Conjugated Bis-Guanidinate (CBG) Stabilized Aluminum Complexes: Synthesis and Their Catalytic Applications

By

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DOCTOR OF PHILOSOPHY

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Recommendations of the Viva Voce Committee

As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by **Nabin Sarkar** entitled **"Conjugated Bis-Guanidinate (CBG) Stabilized Aluminum Complexes: Synthesis and Their Catalytic Applications"** and recommend that it may be accepted as fulfilling the thesis requirement for the awardof Degree of Doctor of Philosophy.

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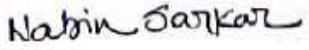

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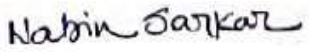
DECLARATION

I hereby declare that I have carried out the investigation presented in the thesis. The work is original and has not been submitted earlier as a whole or in part for a degree/diploma at this or any other Institution / University.



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List of Publications with Complete Details

Journal

(#pertaining to the thesis)

#1. **Sarkar, N.**; Sahoo, R. K.; Mukhopadhyay, S.; Nembenna, S. Organoaluminum Cation Catalyzed Selective Hydrosilylation of Carbonyls, Alkenes, and Alkynes. *Eur. J. Inorg. Chem.* **2022 (*Invited article, part of a joint Special Collection on "Main Group Catalysis"*)**. DOI: https://doi.org/10.1002/ejic.202101030

#2. **Sarkar, N.**; Sahoo, R. K.; Patro, A G.; Nembenna, S. Aluminum-Catalyzed Selective Hydroboration of Carbonyls and Dehydrocoupling of Alcohols, Phenols, Amines, Thiol, Selenol, Silanols with HBpin. *Polyhedron* **2022**, *222*, 115902 **(*Invited, Part of Special Issue: Catalytic Applications of Main group Compounds; Edited by Gerard Parkin*)**.

#3. **Sarkar, N.**; Sahoo, R. K.; Nembenna, S. Aluminum Catalyzed Selective Reduction of Heteroallenes via Hydroboration: Amide Bond Construction and C=X (X= O, S, Se) Bond Activation. *Eur. J. Org. Chem.* **2022 (Accepted). DOI:** https://doi.org/10.1002/ejoc.202200941

#4. **Sarkar, N.**; Sahoo, R. K.; Nembenna, S. Aluminum-Catalyzed Selective Hydroboration of Esters and Epoxides to Alcohols: C-O bond Activation. *Chem. Eur. J.* **2022 (Accepted). DOI:** https://doi.org/10.1002/chem.202203023

5. Khuntia, A. P.; **Sarkar, N.**; Patro, A G.; Sahoo, R. K.; Nembenna, S. Germanium Hydride Catalyzed Selective Hydroboration and Cyanosilyation of Ketones. *Eur. J. Inorg. Chem.* **2022, (*Invited article, part of a joint Special Collection on "Main Group Catalysis"*)**, DOI: https://doi.org/10.1002/ejic.202200209

6. Nayak, D. K; **Sarkar, N.**; Sampath, C. M.; Sahoo, R. K.; Nembenna, S. Organoaluminum Catalyzed Guanylation and Hydroboration Reactions of Carbodiimides. *Z. Anorg. Allg. Chem.* **2022 *(Invited Article)*,** DOI: https://doi.org/10.1002/zaac.202200116

7. Peddarao, T.; Baishya, A.; **Sarkar, N.**; Acharya, R.; Nembenna, S. Conjugated Bis-Guanidines (CBGs) as β-Diketimine Analogues: Synthesis, Characterization of CBGs/Their Lithium Salts and CBG Li Catalyzed Addition of B−H and TMSCN to Carbonyls. *Eur. J. Inorg. Chem.* **2021,** 2034-2046.
8. Sahoo, R. K.; **Sarkar, N.**; Nembenna, S. Zinc Hydride Catalyzed Chemoselective Hydroboration of Isocyanates: Amide Bond Formation and C=O Bond Cleavage. *Angew. Chem. Int. Ed.* **2021,** *60* (21), 11991-12000.
9. **Sarkar, N.**; Mahato, M.; Nembenna, S. Palladium-Catalyzed Selective Reduction of Carbonyl Compounds. *Eur. J. Inorg. Chem.* **2020,** 2295-2301.
10. Peddarao, T.; **Sarkar, N.**; Nembenna, S. Mono- and Bimetallic Aluminum Alkyl, Alkoxide, Halide, and Hydride Complexes of a Bulky Conjugated Bis-Guanidinate (CBG) Ligand, and Aluminum Alkyls as Precatalysts for Carbonyl Hydroboration. *Inorg. Chem.* **2020,** *59* (7), 4693-4702.
11. [#] **Sarkar, N.**; Bera, S.; Nembenna, S. Aluminum-Catalyzed Selective Hydroboration of Nitriles and Alkynes: A Multifunctional Catalyst. *J. Org. Chem.* **2020,** *85* (7), 4999-5009.
12. Sahoo, R. K.; **Sarkar, N.;** Nembenna, S. Intermediates Isolation, and Mechanistic Insights into Zinc Hydride Catalyzed 1, 2-Regioselective Hydrofunctionalization of N-Heteroarenes. *Inorg. Chem.* **2022, (Accepted). DOI:** https://doi.org/10.1021/acs.inorgchem.2c03389
13. Sahoo, R. K.; **Sarkar, N.;** Nembenna, S. Comparing of Two Zinc Hydride Precatalysts for Selective Dehydrogenative Borylation of Terminal Alkynes: A Detailed Mechanistic Study. *ACS Omega* **2022**, **(Accepted).**

Manuscripts in preparation

[#]1. **Sarkar, N.**; Sahoo, R. K.; Nembenna, S. Aluminum-Catalyzed Selective Deoxygenative Hydroboration of Carboxylic Acids and C-O Bond Cleavage of Carbonates, Formates with Pinacolborane *(Manuscript under preparation)*.

[#]2. **Sarkar, N.**; Sahoo, R. K.; Nembenna, S. Aluminum-Catalyzed Double Bond Activation of Alkenes and Isocyanides *(Manuscript under preparation)*.

Other Publications:

a. Book Chapter

1. Nembenna, S.; **Sarkar, N.**; Sahoo, R. K.; Mukhopadhyay, S. *Organometallic Complexes of the Alkaline Earth Metals*, Book Chapter, In Comprehensive Organometallic Chemistry IV **2022 (*Invited*)**. DOI: 10.1016/B978-0-12-820206-7.00173-6

List of Conferences/Seminars Attended with Details

1. Presented poster in **'XVII International Symposium at MTIC- Modern Trends in Inorganic Chemistry'** held at IISER, Pune (11^{th}-14^{th} December 2017).
2. Presented poster in **'ACS on campus conference'** held at NISER, Bhubaneswar (23^{rd} July 2018). **"Achieved Best Poster Award."**
3. Presented poster in **'1^{st} International Symposium on Main Group Molecules to Materials (MMM)'** held at IISc, Bangalore (28^{th}-31^{st} October 2018).
4. Presented poster at **'National Bioinorganic Chemistry Conference (NBCC)'** held at NISER, Bhubaneswar (22^{nd}-24^{th} December 2018).
5. Attended the **'2^{nd} International Conference on Main Group Molecules to Materials (MMM-II)'** held at NISER, Bhubaneswar (13^{th}-15^{th} December 2021).
6. Presented poster in **'1^{st} International RSC-IISER Desktop Seminar with Dalton Transactions'** held at NISER, Bhubaneswar (9^{th}-12^{th} May 2022). **"Achieved Best Poster Award."**

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Dedicated to…….

My Beloved Parents and Family

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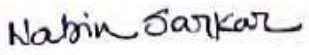
Lastly, I would like to thank my family: my parents, uncle, and brothers for supporting me spiritually throughout the Ph. D. program and my life in general.



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Chapter 4:

Chapter 5A:

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SYNOPSIS OF Ph. D. THESIS

1.	**Name of the Student:** Nabin Sarkar
2.	**Name of the Constituent Institution:** National Institute of Science Education and Research (NISER)
3.	**Enrolment No.:** CHEM11201604005
4.	**Title of the Thesis:** Conjugated Bis-Guanidinate (CBG) Stabilized Aluminum Complexes: Synthesis and Their Catalytic Applications
5.	**Board of Studies:** Chemical Science, NISER

Abstract

Aluminum is cheaper, non-toxic, and abundant on the earth's crust than transition or lanthanide elements. The application of the main group, molecular compounds in catalysis, have been an emerging area of recent research interest. Despite numerous reports on synthesis and reactivity studies of molecular aluminum hydride complexes, surprisingly, only a few reports on aluminum hydride-catalyzed hydrofunctionalization of unsaturated organic transformations are found. Here, in the present work, the synthesis of *N, N'*-chelated conjugated bis-guanidinate (CBG) stabilized mononuclear aluminum dihydride and its catalytic activity towards organic transformations of carbonyls and other unsaturated functionalities with pinacolborane (HBpin) was demonstrated. Additionally, cross-dehydrocoupling reactions of polar functional groups catalyzed by aluminium hydride have been described. In addition, the aluminum dihydride complex has been used for chemoselective and regioselective B-H addition in heteroallenes such as CDIs, isocyanates, isothiocyanates, and selenocyanates. A wide range of N-boryl amides, aminals, and N-methylamines have been isolated. Apart from this, CBG stabilized aluminum alkyls, and the corresponding alkyl cations were isolated. The cationic complex effectively catalyzed the hydrosilylation of carbonyls, alkenes, and alkynes under a low catalyst load. The catalytic outcomes of molecular

CBG aluminum complexes have opened opportunities for understanding the reaction mechanisms and could be extended to other challenging organic transformations.

The thesis has been organized into six chapters.

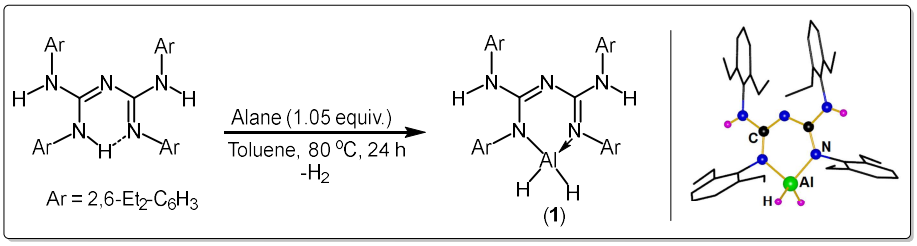
<u>Chapter 1.</u> Introduction

Chapter 1 summarizes literature reports on the work carried out throughout the thesis. This chapter briefly narrates newly synthesized symmetrical and unsymmetrical conjugated bis-guanidine (CBG) ligands, synthesis, coordination, and metalation chemistry with aluminum. A brief introduction of reported N-donor ligand stabilized soluble aluminum hydrides have been discussed. In addition, the synthesis and reactivity of CBG-ligated aluminum dihydride complexes were described. Finally, the current investigation's purpose, scope, and goals were developed based on literature reports.

<u>Chapter 2.</u> Aluminum-Catalyzed Selective Hydroboration of Carbonyls and Dehydrocoupling of Alcohols/Phenols, Amines, Thiol, Selenol, and Silanols with HBpin.

2.1 Synthesis of (^{Diethyl}CBG) Aluminum-Dihydride Complex and its Characterization

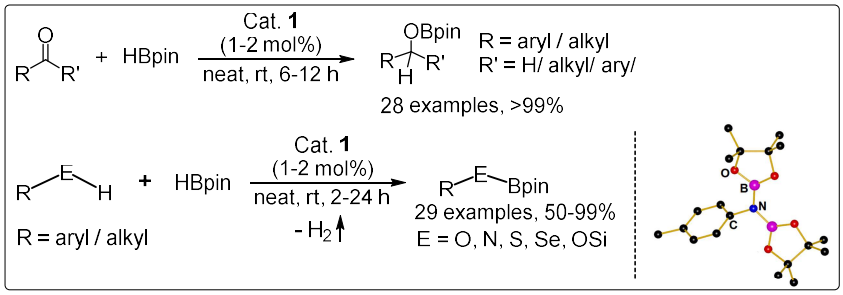
Treatment of a CBG ligand, *i.e.*, LH [L= {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar =2,6-Et_2-C_6H_3] with equimolar alane ($H_3Al{\cdot}NMe_2Et$) solution to yield a mononuclear aluminum–hydride **1** complex ($^{Diethyl}LAlH_2$). Compound **1** is well-characterized by NMR, Mass, IR, and X-ray diffraction studies (Scheme 1).



Scheme 1. Synthesis of compound **1**; the molecular structure of $^{Diethyl}LAlH_2$(**1**).

2.2 Catalytic activity: Hydroboration of Carbonyls and CDC (Cross-Dehydrocoupling) Reactions with Pinacolborane.

The catalytic activity of compound **1** towards B-H addition in aldehydes and ketones was studied. The reduction of carbonyls to boronate esters product in 1-2 mol% of **1** at rt without solvent occurred in excellent yield (Scheme 2). Additionally, the investigation for the catalytic activity of complex **1** towards cross-dehydrocoupling of polar functional groups such as alcohols/phenols (-OH), amines (-NH_2), thiol (-SH), selenol (-SeH), and silanols (-OSiH) with pinacolborane in excellent yield with low catalyst load (Scheme 2).

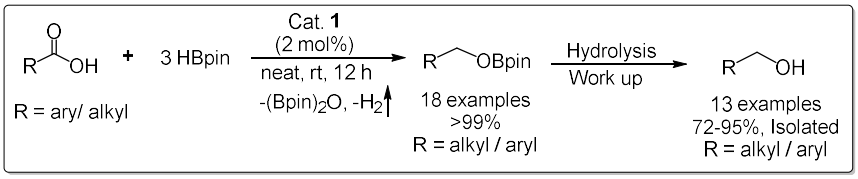


Scheme 2. Hydroboration of carbonyls and CDC reactions catalyzed by **1**.

Chapter 3. This chapter has been divided into two parts.

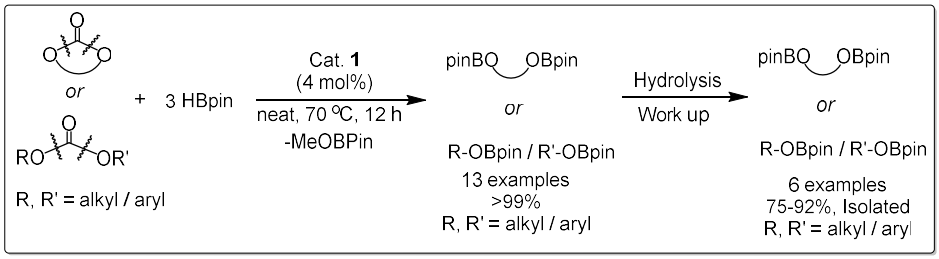
Part A: Aluminum-Catalyzed Selective Deoxygenative Hydroboration of Carboxylic Acids and C-O Bond Cleavage of Carbonates, Formates, Amide, and Anhydride with Pinacolborane.

The effective catalytic performance of aluminum-dihydride **1** for reducing aldehydes and ketones inspires us to explore the further application of compound **1**. In one such example, a full investigation of complex **1** catalyzed deoxygenative reduction of a broad range of carboxylic acids with pinacolborane under mild conditions with good tolerance of halides, nitro, nitrile, amide, alkenes, alkyne, and heteroaryl functionalities (Scheme 3).



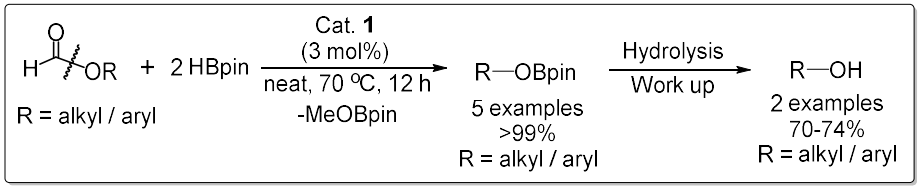
Scheme 3. Deoxygenative hydroboration of carboxylic acids.

Furthermore, C-O bond cleavage of cyclic and acyclic carbonates have been discovered by using compound **1** (Scheme 4). All reactions were performed at the elevated condition with isolation of corresponding alcohols in satisfactory yield.



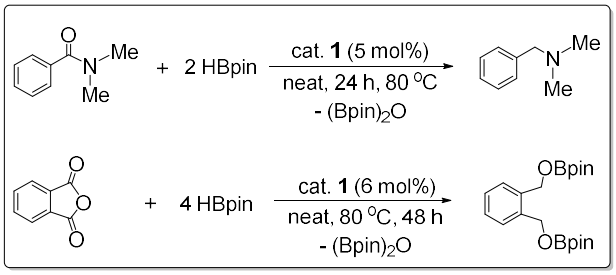
Scheme 4. C-O bond cleavage of carbonates.

In addition, the catalytic performance of CBG aluminum hydride **1** has been explored to reduce formates with pinacolborane (Scheme 5). The reaction resulted in excellent isolation of aryl and alkyl boronate esters at low catalyst load, demonstrating a more comprehensive catalytic application of compound **1**.



Scheme 5. Reduction of formates via hydroboration.

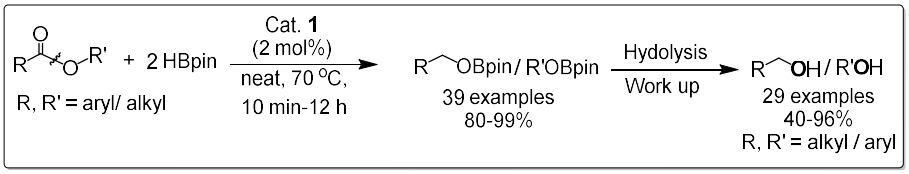
CBG aluminum-dihydride (**1**) was further employed for the deoxygenative reduction of amide and anhydride under mild conditions (Scheme 6). In both reactions, the quantitative formation of hydroborated products has been observed along with BpinOBpin as a side product.



Scheme 6. Hydrodeoxygenation of amide and anhydride.

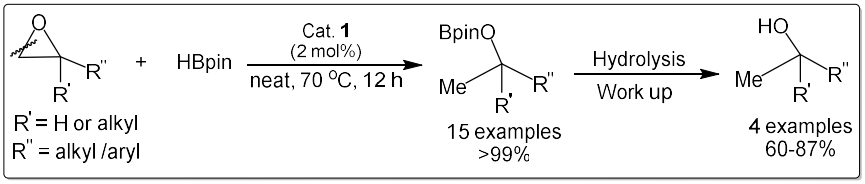
Part B: Aluminum-Catalyzed Selective Hydroboration of Esters and Epoxides to Alcohols: C=O bond reduction and C-O Bond Activation.

In the additional catalytic experiment of compound **1**, the C-O bond reduction of esters with HBpin as a reducer was discovered (Scheme 7). In catalytic outcome, it was found that a wide range of aryl and alkyl esters were hydroborated in a 99% yield.



Scheme 7. C=O bond reduction of esters.

More remarkably, compound **1** was employed for the Markovnikov ring-opening of epoxides into branched boronated ester in the presence of HBpin (Scheme 8).

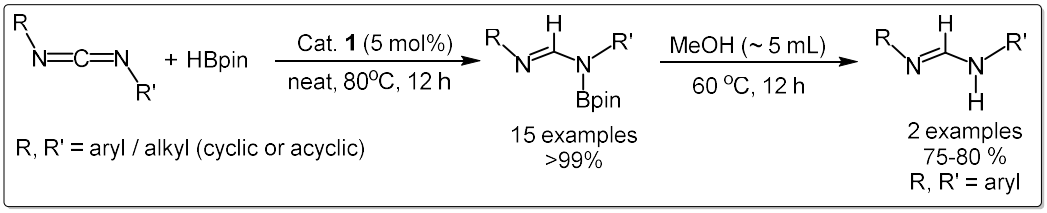


Scheme 8. C-O bond cleavage of epoxides.

The reaction is highly regioselective and more effective than reported transition metal catalysts in these research areas.

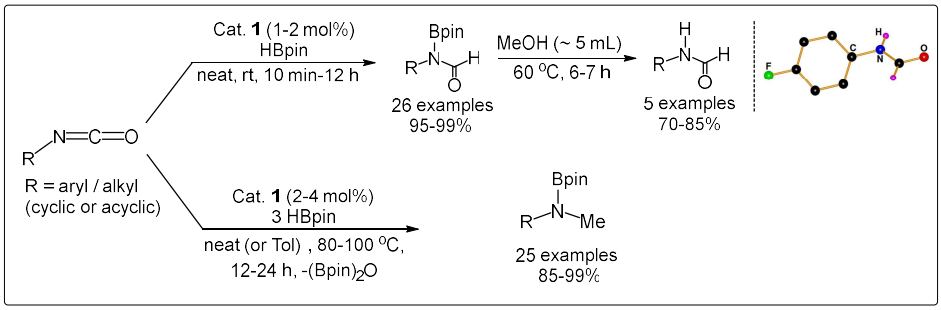
<u>Chapter 4.</u> Aluminum Catalyzed Selective Reduction of Heteroallenes via Hydroboration: Amide Bond Construction and C=X (X= O, S, Se) Bond Activation.

The synthesized aluminum hydride catalyst **1** was effectively used to reduce symmetrical and unsymmetrical carbodiimides into borylated N-formamidines under one equivalent of HBpin (Scheme 9).



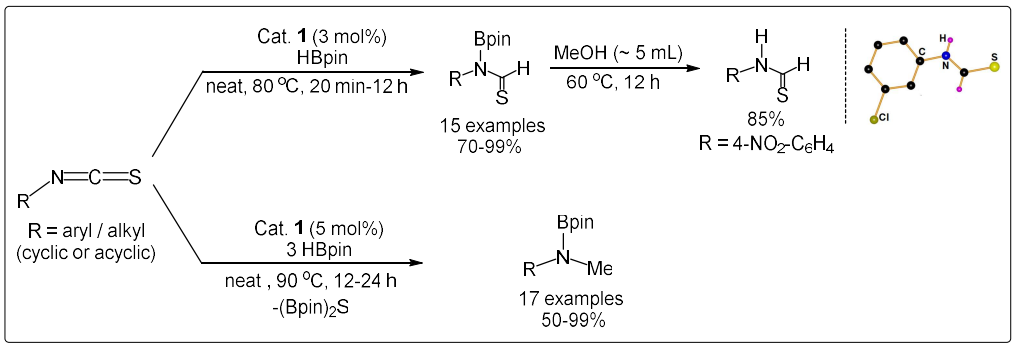
Scheme 9. Monohydroboration of carbodiimides.

In further experiments, compound **1** was employed for partial hydroboration and hydrodeoxygenation of isocyanates into borylated N-formamides and N-methyl amines under low catalyst load **1** (Scheme 10).



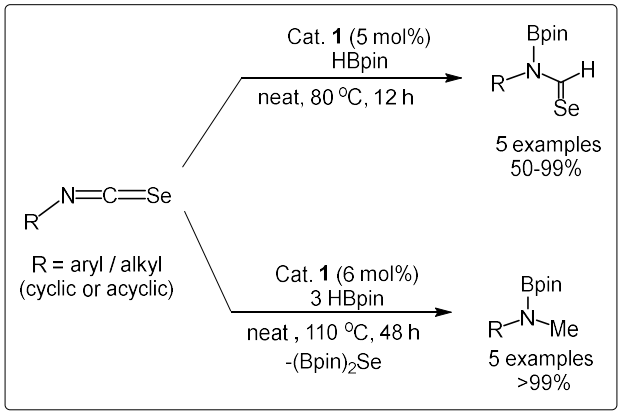
Scheme 10. Synthesis of N-boryl formamides and borylated N-methylamines.

Like isocyanate, catalyst **1** enables the chemoselective monohydroboration and hydrodesulfurization of isothiocyanates to produce borylated N-methyl amines or N-boryl thioamides in excellent yield (Scheme 11).



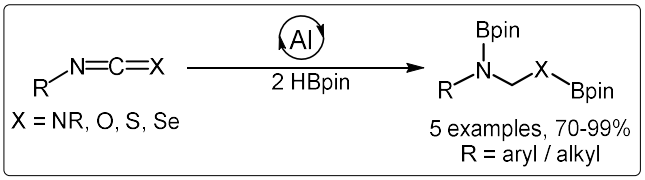
Scheme 11. Partial hydroboration and hydrodesulfurization of isothiocyanates.

In selenocyanate, compound **1** catalyzed the synthesis of borylated selenoformamides and methylamines with pinacolborane as a reducer (Scheme 12). The result is highly adequate, and isolated products in high yields were found.



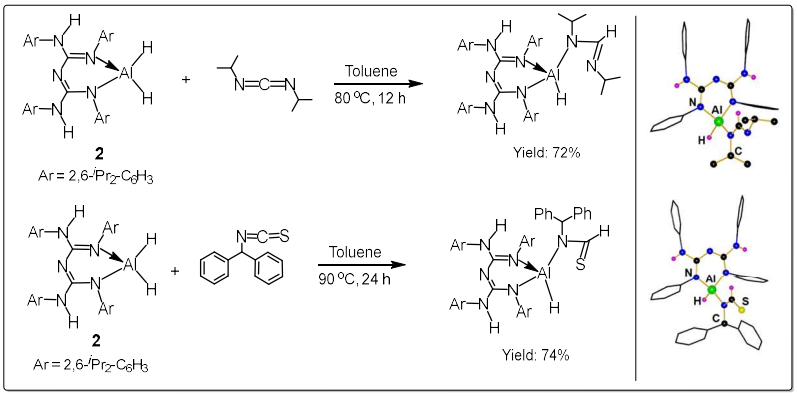
Scheme 12. Partial hydroboration and hydrodeselenization of isoselenocyanates.

Furthermore, complex **1** catalyzed chemoselective di-hydroboration of heteroallenes, i.e., CDI, isocyanate, isothiocyanate, and selenocyanate, have been studied with excellent yield (Scheme 13).



Scheme 13. Synthesis of borylated N-aminals.

The catalytic pathway was confirmed by treating the compound ($^{Dipp}LAlH_2$) with the above heteroallenes, resulting in the isolation of Al-H inserted intermediates confirmed by NMR, HRMS, and Single crystal x-ray diffraction studies (Scheme 14).



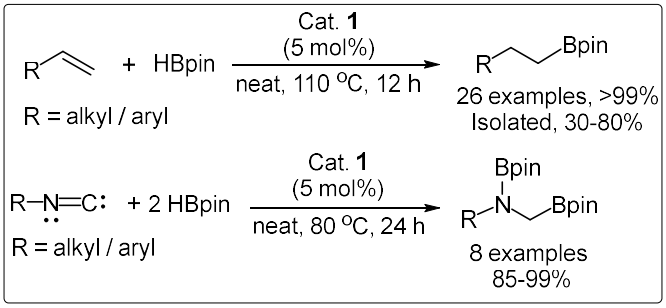
Scheme 14. Control reactions of CDI and NCS hydroboration.

Chapter 5. This chapter has been divided into two parts.

Part A: Aluminum-Catalyzed Double Bond Activation of Alkenes and Isonitriles.

The regioselective anti-Markovnikov B-H addition of alkenes, including terminal, internal and 1,1-disubstituted moieties, was achieved using compound **1** under elevated conditions into linear boronate ester with good yield (Scheme 15).

Additionally, the synthetic route for dihydroboration of isonitriles (*aryl and alkyl*) to diboryl amine esters under two equivalents of HBpin at 80 °C was established (Scheme 15).

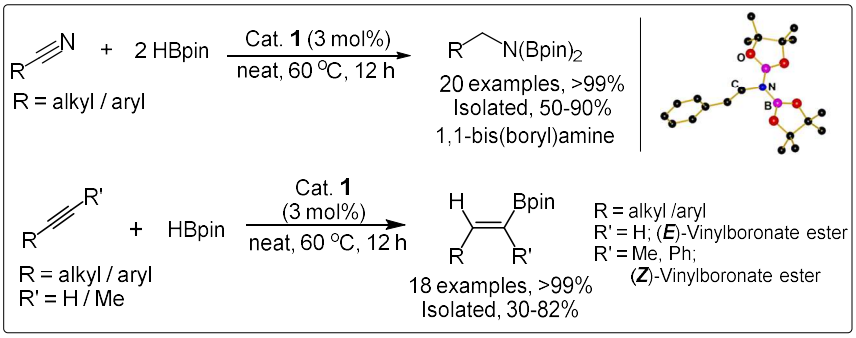


Scheme 15. Hydroboration of alkenes and isonitriles.

Part B: Aluminum-Catalyzed Selective Reduction of Nitriles and Alkynes: A Multifunctional Catalyst.

In this context, a thorough study has been done on the double hydroboration method for isolating bis(boryl) amines from corresponding organic nitriles with a low catalyst **1** load (Scheme 16). Compound **1** was further employed for the syn addition of HBpin across triple bond of both aryl

and alkyl alkynes to afford regioselectively (*E*) and (*Z*) vinyl boronate esters in good yield (Scheme 16).

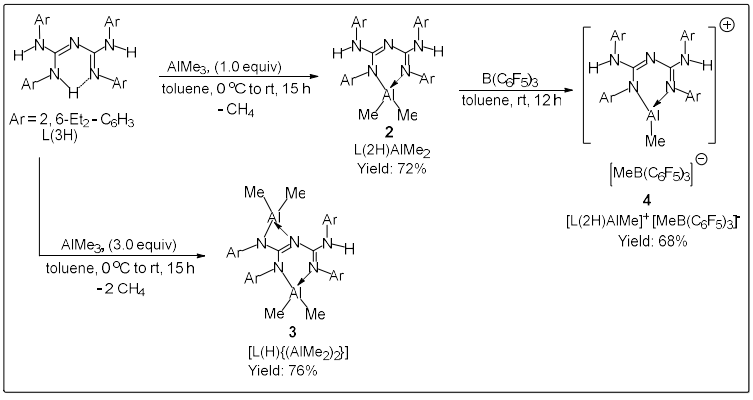


Scheme 16. Synthesis of bis(boryl)amines and vinyl boronates esters.

Chapter 6. Organoaluminum Cation Catalyzed Selective Hydrosilylation of Carbonyls, Alkenes, and Alkyne.

6.1 Synthesis of (^{Diethyl}CBG) Aluminum-Methyls and Methyl Cation Complexes.

The synthesis of CBG stabilized organoaluminum complexes has been achieved by deprotonating the free ligand with $AlMe_3$ solution in toluene (Scheme 17). Single-crystal X-ray structural analysis has established synthetic aluminum methyl compounds **2** and **3** (Figure 1). In addition, treatment of compound **2** with $B(C_6F_5)_3$ in a 1:1 ratio resulted in forming three-coordinate organoaluminum cation **4** in good yield. Multinuclear NMR and HRMS studies confirm the formation of compound **4**.



Scheme 17. Synthesis of CBG stabilized aluminum-alkyl and alkyl cations (**2-4**).

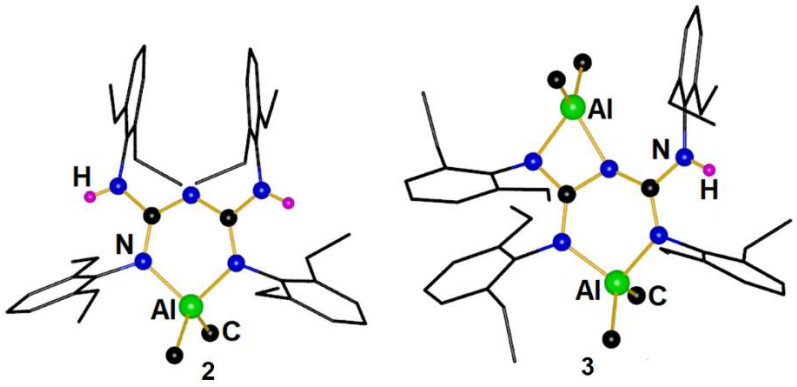
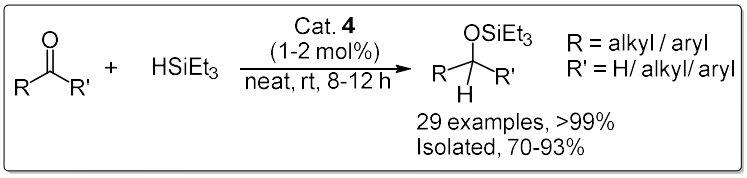


Figure 1. Solid-state structures of compounds **2** and **3**.

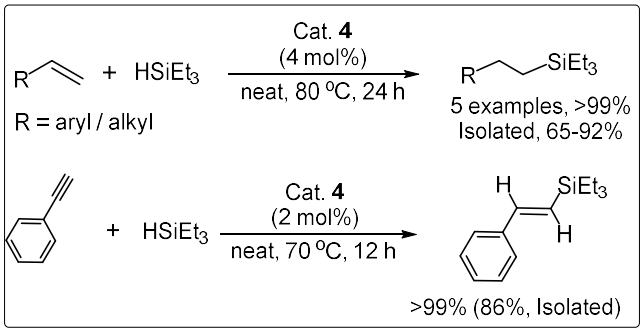
6.2 Catalytic Activity: Hydrosilylation of Carbonyls and other Unsaturated Functionalities with Triethylsilane.

Compound **4** was a robust catalyst for reducing aldehydes and ketones via hydrosilylation into corresponding silyl ethers with a tolerance of halides, nitriles, and heteroaryl (Scheme 18).



Scheme 18. Reduction of aldehydes and ketones via hydrosilylation.

In additional experiments, it was found that complex **4** can be used to reduce alkenes and alkyne to alkyl silane or (*E*) vinyl silane with excellent regioselectivity as per the literature report (Scheme 19).



Scheme 19. Anti-Markovnikov hydrosilylation of alkenes.

Summary of the Work:

- In summary, conjugated bis-guanidinate (CBG) stabilized aluminum-dihydride was synthesized, and studied its catalytic hydroboration of a wide range of unsaturated functionalities (both regioselective and chemoselective).
- CBG-supported aluminum methyl and cationic methyl complexes have been isolated, followed by the catalytic activity of aluminum alkyl cation compound for chemoselective hydrosilylation of carbonyls, alkenes, and alkyne have been analyzed.

List of Abbreviations		
1	Ar	Aryl
2	AN	Acceptor number
3	av.	Average
4	Al	Aluminum
5	( )^{o}	Angle
6	Br	Bromine
7	br	Broad
8	C_6D_6	Deuterated Benzene
9	Å	Bond Distance
10	9-BBN	9-Borabicyclo [3.3.1] nonane
11	δ	Chemical Shift
12	^{o}C	Celsius
13	calcd.	Calculated
14	cat.	Catalyst
15	C	Celsius
16	*J*	Coupling Constant in NMR
17	Cl	Chlorine
18	$CDCl_3$	Deuterated Chloroform
19	HBcat	Catecholborane
20	CDC	Cross-Dehydrocoupling
21	CN (C≡N)	Cyanide / Nitrile
22	CHN	Carbon/Hydrogen/Nitrogen
23	CDIs	Carbodiimide
24	d	Doublet in NMR
25	Et	Ethyl
26	equiv.	Equivalent
27	g	Gram
28	h	Hour
29	Hz	Hertz
30	HRMS	High Resolution Mass Spectrometry
31	HDO	Hydrodeoxygenation
32	HDS	Hydrodesulfurization
33	HDSe	Hydrodeselenization
34	IR	Infrared
35	^{i}Pr	*iso*-propyl
36	I	Iodine
37	NC (N=C)	Isocyanide / Isonitrile / Carbylamine
38	Int	Intermediate
39	IS	Internal standard
40	NCS	Isocyanate
41	NCSe	Isoselenocyanate
42	K	Kelvin
43	*m/z*	Mass/Charge
44	M.P.	Melting Point

45	M^+	Molecular ion
46	Me	Methyl
47	MeO	Methoxy
48	MS	Mass Spectrometry, Mass Spectra
49	m	Multiplet
50	mmol	Millimole
51	mg	Microgram
52	µl	Microlitre
53	min	Minute
54	MHz	Megahertz in NMR
55	M	Molar
56	Mol.	Molecular
57	mL	Milliliter
58	m	Meta
59	NO_2	Nitro
60	NMR	Nuclear Magnetic Resonance
61	o	Ortho
62	ppm	Parts Per Million
63	HBpin	Pinacolborane
64	p	Para
65	q	Quartet in NMR
66	ν	Stretching Frequency
67	s	Singlet in NMR
68	sept	Septet in NMR
69	σ	Sigma
70	TON	Turnover Number
71	TOF	Turnover Frequency
72	CF_3	Trifluoromethyl
73	Tol-d8	Deuterated Toluene
74	t	Triplet
75	Tol	Toluene
76	THF	Tetrahydrofuran
77	OTf	Trifluoromethanesulfonate
78	TS (or T.S)	Transition state
79	T	Temperature
80	t	Time
81	TLC	Thin Layer Chromatography
82	$HSiEt_3$	Triethylsilane
83	rt	Room Temperature
84	XRD	X-ray Diffraction /Crystallography
85	UV	Ultraviolet
86	λ	Wavelength
87	Diethyl	2,6-Et_2-C_6H_3
88	Dipp	2,6-^{i}Pr$_2$-C_6H_3
89	Mes	2,4,6-Me_3-C_6H_2
90	Xyl	2,6-Me_2-C_6H_3

Chapter1: Introduction

This thesis unit gives the background and a brief overview of the area in different sections of the present work.

1.1 Introduction of Conjugated Bis-Guanidine (CBG) Ligands

1.1.1 Summary of Unsubstituted and Substituted Guanidines and Biguanides

Guanidines are the foremost organic compounds with the molecular formula $HNC(NH_2)_2$.[1] Adolph Strecker first discovered this in 1861 in the degradation of guanine.[2] Later, in 1970 Lappert synthesized the first transition metal guanidinate complex[3] followed by main-group metal guanidinates (e*specially aluminum*),[1a, 1c, 4, 3] which opened many research areas of coordination chemistry and material science application.[4-5] In a similar link, organic biguanides have various applications, especially in medicinal chemistry, like oral antihyperglycemic drugs for diabetes (Figure 1.1.).[6] In 1879, Rathke and coworkers prepared the first unsubstituted biguanides,[7] which were actively used in organometallic chemistry to isolate low-valent metal complexes.[3-5] The Maksic[8] research group in 2013 developed hexasubstituted biguanides (Figure 1.1.).

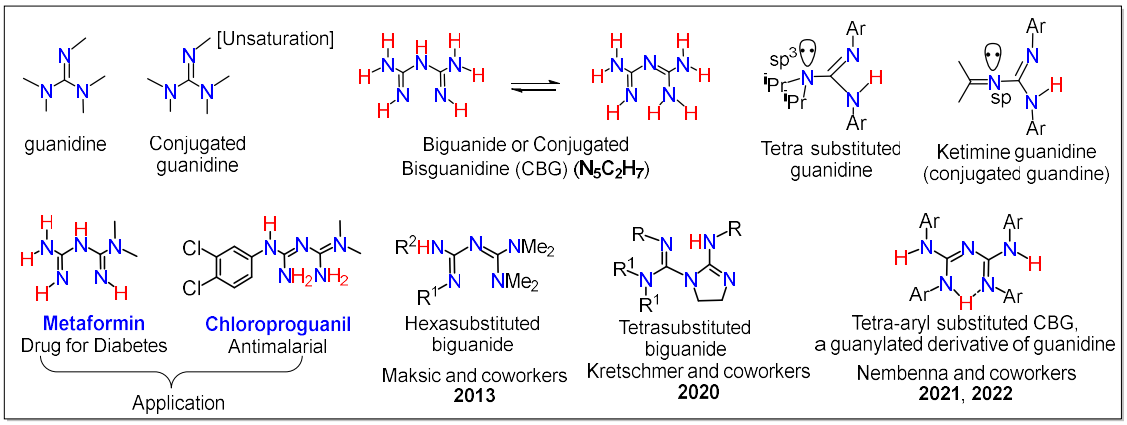


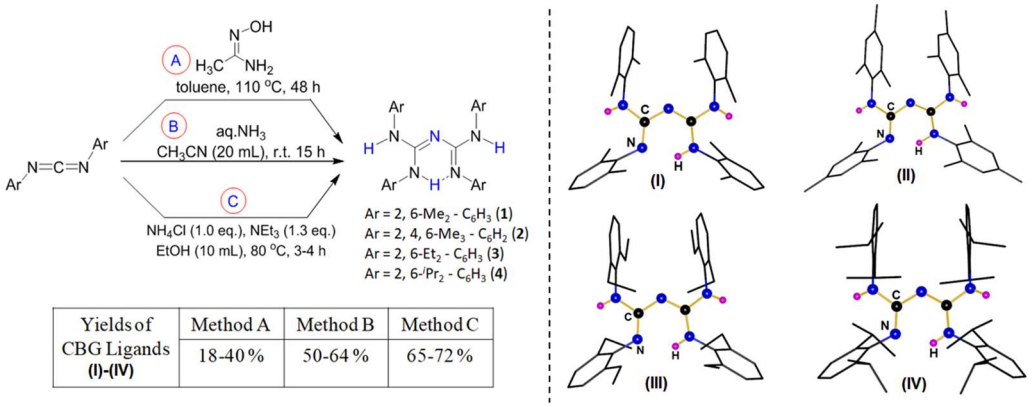
Figure 1.1. Unsubstituted and substituted guanidines and biguanides.

However, biguanide-stabilized aluminum is rare. Nandi[9] introduced the first successful Al(III) biguanide complex in 1864, confirmed by infrared and CHN methods only. Over the past few years, Kretschmer[10] isolated aluminum alkyl complexes supported by tetrasubstituted biguanides. Thereafter our research group synthesized both symmetrical,[11a, 11b] and unsymmetrical[11c] tetra-aryl

substituted conjugated bisguanidines (CBG)[11] and their aluminum complexes.[11c, 12] The newly synthesized CBG ligands are analogs of N-donor β-diketiminate ligands.[13]

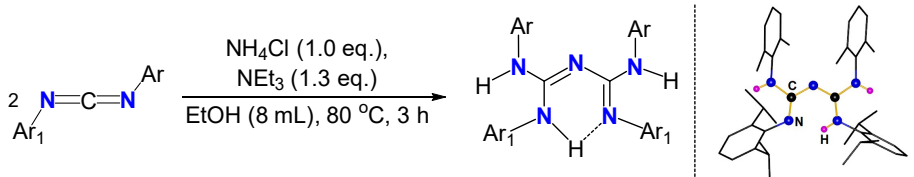
1.1.2 Synthesis, and Coordination Modes of CBG Ligand

There are three synthetic routes to prepare bulky symmetrical aryl-substituted CBG ligands (Scheme 1.1.).[11a] In the first method, *N, N'*-diarylcarbodiimides were treated with acetamidoxime in a 1:2 ratio at rt, resulting in the isolation of required products (**I-IV**) with 18-40% yield. In the second procedure,[11a] the above CDIs mixed with four equivalents of aq. NH_3 under mild conditions ended with 50-64% forming desired CBGs. Besides, in the third method,[11a, 11b] high yield (65-75%) of all CBGs, including both symmetrical and unsymmetrical (Scheme 1.1. and 1.2.), have been found by treating corresponding CDIs with NH_4Cl/Et_3N in ethanol.



Yields of CBG Ligands (I)-(IV)	Method A	Method B	Method C
	18-40 %	50-64 %	65-72 %

Scheme 1.1. Synthetic routes of symmetrical conjugated bis-guanidine ligand (**I-IV**).



Scheme 1.2. Synthesis of unsymmetrical bulky conjugated bis-guanidine ligand **(V)**.

Additionally, five coordination modes[11a] of CBGs have been displayed in Figure 1.2. The present ligand can act as both monodentate (**A-D**) and bidentate (**E**) towards metal chelation, resulting in

mononuclear and binuclear metal complexes. This type of coordination is far superior to previously reported N-donor guanidine and analog β-diketiminate ligands.[14]

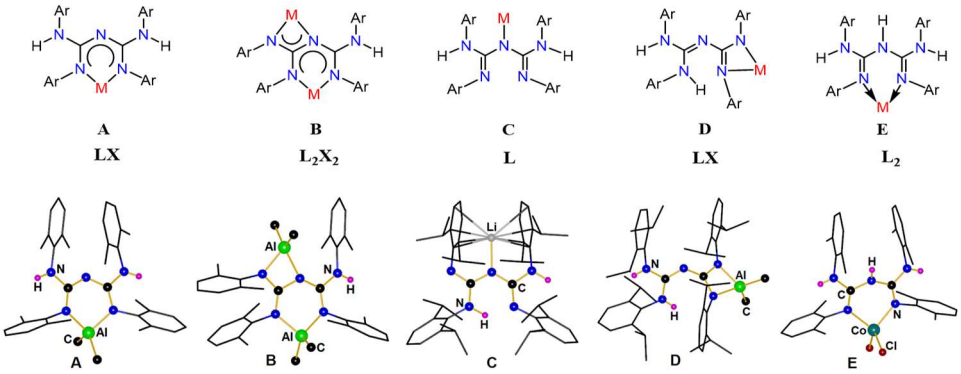


Figure 1.2. Coordination modes of CBGs.

1.2 Complexes of CBGs with Aluminum

1.2.1 Reported *N, N'*-Chelated Soluble Aluminum Hydrides

In recent years, molecular aluminum hydrides have been employed for the catalytic transformation of challenging organic molecules.[15] Previously, several reports on the reactivity of aluminum hydrides, such as deprotonation, hydroalumination, dehydrocoupling, molecular activation, etc., have been well-known.[15c, 15g] But the catalytic applications of molecular complexes are hardly known.[15] In 1942, Stecher and coworkers[16] synthesized AlH_3, which boosted the research area of aluminum chemistry.[15] Later, $LiAlH_4$, a suitable hydride used to reduce various organic functional groups.[17] However, due to high pyrophoricity and uncontrolled reactions,[18] was later overshadowed by transition metal catalysts.[19] In recent times, main-group metal-hydrides[15i, 19c-e, 20] displayed remarkable catalytic activity compared to the transition metal series.[19] Therefore, developing stable metal hydrides is necessary to overcome such challenges.[15i, 20a] Many research groups explored several bulky ligands to synthesize monomeric and dimeric aluminum hydrides.[15a, 15b, 15i, 20a] In Figure 1.3., some selected molecular aluminum hydrides were displayed.[21] Recently, Rivard and coworkers[15i] reviewed one article on possible synthetic routes for preparing main-group metal hydrides. Among all possible synthetic methods, the simplest method is to treat a precursor

with an alane reagent ($AlH_3.N(Me_3)_2$) to synthesize stable aluminum hydride. Such examples are shown[21] in Figure 1.3, where five and six-membered aluminum hydrides are synthesized.

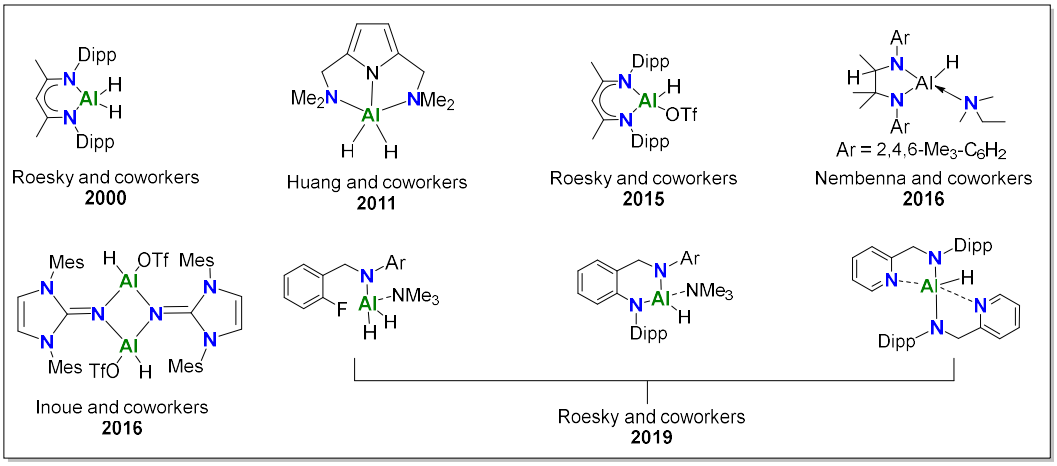
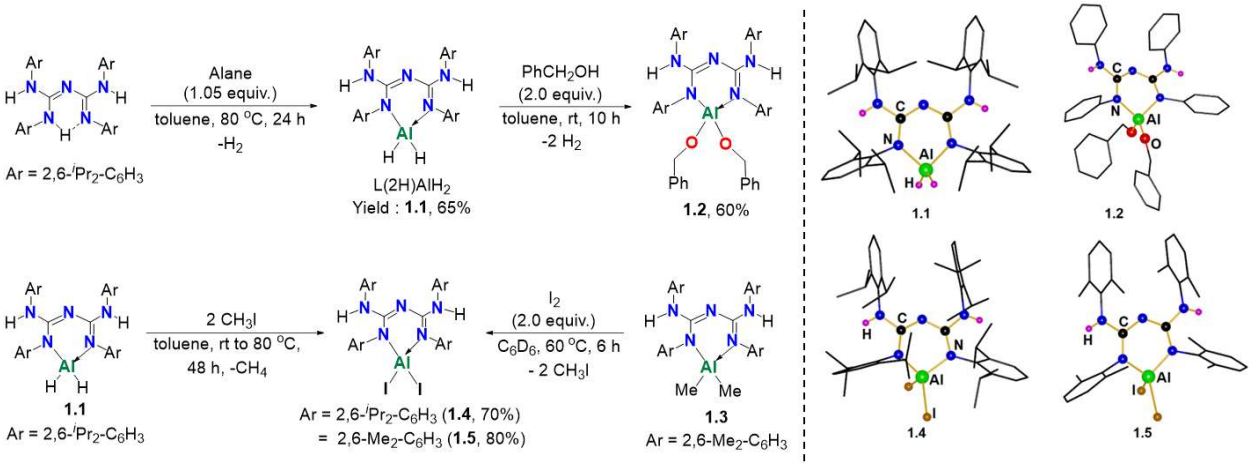


Figure 1.3. Selected report of *N, N'*-chelated soluble aluminum hydrides.

1.2.2 Synthesis and Reactivity of CBG Supported Aluminum Dihydrides

In recent reports, the preparation of aryl conjugated bis-guanidinate chelated $LAlH_2$ complex (**1.1**)[12] by treatment of free ligand (LH) [L= {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar =2,6-^{i}Pr$_2$-C_6H_3] with one equivalent of (0.5 M) Alane solution of toluene was introduced (Scheme 1.3.).



Scheme 1.3. Synthesis and reactivity of (^{Ar}CBG)AlH_2.

The six-membered mononuclear aluminum dihydride **1.1** is well-characterized by NMR, HRMS, infrared spectroscopy, and X-ray diffraction methods. It was found that compound **1.1** is highly reactive toward polar functionalities. In one such example, the dehydrocoupling of **1.1** with benzyl

alcohol in a 1:2 ratio resulted in aluminum alkoxide **1.2** with a 60% yield. Later, CBG-stabilized aluminum-iodide **1.4** was synthesized by reacting compound **1.1** with two equivalent methyl iodide. The reaction ended with a 70% isolation of **1.4** with the evolution of methane gas. Similarly, less bulky ^{xyl}CBG supported aluminum-diiodide (**1.5**)[12b] was prepared by mixing two-fold iodine with one equivalent precursor (^{Xyl}LAlMe$_2$, **1.3**). All four compounds (**1.1-1.2, 1.4-1.5**) exhibited distorted tetrahedral around the central aluminum atom and well agreed with previously reported analog NacNac aluminum complexes.[13, 22]

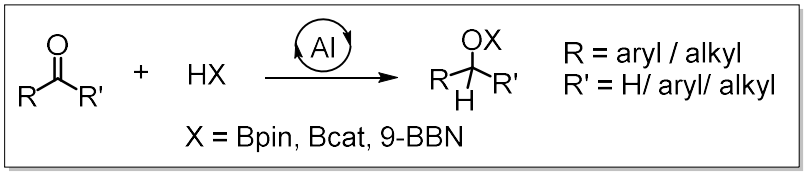
1.3 Catalytic Application of Reagent/Molecular-based Aluminum Complexes

In the earth's crust, aluminum is found as the third most abundant element (~ 8%). Compared to transition and lanthanide metals, it is economical, environmental-friendly, and non-radioactive.[23] Due to these features, aluminum reagents and complexes are most vulnerable and able to mimic other metal catalytic properties. Therefore, over the past few years, aluminum compounds have been extensively used for critical catalytic processes like transfer hydrogenation,[24] hydroelementation,[19c, 21c, 21d, 25] hydroacetylenation,[26] hydroamination,[27] hydrodefluorination,[11c, 28] etc. This broad application-initiated aluminum complexes' development as an effective catalyst for challenging the organic transformation of unsaturated motifs.[15, 19c, 20, 21c, 21d, 24-28]

1.3.1 Hydroboration of Carbonyls and Dehydrocoupling Reactions

Boron species are an essential precursor for synthesizing various important organic compounds such as alcohols, alkyl halides, alkenes, etc.[29] The synthetic route involves hydroboration, directly adding active B-H across the unsaturated functionalities (C-X, where X = C, N, and O) to afford the significant borate derivatives.[30] In 1956, Brown and coworkers reported the first B-H addition in alkenes using $NaBH_4/AlCl_3$ reagents.[31a] After these discoveries, significant development has been found in hydroboration techniques,[19-20] thus opening the gateway to new challenging organic transformations. Transition metal compounds have been used for many years as active catalysts for such reductions.[19] Recently, main-group metals proved efficient catalysts

compared to transition and lanthanide elements due to similar bonding properties and reactivity.[20] In this context, aluminum complexes are suitable contestants for various exciting catalytic applications and thus draw the attention of many research groups to develop molecular aluminum complexes.[32] Several transition metals have been reported regarding carbonyl hydroboration in the past few years.[19c] A vast array of aluminum-based reductions of aldehydes and ketones have been published in this perspective (Scheme 1.4.).[12b, 21b-d, 33]



Scheme 1.4. Hydroboration of carbonyls by using aluminum complexes.

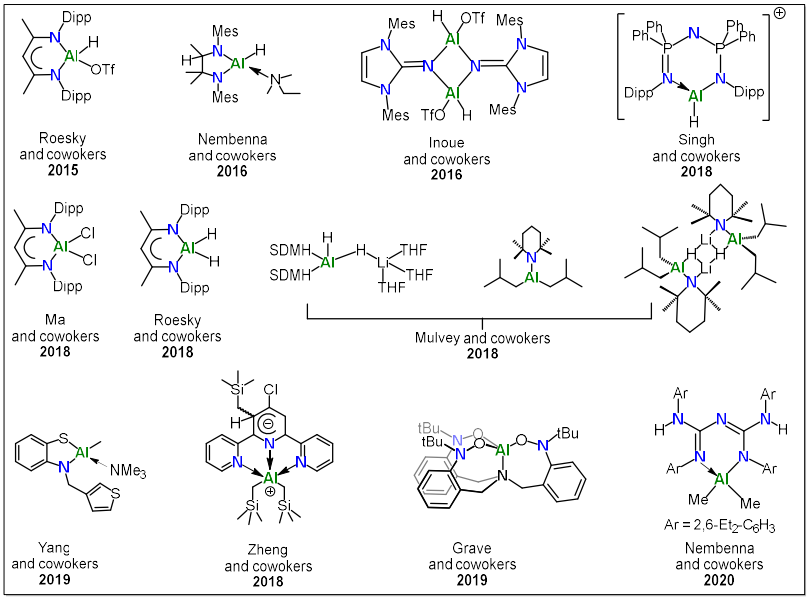
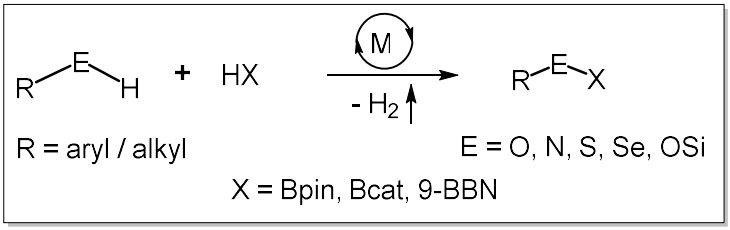


Figure 1.4. Reported molecular aluminum catalysts for hydroboration of carbonyls.

In 2015 Roesky and coworkers[21d] first reported that aluminum-monhydride ^{Dipp}NacNacAlH(OTf); (^{Dipp}NacNac = HC(CMeNAr)$_2$, Dipp = 2,6-^{i}Pr$_2$-C$_6$H$_3$) used for carbonyl hydroboration in benzene-d6 (Figure 1.4.). Subsequently, many main-group research groups synthesized low-valent molecular aluminum complexes, especially metal hydrides and alkyls, which were effectively applied in reducing carbonyl derivatives through hydroboration techniques using HBpin, HBcat, and 9-BBN reagents. [15, 19c, 20, 21c, 21d, 24-28] In this area of research, Leung[34] and

Hreczycho[35] described the metal-free B-H addition in aldehydes and ketone under neat conditions. Both these methods[34-35] require high temperature (>140 ºC) and excessive reducer quantity to afford the boronate ester products.

Boron reagents can also be synthesized by using cross-dehydrocoupling reactions.[36] These reagents are thermally stable and can be stored for a long time under a nitrogen atmosphere, mainly used for various coupling reactions.[36] In this regard, very few main-group metal-based catalysts[37] are known in the literature (Scheme 1.5.). The first transition-metal catalyzed[38] coupling reaction was estabilized by the Nolan research group.[38a] A newly developed ruthenium complex tested the coupling between thiol and boron reagents such as pinacolborane and catecholborane in dry toluene. The next transition metal introduced in this category was osmium.[38b]



Scheme 1.5. Cross-dehydrocoupling of pinacolborane with alcohol/phenol, amine, thiol, silanol, and selenol.

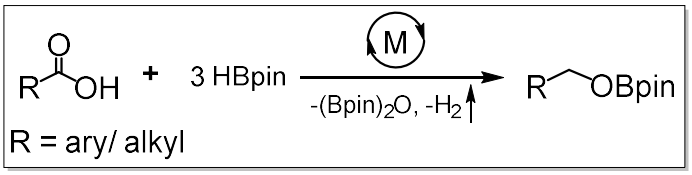
In 2015 Yus described[38b] osmium hydride catalyzed the coupling of alcohols with HBpin. In the same year, Hill[37e] initiates the dehydrocoupling reaction with main-group metals. This NacNac-bound magnesium alkyl complex was used to catalyze the cross-dehydrocoupling of aniline and amine with lewis acid 9-BBN and HBpin at 60 ºC heating. Following this, Panda[37d] proved that alkali metal bis-amides could also be used for the dehydrocoupling of amines with boranes. In 2016, Roesky[37b] expanded the catalytic utilization of the ^{Dipp}NacNac-aluminum dihydride complex. Apart from this, other main-group scientists, i.e., the Power,[37c] and Fontaine[37a] groups, expand the dehydrocoupling reactions of polar functionalities (R-EH) with pinacolborane. In 2016, Bertrand and coworkers[39] reported metal-free cross dehydrocoupling of thiol, alcohol, and amine with HBpin without solvents. The substrates were coupled together using 1 mol% triethylamine at rt temperature. But a longer

duration of time was required for complete conversion, even in some cases required 96 h with 120 ºC heating. So, it was concluded that metal-catalyzed dehydrocoupling is still beneficial over non-metal coupling reactions.

1.3.2 Reductive Hydroboration and C-O Bond Cleavage of Carbonyls

1.3.2.1. Part A: Hydroboration of Carboxylic Acids, Carbonates, and Amides.

The reduction of carboxylic acids to alcohol is an essential industrial procedure.[17] Traditionally, metal hydrides $LiAlH_4$, $NaBH_4$, $Zn(BH_4)_2$ etc., were utilized[17] in stoichiometric ratios with reducing agents like 9-BBN and BMS solution, etc. afford alcohols from organic acids. But the synthetic routes involve many disadvantages like poor waste management, low substrate scope, violent reactions, inadequate selectivity, and pyrophoric reagents that cause fire hazards. Therefore, metal-catalyzed hydrogenation[40] is used to unsaturated carbonyls into corresponding alcohols. But again, these techniques need high pressure and temperature for complete reactions. The method failed severely for aryl carboxylic acids, where less conversion was found. In this circumstance, only hydroelementation techniques for carbonyl reduction, such as hydrosilylation and hydroboration, play a vital role. [15, 19c, 20, 21c, 21d, 24-28] It was found that transition-metal[41] premised carboxylic acid hydrosilylation is known in literature. However, the synthetic route involves poor substrate scope and lower yield%. Therefore, the hydroboration method is the only option (Scheme 1.6.).[42]



Scheme 1.6. Deoxygenative hydroboration of carboxylic acids.

In recent times, molecular manganese,[42c, 42e] and ruthenium[42b, 42d] catalysts were developed to catalyze B-H addition across carboxylic acids in low catalytic amounts (Figure 1.5.). Till today only one report[42a] has been found for aluminum-hydride ($^{Diethyl}NacNacAlH_2$); {where $^{Diethyl}NacNac$ = $HC(CMeNAr)_2$, Diethyl = 2,6-Et_2-C_6H_3) carboxylic acid hydroboration in main-group chemistry.

There are three reports[43] of metal and solvent-free deoxygenative hydroboration of carboxylic acids. All three reports[43] resulted in good chemoselectivity and productivity but were limited by enormous boron reagents. So, it can be concluded that molecular metal complexes[42] are still superior to the metal-free[43] reduction of carboxylic acids.

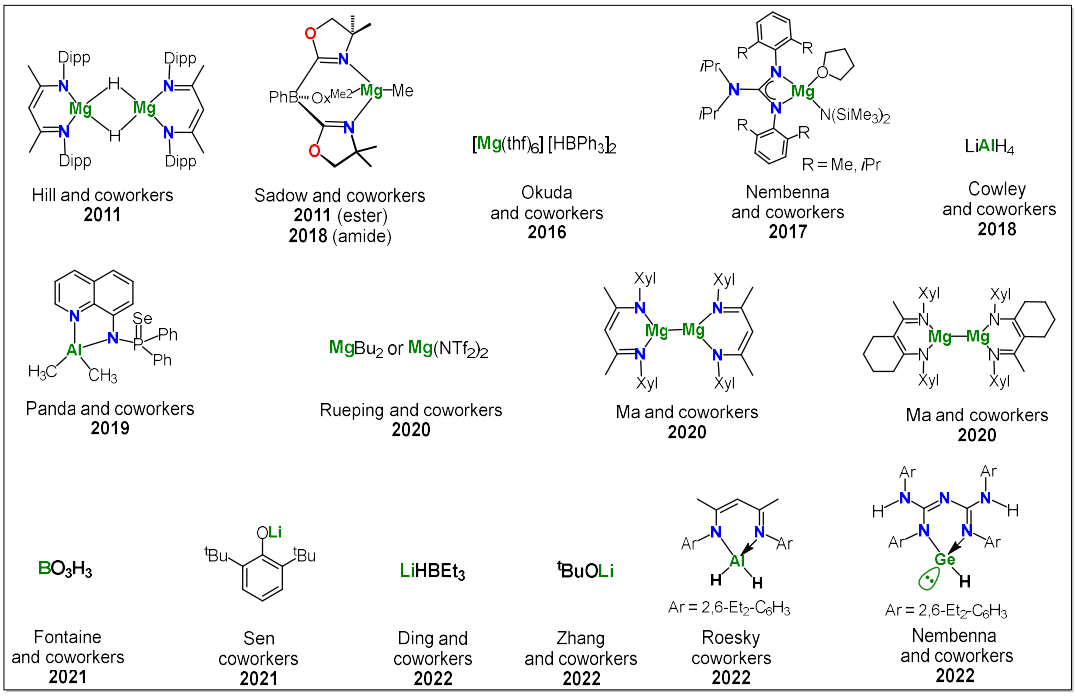
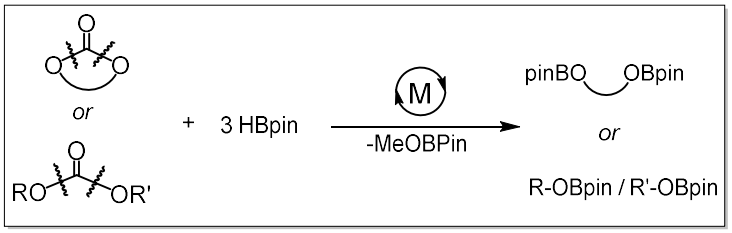


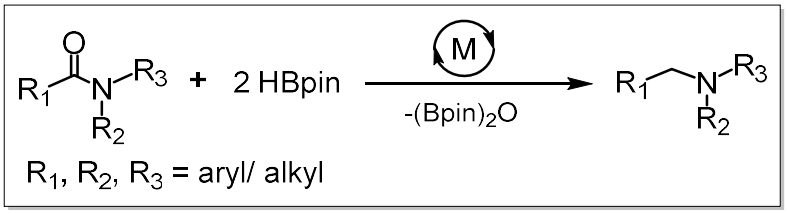
Figure 1.5. Reported main-group metal-based reduction of carboxylic acid, carbonates, amides, esters, and epoxides via hydroboration.

Carbonate hydroboration is being studied alongside carboxylic acids.[42a, 44] Leitner and coworkers[42e] reported the first pincer-supported manganese complex for carbonate reduction using pincer-supported manganese complex for carbonate HBpin as a reducer in 2018. (Scheme 1.7.). Following this, the research groups of Fontaine,[44c] Ma,[44b] and Rueping[44a] introduced magnesium-based C-O cleavage of carbonates into desired boronate esters (Figure 1.5.). The methods described above outperform traditional reduction and transfer hydrogenation procedures for C-O bond breaking in organic carbonates.[45] Our group[44d] recently discovered that monomeric CBG germanium-hydride catalyzed quantitative C-O bond cleavage of diphenyl carbonate to produce corresponding boronate ester and MeOBpin as a byproduct.



Scheme 1.7. C-O bond cleavage of cyclic and acyclic carbonates.

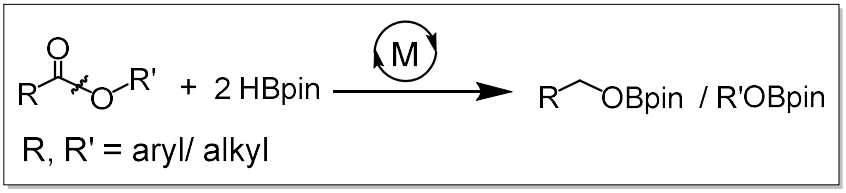
A literature survey summarized that deoxygenative hydroboration of amide is also a complicated procedure (Scheme 1.8.).[46] Only one report has been found for aluminum,[46d] catalyzed reduction of amides to corresponding amines via hydroboration (Figure1.5.).



Scheme 1.8. Reduction of amides to amines.

1.3.2.2. Part B: Hydroboration of Esters and Epoxides.

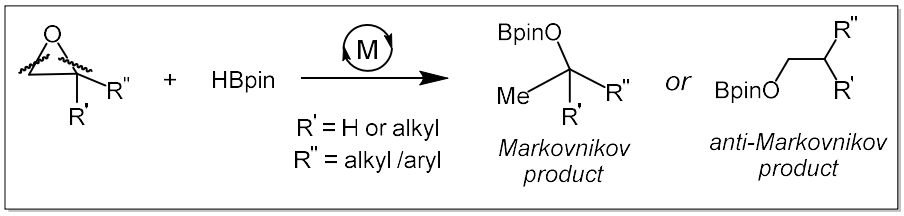
Alcohols can also be synthesized from esters reduction.[17] Previously, esters were reduced by a classical reductant ($LiAlH_4$, $NaBH_4$, etc.)[17] but again overshadowed due to severe disadvantage. Hydroboration[44b, 46e, 47] and hydrosilylation[48] methods were used to overcome these difficulties for the C-O bond reduction of esters (Scheme 1.9.). The above synthetic methods produced non-pyrophoric boronate and silyl esters with high yield, good selectivity, no waste, and high productivity. As a result, these hydroelementation methods [44b, 46e, 47, 48] are more effective for reducing esters than the metal-based hydrogenation procedure.[49]



Scheme 1.9. Chemoselective reduction of esters.

Among the hydroboration category of main-group metals, Sadow's group[47g] first reported a reduction of esters with HBpin under magnesium complex $To^{M}MgMe$ [where To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate]. Following this, other reagents or molecular based main-group metals [47a-47f] were used for C=O bond reduction of esters under mild conditions (Figure 1.5.). In this context, only one aluminum catalyst[42a] has been reported to reduce esters via hydroboration.

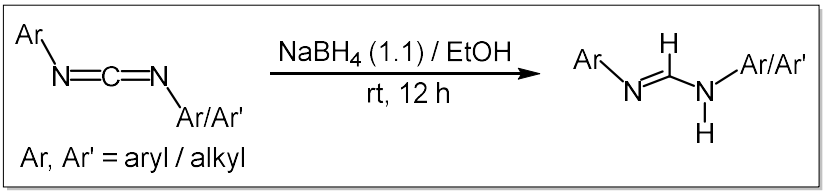
In the current discussion, epoxide reduction is very crucial.[50] Only a handful of main-group metal-based C-O bond cleavage of epoxides[50a-50b, 50f] is reported by Rueping[50a] and Ma[50b] research groups (Scheme 1.10.). The isolated boronate esters follow Markovnikov ring cleavage compared to transition metal[50c-50e] deployed anti-Markovnikov C-O bond activation of epoxides (Figure 1.5.). The preceding discussion concludes that epoxide hydroboration is superior to traditional reducant and hydrogenation techniques.[49]



Scheme 1.10. C-O bond activation for epoxides.

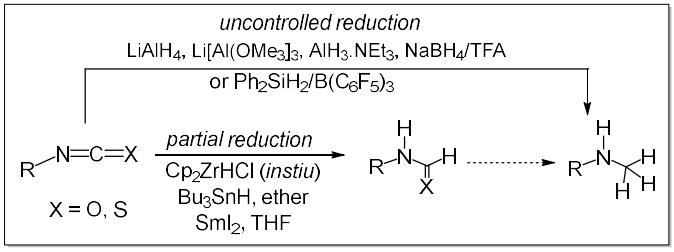
1.3.3 Synthesis of Borylated Amides/ Aminals/ N-Methyl Amines from Heteroallenes

Heteroallenes are the essential building blocks of organic synthesis.[51] Reduction of carbodiimide, isocyanate, isothiocyanate, etc., functionalities play a vital role in synthesizing amide compounds,[52] like formamidines, formamides, and thioformamids. These amides function as a synthon in preparing essential organic functionalities for pharmaceutical drugs and agricultural applications.[51] Therefore, developing a correct synthetic procedure to deduce this amide is significant. Many routes have been published for formamidine preparation[1-2] in the past few years but ended with several drawbacks. Recently our group reported[52c] $NaBH_4$ to catalyze CDI reduction into air-stable isolation of formamidines with excellent yield (Scheme 1.11.).



Scheme 1.11. Synthesis of formamidines from carbodiimides.

The synthetic procedure takes less time with no toxicity. With literature analysis, it is evident that many research groups developed various methods for the partial reduction of isocyanate and isothiocyanates into corresponding formamides and thioformamids.[52b] However, the outcome of reactions is inferior due to uncontrolled reduction in methylamines products (Scheme 1.12.).[52b] In 2016, Pace and coworkers developed the Schwartz reagent (Cp_2ZrClH) for the selective reduction of isocyanate into targeted formamides (Scheme 1.12).[52b] The *insitu* synthesized above reagent shows the remarkable chemoselective synthesis of stable formamides compared to reported reagents such as Grignard reagents and lithium carbenoids.[52b] In 2019, the same author again utilized Schwartz's reagent to prepare thioformamide from its corresponding precursor (isothiocyanates) in a controlled pathway (Scheme 1.12.).[52b] The reaction is more effective than previously reported classical reducing agents like SmI_2 and tributyltin hydride ($(C_4H_9)_3SnH$). [52b]



Scheme 1.12. Reduction of isocyanates and isothiocyanates.

As evident in the modern catalysis field, hydroboration and hydrosilylation techniques have evolved to reduce unsaturated organic functionalities.[21a, 46e, 47e, 53] In one such method, Hill and coworkers[53g] utilized NacNac stabilized organomagnesium complex for reduction of CDI with HBpin into N-boryl formamidines (Figure 1.6.).

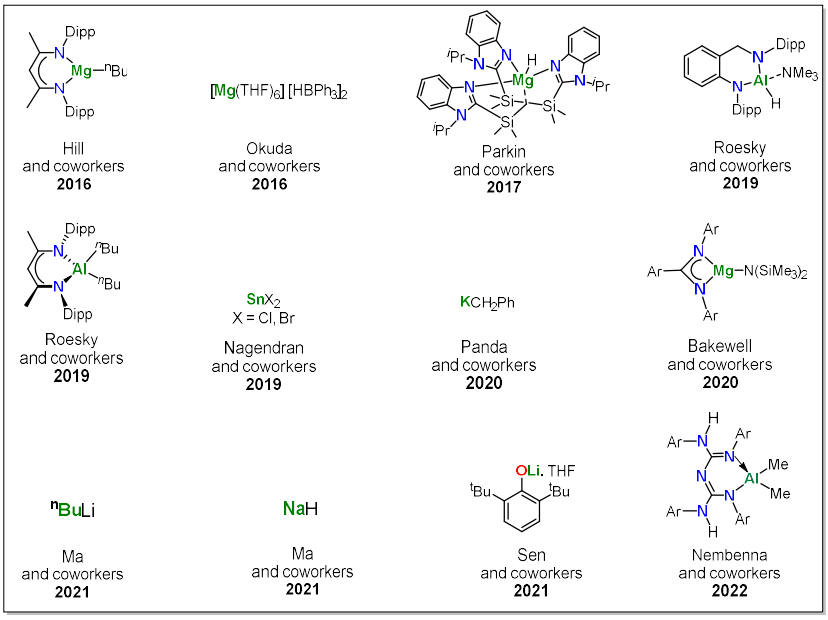
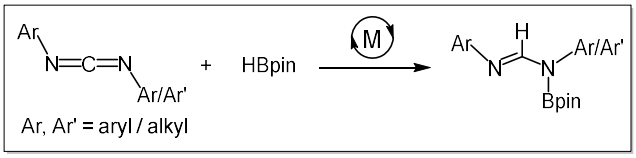


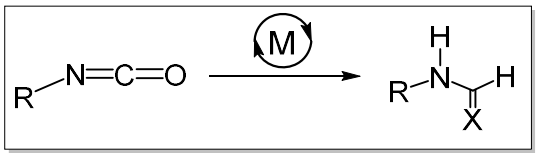
Figure 1.6. Previous report on main-group metal-catalyzed reduction of carbodiimides via hydroboration.

Later, both main-group and lanthanide compounds were employed for the monohydroboration of carbodiimides (Scheme 1.13).[53]



Scheme 1.13. Monohydroboration of carbodiimides.

A detailed literature survey on isocyanate reduction via the hydroboration method was done in this research area. Only a handful of examples are known for B-H addition in organic isocyanates (Figure 1.7.).[11b, 47d, 54] Previously, Okuda[46e] and Hill[54c] introduced magnesium-based hydroboration of isocyanates. Following this, zinc,[11b] lithium,[47d] silver,[54a] and cobalt[54a]



Scheme 1.14. B-H addition in isocyanates.

based reagents, i.e., $LiHBEt_3$ and $AgSbF_6$, catalyzed hydroboration of isocyanate with pinacolborane (Scheme 1.14.).

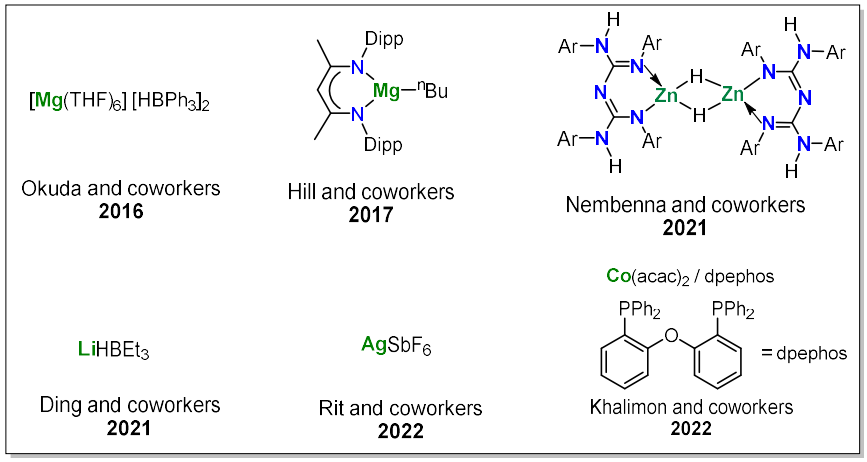
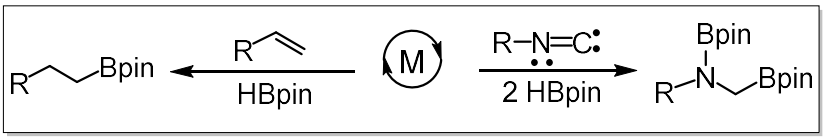


Figure 1.7. Report on metal-catalyzed reduction of isocyanates via hydroboration.

1.3.4 Metal-based Double and Triple Bond Activation

1.3.4.1. Part A: B-H Addition Across Double Bonds, i.e., Alkenes and Isonitriles

Organoboron species are the foremost reagents in organic chemistry for deducing crucial transformations in the C-C bond formation of Suzuki–Miyaura coupling reactions.[29-30] This reaction alternatively helps to isolate industrial and pharmaceutical-based organic species.[30] In the organometallic research area, these organoboron are mainly synthesized by either Grignard reagents or catalytic borylation of alkenes, alkynes, alkyl halides, etc.[29-30] Among these, the safe procedure is the hydroboration of unsaturated bonds. Therefore, many research groups are engaged in developing suitable molecular metal compounds to derive the B-H addition in alkenes (Scheme 1.15.).[33o, 55] The reason for choosing alkene hydroboration is that it is safe to isolate air-stable and non-toxic alkyl boronate compounds in high yields with less impact on the environment. In the literature, it was found that there are several reports on transition and lanthanide-based reduction[19b, 56] of olefins compared to main-group elements. It is evident that only a handful of examples of molecular s and p-block metals are reported in this category (Figure 1.8.).[33o, 55]



Scheme 1.15. Metal catalyzed double bond activation of alkenes and isonitriles.

Among the double bond activations, the next challenging functional group is the isonitrile. In the hydroboration category, no transition metal reports were found (Scheme 1.15.).[55j] However, only one main-group Report on magnesium-based[55j] isocyanide reduction has been described (Figure 1.8.). Hill and coworkers[55j] demonstrated the first report in 2015 by using NacNac magnesium butyl catalyst [CH{C(Me)NAr}$_2$Mg^{n}Bu] (where Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$) based double hydroboration of isonitriles (RNC) to borylated amine {RN(Bpin)CH$_2$(Bpin)}. Before this report, Figueroa and coworkers[55k] attempted a double reduction of m-terphenyl isocyanide with 9-BBN but terminated with the single hydroborated product at a high-temperature reaction (100 °C).

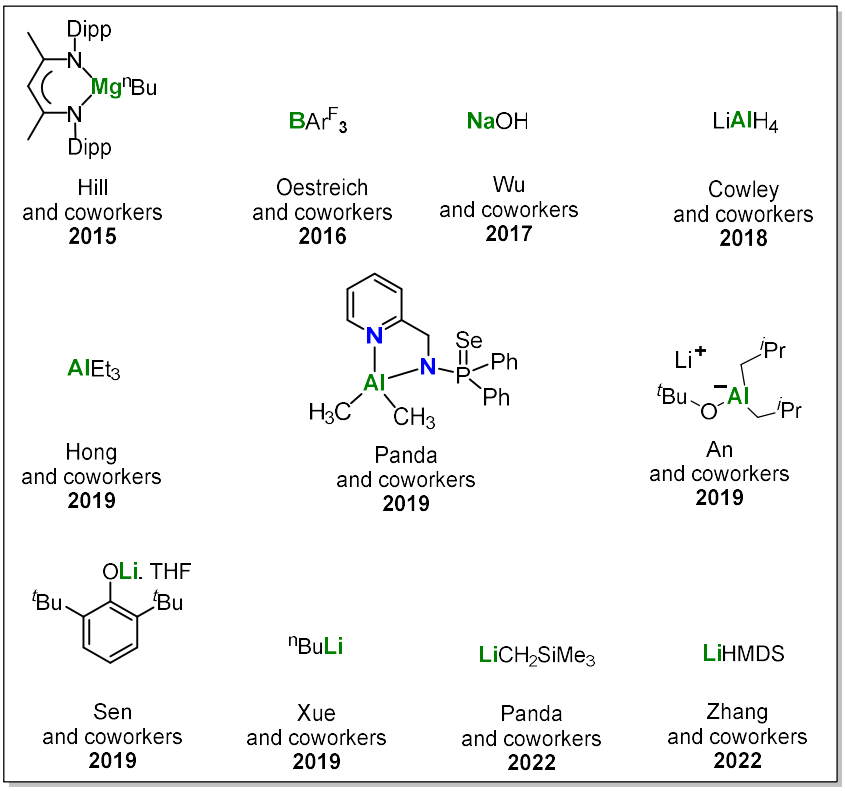
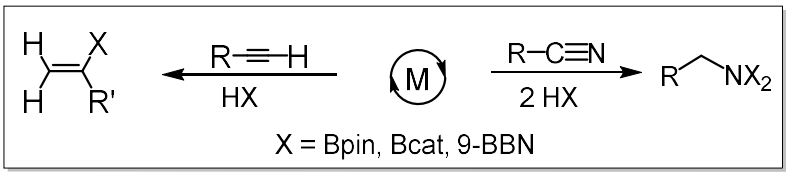


Figure 1.8. Reported main-group metal-catalyzed double bond activation of alkenes and isonitriles.

1.3.4.2. Part B: B-H Addition Across Triple Bonds, i.e., Alkynes and Nitriles

The alkyne hydroboration also afforded stable organoboron compounds apart from alkene reduction. In recent years, many main-group elements[57] have emerged as effective catalysts for alkyne reduction via hydroboration using HBpin, HBcat, and 9-BBN reagents compared to transition metals (Scheme 1.16.).



Scheme 1.16. Metal catalyzed triple bond activation of alkynes and nitriles.

In 2016 Roesky and coworkers[57] described the catalytic activity of six-membered aluminum dihydride for anti-Markovnikov insertion of B-H into terminal C≡C bond of alkynes to yield a vinyl boronate ester with (*E*) selectivity (Figure 1.9.). Next, Blakewell, Inoue, Mulvey, Panda, Ma, and Yang's research groups[57] estabilized molecular aluminum-based syn-reduction of pinacolborane across triple bonds of alkynes under elevated conditions. Apart from this, other main-group metals such as lithium, boron, and phosphorus-based catalysts[57] were used for the selective reduction of alkynes have been found.

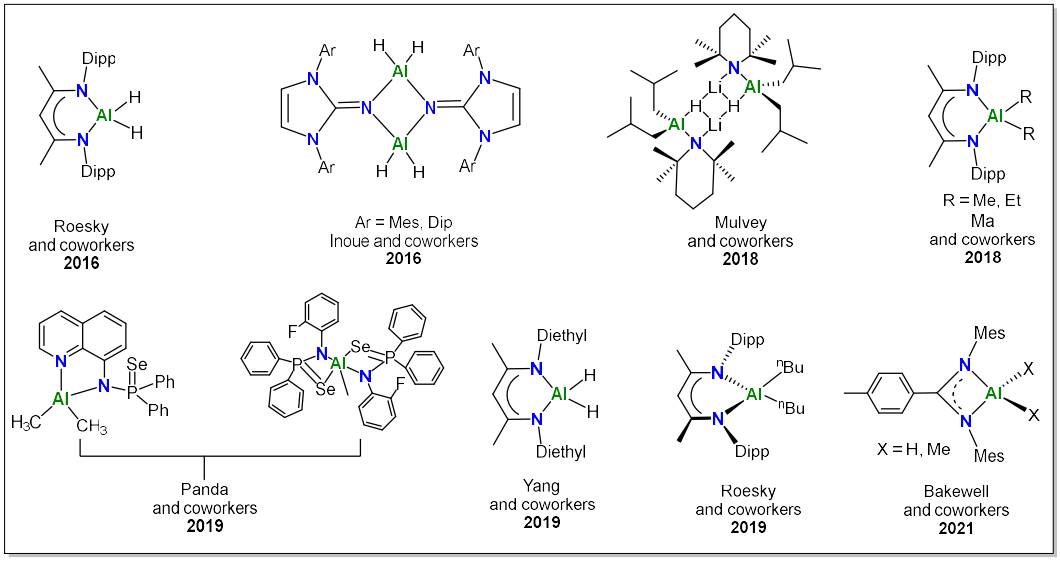
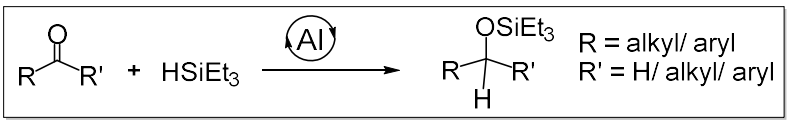


Figure 1.9. Reported molecular aluminum catalyzed triple bond activation of nitriles and alkynes.

Similarly, there are reports of main-group metal-catalyzed double reduction of nitriles using the hydroboration technique (Scheme 1.16.).[19d, 58] In this context, it was found that Hill[19d] first introduced dihydroboration of organic nitriles into 1,1-bis(boryl)amines with a low catalyst load (Figure1.9.). The synthetic procedure is limited by lower substrate scope. Other s-block elements, i.e., magnesium and lithium-based[19d] hydroboration of nitriles, have been described in the literature. However, the first report on molecular aluminum catalysts for chemoselective B-H addition in nitriles was presumed by Roesky in 2019.[19d] Following this, only three reports came forward by Panda, Yang, and Blakewell for aluminum alkyl and hydride-catalyzed nitrile reduction through HBpin addition.[19d]

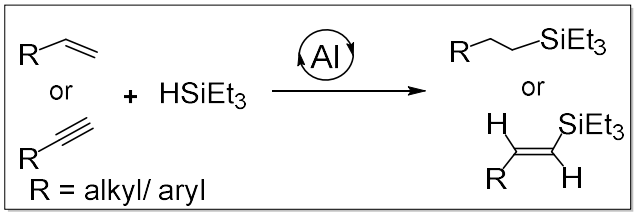
1.3.5 Chemoselective Hydrosilylation of Carbonyls, Alkenes, and Alkynes

The catalytic hydrosilylation of carbonyl compounds with silanes is undoubtedly a sensible approach for synthesizing silyl ethers, which are widely used to synthesize alcohols (Scheme 1.17.).[19c, 21c, 21d, 25]



Scheme 1.17. Organoaluminum cation catalyzed reduction of carbonyls via hydrosilylation.

Developing cheaper and more sustainable metal compounds, particularly aluminum-based catalysts, is beneficial.[23] In this background, inexpensive and earth-abundant aluminum metal fits perfectly. Very few molecular Al cations are reported for hydrosilylation of unsaturated bonds (Scheme 1.18.).[25, 59] Particularly for reducing alkene and alkynes, a mixture of silyated products is often found even by employing Lewis acid catalysts.[59]



Scheme 1.18. Reduction of alkenes and alkynes by aluminum cationic complexes.

Therefore, developing efficient cationic complexes is required to deduce these challenges. Jordan's group first reported a six-membered mononuclear aluminum alkyl complex (Figure 1.10.).[60] Following this, a few examples of molecular Al cationic compounds were published.[59] About hydrosilylation reduction, the Bergmans group[59d] reported first time the carbonyl reduction with Et_3SiH by using [Tp*AlMe][$MeB(C_6F_5)_3$] (Tp* = Tridentate scorpionate ligand) catalyst. After this, Wehmschulte and coworkers[59a-59c] prepared a series of organoaluminum monocations to deduce a deoxygenated reduction of CO_2 to methane gas under a low catalyst load.

In 2016, Nikonov[25c] developed aluminum hydride cation [^{Dipp}NacNacAlH]$^+$ to reduce alkenes and alkynes into vinyl silanes via hydrosilylation. The author proposed a reaction mechanism via lewis acid activation. Recently, Venugopal[25a] explored the ketone hydrosilylation by use of newly synthesized aluminum monocationic complex[$(Me_2NC_6H_4)_2Al(THF)_2$]$^+$ under mild conditions (Figure 1.10.). In 2022, Dagorne[25b] developed NHC ligated Al^{+3} cationic methyl complex to reduce benzaldehyde and alkynes with a simple silane reagent, i.e., triethylsilane.

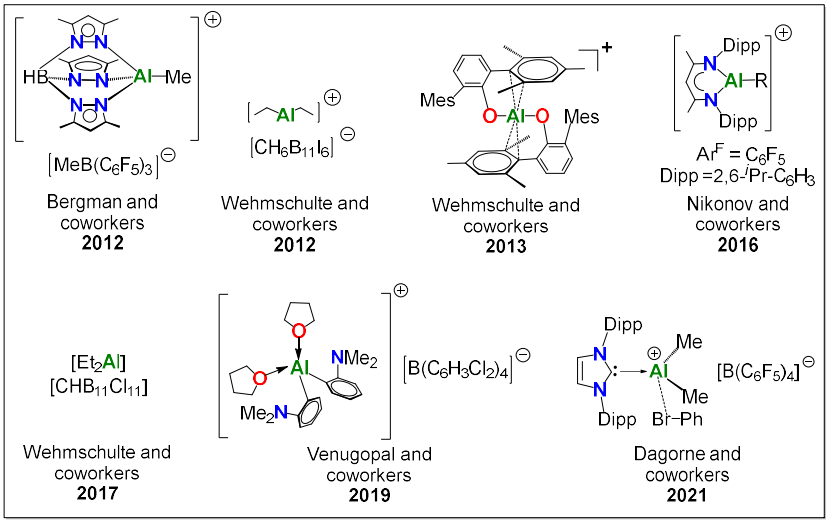


Figure 1.10. Reported molecular aluminum cationic compounds to reduce unsaturated organic substrates via hydrosilylation.

1.4 Aim, Scope, and Objective of the Present Work

The chemistry of aluminum is well estabilized in literature. Various aluminum complexes and cluster molecules are reported. However, very few examples of catalysis reactions with aluminum complexes were known. Schlesinger discovered the first effective Lewis acid catalyst, i.e., $LiAlH_4$, which introduced a powerful reductant for various organic transformations. But due to severe drawbacks, later transition and lanthanide metals overshadowed the utility of aluminum complexes in catalysis. In the past few years, the application of main-group metal complexes in catalysis has emerged in preference of transition elements as aluminum is the cheapest earth-abundant element in the periodic table, which draws attention to its application in catalysis. Roesky's group reported the first effective molecular aluminum-based catalysis reaction for carbonyl reduction with HBpin. The catalytic outcome initiates the utilization of aluminum complexes for challenging organic transformation such as hydroboration, hydrosilylation, hydroamination, transfer hydrogenation, hydrodefluorination, etc. Among these, hydroboration of various functional groups like alkyne, nitrile, imine, and CDI has been well reported. This report shows a comprehensive application of aluminum complexes in the catalysis research area.

In the past few years, hydrosilylation of various organic molecules have been reported. In 2012, Berman and coworkers developed aluminum cation-based hydrosilylation of carbonyls with triethylsilane under mild conditions. Following this, the hydrosilylation method synthesized a few other cationic aluminum complexes to reduce carbon dioxide, alkynes, and alkynes. The reactions are effective with a high yield of product formation. However, only some selected aluminum cations were used for hydrosilylation reactions. This Report makes it understandable that molecular aluminum cations as a catalyst are not well studied.

Based on these facts, the objective of the present work is as follows-

1. To isolate CBG stabilized neutral and cationic aluminum complexes.

2. To investigate the catalytic utilization of aluminum compounds to reduce challenging organic functionalities via hydroboration.
3. To synthesize CBG-supported organoaluminum cations and practical application in hydrosilylation reactions.

1.5 References

1. Selected examples of synthesis and reactivity of guanidines: (a) Cui, X. -Y.; Tan, C. -H.; Leow, D. *Org. Biomol. Chem.* **2019**, *17*, 4689-4699; (b) Zhang, W. -X.; Xu, L.; Xi, Z. *Chem. Commun.* **2015**, *51*, 254-265; (c) Alonso-Moreno, C.; Antinolo, A.; Carrillo-Hermosilla, F.; Otero, A. *Chem. Soc. Rev.* **2014**, *43*, 3406-3425; (d) Barry, S. T. *Coord. Chem. Rev.* **2013**, *257*, 3192-3201.
2. Güthner, T.; Mertschenk, B.; Schulz B. "Guanidine and Derivatives". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH. DoI:10.1002/14356007.a12_545.pub2
3. Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc.* **1970**, 2550-2559.
4. Aplication of Guaindines: (a) Jones, C. *Coord. Chem. Rev.* **2010**, *254*, 1273-1289; (b) Coles, M. P. *Dalton Trans.* **2006**, 985-1001.
5. Chlupatý, T.; Růžička A. *Coord. Chem. Rev.* **2016**, *314*, 103-113.
6. Selected examples of medicinal Applications of Guaindines: (a) Kathuria, D.; Bankar, A. A.; Bharatam, P. V. *J. Mol. Struct.* **2018**, *1152*, 61-78; (b) Bailey, C. J. *Diabetologia* **2017**, *60*, 1566-1576; (c) Wilcock, C.; Bailey, C. J. *J. Pharm. Pharmacol.* **1991**, *43*, 120-121.
7. Rathke, B. *Ber. Dtsch. Chem. Ges.* **1879**, *12*, 776–784.
8. Eckert-Maksić, M.; Margetić, D.; Glasovac, Z.; Trošelj, P.; Jušinski, I. *Synlett* **2013**, *24*, 2540-2544.

9. Nandi, S. D. *Z. Naturforsch. B* **197**, *29*, 347-348.

10. (a) Dehmel, M.; Görls, H.; Kretschmer, R. *Inorganics* **2021**, *9*, 52; (b) Dehmel, M.; Vass, V.; Prock, L.; Gorls, H.; Kretschmer, R. *Inorg. Chem.* **2020**, *59*, 2733-2746.

11. Synthesis of Tetra-aryl Substituted Conjugated Bisguanidines (CBG): (a) Peddarao, T.; Baishya, A.; Sarkar, N.; Acharya, R.; Nembenna, S. *Eur. J. Inorg. Chem.* **2021**, 2034-2046; (b) Sahoo, R. K.; Sarkar, N.; Nembenna, S. *Angew.Chem. Int. Ed.* **2021**, *60*, 11991 –12000; (c) Nayak, D. K.; Sarkar, N.; Sampath, C. M.; Sahoo, R. K.; Nembenna, S. *Z. Anorg. Allg. Chem.* **2022**, DOI: https://doi.org/10.1002/zaac.202200116

12. Peddarao, T.; Sarkar N.; Nembenna, S. *Inorg. Chem.* **2020**, *59*, 4693-4702;

13. Selected References: (a) Bakthavachalam, K.; Reddy, N. D. *Organometallics* **2013**, *32*, 3174-3184; (b) Yang, Y.; Li, H.; Wang, C.; Roesky, H. W. *Inorg. Chem.* **2012**, *51*, 2204-2211.

14. Selected References: (a) Antinolo, A.; Carrillo-Hermosilla, F.; Fernandez-Galan, R.; Montero-Rama, M. P.; Ramos, A.; Villasenor, E.; Rojas R. S.; Rodriguez-Dieguez, A. *Dalton Trans.* **2016**, *45*, 15350-15363; (b) Edelmann, F. T. *Chem. Soc. Rev.* **2012**, *41*, 7657–7672; (c) Willcocks, A. M.; Robinson, T. P.; Roche, C.; Pugh T.; Richards, S. P.; Kingsley, A. J.; Lowe, J. P.; Johnson, A. L. *Inorg. Chem.* **2012**, *51*, 246-257.

15. Review Articles and Book Chapters for Reactivity and Catalysis of molecular Aluminum Chemistry; (a) Ni, C.; Ma X.; Yang, Z.; Roesky, H. W. *Eur. J. Inorg. Chem.* **2022**, DOI: https://doi.org/10.1002/ejic.202100929; (b) Das, A.; Rej, S.; Panda, T. K. *Dalton Trans.* **2022**, ***51***, 3027-3040; (c) Liu, Y.; Li, J.; Ma, X.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2018**, *374*, 387-415; (d) Caise, A.; Jones, D.; Kolychev, E. L.; Hicks, J.; Goicoechea, J. M.; Aldridge, S. *Chem. Eur. J.* **2018**, *24*, 13624-13635; (e) Weetman, C.; Inoue, S. *ChemCatChem* **2018**, *10*, 4213-4228; (f) Dagorne, S.; Wehmschulte, R. *ChemCatChem* **2018**, *10*, 2509-2520; (g) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, *350*, 14-29; (h) Ananikov, V. P. *Angew. Chem. Int. Ed.* **2016**, *55*, 14904-

14904; (i) Roy, M. M. D.; Omaña, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.* **2021**, *121*, 12784-12965.

16. Stecher, O.; Wiberg, E. Ber. deut. chem. Gesellschaft (A and B Series) 75 (1942) **2003–2012**.
17. Selected References on Application of Classical Metal Reductants: (a) Kokotos, G.; Noula, C. *J. Org. Chem.* **1996**, *61*, 6994-6996; (b) Narasimhan, S.; Madhavan, S.; Prasad, K. G. *J. Org. Chem.* **1995**, *60*, 5314-5315; (c) Kanth, J. V. B.; Periasamy, M. *J. Org. Chem.* **1991**, *56*, 5964-5965; (d) Murphy, D. K.; Alumbaugh, R. L.; Rickborn, B. *J. Am. Chem. Soc.* **1969**, *91*, 2649-2653; (e) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464-1472; (f) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197-1199.
18. Eisch, J. J. *J. Am. Chem. Soc.* **1998**, *120*, 6631-6632.
19. Selected Review Articles on Catalytic Application of Transition Metals: (a) Bose, S. K.; Mao, L.; Kuehn, L.; Radius, U.; Nekvinda, J.; Santos, W. L.; Westcott, S. A.; Steel P. G.; Marder, T. B. *Chem. Rev.* **2021**, *121*, 13238-13341; (b) Liu, H.; Eisen, M. S. *Synthesis* **2020**, *52*, 629-644; (c) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307-3336; (d) Tamang, S. R.; Findlater, M. *Molecules* **2019**, *24*, 3194; (e) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, *5*, 3238-3259; (f) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48*, 1995-2003; (g) Maeda, C.; Miyazaki, Y.; Ema, T. *Catal. Sci. Technol.* **2014**, *4*, 1482–1497; (h) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957-5026; (i) Ghosh, P.; Jacobi von Wangelin, A. *Angew. Chem. Int. Ed.* **2021**, *60*, 16035-16043; (j) Marciniec, B.; Pietraszuk, C.; Pawluć, P.; Maciejewski, H. *Chem. Rev.* **2022**, *122*, 3996-4090.
20. Selected Review Articles on Catalytic Application of Main-Group Metals: (a) Magre, M.; Szewczyk, M.; Rueping, M. *Chem. Rev.* **2022**, *122*, 8261–8312; (b) Banerjee, I.; Panda, T. K. *Appl. Organomet. Chem.* **2021**, *35*, e6333; (c) Bage, A. D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas S. P. *ACS Catal.* **2020**, *10*, 13479-13486; (d) Kuciński, K.; Hreczycho,

G. *Green Chem.* **2020**, *22*, 5210-5224; (e) Saptal, V. B.; Wang, R.; Park, S. *RSC Adv* **2020**, *10*, 43539-43565; (f) Hill, M. S.; Liptrot, D. J.; Weetman, C. *Chem. Soc. Rev.* **2016**, *45*, 972-988.

21. Examples of Molecular Aluminum Hydrides: (a) Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J.* **2019**, *25*, 11918-11923; (b) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1245–1250; (c) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, *18*, 4710-4713; (d) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54*, 10225-10229; (e) Chang, J.-C.; Chen, Y.-C.; Datta, A.; Lin C.-H.; Hsiao, C.-S.; Huang, J.-H. *J. Organomet. Chem.* **2011**, *696*, 3673-3680; (f) Cui, C.; Roesky, H. W.; Hao H.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1815-1817.

22. (a) Gianopoulos, C. G.; Kumar, N.; Zhao, Y.; Jia L.; Kirschbaum, K.; Mason, M. R. *Dalton Trans.* **2016**, *45*, 13787-13797; (b) Gianopoulos, C. G.; Kirschbaum, K.; Mason, M. R. *Organometallics* **2014**, *33*, 4503-4511.

23. (a) Ananikov, V. P. *Sustainable Catalysis with Nonendangered Metals*. *Angew. Chem. Int. Ed.* **2016**, *55*, 14904; (b) Aldridge, S. A.; Downs, J. *The Group 13 Metals Aluminium, Gallium, Indium, and Thallium: Chemical Patterns and Peculiarities*. *Angew. Chem. Int. Ed.* **2011**, *50* (49), 11569.

24. Selected References of Aluminum Catalyzed Transfer Hydrogenation: (a) Yeagle, K. P.; Hester, D.; Piro, N. A.; Dougherty, W. G.; Kassel, W. S.; Graves, C. R. *Aust. J. Chem.* **2015**, *68*, 357-365; (b) McNerney, B.; Whittlesey, B.; Cordes, D. B.; Krempner, C. *Chem. Eur. J.* **2014**, *20*, 14959-14964.

25. Selected Review Articles and References of Hydroelemenation Reactions: (a) Kannan, R.; Chambenahalli, R.; Kumar, S.; Krishna, A.; Andrews, A. P.; Jemmis, E. D.; Venugopal, A. *Chem. Commun.* **2019**, *55*, 14629-14632; (b) Bolley, A.; Specklin, D.; Dagorne, S.

Polyhedron **2021**, *194*, 114956; (c) Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.* **2016**, *6*, 7350-7356.

26. Examples of Al Catalyzed Hydroacetylation Reaction: Zhao, Y.; Ma, X.; Yan, B.; Ni, C.; He, X.; Peng, Y.; Yang, Z. *J. Organomet. Chem.* **2021**, *946-947*, 121879.

27. Selected References of Al based Hydroamination Reactions: (a) Chen, J.; Goforth, S. K.; McKeown, B. A.; Gunnoe, T. B. *Dalton Trans.* **2017**, *46*, 2884-2891; (b) Khandelwal, M.; Wehmschulte, R. J. *J. Organomet. Chem.* **2012**, *696*, 4179-4183.

28. Selected References of Al based Hydrfluorination Reactions: (a) Gu, W.; Haneline, M. R.; Douvris, C.; Ozerov, O. V. *J. Am. Chem. Soc.* **2009**, *131*, 11203-11212; (b) Klahn, M.; Fischer, C.; Spannenberg, A.; Rosenthal, U.; Krossing, I. *Tetrahedron Lett.* **2007**, *48*, 8900-8903.

29. References: (a) Sandford, C.; Aggarwal, V. K. *Chem. Commun.* **2017**, *53*, 5481 – 5494; (b) Leonori, D.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2015**, *54*, 1082 – 1096; (c) *Synthesis and application of organoboron compounds*, ed. Fernandez, E.; Whiting, A. Springer, **2015**; Bertrand, C. *Angew. Chem. Int. Ed.* **2015**, *54*, 15010 – 15011.

30. Application of Boron Reagents: (a) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307- 3336; (b) Magano, J.; Dunetz, J. R. *Chem. Rev.* **2011**, *111*, 2177-2250; (c) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457-2483.

31. (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 486-487; (b) Brown, H. C.; Rao, B. C. S. *J. Am. Chem. Soc.* **1956**, *78*, 5694-5695.

32. (a) Willcox, D. R.; De Rosa, D. M.; Howley, J.; Levy, A.; Steven, A.; Nichol, G. S.; Morrison, C. A.; Cowley, M. J.; Thomas, S. P. *Angew. Chem. Int. Ed.* **2021**, *60*, 20672-20677; (b) Caise, A.; Kolychev, E. L.; Hicks, J.; Fuentes, M. Á.; Goicoechea, J. M.; Aldridge, S. *Dalton Trans.* **2019**, *48*, 10845-10852; (c) Caise, A.; Jones, D.; Kolychev, E. L.; Hicks J.; Goicoechea, J. M.; Aldridge, S. *Chem. Eur. J.* **2018**, *24*, 13624-13635.

33. Aluminum Catalyzed Hydroboration of Carbonyls: (a) Titze, M.; Heitkämper, J.; Junge, T.; Kästner, J.; Peters, R. *Angew. Chem. Int. Ed.* **2021**, *60*, 5544-5553; (b) Chia, C. -C.; Teo, Y. -C.; Cham, N.; Ho, S. Y. -F.; Ng, Z. -H.; Toh, H. -M.; Mézailles, N.; So, C. -W. *Inorg. Chem.* **2021**, *60*, 4569-4577; (c) Weetman, C.; Porzelt, A.; Bag, P.; Hanusch, F.; Inoue, S. *Chem. Sci.* **2020**, *11*, 4817-4827; (d) Ould, D. M. C.; Carden, J. L.; Page, R.; Melen, R. L. *Inorg. Chem.* **2020**, *59*, 14891-14898; (e) Franz, D.; Jandl, C.; Stark, C.; Inoue, S. *ChemCatChem* **2019**, *11*, 5275-5281; (f) Lebedev, Y.; Polishchuk, I.; Maity, B.; Guerreiro, M. D. V.; Cavallo, L.; Rueping, M. *J. Am. Chem. Soc.* **2019**, *141*, 19415-19423; (g) Woodside, A. J.; Smith, M. A.; Herb, T. M.; Manor, B. C.; Carroll, P. J.; Rablen, P. R.; Graves, C. R. *Organometallics* **2019**, *38*, 1017-1020; (h) Zhang, G.; Wu, J.; Zeng, H.; Neary, M. C.; Devany, M.; Zheng, S.; Dub, P. A. *ACS Catal.* **2019**, *9*, 874-884; (i) Liu, Y.; Ma, X.; Ding, Y.; Yang, Z.; Roesky, H. W. *Organometallics* **2018**, *37*, 3839-3845; (j) Liu, Y.; Liu, X.; Liu, Y.; Li, W.; Ding, Y.; Zhong, M.; Ma, X.; Yang, Z. *Inorganica Chim. Acta* **2018**, *471*, 244-248; (k) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.* **2018**, *54*, 1233-1236; (l) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. *Chem. Eur. J.* **2018**, *24*, 4794-4799; (m) Lemmerz, L. E.; McLellan, R.; Judge, N. R.; Kennedy, A. R.; Orr, S. A.; Uzelac, M.; Hevia, E.; Robertson, S. D.; Okuda, J.; Mulvey, R. E. *Chem. Eur. J.* **2018**, *24*, 9940-9948; (n) Pollard, V. A.; Fuentes, M. A.; Kennedy, A. R.; McLellan, R.; Mulvey, R. E. *Angew. Chem. Int. Ed.* **2018**, *57*, 10651-10655; (o) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, *8*, 2001-2005.

34. Metal-Free B-H Addition in Ketones: Wang, W.; Luo, M.; Yao, W.; Ma, M.; Pullarkat, S. A.; Xu, L.; Leung, P.-H. *New J. Chem.* **2019**, *43*, 10744-10749.

35. Metal-Free B-H Addition in Aldehydes: Stachowiak, H.; Kaźmierczak J.; Kuciński, K.; Hreczycho, G. *Green Chem.* **2018**, *20*, 1738-1742.

36. Synthesis and Application of Boron Reagents: (a) Prates, J. L. B.; Pavan, A. R.; dos Santos, J. L. *Curr. Org. Chem.* **2021**, *25*, 1853 – 1867; (b) Buskes, M. J.; Blanco, M. -J. *Molecules* **2020**, *25*, 3493.

37. Main-Group Metal Catalyzed CDC Reactions: (a) Rochette, É.; Boutin, H.; Fontaine, F.-G. *Organometallics* **2017**, *36*, 2870-2876; (b) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De S.; Parameswaran, P.; Roesky, H. W. *J. Am. Chem. Soc.* **2016**, *138*, 2548-2551; (c) Erickson, J. D.; Lai, T. Y.; Liptrot, D. J.; Olmstead, M. M.; Power, P. P. *Chem. Commun.* **2016**, *52*, 13656-13659; (d) Harinath, A.; Anga, S.; Panda, T. K. *RSC Adv.* **2016**, *6*, 35648-35653; (e) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; Wilson, A. S. *Angew. Chem. Int. Ed.* **2015**, *54*, 13362-13365.

38. Transistion Metal Catalyzed CDC Reactions: (a) Fernández-Salas, J. A.; Manzini, S.; Nolan, S. P. *Chem. Commun.* **2013**, *49*, 5829-5831; (b) Bolaño, T.; Esteruelas, M. A.; Gay, M. P.; Oñate, E.; Pastor, I. M.; Yus, M. *Organometallics* **2015**, *34*, 3902-3908.

39. Metal-Free CDC Reactions: Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G. *Chem. Commun.* **2016**, *52*, 10563-10565.

40. Selected References of Metal Based Hydrogenation of Carbonyls: (a) Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. *Chem. Soc. Rev.* **2018**, *47*, 1459-1483; (b) Glatz, M.; Stöger, B.; Himmelbauer, D.; Veiros, L. F.; Kirchner, K. *ACS Catal.* **2018**, *8*, 4009-4016.

41. Selected References: Misal Castro, L. C.; Li, H.; Sortais, J. B.; Darcel, C. *Chem. Commun.* **2012**, *48*, 10514-10516.

42. Metal Catalyzed Deoxygenative Hydroboration of Carboxylic Acids: (a) Yan, B.; Dutta, S.; Ma, X.; Ni, C.; Koley, D.; Yang, Z.; Roesky, H. W. *Dalton Trans.* **2022**, *51*, 6756-6765; (b) Wang, Q.; Li, L.; Li, P.; Yue, X.; Yang, Z.; Pu, M.; Lei, M. *New J. Chem.* **2019**, *43*, 11493-11496; (c) Barman, M. K.; Das, K.; Maji, B. *J. Org. Chem.* **2019**, *84*, 1570-1579; (d) Kisan, S.; Krishnakumar, V.; Gunanathan, C. *ACS Catal.* **2018**, *8*, 4772-4776; (e) Erken, C.; Kaithal,

A.; Sen, S.; Weyhermüller, T.; Hölscher, M.; Werlé, C.; Leitner, W. *Nat. Commun.* **2018**, *9*, 4521.

43. Metal-Free Catalyzed Hydroboration of Carboxylic Acids: (a) Wang, W.; Luo, M.; Zhu, D.; Yao, W.; Xu, L.; Ma, M. *Org. Biomol. Chem.* **2019**, *17*, 3604-3608; (b) Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Chem. Commun.* **2019**, *55*, 1386-1388; (c) Xu, X.; Yan, D.; Zhu, Z.; Kang, Z.; Yao, Y.; Shen, Q.; Xue, M. *ACS Omega* **2019**, *4*, 6775-6783.

44. Metal Catalyzed Carbonate Hydroboration: (a) Szewczyk, M.; Magre, M.; Zubar, V.; Rueping, M. *ACS Catal.* **2019**, *9*, 11634-11639; (b) Cao, X.; Wang, W.; Lu, K.; Yao, W.; Xue, F.; Ma, M. *Dalton Trans.* **2020**, *49*, 2776-2780; (c) Légaré Lavergne, J.; To H.-M.; Fontaine F.-G. *RSC Adv.* **2021**, *11*, 31941-31949; (d) Khuntia, A. P.; Sarkar N.; Patro A. G.; Sahoo R. K.; Nembenna S. *Eur. J. Inorg. Chem.* **2022**, ; (e) Thenarukandiyil, R.; Satheesh V.; Shimon L. J. W.; de Ruiter G. *Chem. Asian J.* **2021**, *16*, 999-1006.

45. Metal Catalyzed Hydrogenation of Carbonate: (a) Kaithal, A.; Hçlscher, M.; Leitner, W. *Angew. Chem. Int. Ed.* **2018**, *57*, 13449-13453; (b) Kumar, A.; Janes, T.; Espinosa-Jalapa, N. A.; Milstein, D. *Angew. Chem. Int. Ed.* **2018**, *57*, 12076-12080.

46. Deoxgenative Hydroboration of Amides using Main-Group Metals: (a) Khalimon, A. Y. *Dalton Trans.* **2021**, *50*, 17455-17466; (b) Yu, C.; Guo, C.; Jiang, L.; Gong, M.; Luo, Y. *Organometallics* **2021**, *40*, 1201-1206; (c) Bisai, M. K.; Gour, K.; Das, T.; Vanka, K.; Sen, S. S. *Dalton Trans.* **2021**, *50*, 2354-2358; (d) Das, S.; Karmakar, H.; Bhattacharjee, J.; Panda, T. K. *Dalton Trans.* **2019**, *48*, 11978-11984; (e) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52*, 13155-13158; (f) Schnitzler, S.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2016**, *55*, 12997-13006; (g) Lampland, N. L.; Hovey, M.; Mukherjee, D.; Sadow, A. D. *ACS Catal.* **2015**, *5*, 4219-4226.

47. Main-Group Catalyzed Hydroboration of Esters: (a) Shi, Y.; Wang, Y.; Huang, Z.; Zhang, F.; Shao, Y. *ACS Omega* **2022**, *7*, 18876-18886; (b) Yan, B.; Dutta, S.; Ma, X.; Ni C.; Koley, D.;

Yang, Z.; Roesky, H. W. *Dalton Trans* **2022**, *51*, 6756-6765; (c) Sai Kumar, G.; Bhattacharjee, J.; Kumari, K.; Moorthy, S.; Bandyopadhyay, A.; Kumar Singh, S.; Panda, T. K. *Polyhedron* **2022**, *219*, 115784; (d) Du, Z.; Behera, B.; Kumar, A.; Ding, Y. *J. Organomet. Chem.* **2021**, *950*, 121982; (e) Bisai, M. K.; Gour, K.; Das, T.; Vanka K.; Sen, S. S. *J. Organomet. Chem.* **2021**, *949*, 121924; (f) Barman, M. K.; Baishya A.; Nembenna, S. *Dalton Trans.* **2017**, *46*, 4152-4156; (g) Mukherjee, D.; Ellern A.; Sadow, A. D. *Chem. Sci.* **2014**, *5*, 959-964; (h) Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Köhn, G.; Weetman, C. *Organometallics* **2011**, *30*, 5556-5559; (i) Brown, H. C.; Rao, B. C. S. *J. Am. Chem. Soc.* **1960**, *82*, 681-686.

48. Selected References of Metal-Based Hydrosilylation of Esters: (a) Clarke, J. A.; Est, A.; Nikonov, G. I. *Eur. J. Org. Chem.* **2021**, *2021*, 4434-4439; (b) Behera, R. R.; Ghosh, R.; Panda, S.; Khamari, S.; Bagh, B. *Org. lett.* **2020**, *22*, 3642-3648; (c) Feng, X.; Ji, P.; Li Z.; Drake, T.; Oliveres, P.; Chen, E. Y.; Song, Y.; Wang, C.; Lin, W. *ACS Catal.* **2019**, *9*, 3327-3337.

49. Selected References of Metal-Based Hydrogenation of Esters: (a) Tadiello, L.; Gandini, T.; Stadler, B. M.; Tin, S.; Jiao, H.; de Vries, J. G.; Pignataro, L.; Gennari, C. *ACS Catal.* **2022**, *12*, 235-246; (b) Liu, W.; Li, W.; Spannenberg, A.; Junge, K.; Beller, M. *Nat. Catal.* **2019**, *2*, 523-528; (c) Thiyagarajan, S.; Gunanathan, C. *Org. lett.* **2019**, *21*, 9774-9778.

50. Metal-Based Hydroboration of Epoxides: (a) Magre, M.; Paffenholz, E.; Maity, B.; Cavallo, L.; Rueping, M. *J. Am. Chem. Soc.* **2020**, *142*, 14286-14294; (b) Cao, X.; Li, J.; Zhu, A.; Su, F.; Yao, W.; Xue, F.; Ma, M. *Org. Chem. Front.* **2020**, *7*, 3625-3632; (c) Wang, Z.; Patnaik, S.; Eedugurala, N.; Manzano, J. S.; Slowing, I. I; Kobayashi, T.; Sadow, A. D.; Pruski M. *J. Am. Chem. Soc.* **2020**, *142*, 2935-2947; (d) Desnoyer, A. N.; Geng, J.; Drover, M. W.; Patrick, B. O.; Love, J. A. *Chem. Eur. J.* **2017**, *23*, 11509-11512; (e) Song, H.; Ye, K.; Geng,

P.; Han, X.; Liao, R.; Tung, C.-H.; Wang, W. *ACS Catal.* **2017**, *7*, 7709-7717; (f) Sreekumar, R.; Padmakumar, R.; Rugmini, P. *Tetrahedron Lett.* **1998**, *39*, 5151-5154.

51. Application Heteroallenes: (a) Mitchell, S. M.; Niradha Sachinthani, K. A.; Pulukkody, R.; Pentzer, E. B. *ACS Macro Lett.* **2020**, *9*, 1046-1059; (b) Jurrat, M.; Pointer-Gleadhill, B. J.; Ball, L. T.; Chapman, A.; Adriaenssens, L. *J. Am. Chem. Soc.* **2020**, *142*, 8136-8141.

52. Selected References of Synthesis of Amides (Formamidine, Formamide, and Thioformaide): (a) Su, Z.; Feng, Y.; Zou, R.; Qiu, X.; Wang, J.; Tao, C. *Chem. Commun.* **2020**, *56*, 7483-7486; (b) Pace, V.; Monticelli, S.; de la Vega-Hernandez, K.; Castoldi, L. *Org Biomol Chem* **2016**, *14*, 7848-7854; (c) Peddarao, T.; Baishya, A.; Barman, M. K.; Kumar, A.; Nembenna, S. *New J. Chem.* **2016**, *40*, 7627-7636; (d) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790-792.

53. Main-Group Catalyzed Hydroboration of Carbodiimides: (a) Yan, B.; He, X.; Ni, C.; Yang, Z.; Ma, X. *ChemCatChem* **2020**, *13*, 851-854; (b) He, X.; Yan, B.; Ni, C.; Zhao, Y.; Yang, Z.; Ma, X. *Asian J. Org. Chem.* **2021**, *10*, 196-201; (c) Bakewell, C. *Dalton Trans.* **2020**, *49*, 11354-11360; (d) Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics* **2019**, *38*, 3092-3097; (e) Liu, H.; Kulbitski, K.; Tamm, M.; Eisen, M. S. *Chem. Eur. J.* **2018**, *24*, 5738-5742; (f) Rauch, M.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 13264-13267; (g) Weetman, C.; Hill, M. S.; Mahon, M. F. *Chem. Eur. J.* **2016**, *22*, 7158-7162; (h) Huckaba, A. J.; Hollis, T. K.; Reilly, S. W. *Organometallics* **2013**, *32*, 6248-6256; (i) Ojima, I.; Inaba, S.-I. *J. Organomet. Chem.* **1977**, *140*, 97-111.

54. Metal Catalyzed Hydroboration of Isocyanates: (a) Gudun, Kristina, A.; Tussupbayev, S.; Slamovac, A.; Khalimon, A. Y. *Org. Biomol. Chem.* **2022**, *20*, 6821–6830; (b) Pandey, V. K.; Sahoo, S.; Rit, A. *Chem. Commun.* **2022**, *58*, 5514-5517; (c) Yang, Y.; Anker, M. D.; Fang, J.; Mahon, M. F.; Maron, L.; Weetman, C.; Hill, M. S. *Chem Sci* **2017**, *8*, 3529-3537;

(d) Ma, M.; Wang, W.; Luo, M.; Xiao, Q.; Xu, L. CN Pat 108358959, **2018**; (e) Ma, M.; Xiao, Q.; Cao, X.; Zheng, Y. CN Pat. 111410668, **2020**.

55. Main-Group Metal Catalyzed Hydroboration of Alkenes and Isonitriles: (a) Liu, J.; Wu, C.; Hu, T.; Yang, W.; Xie, Y.; Shi, Y.; Liu, Q.; Shao, Y.; Zhang, F. *J. Org. Chem.* **2022**, *87*, 3442-3452; (b) Wang, Z.-C.; Wang, M.; Gao, J.; Shi, S.-L.; Xu, Y. *Org. Chem. Front.* **2019**, *6*, 2949-2953; (c) Bisai, M. K.; Yadav, S.; Das, T.; Vanka, K.; Sen, S. S. *Chem. Commun.* **2019**, *55*, 11711-11714; (d) Li, F.; Bai, X.; Cai, Y.; Li, H.; Zhang, S.-Q.; Liu, F.-H.; Hong, X.; Xu Y.; Shi, S.-L. *Org. Process Res. Dev.* **2019**, *23*, 1703-1708; (e) Jaladi, A. K.; Shin, W. K.; An, D. K. *RSC Adv.* **2019**, *9*, 26483-26486; (f) Harinath, A.; Banerjee, I.; Bhattacharjee, J.; Panda, T. K. *New J. Chem.* **2019**, *43*, 10531-10536; (g) Wu, Y.; Shan, C.; Ying, J.; Su, J.; Zhu, J.; Liu, L. L.; Zhao, Y. *Green Chem.* **2017**, *19*, 4169-4175; (h) Rauch, M.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 13264-13267; (i) Yin, Q.; Kemper, S.; Klare, H. F.; Oestreich, M. *Chem. Eur. J.* **2016**, *22*, 13840-13844; (j) Weetman, C.; Hill, M. S.; Mahon, M. F. *Chem. Commun.* **2015**, *51*, 14477-14480; (k) Barnett, B. R.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Chem. Commun.* **2015**, *51*, 541 – 544.

56. Selected examples of Transition and Lanthanide Metal Catalyzed Hydroboration of Alkenes: (a) Su, W.; Qiao, R.-X.; Jiang, Y.-Y.; Zhen, X.-L.; Tian, X.; Han, J.-R.; Fan, S.-M.; Cheng, Q.; Liu, S. *ACS Catal.* **2020**, *10*, 11963-11970; (b) Huang, J.; Yan, W.; Tan, C.; Wu, W.; Jiang, H. *Chem. Commun.* **2018**, *54*, 1770-1773.

57. Review of Metal-Based Hydroboration of Alkynes: Rej, S.; Das, A.; Panda, T. K. *Adv. Synth. Catal.* **2021**, *363*, 4818-4840.

58. Review of Metal-Based Hydroboration of Nitriles: (a) Bazkiaei, A. R.; Findlater, M.; Gorden, A. E. V. *Org. Biomol. Chem.* **2022**, *20*, 3675-3702; (b) Hayrapetyan, D.; Khalimon, A. Y. *Chem Asian J.* **2020**, *15*, 2575-2587.

59. Aluminum Catalyzed Hydrosilylation of Unsaturated Functionalties: (a) Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics* **2017**, *36*, 4810-4815; (b) Wehmschulte, R. J.; Saleh, M.; Powell D. R. *Organometallics* **2013**, *32*, 6812-6819; (c) Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 7323-7326; (d) Koller, J.; Bergman, R. G. *Organometallics* **2012**, *31*, 2530-2533.

60. Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673-8674.

Chapter 2

Aluminum-Catalyzed Selective Hydroboration of Carbonyls and Dehydrocoupling of Alcohols, Phenols, Amines, Thiol, Selenol, and Silanols with HBpin

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Sarkar, N.; Sahoo, R. K.; Patro, A G.; Nembenna, S. *Polyhedron* **2022**, *222*, 115902 **(*Invited, Part of Special Issue: Catalytic Applications of Main group Compounds; Edited by Gerard Parkin*)**.

Abstract

A popular *N, N'*-chelated NacNac analog, *i.e*., conjugated bis-guanidinate (CBG)stabilized aluminum dihydride $LAlH_2$(**1**) [L = {(ArHN)(ArN)– C=N–C=(NAr)(NHAr)}; Ar = 2,6-Et_2-C_6H_3], demonstrates excellent catalytic hydroboration of a wide array of carbonyls with pinacolborane (HBpin) under neat conditions with good tolerance of reducible functional groups such as alkyl, alkene, halide, nitrile, nitro, ester, amide, and heteroaryl. In addition, complex **1** catalyzed cross-dehydrocoupling (CDC) of alcohols, phenols, amines, thiol, selenol, and silanols with HBpin under mild reaction conditions was investigated. Furthermore, several control experiments have been performed to understand the mechanisms of hydroboration and CDC reactions. All corresponding catalytic intermediates have been identified and characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic methods. In contrast to several reports on metal-catalyzed hydroboration of carbonyls, to the best of our knowledge, this is the second report for the molecular aluminum catalyzed CDC of organic substrates with HBpin.

2.1. Introduction

Among the p-block elements, aluminum is the highest earth-abundant, cheap and eco-friendly element compared to precious transition metals.[1] Over the past few years, aluminum-based

reagents and molecular compounds were widely used in mimicking the catalytic properties of both transition and lanthanide metals which includes various hydroelementation reactions such as hydrosilylation,[2] hydroboration,[3] hydrostannation[2b] hydroamination[4] along with dehydrogenation,[5] transfer hydrogenation,[6] and hydrodefluorination[7] type reactions. Therefore, the use of aluminum-based catalysts, particularly molecular aluminum catalysts, which help in understanding the reaction mechanisms in homogenous catalysis is significant to the extent of sustainable catalytic pathway.[1] Recently, numerous transition and main-group metal catalysts have been reported for carbonyl hydroboration;[8] however, only a few examples of aluminum catalyzed aldehyde and ketone hydroboration have been reported.[3] In 2015, Roesky and coworkers[3m] reported that six-membered ^{Dipp}NacNac aluminum hydride, LAlH(OTf); (L = $HC(CMeNAr)_2$, Ar = 2,6-$^{i}Pr_2$-C_6H_3)catalyzed carbonyl hydroboration for the first time. Various molecular aluminum catalysts have been synthesized, which were utilized for several unsaturated organic transformations via hydroboration.[3, 8, 9] There are only two reports that have been found of solvent and metal-free carbonyl hydroboration,[10] but the catalytic procedures require an excessive quantity of reducing reagent and very high temperature upto 140 ^{o}C.

Besides hydroboration reactions, it has been discovered that the cross-dehydrocoupling(CDC) reactions can be an alternate route for synthesizing various stable boron reagents, which were used for multiple coupling processes.[11] The first molecular metal-based dehydrocoupling reaction was introduced by Nolan and coworkers.[12] Later, Yus[13] and Hill's[14] research groups developed osmium and group 2 metals catalyzed CDC reactions. Furthermore, Panda,[15] Power,[16] Yang[17] and Fontaine[18] groups extend the CDC reactions in alcohols, amines, selenols, and thiols with HBpin. In 2016 Bertrand and coworkers[19] reported solvent and metal-free cross-dehydrocoupling reactions. However, many substrates require a long duration of time (upto 96 h)

and high heating for complete dehydrocoupling. So, in this context, it can be concluded that metal-based dehydrocoupling reactions are still beneficial over metal-free catalytic reactions.

An earlier report of our group described the catalytic application of well-defined four-coordinated thermally stable aluminum monohydride, $LAlH{\cdot}NMe_2Et$; {L = ($MesNCMe_2C(H)MeNMes$; Mes = 2,4,6-Me_3-C_6H_2)}[3l] for carbonyls reduction via hydroboration with good excellent chemoselectivity. In line with this study, it was delighted that our previously reported NacNac analog, conjugated bis-guanidinate (CBG) stabilized six-membered aluminum dihydride (**1**)[9b], demonstrates good catalytic activity at mild reaction conditions. The complex $LAlH_2$(**1**) [L = {(ArHN)(ArN)– C=N–C=(NAr)(NHAr)}; Ar = 2,6-Et_2-C_6H_3] catalyzed the complete conversion of various functionalized carbonyl substrates to their corresponding boronate esters with a low catalyst loading. Moreover, catalyst **1** has been tested in neat conditions for CDC reactions of various functional groups such as alcohols, phenols, amines, thiol, selenol, and silanols. All selected substrates underwent successful coupling with pinacolborane. To the best of our knowledge, this is the second report[17] on the aluminum-catalyzed wide range of dehydrocoupling reactions with HBpin under mild conditions.

2.2. Result and Discussion

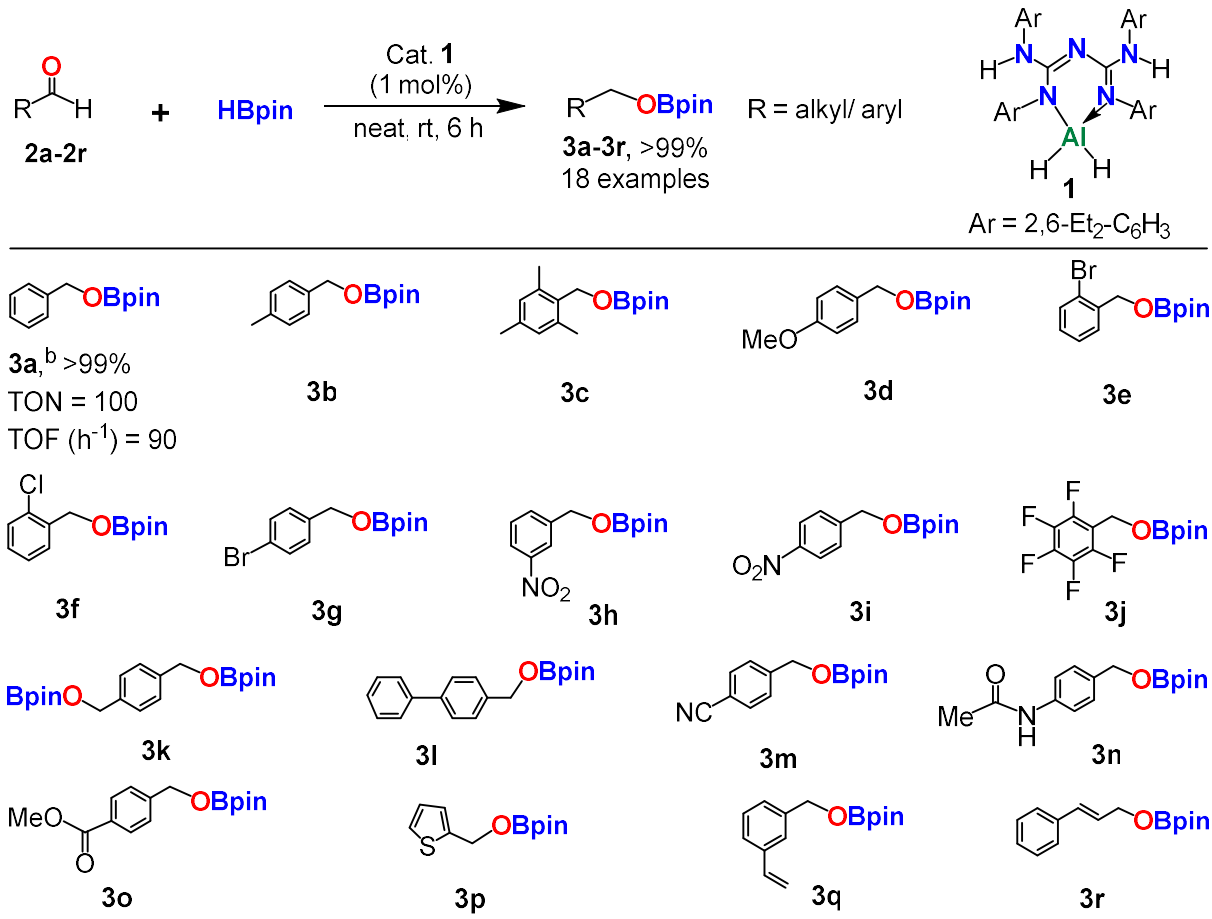
A recent report demonstrated the synthesis of a well-defined six-membered aluminum dihydride (**1**)[9b] bearing an N, N'-chelated conjugated bis-guanidinate ligand. Compound **1** can be easily accessed by the deprotonation of LH with alane, $AlH_3{\cdot}NMe_2Et$. Interesting facts of the reported compound **1** are a robust catalyst as it is being used for hydroboration of challenging functional groups such as nitrile, alkyne, alkene, carbodiimide, and isocyanide. The earlier results prompted us to investigate further the catalytic property of compound **1** in the hydroboration of carbonyls and dehydrocoupling reactions.

2.2.1. Hydroboration of Aldehyde

Our initial examination was started by adding 5 mol% of compound **1** to an equimolar solution of pinacolborane and benzaldehyde at room temperature (Table S1, ESI). It was observed that the complete conversion of benzaldehyde into corresponding boronate ester **3a** $PhCH_2OBpin$ after 12 h in C_6D_6. Further decrease in reaction time and catalyst loadings 3 mol% and 1 mol% afforded the complete formation of **3a** with 99% yield. A similar observation was found under neat conditions (entry 5 of Table S1 of ESI). Further decrease in catalyst load results in low yield%. Interestingly, entry 8 shows high TON (100) and TOF (90 h^{-1}) for benzaldehyde hydroboration. In contrast, the catalyst-free reduction of benzaldehyde displayed only 40% of **3a**. With the final optimization studies in hand, a wide range of aldehydes was explored with good tolerance of reducible functional groups such as alkyl, halide, nitro, alkene, nitrile, amide, ester, and heterocycles by using compound **1** (Table 2.1.).

Under the neat condition, aryl aldehydes with electron-donating groups (**2b-2d**), and electron-withdrawing groups (**2e-2j**), underwent complete hydroboration into corresponding boronate esters (**3b-3j**) in 6h. Recently, Yao *et al.*[20] have reported $KOtBu/BEt_3$ catalyzed deoxygenative reduction of nitroarenes and nitroalkanes with excess HBpin under extreme conditions. Interestingly in our current methodology, a complete reduction of only carbonyl moiety (C=O) was detected in 3-nitrobenzaldehyde (**2h**) and 4-nitrobenzaldehyde (**2i**), with unaffected nitro functional groups for products (**3h** and **3i**). In addition, the hydroboration of terephthaldehdye (**2k**) bearing two reducible carbonyl moieties afforded the diboronate ester (**3k**) in good yield under two equivalents of pinacolborane. Biphenyl-4-carboxaldehyde (**2l**) was efficiently reduced into biphenylborate ester (**3l**) with a 99% yield.

Table 2.1. Substrate scope for aldehyde hydroboration catalyzed by aluminum-dihydride (**1**).[a]

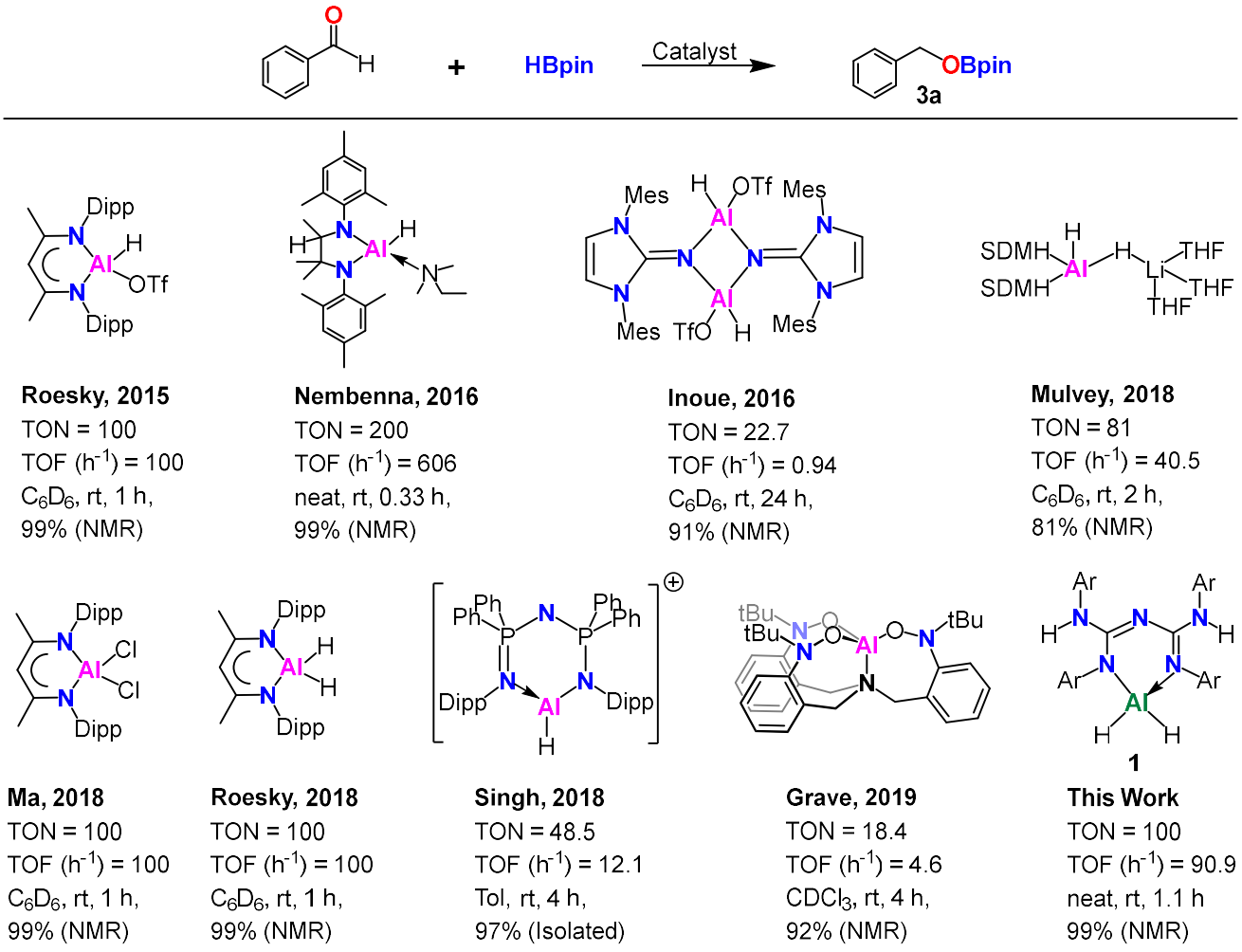


[a]Reaction conditions: aldehyde (1.0 equiv., 0.3 mmol), pinacolborane (1.0 equiv., 0.3 mmol), catalyst **1** (1 mol%), neat, 6 h at room temperature under inert N_2. The yield was examined by ^{1}H NMR spectroscopy based on consumption of starting material and identified newly formed characteristic proton (RCH_2OBpin) signal confirmed the product. [b]For compound **3a**, TOF was 90.9 h-1 resulting in a shorter reaction time (1.1 h). TON was calculated by dividing the number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by the time of reaction.

It was shown that effective chemoselective hydroboration in the additional substrate scope of functionalized aldehydes such as 4-cyanobenzaldehyde, 4-acetamidobenzaldehyde, and methyl 4-formylbenzoate (**2m-2o**), only aldehyde moiety undergoes complete reduction (**3m-3o**). At the same time, nitrile, amide, and ester functional groups were unaffected. Moreover, under the

optimized conditions, hydroboration of the heterocyclic aldehyde, i.e., 2-thiophene carboxaldehyde (**2p**), transformed into corresponding heterocyclic boronate ester product (**3p**). Eventually, the current methodology also affords chemoselective hydroboration of aldehydes in the presence of internal and terminal alkenes (**2q**-**2r**). Alkene groups remain unaltered in both products (**3q** and **3r**).

In the end, the catalytic performance of compound **1** with selected other aluminum-based hydroboration of benzaldehyde was displayed (Scheme 2.1.).



Scheme 2.1. Comparison of catalytic efficiencies of selected aluminum catalysts for hydroboration of benzaldehyde.[a]

[a]TON was calculated by dividing the number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by the time of reaction.

The reaction was performed at rt with low catalyst load and lesser time interval to afford high TON (100) and TOF (90) for reduction of PhCHO into corresponding boronate ester **3a** in comparison of reported Al catalysts (TON = 20-100 and TOF = 0.9-606 h^{-1}).[3b, 3d-3f, 3j-3k, 3l-3m]

2.2.2. Hydroboration of Ketone

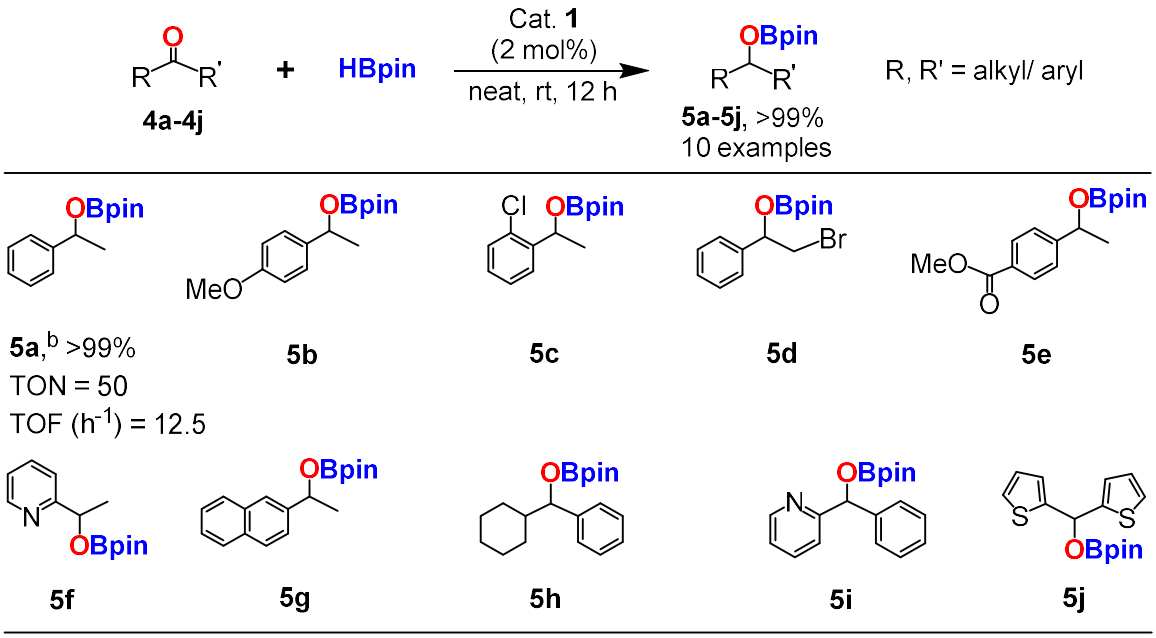
Additionally, compound **1** was used to investigate the B-H addition in ketones. Initial examination for reduction of acetophenone by compound **1** under various conditions was performed (Table S2 of ESI). It was discovered that the most effective way to catalyze the hydroboration of acetophenone is using 2 mol% of compound **1** at room temperature (entry 5 of Table S2, ESI). Lower catalyst amount results in a lesser reduction of acetophenone. Entry 9 displayed a high TON (50) and TOF (12.5 h^{-1}) for acetophenone hydroboration. In catalyst-free conditions, only 30% formation of **5a** was found. With the final optimization of acetophenone reduction, the substrate scope of compound **1** catalyzed ketone hydroboration was thoroughly investigated and summarized in Table 2.2. Analysis of all catalytic reductions revealed a complete formation of hydroborated products (**5a-5j**), including with good tolerance of methoxy, halide, ester, pyridine, heteroaryl groups.

In initial substrate screening, aryl ketones with electron-donating and electron-withdrawing groups were fully hydroborated into corresponding aryl boronate esters (**5b-5d**) unaffected methoxy and halide groups under solvent-free conditions similar to a previously reported analog[3m] of compound **1**.

More importantly, methyl 4-acetylbenzoate (**4e**) affords 99% of corresponding boronate ester (**5e**), demonstrating an effective intramolecular chemoselective hydroboration of ketone moiety over reducible ester functional group. A similar observation was observed in 2-acetylpyridine

(**4f**), where the carbonyl group at ortho position was fully hydroborated (**5f**) with untouched pyridine moiety. Treatment of 2-napthylmethylketone (**4g**) with equimolar HBpin yielded corresponding naphthyl boronate ester (**5g**) in 99% yield.

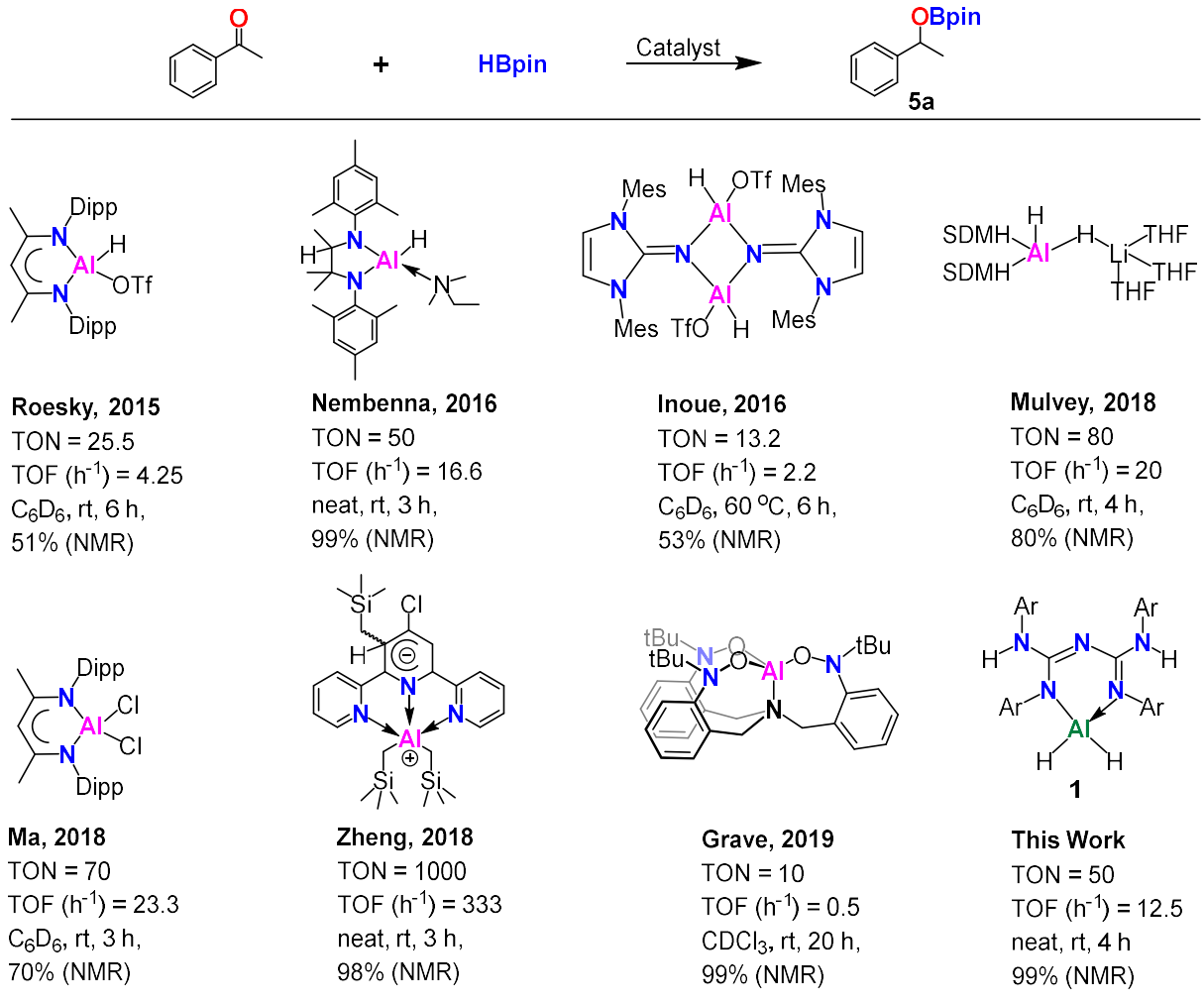
Table 2.2. Substrate scope for ketone hydroboration catalyzed by aluminum-dihydride (**1**).[a]



[a]Reaction conditions: ketones (1.0 equiv., 0.3 mmol), HBpin (1.0 equiv., 0.3 mmol), and catalyst **1** (2 mol%) were stirred in neat for 12 h at rt under N_2. The yield was examined by ^{1}H NMR spectroscopy based on consumption of starting material and identified newly formed characteristic proton (RC*H*R'OBpin) signal confirmed the product. [b]For compound **5a**, TOF was 12.5 h^{-1}, resulting from a shorter reaction time (4 h). TON was calculated by dividing the number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by the time of reaction.

Next, the investigation was conducted for the selective reduction of benzoylcyclohexane and heteroaryl ketones (**4h-4j**). It is worth mentioning that all selected ketones **4h-4j** were quantitatively converted into desired boronates esters (**5h-5j**) with no change in standard conditions.

At last, the catalytic activity of selected aluminum compounds for acetophenone hydroboration was compared with present CBG supported aluminum hydride complex **1** (Scheme 2.2.). The catalytic experiments were done at mild conditions, which resulted in a high turnover number (TON, 50) and TOF (12.5 h^{-1}) of reduction of $PhCOCH_3$ to desired aryl boronate ester **5a** as compared to published aluminum catalysts (TON = 10-1000 and TOF = 0.5-333 h^{-1}).[3b-3c, 3e-3f, 3k-3m]



Scheme 2.2. Comparison of catalytic efficiencies of selected aluminum catalysts for hydroboration of acetophenone.[a]

[a]TON was calculated by dividing the number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by the time of reaction.

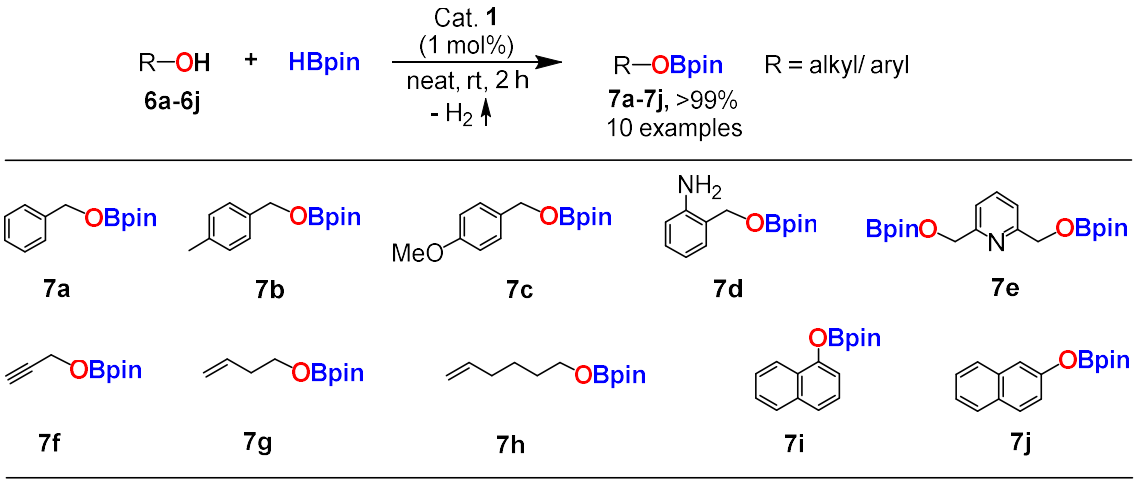
2.2.3. Dehydrocoupling of Alcohols and Phenols

As mentioned before, as far as aluminum-catalyzed CDC coupling of alcohols and phenols is concerned, only the sole example is known in the literature.[17] Thus, it was decided to investigate the CDC reactions with HBpin.

Our best effort revealed that upto one mol% catalyst (**1**) loading and benzyl alcohol was quantitatively coupled with pinacolborane at rt under neat conditions (entry 7 of Table S3, ESI). The formation of $PhCH_2OBpin$, **7a** was analyzed by ^1H NMR spectroscopy. In addition to experiments, it was noticed that 60% conversion was found under catalyst and solvent-free environments (Table S3, entry 8).

The successful dehydrocoupling of benzyl alcohol by compound **1** encouraged the screening of additional substrates (Table 2.3.).

Table 2.3. Substrate scope for boron-alcohols/phenols dehydrocoupling catalyzed by aluminum-dihydride (**1**).[a]



[a]Reaction conditions: alcohols/ phenols (1.0 equiv., 0.3 mmol), HBpin (1.0 equiv., 0.3 mmol), catalyst **1** (1 mol%) was stirred in neat for 2 h at rt under N_2. The yield was examined by ^1H NMR spectroscopy based on consumption of starting material and identified newly formed characteristic proton signal confirmed the product.

Alcohols with electron-donating (-Me, -MeO) and reducible functionalities such as amine, pyridine, alkyne, and alkenes were successfully coupled with pinacolborane to afford the

corresponding products (**7b-7h**) in excellent yields (>99%). In boronate esters **7d-7h**, compound **1** affords intramolecular chemoselective B-H/H-O CDC of alcohols with unaffected amine, pyridine, alkyne, and alkenes reducible functional groups. The above chemoselective catalytic results are better than reported analogs of Roesky's (NacNac)AlH_2 with even the same aryl substituent on the nitrogen donors[17] aluminum-catalyzed CDC of alcohols. Similarly, a complete cross-coupling of 1-naphthol (**6i**) and 2-naphthol (**6j**) with one equiv. HBpin yielded corresponding boronate esters **7i** and **7j** in quantitative yields.

2.2.4. Dehydrocoupling of Amines

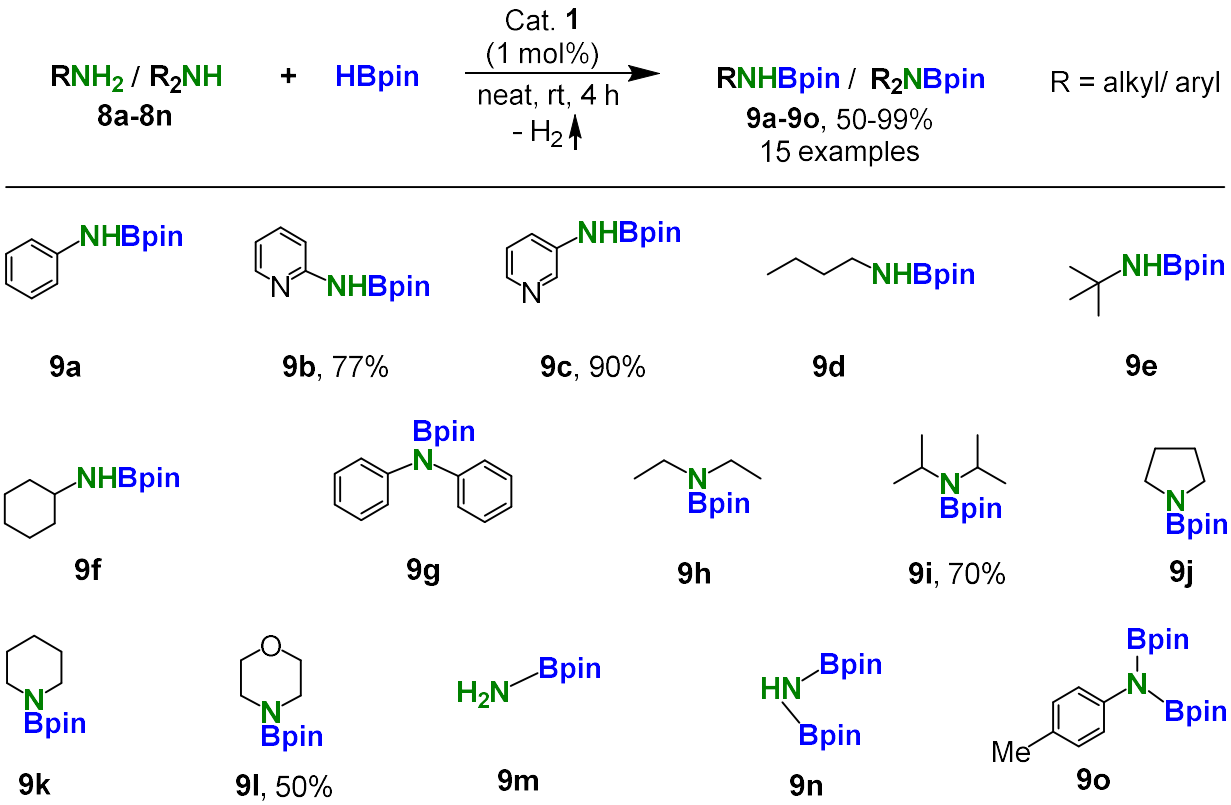
The B-H/H-N CDC using amines as substrates was studied to broaden various cross-dehydrocoupling processes. The NMR-scale experiments revealed a quantitative coupling of aniline with HBpin into corresponding borylated aniline **9a** in 4 h under one mol% catalyst load (entry 5 of Table S4, ESI). This is the best result for CDC of aniline with catalyst **1**. However, only 40% of product **9a** was discovered in solvent and catalyst-free conditions.

With the above-optimized result, the detailed summary of substrate scope for coupling various amines is in Table 2.4. The formation of all aminoboranes (**9a-9o**) was analyzed by ^{1}H NMR spectroscopy with nitromethane as an internal standard. In the initial screening with heterocyclic amines such as 2-aminopyridine and 3-aminopyridine (**8b-8c**), as a coupling participant, there was a moderate conversion observed with yields of 77-90% (**9b-9c**). In the case of aliphatic 1^o amines, i.e., **8d-8f**, in each case, complete conversion was noticed with vigorous evolution of dihydrogen gas to afford amino boranes **9d-9f**. The coupling of diphenylamine **8g** with HBpin in a 1:1 molar ratio yielded a quantitative diphenyl-amino(pinacol)borane**9g** at room temperature.

In addition, 2^o alkyl amines (acyclic and cyclic) were also employed as a coupling participant. Next, the complete formation of corresponding secondary amino boranes for 2^o amine substrates

was detected for diethylamine, piperidine, and pyrrolidine (**9h, 9j,** and **9k**) except diisopropylamine and morpholine, where only 50-70% of amino(pinacol)boranes (**9i** and **9l**) was found.

Table 2.4. Scope of the amine–borane dehydrocoupling reaction catalyzed by aluminum-dihydride (**1**).[a]



[a]Reaction conditions: Conditions: amines (1.0 equiv., 0.3 mmol), HBpin (1.0 equiv., 0.3 mmol), catal. **1** (1 mol%) was stirred in neat for 4 h at rt under N_2. The yield for aminoboranes was analyzed by using nitromethane as an internal standard.

Finally, both mono- and di-coupled products (**9m-9n**) were isolated with ammonia at rt. Both amino-borane products were fully characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, similar to the reported CDC of ammonia by Power and coworkers.[16]

A similar strategy was applied for *p*-toluidine, where two equivalent of pinacolborane affords 1,1-diborylamine ester product (**9o**) with 99% yield. The single-crystal X-ray diffraction method

confirmed compound **9o** (Figure 2.1.) (complete crystal and structure refinement data is provided in supporting information, Table S5).

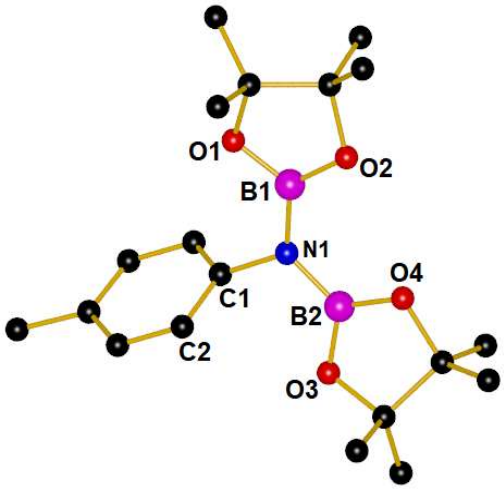
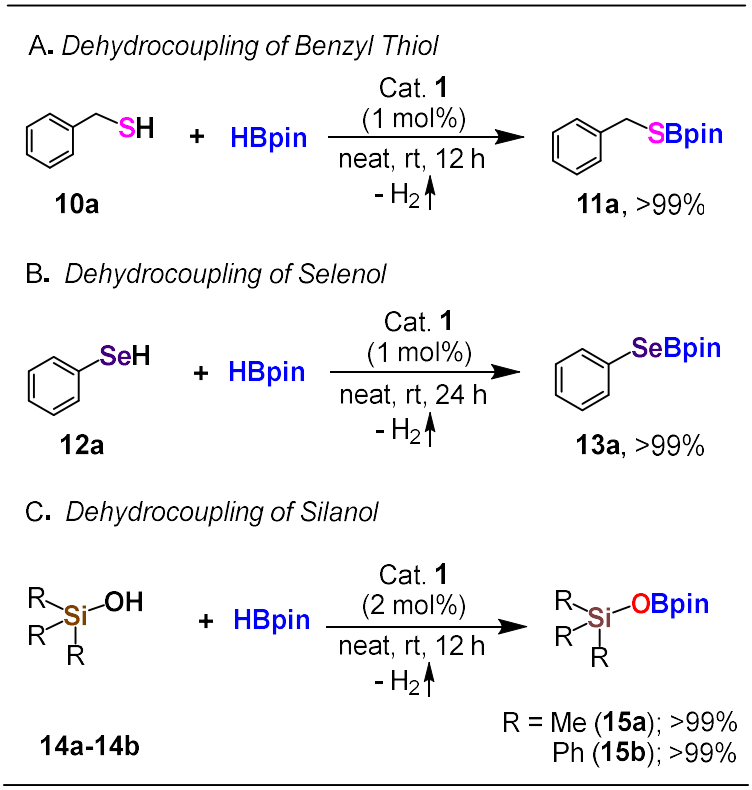


Figure 2.1. Molecular structure of **(9o).** The thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): N1–B1 1.437(2), N1–B2 1.438(2), B1–O1 1.379(2), B1–O2 1.372(2), B2–O3 1.376(2), B2–O4 1.368(2), N1–C1 1.453(2), C1–C2 1.389(2). N1–B1–O1 121.67(16), N1–B1–O2 124.93(16), N1–B2–O3 121.08(16), N1–B2–O4 125.19(16), N1–C1–C2 119.79(16), C1–N1–B1 116.39(14), C1–N1–B2 116.99(14), B1–N1–B2 125.79(15).

2.2.5. Dehydrocoupling of Benzyl Thiol, Selenol, and Silanols

In the past few years, only a handful of examples of metal-catalyzed dehydrocoupling of organic thiols, selenol, and silanols have been reported[12, 17-18, 21] under mild conditions.

To our delight, complex **1** efficiently catalyzed the CDC of above mentioned functional groups at neat conditions with low catalyst loadings (Scheme 2.3.).



Scheme 2.3. Dehydrocoupling of benzyl thiol, selenol, and silanol with pinacolborane catalyzed by aluminum-dihydride (**1**).[a]

[a]Reaction conditions: benzyl thiol/selenol/silanols (1.0 equiv., 0.3 mmol), HBpin (1.0 equiv., 0.3 mmol), catalyst **1** (1-2 mol%) was stirred in neat condition for 12-24 h at rt under N_2. The yield for thiol/selenol/silanol-borane dehydrocoupling was examined by ^{1}H NMR spectroscopy based on consumption of starting material and the newly formed characteristic proton signal confirmed the product.

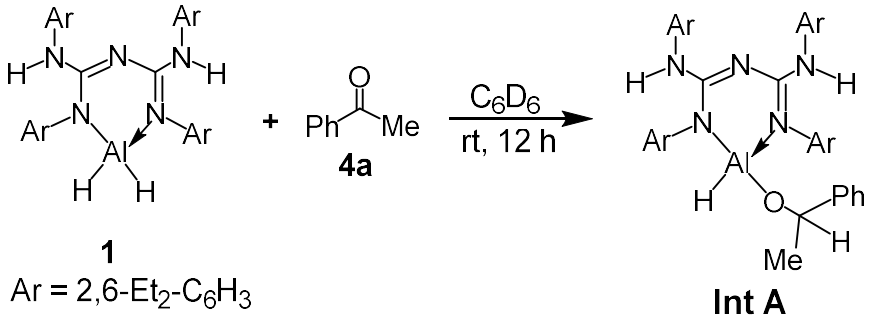
The coupling of benzyl mercaptan **10a** with pinacolborane in 12 h afforded corresponding thioborane (**11a**) with a good yield. Similarly, phenylselenol (**12a**) was quantitatively converted into hydroborated product **13a** at rt. In addition, the dehydrocoupling of trimethylsilanol and triphenylsilanol (**14a-14b**) with pinacolborane yielded the desired borasiloxanes (**15a-15b**) in 99% yields. In solvent and catalyst-free conditions, benzyl mercaptan and phenylselenol (**10a** and **12a**) were not coupled with HBpin except triphenylsilanol (**14b**), where only 5% of

corresponding borasiloxane (**15b**) was found. All cross-dehydrocoupling reactions were analyzed by ^{1}H NMR spectroscopy.

2.2.6. Mechanism for Carbonyl Hydroboration and Dehydrocoupling Reactions

2.2.6.1. Control Reaction of Compound 1's Al-H Insertion in Acetophenone

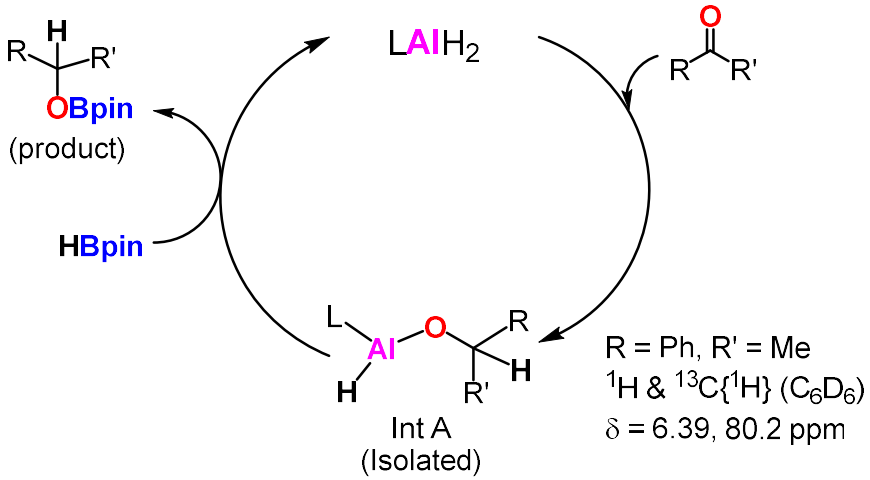
To establish the CBG aluminum-dihydride **1** catalyzed carbonyl hydroboration mechanism, I performed a 1:1 stoichiometric reaction between catalyst **1** and acetophenone in C_6D_6 at rt (Scheme 2.4.). NMR studies monitored the reaction. The ^{1}H NMR spectrum exhibits a characteristic signal of methylene proton for AlHOC(*H*) moiety (**IntA**) at 6.39 ppm, while the $^{13}C\{^{1}H\}$ NMR spectrum displays the carbon signal at 80.2 ppm.



Scheme 2.4. Control reaction for the synthesis of Int A.

2.2.6.2. Catalytic Cycle of Aluminum (1) Catalyzed Carbonyl Hydroboration

Based on the previously established mechanism of aluminum catalyzed hydroboration of carbonyls[3a, 3h, 3j, 3l, 3m] and the above control experiment, suggest an insertion / σ-bond metathesis model reaction mechanism displayed in Scheme 2.5. The C=O group is inserted into the Al-H function that initiates the catalytic cycle to afford the aluminum alkoxide complex (**Int A**). The **IntA** reacts with pinacolborane to yield boronate ester product and rebirth of catalyst **1**. The second step proceeds via TS, where σ-bond (Al-O/B-H) metathesis happens. The control reaction of Int A and HBpin has been carried out to confirm the Al-O/B-H bond metathesis; unfortunately, it was resulting a mixture of products.[22]



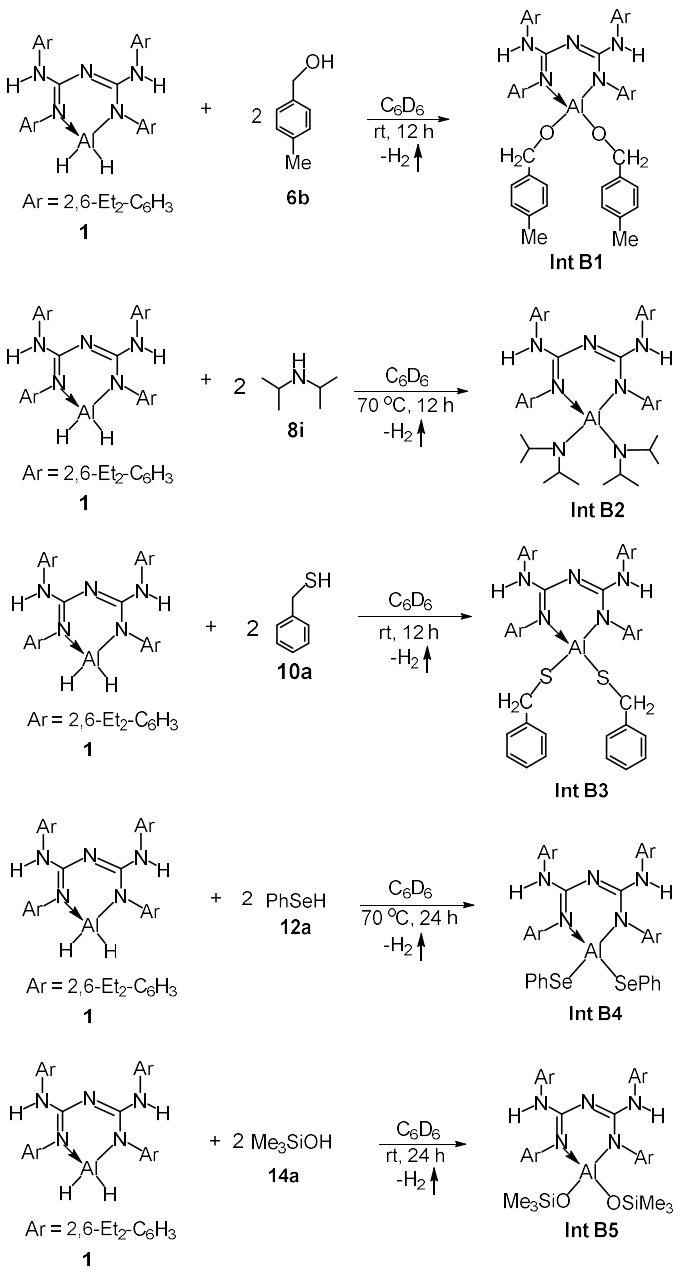
Scheme 2.5. A probable mechanism for $LAlH_2$ (**1**) catalyzed hydroboration of carbonyls.

2.2.6.3. Control Reactions for Cross-Dehydrocoupling Reactions

Five independent control experiments have been performed to gain insights into the mechanism for Al hydride (**1**) catalyzed dehydrocoupling reactions (Scheme 2.6.). All intermediates IntB1-IntB5 were analyzed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, and corresponding spectral data were provided in supporting information. Further, a stoichiometric reaction of **Int B2** and HBpin in a 1:2 molar ratio has been performed in C_6D_6 at 80 °C for 12 h in a J Young valve NMR tube. NMR studies noticed a clean formation of compounds **1** and **9i** (Scheme 2.7.). The Intermediate B2 was further characterized by Heteronuclear Multiple Bond Correlation (HMBC) NMR spectroscopy in which proton interaction with carbon separated by two and three bonds was analyzed in the alkyl and aryl region.

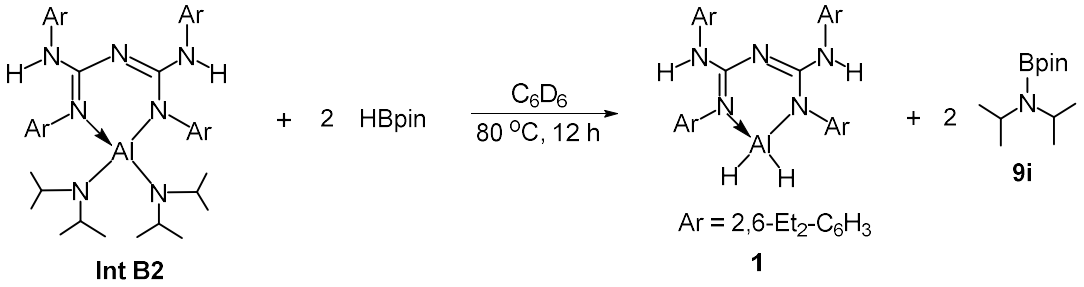
2.2.6.4. Catalytic Cycle of Aluminum (1) Catalyzed Dehydrocoupling Reactions

As examined from the above-control reactions and reported β-diketiminate metal-based CDC, [14, 17] mechanisms for Al hydride **1** catalyzed dehydrocoupling reactions were proposed (shown in Scheme 2.8.).

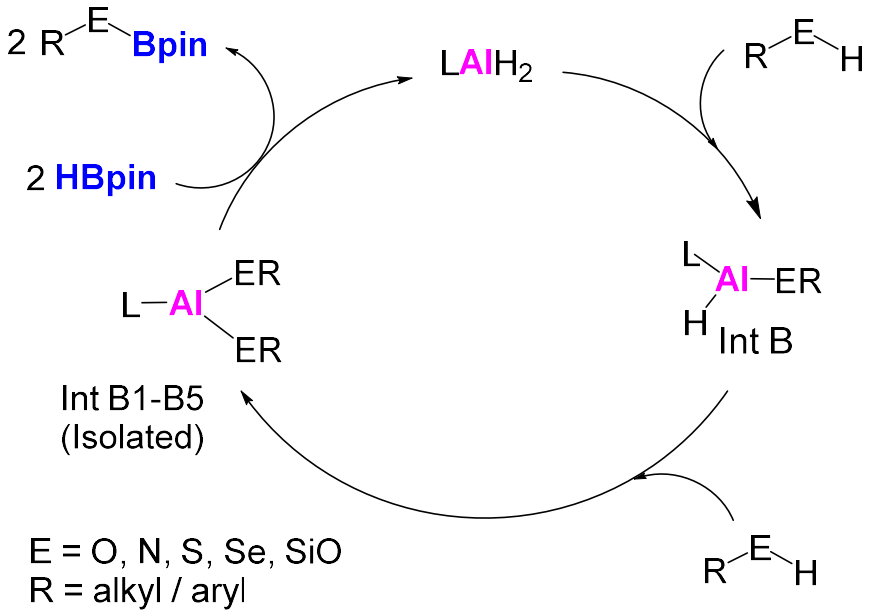


Scheme 2.6. Control reactions for CDC reactions.

At the beginning of the catalytic cycle, the active Al-H (**1**) reacted with polar E-H (E= O, N, S, Se) functional moiety to generate aluminum intermediates (**B1-B5**), LAl-$(ER)_2$ with the elimination of dihydrogen gas. The Int (**B1-B5**) afforded dehydrocoupled product and rebirth of compound **1** to close the catalytic cycle. The final step involves TS, where hydrogen atoms transfer from HBpin to the electron-deficient aluminum metal center.



Scheme 2.7. Control reaction of Int B2 with HBpin.



Scheme 2.8. Proposed mechanism for $LAlH_2$ (**1**) catalyzed dehydrocoupling reactions.

2.3. Conclusion

In conclusion, it summarized the excellent hydroboration of various aldehydes and ketones using CBG aluminum-dihydride (**1**) as a catalyst under solvent-free conditions with pinacolborane. All selected carbonyl compounds underwent complete conversion with low catalyst loading and good tolerance of various reducible functional groups, including halide, nitro, nitrile, amide, ester, and heterocycles. Moreover, catalyst **1** was also employed for the dehydrocoupling of alcohols, phenols, amines, thiol, selenol, and silanols with HBpin at room temperature. All hydroborated and dehydrocoupled products were isolated in good yields and well-characterized by NMR spectroscopy. As far as aluminum catalyzed CDC reaction is concerned, this is the

second report after ^{Dipp}Nacnac aluminum-dihydride for dehydrocoupling reactions. Further studies on compound **1** catalyzed challenging organic transformation are still in progress.

2.4. Appendix: All general experimental information along with analytical data and spectral files of hydroborated products and control reactions were available in published paper: *Polyhedron* **2022**, *222*, 115902. Crystallographic data and structure refinement summary of **9o** were also provided in ESI.

2.5. References

1. (a) Liu, Y.; Li, J.; Ma, X.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2018**, *374*, 387–415; (b) Weetman, C.; Inoue, S. *ChemCatChem* **2018**, *10*, 4213–4228; (c) Dagorne, S.; Wehmschulte, R. *ChemCatChem* **2018**, *10*, 2509–2520; (d) Nikonov, G. I. *ACS Catal.* **2017**, 7, 7257-7266; (e) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, *350*, 14–29; (f) Ananikov, V. P. *Angew. Chem. Int. Ed.* **2016**, *55*, 14904; (g) Aldridge, S. Downs, A. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 11569; (h) Ni, C.; Ma, X.; Yang, Z.; Roesky, H. W. *Eur. J. Inorg. Chem.* **2022**, https://doi. org/10.1002/ejic.202100929; (i) Das, A.; Rej, S.; Panda, T. K. *Dalton Trans.* **2022**, *51*, 3027–3040.

2. Selected examples of aluminum-catalyzed hydrosilylation, see: (a) Bolley, A.; Specklin, D.; Dagorne S. *Polyhedron* **2021**, *194*, 114956; (b) Kannan, R.; Chambenahalli, R.; Kumar, S.; Krishna, A.; Andrews, A. P.; Jemmis, E. D.; Venugopal, A. *Chem. Commun.* **2019**, *55*, 14629–14632; (c) Saleh, M.; Powell, D. R; Wehmschulte, R. J. *Organometallics* **2017**, 36, 4810–4815; (d) Jakobsson, K.; Chu, T.; Nikonov, G. I.; *ACS Catal.* **2016**, *6*, 7350–7356; (e) Stennett, T. E.; Pahl, J.; Zijlstra, H. S.; Seidel, F. W.; Harder, S. *Organometallics* **2016**, *35*, 207–217; (f) Chen, J.; Chen, E.-Y.-X. *Angew. Chem. Int. Ed.* **2015**, *54*, 6842–6846; (g) Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics* **2013**, *32*, 6812–6819; (h) Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 7323–7326; (i) Koller, J.; Bergman, R. G. *Organometallics* **2012**, *31*, 2530–2533; (j) Kato, N.; Tamura, Y.; Kashiwabara, T.; Sanji, T.; Tanaka, M.

Organometallics **2010**, *29*, 5274–5288; (k) Bach, P.; Albright, A.; Laali, K. K.; *Eur. J. Org. Chem.* **2009**, 1961–1966.

3. Aluminum-based catalysts for hydroboration reactions: (a) Peddarao, T.; Sarkar, N.; Nembenna S. *Inorg. Chem.* **2020**, *59*, 4693–4702; (b) Woodside, A. J.; Smith, M. A.; Herb, T. M.; Manor, B. C.; Carroll, P. J.; Rablen, P. R.; Graves, C. R. *Organometallics* **2019**, *38*, 1017–1020; (c) Zhang, G.; Wu, J.; Zeng, H.; Neary, M. C.; Devany, M.; Zheng, S.; Dub, P. A. *ACS Catal.* **2019**, *9*, 874–884; (d) Liu, Y.; Ma, X.; Ding, Y.; Yang, Z.; Roesky, H. W. *Organometallics* **2018**, *37*, 3839–3845; (e) Liu, Y.; Liu, X.; Liu, Y.; Li, W.; Ding, Y.; Zhong, M.; Ma, X.; Yang, Z. *Inorg. Chim. Acta* **2018**, *471*, 244–248; (f) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.* **2018**, *54*, 1233–1236; (g) Lemmerz, L. E.; McLellan, R.; Judge, N. R.; Kennedy, A. R.; Orr, S. A.; Uzelac, M.; Hevia, E.; Robertson, S. D.; Okuda, J.; Mulvey, R. E. *Chem. Eur. J.* **2018**, *24*, 9940–9948; (h) Pollard, V. A.; Fuentes, M. Á.; Kennedy, A. R.; McLellan, R.; Mulvey, R. E. *Angew. Chem. Int. Ed.* **2018**, *57*, 10651–10655; (i) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, *8*, 2001–2005; (j) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. *Chem. Eur. J.* **2018**, *24*, 4794–4799; (k) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. *Z. Anorg. Allg. Chem.* **2016**, 1245–1250; (l) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, *18*, 4710–4713; (m) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54*, 10225–10229.

4. Selected examples of aluminum catalyzed hydroamination, see: (a) Chen, J.; Goforth, S. K.; McKeown, B. A.; Gunnoe, T. B. *Dalton Trans.* **2017**, *46*, 2884–2891; (b) Khandelwal, M.; Wehmschulte, R. J. *J. Organomet. Chem.* **2012**, *696*, 4179–4183; (c) Koller, J.; Bergman, R. G. *Chem. Commun.* **2010**, *46*, 4577–4579; (d) Koller, J.; Bergman, R. G. *Organometallics* **2010**, *29*, 3350–3356; (e) Koller, J.; Bergman, R. G. *Organometallics* **2010**, *29*, 5946–5952; (f) Zhang, W.-X.; Li, D.; Wang, Z.; Xi, Z. *Organometallics* **2009**, *28*, 882–887.

5. Berben, L. A. *Chem. Eur. J.* **2015**, *21*, 2734–2742.

6. Selected aluminum catalyzed transfer hydrogenation examples: (a) Yeagle, K. P.; Hester, D.; Piro, N. A.; Dougherty, W. G.; Kassel, W. S.; Graves, C. R. *Aust. J. Chem.* **2015**, *68*, 357–365; (b) McNerney, B.; Whittlesey, B.; Cordes, D. B.; Krempner, C. *Chem. Eur. J.* **2014**, *20*, 14959–14964; (c) Cha, J. S. *Org. Process Res. Dev.* **2006**, *10*, 1032–1053; (d) Graves, C. R.; Campbell, E. J.; Nguyen, S. T. *Tetrahedron: Asymmetry* **2005**, *16*, 3460–3468; (e) Cohen, R.; Graves, C. R.; Nguyen, S. T.; Martin, J. M. L.; Ratner, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 14796–14803.

7. Selected examples of aluminum-catalyzed hydrodefluorination, see: (a) Gu, W.; Haneline, M. R.; Douvris, C.; Ozerov, O. V.; *J. Am. Chem. Soc.* **2009**, *131*, 11203–11212; (b) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188–1190; (c) Klahn, M.; Fischer, C.; Spannenberg, A.; Rosenthal, U.; Krossing, I. *Tetrahedron Lett.* **2007**, *48*, 8900–8903; (d) Scott, V. J.; Çelenligil-Çetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 2852–2853.

8. (a) Roy, M. M. D.; Omaña, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.* **2021**, *121*, 12784–12965; (b) Wilkins, L. C.; Melen, R. L. *Coord. Chem. Rev.*, **2016**, *324*, 123–139; (c) Dhillion, R. S. *Hydroboration, and Organic Synthesis*, Springer, **2007**; (d) Tamang, S. R.; Findlater, M. *Molecules* **2019**, *24*, 3194; (e) Shegavi, M. L.; Bose, S. K. *Catal. Sci.Technol.* **2019**, *9*, 3307–3336; (f) Chong, C. C.; Kinjo, R. *ACS Catal.*, **2015**, *5*, 3238–3336; (g) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48*, 1995–2003.

9. (a) Hobson, K.; Carmalt, C. J.; Bakewell, C. *Inorg. Chem.* **2021**, *60*, 10958–10969; (b) Sarkar, N.; Bera, S.; Nembenna, S. *J. Org. Chem.* **2020**, *85*, 4999–5009; (c) Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Adv. Synth. Catal.* **2019**, *361*, 850–857; (d) Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J.* **2019**, *25*, 11918–11923; (e) Liu, W.; Ding, Y.; Jin, D.; Shen, Q.; Yan, B.; Ma, X.; Yang, Z. *Green Chem.* **2019**, *21*, 3812–3815; (f) Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics* **2019**, *38*, 3092–3097.

10. (a) Wang, W.; Luo, M.; Yao, W.; Ma, M.; Pullarkat, S. A.; Xu, L.; Leung, P.-H. *New J. Chem.* **2019**, *43*, 10744–10749; (b) Stachowiak, H.; Kaźmierczak, J.; Kuciński, K. Hreczycho, G. *Green Chem.* **2018**, *20*, 1738–1742.

11. (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461–1473; (b) Hall, D. G. **2005**, *Structure, properties, and preparation of boronic acid derivatives. Overview of their reactions and applications*, Wiley-VCH Verlag GmbH & Co. KGaA; (c) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*, Academic Press, New York, **1988**; (d) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412–443.

12. Ferńandez-Salas, J. A.; Manzini, S.; Nolan, S. P. *Chem. Commun.* **2013**, *49*, 5829–5831.

13. Bolãno, T.; Esteruelas, M. A.; Gay, M. P.; Oñate, E.; Pastor, I. M.; Yus, M. *Organometallics* **2015**, *34*, 3902–3908.

14. Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; Wilson, A. S. S. *Angew. Chem. Int. Ed.* **2015**, *54*, 13362–13365.

15. Harinath, A.; Anga, S.; Panda, T. K. *RSC Adv.* **2016**, *6*, 35648–35653.

16. Erickson, J. D.; Lai, T. Y.; Liptrot, D. J.; Olmstead, M. M.; Power, P. P. *Chem. Commun.* **2016**, *52*, 13656–13659.

17. Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H.W. *J. Am. Chem. Soc.* **2016**, *138*, 2548–2551.

18. Rochette, É.; Boutin, H.; Fontaine, F. -G. *Organometallics* **2017**, *36*, 2870–2876.

19. Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G. *Chem. Commun.* **2016**, *52*, 10563–10565.

20. Yao, W.; Wang, J.; Lou, Y.; Wu, H.; Qi, X.; Yang, J.; Zhong, A. *Org. Chem. Front.* **2021**, *8*, 4554–4559.

21. Yoshimura, A.; Yoshinaga, M.; Yamashita, H.; Igarashi, M.; Shimada, S.; Sato, K. *Chem. Commun.* **2017**, *53*, 5822–5825.

22. Al-O/B-H bond metathesis may not proceed to see, Caise, A.; Jones, D.; Kolychev, E. L.; Hicks, J.; Goicoechea, J. M.; Aldridge, S. *Chem. Eur. J.* **2018**, *24*, 13624-13635. Thus, a control reaction of Int A and HBpin has been carried out to confirm the Al- O/B-H bond metathesis; unfortunately, it was resulting a mixture of products.

23. (a) Peddarao, T.; Baishya, A.; Sarkar, N.; Acharya, R.; Nembenna, S. *Eur. J. Inorg. Chem.* **2021**, 2034–2046; (b) Sahoo, R. K.; Sarkar, N.; Nembenna, S. *Angew. Chem. Int. Ed.* **2021**, *60*, 11991–12000.

Chapter 3A

Aluminum-Catalyzed Selective Deoxygenative Hydroboration of Carboxylic Acids and C-O Bond Cleavage of Carbonates, Formates with Pinacolborane

Abstract

Herein, an unprecedented N-donor CBG stabilized aluminum-dihydride, [$LAlH_2$; (L = {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar = 2,6- Et_2-C_6H_3)] (**1**) catalyzed reduction of carboxylic acids, carbonates, and formates via hydroboration under neat condition is reported. A broad range of substrates were screened with effective tolerance of reducible functionalities like halides (F, Cl, and Br), nitro (NO_2), nitrile (C≡N), 2º amide (CONHR), alkene (C=C), alkyne (C≡C), and heteroaryl groups. The boronates esters residues were further hydrolyzed into corresponding pure alcohols with good yield. The isolated intermediates are well-characterized by NMR and mass spectroscopy, which helps to establish the probable catalytic cycles. Furthermore, compound **1** was also used for deoxygenative hydroboration of amide and anhydride under solvent-free conditions. More importantly, the developed aluminum-catalyzed hydroboration method demonstrates effective intra- and intermolecular chemoselective C-O bond cleavage of carbonates compared to other reducible functional groups.

3.A.1. Introduction

Chemoselective reduction of carbonyl compounds to alcohols is one of the essential organic transformations.[1] Various classical metal hydrides,[2] such as $LiAlH_4$, $NaBH_4$, NH_3BH_3, $NaNH_2(BH_3)_2$, B_2H_6, etc., were used to reduce carbonyl compounds to corresponding alcohols. Still, they indirectly offered severe disadvantages such as uncontrolled reduction, limited substrate scope, huge chemical wastes, and, more importantly, highly pyrophoric. Thus, both homogenous and heterogeneous metal-based hydrogenation[3] procedures for carbonyls have been developed to sustain these drawbacks. To some extent, these techniques were successful;

however, it requires high pressurized hydrogen gas and high temperature, usually more than 120 ºC, to complete the reaction. Therefore, new methodologies were developed to overcome these harsh reaction methods. Recently, the metal-catalyzed hydroboration[4] technique has been explored to reduce challenging organic functionalities in their corresponding boronate ester. These stable boron reagents are non-toxic and stored under inert nitrogen gas for further application in organic chemistry, like the Suzuki-Miyaura coupling reaction.[5] Therefore, it is worth mentioning that in the last few years, extraordinary progress has been made for molecular aluminum-based catalysts in carbonyl reduction via hydroboration[6] and hydrosilylation[7] procedures due to substantial properties such as high earth-abundant, economical, and non-radioactive in comparison to lanthanide and transition metal series.[4]

Subsequently, various molecular aluminum complexes have been developed, demonstrating an excellent catalytic transformation of various unsaturated organic functional groups and carbonyl compounds via hydroboration.[4j, 8, 9] In this context, it is of particular interest that only one report registered from the main-group element for the reduction of carboxylic acid reduction via the hydroboration technique.[10a] Although metal-free deoxygenative reduction of carboxylic acids with pinacolborane was well established under neat conditions.[11] The reactions were eventually associated with high substrate scope and selectivity, but it requires an excessive amount of HBpin to complete the process at rt-60 ºC. Recently manganese[10c, 10e] and ruthenium[10b, 10d] and aluminum[10a] based molecular compounds have been reported for carboxylic reduction with low catalyst load. Therefore, it confirms that carboxylic acids' molecular metal-based[10] deoxygenative hydroboration reactions are more effective catalytic routes than metal-free catalytic reductions.[11]

Recently molecular/reagent-based magnesium,[12a,12b] boron,[12c] aluminum,[10a] germanium,[12e] and manganese,[10e, 13] catalysts have been employed for carbonate reduction using pinacolborane as the hydrogen source. Previously carbonates were reduced by the hydrogenation[14] and transfer hydrogenation[15] method at high temperature (80-140 ºC) and pressure (50 bar). Thus, the hydroboration method is an alternate route for reducing carbonate motifs.[10, 12, 13]

To the best of our knowledge, no hydroboration of formates has been reported. Although Milstein,[14h] Hong,[15a] and Werner's[15b] research groups established the reduction of formates by hydrogenation method, which involves high temperatures upto 140 ºC. In 2019 Rueping[12a] mentioned the possibility of formate reduction via hydroboration. So, it can be concluded that reducing formate (ROCHO) via the hydroboration method is a safer and more effective procedure rather than conventional reduction techniques.[14h, 15]

Lately, our research group published CBG aluminum-based reduction of challenging organic compounds.[6e, 7a, 9b] To expand the catalytic hydroboration application, the reduction of the above reducible carbonyl functionalities was tested using CBG aluminum-dihydride compound **1**. The reduction of carboxylic acids, carbonates, and formates with pinacolborane was successfully accomplished using complex (**1**) under mild reaction conditions and with a modest catalyst load.

To the best of our literature analysis, this is the second report of molecular aluminum-based reduction for deoxygenative reduction of carboxylic acid[10a] and C-O bond cleavage of organic carbonates under neat conditions. In addition, compound **1** was also used to reduce formates,[14h, 15a, 15b] amide,[16] and anhydride via hydroboration.

3.A.2. Results and Discussion

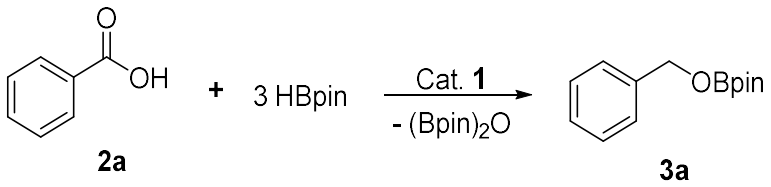
Recent studies established the synthetic routes for high-yield CBG-stabilized aluminum alkyls and hydride complexes.[6e, 7a, 9b] In this context, aluminum-dihydride (**1**) is a multifunctional

catalyst employed for double bond and triple bond activation via hydroboration under mild conditions.[9b] These results motivate us to explore further catalytic utilization of compound **1** for hydroboration of reducible carbonyl functionalities, i.e., carboxylic acids, carbonates, and formates, under neat conditions.

3.A.2.1. Catalytic Hydroboration of Carboxylic Acids

To optimize the carboxylic acid reduction, I chose benzoic acid (**2a**) as an ideal substrate. Initial reaction was performed under solvent and catalyst-free conditions at rt for 12 h with three equiv. pinacolborane. Only a 40% reduction of benzoic acid was observed in hydroborated product **3a** (Table 3.A.1., entry 1).

Table 3.A.1. Optimization table of aluminum catalyzed (**1**) hydroboration of benzoic acid.[a]



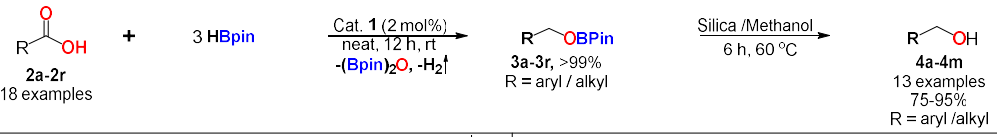
Entry	Cat. (mol%)	Solvent	Time	Yield (%)[b]
1	-	neat	12 h	40
2	0.5	neat	12 h	60
3	1.0	neat	12 h	75
4	1.5	neat	12 h	88
5	2.0	neat	12 h	>99
6	2.0	toluene	12 h	>99
7[c]	2.0	neat	8 h	>99
8	2.0	neat	6 h	80

[a]Reaction conditions: benzoic acid (1.0 equiv., 1.0 mmol), pinacolborane (3.0 equiv., 3.0 mmol), aluminium-hydride **1** (2.0 mol%), under N_2 (solvent-free, 12 h, rt). BpinOBpin is found as a side product. [b]Yield for hydroboration of benzoic acid was analyzed by ^{1}H NMR spectra based on the full vanishing of a carboxyl group (-COOH) followed by the formation of a new characteristic proton resonance for –C*H*$_2$OBpin, a fragment of **2a** at (δ) 4.93 ppm. [c]Entry 7, exhibits TON = 50 and the corresponding TOF = 6.25 h^{-1} for reducing benzoic acid to hydroborated product **3a**. The turnover number was examined by the number of moles of desired boronate ester (**3a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction.

The result was matched with the previously reported catalyst-free hydroboration of carboxylic acids.[11] Next, when the same reaction was performed in 0.5 mol% of catalyst **1**, it afforded 60% of boronate ester **3a** ($PhCH_2OBpin$) along with $(Bpin)_2O$ as a side-product. The reaction progress was solely analyzed by ^{1}H NMR spectroscopy. With the increase of catalyst loading upto 2.0 mol%, the complete formation of product **3a** was observed (Table 3.A.1., entry 5). Solvent (*toluene*) did not affect the catalytic performance of compound **1** for B-H addition in benzoic acid (Table 1, entry 6). Notably, entry 7 (Table 3.A.1.) shows a turnover no, TON (50), and corresponding turnover frequency, TOF (6.25 h^{-1}), for the reduction of a carboxylic acid into boronate ester product **3a**. Further decrease in catalyst load affords a lower yield for product **3a**.

Next, the optimization reaction protocol was used to explore the substrate scope for deoxygenative hydroboration of commercially available carboxylic acids. As indicated in Table 3.A.2., all accessible organic acids (**2a-2r**) were quantitatively reduced into corresponding alkoxyboronate esters (**3a-3r**) under neat conditions with good tolerance of reducible functional groups, i.e., halide, alkene, nitrile, amide, and heteroaryl. Further, these boronate esters were hydrolyzed into corresponding pure 1° alcohols (**4a-4o**) with an isolated yield of 72-95%. In initial substrate screening, it has been found that derivatives of aryl carboxylic acids with

Table 3.A.2. Substrate scope for catalytic deoxygenative hydroboration of carboxylic acids using Al complex (**1**).[a]



entry	carboxylic acid (**2**)	product (**3**)	yield[b]
1	**2a**	**3a**[c] TON = 50 TOF = 6.25 h^{-1}	>99% (**4a**, 94%)
2	**2b**	**3b**	>99% (**4b**, 90%)
3	**2c**	**3c**	>99% (**4c**, 92%)
4	**2d**	**3d**	>99% (**4d**, 93%)
5	**2e**	**3e**	>99% (**4e**, 95%)
6	**2f**	**3f**	>99% (**4f**, 94%)
7	**2g**	**3g**	>99%
8	**2h**	**3h**	>99% (**4g**, 82%)
9	**2i**	**3i**[d]	>99% (**4h**, 94%)
10	**2j**	**3j**	>99% (**4i**, 94%)
11	**2k**	**3k**	>99% (**4j**, 85%)
12	**2l**	**3l**	>99%
13	**2m**	**3m**	>99% (**4k**, 82%)
14	**2n**	**3n**	>99% (**4l**, 75%)
15	**2o**	**3o**	>99% (**4m**, 80%)
16	**2p**	**3p**	>99%
17	**2q**	**3q**	>99%
18	**2r**	**3r**	>99%

[a]Reaction conditions: carboxylic acids (1.0 equiv., 1.0 mmol), pinacolborane (3.0 equiv., 3.0 mmol), aluminium-hydride **1** (2.0 mol%), under N_2 (solvent-free, 12 h, rt). BpinOBpin is found as a side product. The major hydroborated pdts were only marked. [b]Yield for reduction of carboxylic acids was analyzed by ^{1}H NMR spectra based on the full vanishing of a carboxyl group (-COOH) followed by the formation of a new characteristic proton signal for –C*H*$_2$OBpin, a fragment of boronate ester products (**3a-3r**). The yield of isolated alcohols (**4a-4m**) was given in parenthesis after being purified by column chromatography. [c]For compound **3a**, TOF was 6.25 h^{-1} resulting from a shorter reaction time (8 h). The turnover number was examined by the number of moles of desired boronate ester (**3a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction. [d]For **3i**, pinacolborane (6.0 equiv., 6.0 mmol) was used.

electron-rich (methyl, methoxy) and electron-deficient (chloro, bromo) groups(**2b-2f**) underwent smooth deoxygenative reduction with HBpin into corresponding hydroborated products (**3b-3d** and **3e-3f**) at rt. As analyzed by NMR studies, it was found that apart from BpinOBpin, there are no other side products, unlike in some transition metal-catalyzed hydrosilylation of organic

acid.[17] From a steric and electronic point of view, reducing carboxylic acid-containing both electron-rich and electron-poor functionalities was difficult.[18] Next, substrates such as 3-fluoro-2-methyl benzoic acid (**2g**) were selected to sustain this challenge and reacted with three equiv. of HBpin under standard conditions. Both methyl and fluorine functional groups remain untouched, and a total reduction of only the carboxyl group was observed (**3g**). Further, the deoxygenative reduction of heteroaryl or diaryl organic acids like 2-thiophene carboxylic acid, 2,6-pyridine dicarboxylic acid, and biphenyl-4-carboxylic acid (**2h-2j**) was well agreed with the optimized protocol and fully hydroborated into corresponding aryloxy-boronate esters (**3h-3j**). For the complete reduction of 2,6-pyridine carboxylic acid (**2i**), an excess amount of HBpin (six equiv.) was used. Further, some functionalized carboxylic acids with nitrile, amide, and alkenes groups have been explored to widen the substrate scope.[10d] It was delighted to inform that catalyst **1** displayed good chemoselective behavior towards 4-cyanobenzoic acid and 4-acetamidobenzoic acid (**2k-2l**). As evident from Table 3.A.2., in both acids, the reducible functional group, i.e., nitrile (C≡N) and 2^{o} amide (CONHR) remained untouched, followed by chemoselective reduction of a carboxyl group (CO_2H) was only noticed (**3k-3l**). Similar intramolecular chemoselective deoxygenative hydroboration was displayed for substrates having alkene substituents (**2m-2o**; *internal and external alkenes*). Next, linear (**2p-2q**) and cyclic (**2r**) carboxylic acids' hydroboration was analyzed under the standard condition. All three acids were well tolerated and reduced into the required alkyl boronate esters (**3p-3r**) with a yield of 99%.

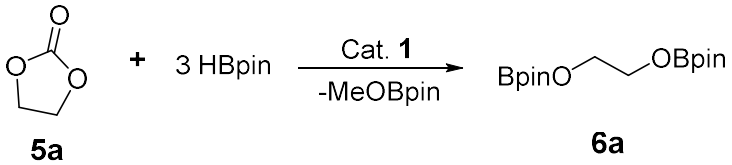
3.A.2.2. Catalytic Hydroboration of Carbonates

Recently few main-group metals have been reported for carbonate hydroboration. [10a, 12] The reduction of carbonates was quite challenging due to the high bond energy of C=O groups compared to aldehydes and ketones. Therefore, next, aimed at B-H addition in carbonates. With

our best effort, it was discovered that using 4 mol% of catalyst **1**; ethylene carbonate was quantitatively converted into corresponding boronate ester (**6a**, pinBOCH$_2$CH$_2$OBpin) along with MeOBpin as a side product under three equiv. of HBpin at neat conditions (Table 3.A.3., entry 4). The above outcome is the best result for catalytic hydroboration of **5a** with compound **1**. Toluene does not affect the catalytic activity of aluminum-hydride (**1**) for the C-O bond activation of ethylene carbonate (Table 3.A.3., entry 5). It was significant to note that entry 6 of Table 2 suggests the high TON (= 25) and TOF (= 3.1 h^{-1}) for reducing ethylene carbonate to boryl ester **6a** with low catalyst load and lower time of reaction. Under a catalyst-free environment, hydroboration of ethylene carbonate was not observed (Table 3.A.3., Entry 8). Among the main-group metal catalysis, this is the second report of molecular aluminum-dihydride[10a] catalyzed C-O bond cleavage of carbonate via hydroboration.[10a, 12] It was noteworthy that our reaction methodology is better than previously reported transition metal catalysts[13] for the reduction of carbonates where high temperature (>100 ^oC) and strong activating reagents (highly pyrophoric) such as sodium tert-butoxide (Na^{t}OBu) were required to complete the reaction.

Next, with no hurdle, a wide range of cyclic and linear carbonates (**5a-5m**) were explored with three-fold of HBpin by using 4 mol % of catalyst **1** under standard conditions (Table 3.A.4.). All reactions were analyzed by ^{1}H NMR spectroscopy. The major

Table 3.A.3. Optimization table of aluminum-hydride (**1**) catalyzed reduction of ethylene carbonate.[a]



5a **6a**

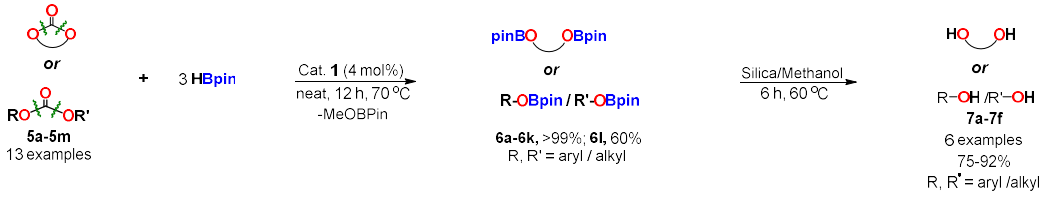
Entry	Cat. (mol%)	Solvent	Time	Yield (%)[b]
1	1.0	neat	12 h	60

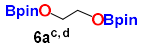
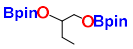
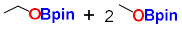
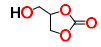
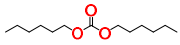
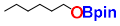
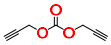
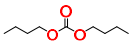
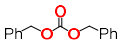
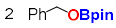
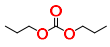
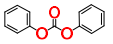
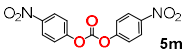
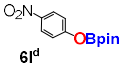
2	2.0	neat	12 h	80
3	3.0	neat	12 h	92
4	4.0	neat	12 h	>99
5	4.0	toluene	12 h	>99
6[c]	4.0	neat	8 h	>99
7	4.0	neat	6 h	75
8	-	neat	12 h	-

[a]Reaction conditions: ethylene carbonate (1.0 equiv., 1.0 mmol), pinacolborane (3.0 equiv., 3.0 mmol), aluminum-hydride (**1**) (4.0 mol%), under N_2 in solvent-free condition at 70 ^oC for 12 h. [b]Yield for reduction of ethylene carbonate was analyzed by ^1H NMR spectra based on the full vanishing of the carbonyl group (C=O) followed by the formation of new characteristic proton resonance for -OCH_2CH_2O-, a fragment of **6a** at (δ) 3.84 ppm. MeOBpin is found as a side product. [c]Entry 6 exhibits TON = 25 and the respective turn over frequency of 3.1 h^{-1} for reducing ethylene carbonate to hydroborated product **6a**. The turnover number was examined by no. of moles of desired pinacol boronate ester (**6a**) formed divided with no. of moles of CBG aluminium-hydride (**1**) consumed. Turnover frequency was analyzed by dividing the Turnover number by the time (h) of the catalytic reaction.

boronate ester products were hydrolyzed by SiO_2/methanol and purified by column chromatography to isolate the desired alcohols (**7a-7f**) in a 75-92% isolated yield. It has been found that five-membered cyclic carbonate with ethyl group, i.e., 1,2-butylene carbonate (**5b**), undergo smooth C-O bond cleavage into diboryl ester (**6b**) along with MeOBpin (by-product) as indicated by ^1H NMR spectrum of δ = 3.52 ppm for methyl protons (-CH_3). The catalytic result is found to be similar to the reported literature.[12b] However, a substrate with hydroxyl groups (**5c**) was not tolerated under standard conditions. Therefore under 4.0 equiv. of HBpin, both C-O bond cleavage and dehydrocoupling reactions of substrate **5c** occur, which resulted in the alkyl boronate ester (**6c**) in 99% yield, like published magnesium catalyzed reduction of carbonates.[12b]

Table 3.A.4. Substrate scope for catalytic hydroboration of carbonates using Al complex (**1**).[a]



entry	carbonate (**5**)		product (**6**)	yield[b]	entry	carbonate (**5**)		product (**6**)	yield[b]
1		**5a**	 **6a**[c,d] TON = 25 TOF = 3.1 h^{-1}	>99% (**7a**, 80%)	7		**5g**	2  **6g**[d]	>99%
2		**5b**	 **6b**[d]	>99%	8		**5h**	 **6g**	>99%
3		**5c**	 **6c**[d,e]	>99%	9		**5i**	3  **6h**	>99%
4		**5d**	2  **6d**[d]	>99% (**7b**, 78%)	10		**5j**	2  **6i**[d]	>99% (**7c**, 75%)
5		**5e**	2  **6e**[d]	>99%	11		**5k**	2  **6j**[d]	>99% (**7d**, 92%)
6		**5f**	2  **6f**[d]	>99%	12		**5l**	2  **6k**[d]	>99% (**7e**, 90%)
					13		**5m**	2  **6l**[d]	60% (**7f**, 86%)

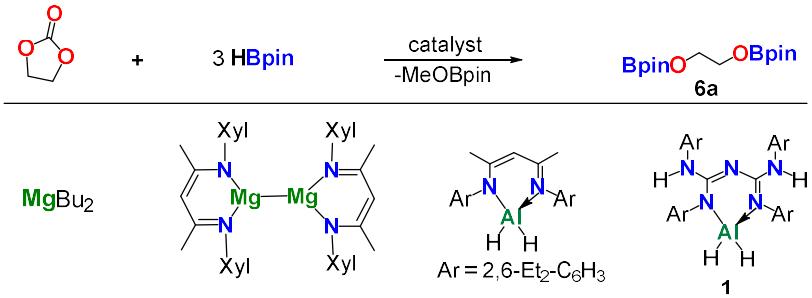
[a]Reaction conditions: carbonates (1.0 equiv., 1.0 mmol), pinacolborane (3.0 equiv., 3.0 mmol), aluminium-hydride (**1**) (4.0 mol%), under N_2 in a 10 mL air-tight vial at 70 °C for 12 h (solvent-free). [b]Yield for reduction of carbonates was analyzed by ^{1}H NMR spectra based on the full vanishing of the carbonyl group (C=O) followed by the formation of a new characteristic proton signal for boronate ester products (**6a-6l**). The yield of isolated alcohols (**7a-7f**) was given in parenthesis after being purified by column chromatography. [c]For compound **5a**, the turnover frequency was found 3.1 h^{-1} in 8h. The turnover number was examined by the number of moles of desired boronate ester (**6a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction. [d]MeOBpin is side product. The major hydroborated pdts were only marked. [e]For **5c**, pinacolborane (4.0 equiv., 4.0 mmol) was used.

In addition, aliphatic carbonates such as dihexyl carbonate (HexO(CO)OHex), dibutyl carbonate (BuO(CO)OBu), dipropyl carbonate(PrO(CO)OPr), diethyl carbonate (EtO(CO)OEt), ethyl methyl carbonate (EtO(CO)OMe), and dimethyl carbonate (MeO(CO)OMe), **5d-5i** were reacted quantitatively with three equiv. of HBpin under a similar reaction condition. As manifested in Table 3.A.4., all six linear alkyl carbonates were selectively converted into desired alkoxy-boronate esters (**6d-6h**) at 70 °C. Following this outcome, it is worth noting that our catalytic

system's hydroboration of linear carbonates is more efficient than the reported manganese[10e] catalyzed reaction protocol, where a yield of less than 50 % was found, especially for alkyl carbonate reduction. Subsequently, one intramolecular chemoselective reduction in alkyl carbonate, such as dipropargyl carbonate (HC≡C)$CH_2O(CO)OCH_2$(C≡CH) **5j**, has been found. In substrate **5j**, hydroboration occurred smoothly, affording borate ester **6i,** where C≡C functional group was well-tolerated and remained unreacted.

Among other aryl carbonates, such as dibenzyl carbonate ($(PhCH_2O)_2CO$) and diphenyl carbonate ($(PhO)_2CO$) **5k-5l**, demanded no change in reaction conditions. Both carbonates (**5k** and **5l**) were quantitatively reduced into corresponding aryl boronate esters $PhCH_2OBpin$ (**6j**) and PhOBpin (**6k**), similar to reported magnesium-catalyzed carbonate reduction.[12b] However, in bis(4-nitrophenyl) carbonate(**5m**), only 60 % reduced boryl ester ($4\text{-}NO_2\text{-}PhCH_2OBpin$) **6l** was noticed due to the possible reduction (*intramolecular chemoselectivity*) of nitro (NO_2)[19] vs. carboxyl group ($-CO_2H$).

Finally, the catalytic activity of reported main-group metals[12a, 12b, 10a] for C-O bond cleavage of ethylene carbonate with three folds of pinacolborane was compared with CBG aluminum hydride (**1**) complex (Scheme 3.A.1.).



Rueping, 2019	Ma, 2020	Roesky, 2022	This Work
TON = 29.3	TON = 100	TON = 20	TON = 25
TOF (h^{-1}) = 9.7	TOF (h^{-1}) = 16.6	TOF (h^{-1}) = 2.0	TOF (h^{-1}) = 3.1
Tol-d8, 65 °C, 3 h	neat, rt, 6 h	neat, 100 °C, 10 h	neat, rt, 8 h
88% (NMR)	99% (NMR)	99% (NMR)	99% (NMR)

Scheme 3.A.1. Catalytic activity comparison of main-group metal catalysts to reduce ethylene carbonate with pinacolborane.[a]

[a]The turnover number was examined by the number of moles of desired boronate ester (**6a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction.

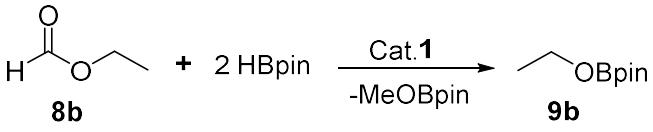
The catalytic reduction was performed at 70 ºC with a lesser time interval (8h) and low catalyst quantity (4.0 mol%), which afforded a TON (25) and TOF (3.1 h^{-1}) for the reduction of ethylene carbonate to corresponding boronate ester **6a** in preference to the previously reported main-group metal catalysts (TON = 20-100 and TOF = 2.0-16.6 h^{-1}).[12a-12b, 10a]

3.A.2.3. Catalytic Hydroboration of Formates

Formates (ROCHO) are usually derived from alcohol and carboxylic acid reaction.[20] The structural core is analogous to an aldehyde (RCHO) in the carbonyl family. A complete literature investigation reveals no reports of metal-catalyzed hydroboration of organic formates besides hydrogenation[14h,15a] techniques.

A series of NMR studies indicate that upto 3.0 mol% catalyst load **1**, ethyl formate was quantitatively cleavaged into EtOBpin (**9b**) with side product MeOBpin under two equiv. of HBpin at 70 ºC (Table 3.A.5., entry 3).

Table 3.A.5. Optimization table of aluminum-hydride (**1**) catalyzed reduction of ethylformate.[a]



Entry	Cat. (mol%)	Solvent	Time	Yield (%)[b]
1	1.0	neat	12 h	68
2	2.0	neat	12 h	89
3	3.0	neat	12 h	>99

4	3.0	toluene	12 h	>99
5[c]	3.0	neat	10 h	>99
6	3.0	neat	8 h	80
7	-	neat	12 h	-

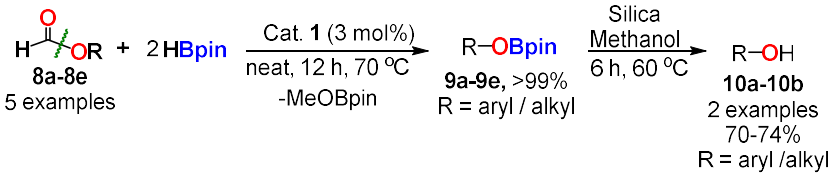
[a]Reaction conditions: ethyl formate (1.0 equiv., 1.0 mmol), pinacolborane (2.0 equiv., 2.0 mmol), aluminium-hydride (**1**) (3.0 mol%), under N_2 in solvent-free condition at 70 °C for 12 h. MeOBpin is found as a by-product. [b]Yield for hydroboration of ethyl formate was analyzed by ^{1}H NMR spectra based on the full vanishing of the carbonyl group (C*H*O) followed by the formation of new characteristic proton resonance for –CH_2OBpin, (**9b**) fragment at (□) 3.91 ppm (quartet signal). [c] Entry 5 exhibits TON = 33 and the respective turn over frequency of 3.3 h^{-1} for the reduction of ethyl formate to hydroborated product **9b**. The turnover number was examined by the number of moles of desired boronate ester (**9b**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction.

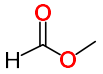
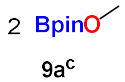
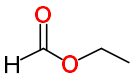
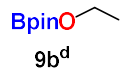
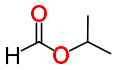
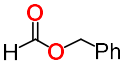
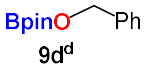
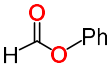
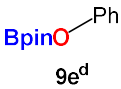
The ^{1}H NMR spectrum thoroughly analyzed the formation of **9b**. It was remarkable that entry 5 (Table 3.A.5.) indicates a Turnover no (33) and the respective turnover frequency (3.1 h^{-1}) for reductive C-O bond cleavage of ethyl formate to corresponding alkyl hydroborated product **9b** using complex **1**. In further experiments, it was confirmed that no reduction of ethyl formate was noticed under the catalyst-free condition with no solvent (Table 3.A.5., entry 7).

Next, the aryl and alkyl formate reduction substrate scope was broadened under standard conditions, summarized in Table 3.A.6.

In initial substrate screening, alkyl formates such as (CHO)OCH_3, (CHO)$OCH(CH_3)_2$, and (CHO)OCH_2Ph, i.e., **8a** or **8c-8d**, were effectively reduced into desired alkyl boronate esters (**9a** and **9c-9d**) with excellent yield (>99%) under two-fold of HBpin. In both isopropyl formate (**8c**) and benzyl formate (**8d**) reduction, the side product was MeOBpin. Similarly, phenyl formate (**8e**) was reduced into an aryl-boronate ester (PhOBpin, **9e**) and by-product MeOBpin in quantitative yield. Besides, synthesized alkyl/aryl boronate esters (**9d-9e**) were further hydrolyzed into corresponding alcohols **10a-10b** with good to excellent yields (70-74%).

Table 3.A.6. Substrate scope for catalytic hydroboration of formates using Al complex (**1**).[a]

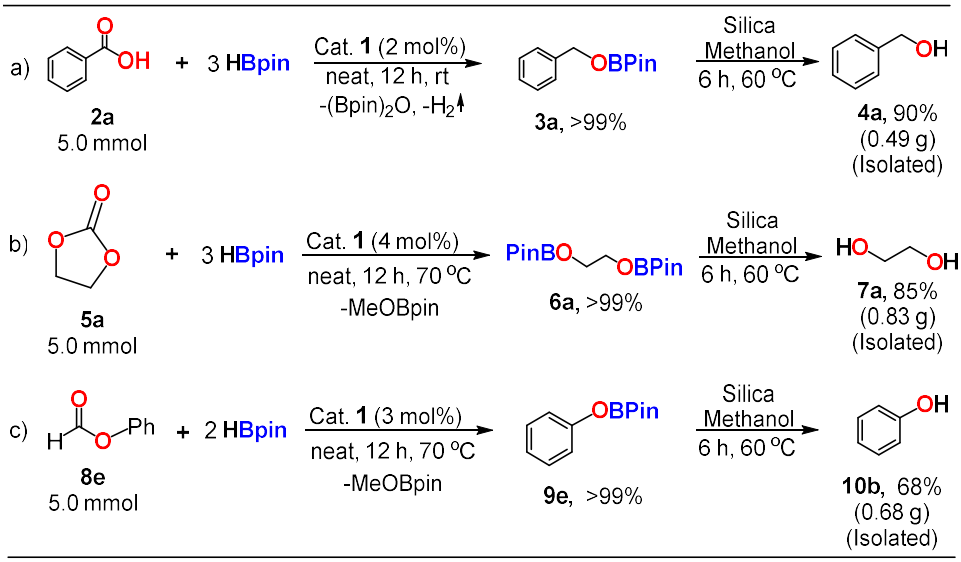


entry	formate (**8**)	product (**9**)	yield[b]
1	 **8a**	2  TON = 33, TOF = 3.3 h^{-1} **9a**[c]	>99%
2	 **8b**	 **9b**[d]	>99%
3	 **8c**	 **9c**[d]	>99%
4	 **8d**	 **9d**[d]	>99% (**10a**, 74%)
5	 **8e**	 **9e**[d]	>99% (**10b**, 70%)

[a]Reaction conditions: formates (1.0 equiv., 1.0 mmol), pinacolborane (2.0 equiv., 2.0 mmol), aluminium-hydride (**1**) (3.0 mol%), under N_2 in solvent-free condition at 70 °C for 12 h. [b]Yield for reduction of formates was analyzed by ^{1}H NMR spectra based on the full vanishing of the carbonyl group (C*H*O) followed by the formation of a new characteristic proton signal for boronate ester products (**9a-9e**). The yield of isolated alcohols (**10a-10b**) was given in parenthesis after being purified by column chromatography. [c]For compound **9a**, the turn over frequency was found 3.3 h^{-1} in 10 h. The turnover number was examined by the number of moles of desired boronate ester (**9a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction. [d]MeOBpin is side product. The major hydroborated pdts were only marked.

3.A.2.4. Large Scale Reaction

Three independent large-scale reductions were performed to analyze the practical application of current catalytic procedures.[11c] Scheme 3.A.2. displayed a gram-scale of 5.0 mmol scale deoxygenative hydroboration of carboxylic acid with three folds of pinacolborane under standard conditions affords complete formation of **3a**, which further hydrolyzed into pure 1° alcohol **4a** in 90% isolated yield. Likewise, ethylene carbonate and phenyl formate (*5.0 mmol scale*) react with 2.0-3.0 equiv. of HBpin under optimized conditions afforded the isolation of corresponding alcohols **7a**, 85%, and **10d**, 68%.

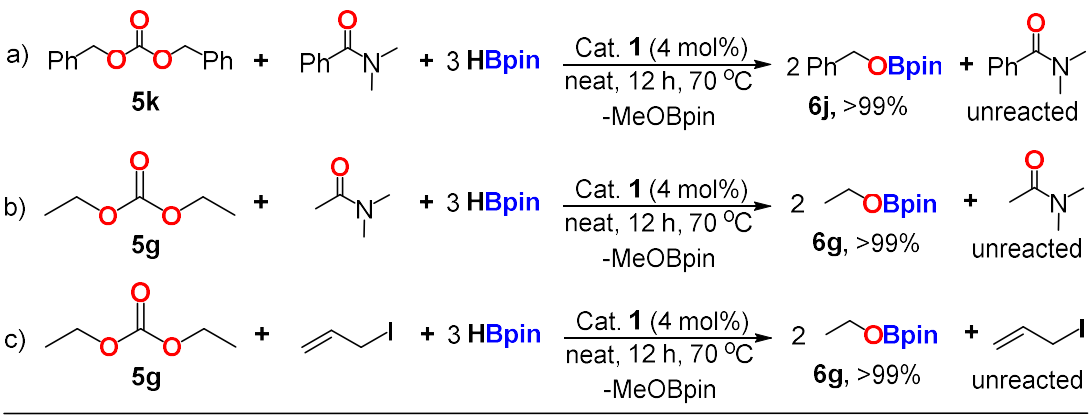


Scheme 3.A.2. Gram-scale hydroboration reactions catalyzed by aluminum-hydride (**1**).

3.A.2.5. Intermolecular C-O Bond Activation Reactions

A chemoselective route is an effective tool for preparing desired products in organic chemistry.[21] Table 3.A.4. shows evidence of the active tolerance of nitro (NO_2) and reducible alkyne (C≡C) groups during the hydroboration of carbonates. This motivates us to examine the intermolecular chemoselective reduction of carbonate vs. amide or olefin (Scheme 3.A.3.).

Therefore, under standard conditions, a reaction between dibenzyl carbonate and *N, N*-dimethylbenzamide with 3.0 equiv. of HBpin afforded product **6j** in 99% yield (Scheme 3.A.3. a). Similar chemoselective behavior was observed when three-folds of pinacolborane was mixed with an equimolar solution of diethyl carbonate and *N, N*-dimethylacetamide, confirming the predominate C-O bond cleavage of carbonate (**5g**) over deoxygenative hydroboration of amide (Scheme 3.A.3. b). Besides, the quantitative reduction of diethyl carbonate into ethyl boronate ester (**6g**) with untouched allyl iodide (C=C bond) was also observed in ^{1}H NMR spectroscopy (Scheme 3.A.3. c).



Scheme 3.A.3. Intermolecular chemoselective hydroboration of carbonates.

3.A.2.6. Kinetic Experiment for Dimethyl Carbonate Hydroboration

The catalytic activity for C-O bond activation of dimethyl carbonate was evaluated by *instu* examination by reaction of three folds of pinacolborane with 1.0 equiv. of dimethyl carbonate (**5i**) catalyzed by 4 mol% of $LAlH_2$ (**1**) at 70 °C (Figure 3.A.1. a).

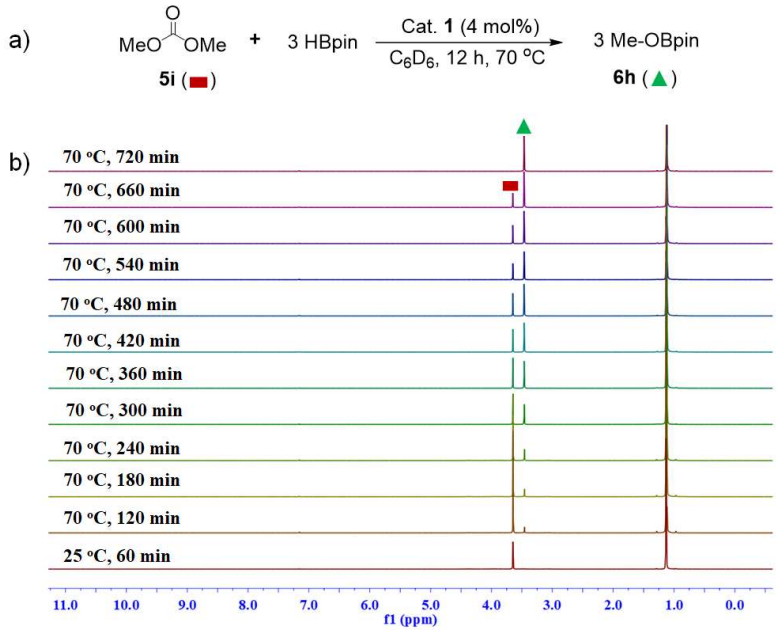


Figure 3.A.1. a) Kinetic study for hydroboration of dimethyl carbonate (**5i**); b) Stacked ^1H NMR spectra (400 MHz, C_6D_6) for the reduction of hydroboration of 1.0 equiv. of dimethyl carbonate (**5i**) (0.3 mmol) with 3.0 equiv. of HBpin (0.9 mmol) using 4 mol% $^{Diethyl}LAlH_2$ (**1**) complex as a catalyst. Spectra were recorded at

different temperatures and time intervals between T = 25 to 70 °C and t = 60 min to 720 min, respectively; ■ = $CO(OMe)_2$ (**5i**); ▲ = Me-OBpin (**6h**).

The reaction development over 720 min displayed the formation of alkyl boronate ester product (MeOBpin) **6h**, as shown in Figure 3.A.1. b. The reaction began at 120 min, where the formation of product MeOBpin (**6h**) was evident by the appearance of methyl proton signal at δ 3.45 ppm (singlet, C_6D_6). Finally, the disappearance of the methoxy (**5i**) resonance peak of starting material (MeO(CO)OMe) at δ 3.63 ppm and exclusive formation of alkyl boronate ester (MeOBpin) **6h** was observed at 720 min, indicating the complete reduction of carbonate **5i** to hydroborated product **6h**. The kinetic experiment confirms the reduction of carbonates proceeds with the probable mechanism sequence.

3.A.2.7. Kinetic Experiment for Ethyl formate Hydroboration

The catalytic performance of 3 mol% of aluminum hydride (**1**) for formate reduction was analyzed by *insitu* inspection of the reaction between three folds of HBpin and 1.0 equiv. of ethyl formate at 70 °C (Figure 3.A.2. a).

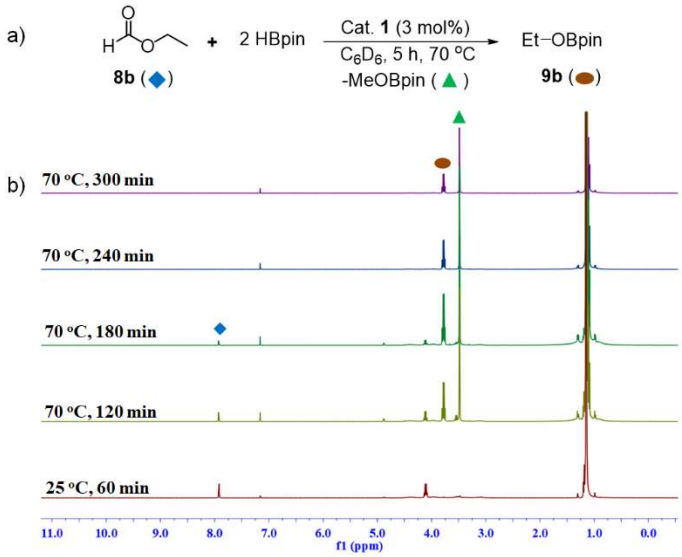


Figure 3.A.2. a) Kinetic study for hydroboration of ethyl formate (**8b**); b) Stacked ^1H NMR spectra (400 MHz, C_6D_6) for the reduction of hydroboration of 1.0 equiv. of ethyl formate (**8b**) (0.3 mmol) with 2.0 equiv. of

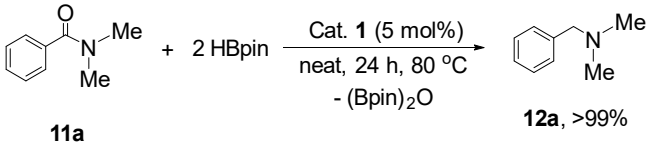
HBpin (0.6 mmol) using 3 mol% $^{Diethyl}LAlH_2$ (**1**) complex as a catalyst. Spectra recorded at different temperatures and time intervals between T = 25-80 °C and t = 60 min to 300 min, respectively; ♦ = (CHO)OEt (**8b**), ● = Et-OBpin (**9b**), ▲ = Me-OBpin (by-product).

Reaction progress in 300 min demonstrates the formation of ethyl boronate ester product (EtOBpin) **9b** and side product MeOBpin (Figure 3.A.2. b). At 120 min, the reaction started, as indicated by the quartet signal for the appearance of methylene proton for –CH_2 fragment of product **9b** at δ 3.76 ppm (C_6D_6) and singlet peak for MeOBpin (*side product*) δ 3.47 ppm. At 240 minutes, the carbonyl peak of ethyl formate at around δ 7.92 ppm completely vanished. The formation of product **9b** confirms the quantitative C-O bond cleavage of ethyl formate. The kinetic reaction suggests the probable mechanism for formate hydroboration under aluminum hydride catalyst **1**.

3.A.2.8. Reduction of Amide and Anhydride via Hydroboration

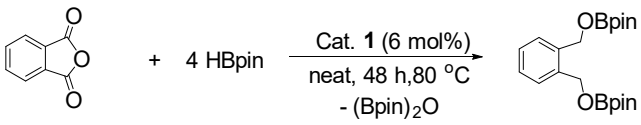
The multifunctional catalytic activity of compound **1** toward unsaturated organic compounds[9b] was established in the earlier work. To further widen such challenging organic transformation, compound **1** was used for deoxygenative hydroboration of amide and anhydride under mild conditions (Scheme 3.A.4.).[16, 23]

A. Hydroboration of Amide



11a **12a**, >99%

B. Hydroboration of Phthalic Anhydride



13a **14a**, >99%

Scheme 3.A.4. Deoxygenative hydroboration of amide and anhydride using aluminum-hydride (**1**).[a]

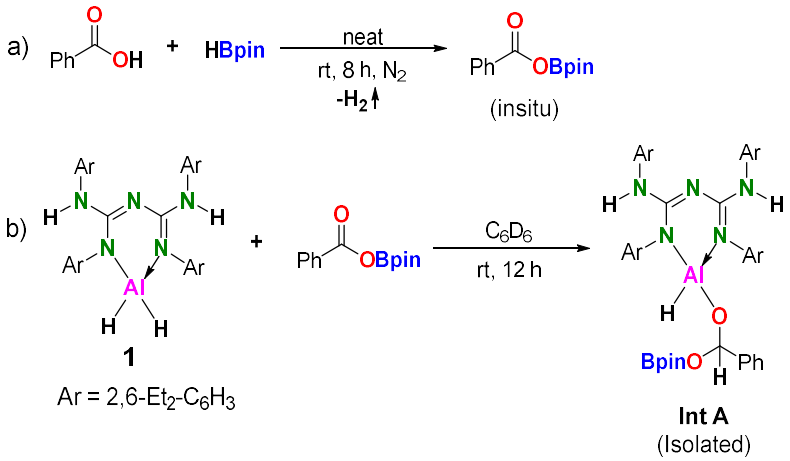
[a]Reaction conditions: 1.0 equiv. of *N, N*-dimethylbenzamide/ phthalic anhydride (1.0 mmol), 2.0-4.0 equiv. of pinacolborane (2.0-4.0 mmol), aluminium-hydride (**1**) (5-6 mol%), under N_2 in solvent-free condition at 80 °C for 24-48 h. [b]Yield was analyzed by NMR spectra (^{1}H) based on the complete vanishing of starting substrate and formation of new characteristic proton resonance for boronate ester products (**12a** and **14a**).

The reduction of *N, N*-dimethylbenzamide proceeded smoothly by 5 mol% catalyst **1** at 80 °C, affording the hydroborated product *N, N*-dimethyl-1-phenylmethanamine **12a** in 99% yield. The catalytic outcome was similar to the reported main-group catalysts[16] for 2° amide reduction (Scheme 3.A.4.).

Next, using compound **1** (6 mol%) and 4.0 equiv. of pinacolborane, the deoxygenative reduction of phthalic anhydride into corresponding hydroborated product **14a** with quantitative yield was observed. It is worthy to note that the present catalytic outcome is the first example of molecular aluminum-based reduction of aryl anhydride via B-H addition.[23]

3.A.2.9. Control reactions for Hydroboration of Benzoic Acid

Two independent control experiments have been conducted to understand the mechanism for CBG Al hydride (**1**) catalyzed reduction of carboxylic acids with HBpin (Scheme 3.A.5.).

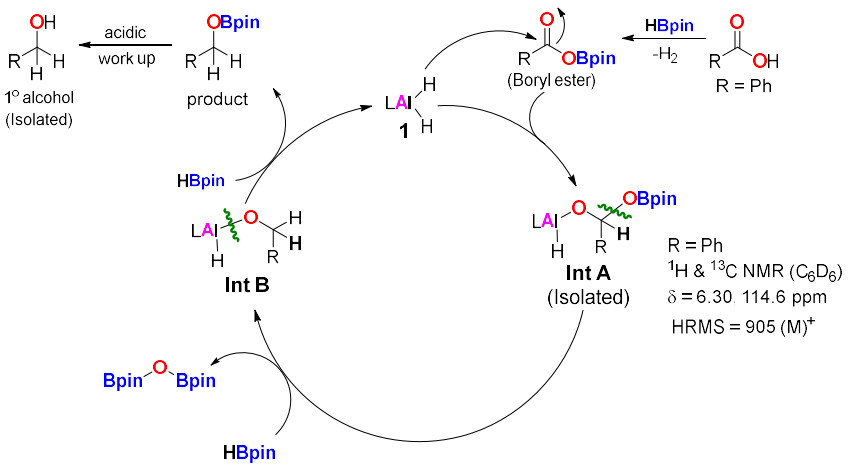


Scheme 3.A.5. Control experiments of hydroboration of benzoic acid.

At first, the boryl ester PhC(O)OBpin was synthesized *insitu* by treating one equiv. of benzoic acid with one equiv. of pinacolborane under neat conditions.[10b] In the second experiment, a stoichiometric reaction between compound **1** and *insitu* generated boryl ester (PhC(O)OBpin) was performed in C_6D_6 at rt. The NMR spectra exhibit a new resonance signal at 6.30 (^{1}H), and 114.6 ppm (^{13}C{^{1}H}) was observed for newly formed methine proton for (–AlOCH) moiety of CBG aluminum-boryl ester intermediate LAlHO(CH)PhOBpin [**IntA**]. In ^{11}B NMR, one new peak was observed at 26.00 ppm for the (-OBpin) fragment of [**IntA**]. The intermediate A was further confirmed by mass spectroscopy.

3.A.2.10. Catalytic Cycle of Aluminum (1) Catalyzed Carboxylic Acid Hydroboration

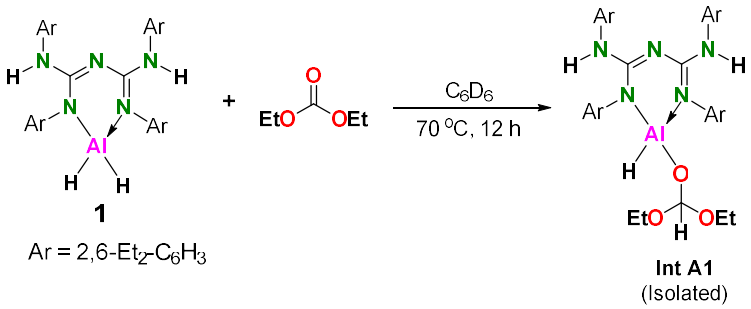
A possible reaction mechanism for the compound 1-catalyzed deoxygenative hydroboration of acids was suggested by an examination of the control reactions and previously described manganese-based[10b] hydroboration of carboxylic acids (Scheme 3.A.6.). The reaction begins with the insertion of active Al–H (**1**) into electron-deficient carbonyl group (-C=O) of boryl ester PhC(O)OBpin (*insitu* prepared), which leads to the formation of aluminum-boryl ester intermediate (**A**). Next, a reaction of **Int A** with pinacolborane afforded metal-alkoxide complex [**Int B**] with the elimination of $(Bpin)_2O$ as a side product. In the final stage of the catalytic cycle, alkoxy intermediate **B** reacts with the third molecule of HBpin to release the boronate ester product of corresponding carboxylic acid and regenerate the catalyst **1**.



Scheme 3.A.6. Proposed mechanism for deoxygenative hydroboration of carboxylic acids.

3.A.2.11. Control Reaction for Al-H (1) Insertion in Diethyl Carbonate

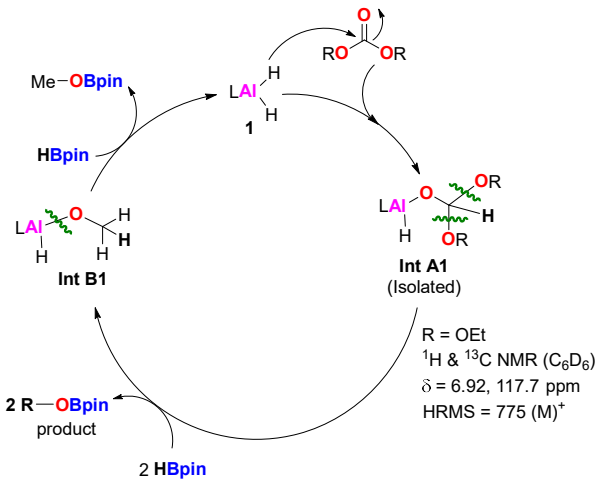
Initially, one control reaction was established, the compound **1** catalyzed carbonate reduction mechanism. A 0.5 mL C_6D_6 solution of 1:1 equimolar ratio of aluminum-dihydride (**1**) and diethyl carbonate, when warmed for 12 h at mild heating (70 °C), resulted in the formation CBG supported aluminum ethoxide complex [**Int A1**] (Scheme 3.A.7.). NMR and HRMS methods help to characterize the formation of **Int A1**. The ^{1}H NMR spectrum displayed one characteristic peak at 6.92 ppm, corresponding to (-AlOC*H*) moiety of [**Int A1**]. The signal for alkoxide carbon of (LAlHO(*C*H)(OEt)$_2$) found at 117.7 ppm (^{13}C{^{1}H}).



Scheme 3.A.7. Control experiment for hydroboration of diethyl carbonate.

3.A.2.12. Catalytic Cycle of Aluminum (1) Catalyzed Carbonate Hydroboration

The probable mechanism for aluminum-dihydride-1 catalyzed C-O cleavage of carbonates via hydroboration reaction was proposed based on the stoichiometric reaction described above (Scheme 3.A.8.).



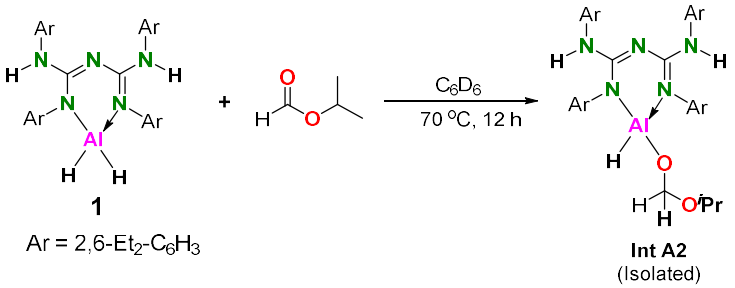
Scheme 3.A.8. Proposed mechanism for hydroboration of carbonates.

At first, the catalytic cycle was initiated by the insertion of $^{Diethyl}LAlH_2$ (**1**) across the C=O bond of carbonate, which resulted in the formation of a CBG aluminum-alkoxide complex (**Int A1**). The intermediate **A1** immediately reacts with two molecules of pinacolborane and generates another metal-alkoxide, **Int B1**, *via* releasing the corresponding alkoxy-boronate ester product. Finally, the **Int B1** is attacked by the third molecule of pinacolborane to liberate MeOBpin of central carbonyl carbon of carbonate and rebirth the catalyst **1**.

3.A.2.13. Control Reaction for Al-H (1) Insertion in Isopropyl Formate

To establish the compound **1** catalyzed formate hydroboration reaction mechanism, a 0.5 mL solution of C_6D_6 was warmed at 70 °C having a 1:1 equimolar ratio of aluminum-dihydride (**1**) and isopropyl formate for 12 h, afforded a new aluminum-alkoxide intermediate (**A2**) (Scheme 3.A.9). The formation of **Int A2** was solely confirmed by NMR spectroscopy, which reveals a

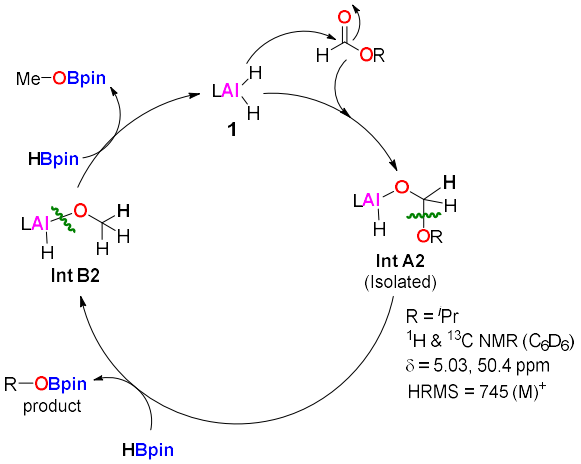
characteristic resonance signal at 5.03 (^{1}H NMR) and 50.04 (^{13}C{^{1}H} NMR) ppm for (–AlOCH$_2$) fragment of newly formed complex [Int A2], LAlHO(CH_2)O^{i}Pr. The intermediate **A2** was further confirmed by high-resolution mass spectroscopy.



Scheme 3.A.9. Control experiment for hydroboration of isopropyl formate.

3.A.2.14. Catalytic Cycle of Aluminum (1) Catalyzed Formate Hydroboration

As examined from the stoichiometric reaction above, a mechanism for aluminum **1** catalyzed formate hydroboration was suggested (Scheme 3.A.10.).



Scheme 3.A.10. Proposed mechanism for hydroboration of formates.

The reaction initiates with active aluminum-hydride (**1**) insertion across the C=O bond of formate, leading to the aluminum-alkoxy compound [**IntA2**]. The intermediate **A2** yielded the desired boronate ester product by reacting with one pinacolborane molecule and forming another aluminum-alkoxide complex (**Int B2**). The Intermediate **B2** reacts with the second molecule of HBpin to afford MeOBpin and regenerates the catalyst **1**.

3.A.3. Conclusion

In conclusion, the outstanding catalytic B-H addition in carboxylic acids, carbonates, and formates using CBG aluminum hydride (**1**) was summarized under neat conditions. All selected substrates of carboxylic acids, carbonates, and formates underwent quantitative hydroboration with practical tolerance for halides (F, Cl, Br), nitro (NO_2), alkene (C=C), alkyne (C≡C), nitrile (C≡N), amide (CONHR), and heteroaryl functional groups have been studied. Both intra- and intermolecular C-O bond cleavage of carbonates have been explored. In addition, large-scale hydroboration reactions were also performed to demonstrate the practical utility of current catalysis. Moreover, compound **1** was further used for deoxygenative hydroboration of challenging unsaturated substrates such as amide and anhydride under mild conditions. Both kinetic study and control reactions confirm the catalytic cycles for reducing carbonates and formate via hydroboration. It was hoped that more challenging and difficult organic transformations of this nature could be documented in the future.

3.A.4. References

1. (a) Leitner, W.; Klankermayer, J.; Pischinger, S.; Pitsch, H.; Kohse-Höinghaus, K. *Angew. Chem. Int. Ed.* **2017**, *56*, 5412 – 5452.; (b) Magano, J.; Dunetz, J. R. *Org. Process Res. Dev.* **2012**, *16*, 1156 – 1184; (c) Cho, B. T. *Chem. Soc. Rev.* **2009**, *38*, 443 – 452; (d) Dhillon, S. R. *Hydroboration and Organic Synthesis*: 9-Borabicyclo [3.3.1] nonane (9-BBN); Springer: Berlin, Germany **2007**; *J. Am. Chem. Soc.* **2008**, *130*, 1, 382 – 384; (e) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411 – 2502.
2. Selected examples of classical metal *reagent*-based carbonyl reduction; (a) Wang, J.; Ju, M. -Y.; Wang, X.; Ma, Y. -N.; Wei, D.; Chen, X. *J. Org. Chem.* **2021**, *86*, 5305 – 5316; (b) Wang, X.; Yao, W.; Zhou, D.; Fan, H. *Mol. Phys.* **2013**, *111*, 3014 – 3024; (c) Shi, L.; Liu, Y.; Liu, Q.; Wei, B.; Zhang, G. *Green Chem.* **2012**, *14*, 1372 – 1375; (d) Yang, X.; Fox, T.;

Berke, H. *Tetrahedron* **2011**, *67*, 7121 – 7127; (e) Seyden-Penne. J. Reductions by the Alumino- and Borohydrides in Organic Synthesis. *Wiley, New York, 2nd edition* **1997**; Eisch, J. J. *J. Am. Chem. Soc.* **1998**, *120*, 6631 – 6632; (f) Brown, H. C.; Heim, P.; Yoon, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 1637 – 1646; (g) Brown, H. C.; Rao, B. C. S. *J. Am. Chem. Soc.* **1960**, *82*, 681 – 686; (h) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947***, 69,* 2548 – 2549.

3. Selected references of metal-based hydrogenation of carbonyls; (a) Filonenko, G. A.; Putten, R. V.; Hensen, E. J. M.; Pidko, E. A. *Chem. Soc. Rev.* **2018**, *47*, 1459 – 1483; (b) Glatz, M.; Stöger, B.; Himmelbauer, D.; Veiros, L. F.; Kirchner, K. *ACS Catal.* **2018**, *8*, 4009 – 4016; (c) Gorgas, N.; Stöger, B.; Veiros, L. F.; Kirchner, K. *ACS Catal.* **2016**, *6*, 2664– 2672; (d) Tan, X.; Wang, G.; Zhu, Z.; Ren, C.; Zhou, J.; Lv, H.; Zhang, X.; Chung, L. W.; Zhang, L.; Zhang, X. *Org. Lett.* **2016**, *18*, 1518 – 1521; (e) Zell, T.; Ben-David, Y.; Milstein, D. *Catal. Sci. Technol.* **2015**, *5*, 822 – 826; (f) Wang, D.; Astruc, D. *Chem. Rev.* **2015**, *115*, 6621 – 6686; (g) Rösler, S.; Obenauf, J.; Kempe, R. *J. Am. Chem. Soc.* **2015**, *137*, 7998 – 8001; (h) Takahashi, K.; Nozaki, K. *Org. Lett.* **2014**, *16*, 5846 – 5849.

4. Selected review articles and book chapter for metal-based hydroboration reactions; (a) Magre, M.; Szewczyk, M.; Rueping, M. *Chem. Rev.* **2022**, *122*, 9, 8261 – 8312; (b) Banerjee, I.; Panda, T. K. *Appl. Organomet. Chem.* **2021**, *35*, e6333; (c) Ghosh, P.; Wangelin, A. J. V. *Angew. Chem. Int. Ed.* **2021**, *60*, 16035 – 16043.; (d) Roy, M. M. D.; Omaña, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S. Rivard, E. *Chem. Rev.* **2021**, *121*, 12784 – 12965; (e) Bose, S. K.; Mao, L.; Kuehn, L.; Radius, U.; Nekvinda, J.; Santos, W. L.; Westcott, S. A.; Steel, P. G.; Marder, T. B. *Chem. Rev.* **2021**, *121*, 13238 – 13341; (f) Liu, H.; Eisen, M. S. *Synthesis* **2020**, *52*, 629 – 644; (g) Sadow, A. D. (**2020**), 201-224. *Alkali and Alkaline Earth Element-Catalyzed Hydroboration Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA; (h) Bage, A.

D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. *ACS Catal.* **2020**, *10*, 13479 – 13486; (i) Kuciński, K.; Hreczycho, G. *Green Chem.* **2020**, *22*, 5210 – 5224; (j) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307 – 3336; (k) Tamang, S. R.; Findlater, M. *Molecules* **2019**, *24*, 3194; (l) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, *5*, 3238 – 3259; (m) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48*, 1995 – 2003; (n) Maeda, C.; Miyazaki, Y.; Ema, T. *Catal. Sci. Technol.* **2014**, *4*, 1482 – 1497; (o) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957 – 5026.

5. Selected examples of synthesis and application of boron reagents; see: (a) Prates, J. L. B.; Pavan, A. R.; dos Santos, J. L. *Curr. Org. Chem.* **2021**, *25*, 1853 – 1867; (b) DeFrancesco, H.; Dudley, J.; Coca, A. *Boron chemistry: overview*, *ACS Symp. Ser.* **2016**, *1236*, 1 – 25; DOI: 10.1021/bk-2016-1236.ch001; (c) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412 – 443; (d) Tobisu, M.; Chatani, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 3565 – 3568; (e) Hall, D. G. *Structure, Properties, Preparation of Boronic Acid Derivatives. Overview of their Reactions and Applications*, Wiley-VCH, Weinheim, **2005**; (f) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*, Academic Press, New York, **1988**.

6. Aluminum-based catalysts for hydroboration of carbonyls; (a) Titze, M.; Heitkämper, J.; Junge, T.; Kästner, J.; Peters, R. *Angew. Chem. Int. Ed.* **2021**, *60*, 5544 – 5553; (b) Chia, C. -C.; Teo, Y. -C.; Cham, N.; Ho, S. Y. -F.; Ng, Z. -H.; Toh, H. -M.; Mèzailles, N.; So, C. -W. *Inorg. Chem.* **2021**, *60*, 4569 – 4577; (c) Weetman, C.; Porzelt, A.; Bag, P.; Hanusch, F.; Inoue, S. *Chem. Sci.* **2020**, *11*, 4817 – 4827; (d) Ould, D. M. C.; Carden, J. L.; Page, R.; Melen, R. L. *Inorg. Chem.* **2020**, *59*, 14891 – 14898; (e) Peddarao, T.; Sarkar, N.; Nembenna, S. *Inorg. Chem.* **2020**, *59*, 4693 – 4702; (f) Franz, D.; Jandl, C.; Stark, C.; Inoue, S. *ChemCatChem* **2019**, *11*, 5275 – 5281; (g) Lebedev, Y.; Polishchuk, I.; Maity, B.; Guerreiro, M. D. V.; Cavallo, L.; Rueping, M. *J. Am. Chem. Soc.* **2019**, *141*, 19415 – 19423; (h) Woodside, A. J.; Smith, M. A.; Herb, T. M.; Manor, B. C.; Carroll, P. J.; Rablen, P. R.;

Graves, C. R. *Organometallics* **2019**, *38*, 1017 – 1020; (i) Zhang, G.; Wu, J.; Zeng, H.; Neary, M. C.; Devany, M.; Zheng, S.; Dub, P. A. *ACS Catal.* **2019**, *9*, 874 – 884; (j) Liu, Y.; Ma, X.; Ding, Y.; Yang, Z.; Roesky, H. W. *Organometallics* **2018**, *37*, 3839 – 3845; (k) Liu, Y.; Liu, X.; Liu, Y.; Li, W.; Ding, Y.; Zhong, M.; Ma, X.; Yang, Z. *Inorg. Chim. Acta* **2018**, *471*, 244 – 248; (l) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.* **2018**, *54*, 1233 – 1236; (m) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. *Chem. Eur. J.* **2018**, *24*, 4794 – 4799; (n) Lemmerz, L. E.; McLellan, R.; Judge, N. R.; Kennedy, A. R.; Orr, S. A.; Uzelac, M.; Hevia, E.; Robertson, S. D.; Okuda, J.; Mulvey, R. E. *Chem. Eur. J.* **2018**, *24*, 9940 – 9948; (o) Pollard, V. A.; Fuentes, M. Á.; Kennedy, A. R.; McLellan, R.; Mulvey, R. E. *Angew. Chem. Int. Ed.* **2018**, *57*, (p) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, *8*, 2001 – 2005; (q) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54*, 10225 – 10229; (r) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, *18*, 4710 – 4713; (s) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1245 – 1250.

7. Selected examples of aluminum catalyzed hydrosilylation of carbonyls and unsaturated organic compounds; (a) Sarkar, N.; Sahoo, R. K.; Mukhopadhyay, S.; Nembenna, S. *Eur. J. Inorg. Chem.* **2022**, DOI: https://doi.org/10.1002/ejic.202101030; (b) Bolley, A.; Specklin, D.; Dagorne, S. *Polyhedron* **2021**, *194*, 114956; (c) Kannan, R.; Chambenahalli, R.; Kumar, S.; Krishna, A.; Andrews, A. P.; Jemmis, E. D.; Venugopal, A. *Chem. Commun.* **2019**, *55*, 14629 – 14632; (d) Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics* **2017**, *36*, 4810 – 4815; (e) Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.* **2016**, *6*, 7350 – 7356; (f) Stennett, T. E.; Pahl, J.; Zijlstra, H. S.; Seidel, F. W.; Harder, S. *Organometallics* **2016**, *35*, 207 – 217; (g) Chen, J.; Chen, E. Y. –X. *Angew. Chem. Int. Ed.* **2015**, *54*, 6842 – 6846; (h) Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics* **2013**, *32*, 6812 – 6819; (i)

Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 7323 – 7326; (j) Koller, J.; Bergman, R. G. *Organometallics* **2012**, *31*, 2530 – 2533; (k) Kato, N.; Tamura, Y.; Kashiwabara, T.; Sanji, T.; Tanaka, M. *Organometallics* **2010**, *29*, 5274 – 5282; (l) Bach, P.; Albright, A.; Laali, K. K. *Eur. J. Org. Chem.* **2009**, 1961 – 1966.

8. Review articles and book chapters for reactivity and catalysis of molecular aluminum chemistry; (a) Ni, C.; Ma, X.; Yang, Z.; Roesky, H. W. *Eur. J. Inorg. Chem.* **2022**, DOI: https://doi.org/10.1002/ejic.202100929**;** (b) Das, A.; Rej, S.; Panda, T. K. *Dalton Trans.* **2022**, *51*, 3027 – 3040; (c) Liu, Y.; Li, J. Ma, X.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2018**, *374*, 387 – 415; (d) Caise, A.; Jones, D.; Kolychev, E. L.; Hicks, J.; Goicoechea, J. M.; Aldridge, S. *Chem. Eur. J.* **2018**, *24*, 13624 – 13635; (e) Weetman, C.; Inoue, S. *ChemCatChem* **2018**, *10*, 4213 – 4228; (f) Dagorne, S.; Wehmschulte, R. *ChemCatChem* **2018**, *10*, 2509 – 2520; (g) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, *350*, 14 – 29; (h) Ananikov, V. P. *Sustainable Catalysis with Nonendangered Metals*. *Angew. Chem. Int. Ed.* **2016**, *55*, 14904; (i) Aldridge, S.; Downs, A. J. *The Group 13 Metals Aluminium, Gallium, Indium, and Thallium: Chemical Patterns and Peculiarities*. *Angew. Chem. Int. Ed.* **2011**, *50* (49), 11569.

9. Selected examples of aluminum catalyzed hydroboration of unsaturated functional groups; (a) Hobson, K.; Carmalt, C. J.; Bakewell, C. *Inorg. Chem.* **2021**, *60*, 10958 − 10969; (b) Sarkar, N.; Bera, S.; Nembenna, S. *J. Org. Chem.* **2020**, *85*, 4999 – 5009; (c) Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Adv. Synth. Catal.* **2019**, *361*, 850 – 857; (d) Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J.* **2019**, *25*, 11918 – 11923; (e) Liu, W.; Ding, Y.; Jin, D.; Shen, Q.; Yan, B.; Ma, X.; Yang, Z. *Green Chem.* **2019**, *21*, 3812 – 3815; (f) Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics* **2019**, *38*, 3092 – 3097.

10. Main-group and transition metal-based catalysts for hydroboration of carboxylic acids; (a) Yan, B.; Dutta, S.; Ma, X.; Ni, C.; Koley, D.; Yang, Z.; Roesky, H. W. *Dalton Trans.* **2022**, *51*, 6756 – 6765; (b) Wang, Q.; Li, L.; Li, P.; Yue, X.; Yang, Z.; Pu, M.; Lei, M. *New J. Chem.* **2019**, *43*, 11493 – 11496; (c) Barman, M. K.; Das, K.; Maji, B. *J. Org. Chem.* **2019**, *84*, 1570 – 1579; (d) Kisan, S.; Krishnakumar, V.; Gunanathan, C. *ACS Catal.* **2018**, *8*, 4772 – 4776; (e) Erken, C.; Kaithal, A.; Sen, S.; Weyhermüller, T.; Hölscher, M.; Werlé, C.; Leitner, W. *Nat. Commun.* **2018**, *9*, 4521.

11. Solvent and metal-free hydroboration of carboxylic acids; (a) Wang, W.; Luo, M.; Zhu, D.; Yao, W.; Xu, L.; Ma, M. *Org. Biomol. Chem.* **2019**, *17*, 3604 – 3608; (b) Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Chem. Commun.* **2019**, *55*, 1386 – 1389; (c) Xu, X.; Yan, D.; Zhu, Z.; Kang, Z.; Yao, Y.; Shen, Q.; Xue, M. *ACS Omega* **2019**, *4*, 6775 – 6783.

12. Main-group metal-catalyzed hydroboration of carbonates; (a) Szewczyk, M.; Magre, M.; Zubar, V.; Rueping, M. *ACS Catal.* **2019**, *9*, 11634 – 11639; (b) Cao, X.; Wang, W.; Lu, K.; Yao, W.; Xue, F.; Ma, M. *Dalton Trans.* **2020**, *49*, 2776 – 2780; (c) Lavergne, J. L.; To, H. -M.; Fontaine, F.-G. *RSC Adv.* **2021**, *11*, 31941 – 31949; (d) Khuntia, A. P.; Sarkar, N.; Patro, A G.; Sahoo, R. K. Nembenna, S. *Eur. J. Inorg. Chem.* **2022**, DOI: https://doi.org/10.1002/ejic.202200209.

13. Transition metal-catalyzed hydroboration of carbonates; see Thenarukandiyil, R.; Satheesh, V.; Shimon, L. J. W.; de Ruiter, G. *Chem. Asian J.* **2021**, *16*, 999 – 1006.

14. Selected examples of metal-catalyzed hydrogenation of carbonates and formates; (a) Li, Y.; Ding, K. *Catalytic Reduction of Carbonates*, **2018**, *1*, 269 – 288; (b) Kaithal, A.; Hölscher, M.; Leitner, W. *Angew. Chem. Int. Ed.* **2018**, *57*, 13449 – 13453; (c) Han, Z.; Rong, L.; Wu, J.; Zhang, L.; Wang, Z.; Ding, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 13041 – 13045; (d) Kumar, A.; Janes, T.; Espinosa-Jalapa, N. A.; Milstein, D. *Angew. Chem. Int. Ed.* **2018**, *57*, 12076 – 12080; (e) Zubar, V.; Lebedev, Y.; Azofra, L. M.; Cavallo, L.; El-Sepelgy, O.;

Rueping, M. *Angew. Chem. Int. Ed.* **2018**, *57*; (f) Stein, T. V.; Meuresch, M.; Limper, D.; Schmitz, M.; Hölscher, M.; Coetzee, J.; Cole-Hamilton, D. J.; Klankermayer, J.; Leitner, W. *J. Am. Chem. Soc.* **2014**, *136*, 13217 – 13225; (g) Dub, P. A.; Ikariya, T. *ACS Catal.* **2012**, *2*, 1718 – 1741; (h) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nat. Chem.* **2011**, *3*, 609 – 614.

15. Selected examples of metal-catalyzed transfer hydrogenation of carbonates and formates; (a) Kim, S. H.; Hong, S. H. *ACS Catal.* **2014**, *4*, 3630 – 3636; (b) Liu, X.; de Vries, J. G.; Werner, T. *Green Chem.* **2019**, *21*, 5248 – 5255.

16. Main group metal-catalyzed reduction of amides to amines *via* hydroboration; (a) Khalimon, A. Y. *Dalton Trans.* **2021**, *50*, 17455 – 17466; (b) Yu, C.; Guo, C.; Jiang, L.; Gong, M.; Luo, Y. *Organometallics* **2021**, *40*, 1201 – 1206; (c) Bisai, M. K.; Gour, K.; Das, T.; Vanka, K.; Sen, S. S. *Dalton Trans.* **2021**, *50*, 2354 – 2358; (d) Yao, W.; Wang, J.; Zhong, A.; Wang, S.; Shao, Y. *Org. Chem. Front.* **2020**, *7*, 3515 – 3520; (e) Bhunia, M.; Sahoo, S. R.; Das, A.; Ahmed, J.; Sreejyothi P., Mandal, S. K. *Chem. Sci.* **2020**, *11*, 1848 – 1854; (f) Das, S.; Karmakar, H.; Bhattacharjee, J.; Panda, T. K. *Dalton Trans.* **2019**, *48*, 11978 – 11984; (g) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52*, 13155 – 13158; (h) Schnitzler, S.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2016**, *55*, 12997 – 13006; (i) Lampland, N. L.; Hovey, M.; Mukherjee, D.; Sadow, A. D. *ACS Catal.* **2015**, *5*, 4219 – 4226.

17. Selected example of hydrosilylation of carboxylic acids; Castro, L. C. M.; Sortais, H. Li, J. -B.; Darcel, C. *Chem. Commun.* **2012**, *48*, 10514 – 10516.

18. Selected examples: (a) Pritchard, J.; Filonenko, G. A.; Putten, R. V.; Hensen, E. J. M.; Pidko, E. A. *Chem. Soc. Rev.* **2015**, *44*, 3808 – 3833; (b) Naruto, M.; Agrawal, S.; Toda, K.; Saito, S. *Sci. Rep.* **2017**, *7*(1), 1-12.

19. Selected references of deoxygenative hydroboration of nitro (NO_2) compounds; (a) Yao, W.; Wang, J.; Lou, Y.; Wu, H.; Qi, X.; Yang, J.; Zhong, A. *Org. Chem. Front.* **2021**, *8*, 4554 – 4559; (b) Zhao, L.; Hu, C.; Cong, X.; Deng, G.; Liu, L. L.; Luo, M.; Zeng, X. *J. Am. Chem. Soc.* **2021**, *143*, 1618 – 1629; (c) Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. *Chem. Rev.* **2019**, *119*, 2611 – 2680; (d) Orlandi, M.; Brenna, D.; Harms, R.; Jost, S.; Benaglia, M. *Org. Process Res. Dev.* **2018**, *22*, 430 – 445.

20. Selected reference: Reutemann; W. Kieczka, H. "Formic Acid" in *Ullmann's Encyclopedia of Industrial Chemistry* **2002**, Wiley-VCH.

21. Selected examples on chemoselectivity reaction; (a) Bergamaschi, E.; Lunic, D.; McLean, L. A.; Hohenadel, M.; Chen, Y. –K.; Teskey, C. J. *Angew. Chem. Int. Ed.* **2022**, DOI: https://doi.org/10.1002/anie.202114482; (b) Sarkar, N.; Mahato, M.; Nembenna, S. *Eur. J. Inorg. Chem.* **2020**, 2295 – 2301; (c) Mahatthananchai, J.; Dumas, A. M.; Bode, J. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 10954 – 10990; (d) Cunningham, A. D.; Ham, E. Y.; Vosburg, D. A. *J. Chem. Educ.* **2011**, *88*, 322 – 324; (e) Ballard, C. E. *J. Chem. Educ.* **2010**, *87*, 190 – 193; (f) Shenvi, R. A.; O'Malley, D. P.; Baran, P. S.; *Acc. Chem. Res.* **2009**, *42*, 530 – 541.

22. References for the Conjugated Bis-guanidine (CBG) ligand; (a) Sahoo, R. K.; Sarkar, N.; Nembenna, S. *Angew. Chem. Int. Ed.* **2021**, *60*, 11991 – 12000; (b) Peddarao, T.; Baishya, A.; Sarkar, N.; Acharya, R.; Nembenna, S. *Eur. J. Inorg. Chem.* **2021**, 2034 – 2046.

23. Selected examples of hydrogenation of amide and phthalic anhydride; (a) Pan, Y.; Luo, Z.; Han, J.; Xu, X.; Chen, C.; Zhao, H.; Xu, L.; Fan, Q.; Xiao, J. *Adv. Synth. Catal.* **2019**, *361*, 2301 – 2308; (b) Coeck, R.; Berden, S.; De Vos, D. E. *Green Chem.* **2019**, *21*, 5326 – 5335; (c) Zhang, L.; Chen, X.; Chen, Y.; Peng, Z.; Liang, C. *Catal. Sci. Technol.* **2019**, *9*, 1108 – 1116; (d) Zou, Y. -Q.; Chakraborty, S.; Nerush, A.; Oren, D.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *ACS Catal.* **2018**, *8*, 8014 – 8019; (e) Zhang, L.; Chen, X.; Jin, S.; Di, X.;

Williams, C. T.; Peng, Z.; Liang, C. *Mater. Chem. Phys.* **2016**, *180*, 89 – 96; (f) Volkov, A.; Tinnis, F.; Slagbrand, T.; Trillo, P.; Adolfsson, H. *Chem. Soc. Rev.* **2016**, *45*, 6685 – 6697; (g) Stein, M.; Breit, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 2231 – 2234; (h) Liu, Y. Xing, T. Wei, Z. Li, X. Yan, W. *Catal. Commun.* **2009**, *10*, 2023 – 2026.

Chapter 3B

Aluminum-Catalyzed Selective Hydroboration of Esters and Epoxides to Alcohols: C-O Bond Activation

Published:

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Abstract

In this work, the molecular aluminum dihydride complex bearing an *N, N'*-chelated conjugated bis-guanidinate (CBG) ligand is used as a catalyst for reducing a wide range of aryl and alkyl esters with good tolerance of alkene (C=C), alkyne (C≡C), halides (Cl, Br, I and F), nitrile (C≡N), and nitro (NO_2) functionalities. Further, it was discovered that the catalytic application of aluminum dihydride in the C-O bond cleavage of alkyl and aryl epoxides into corresponding branched Markovnikov ring-opening products. In addition, the chemoselective intermolecular reduction of esters over other reducible functional groups, such as amides and alkenes, has been established. Intermediates are isolated and characterized by NMR and HRMS studies, which confirm the probable catalytic cycles for the hydroboration of esters and epoxides.

3.B.1. Introduction

The reduction of esters *via* the hydroboration technique to alcohols is one of the crucial processes in organic chemistry.[1] Especially, selective reduction of esters over other reducible functionalities is the foremost challenging and synthetically valuable task.[2] Employing a stoichiometric quantity of classical reductants such as sodium borohydride or lithium aluminum hydride, one can significantly extract alcohols[3] from esters, which may lead to severe drawbacks,

including fire hazards, poor tolerance of functional groups, and generation of a massive quantity of wastes with exhausting isolation steps.[4] Therefore, the metal-based reduction of esters via the hydrogenation method has been developed as a good practice.[5] Nonetheless, it demands combustible H_2 gas and extremely harsh reaction environments. These difficulties can be overcome by metal-catalyzed hydroelementation reactions such as hydroboration,[6] and hydrosilylation.[7]

In the past few years, metal-catalyzed hydroboration of carbonyl compounds has developed rapidly.[6] Among main-group metal catalysis, it was observed that inexpensive molecular aluminum compounds were effectively used for carbonyl reduction via hydroboration[6, 8] and hydrosilylation[9] techniques as alternatives to expensive transition (except 3d metals) and lanthanide metal complexes.[6, 10]

The developed molecular aluminum catalysts have been further explored to reduce challenging unsaturated organic functionalities via B-H or Si-H addition method.[11] As per the literature survey, various metal-mediated hydrosilylations of esters[12] is reported.

However, only a handful of examples of main-group[8j,13] catalyzed hydroboration of esters have been explored compared to transition metal-based catalysts[14] due to less reactivity than aldehydes and ketones (Scheme 1). In this context, it is noteworthy that no reports on aluminum-based hydroboration of esters are found, except for the Cowley group's sole example, $LiAlH_4$ catalyzed hydroboration of ethyl acetate with HBpin.[8j] Moreover, during the preparation of this manuscript, Yan et al. reported aluminum-catalyzed hydroboration of esters.[13b] In 2014, Sadow and coworkers[13j] established the first main-group magnesium; To^MMgMe [where To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate] catalyzed C=O bond reduction of esters. Later, other molecular magnesium catalysts[13i-13j] were used to reduce esters with pinacolborane (HBpin)

under low catalyst loadings. Recently Ma and coworkers[13g] introduced an unsymmetrical NacNac stabilized Mg (I) dimer as a pre-catalyst to synthesize boronate esters from corresponding esters.

As per current research, there have been few reports on main-group[15] and transition[14h, 16] metal-catalyzed hydroboration of epoxides. In main-group metal catalysis, Rueping[15a] and Ma[15b] research groups independently introduced magnesium-based catalysts for the ring-opening of epoxides with HBpin. Classical metal hydrides[17] and hydrogenation

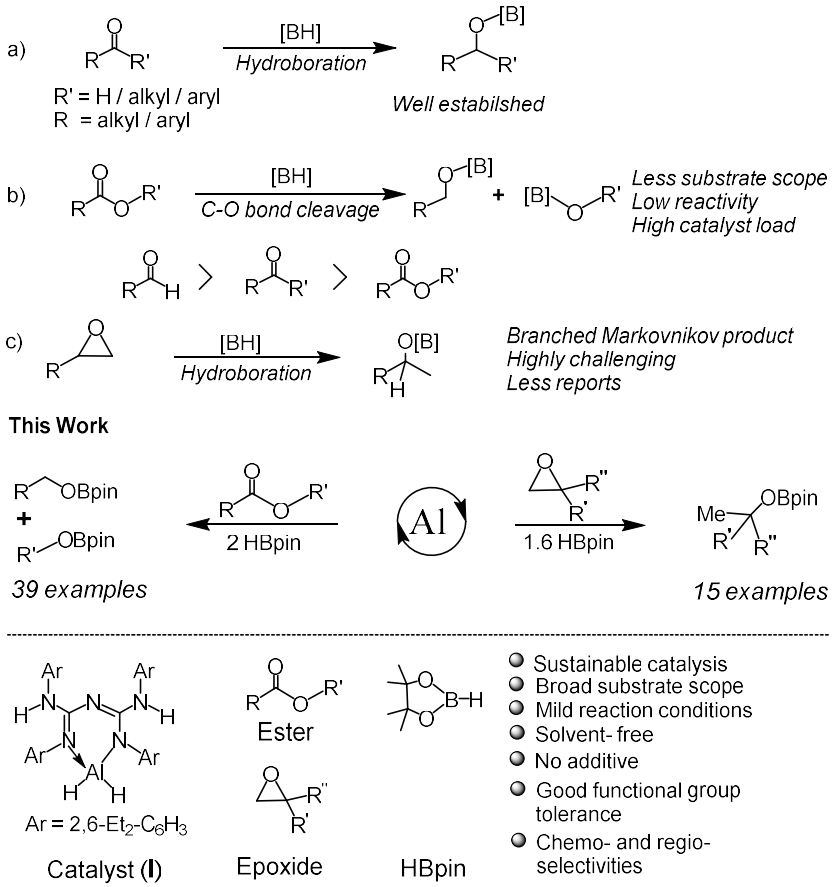


Figure 3.B.1. Metal-catalyzed hydroboration of carbonyls and epoxides.

methods[18] have also been employed for epoxide reduction. Most of these catalysts[16, 17, 18] favor anti-Markovnikov C-O bond activation of epoxides, which restrains the Markovinkov substrate

scope[15] (Figure 3.B.1.). Therefore, developing new sustainable methods for the Markovnikov ring cleavage [15] *via* hydroboration of epoxides is attractive.

Recently our group described a series of structurally characterized conjugated bis-guanidinate (CBG) stabilized aluminum complexes, including CBG aluminum dihydrides.[7a,8a,11b] Moreover, CBG aluminum dialkyls[7a, 8b] and dihydrides[11b] have been utilized as catalysts for organic transformations. Previously, our research group reported the guanidinate magnesium amides as pre-catalysts for the chemoselective reduction of organic esters.[13h] Apart from (^{Diethyl}Nacnac)AlH_2 catalyzed B-H addition in ester,[13b] no other reports have been on molecular aluminum-based catalysts to reduce epoxides *via* the hydroboration method.[13,15]

Therefore, we report an aluminum dihydride (**1**) complex bearing a conjugated bis-guanidinate (CBG) for chemoselective C-O bond cleavage of esters and epoxides. Compound **1** catalyzed the selective hydroboration of esters in the presence of other reducible functional groups, which have been thoroughly explored. The present work is the first report on the aluminum-catalyzed Markovinkov ring-opening of epoxides into branched borate esters with HBpin.[15]

3.B.2. Results and Discussion

3.B.2.1. Ester Hydroboration

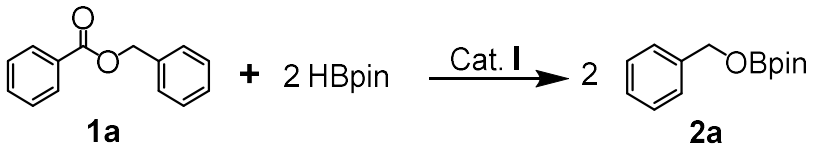
In a recent report, the synthesis of well-characterized conjugated bis-guanidinate supported mononuclear aluminum dihydride (**I**)[11b] complex by deprotonation of ligand LH[19] [L= {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar =2,6-Et_2-C_6H_3] with 1.0 equiv. of alane ($H_3Al{\cdot}NMe_2Et$) was published.

Compound **I** is a highly active catalyst as it is being used for the hydroboration of challenging functional groups[7a, 8a, 11b] such as nitrile, alkyne, alkene, carbodiimide, and isocyanide, which

encouraged us to investigate the catalytic hydroboration of other challenging organic substrates, i.e., esters, and epoxides.

The investigation was started by reducing benzyl benzoate **1a** as a representative substrate with 2.0 equiv. of HBpin (reducer) under solvent and catalyst-free conditions. After 24 h of stirring at rt and 70 ºC, no B-H addition in substrate **1a** was observed (entries 1-2 of Table 3.B.1.). However, by adding 6 mol% of aluminum-hydride catalyst (**1**) to the reaction mixture of benzyl benzoate and HBpin, leads to a complete reduction of benzyl benzoate into the corresponding hydroborated product $PhCH_2OBpin$ (**2a**) at 70 ºC. Furthermore, a similar C=O bond reduction of benzyl benzoate was conducted under solvent-free conditions by employing lower catalyst loading (4 mol% and 2 mol%) at 12 h of stirring (entries 6 and 7 in Table 3.B.1.). Similar catalytic activity of compound **I** for benzyl benzoate reduction for different solvents (Table 3.B.1., entries 8-10). Reaction progress was monitored by multinuclear NMR spectra (^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{11}B\}$.

Table 3.B.1. Optimization table of aluminum-hydride (**I**) catalyzed reduction of benzyl benzoate.[a]



1a **2a**

Entry	Cat. (mol%)	Solvent	Temp	Time	Yield (%)[b]
1	-	neat	rt	24 h	-
2	-	neat	70 ºC	24 h	-
3	6	neat	70 ºC	24 h	>99
4	6	neat	70 ºC	12 h	>99
5	6	neat	70 ºC	8 h	88
6	4	neat	70 ºC	12 h	>99

7	**2**	**neat**	70 °C	**12 h**	**>99**
8	2	toluene	70 °C	12 h	>99
9	2	THF	70 °C	12 h	>99
10	2	benzene	70 °C	12 h	>99
11	1	neat	70 °C	12 h	75

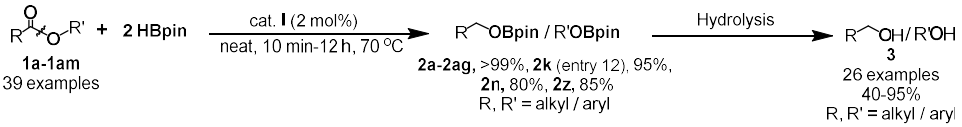
[a]Reactions were conducted with benzyl benzoate (1.0 equiv., 1.0 mmol), HBpin (2.0 equiv., 2.0 mmol), and cat. **I** (2 mol%), in 10 mL air-tight vial under N_2 and stirred in an oil bath of 70 °C heating for 12 h. [b]Yield for reduction of compound **1a** was determined by NMR spectroscopy (^{1}H and ^{13}C{^{1}H}) based on the disappearance of C=O bond and formation of typical new proton signal for (-C*H*$_2$OBpin) moiety of **2a** at (δ) 4.94 ppm.

The successful optimization of reaction conditions to reduce benzyl benzoate (**1a**) motivated us to explore a wide range of esters, and the corresponding reaction outcomes are depicted in Table 3.B.2. All commercially available esters fully underwent reduction with C-O bond activation *via* hydroboration with good tolerance of halide, nitro, nitrile, alkene, and alkyne functional groups. The major boronate ester residues were hydrolyzed and purified into pure alcohols (**3**) using column chromatography. In initial substrate screening, it was discovered that methyl benzoate (**1b**) achieved quantitative conversion (**2a**), like benzyl benzoate reduction. Remarkably under neat conditions, substituted methyl benzoate at para-position either with electron-donating (Me, OMe; **1c-1d**) or electron-withdrawing (Cl, Br, I, NO_2, CF_3; **1e-1i**) groups afforded high yields of benzyl boronates (**2b-2h**) in 12 h. Notably, no over-reduction was found in all boronate ester products **2b-2h**.

In addition, in the case of functionalized ester, 4-cyanobenzoate (**1j**), compound **I** displayed an effective intramolecular chemoselective reduction of ester moiety in preference to nitrile (C≡N) functional group to afford corresponding boronate ester product **2i** in 99% yield. However, the

highly reactive reducible carbonyl functionalities such as aldehyde (CHO), ketone (COMe), and

Table 3.B.2. Substrate scope for catalytic C=O bond reduction of esters using aluminum hydride (**I**).[a]



Entry	Ester (1)	Product (2)	Yield[b]
1	1a	2 2a	>99% (**3a**, 94%)
2	1b	2a + MeOBpin	>99% (**3a**, 88%)
3	1c	2b[c]	>99% (**3b**, 93%)
4	1d	2c[c]	>99% (**3c**, 90%)
5	1e	2d[c]	>99% (**3d**, 94%)
6	1f	2e[c]	>99% (**3e**, 96%)
7	1g	2f[c]	>99%
8	1h	2g[c]	>99% (**3g**, 95%)
9	1i	2h[c]	>99% (**3h**, 86%)
10	1j	2i[c]	>99% (**3i**, 87%)
11	1k	2j[c, d]	>99% (**3j**, 72%)
12	1l	2k[c, d]	95%
13	1m	2j[c, d] + $(Bpin)_2O$ + H_2	>99% (**3j**, 75%)
14	1n	2k[d] + EtOBpin	>99%
15	1o	2e[e]	>99% (**3e**, 84%)
16	1p	2l + $PhCH_2OBpin$ 2a	>99% (**3l**, 42%)
17	1q	2m[f]	>99% (**3m**, 40%)
18	1r	2n[f]	80% (**3n**, 46%)
19	1s	2o[e]	>99% (**3o**, 82%)
20	1t	2p[e]	>99% (**3p**, 78%)
21	1u	2q[f]	>99%
22	1v	2r[c]	>99% (**3r**, 85%)
23	1w	2s[c]	>99% (**3s**, 68%)
24	1x	2s[e]	>99% (**3s**, 62%)
25	1y	2t[e]	90%
26	1z	2u[c]	>99% (**3u**, 80%)
27	1aa	2v[c]	>99% (**3v**, 78%)
28	1ab	2 2w[g]	>99%
29	1ac	2 2x[g]	>99%
30	1ad	2w[c, g]	>99%
31	1ae	2y[e, g]	>99%
32	1af	2z[e]	85% (**3z**, 52%)
33	1ag	2aa	>99%
34	1ah	2ab	>99%
35	1ai	2ac	>99% (**3ac**, 73%)
36	1aj	2 2ad	>99%
37	1ak	2ae	>99%
38	1al	2af	>99% (**3af**, 71%)
39	1am	2ag	>99%

[a]Reactions were conducted with esters (1.0 equiv., 1.0 mmol), HBpin (2.0 equiv., 2.0 mmol), and cat. **I** (2 mol%), in 10 mL air-tight vial under N_2 and stirred in an oil bath of 70 °C heating for 12 h. [b]Yield for reduction of esters (**1a-1am**) was determined by NMR spectroscopy (^{1}H and ^{13}C{^{1}H}) based on the disappearance of C=O bond and formation of typical new proton signal for (-C*H*$_2$OBpin) moiety of boronate ester products (**2a-2ag**). The yield of primary isolated alcohol was given in parenthesis after being purified by column chromatography. [c]MeOBpin is the by-product. Only major hydroboration products were labeled. [d]For **1k-1n,** HBpin (3.0-5.0 equiv.) used. [e]EtOBpin is the by-product. [f]PhCH$_2$OBpin is the by-product. [g]For **1ab-1ae,** the reactions were completed within 10 min.

carboxylic acid (COOH) groups were unprotected; therefore, under excess pincolborane (3.0-5.0 equiv.), **1k-1n** were fully converted into hydroborated products **2j-2k** and MeOBpin (or EtOBpin) as a by-product with high yields.

Moreover, the analogous substrate of methyl 4-bromobenzoate (**1f**), i.e.,**1o**, also yielded the boronate ester **2e** with good isolation of hydrolyzed 1° alcohol in 84% yield (**3e**) and the side-product EtOBpin.

Additionally, for aryl benzoates such as phenyl benzoate, 4-methyl phenyl benzoate, 2-naphthyl acetate, and 1-naphthyl acetate (**1p-1q, 1s-1t**), 99% yields for desired boronate ester products (**2l-2m, 2o-2p**) in 12 h was noticed except in 4-nitrophenyl benzoate (**1r**) where 80% conversion of aryl boronic ester **2n** was found.[20] Next, our focus shifted towards reducing alkyl esters. The benzyl phenylacetate (**1u**) undergoes C-O cleavage to afford the desired aryl borate esters **2q** and **2a** in a 99% yield. Interestingly, functionalized alkyl esters **1v-1aa** sustain smooth intramolecular chemoselective reduction into desired borylated products **2r-2v** with unaffected, double (C=C), and triple (C≡C) bonds. The above- results are consistent with previous reports.[13g-13h,14g]

In additional experiments, it was discovered that smaller alkyl esters (**1ab-1ae**) underwent faster hydroboration than the aryl esters.[14h] Therefore, in hydroboration of ethyl acetate, ethyl propionate, methyl acetate, and isopropyl acetate, affords the complete reduction into relevant alkyl hydroborated products (**2w-2y**) in 10 min with no trace of starting substrate. Nevertheless,

tert-butyl acetate (**1af**) was reduced by only 85% in **2z** due to the steric bulk of the CMe_3 group at the acyl position, which ultimately slows down the hydroboration reaction. In addition, the reduction of cyclic esters (*called lactones*), which serve as the primary building blocks to produce synthetic chemicals,[1] was studied. In this regard, it was found that all selected cyclic esters (**1ag-1al**) were completely hydroborated into alkoxy boronate esters (**2aa-2af**) with no competition reaction such as polymerization of esters which was a typical example.[13j]

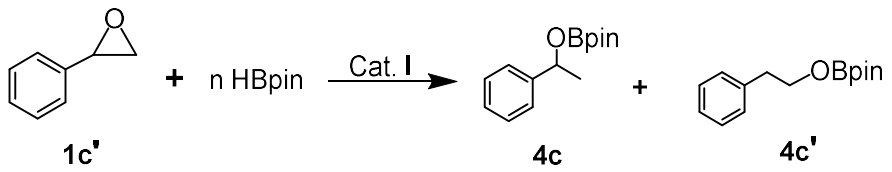
Next, the selective reduction of γ-decalactone (**1am**) was examined, where quantitative C-O bond reduction into hydroborated product **2ag** under standard conditions was discovered.

3.B.2.2. Epoxide Hydroboration

As it was mentioned earlier, a few reports have been known on metal-catalyzed hydroboration of epoxides.[15, 16] With compound **I** success in catalytic ester hydroboration; next, I aimed to explore the epoxide ring cleavage via hydroboration.

The examination began with treating styrene oxide **1c'** as a representative substrate for epoxide hydroboration with 1.2 equiv. HBpin under 10 mol% catalyst, **I** loading to afford the **4c** in 87% yield (entry 1, Table 3.B.3.). Gradually increasing the equivalency of HBpin resulted in the formation of alkoxy boronate ester (**4c**) in 99% yields, respectively, under neat conditions in low catalyst load (Table 3.B.3., Entry 6). Besides, the solvent does not affect the catalytic activity of epoxide reduction (entries 7-9 of Table 3.B.3.). Both linear and branched products were formed in low yield% at catalyst-free environments at 70 ºC (Table 3.B.3., entry 10). With the help of NMR (^1H and $^{13}C\{^1H\}$) spectroscopy, the progress in the reaction was investigated. Further, hydrolysis of boronate esters followed by column chromatography afforded corresponding pure alcohols (**5c**, **5j**) with good yields.

Table 3.B.3. Optimization table of aluminum hydride (**I**) catalyzed reduction of styrene oxide.[a]



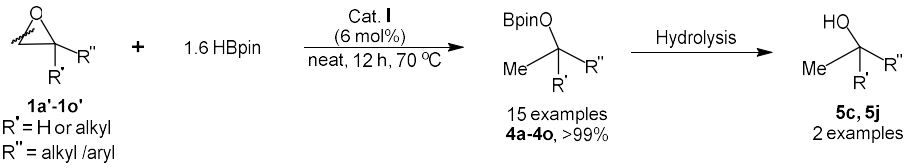
1c' **4c** **4c'**

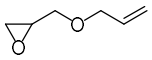
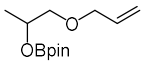
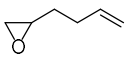
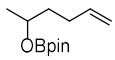
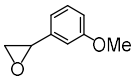
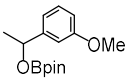
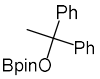
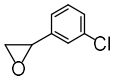
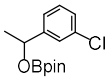
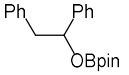
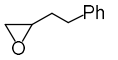
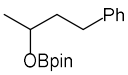
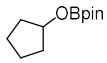
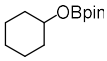
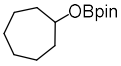
Entry	Cat. (mol%)	HBpin (equiv.)	Solvent	Temp	Time	Yield (%) (**4c:4c'**)[b]
1	10	1.2	neat	70 °C	24 h	87:12
2	10	1.4	neat	70 °C	24 h	95:5
3	10	1.6	neat	70 °C	24 h	>99:0
4	10	1.6	neat	70 °C	12 h	>99:0
5	8	1.6	neat	70 °C	12 h	>99:0
6	**6**	**1.6**	**neat**	70 °C	**12 h**	**>99:0**
7	6	1.6	toluene	70 °C	12 h	>99:0
8	6	1.6	THF	70 °C	12 h	>99:0
9	6	1.6	benzene	70 °C	12 h	>99:0
10	-	1.6	neat	70 °C	12 h	6:4
11	-	1.6	neat	rt	12	-

[a]Reactions were conducted with styrene oxide (1.0 equiv., 1.0 mmol), HBpin (1.6 equiv., 1.6 mmol), and cat. **I** (6 mol%), in 10 mL air-tight vial under N_2 and stirred in an oil bath of 70 °C heating for 12 h. [b]Yield for reduction of styrene oxide was determined by ^{1}H NMR spectra based on the disappearance of starting material and formation of new proton signal for boronate ester product.

With this optimization, the substrate scope in the C-O bond cleavage of epoxides was investigated, and the results are shown in Table 3. B.4.

Table 3.B.4. Substrate scope for catalytic C-O bond cleavage of epoxides using aluminum hydride (**I**).[a]



Entry	Epoxide		Product (4)	Yield[b]	Entry	Epoxide		Product (4)	Yield[b]
1		**1a'**		**4a**, >99%	8		**1h'**		**4h**, >99%
2		**1b'**		**4b**, >99%	9		**1i'**		**4i**, >99%
3		**1c'**		**4c**, >99% (**5c**, 87%)	10		**1j'**		**4j**,[c] >99% (**5j**, 60%)
4		**1d'**		**4d**, >99%	11		**1k'**		**4k**, >99%
5		**1e'**		**4e**, >99%	12		**1l'**		**4l**,[d] >99%
6		**1f'**		**4f**, >99%	13		**1m'**		**4m**, >99%
7		**1g'**		**4g**, >99%	14		**1n'**		**4n**, >99%
					15		**1o'**		**4o**, >99%

[a]Reactions were conducted with epoxides (1.0 equiv., 1.0 mmol), HBpin (1.6 equiv., 1.6 mmol), and cat. **I** (6 mol%), in 10 mL air-tight vial under N_2 and stirred in an oil bath of 70 °C heating for 12 h. [b]Yield for reduction for epoxides (**1a'-1o'**) was determined by ^{1}H NMR spectra based on the disappearance of starting material and formation of new proton signal for boronate ester products (**4a-4o**). The yield of isolated alcohol was given in parenthesis after being purified by column chromatography. [c]For **1j'**, the reactions were done at 2.0 mmol scale. [d]For **1l'**, reaction has been done at 80 °C for 24 h.

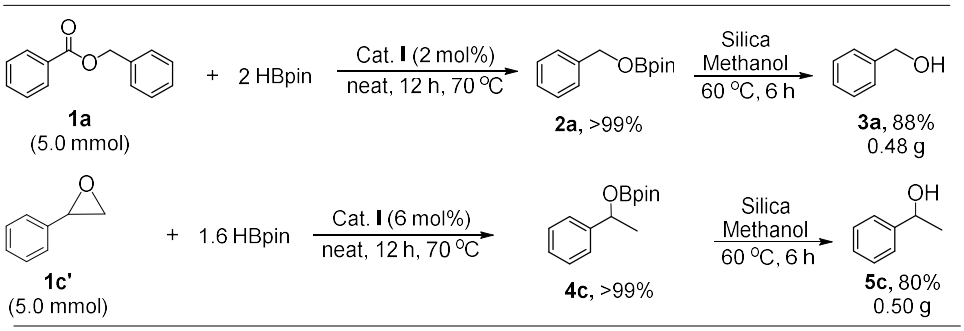
Under standard conditions, ethylene oxide (**1a'**) was converted into corresponding alkoxy boronate ester (**4a**). Following this, the ring-opening of mono-substituted ethylene oxide (**1b'**, **1d'-1g'**) was also explored. It was discovered that the catalytic regioselective ring-opening was successful for both aryl and alkyl substituents to afford the corresponding branched boronate ester products (**4b**, **4d-4g**) in quantitative yield. In addition, the chemoselective C-O bond

cleavage of epoxide in preference over C=C bond reduction was observed for alkenyl substrates (**1h'-1i'**) to yield the respective boryl esters (**4h-4i**). Next, substrates like 2,2-disubstituted terminal oxiranes (**1j'-1k'**) within optimized conditions were screened. As displayed in Table 3.B.4., both 1,2-epoxy-2-methylpropane and 1,1-diphenylcyclopropane substrates transformed into Markovnikov branched boronate esters (**4j-4k**).

Eventually, trans-stilbene oxide (**1l'**) cleavage into a single 1,2-diphenyl borate ester product (**4l**). The reaction also influenced the ring-opening of cyclic epoxides such as cyclopentene oxide, cyclohexene oxide, and cycloheptene oxide (**1m'-1o'**). All three cyclic epoxides were well converted into corresponding alkoxy boronate esters (**4m-4o**), as shown in Table 3.B.4.

3.B.2.3. Scale-up Reactions

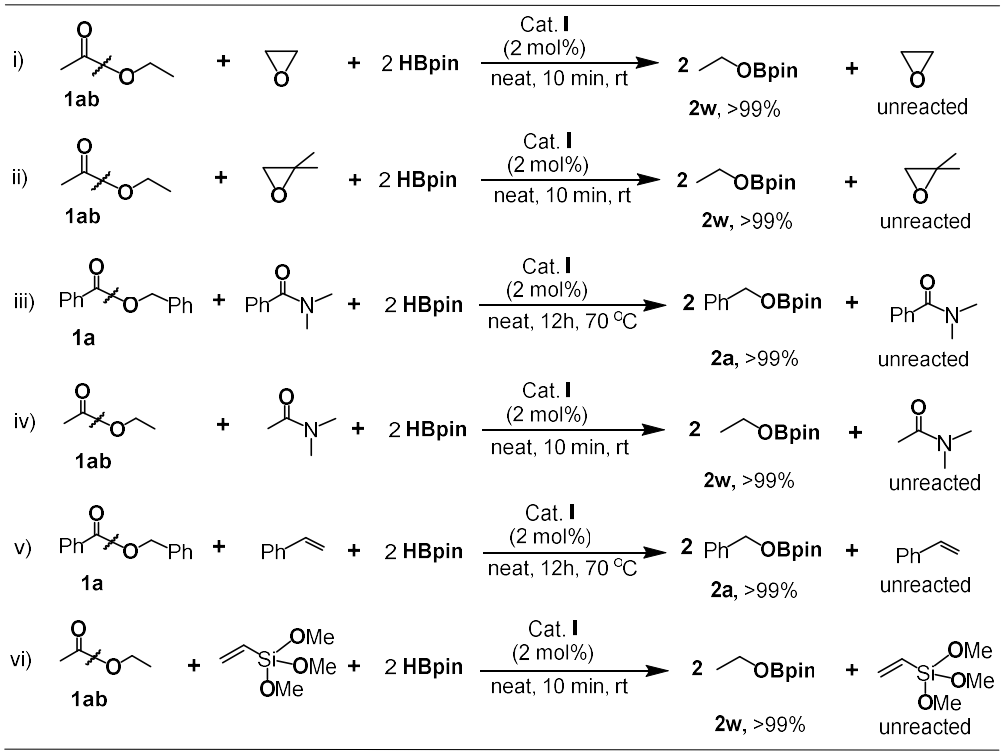
Two independent gram-scale hydroboration reactions were conducted to study the practical utilization of the present catalytic procedures (Scheme 3.B.1.). In the first experiment, a 5.0 mmol scale reaction of benzyl benzoate with two-fold HBpin under standard conditions afforded the corresponding aryl boronate ester product **2a** in 99%, which was later hydrolyzed into 1° alcohol (**3a**) with 88% (0.48 g) isolated yield. Likewise, the ring-opening of styrene oxide (**1c'**) with 1.6 equiv. pinacolborane leads to branched Markovnikov aryl boronate ester product **4c** in quantitative yield on a similar scale. The borate ester **4c** was hydrolyzed by SiO_2/methanol (~ 4 mL) to respective pure 2° alcohol product **5c** in 80% (0.50 g) yield (isolated).



Scheme 3.B.1. Scale-up reactions catalyzed compound **I**.

3.B.2.4. Intermolecular Chemoselective Reactions

In organic synthesis, chemoselectivity plays a vital role in the various chemical transformations to isolate the desired compounds.[21] During ester hydroboration, an exceptional tolerance of nitrile (C≡N), alkene (C=C), and alkyne (C≡C) functional groups have been noticed, which motivates us to explore the chemoselective intermolecular C=O bond reduction of ester vs. epoxide or amide or alkene functionalities (Scheme 3.B.2.).



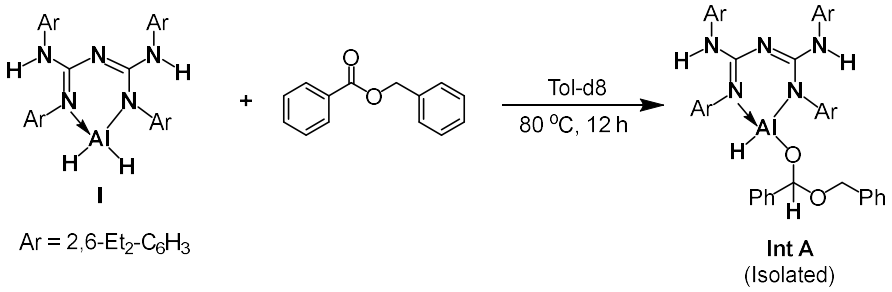
Scheme 3.B.2. Intermolecular chemoselective hydroboration of esters.

Therefore, a one-pot reaction of ethyl acetate and ethylene oxide, or 1,2-epoxy-2-methylpropane with HBpin (2.0 equiv.) at optimized conditions afforded the desired alkoxy boronate ester **2w** with 99% yield in preference to unreacted epoxides (Scheme 3.B.2., i) and ii)). Additionally, a reaction of benzyl benzoate (or ethyl acetate), N, N-dimethylbenzamide (or N, N-dimethylacetamide), and two-folds of pinacolborane yielded the complete formation of **2a** (or

2w) with untouched reducible amide functional groups {iii) and iv) of Scheme 3.B.2.}. Furthermore, exclusive hydroboration of ester with the unreacted alkene group (C=C) was also observed in the reaction between benzyl benzoate (or ethyl acetate) and styrene (or vinyltrimethoxysilane) with 2.0 equiv. HBpin {Scheme 3.B.2., v) and vi)}.

3.B.2.5. Control Reaction for Ester Reduction

To establish the ester hydroboration reaction mechanism, I conducted a control reaction of a 1:1 stoichiometric ratio of benzyl benzoate (**1a**) and aluminum-hydride (**I**) in Tol-d8 at 80 °C. The reaction afforded the desired aluminum alkoxide complex, [**Int A**] in a 99% yield (Scheme 3.B.3.). The **Int A** was confirmed by NMR and HRMS studies. The ^{1}H NMR spectrum exhibits a new proton signal for Al-OC*H*Ph moiety of Int A in 6.18 ppm, and the ^{13}C{^{1}H} NMR spectra revealed the alkoxide carbon signal of LAlHO*C*(H)PhOCH$_2$Ph complex, [**Int A**] at δ 116.7 ppm.



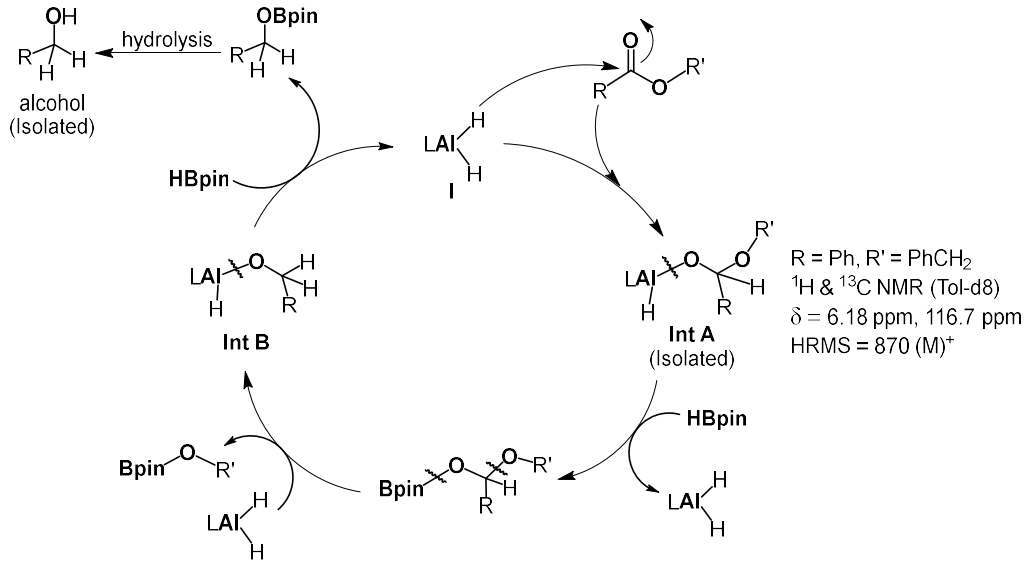
Scheme 3.B.3. Control experiment for hydroboration of benzyl benzoate.

3.B.2.6. Catalytic Cycle for C=O Reduction of Esters

Based on the previously established mechanism of main group-catalyzed hydroboration of esters[13h, 13j] and the above control experiment, I propose a probable reaction mechanism for aluminum hydride **I** catalyzed ester reduction via hydroboration (Scheme 3.B.4.).

The catalytic cycle was initiated by inserting active Al–H into the ester's carbonyl bond (C=O) to afford the aluminum-alkoxide complex [**Int A**]. Int A immediately reacts with HBpin to afford alkoxyboronate ester in the next step, which reacts with **I** to produce another aluminum-alkoxide

intermediate [**Int B**]. The Int B again reacts with the HBpin to afford boronate ester product and regenerates catalyst **I**.



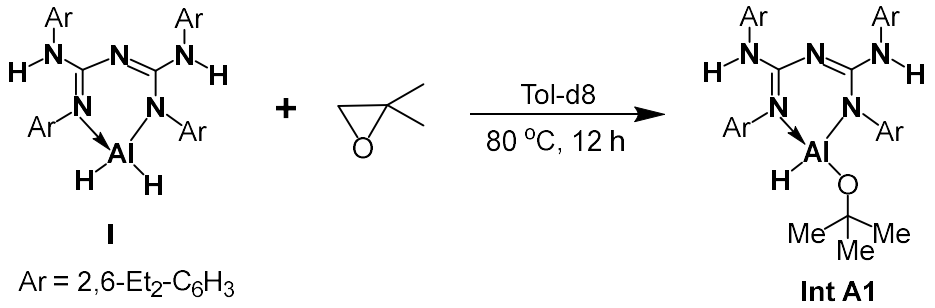
Scheme 3.B.4. Catalytic cycle for ester hydroboration.

In the above two steps, σ -bond metathesis (Al-O/B-H) occurs. Therefore, one controlled reaction between **Int A** and pinacolborane in 1:1 was conducted, resulting in a mixture of products according to literature study.[8a, 10b]

3.B.2.7. Control Reaction for Epoxide Reduction

To understand the mechanism for the compound, **I** catalyzed epoxide hydroboration, and one control reaction between **I** and 1,2-epoxy-2-methylpropane was performed in Tol-d8 to establish the formation of **Int A1** (Scheme 3.B.5.).

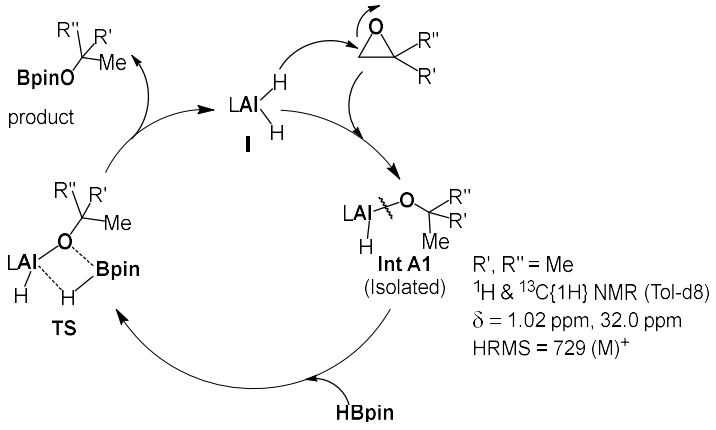
NMR and mass spectroscopy studies analyzed the intermediate **A1**. The ^{1}H NMR spectrum exhibits a characteristic methyl proton signal of Al-OC(CH_3)$_3$ moiety at 1.02 ppm. A new characteristic carbon signal at δ 32.0 ppm corresponds to Al-OC(CH_3)$_3$ group of **Int A1** in the $^{13}C\{^{1}H\}$ NMR spectrum. Further, **Int A1** was confirmed by 2D HMBC NMR experiment.



Scheme 3.B.5. Control experiment for hydroboration of 1,2-epoxy-2-methylpropane.

3.B.2.8. Catalytic Cycle for C-O Bond Cleavage of Epoxides

Based on the above stoichiometric reaction and previous literature report,[15b] a plausible mechanism for Al hydride **I** catalyzed hydroboration of epoxide was displayed in Scheme 3.B.6.



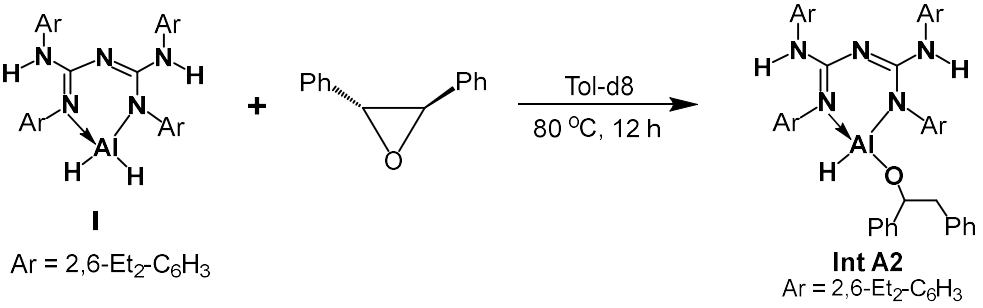
Scheme 3.B.6. Catalytic cycle for reduction of epoxides.

Initially, the catalyst **I** react with less substituted methylene carbon of epoxide to afford one aluminum alkoxy complex (Int A1). The Int A1 immediately reacts with HBpin to afford branched boronate ester product and reforms the catalyst (**I**) for active participation in the catalytic cycle. The second step involves one TS, where σ-bond metathesis happens. To confirm this, Int A1 was reacted with pinacolborane, resulting in a mixture of products as per literature. 8a, 10b

3.B.2.9. Control Reaction for Internal Epoxide Reduction

To prove the mechanism for aluminum-hydride (**I**) catalyzed C-O bond cleavage of stilbene oxide via hydroboration, one stoichiometric reaction between catalyst (**I**) and stilbene oxide in Tol-d8 was performed to demonstrate the **Int A2** (Scheme 3.B.7.).

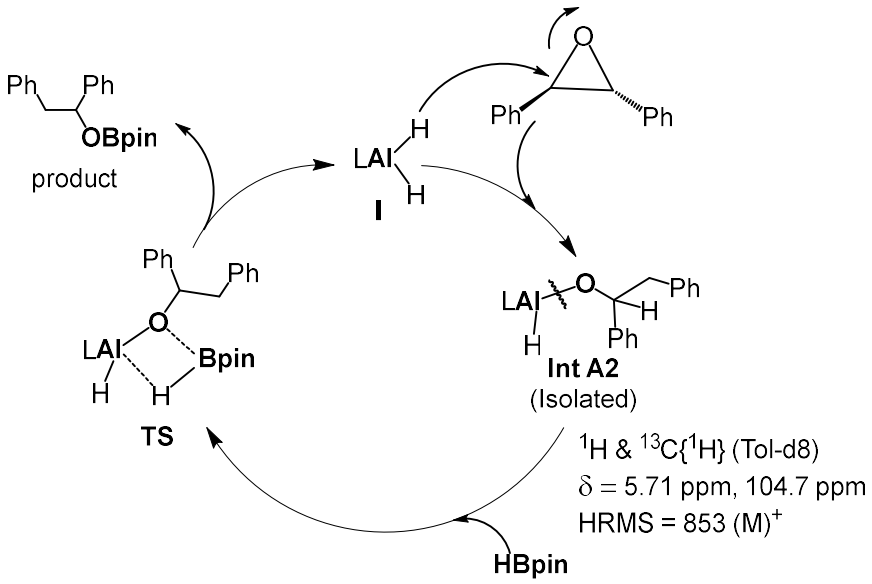
Intermediate A2 was examined by NMR and mass spectroscopy analysis. In the ^{1}H NMR spectrum, the characteristic methine proton signal for Al-OC*H*(Ph)CH_2Ph moiety was noticed at 5.71 ppm and the corresponding carbon signal was found at 104.7 ppm for Al-O*C*H(Ph)CH_2Ph fragment of **Int A2**. In addition, intermediate A2 was confirmed by the HMBC NMR study.



Scheme 3.B.7. Control experiment for hydroboration of stilbene oxide.

3.B.2.10. Catalytic Cycle for C-O Bond Cleavage of Symmetrical Epoxides

Based on the controlled reaction and literature report,[15b] the plausible mechanism for the hydroboration of stilbene oxide demonstrated in Scheme 3.B.8. In the initial catalytic cycle, the insertion of the Al-H bond into either side of symmetrical epoxide to afford aluminum alkoxide complex (**Int A2**). Next, the **Int A2** reacts with pinacolborane to lead the corresponding boronate ester product and regenerates the catalyst (**I**) via σ-bond metathesis.[8a, 10b]



Scheme 3.B.8. Catalytic cycle for reduction of epoxides.

3.B.3. Conclusion

In conclusion, I have demonstrated that the CBG aluminum-dihydride compound (**I**) acts as an efficient catalyst for reducing a wide range of esters and epoxides with pinacolborane (HBpin) in high yields. Catalyst **I** tolerated the reducible alkene (C=C), alkyne (C≡C), halides (F, Cl, Br, and I), nitrile (C≡N), and nitro (NO_2) groups in the C=O bond reduction of aryl and alkyl esters under solvent-free conditions. In addition, compound **I** catalyzed the branched Markovnikov ring-opening of epoxides with HBpin in high yields. Furthermore, the gram-scale reductions of ester and epoxides have been studied under standard conditions. Besides, I have also displayed the effective utilization of compound **I** in intermolecular chemoselective hydroboration of esters vs. epoxides or amides, or alkenes. Intermediates were isolated and well-characterized during control experiments by NMR and high-resolution mass spectroscopy, confirming the catalytic cycles for reducing esters and epoxides with HBpin under catalyst **I**. As far as hydroboration is concerned, guanidine-stabilized aluminum-based catalysis of ester and epoxide has not been

reported. Further investigation on other exciting catalytic applications of the CBG aluminum-dihydride (**I**) complex is still in progress.

3.B.4 Appendix: All general experimental information along with analytical data and spectral files of hydroborated products and control reactions were available in published paper: *Chem. Eur. J.* **2022 (Accepted). DOI:** https://doi.org/10.1002/chem.202203023

3.B.5. References

1. (a) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412 – 443; (b) Magano, J.; Dunetz, J. R. *Org. Process Res. Dev.* **2012**, *16*, 1156 – 1184; (c) Cho, B. T. *Chem. Soc. Rev.* **2009**, *38*, 443 – 452; (d) Dhillon, S. R. *Hydroboration and Organic Synthesis*; Springer: Berlin, Germany **2007**; *J. Am. Chem. Soc.* **2008**, *130*, 382 – 384; (e) Andersson, P. G.; Munslow, I. J. *Modern Reduction Methods*, Wiley-VCH, Weinheim, **2008**; Waldvogel, S. R. *Synthesis* **2009**, (3), 511.
2. (a) Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.***1991**, *113*, 3447 – 3450; (b) Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.***1991**, *113*, 7697 – 7705.
3. (a) Das, K. K.; Paul, S.; Panda, S. *Org. Biomol. Chem.* **2020**, *18*, 8939 –8974; (b) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.***1947**, *69*, 1197 – 1199.
4. Seyden-Penne, J. *Reductions by the Alumino- and Borohydrides in Organic Synthesis*, Wiley, New York, 2nd edition **1997**; Smith, K. *Appl. Organomet. Chem.* **1998**, *12*, 881.
5. Selected references for hydrogenation of esters, (a) Yuwen, J.; Chakraborty, S.; Brennessel, W. W.; Jones, W. D. *ACS Catal.***2017**, *7*, 3735 – 3740; (b) Wang, Z.; Chen, X.; Liu, B.; Liu, Q.-b.; Solan, G. A.; Yang, X.; Sun, W. -H. *Catal. Sci. Technol.***2017**, *7*, 1297 – 1304; (c) Espinso-Jalapa, N. A.; Nerush, A.; Shimon, L. J. W.; Leitus, G.; Avram, L.; Ben-David, Y. Milstein, D. *Chem. Eur. J.* **2017**, *23*, 5934 – 5938; (d) Srimani, D.; Mukherjee, A.; Goldberg, A. F. G.; Leitus, G.; Diskin-Posner, Y.; Shimon, L. J. W.; David, Y. B.; Milstein, D. *Angew. Chem. Int.*

*Ed.***2015**, *54*, 12357 – 12360; (e) vom Stein, T.; Meuresch, M.; Limper, D.; Schmitz, M.; Hölscher, M.; Coetzee, J.; Cole-Hamilton, D. J.; Klankermayer, J.; Leitner, W. *J. Am. Chem. Soc.* **2014**, *136*, 13217 – 13225; (f) Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem. Int. Ed.* **2012**, *51*, 2772 – 2775.

6. Metal-based hydroboration reactions; (a) Magre, M.; Szewczyk, M.; Rueping, M. *Chem. Rev.* **2022**, *122*, 8261–8312; (b) Roy, M. M. D.; Omaña, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.* **2021**, *121*, 12784 – 12965; (c) Dicken, R. D.; Motta, A.; Marks, T. J. *ACS Catal.* **2021**, *11*, 2715 − 2734; (d) Dixit, R.; Bisai, M. K.; Yadav, S.; Yadav, V.; Sen, S. S.; Vanka, K. *Organometallics* **2021**, *40*, 1104 – 1112; (e) Liu, H.; Eisen, M. S. *Synthesis* **2020**, *52*, 629 – 644; (f) Sadow, A. D. (**2020**), 201-224. *Alkali and Alkaline Earth Element-Catalyzed Hydroboration Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA; (g) Kuciński, K.; Hreczycho, G. *Green Chem.* **2020**, *22*, 5210 – 5224; h) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307 – 3336; (i) Tamang, S. R.; Findlater, M. *Molecules* **2019**, *24*, 3194; (j) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, *5*, 3238 – 3259; (k) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48*, 1995 – 2003.

7. Selected examples of metal-based catalysts for hydrosilylation reactions; (a) Sarkar, N.; Sahoo, R. K.; Mukhopadhyay, S.; Nembenna, S. *Eur. J. Inorg. Chem.***2022**, DOI: https://doi.org/10.1002/ejic.202101030; (b) Takaya, J.; Ogawa, K.; Nakaya, R.; Iwasawa, N. *ACS Catal.* **2020**, *10*, 12223 − 12228; (c) Zaranek, M.; Pawluc, P. *ACS Catal.***2018**, *8*, 9865 − 9876; (d) Königs, C. D. F.; Klare, H. F. T.; Oestreich, M. *Angew. Chem. Int. Ed.***2013**, *52*, 10076 – 10079; (e) Riener, K.; Högerl, M. P.; Gigler, P.; Kühn, F. E. *ACS Catal.* **2012**, *2*, 613 − 621; (f) Chakraborty, S.; Krause, J. A.; Guan, H. *Organometallics* **2009**, *28*, 582 – 586; (g) Bo, G. D.; Berthon-Gelloz, G.; Tinant, B.; Markó, I. E. *Organometallics* **2006**, *25*, 1881 – 1890; (h) Ojima, I.; Inaha, S. -I. *J. Organomet. Chem.***1977**, *140*, 97 – 111.

8. Aluminum-based catalysts for hydroboration of carbonyls; (a) Sarkar, N.; Sahoo, R. K.; Patro, A. G.; Nembenna, S. *Polyhedron* **2022**, *222*, 115902; (b) Peddarao, T.; Sarkar, N.; Nembenna, S. *Inorg. Chem.* **2020**, *59*, 4693 – 4702; (c) Woodside, A. J.; Smith, M. A.; Herb, T. M.; Manor, B. C.; Carroll, P. J.; Rablen, P. R.; Graves, C. R. *Organometallics* **2019**, *38*, 1017 – 1020; (d) Zhang, G.; Wu, J.; Zeng, H.; Neary, M. C.; Devany, M.; Zheng, S.; Dub, P. A. *ACS Catal.* **2019**, *9*, 874 – 884; (e) Liu, Y.; Ma, X.; Ding, Y.; Yang, Z.; Roesky, H. W. *Organometallics* **2018**, *37*, 3839 – 3845; (f) Liu, Y.; Liu, X.; Liu, Y.; Li, W.; Ding, Y.; Zhong, M.; Ma, X.; Yang, Z. *Inorg. Chim. Acta* **2018**, *471*, 244 – 248; (g) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.***2018**, *54*, 1233 – 1236; (h) Pollard, V. A.; Fuentes, M. A.; Kennedy, A. R.; McLellan, R.; Mulvey, R. E. *Angew. Chem. Int. Ed.* **2018**, *57*, 10651 – 10655; (i) Lemmerz, L. E.; McLellan, R.; Judge, N. R.; Kennedy, A. R.; Orr, S. A.; Uzelac, M.; Hevia, E.; Robertson, S. D.; Okuda, J.; Mulvey, R. E. *Chem. Eur. J.* **2018**, *24*, 9940 – 9948; (j) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, *8*, 2001 – 2005; (k) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, *18*, 4710 – 4713; (l) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. *Z. Anorg. Allg. Chem.***2016**, 1245 – 1250; (m) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54*, 10225 – 10229; (n) Titze, M.; Heitkämper, J.; Junge, T.; Kästner, J. R. *Chem. Int. Ed.* **2021**, *60*, 5544 – 5553; (o) Chia, C. -C.; Teo, Y. -C.; Cham, N.; Ho, S. Y. -F.; Ng, Z. -H.; Toh, H. -M.; Mézailles, N.; So, C. -W. *Inorg. Chem.* **2021**, *60*, 4569 – 4577; (p) Weetman, C.; Porzelt, A.; Bag, P.; Hanusch, F.; Inoue, S. *Chem. Sci.* **2020**, *11*, 4817 – 4827; (q) Ould, D. M. C.; Carden, J. L.; Page, R.; Melen, R. L. *Inorg. Chem.* **2020**, *59*, 14891 – 14898; (r) Franz, D.; Jandl, C.; Stark, C. Inoue, S. *ChemCatChem* **2019**, *11*, 5275 – 5281; (s) Lebedev, Y. N.; Polishchuk, I.; Maity, B.; Cavallo, L.; Rueping, M. *J. Am. Chem. Soc.* **2019**, *141*, 19415 – 19423.

9. Selected examples of aluminum-based catalysts for hydrosilylation of carbonyls, see (a) Bolley, A.; Specklin, D. Dagorne, S. *Polyhedron* **2021**, *194*, 11496; (b) Kannan, R.; Chambenahalli, R.;

Kumar, S.; Krishna, A.; Andrews, A. P.; Jemmis, E. D.; Venugopal, A. *Chem. Commun.* **2019**, *55*, 14629 – 14632; (c) Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics* **2017**, *36*, 4810 – 4815; (d) Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.* **2016**, *6*, 7350 – 7356; (e) Stennett, T. E.; Pahl, J.; Zijlstra, H. S.; Seidel, F. W.; Harder, S. *Organometallics* **2016**, *35*, 207 – 217; (f) Chen, J.; Chen, E. Y.-X. *Angew. Chem. Int. Ed.* **2015**, *54*, 6842 – 6846; (g) Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics* **2013**, *32*, 6812 – 6819; (h) Koller, J.; Bergman, R. G. *Organometallics* **2012**, *31*, 2530 – 2533; (i) Kato, N.; Tamura, Y.; Kashiwabara, T.; Sanji, T.; Tanaka, M. *Organometallics* **2010**, *29*, 5274 – 5282; (j) Bach, P.; Albright, A.; Laali, K. K. *Eur. J. Org. Chem.* **2009**,1961 – 1966.

10. (a) Ni, C.; Ma, X.; Yang, Z.; Roesky, H. W. *Eur. J. Inorg. Chem.***2022**, DOI: https://doi.org/10.1002/ejic.202100929; (b) Caise, A.; Jones, D.; Kolychev, E. L.; Hicks, J.; Goicoechea, J. M.; Aldridge, S. *Chem. Eur. J.* **2018**, *24*, 13624 – 13635; (c) Das, A.; Rej, S.; Panda, T. K. *Dalton Trans.* **2022**, *51*, 3027 – 3040; (d) Liu, Y.; Li, J.; Ma, X.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2018**, *374*, 387 – 415; (e) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, *350*, 14 – 29; (f) Weetman, C.; Inoue, S. *ChemCatChem* **2018**, *10*, 4213 – 4228; (g) Dagorne, S.; Wehmschulte, R. *ChemCatChem* **2018**, *10*, 2509 – 2520; (h) Ananikov, V. P. *Sustainable Catalysis. With Nonendangered Metals*. *Angew. Chem. Int. Ed.* **2016**, *55* (48), 14904; (i) Aldridge, S.; Downs, A. J. *The Group 13 Metals Aluminium, Gallium, Indium, and Thallium: Chemical Patterns and Peculiarities*. *Angew. Chem. Int. Ed.* **2011**, *50* (49), 11569.
11. Selected examples of aluminum-based catalysis of unsaturated functional groups: (a) Hobson, K.; Carmalt, C. J.; Bakewell, C. *Inorg. Chem.* **2021**, *60*, 10958 − 10969; (b) Sarkar, N.; Bera, S.; Nembenna, S. *J. Org. Chem.* **2020**, *85*, 4999 – 5009; (c) Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Adv. Synth. Catal.* **2019**, *361*, 850 – 857; (d) Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J* .**2019**, *25*, 11918 – 11923; (e) Liu, W.; Ding, Y.; Jin, D.;

Shen, Q.; Yan, B.; Ma, X.; Yang, Z. *Green Chem.* **2019**, *21*, 3812 – 3815; (f) Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics* **2019**, *38*, 3092 – 3097; (g) Itazaki, M.; Nakazawa, H. *Molecules* **2018**, *23*, 2769; (h) Bismuto, A.; Thomas, S. P.; Cowley, M. J. *Angew. Chem. Int. Ed.* **2016**, *55*, 15356 – 15359.

12. Selected references for metal-based hydrosilylation of esters, see; (a) Clarke, J. A.; van der Est, A.; Nikonov, G. I. *Eur. J. Org. Chem.* **2021**, 4434 – 4439; (b) Behera, R. R.; Ghosh, R.; Panda, S.; Khamari, S.; Bagh, B. *Org. Lett.* **2020**, *22*, 3642 – 3648; (c) Ohta, T.; Kamiya, M.; Kusui, K.; Michibata, T.; Nobutomo, M.; Furukawa, I. *Tetrahedron Lett.* **1999**, *49*, 6963 – 6966; (d) Feng, X.; Ji, P.; Li, Z.; Drake, T.; Oliveres, P.; Chen, E. Y.; Song, Y.; Wang, C.; Lin, W. *ACS Catal.* **2019**, *9*, 3327 – 3337; (e) Martínez-Ferraté, O.; Chatterjee, B.; Werlé, C.; Leitner, W. *Catal. Sci. Technol.* **2019**, *9*, 6370 – 6378; (f) Fernández-Salas, J. A.; Manzini, S.; Nolan, S. P. *Chem. Commun.* **2013**, *49*, 9758 – 9760; (g) Bézier, D.; Venkanna, G. T.; Castro, L. C. M.; Zheng, J.; Roisnel, T.; Sortais, J. -B.; Darcel, C. *Adv. Synth. Catal.* **2012**, *354*, 1879 – 1884; (h) Pehlivan, L.; Métay, E.; Laval, S.; Dayoub, W.; Delbrayelle, D.; Mignani, G.; Lemaire, M. *Eur. J. Org. Chem.* **2011**, 7400 – 7406; (i) Verdaguer, X.; Hansen, M. C.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 8522 – 8528; (j) Mao, Z.; Gregg, B. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 10139 – 10140.

13. Main-group metals for hydroboration of esters; (a) Shi, Y.; Wang, Y.; Huang, Z.; Zhang, F.; Shao, Y. *ACS Omega* **2022**, *7*, 18876 – 18886; (b) Yan, B.; Dutta, S.; Ma, X.; Ni, C.; Koley, D.; Yang, Z.; Roesky, H. W. *Dalton Trans.* **2022**, *51*, 6756 – 6765; (c) Kumar, G. S.; Bhattacharjee, J.; Kumari, K.; Moorthy, S.; Bandyopadhyay, A.; Kumar Singh, S.; Panda, T. K. *Polyhedron* **2022**, *219*, 115784; (d) Du, Z.; Behera, B.; Kumar, A.; Ding, Y. *J. Organomet. Chem.* **2021**, *950*, 121982; (e) Bisai, M. K.; Gour, K.; Das, T.; Vanka, K.; Sen, S. S. *J. Organomet. Chem.* **2021**, *949*, 121924; (f) Lavergne, J. L.; To, H.-M.; Fontaine, F.-G. *RSC Adv.* **2021**, *11*, 31941 – 31949; (g) Cao, X.; Wang, W.; Lu, K.; Yao, W.; Xue, F. Ma, M. *Dalton Trans.***2020**, *49*, 2776 –

2780; (h) Barman, M. K.; Baishya, A.; Nembenna, S. *Dalton Trans.* **2017**, *46*, 4152 – 4156; (i) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52*, 13155 – 13158; (j) Mukherjee, D.; Ellern, A.; Sadow, A. D. *Chem. Sci.* **2014**, *5*, 959 – 964; (k) Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Köhn, G.; Weetman, C. *Organometallics* **2011**, *30*, 5556 – 5559; (l) Brown, H. C.; Rao, B. C. S. *J. Am. Chem. Soc.* **1960**, *82*, 681 – 686.

14. Transition metal-based catalysts for hydroboration of esters; (a) Wei, Y.; Bao, Q.; Song, L.; Hong, D.; Gao, J.; Wang, S.; Zhu, X.; Zhou, S.; Mua, X. *Dalton Trans.* **2022**, *51*, 2953 – 2961; (b) Makarov, K.; Kaushansky, A.; Eisen, M. S. *ACS Catal.* **2022**, *12*, 273 – 284; (c) Bhattacharjee, J.; Bockfeld, D.; Tamm, M. *J. Org. Chem.* **2022**, *87*, 1098 – 1109; (d) Thenarukandiyil, R.; Satheesh, V.; Shimon, L. J. W.; de Ruiter, G. *Chem. Asian J.* **2021**, *16*, 999 – 1006; (e) Tamang, S. R.; Singh, A.; Bedi, D.; Bazkiaei, A. R.; Warner, A. A.; Glogau, K.; McDonald, C.; Unruh, D. K.; Findlater, M. *Nature Catal.* **2020**, *3*, 154 – 162; f) Xu, X.; Kang, Z.; Yan, D.; Xue, M. *Chin. J. Chem.* **2019**, *37*, 1142 – 1146; (g) Barger, C. J.; Motta, A.; Weidner, V. L.; Lohr, T. L.; Marks, T. J. *ACS Catal.* **2019**, *9*, 9015 – 9024; (h) Patnaik, S.; Sadow, A. D. *Angew. Chem. Int. Ed.* **2019**, *58*, 2505 – 2509; (i) Khalimon, A. Y.; Farha, P. M.; Nikonov, G. I. *Dalton Trans.* **2015**, *44*, 18945 – 18956; (j) Khalimon, A. Y.; Farha, P.; Kuzmina, L. G.; Nikonov, G. I. *Chem. Commun.* **2012**, *48*, 455 – 457; (k) Makarov, K.; Kaushansky, A.; Eisen, M. S. *ACS Catal.* **2022**, *12*, 273 – 284.
15. Main-group metals for hydroboration of epoxides; (a) Magre, M.; Paffenholz, E.; Maity, B.; Cavallo, L.; Rueping, M. *J. Am. Chem. Soc.* **2020**, *142*, 14286 – 14294; (b) Cao, X.; Li, J.; Zhu, A.; Su, F.; Yao, W.; Xue, F.; Ma, M. *Org. Chem. Front.* **2020**, *7*, 3625 – 3632; (c) Sreekumar, R.; Padmakumar, R.; Rugmini, P. *Tetrahedron Lett.* **1998**, *39*, 5151 – 5154.
16. Transition metals for hydroboration of epoxides; (a) Wang, Z.; Patnaik, S.; Eedugurala, N.; Manzano, J. S.; Slowing, I. I.; Kobayashi, T.; Sadow, A. D.; Pruski, M. *J. Am. Chem. Soc.* **2020**, *142*, 2935 – 2947; (b) Desnoyer, A. N.; Geng, J.; Drover, M. W.; Patrick, B. O.; Love, J. A.

Chem. Eur. J. **2017**, *23*, 11509 – 11512; (c) Song, H.; Ye, K.; Geng, P.; Han, X.; Liao, R.; Tung, C.-H.; Wang, W. *ACS Catal.* **2017**, *7*, 7709 – 7717.

17. Selected examples for classical reagents for hydrogenation of epoxides; (a) Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 3751 – 3753; (b) Brown, H. C.; Narasimhan, S.; Somayaji, V. *J. Org. Chem.* **1983**, *48*, 3091 – 3096; (c) Soai, K.; Oyamada, H.; Ookawa, A. *Synth. Commun.* **1982**, *12*, 463 – 467; (d) Murphy, D. K.; Alumbaugh, R. L.; Rickborn, B. *J. Am. Chem. Soc.* **1969**, *91*, 2649 – 2653; (e) Rickborn, B.; Lamke, W. E. *J. Org. Chem.* **1967**, *32*, 537 – 539; (f) Brown, C. H.; Rao, B. C. S. *J. Am. Chem. Soc.* **1960**, *82*, 681 – 686
18. Selected examples for transition metal catalysts for hydrogenation of epoxides; (a) Tadiello, L.; Gandini, T.; Stadler, B. M.; Tin, S.; Jiao, H.; de Vries, J. G.; Pignataro, L.; Gennari, C. *ACS Catal.* **2022**, *12*, 235 – 246; (b) Liu, W.; Li, W.; Spannenberg, A.; Junge, K.; Beller, M. *Nat. Catal.* **2019**, *2*, 523 – 528; (c) Thiyagarajan, S.; Gunanathan, C. *Org. Lett.* **2019**, *21*, 9774 – 9778; (d) Yao, C.; Dahmen, T.; Gansäuer, A. Norton, J. *Science* **2019**, *364*, 764 – 767; (e) Murru, S.; Nicholas, K. M.; Srivastava, R. S. *J. Mol. Catal. A Chem.* **2012**, *363 – 364*, 460 – 464; (f) Wylie, W. O.; Lough, A. J.; Morris, R. H. *Chem. Commun.* **2010**, *46*, 8240 – 8242; (g) Kwon, M. S.; Park, I. S.; Jang, J. S.; Lee, J. S.; Park, J. *Org. lett.* **2007**, *9*, 3417 – 3419; (h) Ley, S. V.; Mitchell, C.; Pears, D.; Ramarao, C.; Yu, J. -Q.; Zhou, W. *Org. Lett.* **2003**, *5*, 4665 – 4668; (i) Ito, M.; Hirakawa, M.; Osaku, A.; Ikariya, T. *Organometallics* **2003**, *22*, 4190 – 4192; (j) Sajiki, H.; Hattori, K. Hirota, K. *Chem. Commun.* **1999**, (11), 1041 – 1042; (k) Fujitsu, H.; Shirahama, S.; Matsumura, E.; Takeshita, K.; Mochida, I. *J. Org. Chem.* **1981**, *46*, 2287 – 2290.
19. (a) Peddarao, T.; Baishya, A.; Sarkar, N.; Acharya, R.; Nembenna, S. *Eur. J. Inorg. Chem.* **2021**, 2034 – 2046; (b) Sahoo, R. K.; Sarkar, N.; Nembenna, S. *Angew. Chem. Int. Ed.* **2021**, *60*, 11991 – 12000.
20. Selected examples of deoxygentative hydroboration of nitro compounds: (a) Gudun, K. A.; Zakarina, R.; Segizbayev, M.; Hayrapetyan, D.; Slamova, A.; Khalimona, A. Y. *Adv. Synth.*

Catal. **2022**, *364*, 601 – 611; (b) Zhao, L.; Hu, C.; Cong, X.; Deng, G.; Liu, L. L.; Luo, M.; Zeng, X. *J. Am. Chem. Soc.* **2021**, *143*, 1618 – 1629; (c) Yao, W.; Wang, J.; Lou, Y.; Wu, H.; Qi, X.; Yanga, Y.; Zhong, A. *Org. Chem. Front.* **2021**, *8*, 4554 – 4559; (d) Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. *Chem. Rev.* **2019**, *119*, 2611 − 2680.

21. Selected examples on chemoselective catalysis, see (a) Bergamaschi, E.; Lunic, D.; McLean, M.; Hohenadel, L. A.; Chen, Y. -K.; Teskey, C. J. *Angew. Chem. Int. Ed.* **2022**, DOI: https://doi.org/10.1002/anie.202114482; (b) Sarkar, N.; Mahato, M.; Nembenna, S. *Eur. J. Inorg. Chem.* **2020**, 2295 – 2301; (c) Mahatthananchai, J.; Dumas, A. M.; Bode, J. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 10954 – 10990; (d) Cunningham, A. D.; Ham, E. Y.; Vosburg, D. A. *J. Chem. Educ.* **2011**, *88*, 322-324; (e) Ballard, C. E. *J. Chem. Educ.* **2010**, *87*, 190-193; f) Shenvi, R. A.; O'Malley, D. P.; Baran, P. S. *Acc. Chem. Res.* **2009**, *42*, 530 – 541.

Chapter 4

Aluminum-Catalyzed Selective Reduction of Heteroallenes Through Hydroboration: Amide/Thioamide/Selenoamide Bond Construction and C=X (X= O, S, Se) Bond Activation

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Abstract

An unprecedented conjugated bis-guanidinate (CBG) stabilized aluminum dihydride, [$LAlH_2$; (L = {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar = 2,6- Et_2-C_6H_3)] (**I**) catalyzed chemoselective hydroboration of heteroallenes such as carbodiimide (CDI)s, isocyanates, isothiocyanates, and isoselenocyanates is reported. A wide range of heteroallenes, including electron-donating and withdrawing groups, experience hydroboration to obtain selectively N-boryl amide, N-borylaminal, and N-boryl methyl amine products. More importantly, a single sustainable molecular aluminum-based catalyst effectively catalyzes CDIs, isocyanates, isothiocyanates, and isoselenocyanates into formamidines, formamides, thioformamides, and selenoformamides, respectively. Further, heteroallene substrates undergo hydrodeoxygenation (HDO), hydrodesulfurization (HDS), and hydrodeselenization (HDSe) reactions leading to N-boryl methyl amines. In addition, a series of control and kinetic experiments indicate that the aluminum hydride species are essential for all partial and complete reduction steps and breaking the C=X (X = O, S, and Se) bonds in heteroallenes.

4.1. Introduction

The amide or thioamide bond is undoubtedly amongst the most widespread[1] structural units found in natural and synthetic organic molecules with various applications in industrial sectors.[2]

The advancement of more valuable methods for creating amides[3] has been considered one of the top targets for synthetic organic chemists. Traditional methods for amide synthesis can be done *via* C-N[4] and C-C[5] bond formation[4] using acid derivatives and nucleophilic amines. The reduction of heteroallenes such as carbodiimides, isocyanates, and isothiocyanates into formamidines,[6] formamides,[3a, 7] and thioformamides[3a, 8] using stoichiometric metal reagents, have been established in the literature (Figure 4.1., A) under harsh reaction environments with vast amounts of metal waste, resulting in poor yields and insufficient selectivity.[3a, 7, 8]

Recently, metal-catalyzed hydroboration of challenging unsaturated organic substrates,[9, 10] including heteroallenes such as CO_2,[11] carbodiimides,[12] and isocyanates[12k, 13] have been developed (Figure 4.1., B). However, aluminum[12e-12g] catalyzed hydroboration of CDIs is limited with low substrate scope and higher catalyst loading.

In 2016 Okuda and coworkers[12k] introduced magnesium-based $[Mg(thf)_6][HBPh_3]_2$ dihydroboration of ^{tert}butyl isocyanate to corresponding N-, O'-bis (boryl) hemiaminal product. Afterward, a few main-group metal-catalyzed[13] transformations of isocyanates to N-boryl formamides have been reported.

To the best of our knowledge, there have been no reports on the metal-catalyzed reduction of isothiocyanate (RN=C=S) or isoselenocyanate (RN=C=Se) through the hydroboration route (Figure 4.1., B). Previously, various reagents such as Schwartz reagent (Cp_2ZrClH, *insitu*),[3a, 8b] $(C_4H_9)_3SnH$,[8d] SmI_2,[8c] and organolithiums[8a] (RLi and R_2CuLi) were used to reduce isothiocyanates to thioformamides. In addition, a few reports on metal-catalyzed hydrosilylation[14] and hydrogenation[15] techniques are also known for chemoselective reduction of carbodiimides and isocyanates to corresponding N-silyl amides and formamides in extremely harsh reaction conditions (*high temperature and pressure*).

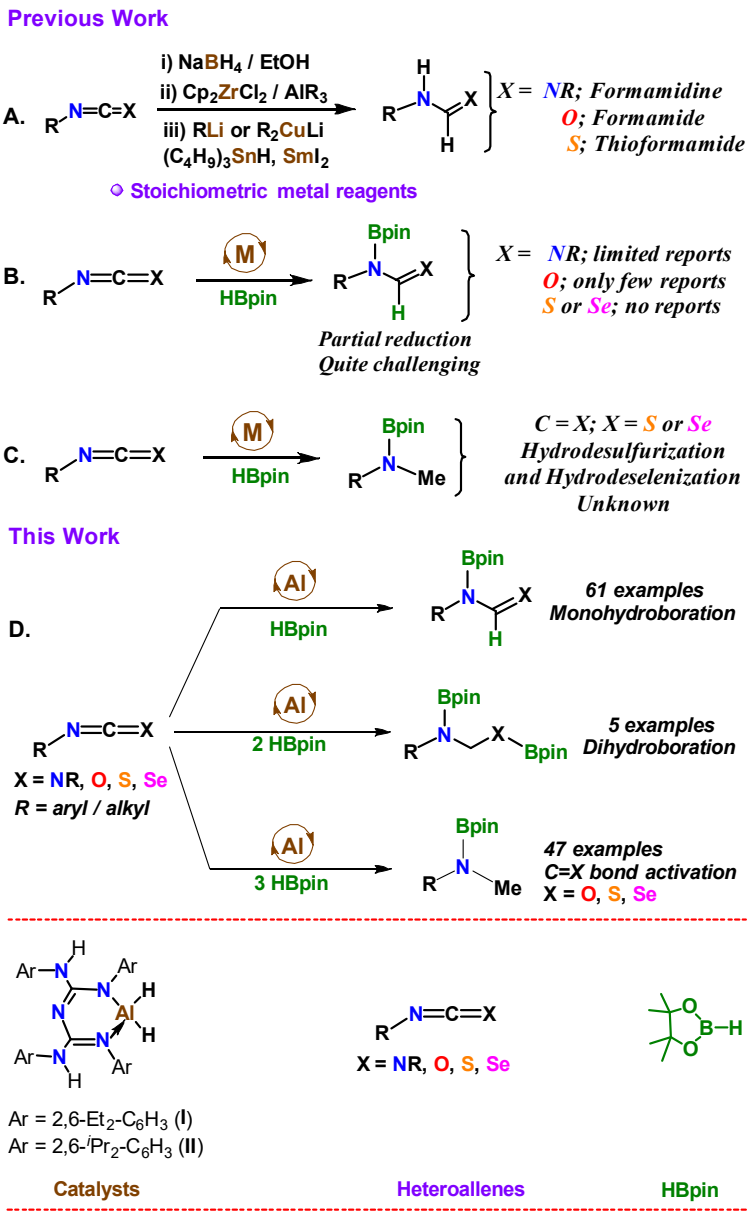


Figure 4.1. Synthesis of amides/aminals / N-methyl amines from heteroallenes.

N-methyl amines are essential reagents for producing biological drugs and other essential chemicals.[16] Usually, carbonyl's reductive methylation[17] and classical metal reagents[18] (like $LiAlH_4$, $Li[Al(OMe)_3]_3$, $NaBH_4$) have been used in stoichiometric amounts to reduce organic isocyanates and isothiocyanates, which suffer from huge chemical waste, narrow substrate scope,

and uncontrollable side reactions. Therefore, developing ideal methods for synthesizing (-NCH_3) amines is necessary.

Following this, metal-catalyzed deoxygenated hydroboration of isocyanates (HDO) to borylated N-methyl amines have been explored with three-fold HBpin.[13] Surprisingly, no reports on hydrodesulfurization (HDS) or hydrodeselenization (HDSe) of isothiocyanates and isoselenocyanates have been found (Figure 4.1., C).

The current trend of sustainable catalysis is using metals with high natural abundance, cheaper, and less toxic; the supporting ligand should contain C, H, and N elements only[20] which can help the main-group metal gain superiority over transition metal in the field of catalysis.[9a-d, 9f, 9h,9j-9k, 10a-b, 19] In this background, our group developed the NacNac analog, conjugated bis-guanidinate (CBG) supported aluminum-based catalysts for the hydroboration of challenging unsaturated organic functionalities.[12e, 21] As mentioned earlier, the selective hydroboration reactions of CDIs[12] and isocyanates[12k, 13] are rare, and surprisingly, there have been no reports on B-H addition in isothiocyanate and isoselenocyanates. Therefore, herein, I report a sustainable aluminum dihydride (**I**) as the catalyst for selective monohydroboration of heteroallenes and C=X (X = O, S, Se) bond cleavage of isocyanates (HDO), isothiocyanates (HDS), and isoselenocyanates (HDSe) to N-boryl methyl amines with excellent yields (Figure 4.1., D).

4.2. Results and Discussion

Previously our group reported a series of aluminum complexes bearing conjugated bis-guanidinate (CBG) ligands,[22] including CBG aluminum dihydride complexes.[12e, 21] The CBG aluminum dihydride complexes **I**[12e] and **II**,[21] $LAlH_2$; (L = {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar = 2,6- Et_2-C_6H_3 (**I**); 2,6- $^iPr_2$-C_6H_3 (**II**)) can be easily accessed by the reaction of LH with $AlH_3 \cdot NMe_2Et$ in toluene. Moreover, CBG aluminum compounds have been

utilized as catalysts for the hydrofunctionalization of unsaturated organic substrates.[12e, 21, 23] As our ongoing interest in the molecular main group metal-based catalysts for organic transformations,[9-13, 24] herein, I report the CBG aluminum dihydride catalyzed hydroboration of heteroallenes.

4.2.1. Hydroboration of Carbodiimide

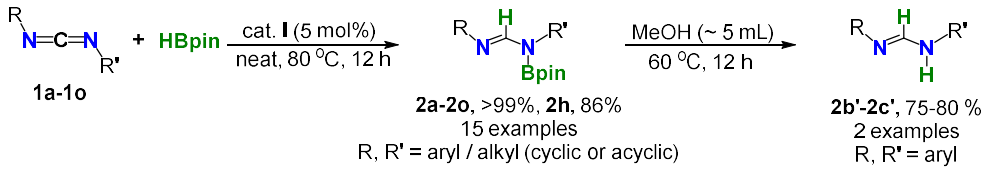
In our previous report the compound **I** catalyzed hydroboration of commercially available aliphatic CDIs,[12e] such as ^{i}PrN=C=N^{i}Pr and ^{t}BuN=C=N^{t}Bu was studied. Considering the importance of *N, N'*-disubstituted formamidines for various applications,[25] I aimed to investigate the hydroboration of a wide array of CDIs.

Subsequently, *N, N'*-dicyclohexylcarbodiimide (DCC) was selected as a representative substrate to optimize CDI reduction with pinacolborane (HBpin) (Table S1 of ESI). The reaction of DCC **1g** with HBpin under catalyst **I** (3 mol%) at 80 ^{o}C for 12 h afforded only 55% of N-borylated formamidine, **2g**, as indicated by ^{1}H NMR analysis. However, a higher quantity of catalyst loading (5 mol%) resulted in **2g** with a 99% yield (entry 3, see Table S1 of ESI). Compound **II** also displayed the same catalytic performance at similar reaction conditions. Besides, no change in the catalytic performance of compound **I** was observed when reactions were done in solvents such as benzene, toluene, and acetonitrile. (Table S1 in ESI, entries 7-9).

With the optimization conditions, the catalytic monohydroboration of symmetrical and unsymmetrical CDIs was explored using catalyst **I** (5 mol%) at 80 ^{o}C in solvent-free conditions (Table 4.1.).

Various symmetrical *N, N'*-diaryl CDIs, ArN=C=NAr (Ar = *p*-tolyl **1a**, xyl **1b**, 3,5-Me$_2$Ph **1c**, mes **1d**, diethyl phenyl **1e**, Dipp **1f**), were converted into corresponding N-boryl formamidines (**2a-2f**) with 98-99% yield about 12 h reaction time interval. Moreover, the symmetrical dialkyl

Table 4.1. Substrate scope in monohydroboration of carbodiimides using $^{Diethyl}LAlH_2$ (**I**) complex as a catalyst.[a]



Entry	Carbodiimide (**1**)	Product (**2**)	Yield (%)[b]
1	**1a**	**2a**	>99%
2	**1b**	**2b** 1.0 mmol scale	>99% (**2b'**, 75%)
3	**1c**	**2c** 1.0 mmol scale	>99% (**2c'**, 80%)
4	**1d**	**2d**	>99%
5	**1e**	**2e**	>99%
6	**1f**	**2f**	98%
7	**1g**	**2g**	>99%
8	**1h**	**2h**[c]	86%
9	**1i**	**2i**	>99%
10	**1j**	**2j**	>99%
11	**1k**	**2k**	>99%
12	**1l**	**2l**	>99%
13	**1m**	**2m**	>99%
14	**1n**	**2n**	>99%
15	**1o**	**2o**	>99%

[a]Reaction conditions: carbodiimide (1.0 equiv., 0.1 mmol), HBpin (1.0 equiv., 0.1 mmol), cat. **I** (5 mol%), neat, 12 h at 80 °C. [b]The yield was determined by ^{1}H NMR spectroscopy based on the consumption of carbodiimide and identified the NC*H*N signal confirmed the product. Formamidines (**2b'-2c'**) were isolated after hydrolysis in methanol. [c]Reaction was stirred at 110 °C for 24 h in neat conditions.

CDIs such as ((*Me*$_3$*Si*)NCN(*Me*$_3$*Si*)) (**1h**), and dibenzylCDI (**1i**) were effectively reduced to corresponding monoborylated products **2h** in 86% and **2i** in 99% yields. Despite the harsh reaction conditions (110 °C in 24 h), product **2h** is obtained in lower yield; due to the steric nature of the substrate. Further, to expand the substrate scope, unsymmetrical diaryl CDIs

ArN=C=NAr' (**1j-1l)** and aryl-alkyl CDIs (Ar-N=C=N-R) (**1m-1o**) were also tested under similar reaction conditions, which afforded unsymmetrical diaryl and aryl-alkyl N-boryl formamidines in quantitative yields (**2j-2l; 2m-2o**). In all these unsymmetrical N-boryl formamidine products, the *Bpin* unit is exclusively attached to the bulkier side of the N atom of the N=C=N core, as Hill[12l] and Eisen[12i] research groups reported.

All newly synthesized N-boryl formamidines (**2a-2o**) were characterized by multinuclear NMR (^{1}H, ^{13}C{^{1}H} and ^{11}B) and high-resolution mass spectrometry (HRMS) analyses. In ^{1}H NMR, all substrates' characteristic NC*H*N resonance signals were observed between 7.82–10.12 ppm. Two representative examples of N-boryl formamidines, i.e., **2b** and **2c,** were further hydrolyzed into corresponding air-stable formamidines (**2b'** and **2c'**)[6a] in 75% and 80% isolated yields, respectively.

Next, I was curious to know the reaction between 1.0 equiv. CDI and 2.0 equiv. HBpin to obtain dihydroborylated products; such reports are rare.[12h]

It was found that by using a 6 mol% catalyst **I** at 80 ^{o}C under neat conditions**,** the substrate DCC **1g** was doubly reduced into corresponding *N, N'*-dicyclohexyl-*N, N'*-bis(Bpin)methanediamine (**3a**) product in 99% yield (see ESI, Scheme S1).

4.2.2. Hydroboration of Isocyanate

Next, it was decided to explore the compound **I** catalyzed mononhydroboration of isocyanates. The examination was initiated by investigating the reaction between *m*-tolyl isocyanate (**4b**) and HBpin under neat conditions. In Table S2, it was found the best result for chemoselective hydroboration of **4b** into N-borylated formamide **5b** using 2% of either catalyst **I** or **II** in 12 h (ESI, Table S2, entries 7-8). No product formation was noticed in the absence of the catalyst.

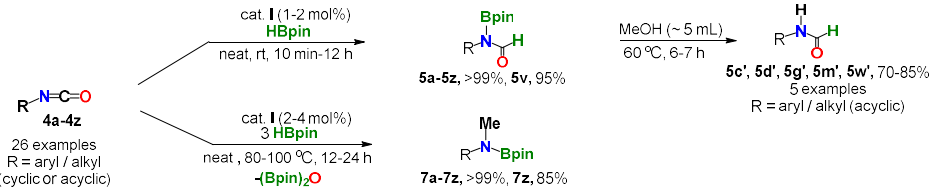
Moreover, the catalytic activity of compound **I** is well tolerated at different solvents (Table S2 of ESI, entries 11-13).

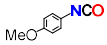
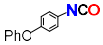
The final optimization condition for the synthesis of N-borylated formamide **5b** leads us to explore the substrate scope for monohydroboration of a wide range of isocyanates (*aryl and alkyl*) into corresponding borylated formamides (**5a-5z**) with excellent tolerance of reducible functional groups such as alkyl, halide, nitro,[26] nitrile, and alkene (Table 4.2.).

In initial substrate screening, it was found that aryl isocyanates with electron-donating (Me, OMe, and OPh) and electron-withdrawing (NO_2, F, Cl, Br, I, and CF_3) functionalities (**4a, 4c-4j**, and **4m-4q**) underwent chemoselective partial reduction into corresponding aryl N-boryl formamide products (**5a, 5c-5j,** and **5m-5q**) with HBpin at room temperature within 10 min-12 h under 1-2 mol% catalyst (**I**) load without any solvent. In addition, catalyst **I** displayed an effective intramolecular chemoselective partial reduction of isocyanate (-NCO) moiety over nitrile (C≡N) functional group for substrates **4k-4l** to afforded N-boryl formamides **5k** and **5l** in 99% yields. Next, the 4-biphenyl isocyanate (**4r**), 1-naphthyl isocyanate (**4s**), and 1,4-phenylene diisocyanate (**4t**) were transferred into corresponding N-boryl formamides (**5r-5t**) in quantitative yields using 1.0-2.0 equiv. HBpin. Additionally, all cyclic and acyclic alkyl isocyanates (**4u-4z**) were also converted into corresponding alkyl N-boryl formamides (**5u-5z**) in 95-99%, yields with an effective chemoselective reduction of NCO over alkene (C=C) functionality in **4z**.[13c]

The ^{1}H NMR spectra of **5a-5z** revealed that the signature proton signal of the NC*H*O unit appears in the range of δ 8.60–10.2 ppm, similar to reported literature values.[13c] Moreover, five selected N-boryl formamides (**5c-5d, 5g, 5m,** and **5w**) were undergo methanolysis (~ 5 mL MeOH) into desired air-stable formamides (**5c'-5d'**, **5g'**, **5m',** and **5w'**) with 70-85% isolated

Table 4.2. Substrate scope for monohydroboration and hydrodeoxygenation (HDO) of isocyanates using catalyst **I**.[a]



Entry	Isocyanate (**4**)	Monohydroboration(**5**)[b]	HDO (**7**)[b, c]
1	 **4a**	 **5a**, 12 h, >99%	 **7a**, 12 h, >99%
2	**4b**	 **5b**, 12 h, >99%	 **7b**, 12 h, >99%
3	 **4c**	 **5c**, 12 h, >99% (1.0 mmo scale, **5c'**, 80%)	 **7c**, 12 h, >99%
4	 **4d**	 **5d**, 12 h, >99% (1.0 mmol scale, **5d'**, 75%)	 **7d**, 12 h, >99%
5	 **4e**	 **5e**, 12 h, >99%	 **7e**, 12 h, >99%
6	 **4f**	 **5f**, 12 h, >99%	 **7f**, 12 h, >99%
7	 **4g**	 **5g**, 12 h, >99% (1.0 mmol scale, **5g'**, 72%)	 **7g**, 12 h, n.r.
8	 **4h**	 **5h**, 12 h, >99%	 **7h**, 12 h, >99%
9	 **4i**	 **5i**, 12 h, >99%	 **7i**, 12 h, >99%
10	 **4j**	 **5j**, 12 h, >99%	 **7j**, 12 h >99%
11	 **4k**	 **5k**, 12 h, >99%	 **7k**, 24 h, >99%
12	 **4l**	 **5l**, 12 h, >99%	 **7l**, 24 h, >99%
13	 **4m**	 **5m**, 12 h, >99% (1.0 mmol scale, **5m'**, 85%)	 **7m**, 12 h, >99%
14	**4n**	**5n**, 10 m, >99%	**7n**, 12 h, >99%
15	**4o**	**5o**, 10 m, >99%	**7o**, 12 h, >99%
16	**4p**	**5p**, 10 m, >99%	**7p**, 12 h, >99%
17	**4q**	**5q**, 10 m, >99%	**7q**, 12 h, >99%
18	**4r**	**5r**, 2 h, >99%	**7r**, 12 h, >99%
19	**4s**	**5s**, 2 h, >99%	**7s**, 12 h, >99%
20	**4t**	**5t**,[d] 2 h, >99%	**7t**,[d] 2 h, >99%
21	**4u**	**5u**, 2 h, >99%	**7u**,[e] 2 h, >99%
22	**4v**	**5v**,[f] 12 h, 95%	**7v**, 2 h, >99%
23	**4w**	**5w**, 12 h, >99% (1.0 mmol scale, **5w'**, 70%)	**7w**, 12 h, >99% (1.0 mmol scale)
24	**4x**	**5x**, 2 h, >99%	**7x**, 12 h, >99%
25	**4y**	**5y**, 2 h, >99%	**7y**, 12 h, >99%
26	**4z**	**5z**, 2 h, >99%	**7z**, 12 h, 85%

[a]Reaction conditions: isocyanates (1.0 equiv., 0.1 mmol), HBpin (1.0-3.0 equiv., 0.1-0.3 mmol), catalyst **I** (1-4 mol%) were stirred in 10 mL sealed vial at rt or 80 °C for 10 min-24 h for all isocyanates under neat condition but in case of **5j-5q** (or **7j-7q**), 1.0 (or 2.0) mol% cat. **I** was used, and **7f** and **7r-7s** were stirred at 100 °C in neat condition.

[b]The yield was determined by ^{1}H NMR spectroscopy based on isocyanate consumption and identified the NC*H*OBpin or NCH_3 signal confirmed the product. After hydrolysis in methanol, formamides (**5c'-5d'**, **5g'**, **5m'**, **5w'**) were isolated. n.r indicates no reaction. [c]$O(Bpin)_2$ is a side-product in all substrates. [d]For **5t** (or **7t**), pinacolborane (2.0-6.0 equiv. 0.2-0.6 mmol) was used. [e]For**7u**, the reaction was performed in ~ 4 mL dry toluene. [f]For **5v**, the yield was determined using an internal standard (nitromethane).

yields (see ESI). In addition, **5m'** was confirmed by a single crystal X-ray diffraction study (*vide supra* Figure S415 in supporting information).

In addition, the dihydroboration of 2,6-diisopropylphenyl isocyanate (**4g)** and 4-bromophenyl isocyanate (**4o**) leads to corresponding N-, O-bis(boryl) hemiaminal products **6a**[13c] and **6b** in 70-99% yields using 2.0 equiv. HBpin under 2 mol% of catalyst **I** (see ESI, Scheme S2). Otherwise, a mixture of boronate esters was observed for other isocyanates.

The reports on metal-catalyzed hydrodeoxygenation (HDO) of isocyanates are rare.[13] Therefore, I determined the complete reduction of isocyanates to N-boryl methyl amines using HBpin. For this *m*-tolyl isocyanate (**4b**) was selected as a model substrate and reacted with three equiv. of HBpin under the different conditions as displayed in Table S3 of ESI. I discovered that under 4 mol% of catalyst **I**, substrate **4b** was quantitatively hydroborated into corresponding N-borylmethyl amine **7b** with BpinOBpin as a by-product at 80 ºC (entry 5, Table S3 of ESI). On lowering the catalyst loadings, a decrease in product yields was observed. Moreover, catalyst **II** exhibits similar catalytic performance at the same reaction conditions.

To expand the substrate scope of HDO of isocyanates, I analyzed the same isocyanates used in the above monohydroboration reactions under optimized conditions (Table 4.2.). All aryl and alkyl isocyanates, including cyclic and acyclic substrates (**4a-4f; 4h-4z**), afforded the desired N-borylmethyl amine products (**7a-7f; 7h-7z**) in 99% yields except **4g** due to bulky isopropyl substituents in the ortho positions at 2-4 mol% of CBG aluminum hydride (**I**) at 80-100 ºC

(solvent-free). The excellent tolerance of halide, nitro (NO_2),[26] nitrile (C≡N), and alkene (C=C) functional groups in the above reactions is notable. It should be noted that substrates, 3-cyanophenyl isocyanate (**4k**) and 4-cyanophenyl isocyanate (**4l**), require a longer reaction time, up to 24 h, than other isocyanates and display the chemoselective formation of products **7k** and **7l** in preference to the nitrile group. Isocyanate **4t** requires six equiv. of HBpin to afford the N-borylated methyl amine **7t** in a 99% yield. [12c]

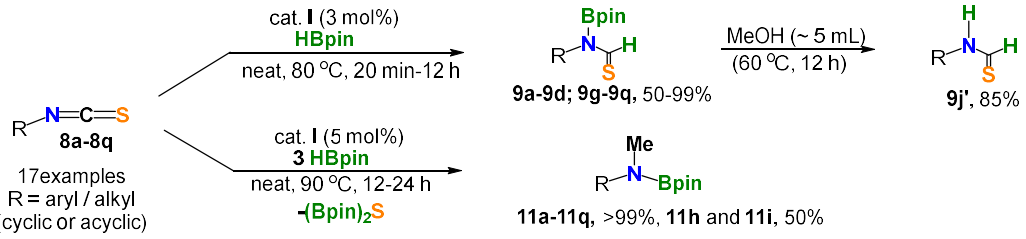
All N-borylated methyl amine products (**7a-7f** and **7h-7z**) were characterized by multinuclear NMR spectroscopy, including the HRMS for two newly synthesized compounds (**7i** and **7k**). The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra disclosed that the characteristic N-methyl amine (-NCH_3) is found in δ 2.47–3.16 ppm and δ 30.8–38.6 ppm as a single sharp peak, with $O(Bpin)_2$ is the only side product found in all reduced products, confirmed by ^{11}B NMR spectra.

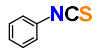
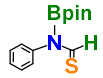
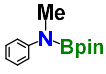
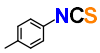
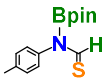
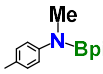
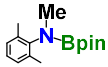
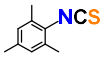
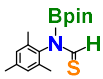
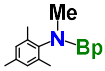
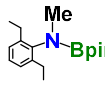
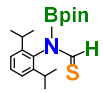
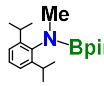
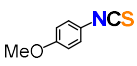
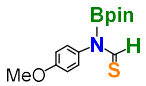
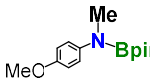
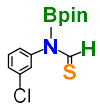
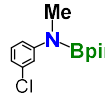
4.2.3. Hydroboration of Isothiocyanate

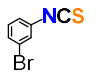
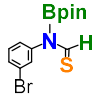
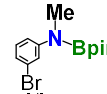
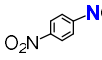
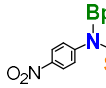
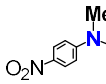
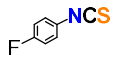
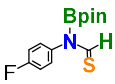
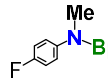
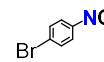
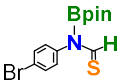
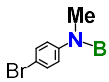
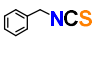
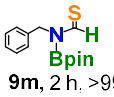
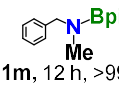
To our knowledge, there have been no reports on metal-catalyzed hydroboration of isothiocyanates. Thus, I investigated the addition of a B-H bond to isothiocyanates using HBpin. As described in Table S4, I optimized the conditions for the compound **I** catalyzed partial reduction of a model substrate, phenyl isothiocyanate (**8a**), to phenyl N-borylthioformamide (**9a**), both neat and different solvents (Table S4, entries 3, 6-8). Catalyst **II** also shows a similar activity as a catalyst **I** at optimized reaction conditions. In the absence of a catalyst, no reduction of substrate **8a** was observed.

As shown in Table 4.3., the substrate scope was summarized for partial reduction of isothiocyanates under optimized reaction conditions with good tolerance of alkyl, halide, NO_2,[26] and C=C groups under 3 mol% of catalyst **I** in 20 min-12 h. Aryl substrates with electron-

Table 4.3. Substrate scope for monohydroboration and hydrodesulfurization (HDS) in isothiocyanates using catalyst **I**.[a]



Entry	Isothiocyanate (**8**)	Monohydroboration (**9**)[b]	HDS (**11**)[b], [c]
1	 **8a**	 **9a**, 12 h, >99%	 **11a**, 12 h, >99%
2	 **8b**	 **9b**, 12 h, >99%	 **11b**, 12 h, >99%
3	 **8c**	 **9c**, 12 h, >99%	 **11c**, 24 h, >99%
4	 **8d**	 **9d**, 12 h, >99%	 **11d**, 24 h, >99%
5	 **8e**	 **9e**, 12 h, 0%	 **11e**, 24 h, >99%
6	 **8f**	 **9f**, 12 h, 0%	 **11f**, 24 h, >99%
7	 **8g**	 **9g**, 12 h, 60%	 **11g**, 12 h, >99%
8	 **8h**	 **9h**, 20 min, >99%	 **11h**,[d] 12 h, 50%

Entry	Isothiocyanate (**8**)	Monohydroboration (**9**)[a]	HDS (**11**)[b], [c]
9	 **8i**	 **9i**, 20 min, >99%	 **11i**,[d] 12 h, 50%
10	 **8j**	 **9j**, 1 h, >99% (1.0 mmol scale, **9j'**, 85%)	 **11j**, 12 h, >99%
11	 **8k**	 **9k**, 1 h, >99%	 **11k**, 12 h, >99%
12	 **8l**	 **9l**, 1 h, >99%	 **11l**, 12 h, >99%
13	 **8m**	 **9m**, 2 h. >99%	 **11m**, 12 h, >99% (1.0 mmol scale)
14	**8n**	**9n**, 1 h, 70%	**11n**, 12 h, >99%
15	**8o**	**9o**, 20 min, 50%	**11o**, 12 h, >99%
16	**8p**	**9p**, 20 min, >99%	**11p**, 12 h, >99%
17	**8q**	**9q**, 20 min, 80%	**11q**, 12 h, >99%

[a]Reaction conditions: isothiocyanates (0.1 mmol, 1.0 equiv.), HBpin (0.1-0.3 mmol, 1.0-3.0 equiv.) and catalyst **I** (3-5 mol%) were stirred in a 10 mL sealed vial for 20 min-24 h at 80-90 °C under neat conditions. [b]The yield was determined by ^{1}H NMR spectroscopy based on isothiocyanate consumption and identified the NC*H*SBpin, or NCH_3 signal confirmed the product. After hydrolysis in methanol, thioformamide (**9j'**) was isolated. [c](Bpin)$_2$S is a side-product in all substrates. [d]Yield was determined using an internal standard (nitromethane).

donating functional groups (Me **8b**, Xyl **8c**, Mes **8d**) require no change in optimized conditions for complete conversion into corresponding aryl N-borylated thioformamides **9b-9d**.

Despite the harsh reaction conditions, substrates **8e** and **8f** could not be reduced due to their steric nature. For *p*-methoxy isothiocyanate **8g**, I found only 60% product formation of *N*-(*p*-methoxy)methane thioamide **9g**. Derivatives of aryl isothiocyanate with electron-withdrawing (F, Cl, Br, NO_2) groups **8h-8l** underwent smooth partial reduction upon treatment with 1.0 equiv. HBpin into corresponding N-borylated aryl thioformamides **9h-9l** within 20 min-1h. Next, alkyl isothiocyanates were screened under standard reaction conditions. At first, benzyl isothiocyanate **8m** was fully reduced into *N*-benzyl-*N*-(Bpin)methane thioamide **9m** in 2 h. Notably, both cyclohexyl methyl isothiocyanate (**8n**) and cyclohexyl isothiocyanate (**8o**) gave 50-70% yields of the respective borylated thioformamides (**9n-9o**). Nevertheless, again 2° alkyl isothiocyanate, i.e., benzhydryl isothiocyanate **8p**, afforded the corresponding 2° alkyl boryl thioformamide **9p** in 99% yield. Next, I screened a challenging substrate, like allyl isothiocyanate (**8q**), containing N=C=S and C=C reducible functional groups. In this case, **8q** got converted into **9q**, in 80 % yield, in which the alkene group (C=C) is untouched.

All newly synthesized N-boryl thioformamides (**9a-9d**; **9g-9q**) were characterized by multinuclear NMR (^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B) and HRMS spectroscopic methods. In ^{1}H NMR spectra of N-boryl thioformamides, the proton resonance signal for NC*H*S moiety was found in δ 9.71–10.55 ppm, while the corresponding carbon signal for the N*C*HS unit observed in the downfield region of δ 187.5–200.6 ppm. Furthermore, a representative example of a thioformamides hydrolyzed product, i.e., **9h'**, is confirmed by a single-crystal X-ray structure. (*vide supra,* ESI, Figure S416).

In dihydroboration of isothiocyanates, substrate, i.e., *p*-methoxyphenyl isothiocyanate (**8g**), was reduced into corresponding dihydroborylated product **10a** under 3% catalyst **I** at 80 ºC for 24 h, confirmed by multinuclear NMR and mass spectroscopic methods (ESI, Scheme S3). A mixture of boronate ester products was noticed for other isocyanates; therefore, additional substrate scope in the dihydroboration of isothiocyanates was not expanded.

Hydrodesulfurization (HDS) is vital to remove sulfur-containing impurities from crude oils due to adverse environmental effects and catalyst poisons.[27] As I mentioned before, no reports have been found in the C=S bond cleavage of isothiocyanates as far as molecular aluminum chemistry is concerned. Using 5 mol % of either catalyst **I** or **II**, I noticed the quantitative hydrodesulfurization of phenyl isothiocyanate **8a** into N-borylated methyl amine **11a** incorporating 3.0 equiv. HBpin at 90 ºC under neat conditions (Table S5, entries 5-6). $S(Bpin)_2$ was found as a by-product. In addition, no C=S bond cleavage was found in **8a** under catalyst and solvent-free environments (Table S5, entry 8). The catalytic activity of compound **I** was unaltered in the presence of other solvents, i.e., toluene, benzene, and acetonitrile.

Motivated by the excellent catalytic activity of compound **I** towards HDS of phenyl isothiocyanate **11a**, a wide range of substrates were screened under standard conditions with good tolerance of alkyl, halide, nitro,[26] and alkene groups (Table 4.3.).

In initial substrate screening, I discovered that aryl isothiocyanates having electron-rich (methyl and methoxy) and deficient groups (nitro, bromo, and fluoro) were fully reduced into corresponding N-borylated methyl amines (**11b-11g**, **11j-11l**) in99% yields using 5 mol% of catalyst (**I**) in 12-24 h (neat condition). Whereas reducing 3-chlorophenyl isothiocyanate and 3-bromophenyl isothiocyanate (**8h** and **8i**), in each case, only 50% of the hydroborated products (**11h** and **11i**) were observed. The 1º and 2º alkyl isothiocyanates (**8m-8p**) were hydroborated

into aliphatic boryl N-methyl amines (**11m-11p**) with excellent yields. Interestingly, for allyl isothiocyanate **8q**, compound **I** effectively borylated only NCS fragments into NMeBpin **11q** without disturbing alkene moiety (C=C).

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra exhibit the characteristic N-methyl amine (-NCH_3) moiety is found in δ 2.01–4.02 and δ 33.0–45.9 ppm as a single sharp peak, with $S(Bpin)_2$ being the side product in all substrates, as identified by ^{11}B NMR spectra.

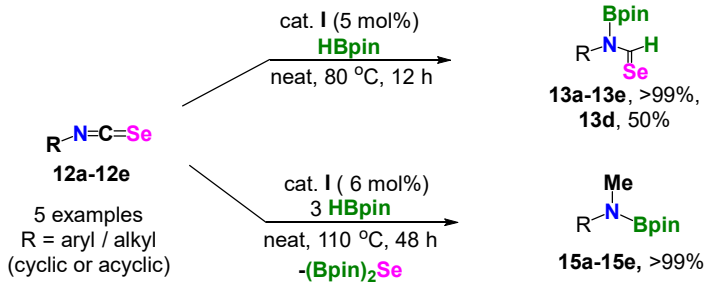
4.2.4. Hydroboration of Isoselenocyanate

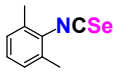
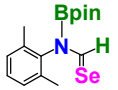
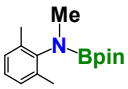
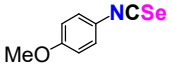
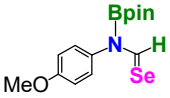
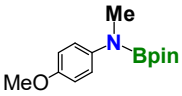
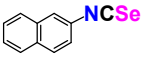
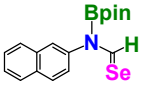
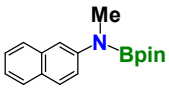
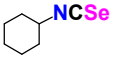
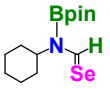
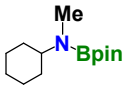
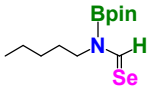
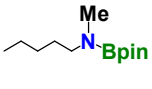
Further, I decided to investigate the reduction of selenocyanates with HBpin as a hydride source. All isoselenocyanates (**12a-12e**) were synthesized as per the literature reports.[28] As shown in Table S6 (Entry 3), the formation of selenoformamide was most efficient in neat conditions using catalyst **I** (5 mol%) at 80 °C for 12 h, which enabled the product in quantitative yield. At the optimized conditions, catalyst **II** shows similar catalytic activity. Moreover, no change in the catalytic activity of compound **I** was discovered in solvents such as toluene, benzene, and acetonitrile. No conversion was found in the absence of the catalyst. Table 4.4. summarizes the scope of the isoselenocyanates studied in this report. All aryl and alkyl isoselenocyanates (**12a-12e**; except **12d**) transformed to N-borylselenoformamide in quantitative yields, while **12d** gave in 50% of **13d**.

In ^{1}H NMR spectra, the characteristic NC*H*Se moiety signal was found in the downfield region at δ 11.90–12.47 ppm, and the distinctive carbon signal of N*C*HSe was found in the range δ 189.7– 207.5 ppm. HRMS further confirmed all newly synthesized N-boryl selenoformamides (**13a-13e**).

Next, I focused on the dihydroboration of isoselenocyanates. For this, 2-isoselenocyanatonaphthalene **12c** was selected as a representative example (Scheme S4 in ESI).

Table 4.4. Using catalyst **I**, substrate scope for monohydroboration and hydrodeoselenization (HDSe) in selenocyanates.[a]



Entry	Isoselenocyanate (**12**)	Monohydroboration (**13**)[b]	HDSe(**15**)[b], [c]
1	 **12a**	 **13a**, >99% (1.0 mmol scale)	 **15a**, >99% (1.0 mmol scale)
2	 **12b**	 **13b**, >99%	 **15b**, >99%
3	 **12c**	 **13c**, >99%	 **15c**, >99%
4	 **12d**	 **13d**, 50%	 **15d**, >99%
5	**12e**	 **13e**, >99%	 **15e**, >99%

[a]Reaction conditions: selenocyanates (0.1 mmol, 1.0 equiv.), HBpin (0.1-0.3 mmol, 1.0-3.0 equiv.), catalyst **I** (5-6 mol%), neat, 12-48 h at 80-110 °C under N_2. [b]The yield was determined by ^{1}H NMR spectroscopy based on selenocyanate consumption and identified the NC*H*SeBpin, or NCH_3 signal, confirmed the product. [c](Bpin)$_2$Se is a side-product.

Under 5 mol% of CBG Al-H (**I**), compound **12c** was smoothly reduced into respective dihydroborylated product **14a** in 99% yield at 80 °C, confirmed by NMR and mass spectroscopy. After this, I focused on the hydrodeselenization (HDSe) reaction using **12a** as a model substrate. The synthesis of N-boryl methyl amine **15a** was most efficient in neat conditions utilizing

catalyst **I** (6 mol%) and 3.0 equiv. HBpin at 110 ºC for 48 h (Table S7, entry 5). $Se(Bpin)_2$ is the side product in the above reaction, confirmed by the ^{11}B NMR spectrum. In addition, I noticed the same catalytic performance by catalyst **II** at the optimized conditions. With optimized reaction conditions in hand, the HDSe reaction was screened for the above selenocyanate substrates (*used in partial reduction*) with three folds of HBpin under standard conditions (Table 4.4.). I noticed the quantitative formation of all four isoselenocyanates **12b-12e** to desired N-methyl boryl amine products (**15b-15e**) (Table 4.4.). In ^{1}H NMR, the N-methyl proton signal of $N(CH_3)Bpin$ moiety was found at 2.13–3.06 ppm, and the carbon signal for the $N(CH_3)Bpin$ unit presented in a range of 33.6– 40.5 ppm. In addition, in ^{11}B NMR, two peaks were found corresponding to N-boryl methyl amine and side product $S(Bpin)_2$.

4.2.5. Intermolecular Chemoselective Reduction of Isocyanates

Chemoselective reactions are highly effective routes for the preparation of desired products.[29] During the hydroboration of isocyanates, I noticed the tolerance of many reducible functional groups such as alkyl, alkene, halide, nitro, and nitrile.

Moreover, only isocyanates are smoothly transformed into corresponding hydroborated products among all heteroallenes under mild conditions. Therefore, I was interested in exploring isocyanates' intermolecular chemoselective hydroboration reactions versus other heteroallenes and alkene (ESI, Scheme S5).

The equimolar solution of 3,5-dimethyl phenyl isocyanate **4e**, 1,3-Bis(2,6-methyl phenyl)carbodiimide, and HBpin, when mixed with 2 mol% catalyst **I** under the solvent-free condition at room temperature, resulted in partial reduction of **4e** into the corresponding N-borylformamide **5e** in 99% yield in preference to unreacted ^{Xyl}CDI (see ESI, Scheme S5 a). Next, 1.0 equiv. 4-methoxyphenyl isocyanate (**4h)** / 4-methoxyphenyl isothiocyanate was treated with

HBpin (1.0 equiv.) under catalyst **I** (1 mol%) at room temperature for 12 h, affording the complete conversion of **4h** into corresponding monoborylated product **5h** over the reducible isothiocyanate (ESI, Scheme S5 b). In additional experiments, a 1:1 molar ratio of 4-fluorophenyl isocyanate(**4m**)/4-bromophenyl isocyanate (**4o**) and 4-fluorophenyl isothiocyanate/4-nitrophenyl isothiocyanate were treated with 1.0 equiv. HBpin reagent at rt for 10 min, resulting in the complete production of borylated N-formamides (**5m**/**5o**) in preference to reducible electron-withdrawing aryl isothiocyanates. Similarly, 3,5-dimethyl phenyl isocyanate **4e** underwent monohydroboration into respective aromatic N-borylformamide **5e** under the standard conditions with unconverted electron-donating aryl selenocyanate (see supporting information, Scheme S5 c). Furthermore, a one-pot reaction of *p*-methoxyphenyl isocyanate (**4h**), *p*-methoxy styrene, and HBpin at optimized conditions gave a quantitative borylated product **5h** in preference to unreacted alkene (Scheme S5 d, ESI).

In addition, one chemoselective dihydroboration reaction was performed between 4-bromophenyl isocyanate (**4o**) and 4-nitrophenyl isothiocyanate. Both reactants mixed in equimolar quantity with two-fold HBpin under 2 mol% compound **I** at rt for 1 h, resulting in N-, O-bis(boryl) hemiaminal product **6a** in quantitative yield in preference over isothiocyanate (ESI, Scheme S5 e). Next, I evaluated the intermolecular chemoselective hydrodeoxygenation reactions with our current catalytic methodology (*NCO vs. NCS, NCSe, or C=C*). The reaction of one equiv. 4-methoxyphenyl isocyanate (**4h**), one equiv. 4-methoxyphenyl isothiocyanate, and three equiv. HBpin under 4 mol% of compound **I** at neat conditions resulted in the complete transformation of **4h** into *p*-methoxy N-boryl methyl amine (**7h**) over unreacted isothiocyanate (Scheme S5 f, ESI). In addition, 4-fluorophenyl isocyanate (**4m**) / 4-bromophenyl isocyanate (**4o**) was reduced fully into corresponding N-boryl amine products (**7m**/**7o**) in comparison to

untouched reducible isothiocyanate substrates under 2 mol% catalyst **I**. At last, **4e** was transformed into corresponding borylated N-methyl amine (**7e**) in 70% yield over selenocyanate under three folds of HBpin (ESI, Scheme S5 g). Moreover, quantitative hydrodeoxygenation of isocyanate **4h** into corresponding borylated N-methyl amine **7h** with unreacted C=C double bond of alkene was noticed for the intramolecular competitive reaction between **4h** and *p*-methoxy styrene with 3.0 equiv. of HBpin (Scheme S5 h, ESI).

4.2.5. Kinetic study

The catalytic performance for B-H addition in carbodiimide was examined by *in situ* reaction of HBpin with 1.0 equiv. of ^{Xyl}CDI (**1b**) catalyzed by 5 mol% of aluminum-hydride (**I**) at 80 °C (Figure 4.2.).

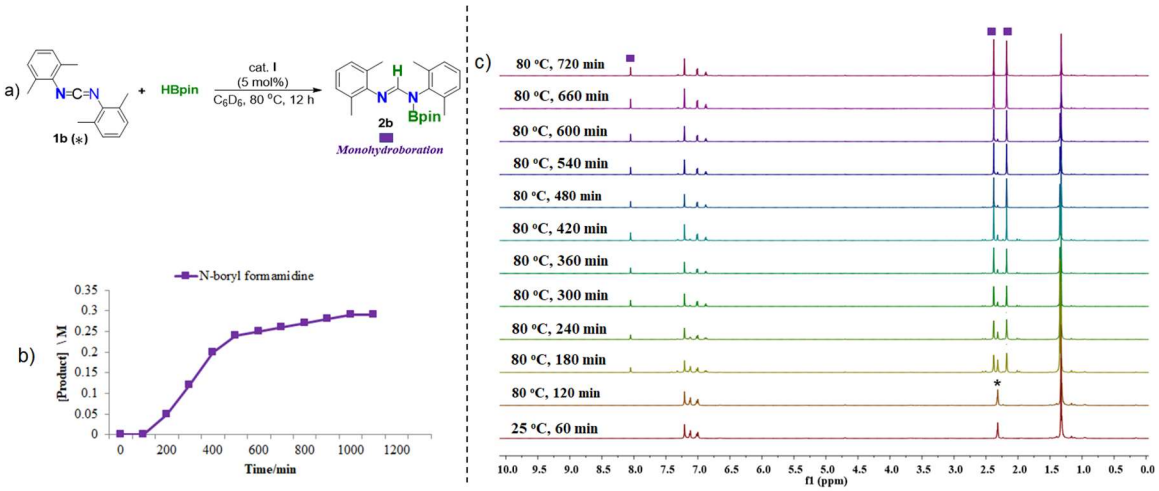


Figure 4.2. a) Kinetic study for hydroboration of ^{Xyl}CDI (**1b**). b) Graphical plot of [product]/M versus time for reduction of (Xyl)N=C=N(Xyl) (**1b**) catalyzed by 5 mol% of complex **I** at rt-80 °C between 60 min-720 min. c) Stacked ^{1}H NMR spectra (400 MHz, C_6D_6) for the reduction of ^{Xyl}CDI (**1b**) (1.0 equiv. 0.3 mmol) and HBpin (1.0 equiv. 0.3 mmol) using 5 mol% aluminum hydride (**I**) complex as a catalyst. Spectra were recorded at different temperatures and time intervals between T = 25-80 °C and t = 60 min -720 min, respectively; ■ = (Xyl)N=CH-N(Bpin)(Xyl) (**2b**).

Reaction progress over 720 min exhibits the formation of N-boryl formamidine (**2b**) (Figure 4.2. a). The reaction began at 120 min, where the formation of hydroborated product **2b** was evident by the NC*H*N proton signal at δ 8.24 ppm (singlet, C_6D_6). Finally, the disappearance of the starting methyl protons at δ 2.32 ppm and exclusive formation of borylated formamidine **2b** was noticed at 720 min, indicating the complete reduction of (Xyl)N=C=N(Xyl) (**1b**) to corresponding reduced product **2b** with no other side product. Figure 4.2.b indicates the sigmoid curve for forming N-boryl formamidine **2b** as per reported literature.[12] Similar observation was found *in situ* B-H addition for (*p*-Toly)N=C=N(*p*-Tolyl) (**1a**), (3,5-Me_2Ph)N=C=N(3,5-Me_2Ph) (**1c**) and (Mes)N=C=N(Mes) (**1d**) carbodiimides (see ESI, Figure S417-S419).

Further, the catalytic activity was assessed by in situ examining (^{1}H NMR spectroscopy) a reaction of HBpin and p-chlorophenyl isocyanate (**4n**) catalyzed by 2 mol % of CBG aluminum dihydride at room temperature to 80 °C. The reaction's evolution over 720 minutes discloses a subsequent formation of amide, hemiaminal, and N-boryl methyl amine products, as shown in Figure 4.3. a.

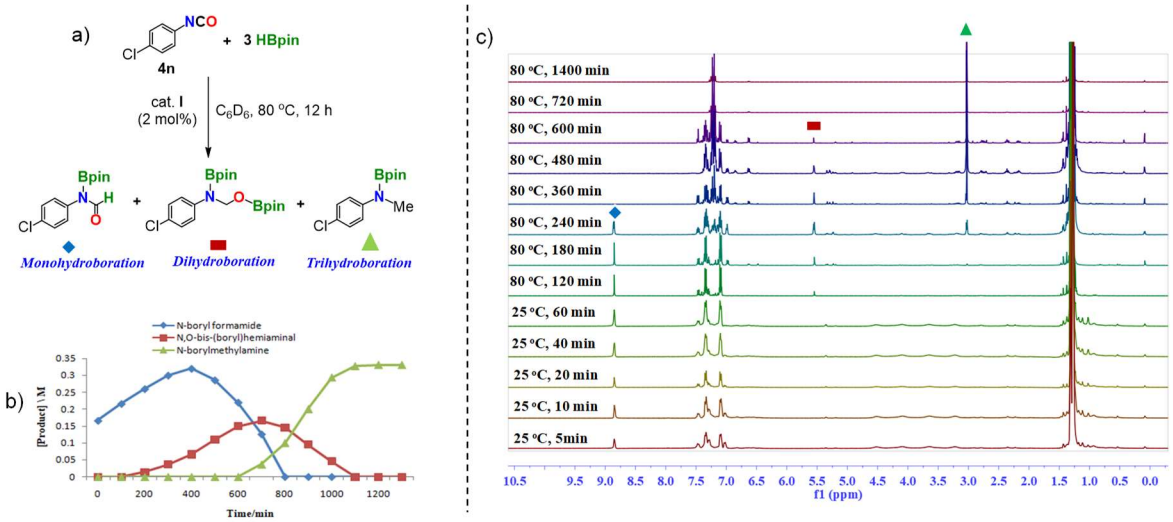


Figure 4.3. a) Kinetic study for hydroboration of p-chlorophenyl isocyanate (**4n**). b) Graphical plot of [Product]/M versus time for reduction of 4-ClPhNCO (**4n**) catalyzed by 2 mol% of complex **I** at rt-80 °C between 5 min-1400 min; c) Stacked ^{1}H NMR spectra (400 MHz, C_6D_6) for the reduction of p-chlorophenyl isocyanate (**4n**) (1.0 equiv. 0.3 mmol) and HBpin (1.0 equiv. 0.3 mmol) using 2 mol% aluminum hydride (**I**) complex as a catalyst. Spectra recorded at different temperature and time intervals between T = 25-80 °C and t = 5min -1400 min, respectively; ◆ = 4-ClPhN(Bpin)CHO (**5n**), ■ = 4-ClPhN(Bpin)CH_2O(Bpin), ▲ = 4-ClPhN(Bpin)CH_3 (**7n**).

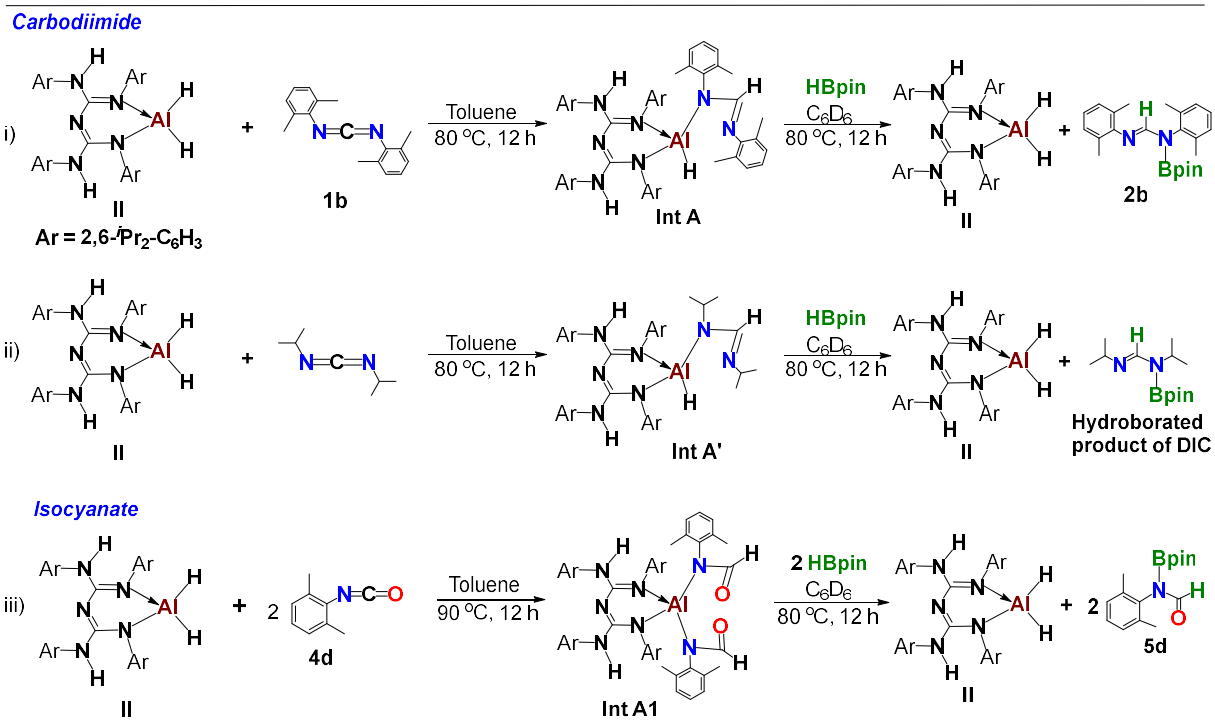
At the beginning of the reaction, the formation of 4-ClPh(Bpin)HC(O) (**7n**) was evidenced by the appearance of a deshielded proton resonance at 8.53 ppm at rt. Later, on the temperature elevation to 80 °C; I noticed the hemiaminal product and amide emergence at 120 minutes. The formation of the hemiaminal product was confirmed by the significant peak at 5.54 ppm. After reaching 240 minutes, N-boryl methyl amine evolved, evidenced by the occurrence of a peak at 3.01 ppm. Finally, a disappearance of amide and hemiaminal species and exclusive formation of HDO product, N-boryl methyl amine, was noticed at 720 minutes. There was no further change when I recorded an NMR after 1400 minutes.

The kinetic experiments indicate that the reaction advances with the subsequent mechanism order. As shown in Figure 4.3. b, I noticed the sigmoid curve of N-boryl methyl amine, **7n**, similar to the reported zinc[13c] and magnesium[13d] catalyzed C=O bond cleavage of organic isocyanates.

4.2.6. Control Experiments

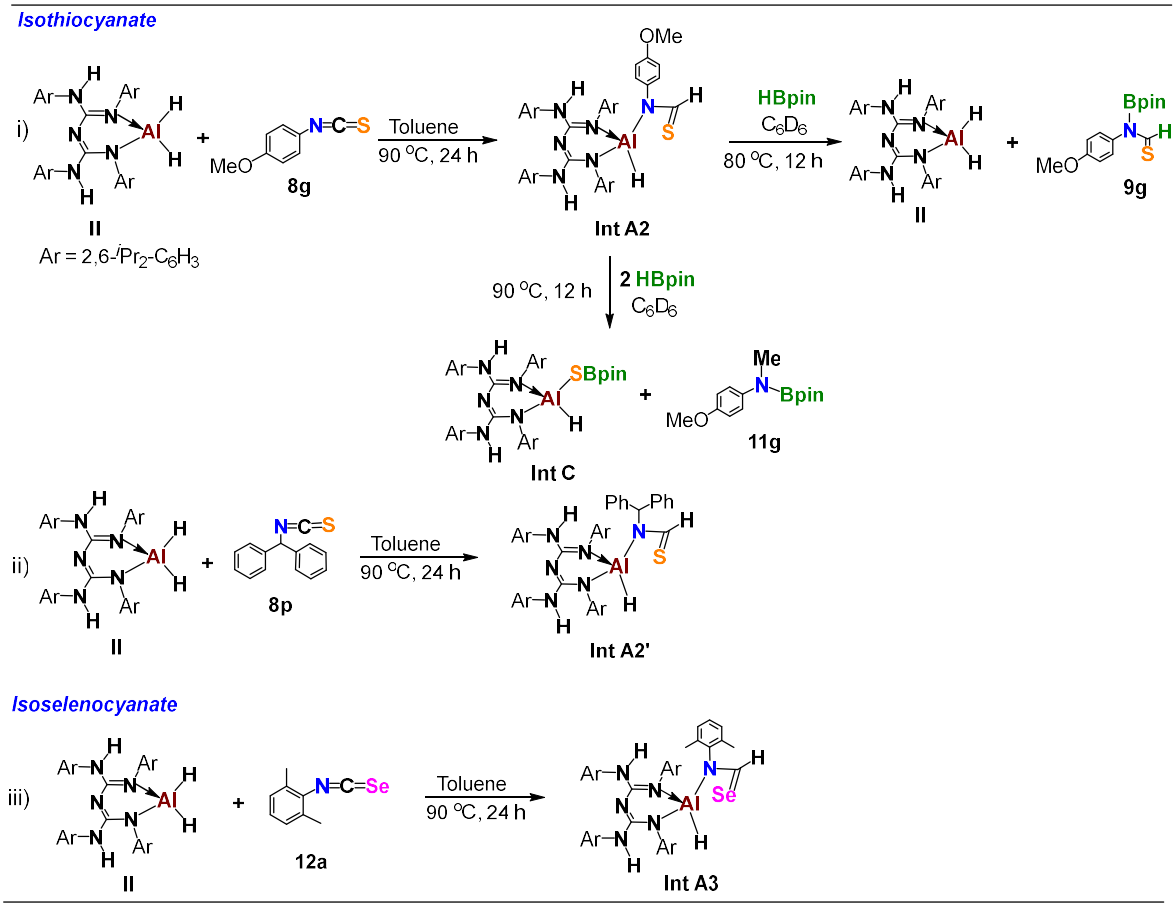
Several control experiments were conducted to deduce that the aluminum hydride catalyzed successive hydroboration of heteroallenes to monoborylated, diborylated, and N-boryl methyl amine products. A 1:1 stoichiometric reaction between catalyst **II** and ^{Xyl}CDI(**1b**) in toluene at 80 °C for 12 h led to CBG Al formamidinate hydride complex, **Int A** (Scheme 4.1.). Here, the insertion of CDI into the Al-H bond happened. NMR and mass spectrometric methods

characterized the intermediate **Int A**. The ^{1}H NMR spectrum of **Int A** reveals a signature peak of -NC*H*N moiety at δ 7.68 ppm, which is good in agreement with reported NacNac stabilized aluminum formamidinate complexes.[12f] The ^{13}C{^{1}H} NMR peaks at δ 153.4 ppm, attributed as N*C*HN. It is noteworthy that when ^{xyl}CDI (**1b**) and compound **II** reacted in a 1:2 ratio, resulting in **Int A** long with unreacted carbodiimide **1b**, which proves that no double hydroalumination happens in carbodiimide reduction. Further, a 1:1 stoichiometric reaction of **Int A** and HBpin has been performed in C_6D_6 at 80 °C for 12 h in a J. Young valve NMR tube. NMR studies noticed a clean formation of compounds **II** and **2b**. Moreover, in the additional experiment, when compound **II** was treated with *N, N'*-diisopropyl carbodiimide (DIC) in the above reaction conditions, it afforded alkyl aluminum formamidinate hydride complex (**Int A'**). The newly synthesized **Int A'** was characterized by NMR, mass, and Single-crystal X-ray diffraction techniques (Scheme 4.1.).



Scheme 4.1. Control experiments for carbodiimide and isocyanate hydroboration.

Additionally, when **Int A'** was treated with 1.0 equiv. of pinacolborane at 80 °C for 12 h in benzene-d6, again regeneration of catalyst **II** and N-boryl formamidine of DIC was observed.



Scheme 4.2. Control experiments for isothiocyanate and isoselenocyanate hydroboration.

In the following experiments, a 1:2 stoichiometric ratio of catalyst **II** and ^{Xyl}NCO (**4d**) in toluene at 90 °C for 12 h yielded CBG bis(formamidinate)Al(III) complex, **Int A1** (Scheme 4.1.). NMR and mass spectrometry methods confirmed the compound **Int A1**. Next, a reaction between **Int A1** and 2.0 equiv. HBpin afforded compound **II** and N-borylated formamide **5d**, confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

In addition, reacting catalyst **II** with 1.0 equiv. *p*-methoxyphenyl isothiocyanate (**8g**) in toluene at 90 °C for 24 h yielded a single hydroaluminumation product LAlHSC(H)N(4-OCH$_3$C$_6$H$_4$), **Int A2** in 68% yield (Scheme 4.2.). The ^{1}H NMR spectrum reveals one singlet resonance at δ 10.03

ppm of SC(*H*)N moiety of **Int A2** in C_6D_6, while the corresponding $^{13}C\{^1H\}$ spectrum shows a single sharp peak in the far downfield region of δ 199.9 ppm for methine carbon atom of S*C*(H)N fragment. Both ^1H and $^{13}C\{^1H\}$ spectral data were well matched with the reported literature[30] and confirmed by mass spectroscopy. Next, the **Int A2** mixed with 1.0 equiv. HBpin in benzene-d6 in a J. Young valve NMR tube and heated at 80 ºC for 12 h, resulting in complex **II** and N-boryl thioformamide **9g** as confirmed by multinuclear NMR studies. Moreover, it was observable when $LAlH_2$ (**II**) was treated with 2.0 equiv. of p-methoxyphenyl isothiocyanate (**8g**), only **Int A2** is found along with unreacted isothiocyanate **8g**. Therefore, it is proved that no double hydroalumination occurs in isothiocyanate reduction. In the following reaction, when a 1:2 molar ratio of **Int A2** and HBpin mixed with 0.5 mL of C_6D_6 and heated at 90 ºC for 12 h, afforded an aluminum-thioboryl hydride type species LAlH(SBpin), **Int C**, and N-borylated methyl amine product **11g**. Multinuclear NMR spectra analyzed the formation of both compounds. Again, a 1:1 molar ratio of compound **II** and benzhydryl isothiocyanate (**8p**) yielded the Single crystals of mononuclear hydroaluminumationcomplex, **Int A2'** (Figure 4.4.). The characteristic thiomethine proton signal of SC(*H*)N moiety is found at δ 10.00 ppm in the ^1H NMR spectrum, while the $^{13}C\{^1H\}$ NMR spectrum reveals the corresponding sharp carbon peak in δ 200.0 ppm in benzene-d6. It is important to note that in the presence of 2.0 equiv. benzhydryl isothiocyanate (**8p**), exclusively **Int A2',** is observed with unconsumed **8p**. In the end, a toluene solution of compound **II** when treated with 2,6-dimethyl phenyl isoselenocyanate(**12a**) in a 1:1 molar ratio at 90 ºC, resulted in a single insertion product LAlHSeC(H)N(2,6-$Me_2C_6H_3$), **Int A3** (Scheme 4.2.). The **Int A3** was isolated in a 74% yield. Both NMR and mass analyses established the existence of **Int A3**. The ^1H NMR spectrum reveals the characteristic selenomethine proton of the SeC(*H*)N component at δ 9.08 ppm in

benzene-d6, while the $^{13}C\{^{1}H\}$ NMR spectrum exhibits the corresponding carbon peak at δ 192.4 ppm. Note that no double hydroalumination reaction happened in the presence of 2.0 equiv. of 2,6-dimethyl phenyl isoselenocyanate (**12a**).

4.2.7. X-ray Study

The newly prepared aluminum intermediates (**Int A'** and **Int A2'**) were crystallized (ether/toluene) in a triclinic (or monoclinic) lattice with $P\bar{1}$and $P2_1$ space groups (crystal and structure refinement data in ESI, Table S8). In both structures (Figure 4.4.), the central aluminum

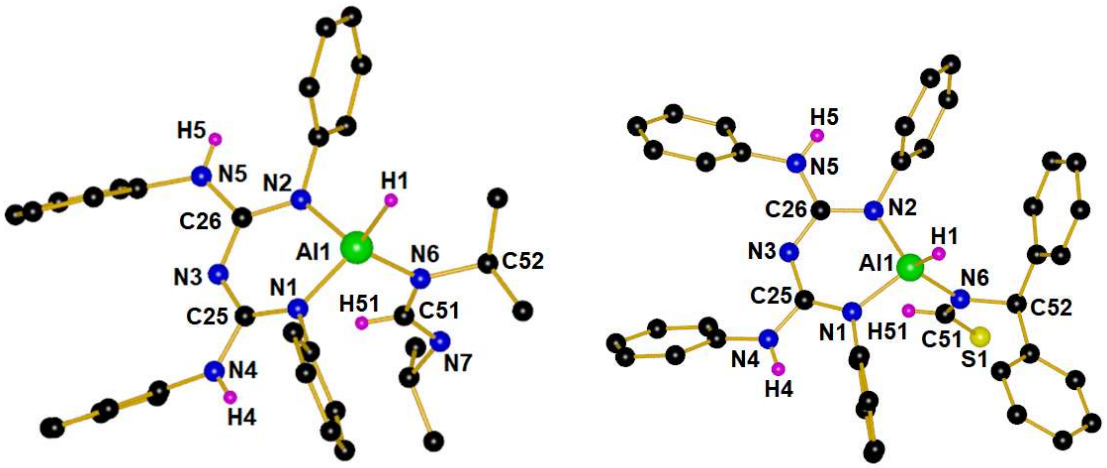


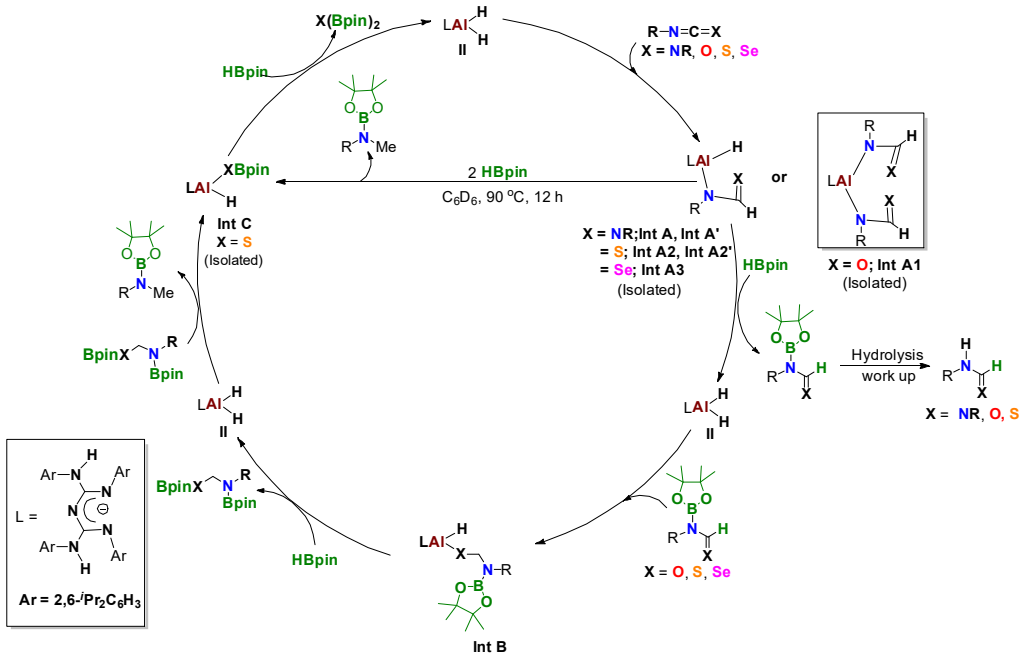
Figure 4.4. Molecular structures of compounds **Int A'** (left) and **Int A2'** (right). All the hydrogen atoms (except for H(4), H(5), and H(51)) and isopropyl groups have been removed for clarity. Selected bond distances (Å) and angles (deg). For **Int A'** (left): Al1−H1 1.919(2), Al1−N1 1.900(2), Al1−N2 1.890(2), Al1−N6 1.854(2), N1−C25 1.344(3), N3−C25 1.342(2), N3−C26 1.334(3), N2−C26 1.350(3), N6-C51 1.359(3), N6−C52 1.492(2), C51−N7 1.283(3), C51−H51 0.930(2); N2−Al1−N1 95.39(9), N2−Al1−H1 115.645(6), N1−Al1−H1 111.812(6), C25−N3−C26 123.9(2), N6−Al1−N2 113.12(10), N6−Al1−N1 110.68(9), N6−Al1−H1 109.515(5), Al1−N6−C51 116.93(17), N6−C51−N7 127.5(2), C51−N6−C52 115.9(2), N6−C51−H51 116.292(2), N7−C51−H51 116.212(2). For **Int A2'** (right): Al1−H1 1.588(3), Al1−N1 1.884(2), Al1−N2 1.874(2), Al1−N6 1.902(2), N1−C25 1.358(4), N3−C25 1.338(3), N3−C26 1.341(3), N2−C26 1.352(4), N6-C51 1.323(4), N6−C52 1.480(4), C51−H51 0.949(2), C51−S1 1.666(3); N2−Al1−N1 96.14(10), N2−Al1−H1 114.196(9), N1−Al1−H1 114.554(9), C25−N3−C26 124.2(2), N6−Al1−N2 109.54(11),

N6−Al1−N1 113.97(11), N6−Al1−H1 108.139(11), Al1−N6−C51 118.7(2), N6−C51−S1 130.1(3), C51−N6−C52 117.6(2).

atom adopts distorted-tetrahedral geometry bonded with an *N, N'*-chelated monoanionic ^{Dipp}CBG ligand, one hydrogen atom, and one amido fragment (-NC*H*N or -NC*H*S). The observed Al1-N6 bond length of **Int A'** (1.854(2) Å) was slightly longer than the reported *N*-donor analog NacNac aluminum formamidinate hydride[12f] {[CH{C(Me)NAr}$_2$Al(H)N(^{i}Pr)CHN(^{i}Pr)], 1.844(3) Å}. The bond distance of Al1-N6 in **Int A2'** (1.902(2) Å) is significantly longer than that of Al1-N6 bond length of **Int A'** (1.854(2) Å) and shorter than the reported pyrrole stabilized aluminum thioformamidiates[30] {[C_4H_2N(2-CH_2NH^tBu)(5-CH_2NMe_2)]Al(SCHNPh)$_2$,[30a] 2.0207(14) Å and [$C_4H_2N(CH_2NMe_2)_2$]Al(SCHNPh)$_2$,[30b] 2.0201(14). The N1–Al1–N2 bite angle of **Int A'**(95.39(9) °) was found moderately acute than the corresponding bond angle noticed in {[(^{Dipp}NacNac)Al(H)N(^{i}Pr)CHN(^{i}Pr)]; N1–Al1–N295.54(13)°}.[12f] As per literature analysis, our current structurally characterized **Int A2'** is the only example of a single hydroalumination product with isothiocyanate fragment (-NC*H*S).[30]

4.2.8. Catalytic Cycle

Based on a series of control and kinetic experiments, a probable catalytic cycle has been suggested for the aluminum-catalyzed hydroboration of heteroallenes such as CDIs, isocyanates, isothiocyanates, and isoselenocyanates to N-borylformamidine, N-borylformamide, N-borylthioformamide, and N-borylselenoformamides, respectively (Scheme 4.3.). The dihydroboration of heteroallenes yielded the formation of bis(boryl) hemiaminal products. The reaction of heteroallenes (except CDI) upon treatment with three equiv. HBpin afforded hydrodeoxygenation (HDO) or hydrodesulfurization (HDS), or hydrodeselenization (HDSe) products, i.e., N-boryl methyl amines.



Scheme 4.3. A plausible mechanism for hydroboration of heteroallenes.

At the first step of the catalytic cycle, the aluminum-dihydride catalyst (**II**) was reacted with carbodiimide, isothiocyanate, and isoselenocyanate in a 1:1 stoichiometric ratio (Scheme 4.3.). In all cases, insertion of heteroallenes into the Al-H bond gave corresponding (^{Dipp}CBG)AlHNR(CHX) {where X = NR, S, Se} complexes. While in the case of a reaction between 1:2 stoichiometric amounts of compound **II** and isocyanate afforded, double isocyanate insertion into Al-H bonds was noticed. The formation of CBG (bis)-formamidinateAl(III) (**Int A1**) was confirmed by NMR and mass spectrometry analysis. This implies the high reactivity of isocyanates compared to other heteroallenes.

Next, reactions between **Int A**, **Int A1**, and **Int A2** with HBpin independently provided chemoselectively N-boryl formamidine, N-boryl formamide, N-borylthioformamide, respectively, and resurgence of the catalyst **II** (Scheme 4.3.). Moreover, I presume that catalyst **II** reacts with corresponding mono N-borylated products in each case, leading to the formation of intermediate **Int B** except N-boryl formamidine. Next, the emergence of bis-(boryl) amine

{RN(Bpin)CH_2(XBpin), X = O, S, Se} and regeneration of catalyst **II** happened by the reaction of **Int B** and HBpin.

Further, in all instances, reactions between N-borylaminal and the catalyst **II** yielded the N-boryl methyl amine products {RN(Bpin)Me} and **Int C**. Alternatively, a 1:2 stoichiometric reactions of **Int A2** and HBpin in C_6D_6 at 90 ºC for 12 h has been carried out. In this case, Int C and N-boryl methyl amine formation was noticed. Lastly, the reaction between **Int C** and HBpin afforded the resurgence of the catalyst **II** and X$(Bpin)_2$ {X= O, S, Se} as a by-product and terminated the catalytic cycle.

4.3. Conclusions

I have established that the molecular aluminum dihydride catalyzed a remarkable partial reduction of heteroallenes for the first time. The prototype aluminum-based reagent synthesizes formamidines/formamides/thio-formamides/seleno-formamides through a B-H bond activation by utilizing CDIs/isocyanates/isothiocyanates/isoselenocyanates as starting materials. Moreover, I have demonstrated aluminum-catalyzed effective hydrodeoxygenation (HDO), hydrodesulfurization (HDS), and hydrodeselenization (HDSe) reactions. Several control and kinetic experiments and structurally characterized intermediates indicate that aluminum species are responsible for the reduction reactions. This work highlights the applicability of CBG aluminum hydride complexes as cheaper, earth-abundant, non-toxic alternatives to stoichiometric metal reagents or molecular transition/lanthanide metal catalysts for the hydroboration of organic substrates. More importantly, the presented aluminum-catalyzed HDO and HDS processes would open new opportunities to convert lignin biomass into value-added chemicals, biofuels and remove sulfur-containing impurities from crude petroleum feedstocks and fuels.

4.4. Appendix: All general experimental information along with analytical data and spectral files of hydroborated products and control reactions were available in supporting information of *Eur. J. Org. Chem.* **2022 (Accepted). DOI:** https://doi.org/10.1002/ejoc.202200941. In addition, the Crystallographic data and structure refinement summary of compounds (**Int A', Int A2', 5m',** and **9h'**) were also provided in ESI.

4.5. References

1. (a) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927 – 1945; (b) Delebecq, E.; Pascault, J. -P.; Boutevin, B.; Ganachaud, F. *Chem. Rev.* **2013**, *113*, 80 – 118; (c) Mitchell, S. M.; Sachinthani, K. A. N.; Pulukkody, R.; Pentzer, E. B. *ACS Macro Lett.* **2020**, *9*, 1046 – 1059; (d) Jurrat, M.; Pointer-Gleadhill, B. J.; Ball, L. T.; Chapman, A.; Adriaenssens, L. *J. Am. Chem. Soc.* **2020**, *142*, 8136 – 8141; (e) Eckert, H. *Angew. Chem. Int. Ed.* **1997**, *36*, 1909.
2. Application of amides: (a) Bruffaerts, J.; Wolff, N. v.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2019**, *141*, 16486 – 16493; (b) Majewski, M. W.; Miller, P. A.; Oliver, A. G.; Miller, M. J. *J. Org. Chem.* **2017**, *82*, 737 – 744.
3. (a) Pace, V.; Monticelli, S.; de la Vega-Hernández, K.; Castoldi, L. *Org. Biomol. Chem.* **2016**, *14*, 7848 – 7854; (b) Yang, L.; Huang, H. *Chem. Rev.* **2015**, *115*, 3468 – 3517; (c) Miura, T.; Takahashi, Y.; Murakami, M. *Chem. Commun.* **2007**, (34), 3577 – 3579; (d) Spino, C.; Joly, M. -A.; Godbout, C.; Arbour, M. *J. Org. Chem.* **2005**, *70*, 6118 – 6121; (e) Sasaki, K.; Crich, D. *Org. Lett.* **2011**, *13*, 2256 – 2259.
4. Selected examples of amides synthesis via C-N bond formation: (a) Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009,** *38*, 606 – 631; (b) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007,** *317*, 790 – 792; (c) Chakraborty, S.; Gellrich, U.; Diskin-Posner, Y.; Leitus, G.; Avram, L. Milstein, D. *Angew. Chem. Int. Ed.* **2017,** *56*, 4229 – 4233; (d) Pattabiraman, V. R.; Bode, J. W. *Nature* **2011,** *480*, 471 – 479.

5. Selected examples of amides synthesis via C-C bond formation: (a) Serrano, E.; Martin, R. *Eur. J. Org. Chem.* **2018,** (24), 3051 – 3064; (b) Su, Z.; Feng, Y.; Zou, R.; Qiu, X.; Wang, J.; Tao, C. *Chem. Commun.* **2020,** *56*, 7483 – 7486; (c) Fiorito, D.; Liu, Y.; Besnard, C.; Mazet, C. *J. Am. Chem. Soc.* **2020,** *142*, 623 – 632.
6. Synthesis of formamidines by employing stoichiometric metal reagents: (a) Peddarao, T.; Baishya, A.; Barman, M. K.; Kumar, A.; Nembenna, S. *New J. Chem.* **2016,** *40*, 7627 – 7636; (b) Kaji, K.; Matsubara, H.; Nagashima, H.; Kikugawa, Y.; Yamada, S. *Chem. Pharm. Bull.* **1978,** *26*, 2246 – 2249.
7. Synthesis of formamides by employing stoichiometric metal reagents: (a) Pace, V.; de la Vega-Hernández, K.; Urban, E.; Langer, T. *Org. Lett.* **2016**, *18*, 2750 – 2753; (b) Pace, V.; Castoldi, L.; Holzer, W. *Chem. Commun.* **2013**, *49*, 8383 – 8386; (c) Schäfer, G.; Matthey, C.; Bode, J. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 9173 – 9175.
8. Synthesis of thioformamide by employing stoichiometric metal reagents: (a) Pace, V.; Castoldi, L.; Monticelli, S.; Safranek, S.; Roller, A.; Langer, T.; Holzer, W. *Chem. Eur. J.* **2015**, *21*, 18966 – 18970; (b) de la Vega-Hernández, K.; Senatore, R.; Miele, M.; Urban, E.; Holzer, W.; Pace, V. *Org. Biomol. Chem.* **2019**, *17*, 1970 – 1978; (c) Park, H. S.; Lee, I. S.; Kim, Y. H. *Chem. Commun.* **1996**, (15), 1805 –1806; (d) Avalos, M.; Babiano, R.; García-Verdugo, C.; Jiménez, J. L.; Palacios, J. C. *Tetrahedron Lett.* **1990**, *31*, 2467 – 2470; (e) Moltzen, E. K.; Kramer, M. P.; Senning, A.; Klabunde, K. J. *J. Org. Chem.* **1987**, *52*, 1156 – 1161; (f) Petermann, J.; Plieninger, H. *Tetrahedron* **1975**, *31*, 1209 – 1216; (g) Borths, C. J.; Chan, J.; Burke, B. J.; Larsen, R. D. *Synlett* **2009**, (19), 3139 – 3142; (h) Yde, B.; Yousif, N. M.; Pedersen, U.; Thomsen, I.; Layesson, S. -O. *Tetrahedron* **1984**, *40*, 2047 – 2052; (i) Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061 – 5087; (j) Hurd, R. N.; Delamater, G. *Chem. Rev.* **1961**, *61*, 45 – 86; (k) Shibahara, F.; Sugiura, R.; Murai, T. *Org. Lett.* **2009**, *11*, 3064 – 3067.

9. Selected references for metal-catalyzed hydroboration of carbonyls: (a) Magre, M.; Szewczyk, M.; Rueping, M. *Chem. Rev.* **2022,** *122*, 8261 –8312; (b) Roy, M. M. D.; Omaña, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.* **2021,** *121*, 12784 – 12965; (c) Bage, A. D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. *ACS Catal.* **2020**, *10*, 13479 – 13486; (d) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019,** *9*, 3307 – 3336; (e) Tamang, S. R.; Findlater, M. *Molecules* **2019,** *24*, 3194; (f) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015,** *5*, 3238 – 3259; (g) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015,** *48*, 1995 – 2003; (h) Maeda, C.; Miyazaki, Y.; Ema, T. *Catal. Sci. Technol.* **2014,** *4*, 1482 – 1497; (i) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997,** *53*, 4957 – 5026; (j) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016,** *18*, 4710 – 4713; (k) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54*, 10225 – 10229.

10. Selected references for metal-catalyzed hydroboration of unsaturated motifs: (a) Bazkiaei, A. R.; Findlater, M.; Gorden, A. E. V. *Org. Biomol. Chem*. **2022**, *20*, 3675 – 3702; (b) Banerjee, I.; Panda, T. K. *Appl. Organomet. Chem.* **2021**, *35* (9), e6333; (c) Bose, S. K.; Mao, L.; Kuehn, L.; Radius, U.; Nekvinda, J.; Santos, W. L.; Westcott, S. A.; Steel, P. G.; Marder, T. B. *Chem. Rev.* **2021,** *121*, 13238 – 13341; (d) Brand, S.; Causero, A.; Elsen, H.; Pahl, J.; Langer, J.; Harder, S. *Eur. J. Inorg. Chem.* **2020,** (18), 1728 – 1735; (e) Wang, M.; Shi, Z. *Chem. Rev.* **2020,** *120*, 7348 – 7398; (f) Hayrapetyan, D.; Khalimon, A. Y. *Chem. Asian J.* **2020,** *15*, 2575 – 2587; g) Wei, D.; Darcel, C. *Chem. Rev.* **2019,** *119*, 2550 – 2610; (h) Mukherjee, A.; Milstein, D. *ACS Catal.* **2018,** *8*, 11435–11469; (i) Nikonov, G. I. *ACS Catal.* **2017,** *7*, 7257 – 7266; (j) Ai, W.; Zhong, R.; Liu, X.; Liu, Q. *Chem. Rev.* **2019,** *119*, 2876 – 2953; (k) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017,** *350*, 14 – 29; (l) Liu, Y.; Li, J.; Ma, X.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2018,** *374*, 387 – 415; (m) Ni, C.; Ma, X.; Yang, Z.; Roesky, H. W. *Eur. J. Inorg. Chem.* **2022,** DOI:

https://doi.org/10.1002/ejic.202100929; **(**n) Dagorne, S.; Wehmschulte, R. *ChemCatChem* **2018,** *10*, 2509 – 2520; (o) Hobson, K.; Carmalt, C. J.; Bakewell, C. *Inorg. Chem.* **2021,** *60*, 10958 – 10969; (p) Liu, W.; Ding, Y.; Jin, D.; Shen, Q.; Yan, B.; Ma, X.; Yang, Z. *Green Chem.* **2019,** *21*, 3812 – 3815; (q) Sadow, A. D. *Early Main Group Metal Catalysis: Concepts and Reactions* (Ed: S. Harder), Wiley-VCH, Weinheim, **2020**, pp. 201 – 224; *Angew. Chem. Int. Ed.* **2021**, *60* (37), 20092 – 20093; (r) Ananikov, V. P. *Sustainable Catalysis With Nonendangered Metals*. *Angew. Chem. Int. Ed.* **2016**, *55*, 14904; (s) Aldridge, S. Downs, A. J. *The Group 13 Metals Aluminium, Gallium, Indium, and Thallium: Chemical Patterns and Peculiarities*. *Angew. Chem. Int. Ed.* **2011**, *50* (49), 11569.

11. Selected examples for metal-catalyzed hydroboration of carbon dioxide: (a) Leong, B. -X.; Lee, J.; Li, Y.; Yang, M. -C.; Siu, C. -K.; Su, M. -D.; So, C. -W. *J. Am. Chem. Soc.* **2019**, *141,* 17629 – 17636; (b) Franz, D.; Jandl, C.; Stark, C.; Inoue, S. *ChemCatChem* **2019**, *11*, 5275 – 5281; (c) Erken, C.; Kaithal, A.; Sen, S.; Weyhermüller, T.; Hölscher, M.; Werlè, C.; Leitner, W. *Nat. Commun.* **2018**, *9,* 4521; (d) von Wolff, N.; Lefèvre, G.; Berthet, J. -C.; Thuéry, P.; Cantat, T. *ACS Catal.* **2016**, *6*, 4526 – 4535; (e) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. *ACS Catal.* **2017**, *7*, 1853 – 1859.
12. Metal catalyzed hydroboration of carbodiimides: (a) Yan, B.; He, X.; Ni, C.; Yang, Z.; Ma, X. *ChemCatChem* **2021**, *13*, 851 – 854; (b) Bisai, M. K.; Gour, K.; Das, T.; Vanka, K.; Sen, S. S. *J. Organomet. Chem.* **2021,** *949*, 121924; (c) He, X.; Yan, B.; Ni, C.; Zhao, Y.; Yang, Z. Ma, X. *Asian J. Org. Chem.* **2021,** *10*, 196 – 201; (d) Bakewell, C. *Dalton Trans.* **2020,** *49*, 11354 – 11360; (e) Sarkar, N.; Bera, S.; Nembenna, S. *J. Org. Chem.* **2020,** *85*, 4999 – 5009; (f) Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J.* **2019**, *25*, 11918 – 11923; (g) Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics* **2019**, *38*, 3092 – 3097; (h) Mahawar, P.; Yadav, D.; Singh, D.; Sharma, M. K.; Selvarajain, N. *ChemRxiv* **2019,** 1 – 3; (i) Liu, H.; Kulbitski, K.; Tamm, M.; Eisen, M. S. *Chem. Eur. J.* **2018**,

24, 5738 – 5742; (j) Rauch, M.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 13264 – 13267; (k) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52*, 13155 – 13158; (l) Weetman, C.; Hill, M. S.; Mahon, M. F. *Chem. Eur. J.* **2016**, *22*, 7158 – 7162.

13. Metal catalyzed hydroboration of isocyanates: (a) Pandey, V. K.; Sahoo, S.; Rit, A. *Chem. Commun.* **2022**, *58*, 5514 – 5517; (b) Du, Z.; Behera, B.; Kumar, A.; Ding, Y. *J. Organomet. Chem.* **2021,** *950*, 121982; (c) Sahoo, R. K.; Sarkar, N.; Nembenna, S. *Angew.Chem. Int. Ed.* **2021,** *60*, 11991 – 12000; (d) Yang, Y.; Anker, M. D.; Fang, J.; Mahon, M. F.; Maron, L.; Weetman, C.; Hill, M. S. *Chem. Sci.* **2017**, *8*, 3529 – 3537; (e) Ma, M.; Wang, W.; Luo, M.; Xiao, Q.; Xu, L. CN Pat 108358959, **2018**; (f) Ma, M.; Xiao, Q.; Cao, X.; Zheng, Y. CN Pat. 111410668, **2020**.
14. Metal catalyzed hydrosilylation of carbodiimides and isocyanates: (a) Marschner, C. *Hydrosilation catalysis*, John Wiley & Sons Ltd.: **2011**; pp 1 – 12; (b) Huckaba, A. J.; Hollis, T. K.; Reilly, S. W. *Organometallics* **2013**, *32*, 6248 – 6256; (c) Ojima, I.; Inaba, S. -I. *J. Organomet. Chem.* **1974**, *72*, C11-C13; (d) Ojima, I.; Inaba, S. -I. *J. Organomet. Chem.* **1977,** *140*, 97 – 111; (e) Tan, M.; Zhang, Y. *Tetrahedron Lett.* **2009,** *50*, 4912 – 4915.
15. Metal catalyzed hydrogenation of carbodiimides and isocyanates: (a) Holthausen, M. H. Colussi, M. Stephan, D. W. *Chem. Eur. J.* **2015,** *21*, 2193 – 2199; (b) Howell, H. G. *Synth. Commun.* **1983,** *13*, 635 – 637.
16. Application of preparation of N-methyl amine compounds: Chen, Y. *Chem. Eur. J.* **2019,** *25*, 3405 – 3439.
17. Selected examples of the preparation of N-methyl amine compounds: (a) Magre, M.; Szewczyk, M.; Rueping, M. *Org. Lett.* **2020,** *22*, 3209 – 3214; (b) Cabrero-Antonino, J. R.; Adam, R.; Beller, M. *Angew. Chem. Int. Ed.* **2019,** *58*, 12820 – 12838; (c) Ogata, O.; Nara, H.; Fujiwhara,

M.; Matsumura, K.; Kayaki, Y. *Org. Lett.* **2018**, *20*, 3866 – 3870; (d) Li, Y.; Sorribes, I.; Vicent, C.; Junge, K.; Beller, M. *Chem. Eur. J.* **2015**, *21*, 16759 – 16763.

18. Synthesis of N-methyl amine compounds by using classical metal reagents: (a) Finholt, A. E.; Andreson, C. D.; Agre, C. L. *J. Org. Chem.* **1953,** *18*, 1338 – 1340; (b) Ellzey, S. E. Jr.; Mack, C. H. *J. Org. Chem.* **1963,** *28*, 1600 – 1604.
19. Ghosh, P. von Wangelin, A. J. *Angew. Chem. Int. Ed.* **2021,** *60*, 16035 – 16043.
20. (a) Harder, S. *Chem. Rev.* **2010,** *110*, 3852 – 3876; (b) Hill, M. S.; Liptrot, D. J.; Weetman, C. *Chem. Soc. Rev.* **2016,** *45*, 972 – 988; (c) Power, P. P. *Nature* **2010,** *463*, 171-177; (d) Wilkins, L. C.; Melen, R. L. *Coord. Chem. Rev.* **2016,** *324*, 123 – 139.
21. Peddarao, T.; Sarkar, N.; Nembenna, S. *Inorg. Chem.* **2020,** *59*, 4693 – 4702.
22. Peddarao, T.; Baishya, A.; Sarkar, N.; Acharya, R.; Nembenna, S. *Eur. J. Inorg. Chem.* **2021,** 2034 – 2046.
23. Sarkar, N.; Sahoo, R. K.; Mukhopadhyay, S.; Nembenna, S. *Eur. J. Inorg. Chem.* **2022,** (8), DOI: https://doi.org/10.1002/ejic.202101030.
24. Selected examples of Phosphorous-based hydroboration of unsaturated motifs and carbon dioxide: (a) Aversa-Fleener, C. R.; Chang, D. K.; Liberman-Martin, A. L. *Organometallics* **2021**, *40*, 4050 –4054; (b) Speed, A. W. H. *Chem. Soc. Rev.* **2020**, *49*, 8335 – 8353; (c) Hynes, T.; Welsh, E. N.; McDonald, R.; Ferguson, M. J.; Speed, A. W. H. *Organometallics* **2018**, *37*, 841 – 844; (d) Rao, B.; Chong, C. C.; Kinjo, R. *J. Am. Chem. Soc.* **2018**, *140*, 652 – 656; (e) Chong, C. C.; Rao, B.; Kinjo, R. *ACS Catal.* **2017**, *7*, 5814 – 5819; (f) Lin, Y. -C.; Hatzakis, E.; McCarthy, S. M.; Reichl, K. D.; Lai, T. -Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2017**, *139*, 6008 – 6016; (g) Tien, C. -H.; Adams, M. R.; Ferguson, M. J.; Johnson, E. R.; Speed, A. W. H. *Org. Lett.* **2017**, *19*, 5565 – 5568; (h) Declercq, R.; Bouhadir, G.; Bourissou, D.; Légaré, M. -A.; Courtemanche, M. -A.; Nahi, K. S.; Bouchard, N.; Fontaine, F. -G.; Maron, L. *ACS Catal.* **2015**, *5*, 2513 – 2520; (i) Wanga, T.; Stephan, D. W. *Chem. Commun.* **2014**, *50*,

7007 – 7010; (j) Courtemanche, M. -A.; Légaré, M. -A.; Maron, L.; Fontaine, F. -G. *J. Am. Chem. Soc.* **2014**, *136*, 10708 – 10717; (k) Enders, D.; Rembiak, A.; Seppelt, M. *Tetrahedron Lett.* **2013**, *54*, 470 – 473.

25. (a) Ramos, A.; Antiñolo, A.; Carrillo-Hermosilla, F.; Fernández-Galán, R.; Rodríguez-Diéguez, A.; García-Vivó, D. *Chem. Commun.* **2018**, *54*, 4700 –4703; (b) Oladipo, S. D.; Omondi, B.; Mocktar, C. *Appl. Organomet. Chem.* **2020,** *34* (5), e5610; (c) Kulkarni, N. V.; Elkin, T.; Tumaniskii, B.; Botoshansky, M.; Shimon, L. J. W.; Eisen, M. S. *Organometallics* **2014,** *33* (12), 3119 – 3136; (d) Enthaler, S.; Schröder, K.; Inoue, S.; Eckhardt, B.; Junge, K.; Beller, M.; Drieß, M. *Eur. J. Org. Chem.* **2010,** (25), 4893 – 4901; (e) Evans, P. D.; Gee, J. D. *Nature* **1980,** *287* (5777), 60-62; (f) Hollingworth, R. M. *Environ. Health Perspect.* **1976,** *14*, 57 –69.
26. Selected examples of deoxygentative hydroboration of nitro compounds: (a) Zhao, L.; Hu, C.; Cong, X.; Deng, G.; Liu, L. L.; Luo, M.; Zeng, X. *J. Am. Chem. Soc.* **2021,** *143*, 1618 – 1629; (b) Yao, W.; Wang, J.; Lou, Y.; Wu, H.; Qi, X.; Yanga, Y.; Zhong, A. *Org. Chem. Front.* **2021,** *8*, 4554 – 4559; (c) Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. *Chem. Rev.* **2019**, *119*, 2611 – 2680; (d) Orlandi, M.; Brenna, D.; Harms, R.; Jost, S.; Benaglia, M. *Org. Process Res. Dev.* **2018**, *22*, 430 – 445.
27. Selected examples: (a) Shafiq, I.; Shafique, S.; Akhter, P.; Yang, W.; Hussain, M. *Catal. Rev.* **2022**, *64*, 1 – 86; (b) Glass, N. R.; Glass, G. E.; Rennie, P. J. *Environ. Sci. Technol.* **1979,** *13*, 1350–1355; (c) Hofmann, M.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1994**, *116*, 4947 – 4952.
28. References for the synthesis of isoselenocyanates: (a) Angeli, A.; Tanini, D.; Peat, T. S.; Mannelli, L. D. C.; Bartolucci, G.; Capperucci, A.; Ghelardini, C.; Supuran, C. T.; Carta, F. *ACS Med. Chem. Lett.* **2017**, *8*, 963 – 968; (b) Zakrzewski, J.; Huras, B.; Kiełczewska, A. *Synthesis* **2016**, *48*, 85 – 96; (c) Barton, D. H. R.; Parekh, S. I.; Tajbakhsh, M.; Theodorakis, E. A.; Tse, T. C. -L. *Tetrahedron* **1994**, *50*, 639 – 654.

29. Selected examples of chemoselectivity reaction; (a) Bergamaschi, E.; Lunic, D.; McLean, L. A.; Hohenadel, M.; Chen, Y. -K.; Teskey, C. J. *Angew. Chem. Int. Ed.* **2022**, *61* (8), DOI: https://doi.org/10.1002/anie.202114482; (b) Mahatthananchai, J.; Dumas, A. M.; Bode, J. W. Angew. Chem. Int. *Ed.* **2012**, *51*, 10954 – 10990; (c) Shenvi, R. A.; O' Malley, D. P.; Baran, P. S. *Acc. Chem. Res.* **2009**, *42*, 530 – 541.
30. (a) Lien, Y. -L.; Chang, Y. -C.; Chuang, N. -T.; Datta, A.; Chen, S. -J.; Hu, C. -H.; Huang, W. -Y.; Lin, C. -H.; Huang, J. -H. *Inorg. Chem.* **2010**, *49*, 136 – 143; (b) Chen, I. -C.; Ho, S. -M.; Chen, Y. -C.; Lin, C. -Y.; Hu, C. -H.; Tu, C. -Y.; Datta, A.; Huang, J.-H.; Lin, C.-H. *Dalton Trans.* **2009**, (40), 8631 – 8643.

Chapter 5A

Aluminum-Catalyzed Reduction of Alkenes and Isocyanides via Hydroboration: C=C and N=C Double Bond Activation

Abstract

Herein, a remarkable *N, N'*-chelated CBG aluminum dihydride [$LAlH_2$; L = {(ArHN)-(ArN)C=NC=(NAr)(NHAr); Ar= 2,6-Et_2-C_6H_3}] (**1**) catalyzed selective B-H addition across the double bond of alkenes and isocyanides is studied. A wide range of alkenes, including terminal, internal, 1,1-disubstituted to α-substituted, underwent exclusively anti-Markovnikov hydroboration reaction with excellent yield and high regioselectivity. The isolated linear boronic esters (RCH_2CH_2Bpin, R = aryl/alkyl) are air-stable and non-toxic, therefore well preserved for further application in coupling reaction (*Suzuki coupling*) partner to synthesis industrially important organic synthons. In addition, compound **1** was employed for double hydroboration of aryl and alkyl organic isonitriles into corresponding diboronate amine esters ($RNBpinCH_2Bpin$, R = aryl/alkyl) in good yield. Moreover, the developed catalytic methodology demonstrates effective gram-scale hydroboration of alkenes and isocyanides under neat conditions.

5.A.1. Introduction

Boron reagents are the vital feedstocks of the organic synthetic field due to their coupling reactions to generate new C-C bonded valuable organic molecules.[1] In addition, these organic components are also used in the medicinal industry and for valuable bioactive molecules.[2] Therefore past few years, adequate research has been done to develop good synthetic routes to prepare stable boron species. As evident from the literature study, I noticed that alkyl boronic esters were synthesized by various methods, which include coupling reactions of Grignard reagents,[3a] hydroboration of alkenes,[3b] alkynes,[3c] alkyl halides,[3d] and more importantly

borylation of C-*H* bond of simple organic motifs using molecular metal complexes.[4] Olefin reduction via hydroboration technique provides the best gateway to synthesize air-stable and less-toxic boronic ester precursors, as the synthetic route is safer and highly selective.[5] According to the literature survey, various transition metal complexes[6] were developed to afford suitable boron species from corresponding olefins. In this regard, it should be noted that only a handful of examples of s and p block elements[7] are reported for the chemoselective transformation of alkenes to desired hydroborated products.

In recent main-group metal catalysis, it was discovered that various molecular aluminum complexes have been used for the reduction of unsaturated organic compounds using hydroboration,[7, 8] hydrosilylation,[9] hydrostannylation,[9c] hydroamination,[10] and transfer hydrogenation[11] methods. The rise of aluminum chemistry is due to its unusual properties, such as being highly earth-abundant, cheap, and non-radioactive compared to lanthanide and transition metal complexes.[12]

In 2016, Oestreich[7k] group reported the first alkene hydroboration among main-group elements. The author used a pre-catalyst to reduce the olefin into linear boronate, and the author employed commercially available BAr^F_3 (Ar^F=3,5-bis(trifluoromethyl)phenyl) ester via the anti-Markovnikov addition of pinacolborane. However, the boronate esters were isolated in a lower yield. More importantly, a trace quantity of hydroborated products was noticed. Later, other main-group metal reagents were introduced for alkene reduction by Zhang,[7a] Wu,[7i] Cowley,[7h] Hong,[7d] Xue,[7b] An,[7e, 7g] and Thomas[7l] research groups respectively. However, the catalysts were highly pyrophoric; quenching, reaction waste disposal, and proper handling are quite challenging.[13] Therefore, based on the above work and their restriction, it increases the demand for sustainable catalysts. In 2017, Parkin and cowokers[7j] employed terminal monomeric

magnesium hydride [Tism$^{Pri\ Benz}$]MgH catalyst for hydroboration of styrene to 1-phenylethyl isomer Ph(Me)C(H)Bpin (*branched product*) with Markovnikov selectivity. Recently, Sen[7c] and Panda's[7f] research group demonstrated an anti-Markovnikov HBpin addition in alkenes by using molecular lithium and aluminum alkyl complexes as pre-catalysts. So, it indicates that molecular metal complexes[7c, 7f, 7j] are better and more efficient catalysts than metal reagents [7a-7b, 7d-7e, 7g-7i, 7k] for the reduction of olefins.

In organic chemistry, isocyanide reduction is quite an attractive research area.[14] Only one main-group catalyst[15] has been reported to reduce isonitriles. The reaction was first initiated by Figueroa and coworkers[16] where they mixed the equimolar amount of 9-BBN (*9-Borabicyclo[3.3.1]nonane*) and m-terphenyl isocyanide to synthesize the corresponding bis(boryl)amine ester product. The author also prepared a partially reduced boroyl-imine product by using half equiv. 9-BBN in dry ether. Several experiments were done for the complete reduction with pinacolborane but ended with a singly reduced boronate ester product only at 100 ^{0}C. In 2015, Hill[15] reported selective dihydroboration of various isocyanides with two equiv. of pinacolborane using ^{Dipp}Nacnac supported magnesium butyl complex [CH{C(Me)NAr}$_2$Mg^{n}Bu] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$). The reaction is highly successful but limited, with poor catalytic performance towards alkyl isocyanides (*cyclic and acyclic substrates*).

In recent years our group synthesized conjugated bis-guanidine ligands (CBG)[17] and the corresponding aluminum methyl,[8c, 9a] and hydride[8p] complexes. These compounds are highly active catalysts for reducing carbonyls and challenging unsaturated functional groups under mild reaction conditions.[8c, 8p, 9a]

Therefore, herein I displayed my recent work on catalytic hydroboration of alkene and isonitrile with pinacolborane using aluminum hydride complex (**1**)[17] in standard conditions. To

the best of our literature investigation, I conclude that this is the first report of molecular aluminum-hydride catalysis for di-hydroboration of organic aryl and alkyl isocyanides to 1,1-bis(boryl)amine ester products in high-yield.

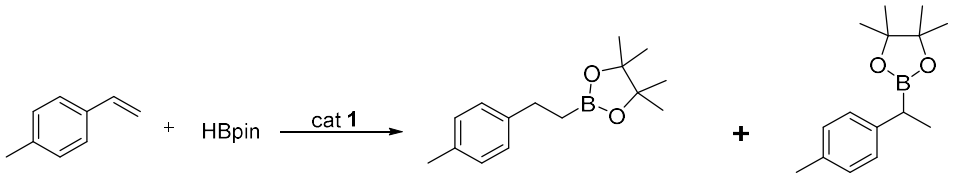
5.A.2. Results and Discussion

5.A.2.1. Anti-Markovnikov Hydroboration of Alkenes

Previously, CBG aluminum-hydride (**1**) catalyzed[8p] reduction of commercially purchased styrene with 1.0 equiv. of pinacolborane has been studied. Given the industrial importance[2] of air-stable alkyl boronate esters (RCH_2CH_2Bpin, R = alkyl/aryl), I aimed to explore the B-H addition in a broad range of alkenes.

For this study 4-methyl styrene (*representative substrate*) optimizes alkene reduction with pinacolborane as a reducer. An initial experiment was performed in solvent-free condition with no catalyst at 110 ^oC heating for 12 h, where only 30% conversion of 4-methyl styrene to corresponding hydroborated product **3a** was noticed (Entry 1, Table 5.A.1.).

Table 5.A.1. Optimization table for aluminum-hydride catalyzed (**1**) reduction of 4-methyl styrene.[a]



2a **3a** **3a'**

Entry	Cat. (mol%)	Solvent	Time	Yield (%) (**3a:3a'**)[b]
1	-	neat	12 h	30:0
2	1	neat	12 h	75:0
3	3	neat	12 h	95:0
4	**5**	**neat**	**12 h**	**>99:0**
5	5	Toluene	12 h	>99:0
6[c]	5	neat	9 h	>99:0

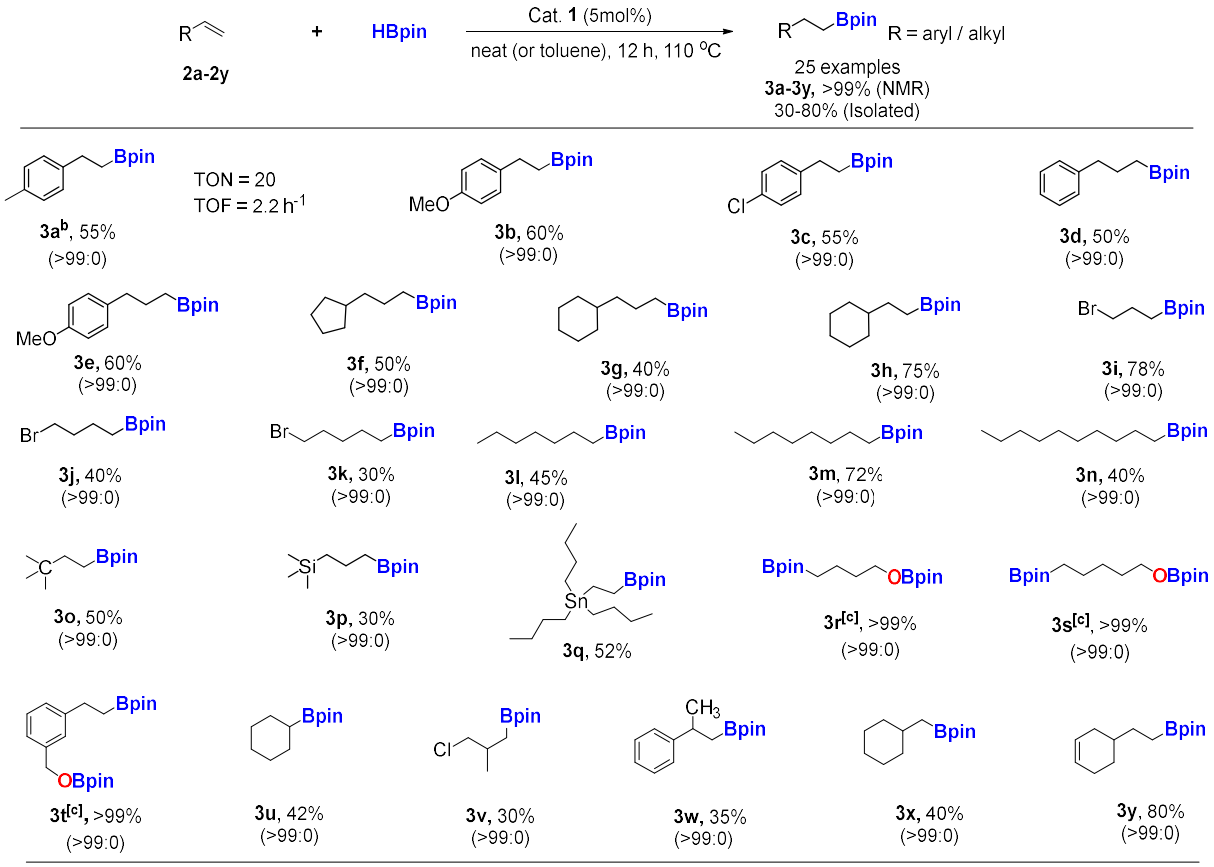
7	5	neat	5 h	80:0

[a]Reactions were performed with 1.0 equiv. of 4-methyl styrene (1.0 mmol), 1.0 equiv. of pincolborane (1.0 mmol), aluminum-hydride (cat.) **1** (5 mol%), neat (or toluene for solid substrate) under N_2 in a 10 mL air-tight vial at 110 °C within 12 h. [b]The yield for reduction of styrene was examined by ^{1}H NMR spectra based on the full vanishing of C=C double bond followed by the formation of new characteristic proton resonance (*triplet*) for –C*H*$_2$CH$_2$Bpin, a fragment of product **3a** at (δ) 2.73 ppm. [c]Entry 6, exhibits high TON = 20 and the corresponding TOF = 2.2 h-1. The turnover number was examined by the number of desired boronate ester (**3a**) formed divided by the number of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction.

In the presence of 1 mol% aluminum-hydride catalyst (**1**) under similar conditions, 75% of boronate ester product **3a** (4-Me-PhCH$_2$CH$_2$Bpin) was formed. The reduced boronate ester product (**3a**) is linear, with anti-Markovnikov selectivity, which confirms the exclusive formation of a single regio-isomer in preference of branched product **3a'**. With an increase of catalyst loading upto 5 mol% in neat conditions, the quantitative formation of **3a** was observed in ^{1}H NMR spectroscopy (entry 4 of Table 5.A.1.). The use of toluene in the reaction did not affect the *p*-methyl styrene reduction. In further experiments, it was discovered that entry 6 of Table 5.A.1. indicates a high turnover no. (20) and eventually the turnover frequency (2.2 h^{-1}) for complete conversion of styrene to respective linear boronate ester product **3a**. The yield% decreases for further lowering in catalyst load. It should be noted that, in a crude reaction mixture of styrene hydroboration, no Markovnikov or dehydrogenative borylation products were found, as confirmed by ^{1}H NMR spectra.

With the final optimization of styrene reduction in hand, next the substrate scope of alkenes reduction was widened via hydroboration. In all experiments, the complete formation of linear boronate esters was observed, further purified by column chromatography to afford the isolation of pure anti-Markovnikov hydroborated products **3a-3y**, summarized in Table 5.A.2. In the initial screening, I discovered that styrene with electron-donating (-MeO) and electron-

Table 5.A.2. Substrate scope for reduction of alkenes via hydroboration catalyzed by aluminum-hydride (**1**) complex.[a]



[a]Reaction was performed with 1.0 equiv. of alkenes (1.0 mmol), 1.0 equiv. of pinacolborane (1.0 mmol), aluminum-hydride (cat.) **1** (5 mol%), neat (or toluene for solid substrate) under N_2 in a 10 mL air-tight vial at 110 °C within 12 h. The distribution of regioisomers ratios (linear vs. branched) is presented in parenthesis and was analyzed by ^{1}H NMR spectra based on the complete vanishing of the C=C double bond followed by the formation of a new characteristic proton resonance signal (*triplet*) for –C*H*$_2$CH$_2$Bpin, a fragment of anti-Markovnikov boronate ester product (**3a-3y**). The linear boronate ester products were isolated after being purified by column chromatography, except **3r-3t**. Yield for (**3r-3t**) products based on ^{1}H NMR integration of product resonance peak. [b]For compound **3a**, TOF was 2.2 h^{-1} resulting from a shorter reaction time (9 h). The turnover number was examined by the number of moles of desired boronate ester (**3a**) formed divided by the number of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction. [c]For **3r**, **3s** and **3t**, pinacolborane (2.0 equiv.) was used.

withdrawing (-Cl) substituents was hydroborated to corresponding linear aryl boronic ester with good yields of 55-60% (entries **3b** and **3c** of Table 5.A.2.).

Additionally, it was noticed that our reaction methodology works well for alkyl-substituted terminal alkenes (*both cyclic and acyclic substrates*). Therefore, when cyclic aliphatic alkenes

such as allylbenzene, 4-allylanisole, allylcyclopentane, allyl cyclohexene, and vinyl cyclohexane (**2d-2h**) when reacted with pinacolborane, it resulted in the entire reduction to linear alkyl boronate ester (Table 5.A.2., entries **3d-3h,** 40-75%) with 5 mol% catalyst (**1**) loading. The catalytic result indicates the high efficiency of the CBG aluminum-hydride catalyst, similar to the reported molecular metal catalyst.[7f]

Similarly, the acyclic short and long-chain alkenes (**2i-2p**) show no change in catalytic efficiency of compound **1** and, therefore, well hydroborated into analogous anti-Markovnikov boronate esters (Table 5.A.2., entries **3i-3p**). The quantitative reduction of vinyl tributyltin (**2q**) to linear pinacol alkyl boronate ester (**3q**) shows adequate anti-Markovnikov selectivity and therefore isolated with 52% yield (*linear boronate ester*). NMR spectra and HRMS studies characterized product **3q**.

Next, for alkenols substrates (**2r-2t**), it was noticed that under one equiv. of pinacolborane, a mixture of products was found due to the high reactivity of carbonyl groups. Therefore, when two equiv. of HBpin were introduced in the reaction system, both carbonyl (-CHO) and alkene (-$CH{=}CH_2$) groups were quantitatively hydroborated into corresponding diboronate ester products **(**Table 5.A.2., entries **3r-3t**) with 99% yield. The reaction outcome was similar to the ruthenium-based reduction of alkenols with pinacolborane.[6f]

Next, an example of internal olefin was subjected to expand the substrate scope of B-H in alkene. In this context, when 1.0 equiv. cyclohexene was added to the reaction mixture of 5 mol% compound **1** and one equiv. of HBpin at 110 ^{o}C, the quantitative formation of respective hydroborated linear product **3u** was observed with 42% isolation after column chromatography. It was remarkable to inform for 1,1-disubstituted olefin (*3-chloro-2-methyl-1-propene*) and α-methyl styrenes (**2v-2w**), the present catalyst methodology afforded an

exclusive formation of anti-Markovnikov boronate esters (Table 5.A.2., entries **3v-3w**) was detected in NMR spectroscopy and isolated in 30-35 % yield. Similarly, for methylenecyclohexene **2x**, the respective linear boronate ester **3x** was isolated in colorless oil (40%). In addition, one chemoselective hydroboration was also documented in Table 5.A.2. by choosing 4-vinyl-1-cyclohexene substrate **2y** where exclusively terminal –CH=CH_2 was reduced with internal alkene remaining unaffected similar to the reported literature.[7h] The respective boronate ester (**3y**) was isolated in an 80% yield.

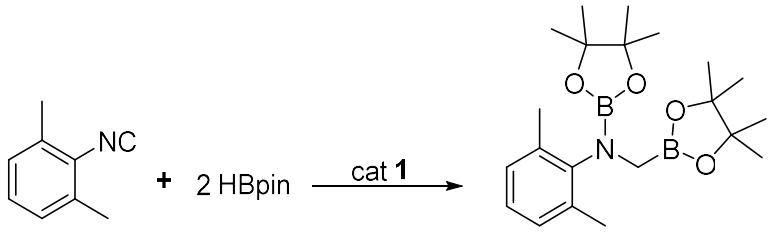
Next, the catalytic activity of the main-group molecular catalysts[7c, 7f] for the anti-Markovnikov reduction of styrene with pinacolborane was correlated with CBG Al-hydride (**1**) compound. The catalytic hydroboration was conducted at 100 ºC with a low catalyst load and shorter reaction time interval, resulting in a TON (20) and TOF (2.2 h^{-1}) for reduction of styrene to linear boronate ester product **3a** in comparison to previously reported molecular aluminum (TON = 33, TOF = 4.0 h-1)[7f] and lithium (TON = 24, TOF = 2.0 h-1)[7c] catalysts.

5.A.2.2. Dihydroboration of Isonitriles

Previously aluminum-hydride (**1**) was used for dihydroboration[8p] of cyclohexyl (CyN≡C) and 1-pentylisocyanide ($C_5H_{11}N$≡C) to corresponding alkyl hydroborated amine in >99% yield. Considering the importance of isocyanide in modern industrial applications,[14] I focused on chemoselective B-H addition in a wide range of aryl and alkyl isocyanides.

For this investigation, 2,6-dimethyl phenyl isocyanide was used as a testing substrate to investigate reducing isonitriles. Initial experiments were done in the absence of a catalyst with two equiv. of pinacolborane under a solvent-free environment. No change was found in the reaction mixture after boiling (80 ºC) the solution for 48 h (Table 5.A.3., entry 1).[15] However, when 7 mol% aluminum dihydride **1** was added to the same reaction mixture

Table 5.A.3. Optimization table for aluminum catalyzed (**1**) hydroboration of 2,6-dimethylphenyl isocyanide.[a]



4a **5a**

Entry	Cat (mol%)	Time	Solvent	Yield (%)[b]
1	-	24 h	neat	-
2	7	48 h	neat	>99
3	7	24 h	neat	>99
4	**5**	**24 h**	**neat**	**>99**
5	5	24 h	Toluene	>99
6[c]	5	12 h	neat	>99
7	5	10 h	neat	88

[a]Reactions were conducted with 2,6-dimethyl phenyl isocyanide (1.0 mmol, 1.0 equiv.), HBpin (2.0 mmol, 2.0 equiv.), aluminum-hydride (cat.) **1** (5 mol%), neat under N_2 in a 10 mL air-tight vial at 80 °C within 24 h. [b]The yield for reduction of xylisonitrile was examined by ^{1}H NMR spectra based on the full vanishing of N=C double bond followed by the appearance of a new proton signal for –N(Bpin)CH_2Bpin moiety of product **5a**. [c]Entry 6, exhibits high TON = 20 and the corresponding TOF = 1.6 h^{-1}. The turnover number was examined by the number of moles of desired bis(boryl)amine ester (**5a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction.

heated at 80 °C for 24 h, it resulted in the quantitative formation of diboryl ester **5a** (RNBpinCH_2Bpin, R = Xyl) confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectra (Table 5.A.3., entry 4). The boronate ester **5a** was further characterized by the ^{11}B NMR spectrum, where two peaks at (δ) 32.69 (RN*Bpin*CH_2Bpin) and 23.53 (RNBpinCH_2*Bpin*) ppm were noticed with no additional peak. Lowering catalyst load upto 5 mol% afforded the complete reduction of xylisocyanide into corresponding diboronate ester (**5a**) within 24 h time interval (Entry 4 of Table 5.A.3.). It was

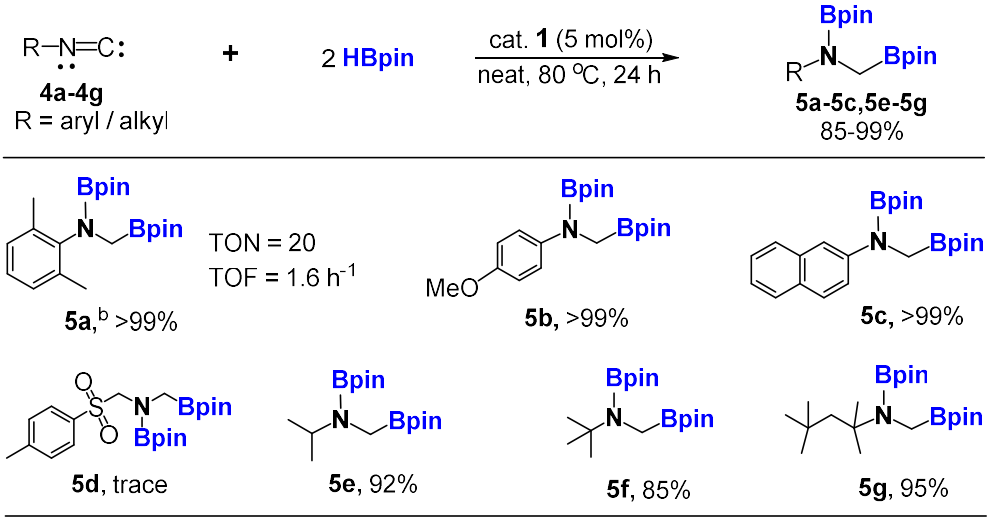
notable that the entry 6 of Table 5.A.3. indicates the TON (20) and corresponding turn over frequency of 1.6 h^{-1} for the reduction of xylisonitrile to borylamine ester **5a** with a low catalyst quantity and shorter reaction time interval.

After completing the optimized condition for reducing xylisocyanide, I investigated the double hydroboration of various organic isocyanides with pinacolborane as a reducer under 5 mol% of catalyst **1** load in neat condition, as summarized in Table 5.A.4. All organic isocyanides were commercially available and used for catalysis reaction without further purification. The yield of all synthesized 1,2-diboranate amines esters was based on ^{1}H NMR spectroscopy. The new boronate esters were characterized by both NMR and mass spectroscopy.

At the beginning of substrate screening, it was discovered that N-aryl isocyanides such as *p*-methoxyphenyl isocyanide and 2-napthylisocyanides were fully converted into corresponding 1,2-bis(boryl)amines (Table 5.A.4., entries **5b-5c**) within stipulated time interval at 5 mol% catalyst **1** load. Here I can conclude that catalyst **1** is better than the reported magnesium-catalyzed dihydroboration for N-aryl isonitriles at 100 ^{o}C for 48 h resulting in only a 50 % yield. However, the present methodology did not successfully reduce *p*-toluenesulfonylmethyl isocyanide (**5d,** trace amount). The possible reason for this failure is due to steric hindrance and electronic resistance of sulfonyl moiety, which blocks the approach of the catalyst towards the isocyanide functional group.

In additional experiments, hydroboration of N-alkyl isocyanides was explored. But a gradual decrease in catalytic conversion for 2^o and 3^o aliphatic isocyanides was observed compared to aryl substrates.

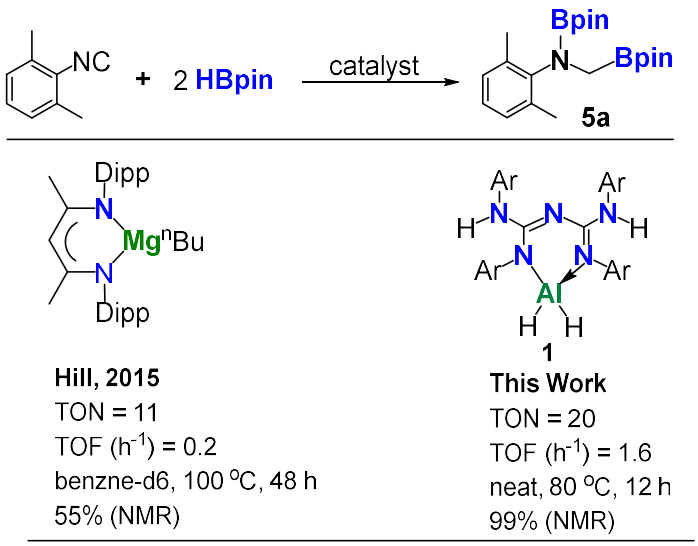
Table 5.A.4. Substrate scope for dihydroboration of isonitriles catalyzed by aluminum-hydride (**1**) complex.[a]



[a]Reaction were performed with 1.0 equiv. of isonitriles (1.0 mmol), 2.0 equiv. of pinacolborane (2.0 mmol), aluminum-hydride (cat.) **1** (5 mol%), neat under N_2 in a 10 mL air-tight vial at 80 °C within 24 h. The yield for reduction of xylisonitrile was examined by ^{1}H NMR spectra based on the full vanishing of N=C double bond followed by the appearance of a new proton signal for –N(Bpin)CH_2Bpin moiety of bis(boryl)amine ester product **5a-5g**. [b]For compound **5a**, TOF was 1.6 h^{-1} resulting from a shorter reaction time (12 h). The turnover number was examined by the number of moles of desired bis(boryl)amine ester (**5a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction.

Therefore, under the prescribed standard reaction conditions (Table 5.A.4.), all three alkylisonitrile, i.e., isopropyl, tertbutyl, and 1,1,3,3-tertbutylisocyanides (**4e-4g**), underwent an effective double reduction with 2.0 equiv. of pinacolborane, which afforded the diborylamine in only 85-95% yields (Table 5.A.4., entries **5e-5g**).

Finally, in the end, the catalytic performance of the aluminum-dihydride (**1**) complex for double hydroboration of 2,6-dimethyl phenyl isocyanide was compared with the reported magnesium catalyst [15a] (Scheme 5.A.1.).



Scheme 5.A.1. Catalytic activity comparison of reported magnesium complex with aluminum hydride (**1**) for double-hydroboration of 2,6-dimethyl phenyl isocyanide with pinacolborane.[a]

[a]The turnover number was examined by the number of moles of desired bis(boryl)amine ester (**5a**) formed divided by the number of moles of aluminum-hydride (**1**) consumed. Turnover frequency was analyzed by the Turnover number divided by the time (h) of the catalytic reaction.

The reaction was performed at 80 °C with less time of reaction and low catalyst quantity, affording the high turnover no. (20) and turnover frequency (1.6 h^{-1}) for the dihydroboration of 2,6-dimethyl phenyl isocyanide to 1,2-bis(boryl)amine **5a** in comparison of β-diketiminate magnesium butyl catalyst (TON = 11 and TOF = 0.2 h^{-1}).[15a]

5.A.2.3. *Insitu* Hydroboration of 2,6-Dimethyl isocyanide

The catalytic activity for B-H addition isocyanide was examined by *insitu* reaction of pinacolborane with 2.0 equiv. of ^{Xyl}NC (**4a**) catalyzed by 5 mol% of aluminum-hydride (**1**) at 80 °C. Reaction progress over 1440 min exhibits the formation of bisborylamine (**4b**), {Figure 5.A.1. a}.

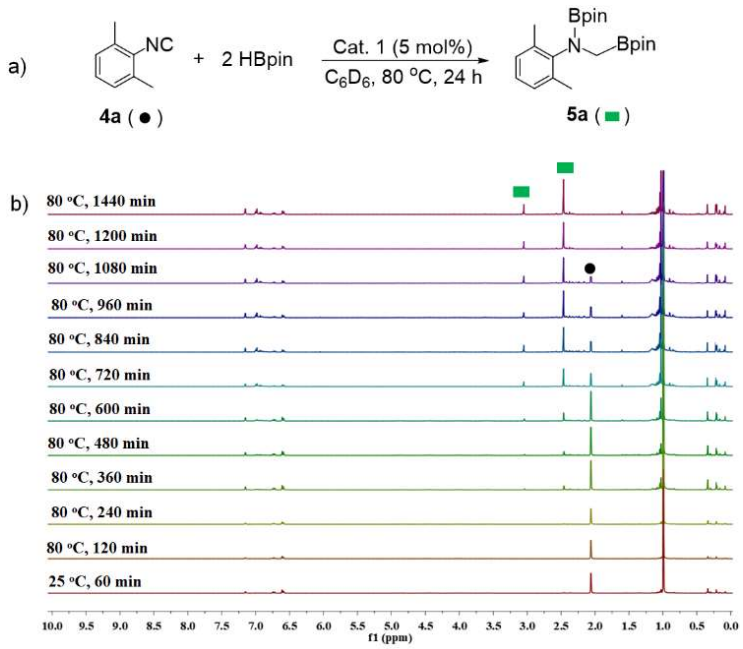


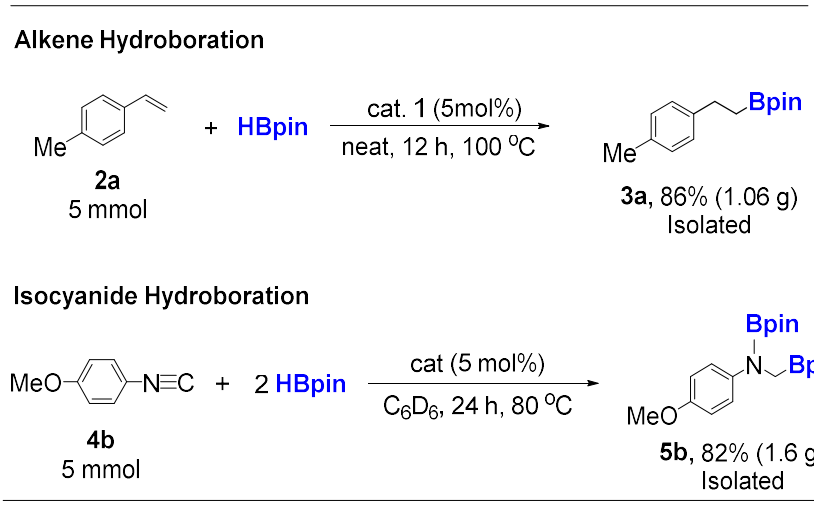
Figure 5.A.1. a) *Insitu* hydroboration of 2,6-dimethyl phenyl isocyanide (**4a**); b) Stacked ^{1}H NMR spectra (400 MHz, C_6D_6) for the hydroboration of 1.0 equiv. of 2,6-dimethyl phenyl isocyanide (**4a**) (0.3 mmol) with 2.0 equiv. of pinacolborane (0.6 mmol) using 5 mol% ^{Diethyl}LAlH$_2$ (**1**) complex as a catalyst. Spectra recorded at different temperatures and time intervals between T = 25 to 80 °C and t = 60 min to 1440 min, respectively; ● = (2,6-Me_2-C_6H_3)-NC (**4a**); ■ = (2,6-Me_2-C_6H_3)-NBpinCH$_2$*Bpin* (**5a**).

The reaction began at 360 min, where the formation of hydroborated product **5a** was evident by the NBpinCH$_2$*Bpin* proton signal at δ 3.05 ppm (singlet, C_6D_6). Finally, the disappearance of the starting methyl protons at δ 2.06 ppm and exclusive formation of borylamine **5a** was noticed at 1440 min, indicating the complete reduction of (2,6-Me_2-C_6H_3)-NC (**4a**) to corresponding reduced product **5a** with no other side product.

5.A.2.4. Scale-up Reactions

To explore the constructive application of the present methodology, I performed two large-scale B-H addition in aryl alkene and isocyanide (Scheme 5.A.2.).[7g, 7j] As demonstrated in Scheme 5.A.2., a 5.0 mmol scale anti-Markovnikov reduction of 4-methyl styrene under the standard condition with 86% isolation of pure linear boronate ester **3a**.

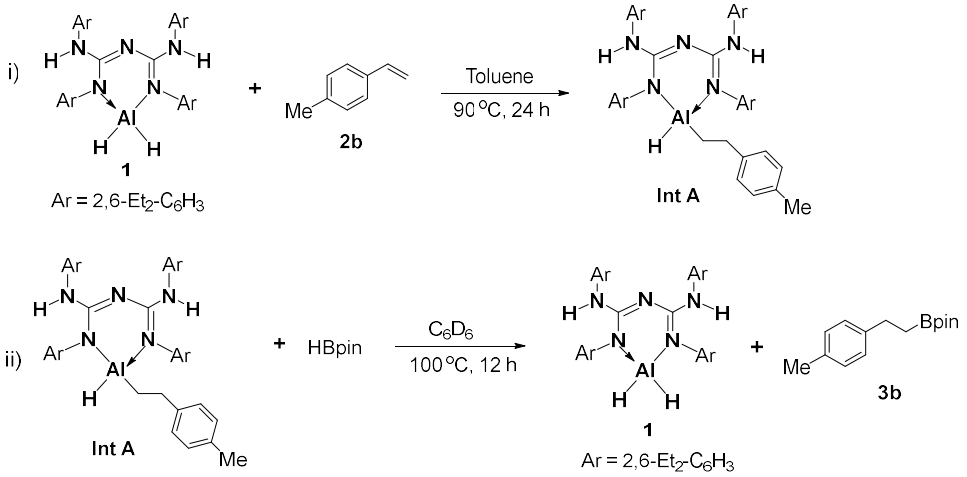
On a similar scale (5.0 mmol), the reduction was successful in the double reduction of 4-methoxyphenyl isocyanide with two equiv. HBpin yielded into corresponding amine boryl ester **5b** in 82% isoalted yield.



Scheme 5.A.2. Large-scale hydroboration of alkene and isocyanide catalyzed by **1**.

5.A.2.5. Control Reactions for Hydroboration of 4-Methoxystyrene

Two stoichiometric reactions have been studied to analyze aluminum-hydride **1** catalyzed alkene reduction via hydroboration (Scheme 5.A.3.).

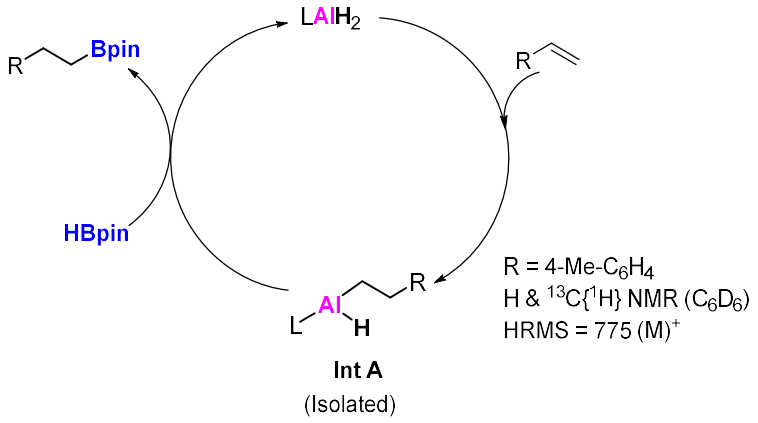


Scheme 5.A.3. Control experiments for hydroboration of *p*-methylstyrene.

In the first set of control reactions, 42 µl of 4-methyl styrene (0.32 mmol) was reacted with catalyst **1** (0.250 g, 0.32 mmol) in a 25 mL Schlenk tube using 10 mL of dry toluene at 90 °C for 24 h. Both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra confirmed the formation of newly synthesized aluminum-alkyl complex, [**IntA**] LAl(H)CH_2CH_2Ph(*p*-Me) {colorless oil}. The ^{1}H NMR spectra displayed resonance signals (δ) at 0.97 and 2.48 ppm corresponding to methylene (CH_2) and methyl (*p*-CH_3) protons of **Int A**. The $^{13}C\{^{1}H\}$ (101 MHz, 298 K) NMR displayed two characteristic signals (δ) at the upfield region of 19.4 and 40.0 ppm corresponding to the LAl(H)CH_2CH_2Ph(*p*-*Me*) complex [**Int A**]. Due to high quadrupolar moment, the Al-H signal is not found in ^{1}H NMR. The isolated intermediate is also characterized by mass spectroscopy. In the second reaction, the **Int A** is mixed with pinacolborane in 0.5 mL of C_6D_6 and warmed at 100 °C for 12 h, which results in the regeneration of catalyst **1** and anti-Markovnikov linear boronate ester **3b**, confirmed by NMR (^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B) spectroscopy.

5.A.2.6. Catalytic Cycle of Aluminum (1) Catalyzed Reduction of Alkenes

Based on the above control reactions and the published report on aluminum-alkyl catalyzed B-H addition across the double bond of olefins by Panda's research group,[7f] I propose the probable catalytic cycle for reduction of alkenes using catalyst **1** displayed in Scheme 5.A.4.

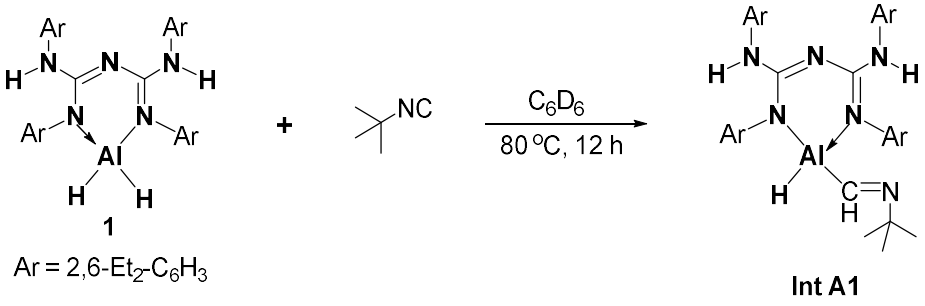


Scheme 5.A.4. Proposed mechanism for anti-Markovnikov hydroboration of alkenes.

At the initial stage of the catalytic cycle, the insertion of active Al-H across the double bond of alkene happens, resulting in forming the aluminum-alkyl complex, Intermediate A. In the second step of the catalytic cycle, the intermediate A immediately reacts with pinacolborane, resulting in linear boronate ester products (anti-Markovnikov) and the rebirth of catalyst **1** for participating in the catalytic cycle.

5.A.2.7. Control Reaction for Al-H (1) Insertion in tert-Butyl isocyanide

One stoichiometric reaction has been done to understand the reduction mechanism for aluminum hydride **1** catalyzed double hydroboration of isocyanides. Thus, when aluminum dihydride **1** (0.250 g, 0.32 mmol) was mixed with tertbutyl isocyanide (36 μL, 0.32 mmol) in 10 mL of toluene followed by heating in an oil bath (80 ºC) for 12 h using 25 mL Schlenk tube, afforded the CBG aluminum-formimidoyl complex (**Int A1**). The isolated corresponding metal formimidoyl complex (LAlH(CH)=N(CMe_3)) (colorless oil) was characterized by NMR and mass spectroscopic methods (Scheme 5.A.5.). The ^{1}H NMR spectra displayed a characteristic methylene proton signal of (LAlH(C*H*)=N(CMe_3)) at (δ) 8.13 ppm. In ^{13}C {^{1}H} NMR spectroscopy, the corresponding carbon signal of formimidoyl complex (LAlH(*C*H)=N(CMe_3)) at the region of (δ) 165.2 ppm. Furthermore, **Int A1** was characterized by HRMS.

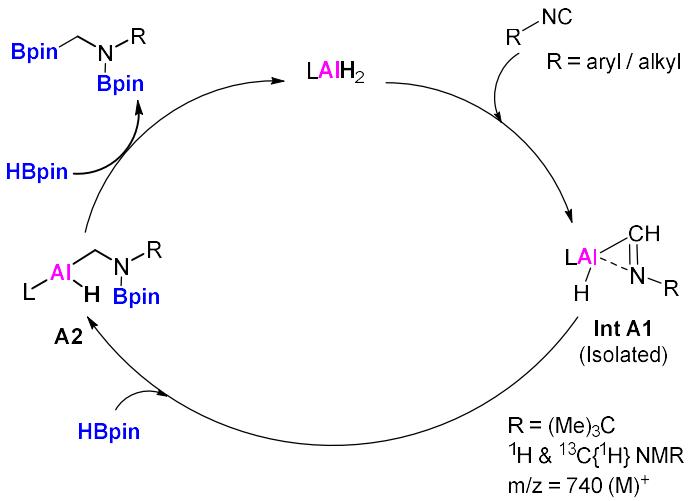


Scheme 5.A.5. Control experiment for hydroboration of ^{tert}butyl isocyanide.

5.A.2.8. Mechanism of Aluminum (1) Catalyzed Double Reduction of Isonitriles

A well-established insertion/σ-bond double decomposition type mechanism is previously reported by Hill[15a] for the dihydroboration of isocyanides. Following the reported mechanism and the above stoichiometric reaction, the catalytic cycle was demonstrated for aluminum (**1**) based on double hydroboration of organic isocyanides, as shown in Scheme 5.A.6. Initially, aluminum-dihydride **1** reacts with isocyanide to generate aluminum formimidoyl complex (LAlH(CH)=N(CMe_3)) **Int A1**. In the second step, the corresponding imine complex (**Int A1**) reacts with one pinacolborane molecule, leading to the generation of five-membered species.

The five-membered aluminum complex is highly unstable; therefore, it immediately rearranges into aluminum amine boronate ester (**Int A2**). Finally, the amine boronate ester (**Int A2**) reacts with the second molecule of pinacolborane to yield the diboryl amine ester (RNBpinCH_2Bpin) product via σ-bond metathesis and regenerates the aluminum catalyst **1**.



Scheme 5.A.6. Proposed mechanism for dihydroboration of isocyanides.

5.A.3. Conclusion

Here I summarized the application of CBG stabilized aluminum-dihydride complex (**1**) for anti-Markovnikov reduction of alkenes, including terminal, internal, 1,1-disubstituted, and α-substituents with pinacolborane under neat conditions. The reaction methodology is highly

regioselective, as confirmed by ^{1}H NMR spectra where no Markovnikov or dehydrogenative borylation products were observed. Therefore, all corresponding air-stable linear boronate esters (RCH_2CH_2Bpin, R = aryl/alkyl) were isolated in good yields. Moreover, complex **1** was also used for double hydroboration of highly challenging isocyanides (R-N≡C) into diboryl amine esters in good yields. In main-group organometallic catalysis, this is the first report of molecular aluminum-based double-bond reduction of isonitriles with HBpin. Besides, gram-scale reduction of alkene and isonitrile have been studied to display the practical benefit of the present methodology. The intermediates in catalytic cycles were isolated in good yield and well-characterized (NMR, HRMS). Further aluminum-mediated catalytic application for challenging organic reactions is in progress.

5.A.4. References

1. Selected examples: (a) Sandford, C.; Aggarwal, V. K. *Chem. Commun.* **2017**, *53*, 5481 – 5494; (b) Leonori, D.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2015**, *54*, 1082 – 1096; (c) *Synthesis and application of organoboron compounds*, ed. Fernandez E.; and Whiting, A.; Springer, Heidelberg, **2015**; B. Carboni, *Angew. Chem. Int. Ed.* **2015**, *54*, 15010 – 15011; (d) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147 – 168; (e) Matteson, D. S. *Stereodirected synthesis with organoboranes*, Springer Science & Business Media, **2012**; Burgess, K. *Synthesis*, **1996**, (4), 551 – 552.
2. Application of boron reagents: (a) Prates, J. L. B.; Pavan, A. R.; dos Santos, J. L. *Curr. Org. Chem.* **2021**, *25*, 1853 – 1867; (b) Buskes, M. J.; Blanco, M. -J. *Molecules* **2020**, *25*, 3493; (c) Boström, J.; Brown, D. G.; Young, R. J.; Keserü, G. M. *Nat. Rev. Drug Discov.* **2018**, *17*, 709 – 727; (d) DeFrancesco, H.; Dudley, J.; Coca, A. *Boron chemistry: overview*, *ACS Symp. Ser.* **2016**, *1236*, 1 – 25; (e) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412 – 443; (f) Magano, J.; Dunetz, J. R. *Chem. Rev.* **2011**, *111*, 2177 – 2250; (g) Tobisu, M.; Chatani, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 3565 – 3568; (h) Hall, D. G. *Structure, Properties, Preparation of Boronic Acid*

Derivatives. Overview of their Reactions and Applications, Wiley-VCH, Weinheim, **2005**; (i) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*, Academic Press, New York, **1988**.

3. Synthetic routes for preparing boronic esters: (a) Volochnyuk, D. M.; Gorlova, A. O.; Grygorenko, O.O. *Chem. Eur. J.* **2021**, *27*, 15277 – 15326; (b) Zhang, G.; Wu, J.; Li, S.; Cass, S.; Zheng, S. *Org. Lett.* **2018**, *20*, 7893 – 7897; (c) Guo, J.; Cheng, B.; Shen, X.; Lu, Z. *J. Am. Chem. Soc.* **2017**, *139*, 15316 – 15319; (d) Pintaric, C.; Olivero, S.; Gimbert, Y.; Chavant, P. Y.; Duñach, E. *J. Am. Chem. Soc.* **2010**, *132*, 11825 – 11827; (e) Brown, H. C.; Kramer, G. W.; Levy A. B.; Midland, M. M. *Organic Syntheses via Boranes*, Wiley, New York, **1975**.
4. Selected examples of metal-catalyzed borylation of C-H bond, see (a) Ghosh, P.; Schoch, R.; Bauer, M.; von Wangelin, A. J. *Angew. Chem. Int. Ed.* **2022**, DOI: doi.org/10.1002/anie.202110821; (b) Zhang, M.; Wu, H.; Yang, J.; Huang, G. *ACS Catal.* **2021**, *11*, 4833 – 4847; (c) Haldar, C.; Hoque, M. E.; Chaturvedi, J.; Hassan, M. M. M.; Chattopadhyay, B. *Chem. Commun.* **2021**, *57*, 13059 – 13074; (d) Hoque, M. E.; Hassan, M. M. M.; Chattopadhyay, B. *J. Am. Chem. Soc.* **2021**, *143*, 5022 – 5037; (e) Hung, M.-U.; Press, L. P.; Bhuvanesh, N.; Ozerov, O. V. *Organometallics* **2021**, *40*, 1004 – 1013; (f) Larsen, M. A.; Cho, S. H.; Hartwig, J. *J. Am. Chem. Soc.* **2016**, *138*, 762 – 765.
5. Selected review articles and book chapter for metal-based hydroboration reactions; (a) Magre, M.; Szewczyk, M.; Rueping, M. *Chem. Rev.* **2022**, *122*, 8261 – 8312; (b) Buono, F.; Nguyen, T.; Qu, B.; Wu, H.; Haddad, N. *Org. Process Res. Dev.* **2021**, *25*, 1471 – 1495; (c) Ankur, R. Kannan; Chambenahalli, R.; Banerjee, S.; Yang, Y.; Maron, L.; Venugopal, A. *Eur. J. Inorg. Chem.* **2021**, 4632 – 4638; (d) Banerjee, I.; Panda, T. K. *Appl. Organomet. Chem.* **2021**, *35*, e6333; (e) Ghosh, P.; Wangelin, A. J. V. *Angew. Chem. Int. Ed.* **2021**, *60*, 16035 – 16043; (f) Roy, M. M. D.; Omaña, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.* **2021**, *121*, 12784 – 12965; (g) Bose, S. K.; Mao, Kuehn, L. L.; Radius, U.; Nekvinda, J.; Santos, W. L.; Westcott, S. A.; Steel, P. G.; Marder, T. B. *Chem. Rev.* **2021**, *121*, 13238 – 13341; (h) Das, K. K.; Paul, S.; Panda, S. *Org. Biomol. Chem.* **2020**, *18*, 8939 – 8974; (i) Liu, H.; Eisen, M. S. *Synthesis* **2020**, *52*, 629 – 644; (j) Bage, A. D.; Hunt, T. A.; Thomas, S. P. *Org. Lett.* **2020**, *22*, 4107 – 4112; (k) Sadow A. D. (**2020**),

201 – 224. *Alkali and Alkaline Earth Element-Catalyzed Hydroboration Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA; (l) Bage, A. D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. *ACS Catal.* **2020**, *10*, 13479 – 13486; (m) Kuciński, K.; Hreczycho, G. *Green Chem.* **2020**, *22*, 5210 – 5224; (n) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307 – 3336; (o) Tamang, S. R.; Findlater, M. *Molecules* **2019**, *24*, 3194; (p) Obligacion, J. V.; Chirik, P. J. *Nat. Rev. Chem.* **2018**, *2*, 15 – 34; (q) Collins, B. S. L.; Wilson, C. M.; Myers, E. L.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2017**, *56*, 11700 – 11733; (r) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, *5*, 3238 – 3259; (s) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48*, 1995 – 2003; (t) Maeda, C.; Miyazaki, Y.; Ema, T. *Catal. Sci. Technol.* **2014**, *4*, 1482 – 1497; (u) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957 – 5026; (v) Saptal, V. B.; Wang, R.; Park, S. *RSC Adv.* **2020**, *10*, 43539 – 43565.

6. Selected transition metal-catalyzed alkene hydroboration: (a) Su, W.; Qiao, R. –X.; Jiang, Y. –Y.; Zhen, X. –L.; Tian, X.; Han, J. –R.; Fan, S. –M.; Cheng, Q.; Liu, S. *ACS Catal.* **2020**, *10*, 11963 – 11970; (b) Huang, J.; Yan, W. C.; Tan, W.; Wu, Jiang, H.; *Chem. Commun* .**2018**, *54*, 1770 – 1773; (c) Tamang, S. R.; Bedi, D.; Shafiei-Haghighi, S.; Smith, C. R.; Crawford, C. Findlater, M. *Org. Lett.* **2018**, *20*, 6695 – 6700; (d) Wang, Z.; He, X.; Zhang, R.; Zhang, G.; Xu, G.; Zhang, Q.; Xiong, T.; Zhang, Q. *Org. Lett.* **2017**, 19, 3067 – 3070; (e) Li, J. –F.; Wei, Z. –Z.; Wang, Y. –Q.; Ye, M. *Green Chem.* **2017**, *19*, 4498 – 4502; (f) Kisan, S.; Krishnakumar, V.; Gunanathan, C. *ACS Catal.* **2017**, *7*, 5950 − 5954.; (g) Pereira, S.; Srebnik, M. *Tetrahedron Lett.* **1996**, *37*, 3283 – 3286; (h) Burgess, K.; Jaspars, M. *Organometallics* **1993**, *12*, 4197 − 4200.

7. Main-group metal-based hydroboration of alkenes: (a) Liu, J.; Wu, C.; Hu, T.; Yang, W.; Xie, Y.; Shi, Y.; Liu, Q.; Shao, Y.; Zhang, F. *J. Org. Chem.* **2022**, *87*, 3442 – 3452; (b) Wang, Z.-C.; Wang, M.; Gao, J.; Shi, S. -L.; Xu, Y. *Org. Chem. Front.* **2019**, *6*, 2949 – 2953; (c) Bisai, M. K.; Yadav, S.; Das, T.; Vanka, K.; Sen, S. S. *Chem. Commun.* **2019**, *55*, 11711 – 11714; (d) Li, F.; Bai, X.; Cai, Y.; Li, H.; Zhang, S. -Q.; Liu, F. -H.; Hong, X.; Xu, Y.; Shi, S. -L. *Org. Process Res. Dev.* **2019**, *23*, 1703 – 1708; (e) Jaladi, A. K.; Shin, W. K.; An, D. K. *RSC Adv.* **2019**, *9*, 26483 – 26486; (f)

Harinath, A.; Banerjee, I.; Bhattacharjee, J.; Panda, T. K. *New J. Chem.* **2019**, *43*, 10531 – 10536; (g) Ma, D. H.; Jaladi, A. K.; Lee, J. H.; Kim, T. S.; Shin, W. K.; Hwang, H.; An, D. K. *ACS Omega* **2019**, *4*, 15893 – 15903; (h) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, *8*, 2001 – 2005; (i) Wu, Y.; Shan, C.; Ying, J.; Su, J.; Zhu, J.; Liu, L. L.; Zhao, Y. *Green Chem.* **2017**, *19*, 4169 – 4175; (j) Rauch, M.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 13264 – 13267; (k) Yin, Q.; Kemper, S.; Klare, H. F. T.; Oestreich, M. *Chem. Eur. J.* **2016**, *22*, 13840 – 13844; (l) Ang, N. W. J.; Buettner, C. S.; Docherty, S.; Bismuto, A.; Carney, J. R.; Docherty, J. H.; Cowley, M. J.; Thomas, S. P. *Synthesis* **2018**, *50*, 803 – 808.

8. Selected aluminum-based catalysts for hydroboration of carbonyls and unsaturated organic motifs: (a) Wang, R.; Park, S. *ChemCatChem* **2021**, *13*, 1898 – 1919; (b) Chia, C. -C.; Teo, Y. -C.; Cham, N.; Ho, S. Y. -F.; Ng, Z. -H.; Toh, H. -M.; Mézailles, N.; So, C. -W. *Inorg. Chem.* **2021**, *60*, 4569 – 4577; (c) Peddarao, T.; Sarkar, N.; Nembenna, S. *Inorg. Chem.* **2020**, *59*, 4693 – 4702; (d) Woodside, A. J.; Smith, M. A.; Herb, T. M.; Manor, B. C.; Carroll, P. J.; Rablen, P. R.; Graves, C. R. *Organometallics* **2019**, *38*, 1017 – 1020; (e) Zhang, G.; Wu, J.; Zeng, H.; Neary, M. C.; Devany, M.; Zheng, S.; Dub, P. A. *ACS Catal.* **2019**, *9*, 874 – 884; (f) Liu, Y.; Ma, X.; Ding, Y.; Yang, Z.; Roesky, H. W. *Organometallics* **2018**, *37*, 3839 – 3845; (g) Liu, Y.; Liu, X.; Liu, Y.; Li, W.; Ding, Y.; Zhong, M.; Ma, X.; Yang, Z. *Inorg. Chim. Acta* **2018**, *471*, 244 – 248; (h) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.* **2018**, *54*, 1233 – 1236; (i) Pollard, V. A.; Fuentes, M. Á.; Kennedy, A. R.; McLellan, R.; Mulvey, R. E. *Angew. Chem. Int. Ed.* **2018**, *57*, 10651 – 10655; (j) Lemmerz, L. E.; McLellan, R.; Judge, N. R.; Kennedy, A. R.; Orr, S. A.; Uzelac, M.; Hevia, E.; Robertson, S. D.; Okuda, J.; Mulvey, R. E. *Chem. Eur. J.* **2018**, *24*, 9940 – 9948; (k) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. *Chem. Eur. J.* **2018**, *24*, 4794 – 4799; (l) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54*, 10225 – 10229; (m) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org Lett.* **2016**, *18*, 4710 – 4713; (n) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1245 – 1250; 9o) Hobson, K.; Carmalt, C.; Bakewell, J. *Inorg. Chem.*

2021, *60*, 10958 – 10969; (p) Sarkar, N.; Bera, S.; Nembenna, S. *J. Org. Chem.* **2020**, *85*, 4999 – 5009; (q) Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Adv. Synth. Catal.* **2019**, *361*, 850 – 857; (r) Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics* **2019**, *38*, 3092 – 3097; (s) Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J.* **2019**, *25*, 11918 – 11923; (t) Liu, W.; Ding, Y.; Jin, D.; Shen, Q.; Yan, B.; Ma, X.; Yang, Z. *Green Chem.* **2019**, *21*, 3812 – 3815.

9. Selected aluminum catalyzed hydrosilylation of carbonyls and unsaturated organic compounds: (a) Sarkar, N.; Sahoo, R. K.; Mukhopadhyay, S.; Nembenna, S. *Eur. J. Inorg. Chem.* **2022**, DOI: https://doi.org/10.1002/ejic.202101030; (b) Bolley, A.; Specklin, D.; Dagorne, S. *Polyhedron* **2021**, *194*, 114956; (c) Kannan, R.; Chambenahalli, R.; Kumar, S.; Krishna, A.; Andrews, A. P.; Jemmis, E. D.; Venugopal, A. *Chem. Commun.* **2019**, *55*, 14629 – 14632; (d) Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics* **2017**, *36*, 4810 – 4815; (e) Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.* **2016**, *6*, 7350 – 7356; (f) Stennett, T. E.; Pahl, J.; Zijlstra, H. S.; Seidel, F. W.; Harder, S. *Organometallics* **2016**, *35*, 207 – 217; (g) Chen, J. Chen, E. Y. –X. *Angew. Chem. Int. Ed.* **2015**, *54*, 6842 – 6846; (h) Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics* **2013**, *32*, 6812 – 6819; (i) Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 7323 – 7326; (j) Koller, J.; Bergman, R. G. *Organometallics* **2012**, *31*, 2530 – 2533; (k) Kato, N.; Tamura, Y.; Kashiwabara, T.; Sanji, T.; Tanaka, M. *Organometallics* **2010**, *29*, 5274 – 5282; (l) Bach, P.; Albright, A.; Laali, K. K. *Eur. J. Org. Chem.* **2009**, 1961 – 1966.

10. Selected examples of metal-catalyzed hydroamination reactions and the corresponding application: (a) H. Karmakar, S. Anga, T. K. Panda, V. Chandrasekhar, *RSC Adv.* **2022**, *12*, 4501 – 4509; (b) P. K. Vardhanapu, V. Bheemireddy, M. Bhunia, G. Vijaykumar, S. K. Mandal, *Organometallics* **2018**, *37*, 2602 – 2608; (c) J. Chen, S. K. Goforth, B. A. McKeown, T. B. Gunnoe, *Dalton Trans.* **2017**, *46*, 2884 – 2891; (d) Y. Wei, S. Wang, S. Zhou, Z. Feng, L. Guo, X. Zhu, X. Mu, F. Yao, *Organometallics* **2015**, *34*, 1882 – 1889; (e) S. T. Barry, *Coord. Chem. Rev.* **2013**, *257*, 3192 – 3201; (f) Z. X. Huaa, X. Fan, S. Qi, *Chin. Sci. Bull.* **2012**, *57*, 3419 – 3422; (g) R. G. S. Berlinck, A. E.

Trindade-Silva, M. F. C. Santos, *Nat. Prod. Rep.* **2012**, *29*, 1382 – 1406; (h) J. Koller, R. G. Bergman, *Chem. Commun.* **2010**, *46*, 4577 – 4579; (i) J. Koller, R. G. Bergman, *Organometallics* **2010**, *29*, 5946 – 5952; (j) J. Koller, R. G. Bergman, *Organometallics* **2010**, *29*, 3350 – 3356; (k) W. -X. Zhang, D. Li, Z. Wang, Z. Xi, *Organometallics* **2009**, *28*, 882 – 887; (l) C. N. Rowley, T. -G. Ong, J. Priem, T. K. Woo, D. S. Richeson, *Inorg. Chem.* **2008**, *47*, 9660 – 9668; (m) M. P. Coles, *Dalton Trans.* **2006**, 985 – 1001.

11. Selected examples of aluminum catalyzed transfer hydrogenation: (a) L. Zheng, X. Yin, A. Mohammadlou, R. P. Sullivan, Y. Guan, R. Staples, W. D. Wulff, *ACS Catal.* **2020**, *10*, 7188 – 7194; (b) R. A. Farrar-Tobar, A. Dell'Acqua, S. Tin, J. G. de Vries, *Green Chem.* **2020**, *22*, 3323 – 3357; (c) P. J. Larson, J. L. Cheney, A. D. French, D. M. Klein, B. J. Wylie, A. F. Cozzolino, *Inorg. Chem.* **2018**, *57*, 6825 – 6832; (d) B. McNerney, B. Whittlesey, D. B. Cordes, C. Krempner, *Chem. Eur. J.* **2014**, *20*, 14959 – 14964.
12. Review articles and book chapters for reactivity and catalysis of molecular aluminum chemistry; (a) C. Ni, X. Ma, Z. Yang, H. W. Roesky, *Eur. J. Inorg. Chem.* **2022**, DOI: https://doi.org/10.1002/ejic.202100929; (b) Amrita Das, Supriya Rej, Tarun K. Panda, *Dalton Trans.* **2022**, *51*, 3027 – 3040; (c) Y. Liu, J. Li, X. Ma, Z. Yang, H. W. Roesky, *Coord. Chem. Rev.* **2018**, *374*, 387 – 415; (d) A. Caise, D. Jones, E. L. Kolychev, J. Hicks, J. M. Goicoechea, S. Aldridge, *Chem. Eur. J.* **2018**, *24*, 13624 – 13635; (e) C. Weetman, S. Inoue, *ChemCatChem* **2018**, *10*, 4213 – 4228; (f) S. Dagorne, R. Wehmschulte, *ChemCatChem* **2018**, *10*, 2509 – 2520; (g) W. Li, X. Ma, M. G. Walawalkar, Z. Yang, H. W. Roesky, *Coord. Chem. Rev.***2017**, *350*, 14 – 29; (h) V. P. Ananikov, *Sustainable Catalysis with Nonendangered Metals*. *Angew. Chem. Int. Ed.* **2016**, *55*, 14904; (i) S. Aldridge, A. J. Downs, *The Group 13 Metals Aluminium, Gallium, Indium, and Thallium: Chemical Patterns and Peculiarities*. *Angew. Chem. Int. Ed.* **2011**, *50* (49), 11569.
13. Selected example: K. Burgess, *Synthesis* **1996**, 551 – 552.
14. Selected review articles on the synthesis and reactivity of isocyanide: (a) P. Patil, M. Ahmadian-Moghaddam, A. Dömling, *Green Chem.* **2020**, *22*, 6902 – 6911; (b) U. Galli, G. C. Tron, B. Purghè,

G. Grosa, S. Aprile, *Chem. Res. Toxicol.* **2020**, *33*, 955 – 966; (c) V. P. Boyarskiy, N. A. Bokach, K. V. Luzyanin, V. Y. Kukushkin, *Chem. Rev.* **2015**, *115*, 2698 – 2779.

15. Main-group metal-catalyzed isonitriles hydroboration: C. Weetman, M. S. Hill, M. F. Mahon, *Chem. Commun.* **2015**, *51*, 14477 – 14480.
16. B. R. Barnett, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Chem. Commun.* **2015**, *51*, 541 – 544.
17. References for the Conjugated Bis-guanidine (CBG) ligand synthesis: (a) R. K. Sahoo, N. Sarkar, S. Nembenna, *Angew. Chem. Int. Ed.* **2021**, *60*, 11991 – 12000; (b) T. Peddarao, A. Baishya, N. Sarkar, R. Acharya, S. Nembenna, *Eur. J. Inorg. Chem.* **2021**, 2034 – 2046.

Chapter 5B

Aluminum-Catalyzed Selective Reduction of Nitriles and Alkynes: A Multifunctional Catalyst

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Abstract

The reaction of LH [L= {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar =2,6-Et_2-C_6H_3] with commercially available alane amine adduct ($H_3Al{\cdot}NMe_2Et$) in toluene resulted in the formation of a conjugated bis-guanidinate (CBG) supported aluminum dihydride complex, *i.e.*, $LAlH_2$ (**1**) in good yield. The new complex has been thoroughly characterized by multinuclear NMR, IR, mass and elemental analyses, including single-crystal structural studies. Further, the aluminum-catalyzed hydroboration of a variety of nitriles and alkynes was demonstrated. Moreover, aluminum-catalyzed hydroboration is expanded to more challenging substrates such as alkene, pyridine, imine, carbodiimide, and isocyanides. More importantly, the aluminum dihydride was used for both intra- and intermolecular chemoselective hydroboration of nitriles and alkynes over other reducible functionalities for the first time.

5.B.1. Introduction

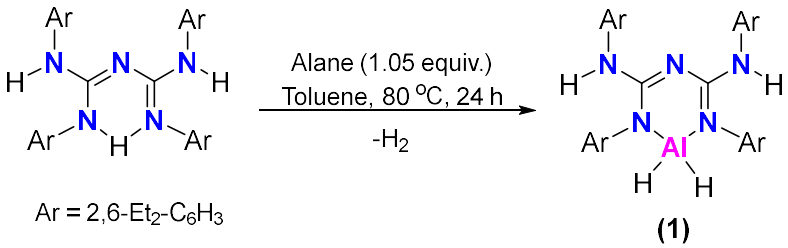
Aluminum is the third most abundant metallic element after oxygen and silicon in the Earth's crust and also cheaper, less toxic when compared to transition or lanthanide elements. The sustainable and environmentally friendly aluminum-based reagents/molecules are ideal for applications in catalysis.[1] Hence, the development of well-defined aluminum-based catalysts is quite attractive.[2] In recent years there has been substantial progress in the development of the main group- or transition metal-catalyzed hydroboration of carbonyl compounds;[3,4] however,

relatively few examples of the main group catalyzed nitrile and alkyne hydroboration have been documented. Nonetheless, aluminum-catalyzed reduction of organic nitriles has been rarely documented. Nonetheless, aluminum-catalyzed reduction of organic nitriles has been rarely documented. In 2016, Hill *et al.* reported the first main-group catalyzed, Nacnac Mg alkyl catalyzed hydroboration of nitriles.[5] Recently, Okuda,[6] Thomas,[4i] and Ma[7] research groups independently reported the main group catalyzed hydroboration of nitriles. During the preparation of this manuscript, Yang,[8] and Roesky[9] groups reported Nacnac supported aluminum dialkyl and dihydride complexes as (pre)catalysts for the hydroboration of nitriles and also, Panda *et al*. [10] reported aluminum alkyl as a pre-catalyst for the hydroboration of nitriles. There have been several reports on the main-group,[4,7,11] transition[12] metal-catalyzed hydroboration of alkynes, while a few reports on aluminum[13] catalyzed hydroboration of alkynes. Moreover, very few reports of aluminum catalyzed hydroboration of alkene,[4i,13a,14] carbodiimide,[9,15]and imine.[4g,16]

The reports mentioned above are having drawbacks such as very limited substrate scope, high catalyst loading, ligand containing elements such as C, H, and N, etc. Therefore, the design of a sustainable catalyst is very desirable because catalysts should be easily accessible, efficient, and tolerance of more functional groups. Moreover, to our knowledge, there have been no reports on aluminum catalyzed hydroboration of pyridine,[17] and isonitrile[18] functionalities. Thus, herein, I report a well-defined aluminum dihydride complex bearing conjugated bis-guanidinate ligand catalyzed selective reduction of a wide range of nitriles and alkynes. Moreover, this protocol further extended to other reducible functionalities such as alkene, carbodiimide, imine, isocyanide, and pyridine. To the best of our knowledge, this is the first report of aluminum-based multifunctional catalysts for the hydroboration of unsaturated organic substrates.

5.B.2. Results and Discussion

Treatment of the free conjugated bis-guanidine (CBG), LH[19] ligand with one equiv. of Alane, $H_3Al{\cdot}NMe_2Et$ in toluene at room temperature and followed by heating at 80 °C cleanly yields the CBG supported aluminum dihydride complex (**1**) in good yield (84%) (Scheme 5.B.1.).



Scheme 5.B.1. Synthesis of conjugated bis-guanidinate (CBG) supported aluminum-dihydride complex (**1**).

The new complex **1** was fully characterized by multinuclear (^1H, $^{13}C\{^1H\}$, and ^{27}Al) NMR, IR, mass, and elemental analyses. In addition, the crystallographic analysis (Figure 5.B.1.) confirmed the solid-state structure of **1**, which is monomeric (Crystallographic data and structure refinement parameters are available in Table S3, ESI)

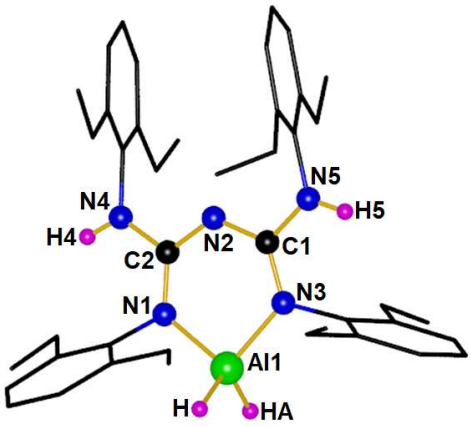


Figure 5.B.1. Molecular structure of catalyst **1**. Selected bond distances (Å) and angles (deg): C1-N2 1.332(4), C1-N5 1.351(4), C1-N3 1.326(4), N3-Al1 1.894(3), N1-Al1 1.879(3), C2-N1 1.336(4), C2-N2 1.342(4), C2-N4 1.355(4), Al1-H 1.411(3), Al1-HA 1.622(3). N2-C1-N3 127.0(3), N2-C1-N5 113.7(3), N3-C1-N5 119.2(3), N1-C2-N2 126.6(3), N2-C2-N4 114.5(3), N1-C2-N4 118.9(3), N3-Al1-N1 94.73(12), N3-Al1-H 112.516(18), N1-Al1-H 113.93(9), N3-Al1-HA 110.88(12), N1-Al1-HA 117.12(12), H-Al1-HA 107.220(21).

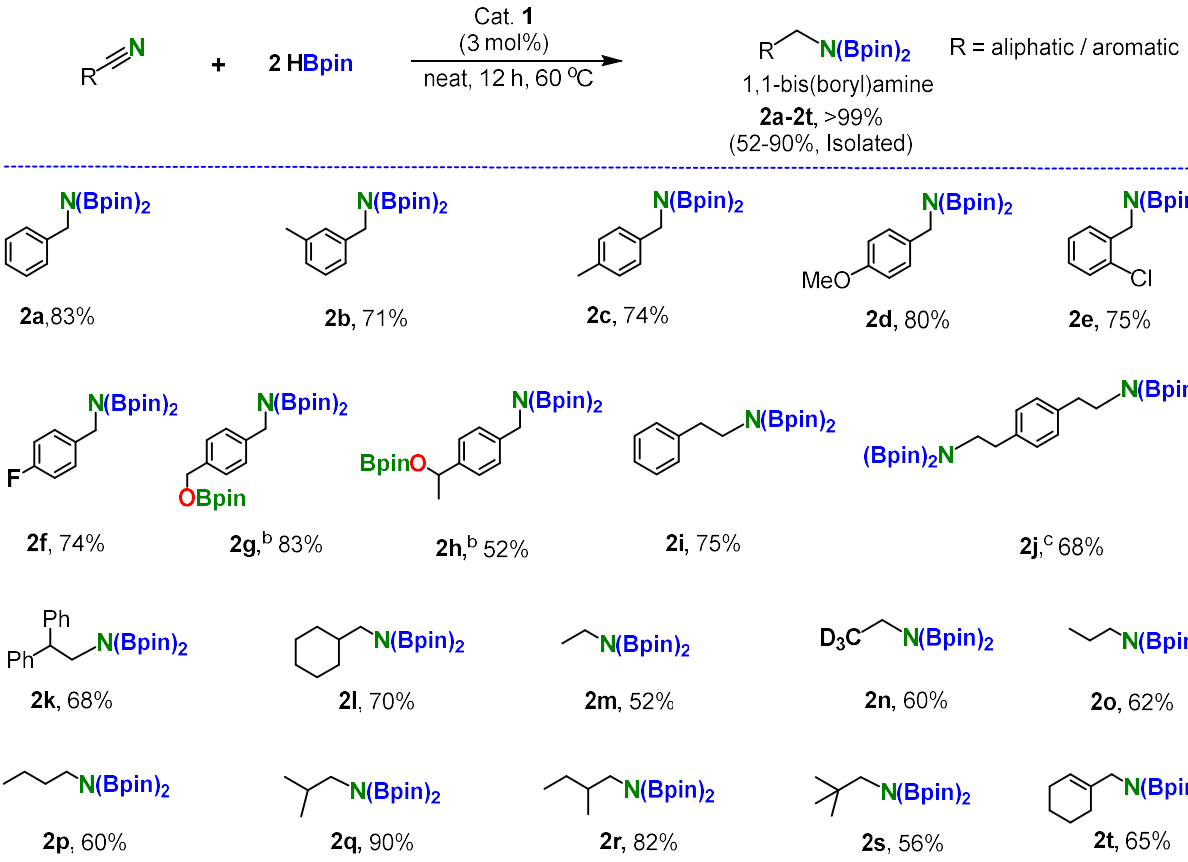
The ^{1}H NMR spectrum reveals a complete disappearance of a free ligand N–*H*–N peak at 12.97 ppm, which indicates the formation of complex **1**. Moreover, a singlet resonance is displayed at 5.14 ppm, which corresponds to two protons of sidearm ArN–*H* moieties. Besides, other expected signals for the CBG ligand were observed. The ^{13}C{^{1}H} NMR spectrum exhibits a characteristic N_3C peak at 158.62 ppm, which is downfield when compared to free ligand (155.0 ppm). The Al–H resonances were not obtained in ^{1}H NMR spectroscopy of compound (**1**) because of quadrupolar broadening on the ^{27}Al center (nuclear spin = 5/2).[20] Nonetheless, the existence of an Al−H bond was confirmed by IR spectroscopy, which exhibits two broad bands at 1813 and 1926 cm^{-1}, referred to as the Al−H stretching frequencies.[4,21]

5.B.2.1. Nitrile Hydroboration

The initial study began by examining the role of aluminum dihydride compound (**1**) in the catalytic hydroboration of benzonitrile with 2 equiv. HBpin (Table S1, ESI). At a loading of 5 mol % of **1** in benzene-d_6 at 60 ºC, benzonitrile was hydroborated to afford 1,1-bis(boryl) amine in 98 % yield within 12 h (Entry 4 of TableS1, ESI). No reaction took place at similar reaction conditions in the absence of catalyst **1**, showing that the aluminum dihydride compound is responsible for this conversion. Further, the same reaction was performed under similar conditions by using lower catalyst loadings (1 mol % and 3 mol %). The formation of 1,1-bis(boryl) amine was found in 50 % and 97 % yields, respectively. However, the same reaction was accomplished under neat conditions by using a 3 mol % catalyst; in this case, I noticed the formation of the desired product in quantitative yield (Entry 7 of Table S1, ESI).

Therefore, I investigated the reduction of a wide range of organic nitriles (**2a-2t**) with HBpin by using 3 mol % of catalyst **1** under neat conditions (Table 5.B.1.).

Table 5.B.1. Hydroboration of nitriles catalyzed by $LAlH_2$ complex (**1**).[a]



[a]Reaction conditions: nitrile (1.0 mmol, 1.0 equiv.), pinacolborane (2.0 mmol, 2.0 equiv.), catalyst (**1**) (3 mol%), 12 h at 60 °C under N_2. Reported numbers are the isolated yields. [b]For **2g** and **2h**, pinacolborane (3.0 equiv.) used. [c]For **2j**, pinacolborane (4.0 equiv.).

Aryl nitriles with electron-donating or electron-withdrawing groups undergo reduction efficiently, yielding the corresponding 1,1-bis(boryl) amine products. Functional groups such as OMe, Cl, and F were all found to be tolerant under reaction conditions. Primary, secondary, and tertiary alkyl nitriles were efficiently reduced to corresponding 1,1-bis(boryl) amines in 52-90 % yields (**2m-2s**). More importantly, the intramolecular chemoselectivity hydroboration reaction was explored by choosing 1-cyanocyclohexene (or cyclohexene-1-carbonitrile) substrates, as an example — the reaction of 1-cyanocyclohexene with two equiv. HBpin and catalyst **1** (3 mol %) in neat condition at 60 °C was executed. The ^{1}H NMR analysis of this reaction mixture indicated the chemoselective hydroboration of nitrile with the quantitative conversion over alkene (**2t**).

Unsurprisingly, substrates bearing reducible carbonyl functional group (**2g** and **2h**) were not tolerated under the conditions.

All 1,1-bis(boryl)amine products were characterized by multinuclear (^{1}H, ^{13}C, and ^{11}B) NMR spectroscopy. HRMS confirmed the purity of new 1,1-bis(aryl) amines. Further, compound **2i** was confirmed by single X-ray crystal structural analysis (Figure 5.B.2.). All Crystallographic data and structure refinement parameters of compound **2i** are available in Table S4 of supporting information.

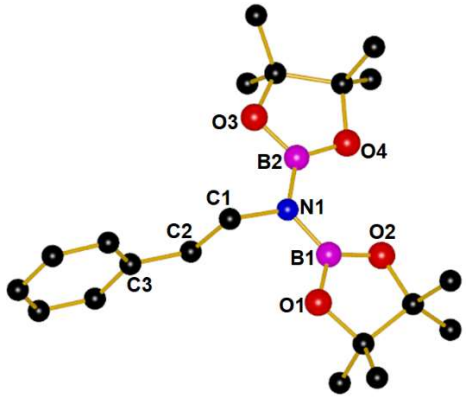
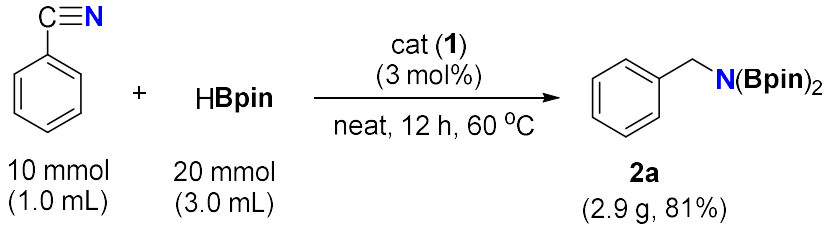


Figure 5.B.2. Molecular structure of compound **2i**. Selected bond distances (Å) and angles (deg): N1–B1 1.4238(16), N1–B2 1.4285(16), B1–O1 1.3753(15), B1–O2 1.3688(16), B2–O3 1.3679(16), B2–O4 1.3612(17), N1–C1 1.4818(16), C1–C2 1.515(2), C2–C3 1.5150(19). N1–B1–O1 121.88(11), N1–B1–O2 124.85(11), N1–B2–O3 122.07(12), N1–B2–O4 124.58(12), N1–C1–C2 111.32(11), C1–C2–C3 116.63(11).

Notably, this protocol also works for large-scale synthesis as established by a 10 mmol scale reaction of benzonitrile under optimized conditions producing corresponding 1,1-bis(boryl)amine (**2a**) in 81% isolated yield (Scheme 5.B.2.).



Scheme 5.B.2. Large-scale hydroboration of benzonitrile with HBpin.

5.B.2.2. Alkyne Hydroboration

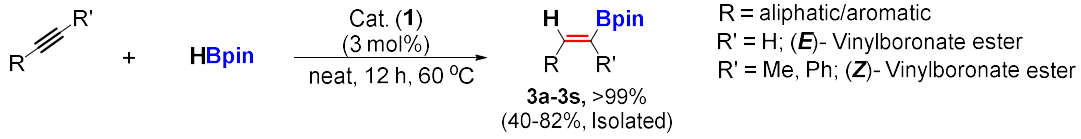
Next, I decided to explore the catalytic activity of compound **1** for the hydroboration of alkynes. I chose phenylacetylene as a substrate for the hydroboration with 1 equiv. HBpin. At a loading of 5 mol % catalyst **1** in benzene-d6 at 60 ^{o}C, phenylacetylene hydroborated to afford the cis-hydroborated product, (***E***)-vinyl boronate ester in quantitative yield within 12 h (Table S2, ESI). No conversion took place in the absence of catalyst **1**. Further, when the same reaction was performed at lower catalyst loadings, lesser conversion was observed (1 mol %, 70% yield, and 3 mol %, 95 % yield). However, a quantitative conversion was displayed when the same reaction operated under neat conditions using a 3 mol % catalyst.

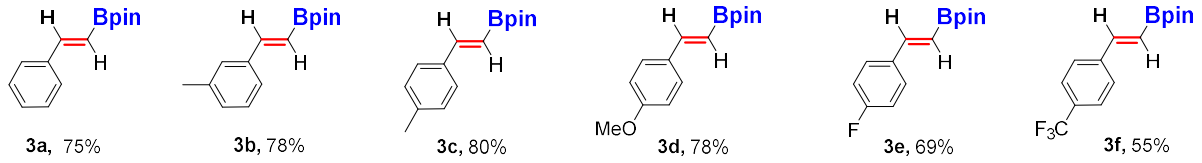
With the optimized reactions conditions in hand, I investigated the scope of the aluminum-catalyzed hydroboration of terminal alkynes (Table 5.B.2.). I began inspecting different phenylacetylene derivatives and were satisfied to see that substituents with electron-donating or electron-withdrawing groups on the aromatic ring did not influence the catalytic activity (**3a-3e,** 69-80 %**)**. However, a slightly lower yield was obtained for the phenylacetylene derivative **3f,** containing CF_3 at the para position of the aromatic ring.

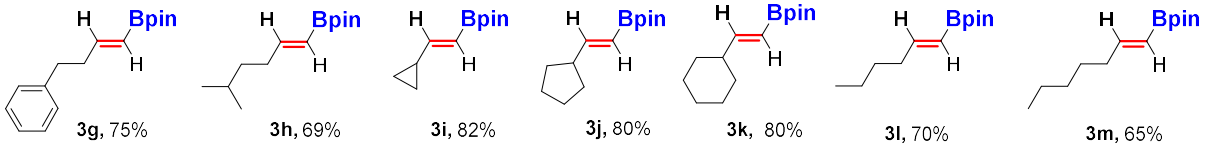
Subsequently, I considered the scope of the transformation by employing terminal alkynes bearing alkyl substituents (**3g-3o**), which performed similarly to the corresponding phenylacetylene derivatives (60-82%).

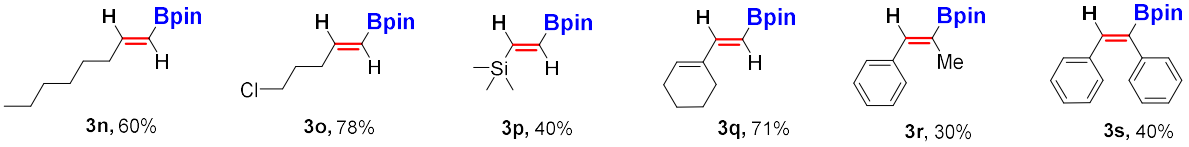
Hydroboration of trimethylsilylacetylene took place, providing **3p** in 40 % yield. More importantly, another interesting intramolecular chemoselective hydroboration of terminal alkyne by choosing 1-ethynylcyclohexene, as an example was carried out. Hydroboration took place smoothly, providing **3q** in 71 % yield, in which C=C tolerated. To further broaden the substrate scope, I decided to test the aluminum catalyzed hydroboration of internal alkyne.

Table 5.B.2. Hydroboration of alkynes catalyzed by $LAlH_2$ complex (**1**).[a]







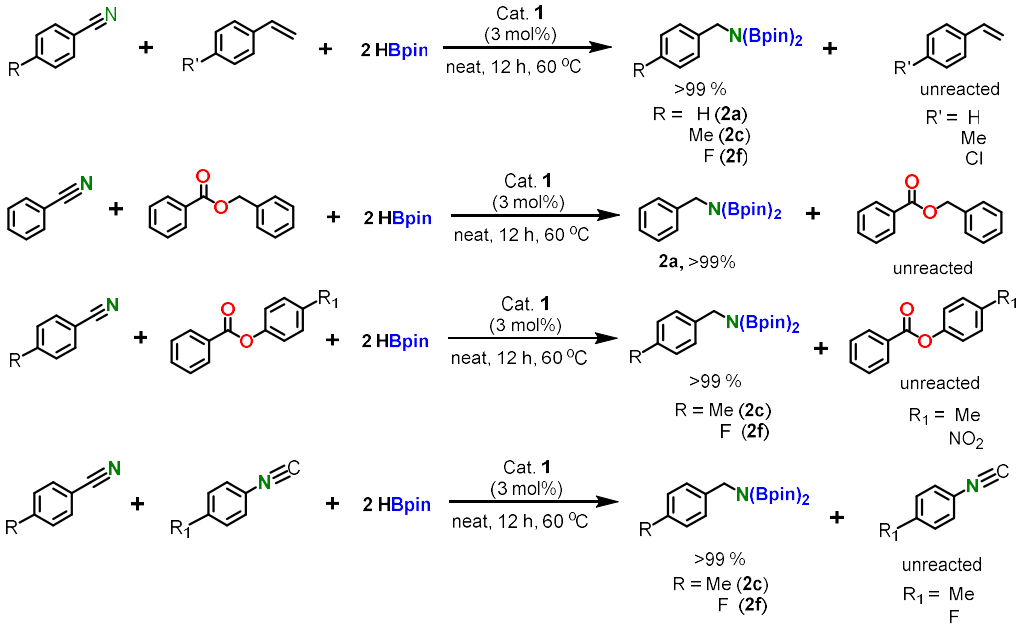


[a]Reaction conditions: alkyne (1.0 mmol, 1.0 equiv.), pinacolborane (1.0 mmol, 1.0 equiv.), catalyst (**1**) (3 mol%), 12 h at 60 °C under N_2. Products are isolated after column chromatography. The ***E*** selectivity was determined by NMR spectroscopy except for **3r** and **3s**, which show ***Z*** selectivity.

Hydroboration of unsymmetrical and symmetrical internal alkynes, like 1-phenyl-1-propyne and diphenylacetylene, took place, providing (***Z***)-vinyl boronate esters in 30% and 40 % yields, respectively. It is interesting to note that CBG supported aluminum dihydride catalyzes the challenging substrates such as symmetrical and unsymmetrical internal alkynes, in contrast to previously reported Nacnac AlH_2, which is less effective in reducing the internal alkynes.[13c]

5.B.2.3. Nitrile Intermolecular Chemoselectivity

More importantly, the application of aluminum-dihydride **1** catalyzed intermolecular chemoselective hydroboration of nitriles over alkenes containing both electron-donating and electron-withdrawing substituents, esters, and isonitriles was explored (Scheme 5.B.3.).



Scheme 5.B.3. Nitrile intermolecular chemoselective reactions catalyzed by **1**.

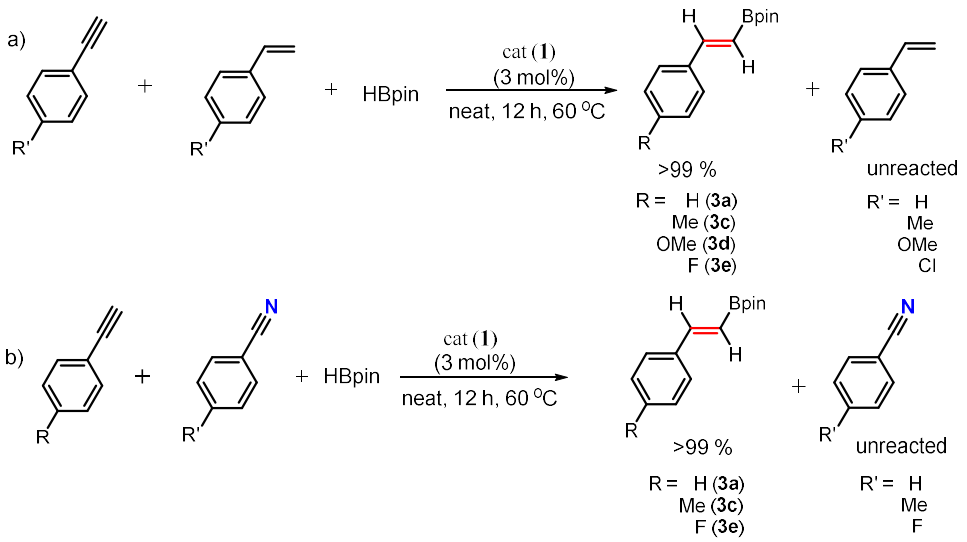
One equivalent of benzonitrile, 1 equivalent of styrene, and 2 equivalent of HBpin were mixed with catalyst **1** (3 mol %) under solvent-free conditions at 60 ºC, which produced the diborylated product 1,1-bis(boryl)amine in the quantitative conversion of benzonitrile, in preference to the alkene (Scheme 5.B.3.).

Similarly, either the reaction of aryl nitrile containing an electron-donating group, 4-methyl benzonitrile, or electron-withdrawing group, 4-flurobenzonitrile gives corresponding 1,1-bis(boryl) amine in preference to the alkene. Moreover, the reaction of 1 equiv. benzonitrile, 1 equiv. of benzyl benzoate and 2 equiv. of HBpin were reacted together with catalyst **1** (3 mol %) under neat conditions at 60 ºC, which yielded the diborylated product 1,1-bis(boryl) amine in the quantitative conversion of benzonitrile over benzyl benzoate. Similarly, 4-methyl benzonitrile and 4-Fluro benzonitrile gave the corresponding 1,1-bis(boryl) amines in preference to the esters (Scheme 5.B.3.). Further, at similar reaction conditions, 4-methyl benzonitrile and 4-fluoro benzonitrile yielded the corresponding 1,1-bis(boryl) amines over aryl isonitriles.

5.B.2.4. Alkyne Intermolecular Chemoselectivity

Equimolar amounts of phenylacetylene, styrene, and HBpin were reacted together with catalyst **1** (3 mol %) under neat conditions at 60 °C, which produced the (*E)* vinyl boronate ester in preference to the alkene. Similarly, 4-methyl phenylacetylene, 4-methoxy phenylacetylene, and 4-fluorophenylacetylene were hydroborated at the same reaction conditions over alkenes (Scheme 5.B.4.).

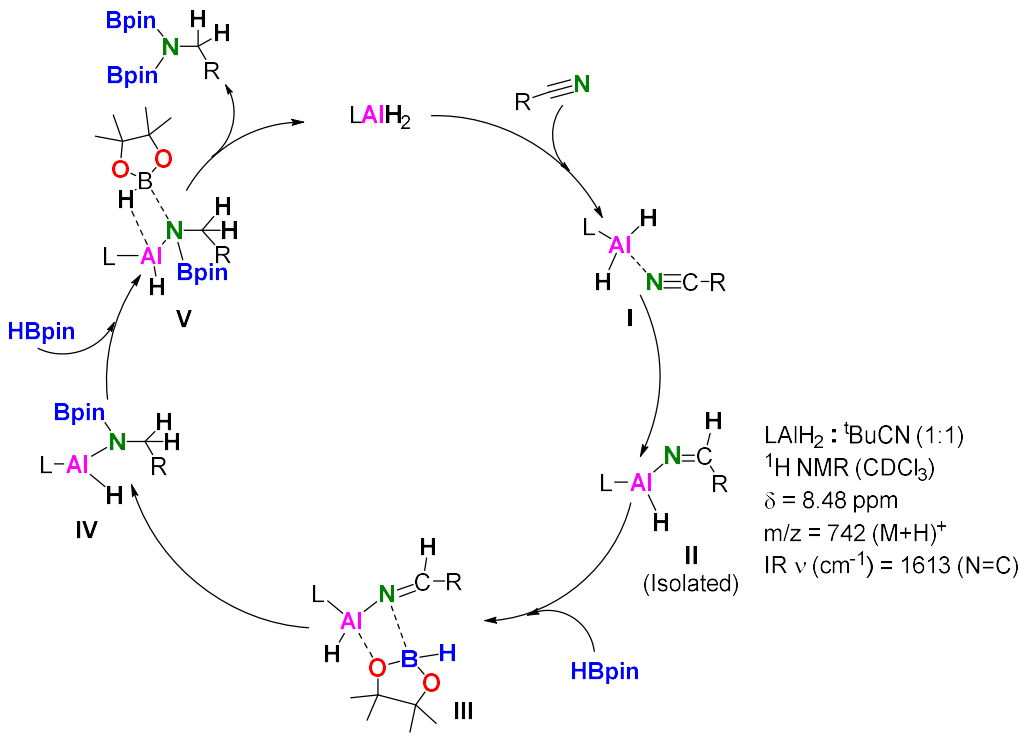
Equimolar amounts of phenylacetylene, benzonitrile, and HBpin were reacted with catalyst **1** under neat conditions at 60 °C, which yielded the (*E*)-vinyl boronate ester over nitrile functionality. Similarly, equimolar amounts of aryl alkynes and aryl nitrile with either electron-donating or electron-withdrawing groups, and HBpin were reacted together, independently, in which exclusively alkyne was hydroborated over nitrile.



Scheme 5.B.4. Alkyne intermolecular chemoselective reaction catalyzed by **1**.

5.B.2.5. Mechanism of $LAlH_2$(1) Catalyzed Hydroboration of Nitrile

Initially, catalyst **1** reacts with the nitrile to form transition species (I), followed by σ bond metathesis to yield the corresponding imine (II) (Scheme 5.B.5.).



Scheme 5.B.5. Proposed mechanism for hydroboration of nitrile.

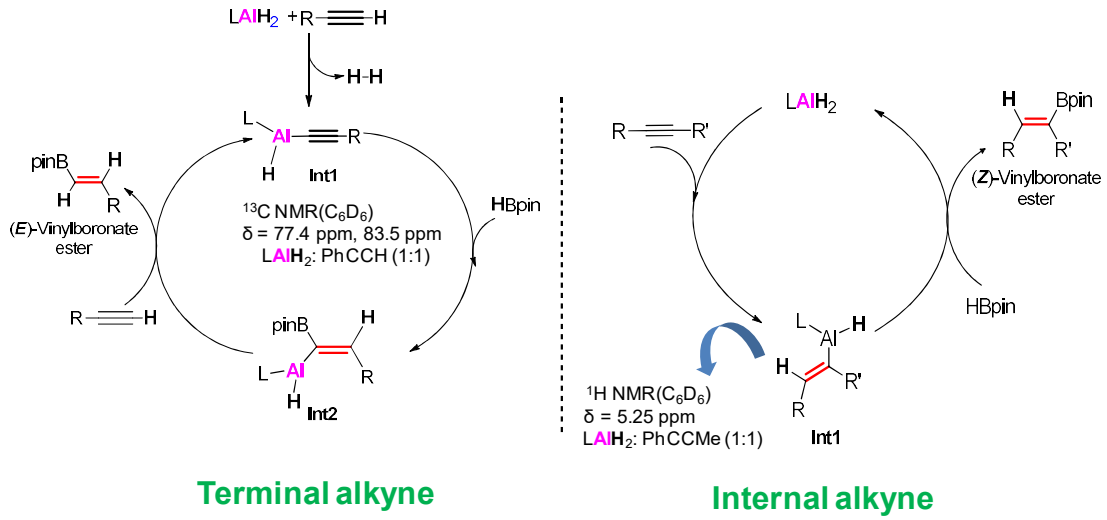
This imine complex further reacts with HBpin to produce the four-membered species (III), which rearranges to give boryl amine (IV). Further, it reacts with another molecule of HBpin to give intermediate species (V), which undergoes sigma bond metathesis to yield the product 1,1-bis(boryl) amine and regeneration of the ligated aluminum dihydride catalyst (Scheme 5.B.5.). Moreover, the aluminum imine species (II) was confirmed by ^{1}H and ^{13}C{^{1}H} NMR analyses by the stoichiometric reaction between catalyst **1** and trimethylacetonitrile in $CDCl_3$ at 70 °C. The ^{1}H NMR spectrum exhibits a characteristic imine, Al-N=C*H*-R peak at 8.48 ppm, while the Al-H signal was silent. The ^{13}C{^{1}H} NMR spectrum displays a typical Al-N=*C*-HR peak at the far downfield region at 160.4 ppm.

5.B.2.6. Mechanism of $LAlH_2$ (1) Catalyzed Hydroboration of Alkyne

Considering the previously established mechanisms of aluminum-catalyzed hydroboration of terminal alkynes [13a,c] I propose that the hydroboration reaction proceeds according to the

mechanism shown in Scheme 5.B.6. First, the deprotonation of alkyne with aluminum-dihydride **1** leads to the formation of aluminum acetylide (Int 1). Further, a stoichiometric reaction of catalyst **1** and phenylacetylene in C_6D_6 at 70 ºC was carried out to confirm the formation of Int 1. ^1H and $^{13}C\{^1H\}$ NMR analyses confirmed the formation of aluminum acetylide, LAl(H)CCPh. The ^1H NMR shows sidearm ArN*H* resonance at 4.90 ppm in the upfield region compared to the $LAlH_2$ (ArN*H* 5.13 ppm). The ^{13}C $\{^1H\}$ NMR displays two peaks at 77.4 and 83.5 ppm, corresponding to Al-*CC*Ph carbon atoms, respectively. The second step involves the cycloaddition reaction, in which the B-H bond of HBpin adds to the C-C triple of **Int 1**, leading to alkene **Int 2**. In the third step, Int 2 reacts with another molecule of phenylacetylene, in which sigma bond metathesis occurs that leads to the formation of product and regeneration of the active catalyst Int 1.

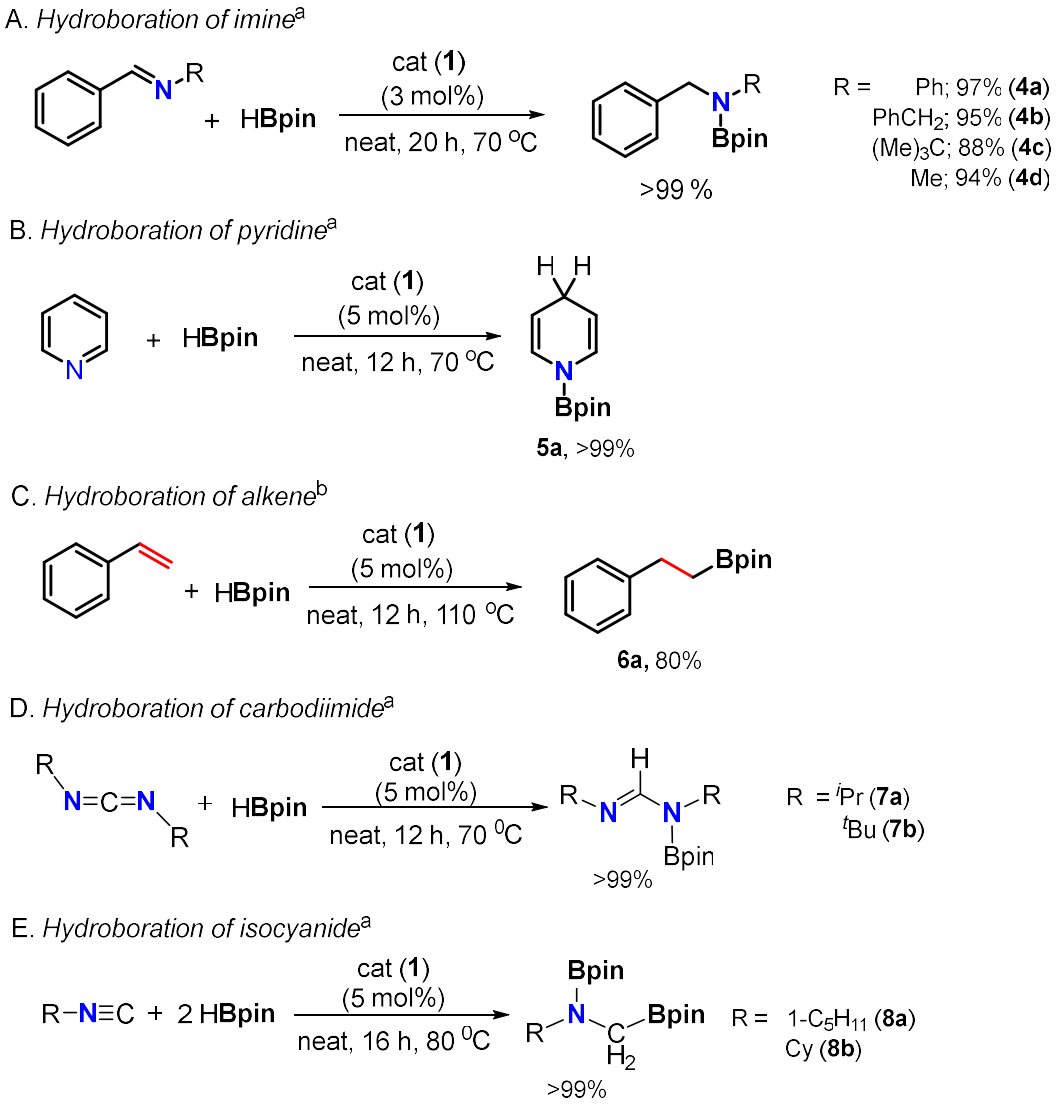
A different mechanism is operative for the internal alkynes, which is previously reported by Thomas, and coworkers.[13b] Accordingly, I propose the catalytic cycle starting with Al-H insertion in alkyne C≡C triple bond to form Int 1, which undergoes transmetallation to regenerate the catalyst and (*Z*)-vinyl boronate ester (Scheme 5.B.6.). Further, a controlled reaction was carried out to confirm the proposed reaction mechanism. Thus, the treatment of catalyst **1** with 1-phenyl-1-propyne in a 1:1 ratio in C_6D_6 at 80 ºC resulted in the formation of Int 1, which is confirmed by ^1H and ^{13}C NMR spectroscopy analyses. The ^1H NMR reveals two singlets at 1.85 and 5.25 ppm, which correspond to methyl and H signals of Al-C*Me*=C*H*Ph moiety. The $^{13}C\{^1H\}$ NMR spectrum shows a typical signal in the upfield region at 3.2 ppm, which corresponds to the carbon atom of Al-C*Me*=CHPh moiety.



Scheme 5.B.6. Proposed mechanism for hydroboration of alkyne.

5.B.2.7. Aluminum Catalyzed Hydroboration of Imines, Alkenes, Pyridine, Carbodiimides, and Isonitriles

To the best of our knowledge, there have been no reports on aluminum-catalyzed hydroboration of heterocycles and isonitriles. To further establish the relevance of this procedure, I utilized aluminum-dihydride catalyzed hydroboration to more challenging substrates (Scheme 5.B.7.).To our delight, compound **1** efficiently catalyzes the hydroboration of imine, pyridine, alkene, carbodiimide, and isonitrile substrates at neat and mild reaction conditions (Scheme 5.B.7.). Hydroboration of imine was successfully achieved for aldimines like N-Benzylideneaniline by 3 mol % of catalyst **1** at 70 ^{o}C within 20 h. Similarly, other imines such as benzyl, ^{t}butyl, and methyl were also hydroborated at the same reaction conditions (**4a-4d**). Equimolar amounts of pyridine and HBpin were reacted together with catalyst **1** in C_6D_6, which afforded exclusively N-borylated 1,4- reduced product (**5a)**. Next, using catalyst **1** (5 mol %) and HBpin (1.0 equiv), the hydroboration of styrene proceeded in an 80 % yield to give the anti-Markovnikov (linear) alkyl boronic ester (**6a**) within 12 h at 110 ^{o}C. Further, compound **1** catalyzed the more challenging organic substrates such as carbodiimides and isonitriles has been investigated.



Scheme 5.B.7. Hydroboration of imines, alkene, pyridine, carbodiimide, and isonitriles by using Al complex (**1**) as a catalyst.[a]

[a]Reaction conditions: all reactions were done on a 1.0 mmol scale. For isocyanide, 2.0 mmol of pinacolborane was used. Conversion was based on ^{1}H NMR spectroscopy. For imine, the yield was determined by using nitromethane as an internal standard. [b]Isolated yield of alkene hydroboration was based on column chromatography.

Aliphatic substrates such as *N, N′*-diisopropyl carbodiimide and *N, N′*-di-tertbutyl carbodiimide reduced to corresponding monohydroborated ester (**7a** and **7b,** respectively) when treated with 1 equiv. of HBpin. Following this, the inert isocyanides such as acyclic and cyclic alkyl isonitriles, i.e., 1-pentylisoniitrile and cycloisonitrile, efficiently converted to corresponding hydroborated amine (**8a** and **8b**, respectively).

5.B.3. Conclusion

In summary, I have demonstrated a newly synthesized *β*-diketiminate analogue of well-defined conjugated bis-guanidinate (CBG)-supported aluminum dihydride (**1**)-catalyzed dihydroboration of a large number of organonitriles with HBpin. It was noticed that catalyst **1** is more efficient for the hydroboration of nitriles than that of *β*-diketiminate (Nacnac) supported aluminum dihydride complex. Further, compound **1**-catalyzed hydroboration of both terminal and internal alkynes with HBpin has been investigated. In contrast to Nacnac Al dihydride catalysis, two different mechanisms are operative for CBG aluminum dihydride catalyzed alkyne hydroboration reaction.

Further, compound **1**-catalyzed hydroboration of alkene, pyridine, imine, carbodiimide, and isocyanide substrates with HBpin has been studied. Overall, compound **1** was found to be a highly efficient (low catalyst loadings and mild reaction conditions) and multifunctional catalyst with a broad substrate scope. Further studies on the aluminum dihydride catalyzing other organic transformations are ongoing in our laboratory.

5.B.4. Synthesis of $LAlH_2$(1)

To a solution of LH (1.0 g, 1.58 mmol) in toluene (~30 mL) at room temperature was added dropwise a solution of an alane-N, N-dimethylethylamine complex (0.5 M) in toluene (3.32 mL, 1.66 mmol). The reaction mixture was heated at 80 ºC and stirred for a further 24 h. The reaction mixture was allowed to attain room temperature and filtered through Celite. Then volatiles were removed in vacuo to yield a colorless solid. The residue was extracted into toluene, and colorless crystals suitable for X-ray diffraction studies were obtained from the storage of a saturated solution in toluene at 5 ºC. The second crop of crystals was obtained on a further concentration of the supernatant solution at -30 ºC. (0.87 g, yield 84%). ^{1}H NMR (C_6D_6, 400 MHz, 273K): δ

(ppm) 0.94 (t, $^{3}J_{HH}$ = 8 Hz, 12H, $PhCH_2CH_3$), 1.36 (t, $^{3}J_{HH}$ = 8 Hz, 12H, $PhCH_2CH_3$), 2.20 – 2.24 (m, 4H, $PhCH_2CH_3$), 2.32 – 2.34 (m, 4H, $PhCH_2CH_3$), 2.84 – 2.86 (m, 4H, $PhCH_2CH_3$), 3.33 – 3.37 (m, 4H, $PhCH_2CH_3$), 5.13 (s, 2H, Ar N*H*), 6.61– 6.63 (d, $^{3}J_{HH}$ = 8 Hz, 4H, Ar*H*), 6.87 (t, $^{3}J_{HH}$ = 8 Hz, 2H, Ar*H*), 7.00 – 7.05 (m, 2H, Ar*H*), 7.12 – 7.14 (m, 2H, Ar*H*), 7.15 – 7.16 (m, 2H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 273K): δ 14.4, 14.5, 23.8, 25.1, 125.4, 126.8, 127.0, 127.5, 134.6, 138.0, 141.3, 141.3, 158.6. ^{27}Al NMR (104 MHz, C_6D_6, 273K) δ 56.35. Mp - 260 – 264 °C. IR (Nujol mull) ν (cm^{-1}): 1813 and 1926 (br, Al-H). HRMS (ESI-TOF-Q) m/z: $[M+H]^+$ calc'd. for $C_{42}H_{56}AlN_5$:658.4797, found: 658.4424. Elemental analysis (%) for $C_{42}H_{56}AlN_5$: calc'd'. C 76.67 H 8.58 N 10.64; found: C 76.20 H 8.42 N 10.86.

5.B.5. Appendix: All analytical data and spectral files of hydroborated products and control reactions along with Crystallographic data and structure refinement summary of compounds **1** and **2i**, were available in the published paper: *J. Org. Chem.* **2020,** *85* (7), 4999-5009.

5.B.6. References

1. (a) Aldridge, S.; Downs, A. J.; Editors, *The Group 13 Metals Aluminium, Gallium, Indium, and Thallium: Chemical Patterns and Peculiarities*; *Johan Wiley & Sons Ltd.*, **2011**; (b) Aldridge, S.; Downs, A. J. *The Group 13 Metals Aluminium, Gallium, Indium, and Thallium. Chemical Patterns and Peculiarities; Angew. Chem. Int. Ed.* **2011**, *50*, 11569; (c) North, M. Editor, Sustainable Catalysis: *With Non-Endangered Metals, Part* 1; [*In RSC Green Chem. Ser*., ***2016****; 38*], RSC, **2016**; (d) North, M. Editor, *Sustainable Catalysis*: *With NonEndangered Metals, Part 2; [In RSC Green Chem. Ser., 2016; 39], RSC*, **2016**; (e) Ananikov, V. P. *Sustainable Catalysis With Nonendangered Metals, Part 1 and 2 Edited by Michael North. Angew. Chem. Int. Ed.* **2016**, *55*, 14904.

2. (a) Dagorne, S.; Wehmschulte, R. *ChemCatChem*, **2018**, *10*, 2509−2520; (b) Weetman, C.; Inoue, S. *ChemCatChem* **2018**, *10*, 4213−4228; (c) Nikonov, G. I. *ACS Catal.* **2017**, *7*,

7257−7266; (d) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, *350*, 14−29.

3. (a) Tamang, S. R.; Findlater, M. *Molecules* **2019**, *24*, 3194; (b) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307−3336; (c) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, 5, 3238−3259; (d) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48*, 1995−2003.
4. (a) Peddarao, T.; Sarkar, N.; Nembenna, S. *Inorg. Chem.* **2020**, *59*, 4693−4702; (b) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1245−1250; (c) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, *18*, 4710−4713; (d) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2015**, *54*, 10225−10229.
5. Weetman, C.; Anker, M. D.; Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F. *Chem. Sci.* **2016**, *7*, 628−641.
6. Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52*, 13155−13158.
7. Li, J.; Luo, M.; Sheng, X.; Hua, H.; Yao, W.; Pullarkat, S. A.; Xu, L.; Ma, M. *Org. Chem. Front.* **2018**, *5*, 3538−3547.
8. Liu, W.; Ding, Y.; Jin, D.; Shen, Q.; Yan, B.; Ma, X.; Yang, Z. *Green Chem.* **2019**, 21, 3812−3815.
9. Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics* **2019**, *38*, 3092−3097.
10. Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Adv. Synth. Catal.* **2019**, *361*, 850−857.
11. (a) Feng, X.; Ji, P.; Li, Z.; Drake, T.; Oliveres, P.; Chen, E. Y.; Song, Y.; Wang, C.; Lin, W. *ACS Catal.* **2019**, *9*, 3327−3337; (b) Magre, M.; Maity, B.; Falconnet, A.; Cavallo, L.; Rueping, M. *Angew. Chem. Int. Ed.* **2019**, *58*, 7025−7029; (c) Bisai, M. K.; Yadav, S.; Das,

T.; Vanka, K.; Sen, S. S. *Chem. Commun.* **2019**, *55*, 11711−11714; (d) Nagao, K.; Yamazaki, A.; Ohmiya, H.; Sawamura, M. *Org. Lett.* **2018**, 20, 1861−1865; (e) Ang, N. W. J.; Buettner, C. S.; Docherty, S.; Bismuto, A.; Carney, J. R.; Docherty, J. H.; Cowley, M.; Thomas, S. *Synthesis* **2018**, 50, 803−808; (f) Lawson, J. R.; Wilkins, L. C.; Melen, R. L. *Chem. Eur. J.* **2017**, 23, 10997−11000; (g) McGough, J. S.; Butler, S. M.; Cade, I. A.; Ingleson, M. J. *Chem. Sci.* **2016**, 7, 3384−3389.

12. (a) Zhang, G.; Li, S.; Wu, J.; Zeng, H.; Mo, Z.; Davis, K.; Zheng, S. *Org. Chem. Front.* **2019**, *6*, 3228−3233; (b) Mamidala, R.; Pandey, V. K.; Rit, A. *Chem. Commun.* **2019**, *55*, 989−992; (c) Nakajima, K.; Kato, T.; Nishibayashi, Y. *Org. Lett.* **2017**, *19*, 4323−4326; (d) Ben-Daat, H.; Rock, C. L.; Flores, M.; Groy, T. L.; Bowman, A. C.; Trovitch, R. J. *Chem. Commun.* **2017**, *53*, 7333−7336; (e) Khalimon, A. Y.; Farha, P. M.; Nikonov, G. I. *Dalton Trans.* **2015**, *44*, 18945− 18956; (f) Jang, W. J.; Lee, W. L.; Moon, J. H.; Lee, J. Y.; Yun, J. *Org. Lett.* **2016**, *18*, 1390−1393; (g) Gunanathan, C.; Hölscher, M.; Pan, F.; Leitner, W. *J. Am. Chem. Soc.* **2012**, *134*, 14349−14352.

13. (a) Harinath, A.; Banerjee, I.; Bhattacharjee, J.; Panda, T. K. *New J. Chem.* **2019**, *43*, 10531−10536; (b) Bismuto, A.; Thomas, S. P.; Cowley, M. J. *Angew. Chem. Int. Ed.* **2016**, *55*, 15356−15359; (c) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. *J. Am. Chem. Soc.* **2016**, *138*, 2548−2551.

14. (a) Li, F.; Bai, X.; Cai, Y.; Li, H.; Zhang, S.-Q.; Liu, F.-H.; Hong, X.; Xu, Y.; Shi, S.-L. *Org. Process Res. Dev.* **2019**, *23*, 1703−1708; (b) Jaladi, A. K.; Shin, W. K.; An, D. K. *RSC Adv.* **2019**, *9*, 26483−26486.

15. Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J.* **2019**, *25*, 11918−11923.

16. Elsen, H.; Färber, C.; Ballmann, G.; Harder, S. *Angew. Chem. Int. Ed.* **2018**, *57*, 7156−7160.

17. (a) Rao, B.; Chong, C. C.; Kinjo, R. *J. Am. Chem. Soc.* **2018**, *140*, 652−656; (b) Hynes, T.; Welsh, E. N.; McDonald, R.; Ferguson, M. J.; Speed, A. W. H. *Organometallics* **2018**, *37*, 841−844; (c) Keyzer, E. N.; Kang, S. S.; Hanf, S.; Wright, D. S. *Chem. Commun.* **2017**, *53*, 9434−9437; (d) Lortie, J. L.; Dudding, T.; Gabidullin, B. M.; Nikonov, G. I. *ACS Catal.* **2017**, *7*, 8454−8459; (e) Fan, X.; Zheng, J.; Li, Z. H.; Wang, H. *J. Am. Chem. Soc.* **2015**, *137*, 4916−4919; (f) Intemann, J.; Lutz, M.; Harder, S. *Organometallics* **2014**, *33*, 5722−5729; (g) Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Köhn, G.; Weetman, C. *Organometallics* **2011**, *30*, 5556−5559.

18. Weetman, C.; Hill, M. S.; Mahon, M. F. *Chem. Commun.* **2015**, *51*, 14477−14480.

19. Peddarao, T.; Baishya, A.; Sarkar, N.; Acharya, R.; Nembenna, S. *Eur. J. Inorg. Chem.* **2021**, 2034–2046.

20. Chu, T.; Korobkov, I.; Nikonov, G. I. *J. Am. Chem. Soc.* **2014**, *136*, 9195−9202.

21. Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 4274−4276.

Chapter 6

Organoaluminum Cation Catalyzed Selective Hydrosilylation of Carbonyls, Alkenes, and Alkynes

Published:

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Abstract

The *N, N'*-chelated *β*-diketiminate analogue, *i.e.*, conjugated bis-guanidine (CBG) ligand L(3H) [L= {(ArHN)(ArN)– C=N–C=(NAr)(NHAr)}; Ar = 2,6-Et_2-C_6H_3], has been used to synthesize mono- and dinuclear Al (III) dimethyl complexes, [L(2H) $AlMe_2$] (**2**) and[L(H)($AlMe_2$)$_2$] (**3**). Compounds **2** and **3** are synthesized by the deprotonation method using free ligand and appropriate stoichiometric amounts of $AlMe_3$ and are structurally characterized by a single-crystal X-ray diffraction technique. Moreover, the reaction of compound **2** with $B(C_6F_5)_3$ afforded a three-coordinate aluminum methyl cation $[L(2H)AlMe]^+$ $[MeB(C_6F_5)_3]^-$ **4** in good yield. Compound **4** was thermally stable and characterized by multinuclear NMR spectroscopy. Furthermore, compound **4** was used for catalytic hydrosilylation of carbonyls, alkenes, and alkyne with triethylsilane ($HSiEt_3$) under solvent-free conditions. I found that catalyst **4** is also effective for large-scale hydrosilylation reactions. Additionally, I have shown that compound **4** catalyzed benzaldehyde's intermolecular chemoselective hydrosilylation over other reducible functional groups.

6.1. Introduction

The catalytic addition of the Si-H bond to aldehydes and ketones is an essential organic transformation (hydrosilylation) that permits the synthesis of silyl ether-protected alcohols in an

atom-economical manner.[1] Although hydrogenation of carbonyls to alcohols is known, it requires highly flammable molecular hydrogen gas and harsh reaction conditions.[2] Thus, commercially available liquid hydrosilanes are attractive due to their mild and easy handling.[3] Various transition metal-based catalysts have been employed for the hydrosilylation of carbonyls.[4] Despite the stability and efficiency of these catalysts, they raise environmental and safety issues. In recent years, attention turned towards earth-abundant, less toxic, and cheaper main group-based catalysts for numerous organic transformations, including hydrosilylation of carbonyls.[5] Such catalysts are alternatives to late transition metal-based systems.[6] In this context, several well-defined molecular aluminum-based compounds have been used as catalysts for the hydrofunctionalization of unsaturated organic substrates, including hydroboration and hydrosilylation reactions.[7] Roesky and coworkers reported that the neutral NacNac Al hydride (where NacNac = $HC(CMeNAr)_2$, Ar = 2,6-$^{i}Pr_2$-C_6H_3) catalyzed hydroboration of aldehydes and ketones with pinacolborane for the first time.[8]

Later, our group and other research groups developed molecular aluminum-based catalysts for the hydroboration of unsaturated organic substrates.[5b, 9]

As far as the current investigation is concerned, a limited number of reports are known for molecular cationic aluminum complexes and their catalytic application in hydroboration and hydrosilylation reactions.[10] In 1999, Jordan group reported NacNac chelated three coordinate aluminum methyl cationic complex.[11] After that few examples of molecular cationic organoaluminum complexes were documented.[12] Regarding cationic organoaluminum complexes in hydrosilylation, in 2012, Bergman and coworkers manifested that the cationic aluminum alkyl stabilized by the scorpionate ligand catalyzed hydrosilylation of carbonyls for the first time (Figure 6.1.).[13] In the same year, cationic organoaluminum, $[Et_2Al]^{+}[CH_6B_{11}I_6]^{-}$

catalyzed the reduction of CO_2 with Et_3SiH reported by Wehmschulte and coworkers.[14] The same research group reported cationic aluminum diphenolate, which catalyzed hydrosilylation of carbon dioxide.[15] In 2016, Nikonov and coworkers established the cationic NacNac aluminum hydride or alkyl complex catalyzed hydrosilylation of alkenes and alkynes with $HSiEt_3$.[16] Again in 2017, Wehmschulte group employed the structurally characterized $[Et_2Al][CHB_{11}Cl_{11}]$ ion pair as a catalyst for the reduction of CO_2 with triethylsilane.[17]

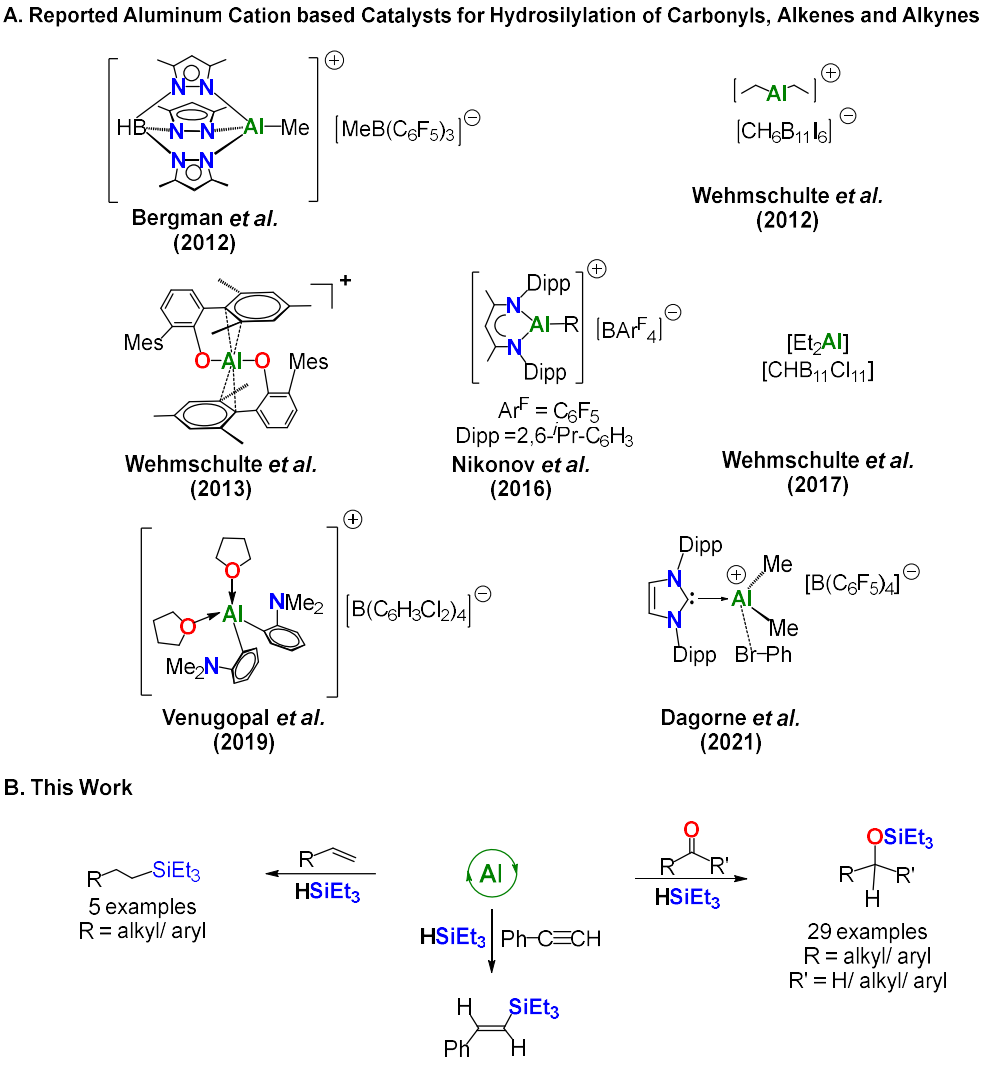


Figure 6.1. Reported molecular cationic aluminum complexes for hydrosilylation of unsaturated organic substrates.

Venugopal and coworkers investigated the catalytic activity of organoaluminum cation, $[(Me_2NC_6H_4)_2Al(THF)_2]^+$ for the hydrosilylation of ketones.[18] Very recently, Dagorne and

coworkers reported N-heterocyclic carbene (NHC) stabilized Al(III) alkyl cation as a catalyst for the hydrosilylation of benzaldehyde, CO_2, and alkynes (Figure 6.1.).[19]

Since the first transition metal guanidinate complex[20] by Lappert in 1970, many guanidinate metal complexes, including aluminum guanidinates, have been documented.[20-21] Moreover, metal complexes bearing guanidinate anions have been utilized as catalysts in organic synthesis.[21c, 22]

The chemistry of biguanides with aluminum is not well developed. Nandi and coworkers reported the first example of Al(III) biguanide.[23] Recently, Kretschmer and coworkers established the aluminum coordination chemistry with tetrasubstituted biguanides.[23b, 24] Our group recently developed well-defined tetra-aryl substituted conjugated bis-guanidinate (CBG)s[25] and CBG stabilized aluminum complexes.[26] In addition, there have been reports on the N-donor stabilized aluminum complexes, including NacNac; CBGs are analogs of popular NacNac ligands.[27]

In 2016, Wei group developed the six-membered monomeric bis-guanidinate aluminum dialkyl complex through two synthetic procedures. i) the reaction of carbodiimide (CDI) with tetrasubstituted guanidinate aluminum dimethyl complex, ii) the reaction of *in situ* generated guanidinate Li salt with $AlMe_2Cl$ followed by the treatment of CDI.[27b]

Recently our group established the first examples of mono- and dinuclear tetrasubstituted aluminum alkyl, halide, and hydride complexes.[26] The deprotonation of free CBG can attain the preparation of CBG aluminum dimethyl complexes with $AlMe_3$ in toluene. However, to our knowledge, there are no examples of cationic CBG aluminum methyl complexes in the literature.

Thus, herein I report two examples of structurally characterized mono- and dinuclear aluminum dimethyl complexes. Moreover, I developed the first example of the CBG aluminum methyl

cationic complex. More importantly, the investigation of organoaluminum cation-catalyzed hydrosilylation of a wide array of aldehydes and ketones. Further, I extended the study of hydrosilylation of alkene and alkyne substrates catalyzed by organoaluminum cation.

6.2. Results and Discussion

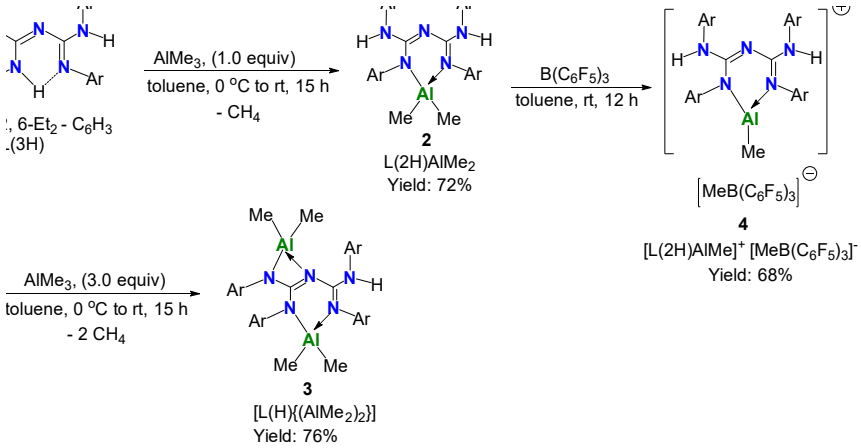
6.2.1. Synthesis and Characterization of Conjugated Bis-Guanidinate (CBG) Stabilized Aluminum Dimethyl and Methyl Cation Complexes

In this article, moderate bulky ^{Diethyl}conjugated bis-guanidine (CBG) ligand L(3H)[25] [L = {(ArHN)(ArHN)C=N-C=NAr(NHAr)}; 2, 6-Et_2-C_6H_3] was selected to synthesize three-coordinate aluminum alkyl cation.

Our group had previously synthesized compound **2;**[26] however, the solid-state structure was not determined. Compound **2** is the precursor for the organoaluminum cation (*vide infra*). Thus, a thorough investigation of the compound mentioned above is justified.

Deprotonation of a free ligand L(3H) with one equivalent trimethylaluminum ($AlMe_3$) in toluene yielded compound [L(2H)$AlMe_2$] **2** in 72 % yield.[26] While a reaction of a 1:3 molar ratio of ligand L(3H) and $AlMe_3$ solution (2.0 M in toluene) in toluene for 15 h led to the formation of dinuclear Al(III) dialkyl compound [L(H)$(AlMe_2)_2$] **3** with 76% yield, as colorless white solid (Scheme 6.1.).

As mentioned earlier, examples of molecular organoaluminum cations are scarce. It should be noted that there have been no reports on biguanide or CBG supported organoaluminum cations, to our knowledge. Thus, it was targeted to prepare CBG aluminum methyl cation.



Scheme 6.1. Synthesis of CBG supported aluminum dimethyl and methyl cation complexes (**2-4**).

Accordingly, the treatment of compound **2** with an equimolar quantity of $B(C_6F_5)_3$ in toluene at room temperature afforded a mononuclear aluminum methyl cationic complex $[L(2H)AlMe]^+$ $[MeB(C_6F_5)_3]^-$ **4** in a 68% yield (Scheme 6.1.).

^1H and $^{13}C\{^1H\}$ NMR spectra of compound **2** are recorded in $CDCl_3$, and corresponding spectra are provided in supporting information. Both compounds $[L(H)(AlMe_2)_2]$ **3** and $[L(2H)AlMe]^+$ $[MeB(C_6F_5)_3]^-$ **4** have been fully characterized by multinuclear NMR spectroscopy.

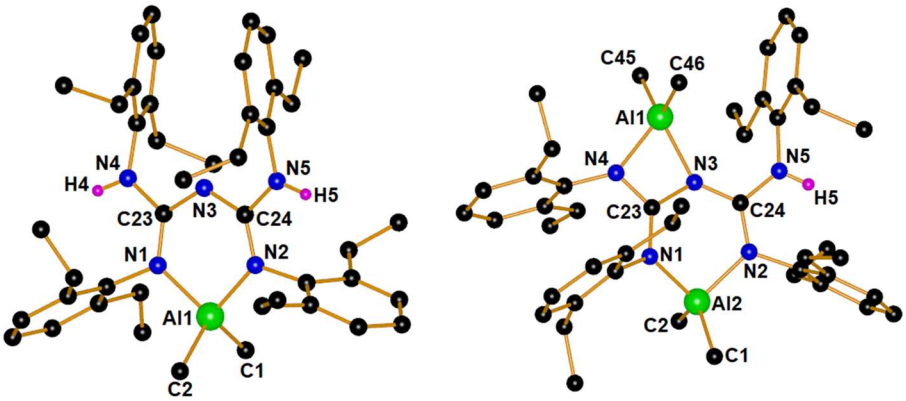


Figure 6.2. Molecular structures of **2** (left) and **3** (right). The thermal ellipsoids are shown at 50% probability, and all the hydrogen atoms except those bound to nitrogen atoms are deleted for clarity. Selected bond lengths (Å) and angles (deg) for **2** (left): Al1− C1 1.9783(14), Al1−C2 1.9716(14), Al1−N1 1.9149(10), Al1−N2 1.9085(10), N1−C23 1.3375(15), N3−C23 1.3406(15), N3−C24 1.3353(15), N2−C24 1.3444(16); N2−Al1−N1 93.82(4), N2−Al1−C1 117.70(5), N1−Al1−C2 116.98(5), C1−Al1−C2 110.54(6), C23−N3−C24 124.22(10).

For **3** (right):Al2−C1 1.9613(15), Al2−C2 1.9731(15), Al1−C45 1.9670(17), Al1−C46 1.9485(16), Al1−N4 1.9238(12), Al2−N1 1.9095(12), Al2−N2 1.9258(12), N1−C23 1.3399(17), N3−C23 1.3977(17), N3−C24 1.3516(17), N2−C24 1.3308(17), N4−C23 1.3368(17), N5−C24 1.3531(18); N1−Al2−N2 93.11(5), N4−Al1−N3 68.24(5), N4−Al1−C45 112.61(6), C46−Al1−C45 117.56(8), C46−Al1−N3 120.84(7), N2−Al2−C2 109.85(6), C24−N3−C23 125.33(11), N4−C23−N3 106.77(11).

The ^{1}H NMR ($CDCl_3$) spectrum of compound **3** displays two sharp singlets at the upfield region, i.e., –1.03 and –1.24 ppm with the integration of six protons each, corresponds to $\{Al(Me_2)\}_2$ fragment, which proves that complex **3** is dinuclear metal alkyl in nature. The result matches the previously reported ^{Xyl}CBG analog of the dialuminum dialkyl complex.[27] The disappearance of resonance signals at 12.63 and 4.97 ppm ($CDCl_3$) corresponds to (N–*H*···N) and one backbone (Ar-N*H*) fragments of free ligand L(3H) and the appearance of one new singlet signal at 5.46 ppm due to the backbone arm Ar-N*H* moieties indicate the complete formation of compound **3**. Due to the unsymmetrical nature of dinuclear metal compound **3,** $^{13}C\{^{1}H\}$ spectrum displays two distinct peaks at 155.2, and 164.0 ppm correspond to the C24 carbon atom of six (AlN3C2) and C23 carbon atom of four-membered (AlN2C) heterocycles (See Figure 6.2.). Both [L(2H)$AlMe_2$] **2** and [L(H)$(AlMe_2)_2$] **3** were additionally characterized with high-resolution mass spectroscopy and single-crystal X-ray analysis (Figure 6.2.). The ^{1}H NMR spectrum of compound **4** showed two sharp singlets at 0.11 and 1.91 ppm, each of the integration of three protons corresponds to Al-Me and B-Me fragments, respectively, compared to the signal for $AlMe_2$ moiety of complex **2** at -0.94 ppm. A similar pattern was observed in the $^{13}C\{^{1}H\}$ spectrum, where the upfield signal at -8.96 ppm due to the $AlMe_2$ moiety of compound **2** split into two signals and shifted towards the downfield region at 2.42 and 5.52 ppm for complex **4** due to the Al-Me and B-Me fragments, respectively.[10b] The ^{11}B and $^{19}F\{^{1}H\}$NMR spectra of complex **4** showed resonances at -15.03 and -134.00, -166.38, and -168.88 ppm, respectively, which proves the existence of counteranion $[MeB(C_6F_5)_3]^-$ of **4.**[10b] The crystallization of molecular cationic aluminum complexes is

extremely difficult. Multiple attempts to obtain the solid-state structure of compound **4** failed because it was impossible to generate crystals of sufficient purity to diffract light. The single-crystal X-ray analysis further provides the conclusive solid-state structures of **2** and **3** (Figure 6.2.). Both the compounds [L(2H)$AlMe_2$] **2** and [L(H)$(AlMe_2)_2$] **3** were grown in toluene as colorless crystals at 5 ºC and crystallized in a monoclinic system with $P2_1/n$ and $P2_1/c$ space groups, respectively. The complete crystallographic data can be seen in the ESI as Table S1. In both **2** and **3**, the central aluminum metal adopts distorted tetrahedral geometry, coordinated with monoanionic *N, N'*-chelated ligand, and two methyl groups, which confirm the four-coordinate structural conformation around the aluminum atom. In addition, the solid-state X-ray crystal structure of **2** further proves the C_2N_3Al six-membered metallacycle ring. The dinuclear compound **3** comprises four and six-membered metallacycle rings, analogous to the previously reported CBG dialuminum alkyl complex.[27] The Al-C and Al-N bond distances lie in complexes **2** and **3** between 1.948-1.978 Å and 1.909-1.923 Å, respectively, similar to reported *N, N'*-chelated aluminum dimethyl complexes.[26-27]

6.2.2. Aldehyde Hydrosilylation

To the best of our literature study, it was noticed that molecular cationic aluminum complexes are robust catalysts for hydroelementation reactions compared to their parent neutral counterparts, which encouraged us to investigate the carbonyl hydrosilylation by employing newly synthesized CBG supported aluminum methyl cation (**4**).

To explore the catalytic performance of compound **4** for hydrosilylation of aldehyde, I chose benzaldehyde as a model substrate and reacted with one equivalent $HSiEt_3$ under solvent-free conditions at room temperature for 12 h (Table 6.1.).

Table 6.1. Optimization table for aluminum catalyzed hydrosilylation of benzaldehyde.[a]

4a **5a**

Entries	Catalysts	mol%	Solvent	Time (h)	Yield (%)[b]
1	-	-	neat	12	-
2	**4**	2.0	neat	12	>99
3	**4**	2.0	neat	8	>99
4	**4**	1.0	neat	8	>99
5	**4**	1.0	Toluene	8	>99
6	**4**	0.5	neat	8	80
7	**3**	1.0	neat	8	-
8	**2**	1.0	neat	8	-

[a]Reaction conditions: benzaldehyde (1.0 equiv., 0.3 mmol), triethylsilane (1.0 equiv., 0.3 mmol), catalyst (x mol%), neat, 8 h at rt under N_2. [b]The yield was determined by ^{1}H NMR spectroscopy based on consumption of starting material and identified newly formed characteristic proton (PhCH_2OSiEt$_3$) signal at (δ) 4.63 ppm.

Initially, no desired silylated ether product was detected in the absence of the catalyst. However, the incorporation of 2 mol% catalyst (**4**) affords quantitative conversion of benzaldehyde (**4a**) into silylated ether PhCH$_2$OSiEt$_3$ (**5a**), which indicates the active participation of compound **4** in this transformation. The further decrease in time up to 8 h leads to a similar result. Inspired by these effective results, the above catalytic reaction was further executed under a lower catalyst loading (1 mol% and 0.5 mol%). I noticed the formation of silylated ether **5a** in 99% and 80% yields.

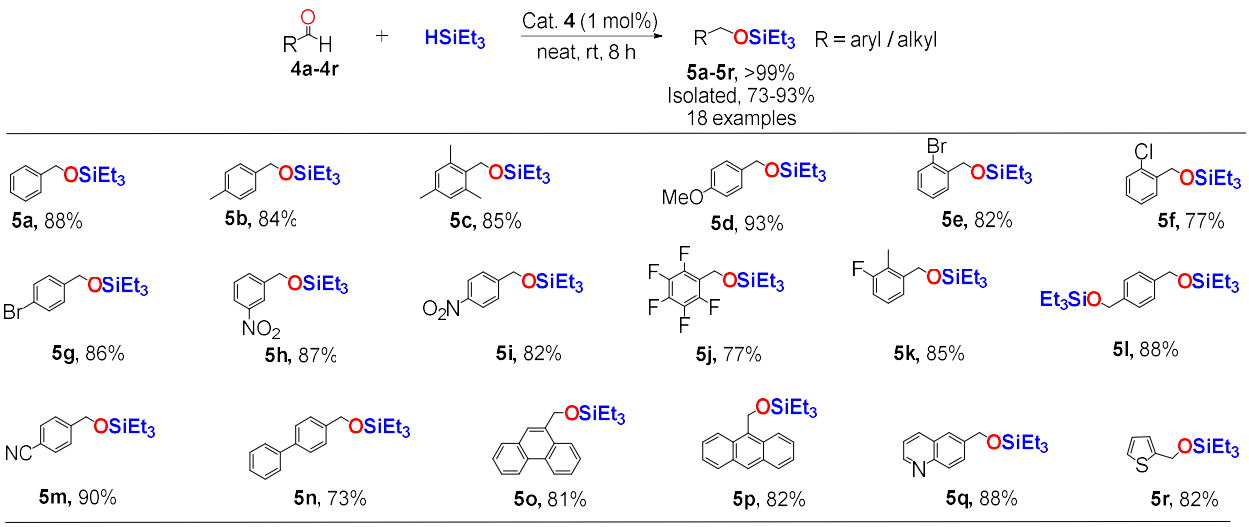
Moreover, the catalytic outcome did not affect by the solvent (entry 5 of Table 6.1.). No conversion was perceived for catalysts **2** and **3**.

With the final optimization in hand, the catalytic hydrosilylation of various commercially available aldehydes was investigated using compound **4,** which reveals a good tolerance of halide, nitrile, nitro, and heterocycles under neat conditions (Scheme 6.2.). I tracked the progress of the hydrosilylation reaction solely by ^{1}H NMR spectroscopy, which established the quantitative formation of silylated ethers. All tertiary silylated ethers (**5a-5r**) were purified by column chromatography and isolated in good yield (73%-93%).

It has been observed that aryl aldehydes with electron-donating (**4b-4d**) or electron-withdrawing (**4e-4k**) groups were fully converted into corresponding silylated ether products (**5b-5k**) as colorless oils. For the hydrosilylation of terephthaldehyde, two-fold triethylsilane was used under similar conditions to isolate the final reduced silylated product (**5l**) in an 88% yield.

Moreover, to explore the potential chemoselectivity of our current catalysis, 4-cyanobenzaldehyde (**4m**) was treated with $HSiEt_3$ and noticed exclusive hydrosilylation of aldehyde (**5m**) with untouched nitrile functional group after 8 h in 90% isolated yield. In addition, I have also investigated the hydrosilylation of biaryl and fused ring aldehydes. As illustrated in scheme 6.2., all three aldehydes, i.e., biphenyl-4-carboxaldehyde, 9-phenanthrenecarboxaldhyde, and 9-anthracenecarboxaldehyde, were quantitatively converted into (**5n-5p**) in 73-82% yields.

Lastly, I examined the hydrosilylation of heteroaryl aldehydes such as quinoline-6-carboxaldehyde and 2-thiophene carboxaldehyde. Both aldehydes were discovered to be smoothly silylated into the related products **5q** and **5r** under the same standard condition.



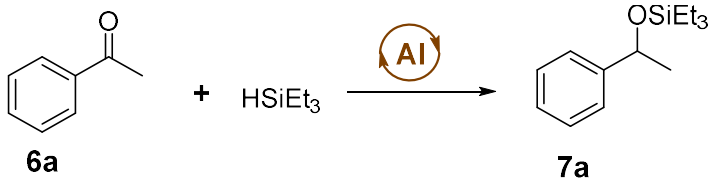
Scheme 6.2. Substrate scope for hydrosilylation of aldehydes catalyzed by **4**.[a]

[a]Reaction conditions: aldehyde (1.0 mmol, 1.0 equiv.), triethylsilane (1.0 mmol, 1.0 equiv.), catalyst **3** (1 mol%), neat, 8 h at rt under N_2. Products are isolated after column chromatography.

6.2.3. Ketone Hydrosilylation

Further, the hydrosilylation scope was additionally extended to ketones. At the outset, acetophenone was treated with $HSiEt_3$ in neat and catalyst-free condition at rt, resulting in no conversion (Table 6.2., entry 1). To our delight, I noticed the full hydrosilylation of acetophenone into corresponding triethyl(1-phenylethoxy)silane **7a** while 4 mol% of catalyst **4** was introduced in the above solution under a similar reaction condition. Additionally, in solvent-free conditions, similar outcomes up to 2 mol% catalyst loading were seen; further lowering in catalyst amount results in poor conversion. It should be noted that entry 8 shows the high turnover frequency (TON) (15). Additionally, both **2** and **3** were inactive to catalyze the acetophenone hydrosilylation reaction.

Table 6.2. Optimization table for aluminum catalyzed hydrosilylation of acetophenone.[a]

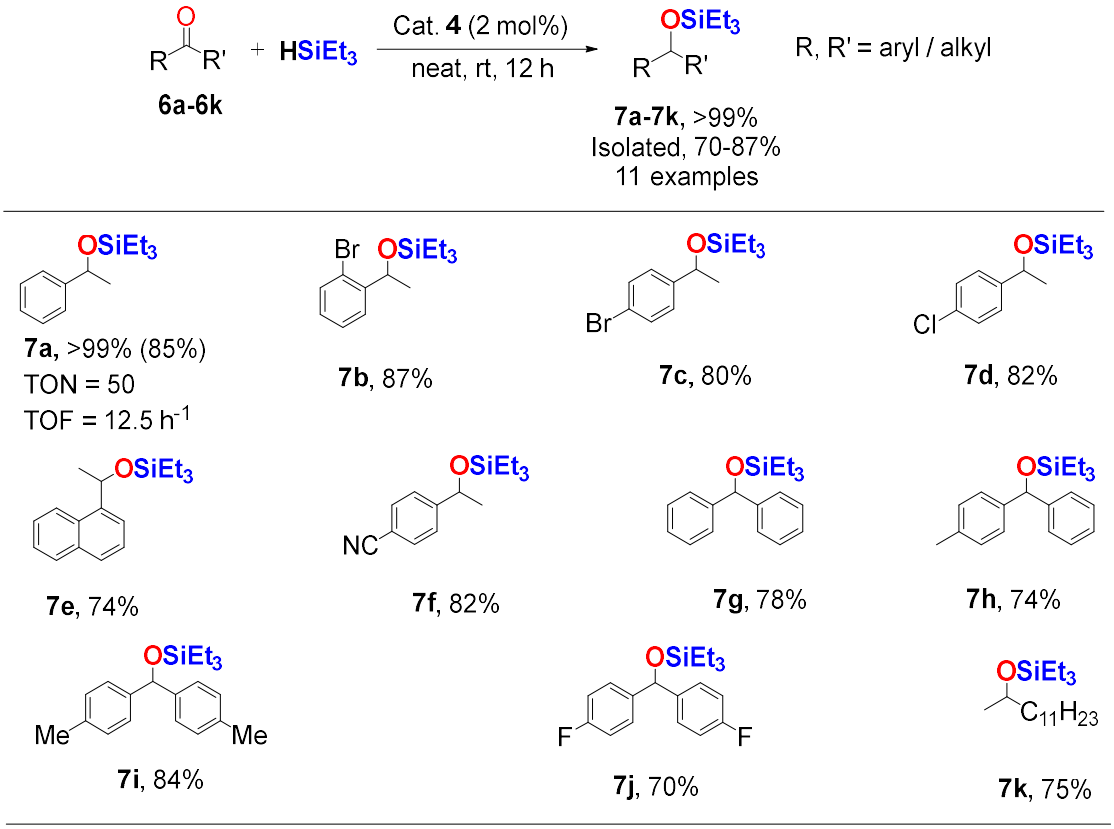


Entries	Catalysts	mol%	Solvent	Time (h)	Yield (%)[b]
1	-	-	neat	24	-
2	**4**	4.0	neat	24	>99
3	**4**	4.0	neat	12	>99
4	**4**	3.0	neat	12	>99
5	**4**	2.0	neat	12	>99
6	**4**	2.0	Toluene	12	>99
7	**4**	2.0	neat	8	>99
8[c]	**4**	2.0	neat	4	>99
9	**4**	1.0	neat	12	60
10	**3**	2.0	neat	12	-
11	**2**	2.0	neat	12	-

[a]Reaction conditions: acetophenone (1.0 equiv., 0.3 mmol), triethylsilane (1.0 equiv., 0.3 mmol), catalyst (x mol%), neat, 12 h at rt under N_2. [b]The yield was determined by ^{1}H NMR spectroscopy based on consumption of starting material and identified newly formed characteristic proton (PhC*H*MeOSiEt$_3$) signal at (δ) 4.79 ppm. TON was calculated by dividing the number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by time of reaction. [c]For entry 8, TON = 50 and TOF = 12.5 h^{-1}.

In Scheme 6.3., I summarized the substrate scope of ketone hydrosilylation with adequate tolerance of alkyl, halide, nitrile, and heterocycle functionalities (**7a-7k**). All reactions were performed in a 1.0 mmol scale and further purified by column chromatography using SiO_2 (100-200 mesh) to isolate silyl ethers in a 70-87% yield. The initial screening revealed that electron-withdrawing aryl ketones, such as 2'-, 4'-, and 4'-chloroacetophenone, completely reduce to their respective silyl ethers (**7b-7d**). These results are well consistent with the reported cationic aluminum catalyzed hydrosilylation reactions.[13] In bulky substrate 1-acetonapthone, I found no change in optimized conditions and therefore afforded the corresponding naphthyl silyl ether (**7e**)

in a quantitative yield. To expand the substrate scope, one intramolecular chemoselective hydrosilylation reaction was performed.



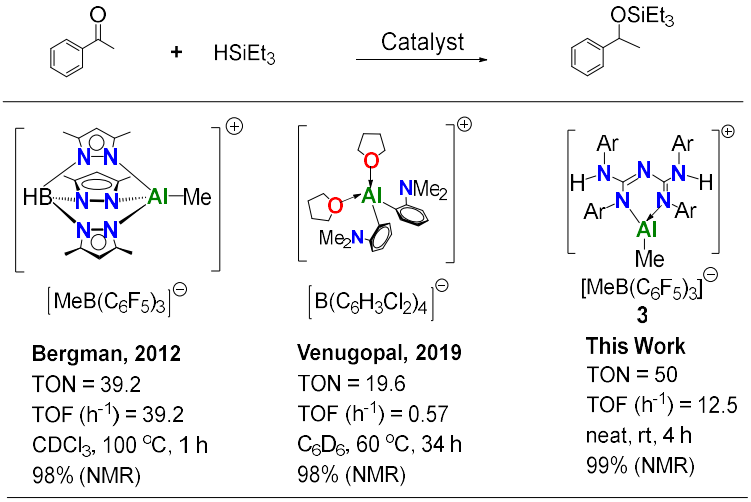
Scheme 6.3. Substrate scope for hydrosilylation of ketones catalyzed by **4**.[a]

[a]Reaction conditions: ketone (1.0 mmol, 1.0 equiv.), triethylsilane (1.0 mmol,1.0 equiv.), catalyst (**3**) (2 mol%), neat, 12 h at rt under N_2. The product was isolated after column chromatography. TON was calculated by dividing the number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by time of reaction.

For this, I chose the commercially available 4'-cyanoacetophenone (**4f**), which is successfully reduced into silyl ether **7f** without disturbing the reducible nitrile functional group. In addition, our catalyst **4** exhibits a good tolerance of bulky disubstituted ketones such as benzophenone, 4-methylbenzophenone, 4,4'-dimethylbenzophenone, and 4,4'-difluorobenzophenone. All four disubstituted ketones underwent full hydrosilylation into desired silyl ethers **7g-7j** with 70-84% isolated yields.

In the end, I also established that compound **4** is adequate towards hydrosilylation of long-chain aliphatic ketones like 2-tridecanone, which is wholly reduced into corresponding triethyl(tridecan-2-yloxy)silane **7k** with 75% isolated yield.

The catalytic activity of **4** in the hydrosilylation of acetophenone displays turn over number (TON), 50 and turn over frequency (TOF), 12.5 h^{-1} as compared to reported Bergman's[13] scorpionate ligand stabilized aluminum methyl cation, 39.2 (TON), and 39.2 h^{-1} (TOF) and Venugopal's[18] $[(Me_2NC_6H_4)_2Al(THF)_2]^+$ 19.6 (TON) and 0.57 h^{-1} catalysts (Scheme 6.4.).



Scheme 6.4. Comparison of catalytic efficiencies of cationic organoaluminum catalysts for hydrosilylation of acetophenone.[a]

[a]TON was calculated through the dividing number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by time of reaction.

It is worth noting that all the above catalytic hydrosilylation reactions were performed in room temperature conditions, while other reported catalysts at higher temperatures (60 -100 °C).

6.2.4. Catalytic Alkene Hydrosilylation

For alkene hydrosilylation, the investigation began with styrene as an example. In the initial screening, I performed a hydrosilylation reaction in the absence of catalyst at 80 °C, where no conversion was recorded (Table 6.3., entry 1). The same reaction when performed in 8 mol% catalyst **4**, >99% of **9a** ($PhCH_2CH_2SiEt_3$), was found exclusively in the crude reaction mixture.

The reduced alkyl silane is linear with anti-Markovnikov selectivity, similar to the results shown by Nikonov and coworkers.[16] With the decrease of catalyst loading up to 4 mol%, I observed the quantitative formation of **9a** in ^{1}H NMR spectroscopy after 12 h stirring in neat conditions. There was no change in the catalytic activity when the reaction was done in toluene. However, both complexes **2** and **3** were inactive to catalyze the hydrosilylation of styrene. It should be noted that all alkyl silanes (**9a-9e**) were further purified by column chromatography. By using the above final optimized conditions, further substrate scope was expanded in alkyl and aryl-substituted alkenes (Scheme 6.5.). The initial experiments were performed using 4-methylstyrene and 4-chlorostryene with $HSiEt_3$ in solvent-free conditions at 80 °C. The corresponding linear alkyl silanes (**9b-9c**) were isolated in 86-88% with no trace of starting material.

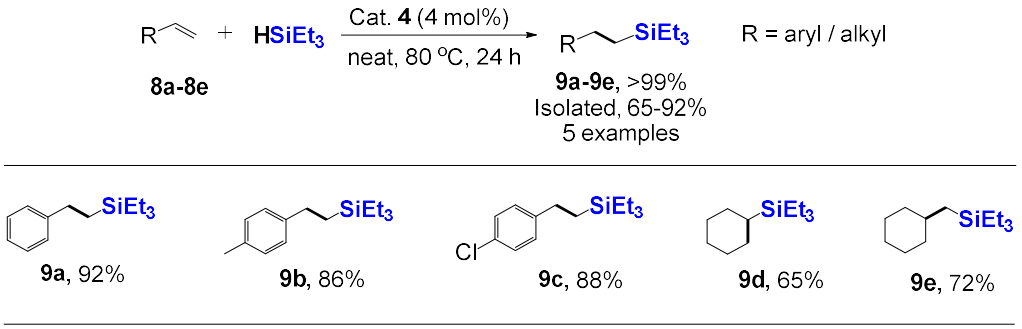
Table 6.3. Optimization table for aluminum catalyzed hydrosilylation of styrene.[a]

8a **9a**

Entries	Catalysts	mol%	Solvent	Time (h)	Yield (%)[b]
1	-	-	neat	24	-
2	**4**	8.0	neat	24	>99
3	**4**	8.0	neat	12	>99
3	**4**	6.0	neat	12	>99
4	**4**	4.0	neat	12	>99
5	**4**	4.0	Toluene	12	>99
6	**4**	2.0	neat	12	75
7	**3**	4.0	neat	12	-
8	**2**	4.0	neat	12	-

[a]Reaction conditions: styrene (1.0 mmol, 1.0 equiv.), triethylsilane (1.0 mmol, 1equiv.), catalyst (x mol%), neat, 24 h at 80 °C under N_2. [b]The yield was determined by ^{1}H NMR spectroscopy based on the consumption of starting material and identified newly formed characteristic proton (PhCH_2CH$_2$SiEt$_3$) signal at (δ) 2.56 ppm.

Furthermore, the reaction with aliphatic alkenes such as cycloalkene and methylenecyclohexane yielded 65-72% corresponding anti-Markovnikov products **9d** and **9e**.

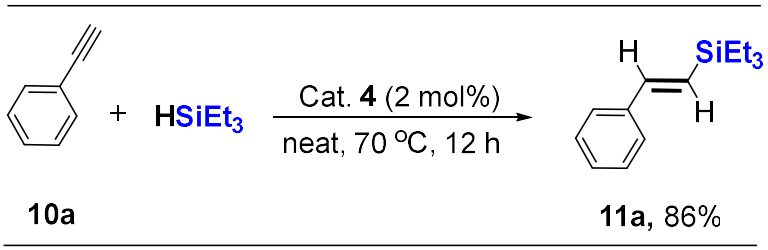


Scheme 6.5. Substrate scope for hydrosilylation of alkenes catalyzed by **4**.[a]

[a]Reaction conditions: alkene (1.0 mmol, 1.0 equiv.), triethylsilane (1.0 mmol,1.0 equiv.), catalyst (**4**) (4 mol%), neat, 24 h at 80 °C under N_2. The products were isolated after column chromatography.

6.2.5. Hydrosilylation of Phenylacetylene

The literature survey revealed that only two molecular cationic aluminum complexes are reported for alkynes' hydrosilylation.[16, 19] However, the analogue catalyst used by Nikonov takes five days to complete the full hydrosilylation of phenylacetylene. To our delight, complex **4** smoothly catalyzed the trans addition of triethylsilane in C≡C bond of phenylacetylene to afford (*E*)-vinyl silane **11a** under mild conditions with 86% isolated yield (Scheme 6.6.).

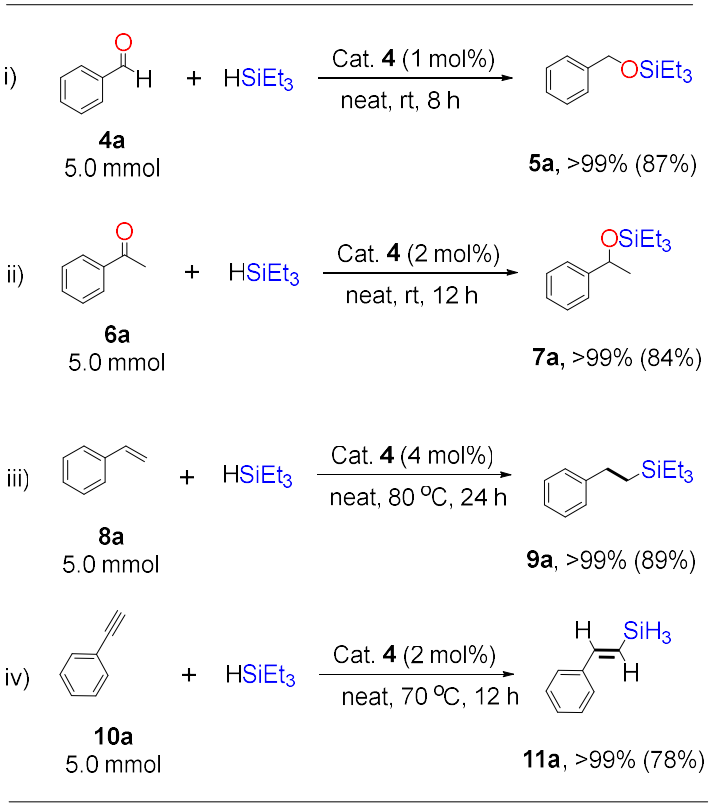


Scheme 6.6. Hydrosilylation of phenylacetylene catalyzed by **4**.[a]

[a]Reaction conditions: phenylacetylene (1.0 mmol, 1.0 equiv.), triethylsilane (1.0 mmol, 1.0 equiv.), catalyst (**4**) (2 mol%), neat, 12 h at 70 °C under N_2. The product was isolated after column chromatography.

6.2.6. Scale-up Reaction

Four independent large-scale experiments at 5.0 mmol were conducted to explore the practical utilization of our current methodology. As shown in scheme 6.7., an equimolar reaction of benzaldehyde with triethylsilane for 8 h afforded a complete hydrosilylation product **5a** with 87% yield. Similarly, the practicable scalability of our current protocol also works well for the hydrosilylation of acetophenone, styrene, and phenylacetylene to isolate the corresponding silylated products **7a**, **9a**, and **11a** in 78-89% yields.



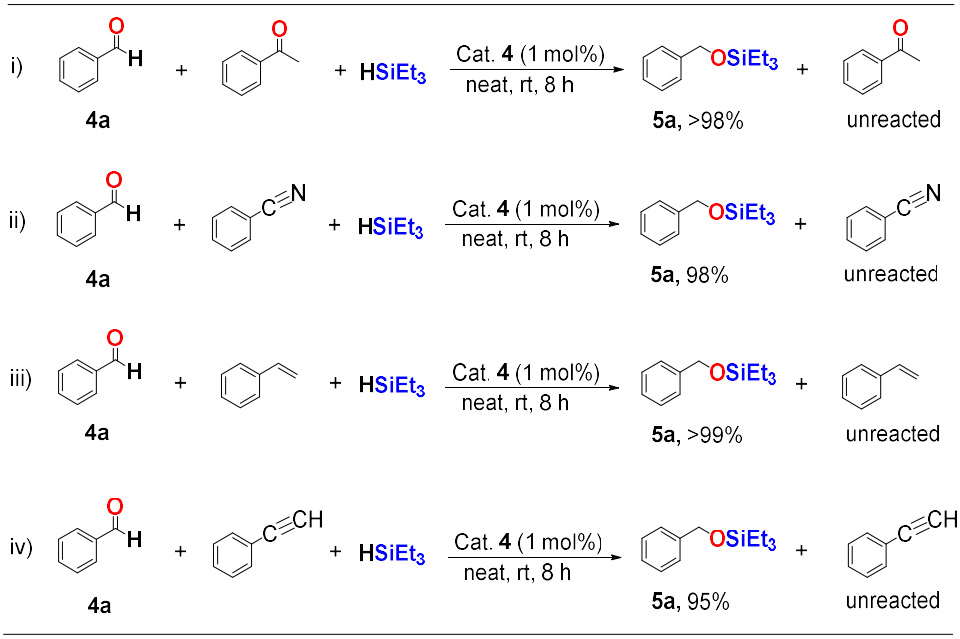
Scheme 6.7. Scale-up reactions with $HSiEt_3$ catalyzed by **4**.

6.2.7. Intermolecular Chemoselective Reactions

Chemoselective reduction is a fundamental transformation for the synthesis of desired products.[28] During hydrosilylation of carbonyls, I introduced the effective intramolecular chemoselective reductions with $HSiEt_3$; therefore, it was curious to investigate the intermolecular

chemoselective hydrosilylation between benzaldehyde and acetophenone or benzonitrile or styrene, or phenylacetylene (Scheme 6.8.).

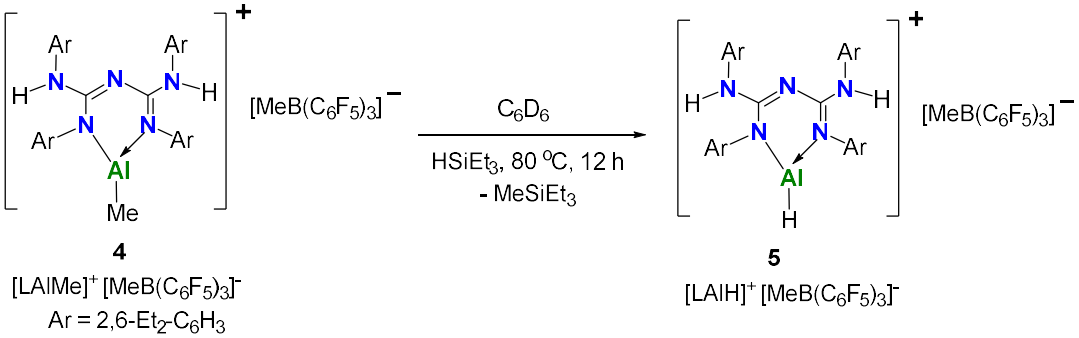
Thus, when I mixed the equimolar solution of benzaldehyde and acetophenone with 1 equivalent of $HSiEt_3$, it affords the almost complete formation of silylated ether **5a** of corresponding benzaldehyde at rt (based on ^1H and $^{13}C\{^1H\}$ NMR analysis). In similar experiments, a 1:1 molar ratio of benzaldehyde and benzonitrile/styrene/phenylacetylene was treated with equimolar triethyl silane under the same condition, resulting in the nearly quantitative hydrosilylation of benzaldehyde into **5a** with intact reducible functionalities was observed.



Scheme 6.8. Intermolecular chemoselective hydrosilylation of benzaldehyde.

6.2.8. Control Experiment

One control reaction was performed to understand the reported CBG aluminum methyl cation catalyzed hydrosilylation reaction mechanism (Scheme 6.9.).



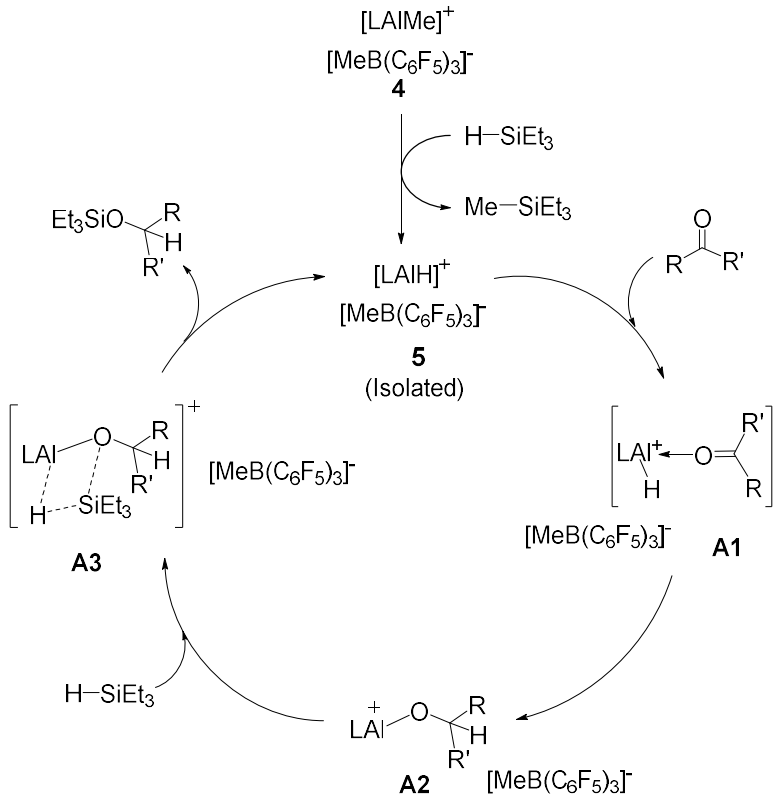
Scheme 6.9. Reaction of compound **4** with triethylsilane.

The reaction of compound **4** with $HSiEt_3$ in a 1:1 molar ratio in benzene-d6 at 80 °C for 12 h afforded CBG aluminum-hydride cation, **5** (Scheme 6.9.). The newly synthesized *in-situ* active catalyst **4** is characterized by multinuclear NMR and high-resolution mass spectroscopy. Further, in the $^{29}Si\{^1H\}$ spectrum, a characteristic signal appeared at 6.38 ppm, ensuring the side product $MeSiEt_3$. The signal is well-matched with reported literatures.[29]

6.2.9. A mechanism for Aluminum (4) Catalyzed Carbonyl Hydrosilylation

Based on the above-control experiment and reported mechanism for carbonyl reduction using cationic aluminum complex,[10b] I suggest an insertion with the σ-bond metathesis model reaction mechanism as displayed in Scheme 6.10.

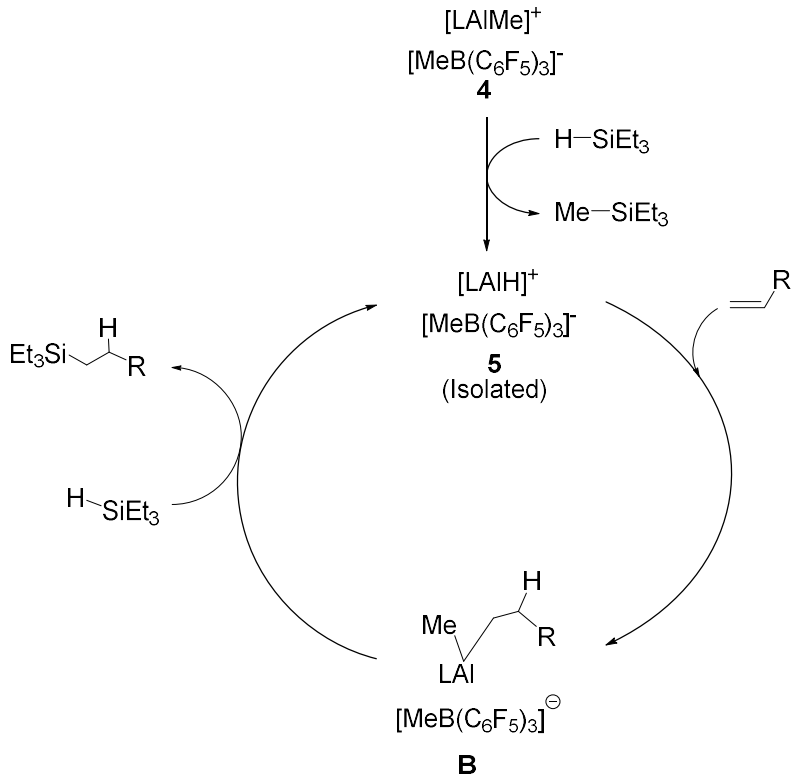
Initially, the aluminum pre-catalyst $[LAlMe]^+$ **4** reacts with $HSiEt_3$ to generate an active catalyst aluminum hydride $[LAlH]^+$ (**5**). In the next step, **4** leads to one labile adduct A1 by reaction with a carbonyl group, where hydride migration from Al center to carbonyl carbon occurs to form stable aluminum alkoxide complex A2, $[LAl\text{-}O\text{-}CHRR']^+$. The intermediate A2 reacts with $HSiEt_3$ and generates one four-membered T.S (intermediate A3). Finally, the intermediate A3 undergoes σ-bond Al-O/Si-H metathesis to release corresponding alkoxy-siloxy ether products and resurgence of catalyst **5**.



Scheme 6.10. Proposed mechanism for hydrosilylation of carbonyl.

6.2.10. A mechanism for Aluminum (3) Catalyzed Alkene Hydrosilylation

Based on the reported mechanism of aluminum-methyl cation catalyzed hydrosilylation of alkenes by Nikonov and coworkers[16] and above stoichiometric reaction, I propose the reduction of alkenes using active catalyst **5** as displayed in Scheme 6.11. The catalytic cycle involves the coordination of compound **5** with an olefin to afford aluminum dialkyl intermediate B. Next, intermediate B reacts with $HSiEt_3$ to afford reduced silyl ether product and regeneration of active catalyst **5**.



Scheme 6.11. Proposed mechanism for hydrosilylation of alkene catalyzed by **4**.

6.2.11. Lewis's acidity determination of compound 4

The Lewis acidity of compound **4** is determined by the Gutmann–Beckett method in which the chemical shift of $^{31}P\{^{1}H\}$ of the Et_3PO probe upon coordination with the Lewis acidic center is measured.[30] I observed that when equimolar amounts of **4** and triethyl phosphine oxide in benzene-d_6 solution is heated at 70 °C, the $^{31}P\{^{1}H\}$ resonance shifts from δ = 45.76 ppm (for uncoordinated Et_3PO) to δ = 74.15 ppm (for **4**.$OPEt_3$). The acceptor number (AN), a measure of Lewis acidity, is calculated according to the reported formula AN = 2.21 (δ_{sample} - 41).[30c] In the present case, the acceptor number of compound **4** is 73.3, as compared to the reported Singh's[10b] bis(phosphinimino)-amine ligand stabilized aluminum methyl cation (AN = 83.1, C_6D_6), Dagorne's[19] $[IPr.AlMe_2]^+$ catalyst (AN = 78.6, C_6D_5Br) and commercially available $B(C_6F_5)_3$ reagent (AN = 76.0, C_6D_6).[30a]

6.3. Conclusions

In conclusion, I have reported the structurally characterized mono- and dinuclear aluminum (III) dialkyl complexes (**2-4**) chelated by NacNac analogue, conjugated bis-guanidinate (CBG)anion. Moreover, this is the first example of the cationic CBG aluminum methyl complex, as per the literature study. The cationic organoaluminum complex **4** was used as a robust catalyst for hydrosilylation of a wide array of aldehydes and ketones with $HSiEt_3$ and well-tolerated the reducible halide, heterocycle, nitro, and nitrile functional groups. All silyl ethers were isolated in excellent yields. Both intra and intermolecular chemoselective hydrosilylation have been performed. In addition, cation was also employed for the hydrosilylation of alkene and alkyne substrates. Furthermore, I have shown large-scale synthesis to illustrate the practical applicability of this methodology. Currently, other challenging organic transformations using compound **4** are still in progress.

6.4. Analytical data of compounds (2-4).

6.4.1. Synthesis of L(2H)AlMe$_2$ (2): To a solution of L(3H) (0.5 g, 0.79 mmol, 1.0 equiv.) in toluene (15 mL), trimethylaluminum (2.0 M in toluene, 0.40 mL, 1.0 equiv.) was added at 0 °C. The solution was allowed to attain the room temperature, and the stirring was extended for 15 h. The solvent was removed completely then washed with *n*-hexane, and was added to the crude solid toluene (∼10 mL) and slowly cooled to room temperature to give **2** as colorless crystals (0.39 g, 0.57 mmol, 72%). Mp: 275 − 285 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.28 (s, 6H, Ar*H*), 6.90 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.68 – 6.66 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 5.20 (s, 2H, N*H*), 3.08 – 3.01 (m, 4H, CH_2CH$_3$), 2.84 – 2.76 (m, 4H, CH_2CH$_3$), 2.42 – 2.33 (m, 4H, CH_2CH$_3$), 2.26 – 2.17 (m, 4H, CH_2CH$_3$), 1.36 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH$_2$CH_3), 0.97 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH$_2$CH_3), -0.94 (s, 6H, Al(CH_3)$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 158.1, 141.1, 140.6, 138.8, 134.3,

126.6 126.4, 125.7, 125.1, 24.6, 23.2, 14.2, 13.8, -8.9 (Al(*C*H$_3$)$_2$). HRMS (ASAP/Q-TOF) *m/z*: [M]$^+$ Calcd. for $C_{44}H_{60}AlN_5$: 685.4899; Found 685.4886.

6.4.2. Synthesis of [L(H){(AlMe$_2$)$_2$}] (3): To a solution of LH (0.5 g, 0.79 mmol, 1.0 equiv.) in toluene (15 mL), trimethylaluminum (2.0 M in toluene, 1.18 mL, 3.0 equiv.) was added at 0 °C. The solution was allowed to warm to room temperature, and the stirring was extended for 15 h. The solvent was removed completely, then washed with *n*-hexane. The crude product was crystallized from toluene at 5 °C to give **3** as colorless crystals (0.445 g, 0.6 mmol, 76%). Mp: 255−260 °C.^{1}H NMR (700 MHz, $CDCl_3$, 298 K) δ (ppm): 7.17 – 7.13 (m, 6H, Ar*H*), 6.77 – 6.72 (m, Ar*H*), 6.64 (t, $^3J_{HH}$ = 8.0 Hz, 3H, Ar*H*), 5.46 (s, 1H, N*H*), 3.02 – 2.98 (m, 4H, C*H*$_2$CH$_3$), 2.79 – 2.74 (m, 2H, C*H*$_2$CH$_3$), 2.72 – 2.65 (m, 2H, C*H*$_2$CH$_3$), 2.42 – 2.37 (m, 4H, C*H*$_2$CH$_3$), 2.28 (m, 4H, C*H*$_2$CH$_3$), 1.33 (t, $^3J_{HH}$ = 8.0 Hz, 6H, CH$_2$C*H*$_3$), 1.14 (t, $^3J_{HH}$ = 8.0 Hz, 6H, CH$_2$C*H*$_3$), 1.10 (t, $^3J_{HH}$ = 8.0 Hz, 6H, CH$_2$C*H*$_3$), 0.99 (t, $^3J_{HH}$ = 8.0 Hz, 6H, CH$_2$C*H*$_3$), -1.03 (s, 6H), -1.24 (s, 6H, (Al(C*H*$_3$)$_2$)$_2$).^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 298 K) δ (ppm): 164.0, 155.2, 143.4, 140.7, 140.6, 138.5, 136.9, 129.7, 127.5, 127.1, 126.1, 124.4, 124.4, 25.1, 23.9, 23.6, 23.4, 14.2, 13.9 13.6, 13.4, 8.5 (Al(*C*H$_3$)$_2$), -9.0(Al(*C*H$_3$)$_2$). HRMS (ASAP/Q-TOF) *m/z*: [M]$^+$ Calcd for $C_{46}H_{66}Al_2N_5$: 742.4949; Found 742.4982.

6.4.3. Synthesis of [L(2H)AlMe]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$(4): To a solution of [L(2H)AlMe$_2$] **2** (0.5 g, 0.73 mmol, 1.0 equiv) in toluene (20 mL), dropwise added solution of B(C$_6$F$_5$)$_3$ (0.37 g, 0.73 mmol, 1.0 equiv) in toluene (10 mL) at rt. The solution was allowed to be stirred for 12 h. The solvent was removed completely under vacuum, and then the oil was washed with n-hexane. The crude product was crystallized from toluene at 0 °C to give **4** colorless crystals (0.43 g, 0.5 mmol, 68%). Mp: 220−225 °C.^{1}H NMR (400 MHz, C_6D_6, 298 K) δ (ppm): 7.20 – 7.14 (m, 6H, Ar*H*), 6.99 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.75 – 6.73 (d, $^3J_{HH}$ = 8.0 Hz, 3H, Ar*H*), 6.31 (s, 2H, Ar*H*), 5.55 (s, 2H, N*H*), 3.37 – 3.28 (m, 4H, C*H*$_2$CH$_3$), 2.63 – 2.56 (m, 4H, C*H*$_2$CH$_3$), 2.37 – 2.34 (m, 4H, C*H*$_2$CH$_3$), 2.22 – 2.17 (m, 4H, C*H*$_2$CH$_3$), 1.91 (s, 3H, C*H*$_3$), 1.32 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH$_2$C*H*$_3$), 0.94 (t, $^3J_{HH}$ = 8.0 Hz,

12H, CH_2CH_3), 0.11 (s, 3H, CH_3).$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ (ppm): 155.2, 147.4, 141.3, 139.8, 137.4, 135.5, 126.9, 126.3, 125.6, 125.5, 125.1, 123.2, 25. 3, 14.0, 14.6, 13.8, 5.5, 2.4.^{11}B NMR (128 MHz, C_6D_6, 298 K) δ (ppm): -15.03.$^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, 298 K) δ (ppm): -134.00, -166.38, -168.88. HRMS (ASAP/Q-TOF) m/z: $[M]^+$ Calcd for $C_{50}H_{61}AlBF_5N_5$: 864.4792; Found 864.4698.

6.5. Appendix: All analytical data and spectral files of hydrosilylated products and compounds **2-4** were available in *Eur. J. Inorg. Chem.* **2022 (*Invited article in Main group catalysis*)**. DOI: https://doi.org/10.1002/ejic.202101030. In addition, the crystallographic data and structure refinement summary of compounds **2** and **3** were provided in ESI.

6.6. References

1. Magano, J.; Dunetz, J. R. *Org. Process Res. Dev.*, **2012**, *16*, 1156–1184.
2. (a) Glatz, M.; Stöger, B.; Himmelbauer, D.; Veiros, L. F.; Kirchner, K. *ACS Catal.*, **2018**, *8*, 4009–4016; (b) Gorgas, N.; Stoger, B.; Veiros, L. F.; Kirchner, K. *ACS Catal.*, **2016**, *6*, 2664–2672; (c) Tan, X.; Wang, G.; Zhu, Z.; Ren, C.; Zhou, J.; Lv, H.; Zhang, X.; Chung, L. W.; Zhang, L.; Zhang, X. *Org. Lett.*; **2016**, *18*, 1518–1521; (d) Rosler, S.; Obenauf, J.; Kempe, R. *J. Am. Chem. Soc.*, **2015**, *137*, 7998–8001; (e) Zell, T.; Ben-David, Y.; Milstein, D. *Catal. Sci. Technol.*, **2015**, *5*, 822–826; (f) Wang, D.; Astruc, D. *Chem. Rev.*, **2015**, 115, 6621–6686; (g) Takahashi, K.; Nozaki, K. *Org. Lett.*, **2014**, *16*, 5846–5849.
3. Li, Z.; Yu, Z.; Luo, X.; Li, C.; Wu, H.; Zhao, W.; Li, H.; Yang, S. *RSC Adv.*, **2020**, *10*, 33972–34005.
4. (a) Verhoeven, D. G. A.; Kwakernaak, J.; van Wiggen, M. A. C.; Lutz, M.; Moret, M. E. *Eur. J. Inorg. Chem.*, **2019**, 660–667; (b) Raya-Barón, Á.; Oña-Burgos, P.; Fernández, I.; *ACS Catal.*, **2019**, *9*, 5400–5417; (c) Wekesa, F. S.; Arias-Ugarte, R.; Kong, L.; Sumner, Z.; McGovern, G. P.; Findlater, M. *Organometallics*, **2015**, *34*, 5051–5056; (d) Junge, K.;

Wendt, B.; Addis, D.; Zhou, S.; Das, S.; Beller, M. *Chem. Eur. J.*, **2010**, *16*, 68–73; (e) Tran, B. L.; Pink, M.; Mindiola, D. J. *Organometallics*, **2009**, *28*, 2234–2243; (f) Diez-Gonzalez, S.; Nolan, S. P. *Acc. Chem. Res.*, **2008**, *41*, 349–358; (g) Du, G.; Abu-Omar, M. M. *Organometallics*, **2006**, *25*, 4920–4923.

5. (a) Roy, M. M. D.; Omaña, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.*, **2021**, *121*, 12784–12965; (b) Shegavi, M. L.; Bose, S. K.; *Catal. Sci. Technol.*, **2019**, *9*, 3307–3336; (c) Wilkins, L. C.; Melen, R. L. *Coord. Chem. Rev.*, **2016**, *324*, 123–139; (d) Hill, M. S.; Liptrot, D. J.; Weetman, C. *Chem. Soc. Rev.*, **2016**, *45*, 972–988; (e) Chong, C. C.; Kinjo, R. *ACS Catal.*, **2015**, *5*, 3238–3259; (f) Harder, S. *Chem. Rev.*, **2010**, *110*, 3852– 3876.

6. Power, P. P. *Nature*, **2010**, *463*, 171–177.

7. Nikonov, G. I. *ACS Catal.* **2017**, *7*, 7257–7266.

8. Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.*, **2015**, *54*, 10225–10229; *Angew. Chem.* **2015**, *127*, 10363–10367.

9. (a) Sarkar, N.; Bera, S.; Nembenna, S. *J. Org. Chem.*, **2020**, *85*, 4999–5009; (b) Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Adv. Synth. Catal.*, **2019**, *361*, 850–857; (c) Shen, Q.; Ma, X.; Li, W.; Liu, W.; Ding, Y.; Yang, Z.; Roesky, H. W. *Chem. Eur. J.*, **2019**, *25*, 11918–11923; (d) Liu, W.; Ding, Y.; Jin, D.; Shen, Q.; Yan, B.; Ma, X.; Yang, Z. *Green Chem.*, **2019**, *21*, 3812–3815; (e) Ding, Y.; Ma, X.; Liu, Y.; Liu, W.; Yang, Z.; Roesky, H. W. *Organometallics*, **2019**, *38*, 3092–3097; (f) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. *J. Am. Chem. Soc.*, **2016**, *138*, 2548–2551.

10. (a) Zhang, G.; Wu, J.; Zeng, H.; Neary, M. C.; Devany, M.; Zheng, S.; Dub, P. A. *ACS Catal.*, **2019**, *9*, 874–884; (b) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. *Chem. Eur. J.*, **2018**, *24*, 4794–4799.

11. Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.*, **1999**, *121*, 8673–8674.

12. (a) Issenhuth, J.-T.; Pluvinage, J.; Welter, R.; Bellemin-Laponnaz, S.; Dagorne, S. *Eur. J. Inorg. Chem.*, **2009**, 4701–4709; (b) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G.; Jr., Jordan, R. F. *J. Am. Chem. Soc.*, **2001**, *123*, 8291–8309; (c) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.*, **1997**, 119, 8125–8126.

13. Koller, J.; Bergman, R. G. *Organometallics*, **2012**, *31*, 2530–2533.

14. Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem. Int. Ed.*, **2012**, *51*, 7323–7326.

15. Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics*, **2013**, *32*, 6812–6819.

16. Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.*, **2016**, *6*, 7350–7356.

17. Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics*, **2017**, *36*, 4810–4815.

18. Kannan, R.; Chambenahalli, R.; Kumar, S.; Krishna, A.; Andrews, A. P.; Jemmis, E. D.; Venugopal, A. *Chem. Commun.*, **2019**, *55*, 14629–14632.

19. Bolley, A.; Specklin, D.; Dagorne, S. *Polyhedron*, **2021**, *194*, 114956.

20. Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc.*, **1970**, 2550–2558.

21. (a) Cui, X. Y.; Tan, C. H.; Leow, D. *Org. Biomol. Chem.*, **2019**, *17*, 4689–4699; (b) Alonso-Moreno, C.; Antinolo, A.; Carrillo-Hermosilla, F.; Otero, A. *Chem. Soc. Rev.*, **2014**, *43*, 3406–3425; (c) Barry, S. T. *Coord. Chem. Rev.*, **2013**, *257*, 3192–3201; (d) Jones, C. *Coord. Chem. Rev.*, **2010**, *254*, 1273–1289; (e) Coles, M. P. *Dalton Trans.*, **2006**, 985–1001; (f) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.*, **2001**, *214*, 91–141.

22. (a) Han, H.-F.; Zhang, S.-F.; Guo, Z.-Q.; Tong, H.-B.; Wei, X.-H. *Polyhedron*, **2015**, *99*, 71–76; (b) Obenauf, J.; Kretschmer, W. P.; Kempe, R. *Eur. J. Inorg. Chem.*, **2014**, 1446–1453; (c) Koller, J.; Bergman, R. G. *Organometallics*, **2010**, *29*, 3350–3356; (d) Zhang, W.-X.; Li, D.; Wang, Z.; Xi, Z. *Organometallics*, **2009**, *28*, 882–887; (e) Chang, C.-C.; Hsiung, C.-S.; Su, H.-L.; Srinivas, B.; Chiang, M. Y.; Lee, G.-H.; Wang, Y. *Organometallics*, **1998**, *17*, 1595–1601.

23. (a) Nandi, S. D.; Banerjee, P. *Z. Naturforsch.*, B **1974**, *29*, 347–348; (b) Dehmel, M.; Vass, V.; Prock, L.; Gorls, H.; Kretschmer, R. *Inorg. Chem.*, **2020**, *59*, 2733–2746.

24. Dehmel, M.; Görls, H.; Kretschmer, R. *Inorganics*, **2021**, *9*, 52.

25. (a) Peddarao, T.; Baishya, A.; Sarkar, N.; Acharya, R.; Nembenna, S. *Eur. J. Inorg. Chem.*, **2021**, 2034–2046; (b) Sahoo, R. K.; Sarkar, N.; Nembenna, S. *Angew. Chem. Int. Ed.*, **2021**, *60*, 11991–12000.

26. Peddarao, T.; Sarkar, N.; Nembenna, S. *Inorg. Chem.*, **2020**, *59*, 4693–4702.

27. (a) Peddarao, T.; Baishya, A.; Hota, S. K.; Nembenna, S. *J. Chem. Sci.*, **2018**, *130*, 1–7; (b) Han, H.-F.; Guo, Z.-Q.; Zhang, S.-F.; Li, J.; Wei, X.-H. *RSC Adv.*, **2016**, *6*, 101437–101446; (c) Gianopoulos, C. G.; Kirschbaum, K.; Mason, M. R. *Organometallics*, **2014**, *33*, 4503–4511; (d) Bakthavachalam, K.; Reddy, N. D. *Organometallics*, **2013**, *32*, 3174–3184; (e) Yang, Y.; Li, H.; Wang, C.; Roesky, H. W. *Inorg. Chem.*, **2012**, *51*, 2204–2211; (f) Koller, J.; Bergman, R. G. *Organometallics*, **2010**, *29*, 5946–5952.

28. (a) Sarkar, N.; Mahato, M.; Nembenna, S. *Eur. J. Inorg. Chem.*, **2020**, 2295– 2301; (b) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.*, **2016**, *18*, 4710–4713; (c) Shenvi, R. A.; O'Malley, D. P.; Baran, P. S. *Acc. Chem. Res.*, **2009**, *42*, 530–541.

29. (a) Thompson, S. M.; Stohr, F.; Sturmayr, D.; Kickelbick, G.; Schubert, U. *J. Organomet. Chem.*, **2003**, *686*, 183–191; (b) Schraml, J.; Chvalovsky, V.; Magi, M.; Lippmaa, E. *Chem. Commun.*, **1979**, *44*, 854–865.

30. (a) Sivaev, I. B.; Bregadze, V. I. *Coord. Chem. Rev.*, **2014**, *270–271*, 75–88; (b) Beckett, M. A.; Brassington, D. S.; Light, M. E.; Hursthouse, M. B. *J. Chem. Soc.*; *Dalton Trans.* **2001**, 1768–1772; (c) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Varma, K. S. *Polymer*, **1996**, *37*, 4629–4631; (d) Gutmann, V. *Coord. Chem. Rev.*, **1976**, *18*, 225–255.

Thesis Highlights

In recent years, the use of main-group metal complexes in catalysis has surpassed that of transition elements, as aluminum is the cheapest earth-abundant element in the periodic table, drawing attention to its use in catalysis. This thesis is based on a thorough application of aluminum complexes in catalysis research. At first CBG-stabilized neutral and cationic aluminum hydrides and alkyl complexes were isolated Following that, the CBG aluminum-hydride was employed for catalytic hydroboration of carbonyl compounds and various cross-dehydrocoupling reactions to corresponding hydroborated products using HBpin as reducer. Additionally, the chemoselective synthesis of amides, aminals, and N-methyl amines from respective heteroallenes such as carbodiimides, isocyanates, isothiocyanates, and isoselenocyanates was investigated under solvent-free conditions at low catalyst load. Moreover, B-H addition across the double bond (alkene, isonitrile) and a triple bond (alkyne, nitrile) were investigated to produce high-yielding borylamine and vinyl boronate ester products. Furthermore, the addition of CBG aluminum methyl cation-based Si-H ($HSiEt_3$) in carbonyls (aldehyde, ketone), alkenes, and phenylacetylene were investigated. Finally, it was concluded that thesis will provide excellent guidelines for reducing challenging unsaturated functional groups via hydroboration and hydrosilylation methods using CBG aluminum complexes under mild conditions.

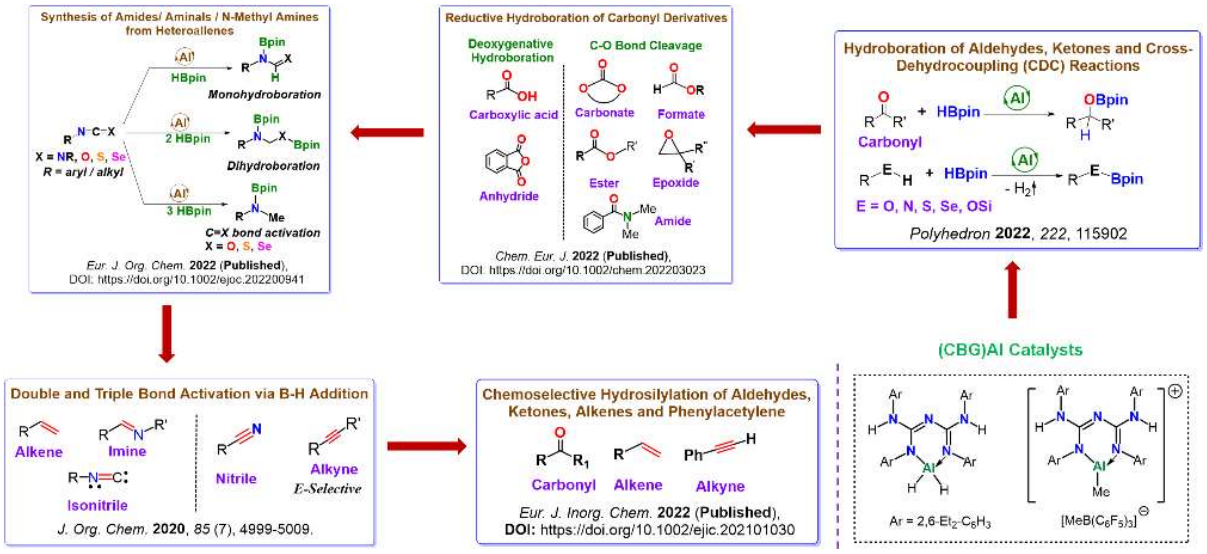


Figure 1. Sustainable approaches for the reduction of unsaturated organic functionalties.

Conclusion and Outlook for Future Research

Main group elements are cheaper, non-toxic, and abundant on the earth's crust than transition or lanthanide elements. In recent years, the application of molecular compounds containing main group elements in catalysis has been an emerging area of recent research interest. In view of this, in the present thesis, various sustainable approaches have been used to synthesize boron derivatives from the corresponding unsaturated organic functionalities using newly synthesized CBG ligand-stabilized aluminum complexes under mild conditions. Every chapter includes a description of the scope of the reaction, mechanistic research, and a synthetic application of our improved methods for hydroboration and hydrosilylation reactions. For the chemistry group working on organic synthesis, this suggests that these efficient and cost-effective methodologies will considerably impact the field of organic synthesis. We hope that these environmentally friendly methods will be beneficial to researchers conducting related research as well as a good manual for building smaller organic building blocks. I have primarily developed cross-dehydrocoupled boron derivatives, vinyl boronate esters, alkoxyboronate esters, N-boryl amides, aminals, and bis-arylamines. These boron derivatives were helpful in various coupling reactions, including Suzuki reactions, pharmaceuticals, the agricultural, and cosmetics sectors. Therefore, our work establishes a connection between organic synthesis and its industrial application. We believe that the study described here will significantly impact organic chemistry research. In the near future, this study endeavor might also have commercial relevance.