Lithium, Aluminum and Gallium Complexes of Sterically Bulky Conjugated Bis-Guanidine Ligands and Aluminum Complexes of Bridged Bis-Guanidines: Synthesis, Characterization and Their Reactivity Studies

By

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I, hereby declare that the investigation presented in the thesis has been carried out by me. 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

1. Metal-free access of bulky *N, N'*-diarylcarbodiimides and their reduction: Bulky *N, N'*-diarylformamidines. **T. Peddarao,** A. Baishya, M. K. Barman, A. Kumar and S. Nembenna*, *New J. Chem,* **2016, 40,** 7627-7636.

2. Bimetallic aluminum alkyl and iodide complexes stabilized by a bulky bis-guanidinate ligand. **T. Peddarao,** A. Baishya, S. K. Hota, and S. Nembenna*, *J. Chem. Sci.,* **2018,** 130:97

3. A New Class of Guanidine Ligands: Synthesis and Characterization of "Conjugated Bis–Guanidines" and Their Lithium Salts. **T. Peddarao,** A. Baishya and S. Nembenna* (*Manuscript under preparation*)

4. Mono-and Bimetallic Aluminum Alkyl, Alkoxide, Halide and Hydride Complexes Stabilized by a Bulky Conjugated Bis-Guanidinate Ligand **T. Peddarao** and S. Nembenna* (*Manuscript under preparation*)

Conferences

- Presented poster in **'21st CRSI National Symposium'** held at IICT, Hyderabad (14-16 July 2017).

  Title of the poster:

  - A New Class of Guanidine Ligands: Synthesis, Characterization of "Conjugated Bis-Guanidines" and Their Metal Complexes.

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    School of Chemical Sciences, National Institute of Science Education and Research (NISER), Bhubaneswar 751005, India.

- Presented poster in **'Indo-French Symposium** on **Functional Metal-Organics'** held at NISER, Bhubaneswar (24-26 February 2014).

  Title of the poster:

  - Guanidinato stabilized aluminum amides as efficient homogeneous catalysts for Tischenko reaction.

    Authors: Milan Kr Barman, Ashim Baishya, **Thota Peddarao**, Sharanappa Nembenna

- Attended **'13th CRSI National Symposium** in Chemistry & **5th CRSI-RSC Symposium'** in Chemistry held at KIIT, Bhubaneswar (02-06 February 2011).
- Participated in **"Chemical Research Scholars Meeting"** (CRSM -2011) organized by IGCAR from July 14-15th 2011.
- Attended **'Indo-European Symposium** on **Frontiers in Chemistry'** held at NISER, Bhubaneswar (12-16 February 2012).

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Dedicated to……..

Sri Sainadh Maharaj and my family members

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Chapter 5.

Summary

Bulky diaryl carbodiimides are ideal precursors to prepare various bulky N-donor ligands such as formamidines, amidines, guanidines, and NHC-CDI adducts, etc. These bulky N-donor ligands are ideal precursors for isolation of unusual metal complexes, particularly low valent and/or low oxidation state metal complexes. In this regard, we have reported the facile synthesis of 15 examples of various symmetrical and unsymmetrical bulky *N,N'*-diaryl carbodiimides by the dehydrosulfurisation of corresponding thioureas by using a base and iodine in THF at mild reaction conditions in moderate to high yields. Further, we produced ten examples of 1, 3-disubstituted symmetrical and unsymmetrical bulky aryl formamidines under mild reaction conditions in excellent yields, upon reduction of corresponding carbodiimides with readily available sodium borohydride. The bulky bis-guanidine ligands $L^1(2H)$, $L^2(2H)$ and $L^3(2H)$ where L = $\{ArNCNAr\}_2\{\mu\text{-}N(C_2H_4)_2N\}$, for $L^1(2H)$ Ar = 2, 6-Me_2 - C_6H_3), $L^2(2H)$ (Ar = 2, 4, 6-Me_3 - C_6H_2) and for $L^3(2H)$ (Ar = 2, 6-$^iPr_2$ - C_6H_3) have been prepared by following the literature procedure. The bimetallic aluminum alkyl compounds supported by Dipp and Mes bulky bis-guanidines were synthesized and characterized. We have shown the synthesis of bulky aryl 5 – amino tetrazoles and these were prepared by treating the bulky diaryl carbodiimides with trimethylsilylazide in thf. The main group metal complexes stabilized by tetrazole ligands are not known in the literature. So in this regard, we have prepared bulky aryl tetrazoles to stabilize various main group metal complexes. We are looking forward in exploring the coordination chemistry of these ligand systems towards the main group as well as transition metals. The systems in which conjugation connected to the guanidine units and their coordination chemistry has received attracted attention in recent years. The term “conjugated guanidine function” can be described as a guanidine function carrying an unsaturation in the alpha–position to the nitrogen

of its imine group. So far tetra substituted bulky bis-guanidines are known in the literature. Interestingly the chemistry of symmetrical conjugated bisguanidines has not been well established. In this aspect, we would like to present our efforts to explore much chemistry of these unique ligand systems and have been successfully ended up with a convenient synthetic protocol and some exciting features in their coordination chemistry towards the lithium metal.

The ligands can be used to synthesize mononuclear six-membered thf and ether coordinated lithium complexes. The thf and ether coordinated lithium complexes are ideal precursors for the preparation of CBG stabilized various main group metal halides. Mononuclear aluminum halide, hydride, alkoxide, and gallium di iodide complexes bearing CBG ligands have been synthesized and structurally characterized. The conjugated bis-guanidine ligands possess the unique capability of forming both four- and six-membered heterocycles binding multi-metal centers within the same molecule; this is attributed to the presence of three acidic protons, among them, two protons can be easily deprotonated upon treatment with metal reagents. The CBG supported bimetallic aluminum alkyl complexes may also be an efficient catalyst for the ROP of cyclic esters. The aluminum diiodide complex is an ideal precursor to synthesize low valent Al (I) heterocycle. We have successfully synthesized and well characterized CBG supported molecular aluminum dihydride. As per our expectation, it has been confirmed that the CBG stabilized molecular aluminum hydride is a good catalyst for hydroboration of carbonyl compounds. We have extended our interest towards the synthesis of low valent Ga (I). In this context, we synthesized of CBG supported Gallium di iodide complex. Currently, the efforts are under way in our laboratory to achieve the fascinating CBG supported low valent Gallium (I) heterocycle. Which will be the only third example of this kind in the literature.

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List of Abbreviations

δ	chemical shift
λ	wavelength
μ	bridging
$\tilde{\nu}$	wave number
Ar	Aryl
CBG	Conjugated bis–guanidine
CDI	Carbodiimide
Form H	Formamidines
Xylyl	2, 6 dimethyl phenyl
Dipp	2, 6 diisopropyl phenyl
Mes	2, 4, 6 trimethyl methyl phenyl
Diethyl	2, 6 diethyl phenyl
av	average
b	broad
^{o}C	Celsius
calcd.	calculated
d	doublet
dd	doublet of doublet
decomp.	decomposition
EI	electron impact ionization
equiv/eq.	equivalents
Et	ethyl

eV	electron volt
g	grams
h	hours
Hz	Hertz
*i*Pr	*i*so-propyl
IR	infrared
J	coupling constant
K	Kelvin
m	multiplet
M	metal
m/z	mass/charge
Mp	melting point
M^+	molecular ion
Me	methyl
MS	mass spectrometry, mass spectra
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
q	quartet
quant.	quantitative
^{t}Bu	*tert*-butyl
s	singlet
sept	septet
t	triplet

THF	tetrahydrofuran
V	volume
w	weak
XRD	X-ray diffraction
Z	number of molecules in the unit cell

Chapter 1. General Introduction

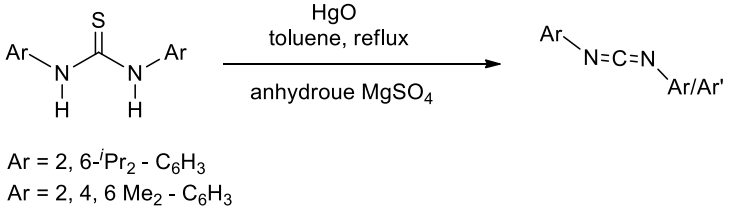
1.1 Carbodiimides

Carbodiimides (CDIs) are unique organic compounds containing an N=C=N core included in the category of heterocumulenes. The synthesis of carbodiimide from isocyanate with the loss of carbon dioxide allowed the industrial scale production. The utilization of carbodiimides in polymeric materials probably the bulk consumption of world production. The most important feature of carbodiimides is their low uncatalyzed reactivity which favours their easy storage. The driving force for the reactivity of carbodiimides towards most of the reactions is the very powerful saturating ability of the C=N bond and ability to form very stable product in dehydrations. The carbodiimide can fulfil most of the properties of an ideal reagent. It is unreactive till a catalyst is employed but can provide a powerful driving force for a reaction to proceed. The major drawback for the utility of carbodiimides is their powerful action as contact allergens. Apart from the synthesis of nucleotides, peptides, and heterocycle, the utilization of carbodiimides was extended to synthesize several *N,N'* donor ligands such as amidinate, guanidinate, formamidines. The tunability of *N,N'* substituent's in carbodiimides makes more promising to synthesize ligands ranging from small, medium, more bulky and extremely bulkiness. On the other hand, the commercial availability of bulky *N, N'*-diaryl CDIs is very limited. It is needless to mention that these ligands with diversity in their bulkiness are the perfect precursors to stabilize main group metals in their low oxidation states, thus carbodiimides became the important synthetic tool for a main group chemist.

Synthesis of N, N'-diarylcarbodiimides

Andrew Williams et al discussed some general synthetic protocols for the synthesis of *N, N'*-substituted carbodiimides.[1] the commercial availability of bulky *N, N'*-diaryl CDIs is very limited. In the synthesis of carbodiimides the classical method involves the elimination of

ligands from the N-C-N skeleton. The synthetic strategies of carbodiimides mainly include (a) the dehydrosulfurisation of 1,3-disubstituted thioureas, (b) the dehydration of ureas, (c) preparation from cyanamides, (d) preparation from isocyanates or isothiocyanates, (e) the nitrene rearrangement and (f) preparation from haloformates and thermolysis reactions. Dehydrosulfurisation of thiourea is the conventional method used to prepare aryl CDIs among all the procedures mentioned above. Literature explored that harsh reaction conditions such as a toxic metal oxide (HgO) and magnesium sulfate ($MgSO_4$) at high temperatures have been employed to convert bulky *N, N'*-diarylthiourea to *N, N'*-diarylcarbodiimide. The greener synthetic protocol for the preparation of CDIs, by Patel and co-workers,[2] is an inspirational move for us, and in which the authors employed dehydrosulfurisation of thiourea in the presence of triethylamine/iodine in mild reaction conditions to produce 15 compounds of aryl CDIs. Symmetrical (R-N=C=N-R; R= p-tolylphenyl) and unsymmetrical (N- (2, 6- dimethylphenyl)-N'-(phenyl)) CDIs have been prepared quite effectively by following the above mentioned synthetic protocol. The same method would also have been efficient for the synthesis of bulky aromatic CDIs with aromatic substituent's at ortho-position, but the reported yields are lower in these cases (vide infra). Both symmetrical and unsymmetrical bulky *N, N'* diaryl carbodiimides of 15 examples have been synthesized in our laboratory.[3]



Scheme 1.1 Dehydrosulfurisation of 1, 3-di-substituted thioureas.

1.2 Formamidines

The compound NH=CH-NH_2 which is the amidine of formic acid is generally known as fformamidines. It acts as a monoanionic and bidentate ligand upon displacement of 'H' atom by R group which is attached go the nitrogen atom, formamidinato ligand. The *N, N'*-disubstituted basic structure of formamidines is shown in the (Figure **1.2**).

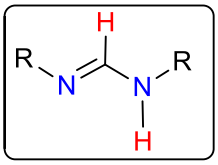
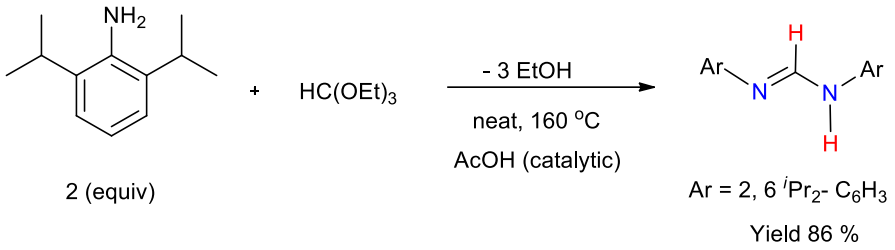


Figure: 1.2 Basic structure of formamidine

Formamidines have their importance in synthetic chemistry[4,5] and can be used extensively as pesticides (e.g., chlordimeform, formetanate, amitraz)[6-10] and as pharmacological agents.[11-13] Formamidines have also been reported as biochemical targets of adrenergic, histamine and neurochemical receptors,[14-18] monoamine oxidase[19] and prostaglandin E2 synthesis.[20] Their utility as ligands in transition-metal complexes has also been reported.[21,22] Variation of the substituent's on the aryl rings can modulate the steric and electronic effect of the ligands as well as their solubilities.[23-26] The utility of formamidines in organic synthesis was quite expanded, playing roles such as auxiliaries in asymmetric synthesis,[27,28] protecting groups for primary amines,[29] electrophiles,[30] and linkers in solid phase synthesis.[31] General routes to formamidines and related compounds are dominated by condensation (amine+form-amide)[32-34] and exchange (amine+formamidine acetals)[35] processes. Formamidines derivatives have been used as ligands to prepare complexes of main group metals such as aluminum and gallium.[36]

Scheme 1.2 The frequently followed synthetic protocol for formamidines.



1.3 Aryl 5-amino tetrazoles

The heterocyclic compounds are interesting synthetic organic molecules and tetrazoles are a class of heterocycles with a wide span of applications and currently receiving considerable attention and the literature on tetrazole has been expanding rapidly.[37-38] These tetrazole heterocyclic compounds, contains a 5-member ring of four nitrogen and one carbon atom. The basic structures of 1H-tetrazoles, 5-substituted-1H-tetrazoles, 5-amino-1(Ar)-tetrazoles were shown in the (Figure **1.3**). Tetrazoles are known for a wide scope of biological activity.[39]

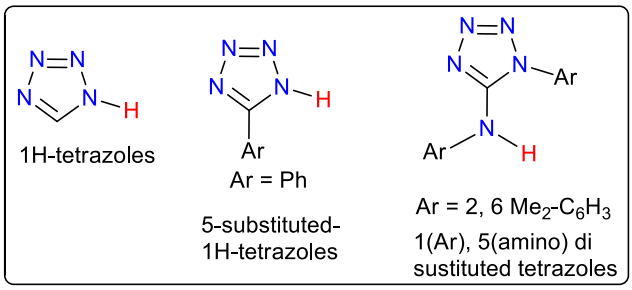


Figure: 1.3 Structures 1H-tetrazoles of 5-substituted-1H-tetrazoles, 5-amino-1(Ar)-tetrazoles

A glut of examples have been reported for the synthesis of tetrazoles the vast majority of which depends on the use of heterocumulenes, nitriles, thioamides, amides, imidoyl chlorides, ketones, amines, and alkenes as the starting material.[40-44] The growing importance of 1, 5-disubstituted tetrazoles in different applications, including as bioactive agents[45] drugs such as cilostazol,

pentylenetetrazole, and latamoxef; and *cis*-amide bond isosteres in peptides, has driven the need for efficient synthetic routes. Direct access to different 1,5-disubstituted tetrazoles is predominantly, possible from amides and thioamides.[46] Other methods include the use of ketones and oximes with suitable azide sources or amidrazones with N_2O_4 or HNO_2.[47] Recently, various methods were developed for the synthesis of 1,5-disubstituted tetrazoles from amides.[45] These methods mainly utilize chlorinating agents to form imidoyl chlorides, and this is then followed by the addition of an azide source to give the disubstituted tetrazoles. Since the availability of diverse amides is limited the synthesis of amides compels an additional step from carbonyl compounds such as acids and acetyl chlorides. Apart from this, the formation of direct amide bond from unactivated acids is challenging.[48] Formation of direct amide bond is favoured in basic conditions, but formation of tetrazole requires acidic conditions through the formation of the imidoyl chloride, and is a tough condition to make one-pot tetrazole synthesis. Also, a one-pot synthesis of tetrazoles from amides is challenging, as hydrogen chloride which is formed in the chlorination step can be harmful to the acid-sensitive functional groups.[49]

1.4 Guanidine

Guanidine is an important organic molecule containing 'CN_3' core, in which carbon atom is sp^2 hybridized and connected to one imine and two amine nitrogen atoms

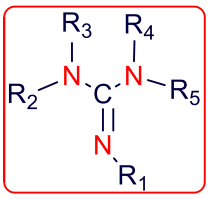


Figure: 1.4.a the structure of guanidine unit

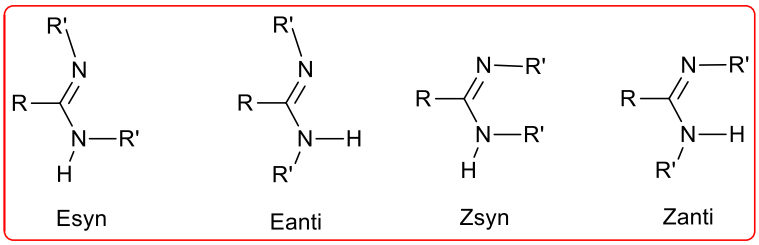


Figure: 1.4.b isomers of tetra substituted guanidines

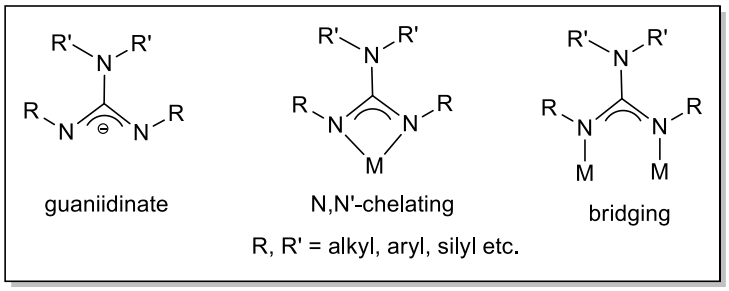


Figure: 1.4.c Coordination modes of guanidinate anions

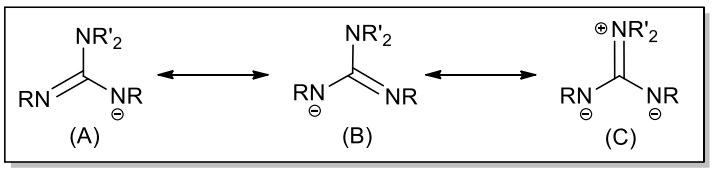


Figure: 1.4.d Resonance forms of guanidinate anions

1.5 Bulky bisguanidines

These are kind of guanidine molecules consisting of two tetra substituted guanidine units in a single molecule connected through piperazine moiety and is show in (Figure **1.5**).

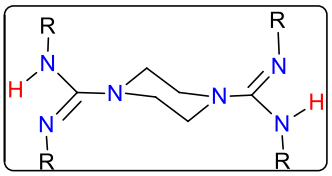
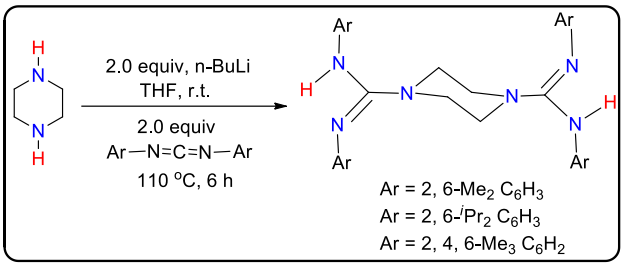


Figure: 1.5 the structure of bulky bis-guanidine unit

Several synthetic procedures are known for the preparation of guanidines.[50-54] the addition of metallated amides to carbodiimides (RN=C=NR), followed by aqueous work-up is one of the

most versatile method (Scheme **1.5)**. It seems that there are no steric and electronic limitations involved in this route but when jones et al attempted the addition of lithiated cis-2,6- dimethyl piperidine, 2,2,6,6-tetramethyl piperidine to ArN=C=NAr (Ar = 2,6-$^{i}Pr_2$-C_6H_3) in THF at reflux these were not successful.[55] Moreover, M [$N(SiMe3)_2$] (M = Li, Na or K) are well known to involve addition reactions to smaller carbodiimides at room temperature, do not react with ArN=C=NAr (Ar = 2,6-$^{i}Pr_2$-C_6H_3) under similar conditions.[56]

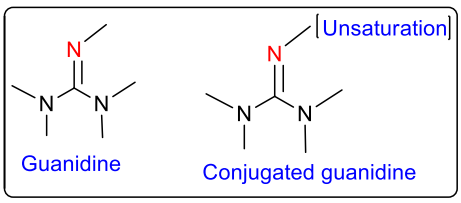
Scheme 1.5 Synthetic protocol for bulky bis-guanidines



1.6 Conjugated bis–guanidine

The systems having conjugation attached to the guanidine units are known as conjugated guanidines. The term "conjugated guanidine function" can be best described as a guanidine function that possess an unsaturation in the alpha–position with respect to the nitrogen (Figure **1.6.a**) of its imine group. "Conjugated guanidine function" carries an unsaturation in the alpha-position with respect to the nitrogen of its imine group.[57]

Figure: 1.6.a guanidine and conjugated guanidine



"Guanidines conjugated to one another" Where the alpha unsaturation of each of the imine groups of the two guanidines are linked to one another in the form of an unsaturated chain allowing conjugation between the two guanidines (Figure **1.6.b)**

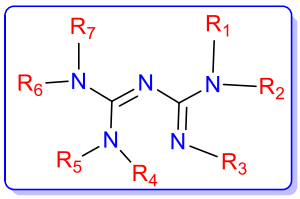


Figure: 1.6.b structure of conjugated bis–guanidine

The term conjugated bis–guanidine is defined as a conjugated structure constitute of five nitrogen atoms, consonant with the following formula' as shown in the (Figure **1.6.c**).

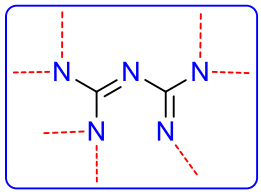


Figure: 1.6.c general formula for conjugated bis–guanidine.

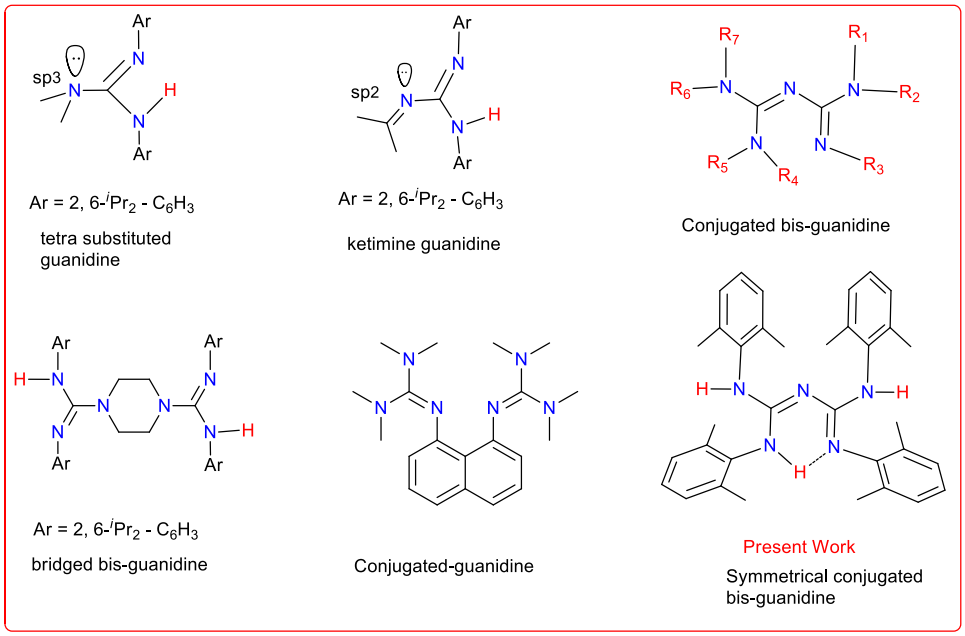


Figure: 1.6.d previous reports on guanidines, bifunctional guanidine, conjugated guanidines and conjugated bis–guanidine.

A.K. Maity et.al in 2015 reported the ketamine-guanidinates and their metal chemistry demonstrating their distinctive contribution the metal chemistry unlike amidinate variants.[58] interestingly, the chemistry of symmetrical conjugated bisguanidines has not been well established, these were first observed as by products by, V. Yu. Kukushkin et.al. In which the phenyl substituted conjugated bisguanidines was the side products.[59] some unsymmetrical alkyl substituted conjugated bisguanidine ligands[1] were documented in 2013. In this aspect we would like to present our efforts to explore much chemistry of these peculiar ligand systems and have been successfully ended up with a convenient synthetic route and some absorbing features in their coordination chemistry towards the lithium, aluminum and gallium metals.

1.7 References

1 A. Williams and I. T. Ibrahim, *Chem. Rev.*, 1981, **81,** 589-636.

2 A. R. Ali, H. Ghosh and B. K. Patel, *Tetrahedron Lett.*, 2010, **51**, 1019-1021.

3 T. Peddarao, A. Baishya, M. K. Barman, A. Kumar and S. Nembenna, *New J. Chem*. 2016, **40**, 7627-7636.

3 A. I. Meyers and R. H. Hutchings, *Tetrahedron.*, 1993, **49**, 1807 - 1820;

4 A. I. Meyers and T. R. Elworthy, *J. Org. Chem.*, 1992, **57**, 4732-4780.

5 V. K. S. Leung, T. Y. K. Chan and V. T. F. Yeung, *Clin. Toxicol.*, 1999, **37**, 513 - 514;

6 A. Nakayama, M. Sukekawa and Y. Eguchi, *Pestic. Sci.*, 1997, **51**, 157 -164;

7 G. D. Baxter and S. C. Barker, *Insect Biochem. Mol. Biol.*, 1999, **29**, 461 - 467;

8 J. I. Moss, *J. Econ. Entomol.,* 1996, **89**, 1151 - 1155;

9 R. W. Beeman and F. Matsumura, *Nature.,* 1973, **242**, 273 – 274.

10 M. Gall, J. M. McCall, R. E. TenBrink, P. F. VonVoigtlander and S. Mohrland, *J. Med. Chem.,* 1988, **31**, 1816-1820.

11 A. Donetti, E. Cereda, E. Bellora, A. Gallazzi, C. Bazzano, P. Vanoni, P. Del Solda-to, R. Micheletti, F. Pagani and A. Giachetti, *J. Med. Chem.,* 1984, **27**, 380-386.

12 M. K. Scott, H. I. Jacoby, J. E. Mills, A. C. Bonfilio and C. R. Rasmussen, *J. Med. Chem.,* 1983, **26**, 535-538.

13 T. Goto, H. Sakashita, K. Murakami, M. Sugiura, T. Kondo and C. Fukaya, *Chem. Pharm. Bull.,* 1997, **45**, 305 - 311;

14 M. Tomizawa and I. Yamamoto, *J. Pestic. Sci.,* 1993, **18**, 91-98.

15 W. H. Hsu and T. J. Kakuk, *Toxicol. Appl. Pharmacol.,* 1984, **73**, 411 – 415.

16 L. G. Costa, G. Olibet and S. D. Murphy, *Toxicol. Appl. Pharmacol.,* 1988, **93**, 319 - 328.

17 L. G. Costa, D. S. Wu, G. Olibet and S. D. Murphy, *Neurotoxicol. Ter-atol.,* 1989, **11**, 405 – 411.

18 S. A. Aziz and C. O. Knowles, *Nature.,* 1973, **242**, 417-418,

19 G. K. Yim, M. P. Holsapple, W. R. Pfister and R. M. Hollingsworth, *Life Sci.,* 1978, **23**, 2509 -2515.

20 D. I. Arnold, F. A. Cotton, J. H. Matonic and C. A. Murillo, *Polyhedron.*, 1997, **16**, 1837-1841.

21 D. B. Mitzi and K. Liang, *J. Solid State Chem.*, 1997, **134**, 376-381.

22 M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas and J.Wang, *Chem. Eur. J.*, 2007, **13**, 8092–8110.

23 R. M. Roberts, *J. Org. Chem.*, 1949, **14**, 277–284.

24 K. M. Kuhn and R. H. Grubbs, *Org. Lett.*, 2008, **10**, 2075–2077.

25 P. C. Junk and M. L. Cole, *Chem. Commun.*, 2007, 1579–1590.

26 A. I. Meyers and R. Hutchings, *Heterocycles.*, 1996, **42**, 475-478.

27 M. A. Matulenko and A. I. Meyers, *J. Org. Chem.*, 1996, **61**, 573-580.

28 S. Vincent, S. Mons, L. Lebeau and C. Mioskowski, *Tetrahedron Lett.*, 1997, **38**, 7527-7530.

29 S. J. Benkovic, T. H. Barrows and P. R. Farina, *J. Am. Chem. Soc.*, 1973, **95**, 8414-8420.

30 P. S. Furth, M. S. Reitman and A. F. Cook, *Tetrahedron Lett.*, 1997, **38**, 54035406.

31 S. Delarue and C. Sergheraert, *Tetrahedron Lett.*, 1999, **40**, 5487-5490.

32 J. Bÿsµn, L. Kulcsµr and M. Kovµcs, *Synthesis.*, 1980, 883-884;

33 Y. Han and L. Cai, *Tetrahedron Lett.*, 1997, **38**, 5423-5426.

34 R. F. Abdulla and R. S. Brinkmeyer, *Tetrahedron.*, 1979, **35**, 1675-1735.

35 A. B. Charette and M. Grenon, *Tetrahedron Lett.,* 2000, **41**, 1677-1680.

36 S. Hamidi, H. M. Dietrich, D. Werner, L. N. Jende, C. Maichle-Mössmer, K . W. Törnroos, G. B. Deacon, P. C. Junk and R. Anwander, *E. J. Inorg. Chem.,* 2013, 2460-2466.

37 R. N. Butler, in Comprehensive Heterocyclic Chemistry II; A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Eds., Pergamon Press: Oxford, 1996, 4, 621, 905.

38 R. N. Butler, in Comprehensive Heterocyclic Chemistry II; A. R. Katritzky, Rees, C. W. Eds., Pergamon Press: Oxford, 1984, 5, 791.

39 S. J. Wittenberger, *Org. Prep. Proced. Int.* **1994**, *26*, 499.

40 M. Malik, M. Wani, S. Al-Thabaiti and R. Shiekh, *J. Inclusion Phenom. Macrocyclic Chem.*, 2014, **78**, 15–37.

41 G. I. Koldobskii, Russ. *J. Org. Chem.*, 2006, **42**, 469–486.

42 R. J. Herr, *Bioorg. Med. Chem.,* 2002, **10**, 3379–3393.

43 V. Y. Zubarev, V. A. Ostrovskii, *Chem. Heterocycl. Compd., (N. Y., NY, U. S.)* 2000, **36**, 759–774.

44 S. J. Wittenberger, *Org. Prep. Proced. Int.*, 1994, *26*, 499–531.

45 A. Sarvary, A. Maleki, *Mol. Diversity.*, **2015**, **19**, 189–212.

46 S. Lehnhoff and I. Ugi, *Heterocycles.,* 1995**, 40**, 801–808.

47 A. R. Katritzky, C. Cai and N. K. Meher, *Synthesis.*, 2007, 1204–1208.

48 C. A. G. N. Montalbetti and V. Falque, *Tetrahedron.,* 2005, **61**, 10827–10852.

49 L. J. Kennedy, *Tetrahedron Lett.,* 2010, **51**, 2010–2013.

50 J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.

51 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403.

52 P. J. Bailey and S. Price, *Coord. Chem. Rev.,* 2001, **214**, 91.

53 M. P. Coles, *Dalton Trans.*, 2006, 985.

54 P. C. Junk and M. L. Cole, *Chem. Commun.,* 2007, 1579.

55 G. Jin, C. Jones, P. C. Junk, K. A. Lippert, R. P. Rose and A. Stasch, *New. J. Chem.*, 2009, **33,** 64-75.

56 Z. Lu, G. P. A. Yap and D. S. Richeson, *Inorg. Chem.,* 1999, **38**, 5788.

57 V. Gaud and F. Rouge, US8530544 B2, September 10, 2013.

58 A. K. Maity, J. Alejandro, M. Magana and S. Fortier, *Inorg.Chem.,* 2015, **54**, 10030−10041.

59 P. V. Gushchin, M. R. Tyan, N. A. Bokach, M. D. Revenco, M. Haukka, M. J. Wang, C.H. Lai, P. T. Chou and V. Y. Kukushkin, *Inorg. Chem.,* 2008**, 47***,* 11487-11500.

Chapter 2

Metal-free access of bulky *N, N'*-diarylcarbodiimides and their reduction: Bulky *N, N'*-diarylformamidines.

Abstract

A metal-free synthesis of symmetrical and unsymmetrical bulky *N,N'*-diaryl carbodiimides from the dehydrosulfurisation of corresponding *N,N'*-diarylthiourea with 4-dimethylaminopyridine (DMAP) and iodine at mild reaction conditions with moderate to excellent yields was established. In the literature, the classical method of dehydrosulfurisation of bulky *N,N'*-diarylthiourea to *N,N'*-diarylcarbodiimide was reported by using toxic metal oxide (HgO) and magnesium sulphate ($MgSO_4$) at harsh reaction conditions. Further, an easy access of 1, 3-disubstituted symmetric and unsymmetrical *N, N'* -diaryl formamidines that involves reaction of symmetrical and unsymmetrical *N, N'* -diaryl carbodiimides with sodium borohydride is described. The widely used method for the preparation of bulky *N, N'* -diaryl formamidines is the treatment of primary amine with triethylorthoformate in the presence of acid at high temperature reaction conditions.

Introduction

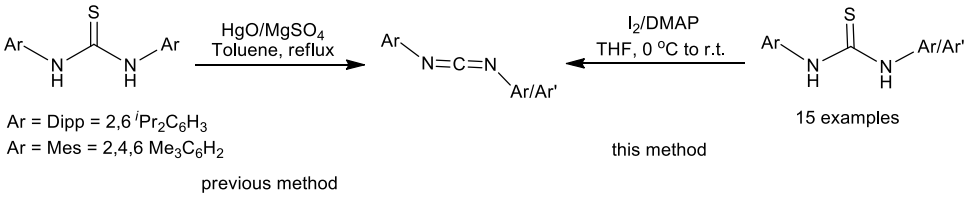
Carbodiimides (CDIs) are a special class of reactive organic compounds containing N=C=N core. In the structure of CDI *i.e.*, R–N=C=N–R, the substituent R can be alkyl, aryl, acyl etc.,[1] many alkyl CDIs such as dicyclohexylCDI (DCC), diisopropyl CDI (DICD) etc., are commercially available and widely used in organic synthesis, in particular**,** as dehydrating agents in the synthesis of lactams, antibiotics, nucleotides and peptides.[2] On the other hand, commercial availability of bulky *N,N'*-diaryl CDIs is very limited. Both alkyl and aryl CDIs, particularly bulky *N,N'* –diaryl CDIs are most important precursors for the preparation of variety of N-donor

ligands, metal complexes and other applications.[3] For instance, compound **1a** (vide infra) (**1a** = DippN=C=NDipp; (Dipp = 2,6-$^{i}Pr_2$-C_6H_3) (vide infra), has been utilized by several research groups for the synthesis of ligands, metal complexes and other applications.[4] And also, *N, N'*-di(2, 6-diethylphenyl) CDI used as a stabilizer for polyester based polyurethanes.[1] In this context, we have previously reported metal-free synthesis of library of bulky guanidines by the reaction of cyclic secondary amines with bulky aryl CDIs and air stable "NHC-CDI" adducts (zwitterions) by the direct addition of N-heterocyclic carbenes (NHCs) to *N,N'* -diaryl CDIs.[5] Thus, it is very clear that bulky *N,N'*-diaryl CDIs are academically as well as industrially very important organic molecules.

Preparation of carbodiimides can be broadly classified into a) dehydrosulfurisation of 1,3 di-substituted thioureas b) from isocyanates or isothiocyanates c) dehydration of ureas d) from cyanamides e) nitrenes rearrangement f) haloformates and thermolysis reactions.[1] Among all methods mentioned above, the classical method of preparation of aryl CDIs is the dehydrosulfurisation of thiourea. And also, in recent years there have been reports on metal catalyzed synthesis of CDIs[6] and this method of synthesis is restricted to only unsymmetrical CDIs (unsymmetrical; R≠R and symmetrical; R=R, in the structure of R–N=C=N–R). However, very recently Ji and Wang et al. reported metal-free synthesis of CDIs by I_2/CHP (cumene hydroperoxide) mediated cross coupling of isocyanides with amines.[7] This is a very attractive method for the synthesis of CDIs but shows poor yields for *N,N'*-diaryl CDIs. Actually, we were inspired by the work of Patel and co-workers,[8] *i.e.,* greener protocol for the preparation of CDIs, in which authors reported 15 examples of aryl CDIs *via* dehydrosulfurisation of thiourea in the presence of triethylamine/iodine in mild reaction conditions. This synthetic route is effectively

employed to prepare both symmetrical (R-N=C=N-R; R= p-tolylphenyl) and unsymmetrical (N-(2,6- dimethylphenyl)-N'-(phenyl)) CDIs. It would also be quite attractive for the syntheses of bulky aromatic CDIs with ortho-substituted aromatic substituent's, but in these cases the reported yields are lower (*vide infra*). In 2010, Akamanchi and co-workers reported o-iodoxybenzoic acid (IBX) mediated oxidative desulfurisation of 1,3- disubstituted thioureas to carbodiimides.[9] Recently, Nakazava and co-workers reported dehydrogenative desulfurisation of thiourea derivatives to produce CDIs by using hydrosilane and an iron complex.[10] In 2007, Cowley et al. reported the synthesis of two examples of bulky aryl CDIs such as DippN=C=NDipp and MesN=C=NMes (Mes=2,4,6-$Me_3C_6H_2$) *via* dehydrosulfurisation of thioureas in the presence toxic HgO and anhydrous $MgSO_4$ in refluxing toluene (Scheme 2.1).[11] Very recently, Fortier and co-workers reported "super bulky" CDI from dehydration of urea derivative in the presence of P_2O_5/Al_2O_3 in pyridine at 115 ^oC.[12] To the best of our knowledge there have been no reports on metal-free synthesis of bulky *N,N'*-diaryl CDIs.

Scheme 2.1 Synthesis of bulky *N, N'*-diaryl CDIs.



In recent years there is a growing interest in the usage of 1,3 di-substituted *N,N'*-diarylformamidines (FormHs) as ligands in organometallic chemistry as well as catalysis due to their unique properties.[13] More importantly, *N,N'*-diaryl FormHs are air and moisture stable and ideal precursors for the preparation cyclic formamidiniums,[14] these salts can be converted into neutral NHCs upon treatment with base. Thus, *N,N'*-diaryl FormHs are very important organic

molecules, which are less sensitive toward hydrolysis than their alkyl substituted congeners. Steric and electronic properties of 1,3 di-substituted diaryl FormHs can be tuned in a wide range by changing the substituent's on the aryl rings. The general formula RN=C(R')NHR R' = H formamidines, CH_3 amidines and NR_2 guanidine type of ligands; of which bulky amidine and guanidine type ligand systems can be prepared by insertion of metal reagents into CDIs and followed by aqueous work up.[15] In contrast, the general method of synthesis of bulky aryl symmetric FormHs is the treatment of aryl amines with triethylorthoformate in the presence of catalytic amount of glacial acetic acid at reflux temperature. This simple method of synthesis was first reported by Roberts in 1949.[16] Unsymmetrical FormHs could also be accessed by the slight modification of the procedure.[14k] Moreover; there have been several reports on preparation of formamidines in the literature. [17] However, the widely employed method of preparation for bulky *N,N'*-diaryl FormH is the treatment of aryl amines with triethylorthoformate in the presence of catalytic amount of glacial acetic acid at reflux temperature.[18] To the best of our knowledge, there have been no reports on the hydrogenation or reduction of symmetrical and unsymmetrical bulky *N,N'*-diaryl CDIs to produce symmetrical and unsymmetrical bulky aryl FormHs. Although, in the year 1978, Yamada and co-workers reported the reduction of alkyl carbodiimides by using sodium borohydride to produce FormHs.[19]

Herein we report a metal-free and facile synthesis of 15 examples of symmetrical and unsymmetrical bulky *N,N'*-diaryl CDIs in good to excellent yields in grams scale. This was achieved by the dehydrosulfurisation of corresponding thioureas by using a dimethylaminopyridine (DMAP) as a base and iodine as a thiophilic agent in THF at mild reaction conditions. Furthermore, reduction of these CDIs with commercially available reducing agent $NaBH_4$ in ethanol afforded bulky *N,N'*-diaryl formamidines in excellent yields.

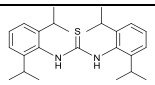
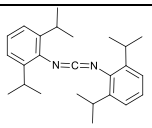
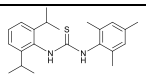
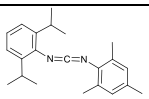
Syntheses of bulky *N,N*'-diaryl carbodiimides

Various symmetrical and unsymmetrical bulky *N,N'*-diaryl thiourea precursors have been utilized for the preparation of bulky *N,N'*-diaryl CDIs and synthesized by following literature methods. Symmetrical *N,N'*-diaryl thioureas were synthesized by the reaction of drop wise addition of carbon disulphide to a solution of aromatic amine and triethylamine in water/acetonitrile,[11, 20] while unsymmetrical *N,N'*-diaryl thioureas were synthesized by the treatment of aryl isothiocyanate with aromatic amine in acetonitrile.[21]

Our investigation began with dehydrosulfurisation of bulky *N,N'*-diaryl thiourea *i.e,* DippN(H)C=SN(H)Dipp (Dipp = 2,6-*i*Pr_2-C_6H_3) by using two equivalents of triethylamine as base and iodine as a thiophilic agent in THF at room temperature conditions. In this case, after work up we were able to isolate 52% yield of corresponding CDI (DippN=C=NDipp) product. The formation of the desired product in the lesser yield might be due to the steric crowding revealed by the two bulky isopropyl substituents from the adjacent ortho positions of aryl groups which may be hampered the deprotonation by the hindered triethylamine base. Next, we chose pyridine (pKa 5.2) as a base, since it is less steric in nature in comparison to triethylamine and performed the reaction maintaining the same reaction conditions along with iodine. We isolated the desired product of CDI in only 37%; this is due to the less basicity of pyridine in comparison to triethylamine (pKa 10.8). Further, dehydrosulfurisation of DippN(H)C=SN(H)Dipp, thiourea derivative was performed using two equivalents of DMAP (pKa 9.7) as a base and one equivalent of iodine at identical reaction conditions, DMAP is a stronger base in comparison to pyridine. To our delight, we successfully isolated the desired CDI product in 90% yield (Table 2.1, entry 3). More importantly, we scale up the reaction up to 8 grams of the bulky thiourea precursor, in which it is observed that a very marginal difference in the isolated yield.

Next, instead of iodine, diiodomethane and diiodoethane were utilized as thiophilic agents for the dehydrosulfurisation of DippN(H)C=SN(H)Dipp and DMAP as base at identical reaction conditions. We noticed the formation of DippN=C=NDipp in 27% (Table **2.1**, entry **4**) and 80% (Table **2.1**, entry **5**) yields, when we employ diiodomethane and diiodoethane as thiophilic agents, respectively.

Table 2.1 Screening of base and thiophilic agent for the dehydrosulfurisation of symmetrical and unsymmetrical thiourea[a,b]

Entry	Thiophilic agent/Base	Substrate	Product	Isolate yield (%)[b]
1	I_2/NEt_3			52
2	I_2/Py			37
3	**I_2/DMAP**			**90**
4	ICH_2I/DMAP			27
5	**ICH_2CH_2I/DMAP**			**80**
6	I_2/NEt_3			50
7	I_2/Py			54
8	**I_2/DMAP**			**89**
9	ICH_2I/DMAP			25
10	**ICH_2CH_2I/DMAP**			**77**

[a] All reactions were performed using 1 equiv. corresponding thiourea (1.0 g), 1. equiv. thiophilic agent and 2 equivs. base in THF; temperature: r.t. and reaction time: 1h [b]Isolated yield

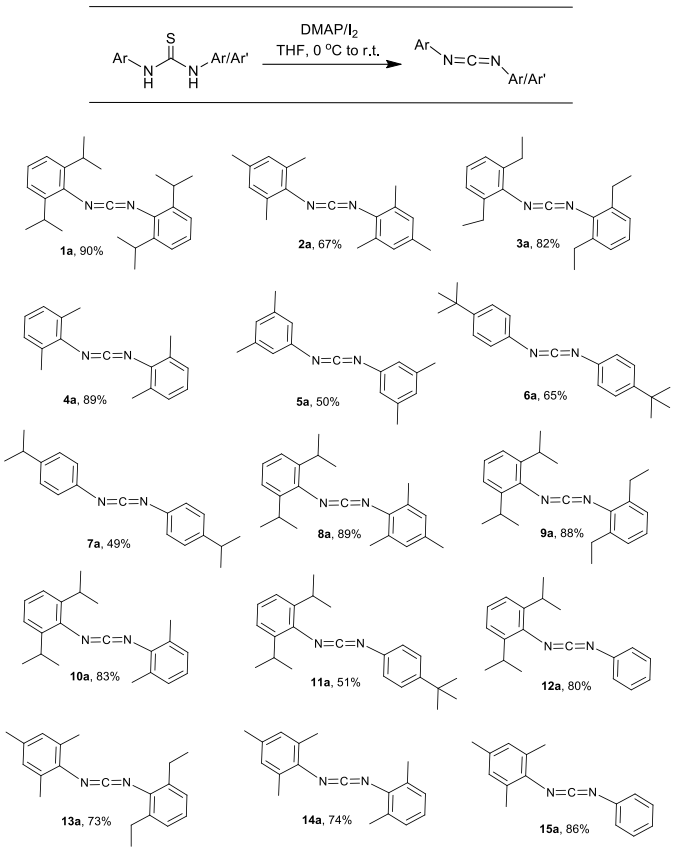
Furthermore, we extended this screening of base and thiophilic agent for the dehydrosulfurisation of unsymmetrical thiourea derivative. For this, we chose DippN(H)C=SN(H)Mes as a precursor and followed the same procedures as described in the above case. From table 2.1 (entries **1-10**), it is very clear that dehydrosulfurisation of both

symmetrical and unsymmetrical thioureas can be effectively performed by using two equivalents of DMAP as base and one equivalent of iodine as a thiophilic agent in THF at room temperature conditions (Table **2.1**, entries **3** and **8**). Dehydrosulfurisation of DippN(H)C=SN(H)Dipp using DMAP/I_2 as base and thiophilic agent was also carried out in different solvents such as ethyl acetate, dichloromethane, and acetonitrile. DippN=C=NDipp was isolated in each case less than 90% yield (Table **2.1**, entry **3**), which indicates that THF is a better solvent for the dehydrosulfurisation of bulky *N,N'*-diarylthiourea. This is due to the better solubility of bulky thoiurea in THF solvent in comparison to other solvents. Further, we extended our studies to dehydrosulfurisation of various less to more bulky symmetrical and unsymmetrical thioureas using DMAP/I_2 to obtain corresponding symmetrical and unsymmetrical diaryl CDIs (Table **2.2**). It is worthy to mention that the reaction of dehydrosulfurisation of [CyN(H)C=SN(H)Cy; (Cy= cyclohexyl)] using DMAP/I_2 in THF to obtain dicyclohexyl carbodiimide (DCC) was attempted; however, we noticed very trace of formation of the desired product.

As can be seen from the table **2.2**, symmetrical CDIs bearing bulky substituent's at their ortho positions of the aryl groups **1a**, **3a**, and **4a** isolated in excellent yields (>82%), while compound **2a** isolated in 67% yield. However, CDI bearing methyl substituents at their adjacent meta positions of the aryl groups yielded in only 50%. And also, CDIs bearing bulky substituents such as tert-butyl (**6a**) and isopropyl (**7a**) groups at their para positions were yielded in 65% and 49%, respectively. Unsymmetrical CDIs are concerned, except compound (2, 6-di-isopropyl-phenyl) - (p-tert-butyl-phenyl)–carbodiimide **11a,** which is isolated in 51% yield, remaining all compounds (2, 6-di-isopropyl-phenyl) - (2, 4, 6-tri-methyl-phenyl) –carbodiimide (**8a;** 89%), 2, 6-di-isopropyl-phenyl) - (2, 6-di-ethyl-phenyl)-carbodiimide (**9a**; 88%), (2, 6-di-isopropyl-phenyl) - (2, 6-di-methyl-phenyl) –carbodiimide, (**10a,** 83%), (2, 6-di-isopropyl-phenyl)-phenyl-

carbodiimide,(**12a**; 80%), (2, 4, 6-tri-methyl-phenyl) - (2, 6-di-ethylphenyl) –carbodiimide, (**13a**; 73%), (2, 4, 6-tri-methyl-phenyl)-(2, 6-di-methyl-phenyl)–carbodiimide,(**14a**; 74%) and (2, 4, 6-tri-methyl-phenyl) - phenyl-carbodiimide(**15a**; 86%) were isolated in very good yields.

Table 2.2 Synthesis of symmetrical and unsymmetrical *N,N'*-diaryl CDIs[a,b]



[a] All reactions were performed using 1 equiv. corresponding thiourea (4.0 g scale), 1. equiv. I_2 and 2 equivs. DMAP in THF
[b]Isolated yield

All these symmetrical and unsymmetrical bulky *N,N'*-diaryl CDIs were characterized by ^1H, ^{13}C, IR and mass spectrometry analyses. The ^1H NMR spectra for compounds **1a-15a** exhibit expected resonances and complete disappearance of N-H protons were observed. ^{13}C NMR spectra show that sp hybridized carbon atom of N=C=N core resonate in the range 134 -148 ppm for symmetrical CDIs and for unsymmetrical CDIs resonate at 136- 147 ppm. These bulky aryl

unsymmetrical CDIs are colorless liquids, while symmetrical CDI are low melting solids and melt in the range 32- 64 ^{o}C. Attempts to prepare extremely bulky *N,N'*-diaryl CDIs are failed, due to the unsuccessful in the preparation of corresponding thiourea precursors.

The proposed mechanism for the formation of *N,N'*-diaryl CDI is depicted in Figure 2.1. The dehydrosulfurisation of thiourea was achieved by using two equivalents of DMAP as base and one equivalent of iodine as thiophilic agent. $DMAPH^{+}I^{-}$ and solid sulfur are side products in this reaction. Sulfur can be easily separated from the desired product by filtration, while DMAP salt removed by column chromatography.

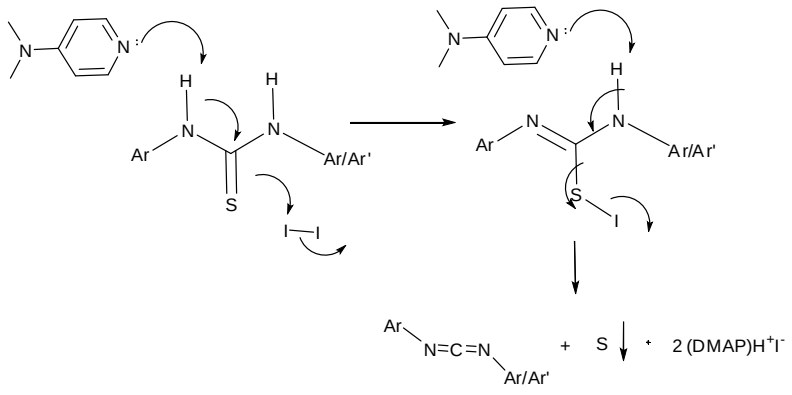


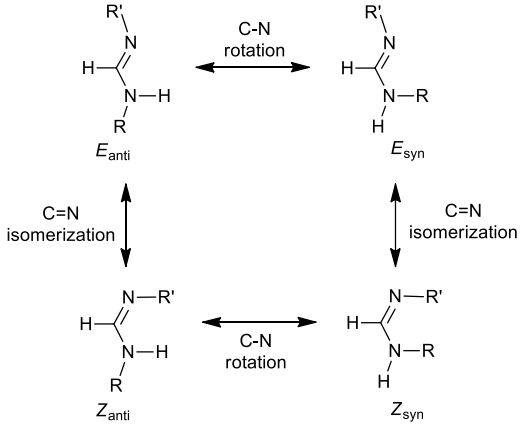
Fig. 2.1 Proposed mechanism for formation of CDI

Reduction of bulky *N,N*'-diaryl carbodiimides: *N,N'*-Diaryl formamidines

Bulky *N,N'*-diaryl CDIs are important precursors for the preparation of variety of bulky N-donor ligand systems such as amidines, guanidine's etc. Bulky amidines and guanidines are used as ligands to construct metal complexes across the periodic table. We have previously shown that these CDIs are ideal precursor for the metal-free synthesis of bulky guanidines that was achieved by the treatment CDIs with secondary cyclic amines.[5a] Very recently, we reported a library of air stable symmetrical and unsymmetrical "NHC-CDI" adducts *i.e,* zwitterions by the direct addition

of NHC to CDIs.[5b] Surprisingly, there have been no reports on the hydrogenation of bulky *N,N'*-diaryl CDIs to produce corresponding FormHs. In view of this, herein we report 10 examples of symmetrical and unsymmetrical FormHs by the reduction of corresponding CDIs. Several symmetrical and unsymmetrical bulky aryl FormHs were isolated in excellent yields (76-98%) by employing simple, straightforward and facile reaction conditions. This was achieved by the reduction of corresponding CDIs with commercially available sodium borohydride in ethanol at ambient reaction temperature. All compounds **(1b-10b)** were characterized by ^{1}H and ^{13}C NMR spectroscopic analyses. For compounds **1b-10b**, they display complicated ^{1}H and ^{13}C NMR spectra. As we described in the introduction section, *N,N'*-diaryl formamidines are widely used in the coordination chemistry, however, their accurate NMR spectra rarely appeared in the literature, due to their complex NMR spectra.[14d] This complexity arises from the presence of more than one isomer in the solution state (Scheme **2.2**).[5a] However, purity of these compounds was confirmed by high performance liquid chromatography (HPLC) analysis.

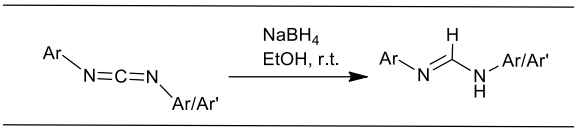
Scheme 2.2 Possible four isomers of formamidines in solution

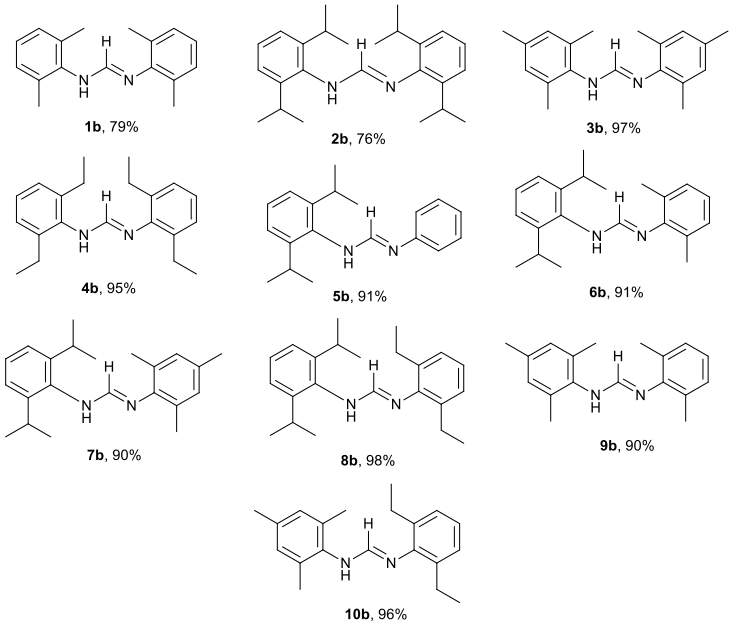


As can be seen from Table 2.3, four symmetrical (**1b-4b**) and six unsymmetrical (**5b-10b**) bulky aryl formamidines were synthesized. However, compounds 1, 3- di (p-tert-butyl-phenyl) carbodiimide (**6a**) and 1, 3- di (p-isopropyl-phenyl) carbodiimide (**7a)** were treated with sodium

borohydride in ethanol, independently to obtain corresponding FormHs. Unfortunately, we did not isolate the desired products–such as–*N*,*N*′-bis (4-tert-butyl-phenyl) formamidine and *N*,*N*′-bis (4-isopropyl-phenyl) formamidine compounds, because several spots were observed in the thin layer chromatography.

Table 2.3 Reduction of symmetrical and unsymmetrical *N,N'*-diaryl CDIs[a,b]





[a] All reactions were performed using 1 equiv. CDI (1.0 g scale) and 1.1 equiv. $NaBH_4$ in ethanol at room temperature

[b]Isolated yield.

Crystallographic information.

Compound **4a** was characterized by single crystal X-ray structural analysis. It crystallizes in the monoclinic space group $P2_1/c$. The molecular structure is depicted in Figure **2.2**. The N2–C1–N1 bond angle is 170.1(2) (º), which deviates from the linearity value 180 (º). The average N–C bond distance in N=C=N core of 1.201(2) Å (**4a**) is well in agreement with Mes and Dipp substituted CDIs (average C–N bond distance1.215 (10) Å).[10]

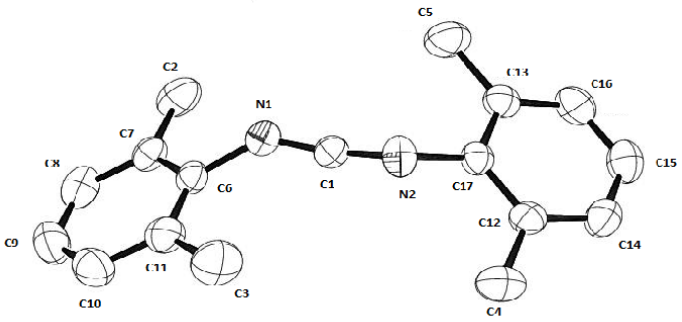


Fig. 2.2 Molecular structure of **4a** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (**º**): N2–C1 1.197(2), N1–C1 1.208(2), N1–C6 1.414(2), N2–C17 1.412(2); N2–C1–N1 170.1(2)

Experimental section

General Information: All reactions were performed in an open atmosphere. Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Spectrochem and used as received unless otherwise stated. Column chromatography and TLC were performed on silica gel (100-200) and

using UV light. ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AV-400 (^{1}H: 400 MHz, $^{13}C\{^{1}H\}$: 100.6 MHz) and were referenced to the resonances of the solvent used. IR Spectra were recorded in Perkin-Elmer FT-IR Spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer. Melting points were taken on an electro thermal apparatus and are uncorrected. All symmetrical and unsymmetrical 1,3-disubstituted thioureas were synthesized according to the literature procedures.[11,20,21] The purity of formamidines was determined by high pressure liquid chromatography (HPLC) with a C18 Agilent ZORBAX GF-450 Eclipse XDB column. Analytical HPLC was performed on an Agilent Technologies 1200 Series (Quaternary Pump) system equipped with a UV detector set at 254nm. Compounds were dissolved in acetonitrile. The following eluent system was used: (70% *n*-hexane/30% isopropanol). HPLC retention times (HPLC tR) were obtained at flow rates of 1 mL/min using a isocratic run.

X-ray crystallographic details

The crystal data for the compound **4a** has been collected on a Bruker SMART CCD diffractometer (MoKα radiation, λ = 0.71073 Å). The structure was solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[22]Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

General procedure for the synthesis of symmetrical and unsymmetrical *N,N'*-diarylcarbodiimides

All reactions were performed by using 4 grams of corresponding 1,3-disubstituted aryl thiourea. The corresponding thiourea 1.0 (equiv.) was dissolved in THF (around 50-80 mL) to this dimethylaminopyridine (DMAP) 2.0 (equiv.) was added. The reaction mixture was cooled to 0 ^{o}C to this iodine 1.1 (equiv.) was added in portions. Once the addition of iodine was completed, allows the reaction mixture to warm to room temperature and continued the stirring for two hours. During this period, progress of the reaction was monitored by thin layer chromatography, once complete consumption of the thiourea was occurred, the reaction mixture was filtered and washed with *n*-hexane (150 mL); the solvent was removed in vacuum. The compound was purified by column chromatography with silica gel in 100% *n*-hexane.

Characterization of CDIs (**1a-15a**)

1, 3- Bis(2, 6- di-isopropyl-phenyl)carbodiimide **(1a)**[11]**.** (Yield: 3.29 g, 9.07 mmol, 90%); m.p. 45-50 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.14 (s, 6H, Ar*H*), 3.50 (m, 4H, C*H* $(CH_3)_2$), 1.29 (d, J = 8 Hz, 24H, CH $(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 142.9 (N*C*N), 133.3 (Ar-*C*), 124.9 (Ar-*C*), 123.3 (Ar-*C*), 29.2 Ar*C*H$(CH_3)_2$, 23.3 ArCH(*C*$H_3)_2$. IR (KBr): ν (cm^{-1}): 3224s, 2920m, 2732m, 2162(C=N)m, 1731s, 1583m, 1470m, 1376m, 1209m, 1146m, 1032m, 956m, 936m, 853m, 769s, 725m, 602s, 537m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{35}N_2$ 363.2795; found: 363.2806.

1, 3- Bis(2, 4, 6- trimethylphenyl) carbodiimide **(2a)**[11]**.** (Yield: 2.38g, 8.576 mmol, 67%); m.p. 40-48 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 6.84 (s, 4H, ArH), 2.34 (s, 12H, *o*-C*H*$_3$), 2.25 (s, 6H, *p*-C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, 25^{o}C): δ 134.0 (N*C*N), 133.4 (Ar-*C*), 132.5 (Ar-*C*), 129.0 (Ar-*C*), 20.8 (*C*H$_3$), 18.9 (*C*H$_3$). IR (KBr): ν (cm^{-1}):3224s, 2920m, 2732m, 2162(C=N)m,

1731s, 1583m, 1470m, 1376m, 1209m, 1146m, 1032m, 956m, 936m, 853m, 769s, 725m, 602s, 537m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{24}N_2$ 279.1856; found: 279.1861.

1, 3- Bis (2, 6- diethyl-phenyl) carbodiimide (**3a).** (Yield: 2.95g, 9.63 mmol, 82%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.09 – 7.05 (m, 6H, Ar*H*), 2.80 (q, *J* = 7.5 Hz, 8H, C*H*$_2$(CH_3), 1.27 (t, *J* = 7.5 Hz, 12H, CH_2(C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 138.8 (N*C*N), 134.5 (Ar-*C*), 126.6 (Ar-*C*), 124.8 (Ar-*C*), 25.8 (*C*$H_2$$CH_3$), 14.7 ($CH_2$*C*$H_3$). IR (KBr): ν (cm^{-1}): 2966m, 2932m, 2163(C=N)m, 1588m, 1450m, 1284m, 1267m, 1215m, 1180m, 1116m, 1101m, 1016, 837m, 661m, 594m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{27}N_2$ 307.2169; found: 307.2185.

1, 3- Bis(2, 6- dimethylphenyl) carbodiimide (**4a)**[20]**.** (Yield: 3.13g, 12.516 mmol, 89%); m.p. 44-53 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.03 (d, *J* = 8 Hz, 4H, Ar*H*), 6.94 - 6.97 (m, 2H, Ar*H*), 2.4 (s, 12H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 135.9 (N*C*N), 132.8 (Ar-*C*), 128.3 (Ar-*C*), 124.5 (Ar-*C*), 19.0 (*C*H_3). IR (KBr): ν (cm^{-1}): 2942s, 2914m, 2205m, 2164(C=N) m, 2106s, 1588m, 1466m, 1262m, 1192m, 1090m, 917m, 769s, 729m, 664s, 582m. HRMS (ESI/TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{19}N_2$ 251.1543; found: 251.1544.

1, 3- Bis(3, 5- dimethylphenyl) carbodiimide (**5a)**[6i]**.** (Yield: 1.760 g, 7.03 mmol, 50%); m.p. 45-49 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 6.81 (s, 6H, Ar*H*), 2.30 (s, 12H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, 25^{o}C): δ 139.3 (N*C*N), 138.4 (Ar-*C*), 135.9 (Ar-*C*), 127.4 (Ar-*C*), 121.9 (Ar-*C*), 21.2 (*C*H_3). IR (KBr): ν (cm^{-1}): 2942s, 2914m, 2205m, 2164(C=N)m, 2106s, 1588m, 1466m, 1262m, 1192m, 1090m, 917m, 769s, 729m, 664s, 582m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{19}N_2$ 251.1543; found: 251.1567.

1, 3- Di (p-tert-butyl-phenyl) carbodiimide (**6a).** (Yield: 2.34g, 7.635 mmol, 65%); m.p. 64-69 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.11 (d, J = 8 Hz, 4H, Ar*H*), 7.4 (d, J = 8 Hz, 4H, Ar*H*), 1.32(s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 148.8 (N*C*N), 135.9 (Ar-*C*), 126.5 (Ar-*C*), 123.8 (Ar-*C*), 34.6 (*C*(CH$_3$)$_3$), 31.4 (*C*(CH$_3$)$_3$). IR (KBr): ν (cm^{-1}): 2965m, 2128(C=N)m, 1601m, 1508m, 1363m, 1284m, 1267m, 1215m, 1180m, 1116m, 1101m, 1016, 837m, 661m, 594m. HRMS (ESI-TOF-Q) *m/z*: [M+H] $^{+}$ calcd. for $C_{21}H_{27}N_2$ 307.2169; found: 307.2202.

1, 3- Di (p-isopropyl-phenyl) carbodiimide (**7a).** (Yield: 1.74 g, 6.27 mmol, 49%); m.p. 50-58 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.18 (d, J = 8.4 Hz, 4H, Ar*H*), 7.12 – 7.09 (m, 4H, Ar*H*), 2.9 (m, 2H, C*H*(CH$_3$)$_2$), 1.24 (d, J = 8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 146.5 (N*C*N), 136.2 (Ar-*C*), 127.5 (Ar-*C*), 124.1 (Ar-*C*), 33.8 (*C*H(CH$_3$)$_2$), 24.1 (*C*H(CH$_3$)$_2$). IR (KBr): ν (cm^{-1}): 3219s, 2961m, 2147(C=N) m, 1895m, 1603m, 1575m, 1505m, 1275m, 1208, 1174m, 1101m, 1054, 1017m, 833m, 729m, 643m, 597m. HRMS (ESI-TOF-Q) *m/z*: [M+H]$^{+}$ calcd. for $C_{19}H_{23}N_2$ 279.1856; found: 279.1867.

(2, 6-Di-isopropyl-phenyl) - (2, 4, 6-Tri-methyl-phenyl) –carbodiimide (**8a).** (Yield: 3.21 g, 10.04mmol, 89%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.16 (s, 3H, Ar*H*), 6.89 (s, 2H, Ar*H*), 3.5 (m, 2H, C*H*(CH$_3$)$_2$), 2.41 (s, 6H, (C*H*$_3$), 2.31 (s, 3H, (C*H*$_3$), 1.31 (d, J = 8 Hz, 12H, CH(C*H*$_3$)$_2$. ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 142.8 (N*C*N), 133.9 (Ar-*C*), 133.5 (Ar-*C*), 133.4 (Ar-*C*), 132.4 (Ar-*C*), 128.9 (Ar-*C*), 127.4 (Ar-*C*), 125.0 (Ar-*C*), 123.4 (Ar-*C*), 29.1 (*C*H(CH$_3$)$_2$, 23.4 (CH(*C*H$_3$)$_2$), 20.8 (CH(*C*H$_3$)$_2$), 18.9 *C*H$_3$. IR (KBr): ν (cm^{-1}): 3227m, 2963m, 2169(C=N)m, 1921m, 1858m, 1589m, 1454m, 1363m, 1323m, 1257m, 1186m, 1159m,

1096m, 1059m, 1040m, 934m, 853m, 794m, 767m, 749m, 730m, 666m, 595m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{29}N_2$ 321.2325; found: 321.2367.

(2, 6-Di-isopropyl-phenyl) - (2, 6-Di-ethyl-phenyl)-carbodiimide **(9a).** (Yield: 3.194 g, 9.55 mmol, 88%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.13 (s, 3H, Ar*H*), 7.06 (q, *J* = 4.2 Hz, 3H, Ar*H*), 3.47 (m, 2H, (C*H* (CH_3)$_2$), 2.81 (q, *J* = 7.5 Hz, 4H, *C*H_2(C*H*$_3$)), 1.28 (dd, *J* = 7.2, 2.1 Hz, 18H, (C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 142.9 (N*C*N), 138.7 (Ar-*C*), 134.6 (Ar-*C*), 133.2 (Ar-*C*), 126.6 (Ar-*C*), 125.9 (Ar-*C*), 125.1 (Ar-*C*), 124.7 (Ar-*C*), 123.4 (Ar-*C*), 29.2 (*C*H(CH_3)$_2$), 25.8 *C*H_2(CH_3), 23.3 (CH(*C*H_3)$_2$), 14.6 (CH_2(*C*H_3)). IR (KBr): ν (cm^{-1}): 3234m, 3063m, 2923m, 2167(C=N) m, 1921m, 1857m, 1587m, 1454m, 1363m, 1324m, 1256m, 1182m, 1101m, 1060m, 1041m, 934m, 872m, 795m, 749m, 593m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{31}N_2$ 335.2409; found: 335.240.

(2, 6-Di-isopropyl-phenyl) - (2, 6-Di-methyl-phenyl) -carbodiimide (**10a).** (Yield: 2.987g, 9.749 mmol, 83%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.13 (s, 3H, Ar*H*), 7.04 (d, *J* = 7.4 Hz, 2H, Ar*H*), 6.97 – 6.95 (m, 1H, Ar*H*), 3.45 (m, 2H, C*H*(CH_3)$_2$), 2.40 (s, 6H, (C*H*$_3$)), 1.27 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 142.9 (N*C*N), 136.2 (Ar-*C*), 133.2 (Ar-*C*), 132.6 (Ar-*C*), 128.3 (Ar-*C*), 127.1 (Ar-*C*), 125.2 (Ar-*C*), 124.3 (Ar-*C*), 123.4 (Ar-*C*), 29.2 (*C*H(CH_3)$_2$), 23.4 (CH(*C*H_3)$_2$), 19.0 (*C*H_3). IR (KBr): ν (cm^{-1}): 3226m, 2962m, 2158(C=N) m, 1590m, 1454m, 1323m, 1258m, 1184m, 1095m, 1060m, 934m, 795m, 766m, 749m, 666m, 594m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{27}N_2$ 307.2169; found: 307.2203.

(2, 6-Di-isopropyl-phenyl) - (p-tert-butyl-phenyl)–carbodiimide (**11a).** (Yield: 1.85 g, 5.534 mmol, 51%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.35 - 7.33 (m, 2H, Ar*H*),

7.14 (d, *J* = 4 Hz, 3H, Ar*H*), 7.13 - 7.07 (m, 2H, Ar*H*), 3.41 (m 2H, C*H*(CH_3)$_2$), 1.32 (s, 9H, C(C*H*$_3$)$_3$), 1.27 (d, *J* = 6.8 Hz, 12H, CH (C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 147.7 (N*C*N), 142.8 (Ar-*C*), 137.2 (Ar-*C*), 132.6 (Ar-*C*), 130.2 (Ar-*C*), 126.5 (Ar-*C*), 125.7(Ar-*C*), 123.4(Ar-*C*), 123.3 (Ar-*C*), 34.5 (*C*(CH_3)$_3$), 31.5 (C(*C*H$_3$)$_3$), 29.4 *C*H(CH_3)$_2$, 23.3 CH(*C*H$_3$)$_2$. IR (KBr): ν (cm^{-1}): 3226m, 3068m, 3030m, 2961m, 2166(C=N) m, 1589m, 1574m, 1470m, 1362s, 1324s, 1257m, 1244m, 1203s, 1179m, 1113m, 1073m, 1041m, 934m, 834m, 795m, 749m, 666m, 594m 551s. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{31}N_2$ 335.2482; found: 335.2503.

(2, 6-Di-isopropyl-phenyl)-phenyl-carbodiimide (**12a**)[21]**.** (Yield: 2.85 g, 10.24 mmol, 80%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.37 – 7.33 (m, 2H, Ar*H*), 7.20 – 7.17 (m, 5H, Ar*H*), 7.14 (d, *J* = 8 Hz, 1H, Ar*H*), 3.44 (m, 2H, CH(*C*H$_3$)$_2$), 1.31 (d, *J* = 8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 142.9 (N*C*N), 140.2 (Ar-*C*), 132.3 (Ar-*C*), 129.6 (Ar-*C*), 125.8 (Ar-*C*), 124.6 (Ar-*C*), 123.8 (Ar-*C*), 123.4 (Ar-*C*), 29.4 *C*H(CH_3)$_2$, 23.2 CH(C*H*$_3$)$_2$. IR (KBr): ν (cm^{-1}): 3746m, 2963m, 2360m, 2158(C=N)m, 1472m, 1244m, 1194m, 1072m, 749m, 689m, 593m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{23}N_2$ 279.1856; found: 279.1881.

(2, 4, 6-tri-methyl-phenyl) - (2, 6-Di-ethylphenyl) –carbodiimide (**13a).** (Yield: 2.615 g, 8.94 mmol, 73%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.08 (s, 3H, Ar*H*), 6.88 (s, 2H, Ar*H*), 2.83 (q, *J* = 7.5 Hz, 4H, C*H*$_2$(CH_3)), 2.40 (s, 6H, *o*-(C*H*$_3$)), 2.29 (s, 3H, *p*-(C*H*$_3$)), 1.29 (t, *J* = 8 Hz , 6H, CH_2(C*H*$_3$)). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 138.7 (N*C*N), 134.8 (Ar-*C*), 134.0 (Ar-*C*), 133.2 (Ar-*C*), 132.5 (Ar-*C*), 129.0 (Ar-*C*), 128.2 (Ar-*C*), 126.6(Ar-*C*), 124.8 (Ar-*C*), 25.8 *o*-*C*H_3, 20.8 (CH(*C*H$_3$)$_2$), 18.9 p-*C*H_3, 14.7 CH_2(*C*H_3). IR (KBr): ν (cm^{-1}): 3226m,

2923m, 2159(C=N) m, 1590m, 1470m, 1377m, 1253m, 1198m, 1159m, 1111m, 1134m, 852m, 750m, 595m. HRMS (ESI-TOF-Q) *m/z*: [M+H] $^{+}$ calcd. for $C_{20}H_{25}N_2$ 293.2012; found: 293.2050.

(2, 4, 6-tri-methyl-phenyl)-(2, 6-Di-methyl-phenyl)–carbodiimide (**14a**)[6d]**.** (Yield: 2.62 g, 9.92 mmol, 74%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.05 (d, J = 8 Hz, 2H, Ar*H*), 6.99 – 6.96 (m, 1H, Ar*H*), 6.88 (s, 2H, Ar*H*), 2.42 (s, 6H, *o*-(CH_3), 2.39 (s, 6H, *o*-(CH_3), 2.29 (s, 3H, *p*-(CH_3)). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 136.2 (N*C*N), 134.1 (Ar-*C*), 133.1 (Ar-*C*), 132.7 (Ar-*C*), 132.6 (Ar-*C*), 129.0 (Ar-*C*), 128.3 (Ar-*C*), 124.4 (Ar-*C*), 20.8 *o*-(CH_3), 19.0 *o*-(CH_3), 18.9 *p*-(CH_3). IR (KBr): ν (cm^{-1}): 3563m, 3220m, 2920m, 2732m, 2147(C=N) m, 1921m, 1731m, 1592m, 1470m, 1377m, 1258m, 1201m, 1161m, 1104m, 1063m, 1032m, 853m, 766m, 733m, 595m. HRMS (ESI-TOF-Q) *m/z*: [M+H] $^{+}$ calcd. for $C_{18}H_{21}N_2$ 265.1749; found: 265.1699.

(2, 4, 6-tri-methyl-phenyl) - phenyl-carbodiimide (**15a).** (Yield: 3.0 g, 12.72 mmol, 86%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.34 – 7.30 (m, 2H, Ar*H*), 7.18 – 7.11 (m, 3H, Ar*H*), 6.87 (s, 2H, Ar*H*), 2.35 (s, 6H, *o*-(CH_3)), 2.27 (s, 3H, *p*-(CH_3)). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 140.3 (N*C*N), 135.0 (Ar-*C*), 132.8 (Ar-*C*), 132.2 (Ar-*C*), 131.9 (Ar-*C*), 129.6 (Ar-*C*), 129.5 (Ar-*C*), 129.0 (Ar-*C*), 128.9 (Ar-*C*), 124.7 (Ar-*C*), 123.7 (Ar-*C*), 20.9 *p*-(CH_3), 19.0 *o*-(CH_3). IR (KBr): ν (cm^{-1}): 3543m, 3221m, 3063m, 2920m, 2148(C=N) m, 1594m, 1485m, 1283m, 1206m, 1161m, 1073m, 1027m, 899m, 853m, 790m, 755m, 724m, 689m, 618m, 547m. HRMS (ESI-TOF-Q) *m/z*: [M+H] $^{+}$ calcd. for $C_{16}H_{17}N_2$ 237.1386; found: 237.1401.

General procedure for the synthesis of symmetrical and unsymmetrical *N,N'*-diaryl formamidines

All reactions were performed by using 1 gram of corresponding *N,N'*- diaryl carbodiimide either symmetrical or unsymmetrical. The corresponding *N, N'*- diaryl carbodiimide 1.0 (equiv.) was dissolved in ethanol (30 mL) to this sodium borohydride 1.1 (equiv.) was added and the reaction mixture was stirred at room temperature for 10 hours. The progress of the reaction was monitored by thin layer chromatography (TLC). When the starting material was completely consumed, the excess sodium borohydride was quenched with aqueous ammonium chloride solution and extracted with diethyl ether. Then the organic portion was dried over anhydrous sodium sulphate. The solvent was removed in vacuum and the compound was dried in high vacuum, and then purified by column chromatography with silica gel (100-200 mesh) with 5% ethyl acetate in *n*-hexane to yield colorless solids in good to excellent (76-98) % yields

Note: *N,N'*-disubstituted formamidines exhibit mixture of isomers in solution therefore their solution NMR spectra always complicated thus it is difficult to assign the accurate peaks. Particularly, large number of peaks than expected were observed for unsymmetrical *N,N'*-disubstituted formamidines in comparison to symmetrical FormHs.

Characterization of Formamidines (**1b-10b**)

Note: Isolated yields of formamidines are reported with respect to carbodiimide

N,N'-Bis(2,6-dimethylphenyl)formamidine (**1b).**[23] (Yield: 0.796 g, 3.155 mmol, 79%); m.p. 180-183 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ 7.10 – 6.92 (m, 4H), 6.91 (dd, 2H), 6.75 (d, 1H), 5.00 (d, 1H), 2.31 (s, 3H), 2.16 (s, 6H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6, 25 ^{o}C): δ 146.6, 145.8, 137.0, 134.2, 128.7, 128.4, 128.3 128.0, 127.8, 126.3, 123.1, 30.2, 18.8, 18.5, 18.2. IR (KBr): ν (cm^{-1}): 3449m, 2940m, 2921m, 1651s, 1638s, 1632s, 1611s, 1589m, 1466m,

1202m, 821s, 771s, 759m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{21}N_2$ 253.1699; found: 253.1666. HPLC: P_{HPLC} 100%, tR 13.28

N,N'-Bis(2,6-diisopropylphenyl)formamidine (**2b**).[14i, 23b] (Yield: 0.764 g, 2.09 mmol, 76%); m.p. 200-205 ºC; ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 10.95 (br, 1H), 7.07 – 7.05 (m, 7H), 3.43 (m, 4H), 1.35 (dd, 1H), 1.12 (d, 22H), 1.05 (d, 1H). ^{13}C NMR (101 MHz, C_6D_6, 25 ºC): δ 155.5, 146.9, 146.1, 143.8, 140.8, 139.6, 138.9, 134.1, 125.8, 123.7, 123.4, 28.3, 23.7. IR (KBr): ν (cm^{-1}): 3131m, 3030m, 2962m, 2929s, 1664s, 1587m, 1462m, 1453m, 1288m, 822s, 799s, 754m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{37}N_2$ 365.2951; found: 365.2967. HPLC: P_{HPLC} 100%, tR 12.93

N,N'-Bis(2,4,6-trimethylphenyl) formamidine (**3b**).[24] (Yield: 0.977g, 3.484 mmol, 97%); m.p. 198 - 200 ºC; ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 6.93 – 6.99 (dd, 2H), 6.78 (s, 2H), 6.59 (s, 1H), 5.04 (d, 1H), 2.34 (s, 3H), 2.26 (s, 1H), 2.20 (s, 6H), 2.16 (s, 3H), 2.06 (s, 2H), 1.89 (s, 3H) . ^{13}C NMR (101 MHz, C_6D_6, 25 ºC): δ 146.4, 144.1, 135.6, 134.5, 134.1, 131.7, 129.4, 129.4, 129.1, 20.9, 20.8, 18.8, 18.5, 18.2. IR (KBr): ν (cm^{-1}): 3434m, 3152m, 2965m, 2944m, 2916m, 1642s, 1614s, 1608s, 1215m, 849s, 776m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{25}N_2$ 281.2012; found: 281.2034. HPLC: P_{HPLC} 100%, tR 12.57

N,N'-Bis (2,6-diethylphenyl) formamidine **(4b)**[23b]**.** (Yield: 0.956g, 3.10 mmol, 95%); m.p. 108-110 ºC; ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 7.0 - 6.90 (m, 7H), 5.21 (d, 1H), 2.62 (q, 8H), 1.15 (t, 12H). ^{13}C NMR (101 MHz, C_6D_6, 25 ºC): δ 154.8, 146.7, 145.3, 140.8, 138.9, 135.6, 134.4, 126.8, 126.6, 125.2, 123.6, 117.9, 116.7, 25.2, 25.0, 24.9, 14.9, 14.8, 14.5. IR (KBr): ν (cm^{-1}): 3158m, 3067m, 2963m, 2934s,1647s, 1630s, 1586m, 1541m, 1453m, 1284m, 864s, 808m, 774s, 755m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{29}N_2$ 309.2325 ;found: 309.2348. HPLC: P_{HPLC} 100%, tR 12.43

N-(2,6-diisopropylphenyl)-N'-phenylformamidine **(5b)**[25]**.** (Yield: 0.916 g, 3.268 mmol, 91%); m.p. 115-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.70 (br, 1H), 7.99 (br, 1H), 7.25 – 6.71 (m, 8H), 3.43 – 3.25 (m, 2H), 1.27 (d, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ 150.5, 149.9, 143.9, 141.6, 141.2, 129.6, 124.8, 123.5, 122.4, 116.4, 48.6, 28.1, 23.7. IR (KBr): ν (cm^{-1}): 3437m, 3376m, 3123m, 3176m, 2962s, 1673s, 1601m, 1589m, 1495m, 1458m, 1362m, 1307m, 885s, 800s, 782s, 752m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{25}N_2$ 281.2012; found: 281.2020.

N-(2,6-diisopropylphenyl)-N'-(2,6-dimethylphenyl)formamidine **(6b).** (Yield: 0.926 g, 3.0 mmol, 91%); m.p. 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.29 – 7.06 (m, 7H), 5.59 (t, 1H), 3.31 – 3.21 (m, 2H), 2.31 (s, 3H), 2.27 (s, 3H), 1.32 (d, 1H), 1.21 (dd, 11H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ 147.8, 146.9, 146.1, 145.2, 142.4, 139.2, 136.4, 133.3, 129.0, 128.9, 128.8, 128.4, 126.3, 126.2, 123.9, 123.7, 123.5, 123.2, 116.3, 28.3, 28.1, 28.1, 24.2, 23.7, 23.2, 18.8, 18.7, 17.8. IR (KBr): ν (cm^{-1}): 3376m, 3330m, 3184m, 3138m, 3063m, 3029m, 2964m, 1645s, 1463m, 1440m, 850s, 824m, 798s, 770m, 750m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{29}N_2$ 309.2325; found: 309.2309.

N-(2,6-Diisopropylphenyl)-N'-(2,4,6-trimethylphenyl)formamidine **(7b)**[14c]**.** (Yield: 0.925 g, 2.87 mmol, 90%); m.p. 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.21 – 6.89 (m, 6H), 5.56 (s, 1H), 3.20 – 3.27 (m, 2H), 2.27 (s, 6H), 2.22 (s, 3H), 1.20 (t, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): δ 150.0, 148.2, 147.4 , 146.2 , 142.4, 139.3, 136.1, 133.8 , 133.6, 129.5, 129.1, 123.9, 123.7 , 123.4, 123.1, 116.3, 28.1, 28.0, 24.2, 23.7, 23.2, 20.9, 18.7, 18.5, 17.8. IR (KBr): ν (cm^{-1}): 3374m, 3243m, 2959m, 2923s, 1644s, 1609s, 1515m, 1460m, 1233m, 850s, 828s, 783m,

762m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{31}N_2$ 323.2482; found: 323.2467. HPLC: P_{HPLC} 100%, tR 12.32

N-(2,6-diethylphenyl)-N'-(2,6-diisopropylphenyl)formamidine **(8b).** (Yield: 0.985g, 2.93 mmol, 98%); m.p. 118-120 ºC; ^{1}H NMR (400 MHz, $CDCl_3$, 25ºC): δ 7.21 (dd, 1H), 7.12 (s, 3H), 7.08 (s, 3H), 5.58 (t, 1H), 3.33 (d, 2H), 2.68 – 2.62 (m, 6H), 1.33 (dd, 4H), 1.19 (dd, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC): δ 147.6, 147.3, 145.8, 144.1, 142.6, 140.6, 139.1, 135.0, 134.5, 133.4, 127.8, 127.2, 126.9, 126.5, 126.3, 123.8, 123.7, 123.5,123.4, 123.2, 28.3, 28.2, 28.1, 24.8, 24.4, 24.1, 23.8, 23.7, 22.8, 15.1, 14.7, 14.3. IR (KBr): ν (cm^{-1}): 3415m, 3296m, 3189m, 2931m, 2868m, 1664s, 1586m, 885s, 876s, 826m, 800m, 768s, 757m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{33}N_2$ 337.2638; found: 337.2654. HPLC: P_{HPLC} 100%, tR 11.70

N-(2,6-dimethylphenyl)-N'-(2,4,6-trimethylphenyl) formamidine (**9b).** (Yield: 0.906g, 3.40 mmol, 90%); m.p. 158-160 ºC; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.05 - 6.89 (m, 6H), 2.26 (s, 15H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC): δ 147.2, 133.9, 130.7, 129.1, 128.4, 117.8, 116.3, 113.4, 29.8, 20.9, 18.8, 18.7. IR (KBr): ν (cm^{-1}): 3362s, 3195m, 2969s, 2916m, 1642s, 1615s, 1608m, 1592m, 850s, 793m, 758m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{23}N_2$ 267.1856; found: 267.1820.

N-(2,6-diethylphenyl)-N'-(2,4,6-trimethylphenyl) formamidine (**10b).** (Yield: 0.966 g, 3.28 mmol, 96%); m.p. 128-130 ºC; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.29 -6.62 (br, 6H), 5.54 (s, 1H), 2.65 (s, 4H), 2.29 (d, 9H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25ºC): δ 136.0, 133.3, 129.5, 129.3, 126.7, 126.4, 123.7, 116.3, 25.0, 20.9, 18.6, 15.0. IR (KBr): ν (cm^{-1}): 3379m, 3187m, 3060m, 2932m, 2874m, 1677s, 1644m, 1609m, 1546m, 863s, 850s, 827m, 810m, 792m,781m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{27}N_2$ 295.2169; found: 295.2192. HPLC: P_{HPLC} 100%, tR 12.71.

Conclusion

In conclusion, we have shown the facile synthesis of various symmetrical and unsymmetrical bulky *N,N'*-diaryl carbodiimides by the dehydrosulfurisation of corresponding thioureas by using a base and iodine in THF at mild reaction conditions in moderate to high yields. Bulky aryl carbodiimides have very broad application in polymer, inorganic and organic syntheses. More importantly, these bulky carbodiimides are ideal precursors to prepare various bulky N-donor ligands such as formamidines, amidines, guanidines and NHC-CDI adducts etc. These bulky N-donor ligands are ideal precursors for isolation of unusual metal complexes, particularly low valent and/or low oxidation state metal complexes. Further, we produced 1, 3- disubstituted symmetrical and unsymmetrical bulky aryl formamidines under mild reaction conditions in excellent yields, upon reduction of corresponding carbodiimides with easily available sodium borohydride. Bulky aryl formamidines are important precursors for the preparation of imidazolinium salts, these salts upon further treatment with base can produce σ- donor N-heterocyclic carbene ligands.

References

1 H. Ulrich and Editor, *Chemistry and Technology Carbodiimides*, John Wiley & Sons, Ltd., 2007.

2 (a) A. Williams and I. T. Ibrahim, *Chem. Rev.*, 1981, **81**, 589-636; (b) A. Williams and I. T. Ibrahim, *J. Am. Chem. Soc.*, 1981, **103**, 7090-7095.

3 (a) M. K. Barman and S. Nembenna, *RSC Adv.*, 2016, **6**, 338-345; (b) L. Xu, W.-X. Zhang and Z. Xi, *Organometallics*, 2015, **34**, 1787-1801; (c) W.-X. Zhang, L. Xu and Z. Xi, *Chem. Commun.*, 2015, **51**, 254-265; (d) Y. Chi, L. Xu, S. Du, H. Yan, W.-X. Zhang

and Z. Xi, *Chem. Eur. J.*, 2015, **21**, 10369-10378; (e) C. Alonso-Moreno, A. Antinolo, F. Carrillo-Hermosilla and A. Otero, *Chem. Soc. Rev.*, 2014, **43**, 3406-3425; (f) W.-X. Zhang and Z. Hou, *Org. Biomol. Chem.*, 2008, **6**, 1720-1730; (g) M. K. Barman, A. Baishya and S. Nembenna, *J. Organomet. Chem.*, 2015, **785**, 52-60; (h) M. K. Barman, A. Baishya, T. Peddarao and S. Nembenna, *J. Organomet. Chem.*, 2014, **772-773**, 265-270; (i) C. Jones, *Coord. Chem. Rev.*, 2010, **254**, 1273-1289; (j) F. T. Edelmann, *Chem. Soc. Rev.*, 2012, **41**, 7657-7672; (k) F. T. Edelmann, *Chem. Soc. Rev.*, 2009, **38**, 2253-2268; (l)A. A. Trifonov, *Coord. Chem. Rev.*, 2010, **254**, 1327-1347.

4 (a) A. K. Maity, A. J. Metta-Magana and S. Fortier, *Inorg. Chem.*, 2015, **54**, 10030-10041; (b) M. H. Holthausen, M. Colussi and D. W. Stephan, *Chem. Eur. J.*, 2015, **21**, 2193-2199; (c) G. B. Deacon, P. C. Junk, J. Wang and D. Werner, *Inorg. Chem.*, 2014, **53**, 12553-12563; (d) W. Yi, S. Huang, J. Zhang, Z. Chen and X. Zhou, *Organometallics*, 2013, **32**, 5409-5415; (e) J. Obenauf, W. P. Kretschmer, T. Bauer and R. Kempe, *Eur. J. Inorg. Chem.*, 2013, 537-544; (f) A. Noor, T. Bauer, T. K. Todorova, B. Weber, L. Gagliardi and R. Kempe, *Chem. - Eur. J.*, 2013, **19**, 9825-9832; (g) R. S. P. Turbervill and J. M. Goicoechea, *Eur. J. Inorg. Chem.*, 2014, 1660-1668; (h) F. Zhang, J. Zhang, Y. Zhang, J. Hong and X. Zhou, *Organometallics*, 2014, **33**, 6186-6192; (i) J. Hong, L. Zhang, K. Wang, Z. Chen, L. Wu and X. Zhou, *Organometallics*, 2013, **32**, 7312-7322; (j) C. Glock, C. Loh, H. Goerls, S. Krieck and M. Westerhausen, *Eur. J. Inorg. Chem.*, 2013, 3261-3269; (k) R. S. P. Turbervill and J. M. Goicoechea, *Organometallics*, 2012, **31**, 2452-2462; (l) C. Jones, S. J. Bonyhady, N. Holzmann, G. Frenking and A. Stasch, *Inorg. Chem.*, 2011, **50**, 12315-12325; (m) R. S. Ghadwal, H. W. Roesky, C. Schulzke

and M. Granitzka, *Organometallics*, 2010, **29**, 6329-6333; (n) F. Zhao, Y. Wang, L. Xu, W.-X. Zhang and Z. Xi, *Tetrahedron Lett.*, 2014, **55**, 4597-4600.

5 (a) A. Baishya, T. Peddarao, M. K. Barman and S. Nembenna, *New J. Chem.*, 2015, **39**, 7503-7510; (b) A. Baishya, L. Kumar, M. K. Barman, T. Peddarao, and S. Nembenna *ChemistrySelect* 2016**, 3,** 498-503.

6 (a) Z. Zhang, Z. Li, B. Fu and Z. Zhang, *Chem. Commun.*, 2015, **51**, 16312-16315; (b) R. E. Cowley, M. R. Golder, N. A. Eckert, M. H. Al-Afyouni and P. L. Holland, *Organometallics*, 2013, **32**, 5289-5298; (c) J. J. Scepaniak, R. P. Bontchev, D. L. Johnson and J. M. Smith, *Angew. Chem., Int. Ed.*, 2011, **50**, 6630-6633; (d) S. Wiese, M. J. B. Aguila, E. Kogut and T. H. Warren, *Organometallics*, 2013, **32**, 2300-2308; (e) C. A. Laskowski and G. L. Hillhouse, *Organometallics*, 2009, **28**, 6114-6120; (f) E. Kogut, H. L. Wiencko, L. Zhang, D. E. Cordeau and T. H. Warren, *J. Am. Chem. Soc.*, 2005, **127**, 11248-11249; (g) N. P. Mankad, P. Mueller and J. C. Peters, *J. Am. Chem. Soc.*, 2010, **132**, 4083-4085; (h) R. E. Cowley, N. A. Eckert, J. Elhaik and P. L. Holland, *Chem. Commun.*, 2009, 1760-1762; (i) Y. M. Badiei, A. Krishnaswamy, M. M. Melzer and T. H. Warren, *J. Am. Chem. Soc.*, 2006, **128**, 15056-15057; (j) I. Pri-Bar and J. Schwartz, *Chem. Commun.*, 1997, 347-348; (k) Y. Ito, T. Hirao and T. Saegusa, *J. Org. Chem.*, 1975, **40**, 2981-2982; (l)T. Saegusa, Y. Ito and T. Shimizu, *J. Org. Chem.*, 1970, **35**, 3995-3996.

7 T.-H. Zhu, S.-Y. Wang, Y.-Q. Tao and S.-J. Ji, *Org. Lett.*, 2015, **17**, 1974-1977.

8 A. R. Ali, H. Ghosh and B. K. Patel, *Tetrahedron Lett.*, 2010, **51**, 1019-1021.

9 P. S. Chaudhari, P. S. Dangate and K. G. Akamanchi, *Synlett*, 2010, **20**,3065-3067.

10 K. Hayasaka, K. Fukumoto and H. Nakazawa, *Dalton Trans.*, 2013, **42**, 10271-10276.

11 M. Findlater, N. J. Hill and A. H. Cowley, *Dalton Trans.*, 2008, 4419-4423.

12 A. K. Maity, S. Fortier, L. Griego and A. J. Metta-Magaña, *Inorg. Chem.*, 2014, **53**, 8155-8164.

13 (a) G. B. Deacon, P. C. Junk, L. K. MacReadie and D. Werner, *Eur. J. Inorg. Chem.*, 2014, 5240-5250; (b) S. Hamidi, L. N. Jende, H. Martin Dietrich, C. Maichle-Mossmer, K. W. Tornroos, G. B. Deacon, P. C. Junk and R. Anwander, *Organometallics*, 2013, **32**, 1209-1223; (c) M. L. Cole, G. B. Deacon, P. C. Junk and J. Wang, *Organometallics*, 2013, **32**, 1370-1378; (d) S. Enthaler, K. Schröder, S. Inoue, B. Eckhardt, K. Junge, M. Beller and M. Drieß, *Eur. J. Org. Chem.*, 2010, 4893-4901; (e) M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, D. Polo-Ceron and J. Wang, *Dalton Trans.*, 2010, **39**, 6732-6738; (f) P. C. Junk and M. L. Cole, *Chem. Commun.*, 2007, 1579-1590; (g) C. Jones, P. C. Junk, M. Kloth, K. M. Proctor and A. Stasch, *Polyhedron*, 2006, **25**, 1592-1600; (h) M. L. Cole, G. B. Deacon, C. M. Forsyth, K. Konstas and P. C. Junk, *Dalton Trans.*, 2006, 3360-3367; (i) H. E. Abdou, A. A. Mohamed and J. P. Fackler, *Inorg. Chem.*, 2006, **46**, 141-146; (j) F. A. Cotton, L. M. Daniels, C. A. Murillo and J. G. Slaton, *J. Am. Chem. Soc.*, 2002, **124**, 2878-2879; (k) L. A. Lesikar and A. F. Richards, *Polyhedron*, 2010, **29**, 1411-1422.

14 (a) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. César, *Chem. Rev.*, 2011, **111**, 2705-2733; (b) R. Jazzar, H. Liang, B. Donnadieu and G. Bertrand, *J. Organomet. Chem.*, 2006, **691**, 3201-3205; (c) K. Hirano, S. Urban, C. Wang and F. Glorius, *Org. Lett.*, 2009, **11**, 1019-1022; (d) K. M. Kuhn and R. H. Grubbs, *Org. Lett.*, 2008, **10**, 2075-2077; (e) M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis,

Organometallics, 2008, **27**, 3279-3289; (f) M. Iglesias, D. J. Beetstra, K. J. Cavell, A. Dervisi, I. A. Fallis, B. Kariuki, R. W. Harrington, W. Clegg, P. N. Horton, S. J. Coles and M. B. Hursthouse, *Eur. J. Inorg. Chem.*, 2010, 1604-1607; (g) E. L. Kolychev, A. F. Asachenko, P. B. Dzhevakov, A. A. Bush, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *Dalton Trans.*, 2013, **42**, 6859-6866; (h) J. Zhang, X. Su, J. Fu and M. Shi, *Chem. Commun.*, 2011, **47**, 12541-12543; (i) E. M. McGarrigle, S. P. Fritz, L. Favereau, M. Yar and V. K. Aggarwal, *Org. Lett.*, 2011, **13**, 3060-3063; (j) E. L. Kolychev, I. A. Portnyagin, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *J. Organomet. Chem.*, 2009, **694**, 2454-2462; (k) A. Binobaid, M. Iglesias, D. J. Beetstra, B. Kariuki, A. Dervisi, I. A. Fallis and K. J. Cavell, *Dalton Trans.*, 2009, 7099-7112; (l) R. Jazzar, J.-B. Bourg, R. D. Dewhurst, B. Donnadieu and G. Bertrand, *J. Org. Chem.*, 2007, **72**, 3492-3499.

15 G. Jin, C. Jones, P. C. Junk, K.-A. Lippert, R. P. Rose and A. Stasch, *New J. Chem.*, 2009, **33**, 64-75.

16 R. M. Roberts, *J. Org. Chem.*, 1949, **14**, 277-284.

17 (a) L. Cai, Y. Han, S. Ren and L. Huang, *Tetrahedron*, 2000, **56**, 8253-8262; (b) C.-H. Lin, C.-H. Tsai and H.-C. Chang, *Cat. Lett.*, 2005, **104**, 135-140; (c) A. Mekhalfia, R. Mutter, W. Heal and B. Chen, *Tetrahedron*, 2006, **62**, 5617-5625; (d) B. M. Reddy and M. K. Patil, *Chem. Rev.*, 2009, **109**, 2185-2208; (e) K. U. Sadek, A. Alnajjar, R. A. Mekheimer, N. K. Mohamed and H. A. Mohamed, *Green and Sustainable Chem.*, 2011, **01**, 92-97; (f) D. R. Patil and D. S. Dalal, *Chin. Chem. Lett.*, 2012, **23**, 1125-1128; (g) M. Sheykhan, M. Mohammadquli and A. Heydari, *J. Mol. Str.*, 2012, **1027**, 156-161.

18 (a) M. L. Cole and P. C. Junk, *Z. Anorg. Allg. Chem.*, 2015, **641**, 2624-2629; (b) M. L. Cole, A. J. Davies, C. Jones, P. C. Junk, A. I. McKay and A. Stasch, *Z. Anorg. Allg. Chem.*, 2015, **641**, 2233-2244.

19 K. Kaji, H. Matsubara, H. Nagashima, Y. Kikugawa and S. Yamada, *Chem. Pharm. Bull.*, 1978, **26**, 2246-2249.

20 J. Obenauf, W. P. Kretschmer and R. Kempe, *Eur. J. Inorg. Chem.*, 2014, 1446-1453.

21 A.-L. Chen, K.-L. Wei, R.-J. Jeng, J.-J. Lin and S. A. Dai, *Macromolecules*, 2011, **44**, 46-59.

22 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A: Fundam. Crystallogr*., 2008, **64**, 112

23 (a) K. E. Krahulic, G. D. Enright, M. Parvez and R. Roesler, *J. Am. Chem. Soc.*, 2005, **127**, 4142-4143; (b) N. Ueda, H. Nikawa, Y. Takano, M. O. Ishitsuka, T. Tsuchiya and T. Akasaka, *Heteroatom Chem.*, 2011, **22**, 426-431.

24 H. Kinuta, M. Tobisu and N. Chatani, *J. Am. Chem. Soc.*, 2015, **137**, 1593-1600.

25 N. V. Kulkarni, T. Elkin, B. Tumaniskii, M. Botoshansky, L. J. W. Shimon and M. S. Eisen, *Organometallics*, 2014, **33**, 3119-3136.

Chapter 3.

Part-A: Bimetallic aluminum alkyl and iodide complexes stabilized by a bulky bis-guanidinate ligand

Abstract.

Bulky bis-guanidine ligands such as $L^2(2H)$ and $L^3(2H)$, where L = $\{ArNCNAr\}_2\{\mu\text{-}N(C_2H_4)_2N\}$, for $L^2(2H)$ (Ar = 2, 4, 6-Me_3 - C_6H_2) and ($L^3(2H)$) (Ar = 2, 6-$^i Pr_2$ - C_6H_3) have been utilized to synthesize four-membered dinuclear aluminum heterocycles. Deprotonation of $L^{2\text{-}3}$ (2H) (1.0 equiv) upon treatment with trimethyl aluminum (2.1 equiv) in toluene led to the formation of bi-metallic aluminum alkyls [$L^2(AlMe_2)_2$] **(1)** and [$L^3(AlMe_2)_2$] **(2)**. Aluminum halide complex *i.e*, **[**$L^3(AlI_2)_2$] **(3)** was obtained by the reaction of compound **2** with four equivalents of molecular iodine in toluene at 80 ^oC, in which alkyl-halide exchange occurred. The identities of compounds (**1-3**) were confirmed by multinuclear (^1H and ^{13}C) magnetic resonance spectroscopy. Furthermore, the structures of compounds **1-3** were confirmed by single crystal X-ray structural analysis. The identities of compounds **1-3** display the expected number of signals in the ^1H and ^{13}C NMR spectra and are consistent with their composition. The crystal structures of compounds **1-3** reveal that each aluminum center is bonded to the monoanionic guanidinate ligand in *N,N'*-chelated fashion and the other two sites are occupied by alkyl or halide ligands, resulting in a distorted tetrahedral geometry.

Introduction

Since the first transition metal guanidinate complex by Lappert and coworkers[1] in 1970, the coordination chemistry of anionic guanidinates has been significantly researched, resulting in various complexes incorporating elements from all blocks of the periodic table.[2-4] Moreover, tetra-substituted bulky guanidinate anions are ideal precursors for the isolation of low valent and/or low oxidation state metal complexes, because these can give steric and/or electronic protection.[5]

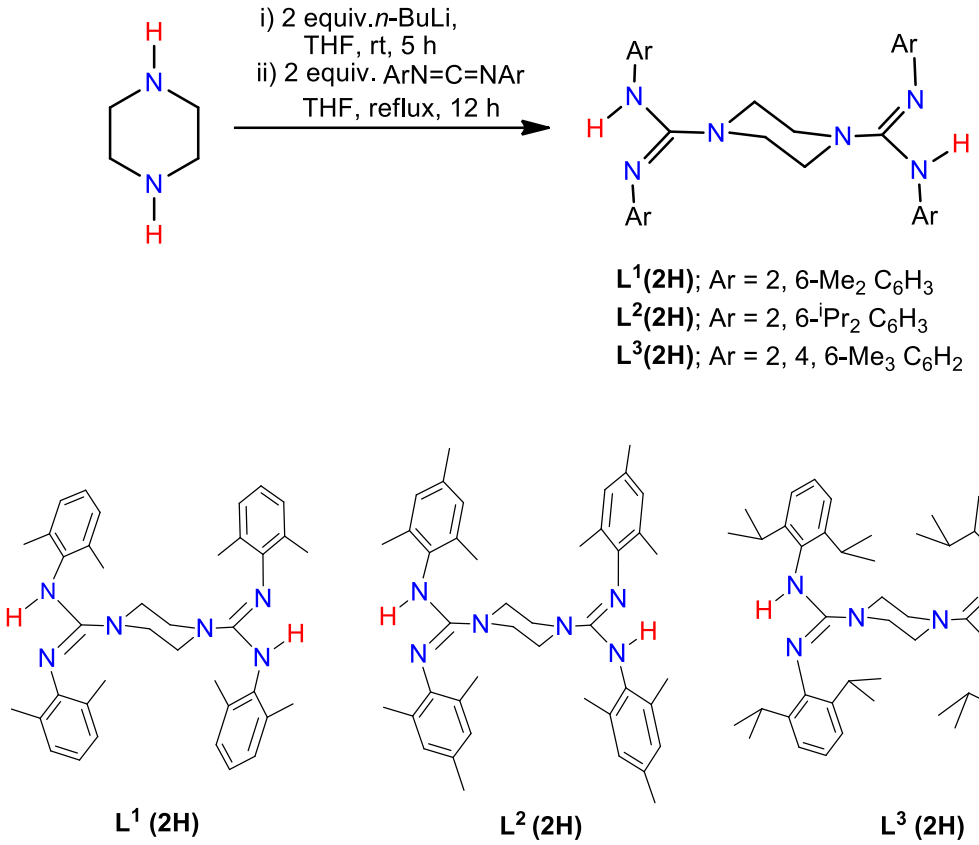
To date, several examples of mononuclear guanidinato aluminum complexes, including aluminum alkyls and halides are known in the literature.[6-13] Recent reports suggest that dinuclear aluminum complexes are more important precursors for ring opening polymerization (ROP) of cyclic esters (e.g., lactide and ε-caprolactone), cyclic ethers (e.g., cyclohexane oxide (CHO) and propylene oxide (PO)) than their monometallic counterparts.[14-16] Despite the prominent role of cooperative effect between two aluminum centers, synthesis and catalytic application of well-characterized dinuclear aluminum complexes remain scarce. To the best our knowledge there has been no reports on dinuclear guanidinates of aluminum complexes. Therefore, we targeted to synthesize dinuclear aluminum complexes by utilizing bi-nuleating ligands.[17]

The application of molecular compounds of aluminum or aluminum based reagents in catalysis is an attractive area of recent research interest.[18] This is due to large abundance, low cost and less toxicity of aluminum element. Recently, it has been demonstrated that aluminum based molecular compounds can be utilized as catalysts for various organic transformations, including hydroboration of carbonyl compounds, hydroboration of olefins and alkynes, cyanosilylation etc.[19-23]

Herein, we report the synthesis and characterization of bi-nucleating bis-guanidine supported dinuclear aluminum (III) alkyl and halide complexes.

Results and Discussion

The bulky bis-guanidine molecules such as $L^1(2H)$, $L^2(2H)$ and $L^3(2H)$, where L = $\{ArNCNAr\}_2\{\mu\text{-}N(C_2H_4)_2N\}$, for $L^1(2H)$ (Ar = 2, 6-Me_2 - C_6H_3), $L^2(2H)$ (Ar = 2, 4, 6-Me_3 - C_6H_2) and $L^3(2H)$ (Ar = 2, 6-$^i Pr_2$ - C_6H_3) have been prepared by previously reported literature procedures by using piperazine (or dilithiated piperazine) and *N,N'*-diaryl carbodiimide as precursors (Scheme **3.A.1**).[24, 25]

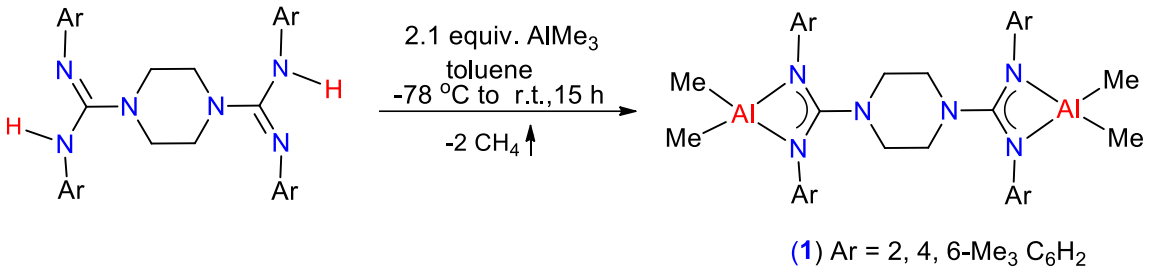


Scheme 3.A.1. Synthesis of bulky bis-guanidine ligands

N,N'-diaryl carbodiimides are important starting materials for the synthesis of several nitrogen-donor ligands such as amidines, formamidines, mono- or bi-guanidines, N-heterocyclic carbene-carbodiimide (NHC-CDI) adducts etc. We have previously reported several bulky nitrogen-donor ligands such as 1, 3-disubstituted formamidines, tetra-substituted guanidines, bis-guanidines, NHC-CDI adducts by using *N,N'*-diaryl CDIs as precursors.[29-31]

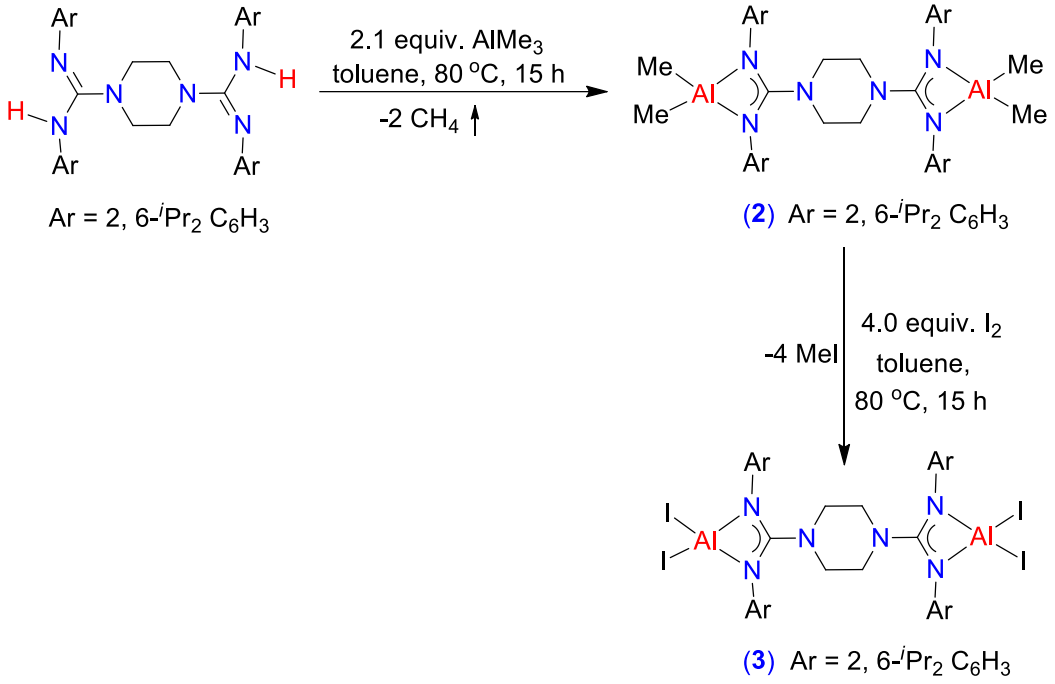
Generally, three procedures allow the synthesis of guanidinates of aluminum metal complexes.[7] i) Metallation of neutral guanidines with aluminum alkyls ii) Salt metathesis reaction of alkali guanidinates with AlX_3 (X = halide) iii) Addition of Al-N bond of $Al_2(NMe_2)_6$ to carbodiimide.[12] By employing the first method, guanidinates of aluminum complexes were prepared. Metallation

of neutral bis-guanidines with AlR_3 (R= alkyl) afforded the guanidinates of aluminum alkyl complexes. The synthesis of organoaluminum compounds **1** [$L^2(AlMe_2)_2$] and **2** [$L^3(AlMe_2)_2$] was achieved by the reaction of corresponding free ligand with trimethyl aluminum in toluene at room temperature (Scheme **3.A.2**).



Scheme 3.A.2. Synthesis of bimetallic aluminum alkyl complex **1**

Whereas, the treatment of $L^3(2H)$ with trimethylaluminum at elevated temeparature (80 °C) in toluene resulted in compound **3.** (Scheme **3.A.3**). Considering the fact that ligated (monoanionic) aluminum dihalides are ideal precursors for isolation of low valent Al(I) heterocycles (NHC analogues),[32] hence, we aimed to prepare *N,N'*-chelated aluminum diiodide complex. This was achieved by alkyl-halide exchange reaction. Compound **3** was prepared from the reaction of **2** with molecular iodine in C_6D_6 at 80 °C for 15 h. Compounds **1, 2** and **3** are isolated as colorless crystalline solids in 60%, 59% and 70% yields, respectively. All compounds found to be thermally stable and melt at the range of 185 – 280 °C. The metal complexes **1-3** were characterized by multinuclear (^1H and ^{13}C) magnetic resonance spectroscopy. Furthermore, compounds **1-3** were confirmed by single crystal X-ray structural analysis. All compounds **1-3** display the expected number of signals in the ^1H and ^{13}C NMR spectra and are consistent with their composition.



Scheme 3.A. 3. Synthesis of bimetallic aluminum alkyl and iodide complexes **2** and **3**

The ^{1}H NMR spectra of compounds **1** exhibit singlet resonances at –0.31 ppm in C_6D_6, respectively corresponding to 12 protons of the two Al*Me*$_2$ groups, *i.e.*, $L^2(AlMe_2)_2$. Similarly, the ^{1}H spectrum of compound **2** shows a singlet resonance at –0.73 ppm in $CDCl_3$ corresponding to 12 protons of the two Al*Me*$_2$ groups, *i.e.*, $L^3(AlMe_2)_2$. In the ^{1}H spectrum, a complete disappearance of singlet resonance at –0.73 ppm in $CDCl_3$, which indicates the formation of compound **3**. ^{13}C NMR spectra of compounds **1**, **2** and **3** show a characteristic peak for the N_3C carbon atom of the bis-guanidinate ligand 163.2, 162.5 and 164.6 ppm (compound **1** in C_6D_6 while **2-3** in $CDCl_3$) respectively. ^{13}C NMR spectra of compounds **1** and **2** exhibit a characteristic peak for the Al(CH_3)$_2$ at –9.2, and –9.4 ppm respectively, which is absent in the case of compound **3**. However, the presence of two iodide ligands which are attached to aluminum atom in compound **3** was further confirmed by single crystal X-ray structural analysis.

The crystals of **1-3** suitable for single crystal X-ray diffraction analysis were recrystallized from the concentrated toluene solution. The compound **1** crystallizes in triclinic system with $P\bar{1}$ space group, while, both compounds **2** and **3** crystallized in the monoclinic system with $P2_1/n$ space group. Both compounds **2** and **3** are isostructural. Molecular structures of these complexes **1-3** are shown in Figures **3.A.1–3.A.3**, respectively. The crystal data and structure refinement details of complexes **1–3** are summarized in Table **3.A.1**. Solid state structures of compounds **2** and **3** reveal that, each of the aluminum centers is coordinated by two carbon atoms from two alkyl groups, as well as two nitrogen atoms from the bis-guanidinate ligand in *N,N'*-chelate fashion to form a distorted tetrahedral geometry. Similarly, in the case of compound **3**, the aluminum center is in distorted tetrahedral geometry, which is surrounded by the nitrogen atoms of chelating bulky bis-guanidine and two iodine moieties. The Al−C bond lengths for the compounds **1** and **2** lie between 1.949(6) Å and 1.962(3) Å, these values are similar to the reported values of Al–C bond lengths.[6-13] The Al−I bond distances in **3** Al1−I1 is 2.507(2) Å and Al1−I2 is 2.521(2) Å which are well in agreement with the reported values.[6-13] The bite angles of the bulky bis-guanidine ligands N1− Al1− N2, which are 68.75(16), 69.33(10) and 71.19(19)° for **1-3** respectively.

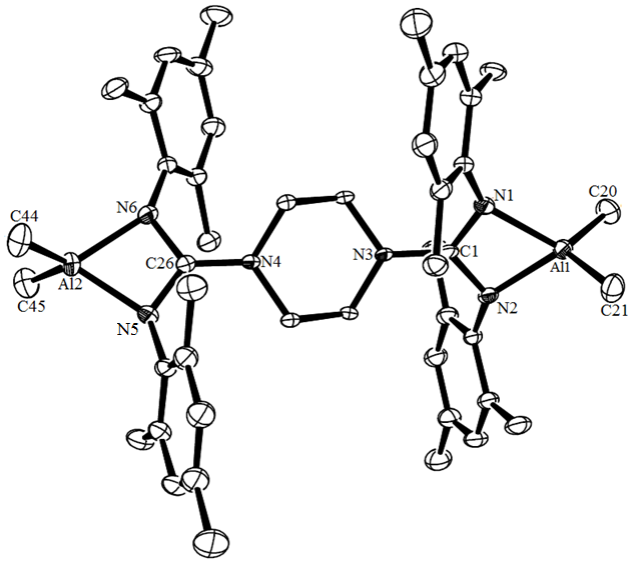


Figure 3.A.1. Molecular structure of **1.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Al1–C20 1.949(6), Al1–C21 1.953(6), Al2– C45 1.925(7), Al2– C44 1.959(6), N1–Al1 1.933(4), N2–Al1 1.933(4), N1 – Al1 – N2 68.75(16), N1 – Al1 – C21 114.1(2), N2–Al1–C21 115.9(2), N6– Al2– N5 69.15(17) N6– Al2– C44 115.0(3) N5– Al2– C44 112.7(2), C45–Al2– N6 113.0(3), C45– Al2– C44 119.2(3).

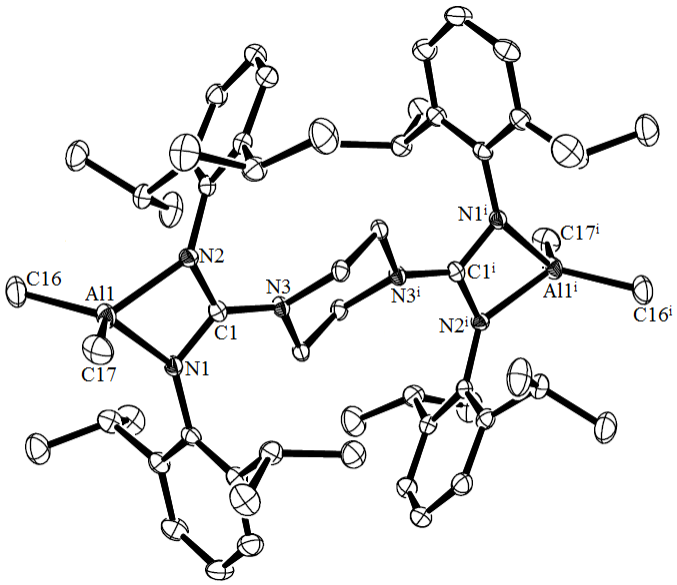


Figure 3.A.2. Molecular structure of **2.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Al1–C16 1.962(3), Al1–C17 1.952(3), N1–Al1 1.941(3), N2–Al1 1.934(2), N1–C1 1.348(3), N2–C1 1.352(4). N2 – Al1 – N1 69.39(10), N2 – Al1 – C17 114.38(13)**,** N2– Al1–C16 118.66(12), C17– Al1– C16 115.24(15).

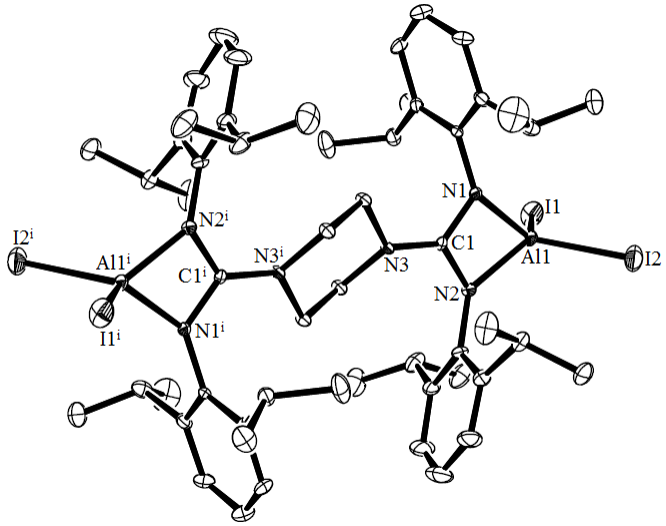


Figure 3.A.3. Molecular structure of **3.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Al1–I1 2.477(2), Al1–I2 2.4555(18), N1–Al1 1.896(5), N2–Al1 1.886(5), N1–C1 1.347(7), N2–C1 1.363(7), N2–Al1–I2 118.07(16), N1–Al1–I1 116.64(16), N1–Al1–I2 121.37(17), I1–Al1–I2 108.28(6). N1−Al1−N2 71.2(19).

Table 3.A.1. Crystallographic and structure refinement data for **1-3**

	1	**2**	**3**
Empirical formula	$C_{46}H_{64}Al_2N_6$	$C_{58}H_{88}Al_2N_6$	$C_{54}H_{76}N_6Al_2I_4$
Formula weight	754.99	923.35	1370.83
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [λ]	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	12.1222(19)	12.528(4)	10.5278(12)
b [Å]	12.893(2)	14.416(6)	20.575(2)
c [Å]	15.790(2)	15.911(6)	14.0056(16)
α [°]	71.271(10)	90	90
β [°]	78.039(10)	95.087(10)	98.131(7)
γ [°]	86.732(11)	90	90
Volume [Å]^3	2286.3(6)	2862.2(19)	3003.2(6)
Z	2	2	2
Calculated Density [g cm^{-3}]	1.097	1.071	1.516
μ (Mo Kα)/mm^{-1}	0.100	0.091	2.142
F (000)	816.0	1008.5	1357.3
Theta range/^{o}	2.40 – 25.5	2.44 – 25.5	2.47 – 26.12
Reflections collected	26359	15753	25353
Independent reflections	8485	5292	5893
GOOF on F^2	1.096	0.995	0.986
R_1/wR_2 [I > 2σ (I)]	0.1039/0.2620	0.0580 /0.1181	0.0618 /0.1872
R_1/wR_2 (all data)	0.1651/0.3421	0.1411/0.1503	0.0829/ 0.1875
Largest diff. peak/ hole [e.Å^{-3}]	0.95/-0.64	0.50/-0.55	2.42/-2.23
R_{int}	0.1017	0.1120	0.1022
Data/restraints/parameters	8485/0/503	5292/0/309	5893/0/306

Experimental section

General procedures

All the reactions dealing with air-and moisture-sensitive compounds were carried out in standard Schlenk line and Glove-box filled with nitrogen gas, unless otherwise noted. The precursors were prepared by following literature procedures.[24, 25] Anhydrous solvents toluene and *n*- hexane were collected from mBRAUN solvent purification system and used as such. Deuterated benzene (C_6D_6) was dried over a sodium mirror in vacuum prior to use. Deuterated chloroform ($CDCl_3$) was dried over $MgSO_4$ and stored on molecular sieves. NMR spectra were {^{1}H (400 MHz), & ^{13}C (101 MHz) were recorded on Bruker AV 400 MHz instrument. The chemical shift values are reported in parts per million (ppm) and are referenced to the residual solvent (7.16, & 7.26 for ^{1}H; 128.09 & 77.16 for ^{13}C; for C_6D_6, $CDCl_3$ respectively). Melting points were recorded on digital melting point apparatus and are uncorrected.

Crystallographic information

Crystals of suitable quality for X-ray diffraction studies of compounds **2** - **4** were withdrawn from Schlenk flask under the atmosphere of nitrogen and covered with a layer of paraffin oil. A good quality single crystal was selected, mounted on a glass fiber, and then placed quickly in a stream of liquid nitrogen on an X-ray diffractometer. The X-ray data were collected on a Bruker 4-circle Kappa APEX-II diffractometer equipped with a CCD detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Data collection was monitored with Apex II software, and preprocessing was done with SADABS integrated with Apex II. Using Olex2,[26] the structures were solved with the ShelXT structure solution program using Direct methods and refined with the ShelXL[27, 28] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated

geometrically and refined using the riding model. The crystal data for all compounds along with the final residuals and other pertaining details are provided in the tables.

Synthesis and characterization of compounds 1-3

Synthesis of compound 1: To a stirred solution of L^2(2H) (0.3 g, 0.466 mmol, 1.0 equiv) in toluene (~10 mL), trimethyl aluminum (2.0 M in toluene, 0.49 mL, and 0.979 mmol, 2.1 equiv) was added at –78 ^{o}C. Then the resulting reaction mixture was slowly warmed to room temperature and continued stirring for 15 h. The volatiles were removed under reduced pressure. The residue was dried *in vacuo* to give the product, which was recrystallized from toluene solution at room temperature to give colorless crystals of complex **2** (Yield: 0.211 g, 0.28 mmol, 60 %). m.p. 230–237 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ – 0.31 (s, 12H, Al(CH_3)$_2$), 2.13 (d, J = 4.0 Hz, 36H, CH_3), 2.44 (s, 8H, (N(CH_2)$_2$N)), 6.63 (s, 8H, ArH). ^{13}C NMR (101 MHz, C_6D_6, 25 ^{o}C): δ – 9.2 Al(CH$_3$)$_2$, 18.8 (ArCH$_3$), 20.9 (ArCH$_3$), 44.8 (N(CH$_2$)$_2$N), 129.6 (ArC), 132.7 (ArC), 133.6 (ArC), 139.1(ArC), 163.2 (N$_3C$).

Synthesis of compound 2: To a stirred solution of L^3(2H) (0.3 g, 0.369 mmol, 1.0 equiv) in toluene (~10 mL), trimethyl aluminum (2.0 M in toluene, 0.38 mL, and 0.776 mmol, 2.1 equiv) was added at room temperature. Then the resulting reaction mixture was heated to 80 ^{o}C and continued the stirring for 24 h. The volatiles were removed under reduced pressure. The solid residue was crystallized from toluene to obtain compound **3** as colorless crystals (Yield: 0.2 g, 0.218 mmol, 59 %). m.p. 215–222 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ – 0.73 (s, 12H, Al(CH_3)$_2$), 1.00 (d, J = 4.0 Hz, 24H), 1.10 (d, J = 4.0 Hz, 24H), 2.30 (s, 8H, (N(CH_2)$_2$N)), 3.21 – 3.27 (sept, 8H), 6.99 (d, J = 4.0 Hz, 3H), 7.01 (s, 5H, ArH), 7.06 (s, 2H, ArH), 7.07 (d, J = 4.0 Hz, 2H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ – 9.4 Al(CH$_3$)$_2$, 23.1, 26.0, 28.0, 44.4 (N(CH$_2$)$_2$N), 123.5 (ArC), 125.5 (ArC), 138.2 (ArC), 144.6 (ArC), 162.5 (N$_3C$).

Synthesis of compound 3*:* In a Glove box, a J Young valve NMR tube was charged with compound **2** (0.030 g, 0.032 mmol, 1.0 equiv), iodine (0.033 g, 0.129 mmol, 4.0 equiv), and C_6D_6 (0.6 mL), and the reaction was run at 80 ºC for 15 h in an oil bath. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Once the ^{1}H NMR spectrum confirms the complete disappearance of $L^3(AlMe_2)_2$ peak. NMR tube kept at room temperature for 2 days, which yielded colorless crystals of compound **3** (Yield: 0.031 g, 0.0227 mmol, 70 %). m.p. 270–280 ºC; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.97 (d, J = 8.0 Hz, 24 H), 1.21 (d, J = 8.0 Hz, 24 H), 2.42 (s, 8 H, ($N(CH_2)_2N$)), 3.33 – 3.40 (sept, 8 H), 7.05 (d, J = 8.0 Hz, 8 H, Ar*H*), 7.15 – 7.19 (m, 4H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC): δ 23.5, 27.5, 28.3, 44.2 ($N(CH_2)_2N$), 124.3 (Ar*C*), 127.4 (Ar*C*), 134.9 (Ar*C*), 145.3 (Ar*C*), 164.6 (N_3C).

Conclusion

A series of new examples of dinuclear aluminum heterocycles have been reported. Synthesis of aluminum alkyl complexes such as $[L^2(AlMe_2)_2]$ (**1)** and $[L^3(AlMe_2)_2]$ (**2)** was achieved by the deprotonation of a corresponding free ligand upon treatment with two equivalents of $AlMe_3$ in toluene. The compound **3** $[L^3(AlI_2)_2]$ has been prepared by the reaction of the compound **2** with four equivalents of molecular iodine in toluene at 80 ºC. Solid state structures for compounds **1-2** reveal that Al is four-coordinated by two nitrogen atoms from the guanidinate ligand and two methyl groups to adopt a distorted tetrahedral geometry. Similarly, in complex **3** aluminum centers adopts a distorted tetrahedral geometry, in which Al is four -coordinated by two N atoms of ligand and two iodine ligands. We presume that compounds **1-3** are ideal precursors for the preparation of four-membered aluminum cations and low valent dinuclear aluminum (I) heterocycles. Currently, such studies are underway in our laboratory.

References

1 G . Chandra, A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *J. Chem. Soc., A* 1970, 2550-2558.

2 M. P. Coles, *Dalton Trans.*, 2006, 985-1001.

3 F. T. Edelmann, and F. H. Anthony and J. F. Mark (Eds.) Advances in organometallic chemistry, Academic Press, 2008, pp. 183-352.

4 F. T. Edelmann, *Chem. Soc. Rev.*, 2012, **41,** 7657-7672.

5 C. Jones, *Coord. Chem. Rev.,* 2010, **254,** 1273-1289.

6 H. Han, Z. Guo, S. Zhang, Y. Hua and X. Wei, *Polyhedron* 2017, **126,** 214-219.

7 H.-F. Han, Z.-Q. Guo, S.-F. Zhang, J. Li and X.-H. Wei, *RSC Adv.,* 2016, **6,** 101437-101446.

8 M. L. Cole, A. J. Davies, C. Jones, P. C. Junk, A. I. McKay and A. Stasch, *Z. Anorg. Allg. Chem.,* 2015, **641,** 2233-2244.

9 S. T. Barry, *Coord. Chem. Rev.,* 2013, **257,** 3192-3201.

10 S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones and A. Stasch, *Nat. Chem.*, 2010, **2,** 865-869.

11 A. P. Kenney, G. P. A. Yap, D. S. Richeson and S. T. Barry, *Inorg. Chem.,* 2005, **44,** 2926-2933.

12 C.-C. Chang, C.-S. Hsiung, H.-L. Su, B. Srinivas, M. Y. Chiang, G.-H. Lee and Y. Wang, *Organometallics,* 1998, **17,** 1595-1601.

13 S. L. Aeilts, M. P. Coles, D. C. Swenson, R. F and Jr. G. Young, *Organometallics,* 1998, **17,** 3265-3270.

14 M. Normand, T. Roisnel, J. F. Carpentier and E. Kirillov, *Chem. Commun.*, 2013, **49,** 11692-11694.

15 W. Li, H. Ouyang, L. Chen, D. Yuan, Y. Zhang and Y. Yao, *Inorg. Chem.*, 2016, **55,** 6520-6524.

16 L. Chen, W. Li, D. Yuan, Y. Zhang, Q. Shen, Y. Yao, *Inorg. Chem.*, 2015, **54**, 4699-4708.

17 A. L. Gavrilova and B. Bosnich, *Chem. Rev.*, 2004, **104**, 349-383.

18 W. Li, X. Ma, M. G. Walawalkar, Z. Yang and H. W. Roesky, *Coord. Chem. Rev.*, 2017, **350,** 14-29.

19 V. K. Jakhar, M. K. Barman and S. Nembenna, *Org. Lett.*, 2016, **18,** 4710-4713.

20 A. Bismuto, M. J. Cowley and S. P. Thomas, *ACS Catal.*, 2018, **8,** 2001-2005.

21 G. I. Nikonov, *ACS Catal.*, 2017, **7,** 7257-7266.

22 M. K. Sharma, S. Sinhababu, G. Mukherjee, G. Rajaraman and S. Nagendran, *Dalton Trans.*, 2017, **46**, 7672-7676.

23 B. Prashanth, M. Bhandari, S. Ravi, K. R. Shamasundar and S. Singh, *Chem. Eur. J.*, 2018, **24**, 4794-4799.

24 A. Baishya, T. Peddarao, M. K. Barman and S. Nembenna, *New J. Chem.*, 2015, **39** 7503-7510.

25 G. Jin, C. Jones, P. C. Junk, K.-A. Lippert, R. P. Rose and A. Stasch, *New J. Chem.*, 2009, **33**, 64-75.

26 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42,** 339-341.

27 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3-8.

28 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64,** 112-122.

29 A. Baishya, L. Kumar, M. K. Barman, T. Peddarao and S. Nembenna, *ChemistrySelect.*, 2016, **1**, 498-503.

30 T. Peddarao, A. Baishya, M. K. Barman, A. Kumar and S. Nembenna, *New J. Chem.*, 2016, **40**, 7627-7636.

31 A. Baishya, L. Kumar, M. K. Barman, H. S. Biswal and S. Nembenna, *Inorg. Chem.*, 2017, **56,** 9535-9546.

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

Chapter 3

Part B: Synthesis of Bulky aryl 5-amino tetrazoles.

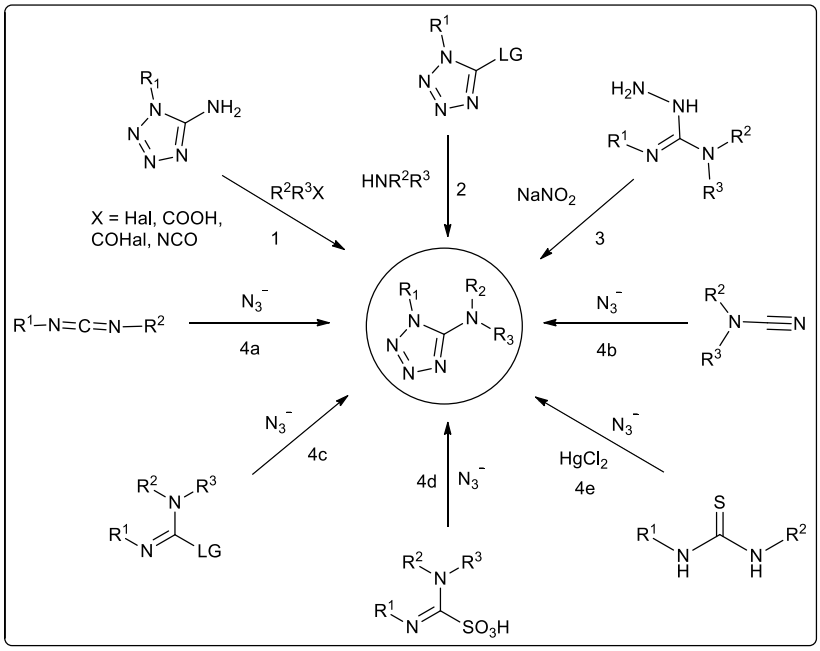
Abstract

A series of 5-(substituted amino)-1(aryl)-tetrazoles (RCN_5R) have been synthesized by cycloaddition reaction of different aryl carbodiimides with azido trimethyl silane in THF. A variety of aryl carbodiimides have undergone [3+2] cycloaddition to produce tetrazoles under mild reaction conditions in good yields. Good yields, safe process, and simple workup make this method an attractive and useful contribution to present the organic synthesis of 5-(substituted amino)-1(aryl)-tetrazoles.

Introduction

The chemistry of heterocyclic compounds has been an exciting field of study for a long time. Tetrazoles as a group of heterocyclic compounds are found to possess a broad spectrum of biological activities such as antibacterial[1] antifungal[2], antiviral[3-5], analgesic[6-7] anti-inflammatory [8-10] antiulcer [11] and antihypertensive[12] activities. Moreover, the tetrazoles can also be used frequently in material chemistry; for example; this structure has been found in explosives, photography and photoimaging chemicals, rocket propellants, polymers, gas generators, and agrochemicals[13-17]. The synthesis of tetrazoles was first reported in 1885[18]. Also, 5-substituted-1*H*-tetrazoles can function as lipophilic spacers and carboxylic acid surrogates[19] and precursors of a variety of nitrogen-containing heterocycles in coordination chemistry[20,21] Since 1901, conventional synthesis of 5-substituted- 1*H*-tetrazoles has been reported to proceed *via* [3 + 2] cycloaddition of azide with nitriles[22]. 5-aminotetrazoles show anti-allergic and anti-asthmatic[23-

[27], antiviral and anti-inflammatory[28]. Antineoplastic[29-30] and cognition disorder activities[31] Activity as CCK antagonists[32] and antibiotics against a range of bacteria[33] has been observed.



Scheme 3.B.1.

The synthesis of 5-aminotetrazole derivatives from various synthetic protocols has been well established by Katritzky et.al[34] and these 5-aminotetrazole derivatives can be synthesized mainly from four types of protocols (Scheme **3.B.1**) 1. Functionalization of amino group or ring in 5-aminotetrazole[35-37] this method frequently results in mixtures of isomers[38,39]. (2) The leaving group in the tetrazole 5-position can be substituted with amines[40] (3) By the reaction of amino guanidine derivatives with sodium nitrite[41-42] and (4) various azide-mediated tetrazole ring constructions. 5-aminotetrazole rings are generated by utilizing azide anion involves the following: (a) NaN_3 addition to carbodiimides[43-44] or cyanamides[45-48] and (b) nucleophilic

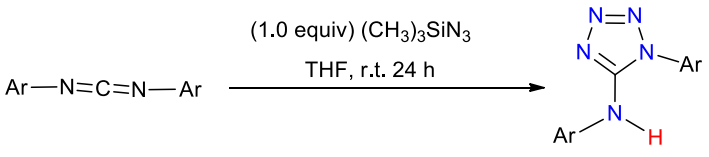
substitution by N_3 of (i) chlorine in R-chloroformamidines[49] which is obtained from nitriles and alkyl halides[50-52] (ii) the sulfite anion in amino imino methanesulfonic acids[53] and (iii) sulfur from thioureas in the presence of mercury[54]. (Scheme **3.B.1**). Hypervalent iodine reagents have been used for desulfurization purposes[55-56]. O-iodoxybenzoic acid (IBX) can be used for oxidative desulfurization of thioureas to carbodiimides and variety of substituted 5-amino tetrazoles have been successfully synthesized from 1,3 di aryl thioureas through the formation of carbodiimide in good yields by chaudhari et. al[57]. The tetrazole functional groups have their role in coordination chemistry[58-61].

Results and discussion

Synthesis of Bulky aryl 5-amino tetrazoles

The required precursors for the synthesis of bulky aryl 5-amino tetrazoles *i.e* symmetrical 1, 3-diaryl carbodiimides were synthesized according to the literature procedures[62.] All reactions were carried out at 1 gram scale of corresponding 1, 3-disubstituted aryl carbodiimide. The corresponding carbodiimide (1.0 equiv.) was dissolved in dry THF (~10 mL) to this trimethylsilylazide (1.1 equiv) was added and the reaction mixture was stirred at 60 ^{o}C for 24 h. The progress of the reaction was monitored by thin layer chromatography. When the complete consumption of the carbodiimde was noticed, the volatiles were removed under reduced pressure. The solid residue so obtained was washed with *n*-hexane (~10 mL) and the crude product was recrystallized from ethyl acetate to yield the compounds **(1a-1f)** as colorless crystals in good yields. These crystals were analyzed by NMR, X–ray, mass, IR melting point.

Scheme 3.B.2; Synthesis of Bulky aryl 5-amino tetrazoles from 1, 3-disubstituted aryl carbodiimides.



NMR spectroscopy confirms the formation of 5-amino tetrazoles. A characteristic N-*H* resonance around 5 ppm was noticed in the products whereas no such N-*H* resonance was noticed in the precursors 1, 3-disubstituted aryl carbodiimides and further the compounds **1a-1d** were characterized by X–ray analysis.

Scheme 3.B.3 Mechanism for the formation of 5-amino tetrazoles.

The formation of 5-amino tetrazoles first involves the nucleophilic addition of azide to the corresponding carbodiimide and followed by electrocyclization to result the desired 5-amino tetrazoles.

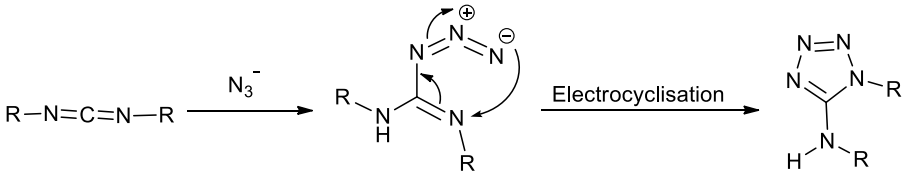
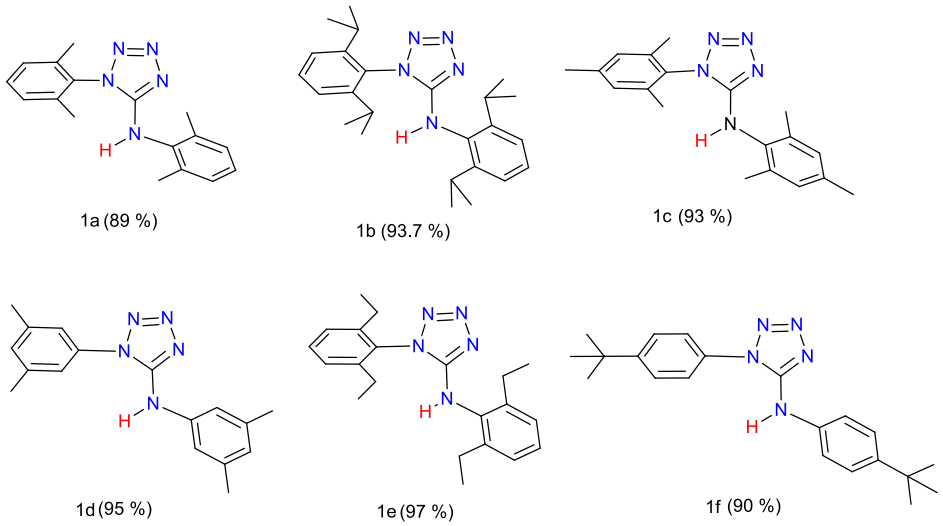


Table 3.B.1 Symmetrically and un symmetrically substituted N,1-bis(phenyl)-1H-tetrazole-5-amine derivatives.



Structural aspects

NMR spectra of these compounds **1a–1d** provided the conclusive evidence of their formation. But, single–crystal X–ray structures were also obtained for further confirmation. The connectivity of atoms in all these compounds **1a–1d** was clearly established by the X–ray studies. Single crystals suitable for X–ray analysis of compounds **1a–1d** were grown from ethyl acetate. Compounds **1a–1d** were crystallized in monoclinic space group P2(1)/n, triclinic space group $P\bar{1}$, orthorhombic space group Pbca, and monoclinic space group P 21/c respectively. There is only one molecule exists in the unit cell of compounds **1a**, **1c**, **1d** and two independent molecules exist in the unit cell of compound **1b**. The ORTEP drawings of compounds **1a–1d** were displayed in (Figures **3.B.1-3.B.4**). X ray analysis revealed that there are total five nitrogen atoms are arranged in conjugation in ligands **(1a–1d)**. The single crystal XRD experiments revealed the molecular structures of **1a–1d** displaying the five membered heterocyclic compound containing four nitrogen atoms and one carbon atom in the ring another nitrogen atom is connected to the carbon atom of the ring. In this 5-amino tetrazole molecular core, there exist two C–N bonds, two N–N bonds one N=N bond and one C=N bond. Among the two C–N bonds one is part of the ring and another one is outside the ring. The C=N, N–N, N=N bonds are part of the ring.

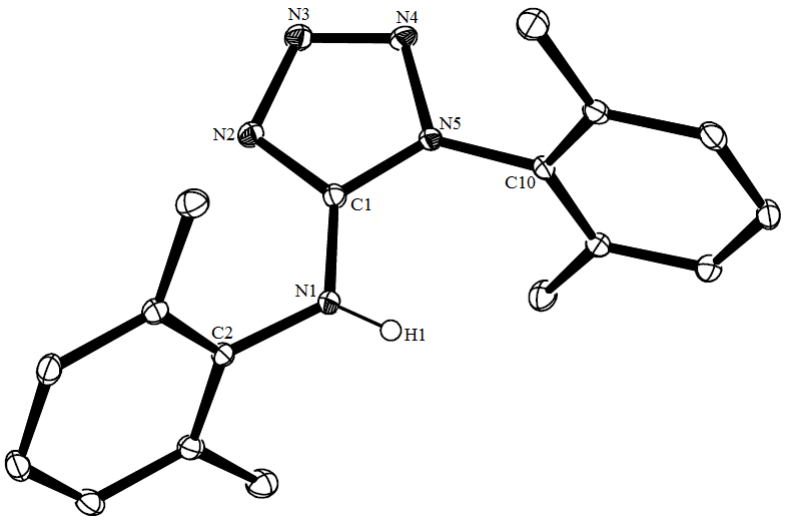


Figure 3.B.1. Molecular structure of **1a.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): N2–N3 1.374(3), N3–N4 1.286(3), N4–N5 1.371(2), C1–N2 1.328(3), C1–N1 1.350(3), C1–N5 1.351(3), N2–C1–N1 126.75(19), N2–C1–N5 109.64(18), N1–C1–N5 123.60(19), C1–N2–N3 104.64(17), N4–N3–N2 111.90(18), N3–N4–N5 106.54(16), C1–N5–N4 107.26(17).

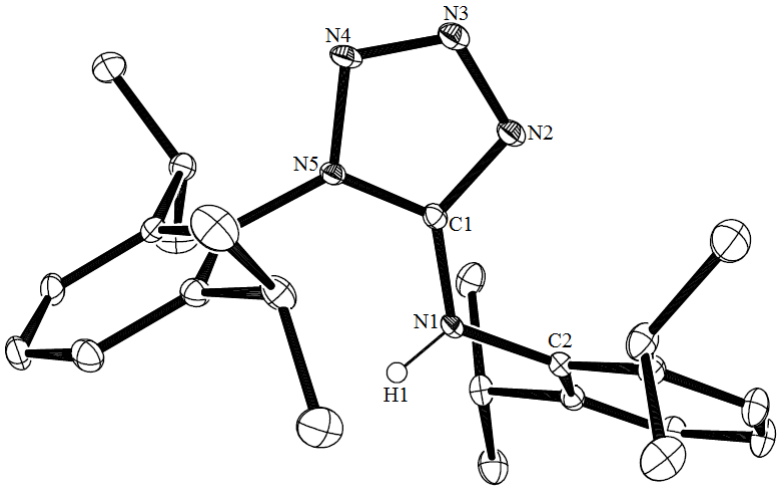


Figure 3.B.2. Molecular structure of **1b.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles

(deg): C1–N1 1.3493(18), C1–N5 1.3503(17), C1–N2 1.3281(18), N2–N3 1.3606(17), N3–N4 1.2927(17), N4–N5 1.3704(16), N2–C1–N1 127.08(13), N2–C1–N5 109.03(12), C1–N2–N3 104.93(11), N4–N3–N2 112.59(11), N3–N4–N5 105.42(11), C1–N5–N4 108.02(11).

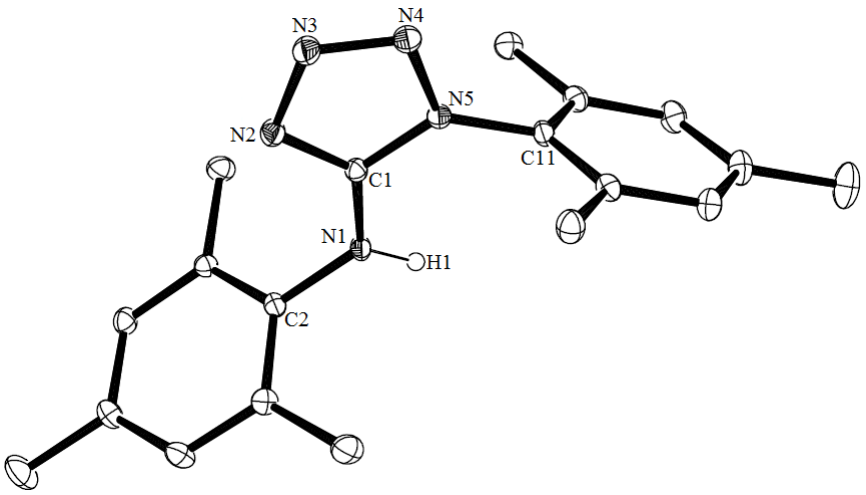


Figure 3.B.3. Molecular structure of **1c.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C1–N1 1.3478(17), C1–N5 1.3443 (17), C1–N2 1.3247(18), N2–N3 1.3626(17), N3–N4 1.2894(17), N4–N5 1.3731(16), N2–C1–N1 127.01(13), N2–C1–N5 109.58(12), C1–N2–N3 105.06(11), N4–N3–N2 111.87(11), N3–N4–N5 106.20(11), C1–N5–N4 107.30(11).

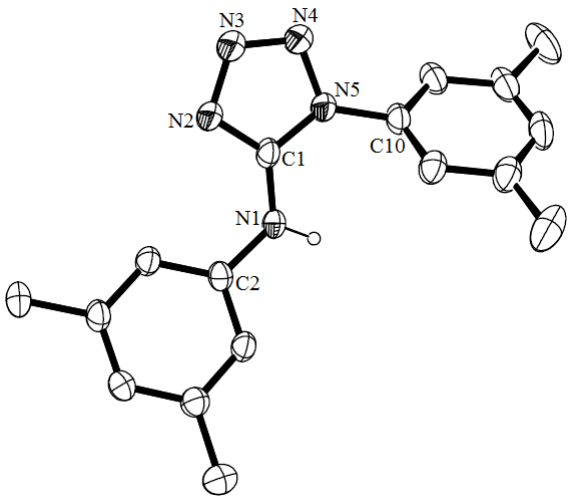


Figure 3.B.4. Molecular structure of **1d.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C1–N1 1.353(18), C1–N5 1.359(3), C1–N2 1.324(3), N2–N3 1.368(3), N3–N4 1.284(3), N4–N5 1.374(3), N2–C1–N1 128.0(2), N2–C1–N5 108.8(2), C1–N2–N3 126.37(18), N4–N3–N2 112.2(2), N3–N4–N5 106.04(19), C1–N5–N4 107.57(18).

Experimental section

General Information: Synthesis of carbodiimides was done in open atmosphere and tetrazoles were prepared in nitrogen atmosphere with dry THF. Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Spectrochem and used as received unless otherwise stated. Column chromatography and TLC were performed on silica gel (100-200) and using UV light. ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AV-400 (^{1}H: 400 MHz, $^{13}C\{^{1}H\}$: 100.6 MHz) and were referenced to the resonances of the solvent used. IR Spectra were recorded in Perkin-Elmer FT-IR Spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer. Melting points were taken on an electro thermal apparatus and are uncorrected. All symmetrical 1, 3-diaryl carbodiimides were synthesized according to the literature procedures[62].

X-ray crystallographic details

Single-crystal X-ray structural study was performed on a Bruker-APEX-II CCD X-ray diffractometer equipped with an Oxford cryosystem 700 Instruments low-temperature attachment. Data were collected at 100(2) K by using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The indexing of frames, integration, and scaling was done by using the

SMART and SAINT software package[63], and the absorption correction for data was performed by using the SADABS program[64]. The structures were solved with ShelXT programe by using direct methods[65], and refined by using the ShellXL with least square minimisation[66] in the olex2[67] software. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystal data for all compounds along with the final residuals and other pertaining details are provided in the tables.

General procedure for the synthesis of symmetrical 5-amino tetrazoles.

All reactions were performed by using 1 gram of corresponding 1,3-disubstituted aryl carbodiimide. The reaction mixture of corresponding carbodiimide (1.0 equiv.) and trimethylsilylazide (1.1 equiv) in dry THF (~10 mL) was stirred at 60 ^{o}C for 2 days. The progress of the reaction was monitored by thin layer chromatography and the volatiles were removed under reduced pressure. The solid residue so obtained was washed with *n*-hexane (~10 mL) and recrystallized from ethyl acetate to get the compounds **(1a-1f)** as colorless crystals. These crystals were analyzed by NMR, X–ray, mass, IR melting point.

Synthesis of N, 1– bis (2, 6-dimethylphenyl)-1H-tetrazole-5-amine (1a)

(Yield: mmol, 89 %); m.p. 199 – 203 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 2.17 (s, 6H, ArC*H*$_3$), 2.22 (s, 6H, ArC*H*$_3$), 5.31 (s, 1H, N–*H*), 7.08 – 7.15 (m, 3H, Ar*H*), 7.29 (d, J = 8.0 Hz, 2H, Ar*H*), 7.41 (t, J = 8.0 Hz, 1H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 17.6 Ar-*C*H_3, 18.4 (Ar-*C*H_3), 127.9 (Ar-*C*H_3), 128.8 (Ar-*C*H_3), 129.3 (Ar-*C*), 130.3 (Ar-*C*), 131.3 (Ar-*C*), 134.3 (Ar-*C*), 135.6 (Ar-*C*), 137.1 (Ar*C*), 153.8 (N_3*C*). IR (KBr): ν (cm^{-1}): 3358s, 2950w,

2921w, 1599s, 1500m, 1473m, 1120w, 1091s, 1033m, 786s, HRMS (ESI/TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{20}N_5$ 294.1713; found: 294.1692.

Synthesis of N, 1-bis (2, 6-diisopropylphenyl)-1H-tetrazole-5-amine (1b).

(Yield: mmol, 93.7%); m.p. 260 - 266 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.16 (d, J = 8.0 Hz, 12H, CH(CH_3)$_2$), 1.20 (d, J = 8.0 Hz, 6H, CH(CH_3)$_2$), 1.31 (d, J = 8.0 Hz, 6H, CH(CH_3)$_2$), 2.45 – 2.55 (sept, 2H, CH(CH$_3$)$_2$)), 2.98 – 3.08 (sept, 2H, CH(CH$_3$)$_2$)), 5.24 (s, 1H, N-*H*), 7.20 (d, J = 8.0 Hz, 2H, Ar*H*), 7.33 (t, J = 8.0 Hz, 1H, Ar*H*), 7.40 (d, J = 8.0 Hz, 2H, Ar*H*), 7.59 (t, J = 8.0 Hz, 1H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ 22.8 (CH(*C*H$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 124.0 (Ar-*C*), 124.8 (Ar-*C*), 127.5 (Ar-*C*), 129.1 (Ar-*C*), 131.3 (Ar-*C*), 132.1 (Ar-*C*), 146.7 (Ar-*C*), 147.8 (Ar-*C*), 155.7 (N$_3$*C*). IR (KBr): ν (cm^{-1}): 3211s, 3077m, 2962s, 1600s, 1467s, 1127m, 1107m, 1095s, 801m, 790m, 756m. HRMS (ESI/TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{36}N_5$ 406.2965; found: 406.2971.

Synthesis of N, 1- bis (2, 4, 6 trimethyl phenyl)-1H-tetrazole-5-amine (1c)

(Yield: mmol, 93 %); m.p. 220 - 230 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.11 (s, 6H, Ar *o*-C*H*$_3$), 2.16 (s, 6H, Ar *o*-C*H*$_3$), 2.27 (s, 3H, Ar *p*-C*H*$_3$), 2.38 (s, 3H, Ar *p*-C*H*$_3$), 5.23 (s, 1H), 6.90 (s, 2H, Ar*H*)), 7.08 (s, 2H, Ar*H*)). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ 17.5 (Ar-*C*H$_3$), 18.3 (Ar-*C*H$_3$), 21.0 (Ar-*C*H$_3$),, 21.3 (Ar-*C*H$_3$), 127.7 (Ar-*C*), 129.5 (Ar-*C*), 130.0 (Ar-*C*), 131.7 (Ar-*C*), 135.3 (Ar-*C*), 136.7 (Ar-*C*), 137.5 (Ar-*C*), 141.5 (Ar-*C*), 154.1 (N$_3$*C*). IR (KBr): ν (cm^{-1}): 3311s, 2978m, 2951m, 2922m, 1612m, 1595s, 1117m, 1097m, 864m, 857m. HRMS (ESI/TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{24}N_5$ 322.2026; found: 322.2003.

Synthesis of N, 1-bis (3, 5-dimethylphenyl)-1H-tetrazol-5-amine (1d)

(Yield: mmol, 95 %); m.p. 210 - 220 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 2.31 (s, 6H, ArCH_3), 2.43 (s, 6H, ArCH_3), 6.27 (s, 1H, N-*H*), 6.73 (s, 1H, Ar*H*), 7.11 (s, 2H, Ar*H*), 7.17 (s, 2H, Ar*H*), 7.21 (s, 1H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 21.3 (Ar-CH_3), 21.4 (Ar-CH_3), 115.9 (Ar-*C*), 122.5 (Ar-*C*), 125.2 (Ar-*C*), 132.2 (Ar-*C*), 132.5 (Ar-*C*), 138.0 (Ar-*C*), 139.2 (Ar-*C*), 140.7 (Ar-*C*), 151.7 (N_3C). IR (KBr): ν (cm^{-1}): 3298s, 3141w, 3099w, 2954w, 2920w, 1622s, 1600s, 1480m, 1119w, 1078m, 1037m, 850m, 842m. HRMS (ESI/TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{20}N_5$ 294.1713; found: 294.1713.

Synthesis of N, 1-bis (2, 6-diethylphenyl)-1H-tetrazol-5-amine (1e)

(Yield: mmol, 97%); m.p. 198 - 205 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 1.13 (t, *J* = 8.0 Hz, 6H, CH_2CH_3), 1.22 (t, *J* = 8.0 Hz, 6H, CH_2CH_3), 2.43 (m, 4H, CH_2CH_3), 2.56 (q, *J* = 8.0 Hz, 4H, CH_2CH_3), 5.26 (s, 1H, N-*H*), 7.14 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.24 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.35 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.52 (t, *J* = 8.0 Hz, 1H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 14.6 (Ar-CH_2CH_3), 23.3 (Ar-CH_2CH_3), 25.8 (Ar-CH_2CH_3), 29.2 (Ar-CH_2CH_3), 123.4 (Ar-*C*), 124.7 (Ar-*C*), 125.1 (Ar-*C*), 125.9 (Ar-*C*), 126.6 (Ar-*C*), 133.2 (Ar-*C*), 134.6 (Ar-*C*), 138.7 (Ar-*C*), 142.9 (Ar-*C*). IR (KBr): ν (cm^{-1}): 3378s, 3048m, 3066m, 2962s, 2933s, 2349s, 2340s, 2361s, 1609m, 1568m, 1514m, 1507m, 1457m, 1423m, 1291s, 1265s, 1222s, 897s, 868s, 789s, 717s. HRMS (ESI/TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{28}N_5$ 350.2339; found: 350.2362.

Synthesis of N, 1-bis (4-(t-butyl) phenyl)-1H-tetrazole-5-amine (1f)

(Yield: mmol, 90%); m.p. 198 - 205 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 1.30 (s, 9H, $(CH_3)_3C$), 1.39 (s, 9H, $(CH_3)_3C$), 6.35 (s, 1H, N-*H*), 7.36 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.45 (t, *J* = 8.0 Hz, 4H, Ar*H*), 7.63 (d, *J* = 8.0 Hz, 2H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 31.3 (Ar-CH_3), 31.4 (Ar-CH_3), 34.4 (Ar-CH_3), 35.1 (Ar-CH_3), 118.2 (Ar-*C*), 124.5 (Ar-*C*), 126.2 (Ar-

C), 127.5 (Ar-*C*), 130.1 (Ar-*C*), 135.6 (Ar-*C*), 146.5 (Ar-*C*), 152.0 (Ar-*C*), 154.1 (N_3C). IR (KBr): ν (cm^{-1}): 3378s, 3048m, 3066m, 2962s, 2933s, 2349s, 2340s, 2361s, 1609m, 1568m, 1514m, 1507m, 1457m, 1423m, 1291s, 1265s, 1222s, 897s, 868s, 789s, 717s. HRMS (ESI/TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{28}N_5$ 350.23; found: 350.25

Conclusion

In conclusion, we have shown the synthesis of various symmetrical bulky N, 1-bis (aryl)-1H-tetrazole-5-amine from symmetrical bulky carbodiimides. These symmetrical bulky carbodiimides were synthesized by the dehydrosulfurisation of corresponding thioureas by using a base and iodine in THF at mild reaction conditions in moderate to high yields. 5-aminotetrazoles show several biological activities such as anti-asthmatic, anti-allergic antiviral and anti-inflammatory. The coordination chemistry of 5-aminotetrazoles was less explored. We are looking forward to explore the coordination chemistry of these ligand systems towards the main group as well transition metals.

References

1 T. Okabayashi, H. Kano and Y. Makisumi, *Chem. Pharm. Bull.,*1960, **8**, 157.

2 S. K. Sangal and A. Ashok Kumar, *J. Indian Chem. Soc.,* 1986, **63**, 351.

3 J. K. Witkowski, R. K. Robins, R.W. Sidwell and L. N. Simon, *J. Med. Chem.,* 1972, **15**, 1150.

4 K. C. Tsov and H. C. F. Su, *J. Med. Chem.*, 1963, **6**, 693.

5 V. C. Bary, M. C. Conalty, J. P. O'Sllivan and D. Twomey, *Chemotherapy.,* 1977, **8**, 103.

6 J. R. Maxwell, D. A. Wasdahl, A. C. Wolfson and V. I. Stenberg, *J. Med. Chem.*, 1984, **27**, 1565.

7 K. D. Stewart, *Bioorg. Med. Chem. Lett.*, 1998, 529.

8 J. S. Shukla, J. Ahmed and S. Saxena, *J. Indian Chem. Soc.,* 1979, **41**, 70.

9 C. J. Shishoo, M. B. Devani, M. D. Karvekar, G. V. Vilas, S. Anantham and V. S Bhaati, *Indian J. Chem.,* Sect B 1982, **21**, 666.

10 S. M. Ray and S. C. Lahiri, *J. Indian Chem. Soc.*, 1990, **67**, 324.

11 S. Hayao, H. J. Havera, W. G. Strycker, T. J. Leipzig and R. Rodriguez, *J. Med. Chem.*, 1965, **10**, 400.

12 S. K. Fig dor and M. S. Von Wittenau, *J. Med. Chem.,* 1967, **10**, 1158.

13 C. X. Wei, M. Bian and G. H. Gong, *Molecules.,* 2015, **20**, 5528–5553;

14 J. Roh, K. Vavrova and A. Hrabalek, *Eur. J. Org. Chem.,* 2012, 6101–6118;

15 P. B. Mohite and V. H. Bhaskar, *Int. J. PharmTech Res.,* 2011, **3**, 1557–1566;

16 L. M. Frija, A. Ismael and M. L. S. Cristiano, *Molecules.,* 2010, **15**, 3757–3774;

17 L. V. Myznikov, A. Hrabalek and G. I. Koldobskii, *Chem. Heterocycl. Compd.,* 2007, **43**, 1–9.

18 J. A. Bladin, *Ber. Dtsch. Chem. Ges.,* 1885, **18**, 1544–1551.

19 H. Singh, A. S. Chala, V. K. Kapoor, D. Paul and R. K. Malhotra, *Prog. Med. Chem.,*1980**,** **17**, 151.

20 R. Huisgen, J. Sauer, H. J. Sturn and J. H. Markgraf, *Chem. Ber.,* 1960, **93**, 2106.

21 D. Moderhack, *J. Prakt. Chem.,* 1988, **340**, 687.

22 A. Hantzsch, A. Vagt, *Justus Liebigs Ann.Chem.,* 1901, **314**, 339.

23 J. Yoshinaga, T. Shogaki, T. Kakita, H. Ozeki, N. Sugimoto and Y. Kato, *Eur. Patent EP* 262873, 1988; *Chem. Abstr.*, 1988, **109**, 54782.

24 W. A. Cetenko, D. T. Connor, M. D. Mullican and R. Sorenson, *J. Eur. Patent EP* 249236, 1987; *Chem. Abstr*., 1988, **108**, 150482.

25 D. T. Connor, P. C. Unangst and R. Weikert, *J. Eur. Patent EP* 279466, 1988; *Chem. Abstr.*, 1988, **109**, 231035.

26 R. E. Ford, P. Knowles, E. Lunt, S. M. Marshall, A. J. Penrose, C. A. Ramsden, A. J. H. Summers, J. L. Walker and D. E. Wright, *J. Med. Chem.*, 1986, **29**, 538.

27 N. P. Peet, L. E. Baugh, S. Sundler, J. E. Lewis, E. H. Matthews, E. L. Olberding and D. N. Shah, *J. Med. Chem.*, 1986, **29**, 2403.

28 V. M. Girijavallabhan, P. A. Pinto, A. K. Ganguly and R. W. Versace, *Eur. Patent EP* 274867, 1988; *Chem. Abstr*., 1989, **110**, 23890.

29 H. Akimoto, K. Ootsu and F. Itoh, *Eur. Patent EP* 530537, 1993; *Chem. Abstr*., 1993, **119**, 226417.

30 A. G. Taveras, A. K. Mallams and A. Afonso, *Int. Patent WO* 9811093, 1998; *Chem. Abstr*., 1998, **128**, 230253.

31 C. H. Mitch and S. J. Quimby, *Int. Patent WO* 9851312, 1998; *Chem. Abstr*., 1998, **130**, 13997.

32 J. L. Castro Pineiro, M. S. Chambers, S. C. Hobbs and V. G. Matassa, *Int. Patent WO* 9319052, 1993; *Chem. Abstr*., 1994, **120**, 134543.

33 A. Andrus, B. Partridge, J. V. Heck and B. G. Christensen, *Tetrahedron Lett.*, 1984, **25**, 911.

34 A. R. Katritzky, B. V. Rogovoy and K. V. Kovalenko, *J. Org. Chem.*, 2003, **68**, 4941-4943.

35 R. E. Ford, P. Knowles, E. Lunt, S. M. Marshall, A. J. Penrose, C. A. Ramsden, A. J. H Summers, J. L. Walker and D. E. Wright, *J. Med. Chem.*, 1986, **29**, 538.

36 N. P. Peet, *J. Heterocycl. Chem.,* 1987, **24**, 223.

37 T. Kato, T. Chiba and M. Daneshtalab, *Chem. Pharm. Bull.,* 1976, 24, 2549.

38 A. Andrus, B. Partridge, J. V. Heck and B. G. Christensen, *Tetrahedron lett.*, 1984, **25**, 911.

39 R. N. Butler and F. L. Scott, *J. Org. Chem.,* 1966, **31**, 3182.

40 M. Klich and G. Teutsch, *Tetrahedron.,* 1986, **42**, 2677.

41 W. G. Finnegan, R. A. Henry and E. Lieber, *J. Org. Chem.,* 1953, **18**, 779.

42 K. A. Jensen, A. Holm and S. Rachlin, *Acta Chem. Scand.,* 1966, **20**, 2795.

43 D. F. Percival and R. M. Herbst, *J. Org. Chem.,* 1957, **22**, 925.

44 Y. X. Ding and W. P. Weber, *Synthesis.,* 1987, 823.

45 D. Moderhack, K. H. Goos and L. Preu, *Chem. Ber.,* 1990, **123**, 1575.

46 W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.,* 1953, **18**, 1014.

47 R. M Herbst, C. W. Roberts and E. J. Harvill, *J. Org. Chem.,* 1951, **16**, 139.

48 M. Marchalin and A. Martvon, *Collect. Czech. Chem. Commun.,* 1980, **45**, 2329.

49 W. Ried and H. E. Erle, *Liebigs Ann. Chem.,* 1982, 201.

50 W. Ried, H. Dietschmann and H. E. Erle, *Synthesis.,* 1980, 619.

51 E. Kuhle, B. Anders, E. Klauke, H. Tarnow and G. Zumach, *Angew. Chem., Int. Ed. Engl.* 1969, **8**, 20.

52 E. Kuhle, B. Anders and G. Zumach, *Angew. Chem., Int. Ed. Engl.* 1967, **6**, 649.

53 A. E. Miller, D. J. Feenay, Y. Ma, L. Zarcone, M. A. Aziz and E. Magnuson, *Synth. Commun.,* 1990, **20,** 217.

54 R. A. Batey and D. A. Powell, *Org. Lett.,* 2000, **2**, 3237.

55 C. Zhu, D. Xu and Y. Wei, *Synthesis.,* 2011, **5,** 711.

56 H. Ghosh, R. Yella, J. Nath and B. K. Patel, *Eur. J. Org. Chem.*, 2008, 6189.

57 P. S. Chaudhari, S. P. Pathare and K. G. Akamanchi *J. Org. Chem.,* 2012, **77**, 3716−3723.

58 P.Lin, W. Clegg, R. W. Harrington and R. A. Henderson, *Dalton Trans.*, 2005, 2388.

59 A. K.Gupta, C. Y. Rim and C. H. Oh, *Synlett.*, 2004, **12**, 2227.

60 P. L. Franke and L. W. Groeneveld, *Inorg. Chem. Acta.*, 1980, **40**, 111.

61 E. H. White and H. Scherrer, *Tetrahedron Lett.*, 1961, **21**,758.

62 T. P. Rao, A. Baishya, M. K. Barman and S. Nembenna, *New J. Chem.*, 2016, **40**, 7627-7636.

63 SAINT+ Software for CCD Diffractometers, Bruker AXS, Madison, WI, 2000.

64 G. M. Sheldrick, SADABS Program for Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1999.

65 G. M. Sheldrick, *Acta Cryst.*, 2015, A71, 3.

66 G. M. Sheldrick, *Acta Cryst.*, 2015, C71, 3.

67 O.V Dolomanov, L.J Bourhis, R.J Gildea, J.A.K Howard; H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, 2009, **42**, 339-341.

Chapter 4: A New Class of Guanidine Ligands: Synthesis and Characterization of "Conjugated Bis–Guanidines" and Their Lithium Salts.

ABSTRACT:

Herein, we report a series of metal-free synthesis of well-defined and novel guanidine molecules named as "conjugated bis–gaunidine(s) **1–4** for the first time. These important nitrogen-rich organic molecules were synthesized by two different procedures (Method **A** and **B**). Bulky aryl carbodiimides are the ideal precursors in both the synthetic protocols. In method A, the desired compounds (**1–4**) were synthesized by refluxing the reaction mixture of acetamidoxime (1.0 equiv) and the corresponding *N,N'*–diaryl carbodiimide (2.1 equiv) in toluene for two days, followed by the purification with column chromatography. Method B, involves the reaction between corresponding *N, N'*–diaryl carbodiimide (1.0 equiv) and aq. ammonia (4.0 equiv) in acetonitrile at room temperature, the pure compound was obtained by crystallization from dichloromethane. Further, two conjugated bis–guanidine ligands such as **1***i.e.*,L^1(3H) [L = {$(ArN)_2C$=N-C= N(Ar)(NAr)}; Ar = 2, 6-Me_2 - C_6H_3] and **4** *i.e.*,L^4(3H) [L^4 = {$(ArN)_2C$=N-C= N(Ar)(NAr)}; Ar = 2, 6-$^iPr_2$ - C_6H_3] have been utilized to prepare their corresponding lithium salts. The ligand **1** [**L^1(3H)**] has been utilized to synthesize, THF adduct of four-coordinated lithium complex **5,** Et_2O adduct of three-coordinated lithium complex **6** and un solvated lithium complex **7.** The reaction between compound **4** [L^4(3H)] (1.0 equiv) and *n*-BuLi (1.1 equiv) at room temperature led to the formation of a mono-coordinated lithium complex **8.** In this compound **8** metal– arene interaction was observed where the lithium is found involving interaction with the carbon atoms of the aromatic rings. All the new conjugated bis-guanidine ligands **1-4**, the THF- solvated lithium complex **5** and the Et_2O-solvated lithium complex **6** were characterized by crystallography. The compound **7** was characterized by multi nuclear ^1H, ^{13}C & ^7Li NMR. The compounds **1-4** are air stable and compounds **5**–**8** are highly sensitive towards air

and moisture. The basic differences between the tetra substituted guanidine and conjugated bis–guanidine has been discussed in the figure **4.4**

Introduction

The chemistry of main group elements has received at most attention and remarkable advancement has been achieved in the past decade. Bulky *N*, *N*' chelating ligands exhibit prominent role in establishing land mark innovations such as stabilizing main group metals in their low oxidation states and designing main group metal catalysts which can function as efficient as transition metals in catalyzing some valuable organic transformations. The designing of new ligands in this field depends on different paths such as new structures, catalytic activity, and volatility. The bulky *N*, *N*' donor ligands such as *β*-diketaminate, guanidinate, amidinate, triaza framework, dipyrromethane ligands have been extensively employed for developing main group chemistry. The coordination chemistry of *β*-diketaminate was developed at the earliest by Bradley,[1-2] Holm[3] and the excellent review article by Lappert.[4] Since then a great deal of interest in this ligand as a host for several metals across the periodic table ranging from alkaline earth metals,[5,6] main group elements,[7] lanthanides and actinides[8-10] and transition metals.[11-15] The main group metal pre-catalysts containing the β-diketiminate moiety, for catalyzing ring-opening polymerization,[16-18] polycarbonate formation[19-21] and olefin polymerization[22-24] documented in the literature. Triaza framework is another kind of *N*, *N*' chelating ligand which closely resemble β-diketiminates structure i (Figure **4.1**)

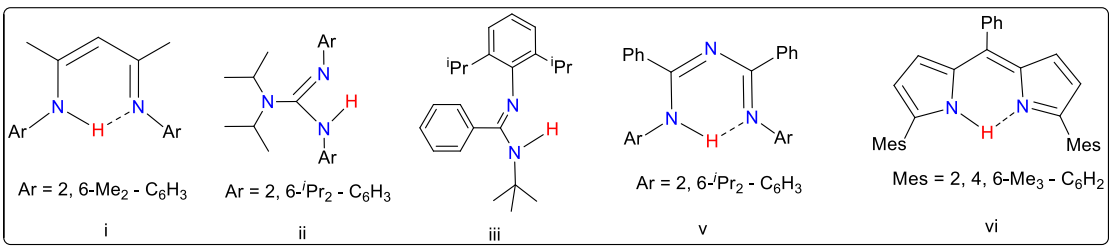


Figure 4.1. Previous reports of various bulky *N, N*' chelating ligands.

have been comparatively less explored.[25-34] Though there have been a good number of Al complexes of triaza framework ligands, such as bis (2-pyridyl)amine[35-37] and phthalocyanin[38,39] reported in the literature the coordination chemistry of triazapentadienate ligands is less known and Al complexes bearing these ligands were reported by Bakthavachalam et al[40] in 2013. Dipyrromethene is also another class of *N, N*' chelating ligand system can form six membered metallocycles (Figure **4.1**). Betley and co-workers reported the imido complexes of iron and cobalt stabilized by sterically demanding α,α′-diaryl or α,α′-dialkyl dipyrromethene ligands.[41-43] The electronic and steric properties in dipyrromethene ligands can be tuned by varying the substituents at the α or β positions of pyrrole and the dipyrromethene meso position.[44-45] The bulky dipyrromethene ligated monomeric aluminum (III) centers was explored by Gianopoulos et al in 2014.[46] Although the BODIPY luminophores are popular the dipyrromethene complexes of the heavier group 13 elements are unexplored and limited to six-coordinate homoleptic complexes of the form $M(N,N)_3$, where (N,N) represents a deprotonated dipyrromethene ligand[47-54]. The groups of Dolphin[47,48] and Cohen[49,50] have focused on Ga and in chemistry and Hsieh reported an organometallic thallium complex of the form[51-54] (N, N) $TlMe_2$. Amidinates are closely related with guanidinate representing a well-established class of N-chelating ligands which can form complexes with almost all metals across the periodic table.[55-59] The real beauty of amidinate and guanidinate (and related) ligands is the fact that the substituents of these motifs can be tunable to allow numerous variations in the substitution pattern. This versatility and easy accessibility of amidinate and guanidinate accounts for their tremendous popularity in recent years. Amidinate and guanidinate stabilized lanthanide metal complexes and their applications in catalysis, materials science have been nicely presented by Frank T. Edelmann.[60-61] Many review

articles have been documented in recent years describing the features and coordination chemistry of bulky guanidinate.[62–64] These bulky guanidinate ligands are the renowned motifs for their potentiality in stabilizing the low oxidation state main group metal complexes.[65, 66]

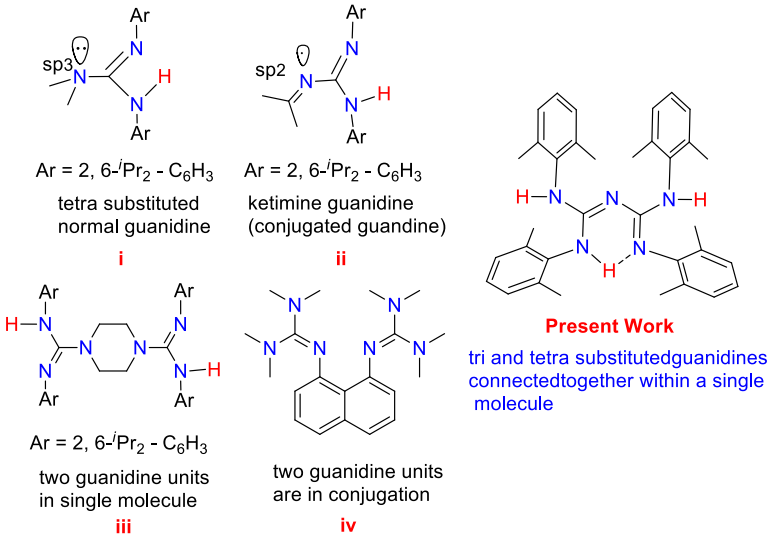


Figure 4.2. Previous reports of various guanidine ligands

Though several synthetic methods are available to prepare guanidinate ligands, a variety of mono– and bifunctional Ar–substituted guanidines can be accessed by following the most common technique *i.e* insertion of carbodiimides into the metal–nitrogen bond of metal amide complexes.[62] The systems are having conjugation attached to the guanidine units and their metal chemistry has received increased attention in recent years. The term "conjugated guanidine function" can be best described as a guanidine function that possesses an unsaturation in the alpha-position to the nitrogen (Figure **4.2**) of its imine group.[67] Several studies have been well established revealing the electronic properties and the proton affinity of the conjugated guanidine 1, 8–Bis (tetramethylguanidino) naphthalene (TMGN).[68–71] Recent studies proved conjugated guanidines as an efficient organocatalyst for the synthesis of polyurethanes.[72] A.K. Maity et.al in

2015 reported the ketimine–guanidinates and their metal chemistry demonstrating their distinctive contribution the metal chemistry unlike amidinate variants.[73] Interestingly the chemistry of symmetrical conjugated bisguanidines has not been well established, these were first observed as byproducts by, V. Yu. Kukushkin et.al. in which the phenyl substituted conjugated bis-guanidine was the side product.[74] Some unsymmetrical alkyl substituted conjugated bisguanidine ligands were documented in 2013.[67] In this aspect we would like to present our efforts to explore much chemistry of these peculiar ligand systems and have been successfully ended up with a convenient synthetic route and some interesting features in their coordination chemistry towards the lithium metal. We accessed the ligands **1**–**4** by using a precise synthetic procedure, not surprisingly the precursors and synthetic protocol for them have not been established so far. They can be easily generated by the reaction between carbodiimide and acetamidoxime in one way and a reaction between carbodiimide and Aqueous ammonia in another method. The term conjugated bis–guanidine is defined as a 'conjugated structure constitute of five nitrogen atoms, consonant with the following formula' as shown in the (Figure **4.3**).[67]

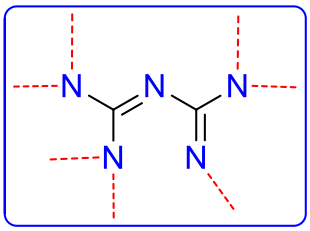
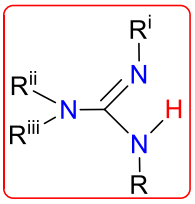
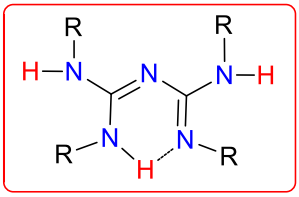


Figure 4.3 standard formula for conjugated bis–guanidine

Figure 4.4 The basic differences between the tetra substituted guanidine and conjugated bis–guanidine



tetra sustituted guanidine



conjugated bisguanidine

Present Work

Presence of one 'N_3C' core	Presence of two 'N_3C' cores
Total three nitrogen atoms	Total five nitrogen atoms
There is no conjugation	Conjugation is observed
Can form only mononuclear metal complexes	Can form mononuclear di nuclear and trinuclear metal complexes also possible.
Can form only four membered metallocycle (CN_2M)	Can form both four & six membered metallocycles (CN_2M) and (C_2N_3M)
Only tetra substituted (Z–anti) Guanidine is observed	Tri and tetra substituted (Z–anti) guanidines are connected together within a single molecule
Less resonating structures	More resonating structures

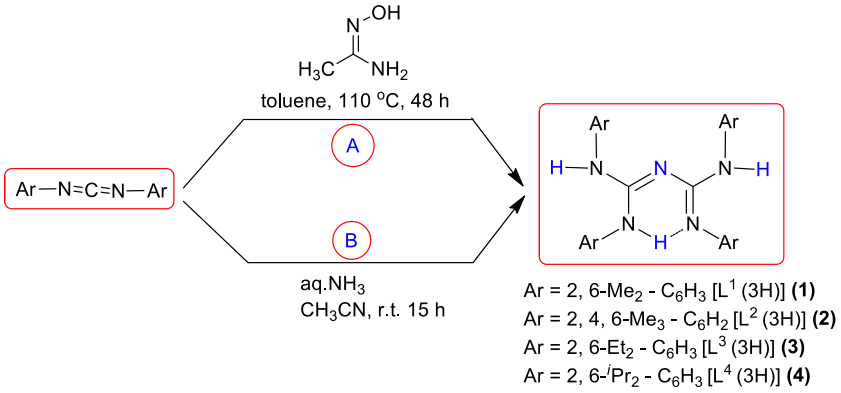
Results and discussion

We have previously reported metal-free access of various symmetrical and unsymmetrical bulky *N, N'*-diarylcarbodiimides. Besides, we reported the catalyst-free synthesis of a library of tetra-substituted guanidines by the reaction of *N, N'*-diarylcarbodiimides with cyclic secondary amines. Thus, *N,N'*-diarylcarbodiimides are ideal precursors for the synthesis of several nitrogen-donor ligands such as formamidines, zwitterionic type amidinates or N-heterocyclic carbene-carbodiimide (NHC-CDI) adducts, amidines, guanidines, etc.

As we mentioned earlier, in 2010 Fylaktakidou, Hadjipavlou-Litina and coworkers reported the synthesis of 5 –amino-substituted 1, 2, 4-oxadiazoles and 1, 3-disubstituted ureas, upon the reactions of amidoximes with carbodiimides. In contrast, the formation of conjugated bis-guanidines (CBG) was observed at the same reaction conditions, upon the reactions of amidoxime with ortho-disubstituted *N, N'*-diarylcarbodiimides. Herein, we report metal-free synthesis of bulky tetra- aryl substituted conjugated bis–guanidines.

These nitrogen rich molecules were accessed conveniently by two new synthetic routes. Bulky *N, N'*-diarylcarbodiimides are the ideal precursors in both the synthetic protocols. In the first method the reaction between corresponding bulky *N, N'*-diarylcarbodiimide (2.1 equiv) and acetamidoxime (1.0 equiv) in toluene at refluxing temperature for two days resulted in the formation of desired product along with some other by-products. The pure compound was obtained by the column chromatography using silica gel with 5:95 % ethyl acetate in *n*-hexane as eluting. We utilized four *N, N'*-diarylcarbodiimides with varying steric bulk to produce the corresponding conjugated bis-guanidine ligands. In all cases the formation of tetra-aryl substituted CBGs in average yields, which is attributed the formation of several other side products in these reactions.

Scheme 4.1. Synthesis of Conjugated bis–guanidine (CBG) ligands



The two carbon atoms of both CDI molecules are connected to one central nitrogen atom and three additional hydrogen atoms which are connected to nitrogen atoms of the CDI molecules (vide infra). Essentially, CBG molecule it is a combination of two CDI and one ammonia molecules. Therefore, we were curious to know the outcome of the reaction between two equiv of CDI and aq. ammonia. Accordingly, we have performed the reaction of one equiv CDI and four equiv of aq. ammonia in acetonitrile at room temperature conditions. To our delight, we observed the formation of CBGs in good yields.

In order to understand the reaction mechanism in both synthetic routes and also the isolation of poor yields in the first method, we had isolated three side products **4a-4c,** when two equiv of ^{dipp}CDI reacted with amidoxime at the same reaction conditions. It should be noted that the reaction was performed by using 6 g of CDI and we were able to isolate the side products in 2.5%, 3% and 1.5% for **4a-4c** respectively.

All CBG ligands **1-4** and the three side products **4a-4c** which are isolated in the reaction between ^{dipp}CDI and amidoxime by method A were confirmed by ^{1}H, ^{13}C NMR, IR and mass spectrometry methods. High-resolution mass spectral and HPLC analysis further confirmed the purity of the CBGs. Furthermore, compounds **1-4** and **4a-4c** were confirmed by single crystal

structure analysis. All CBGs are thermally stable and melt at the range of 165-218 ^{o}C. These are soluble in toluene, THF, dichloromethane and diethyl ether.

Scheme 4.2. Isolation of byproducts, formed in method A.

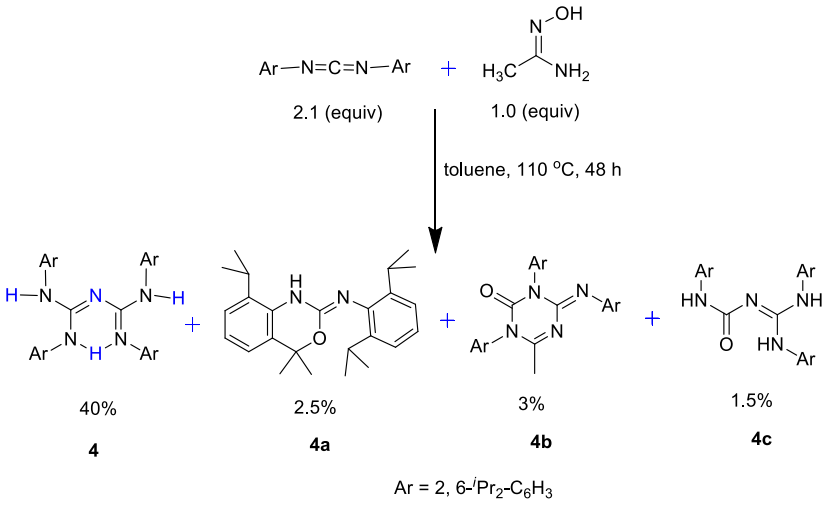
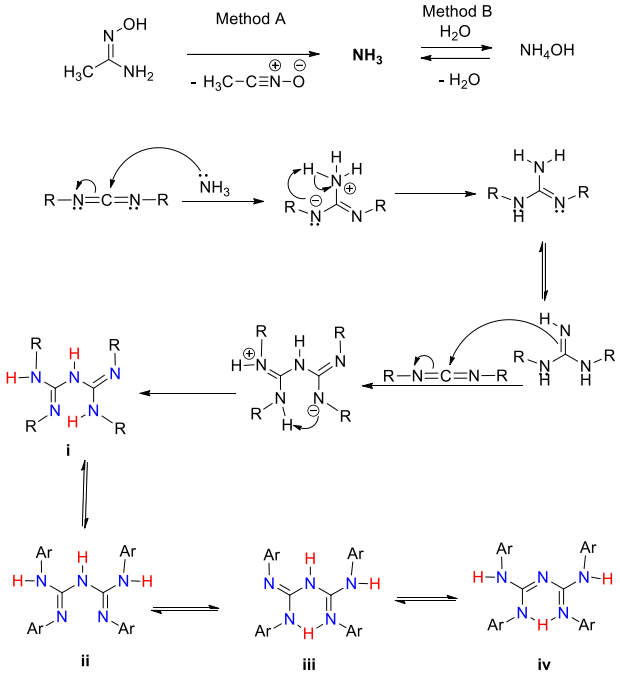


Figure 4.5: Proposed mechanism for the formation of conjugated bisguanidine molecules



Mechanism of formation of CBG

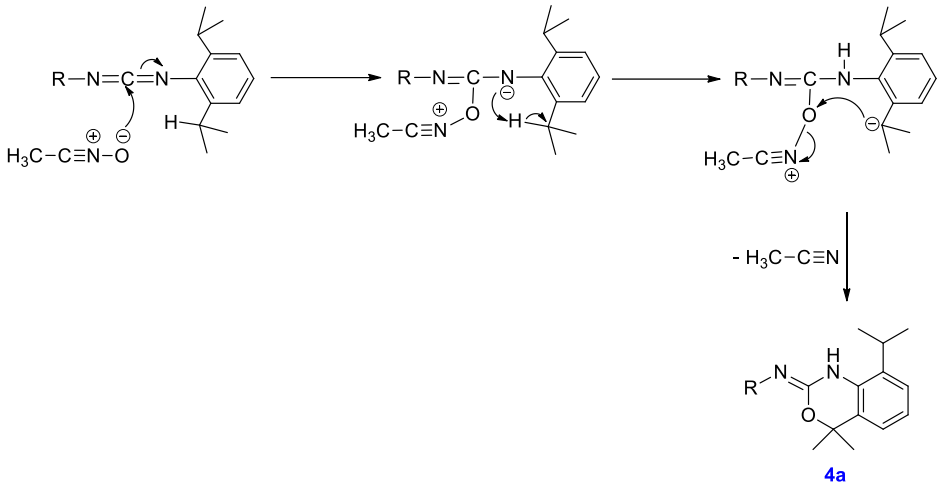
Bulky *N, N'*-diaryl carbodiimide undergoes a nucleophilic addition reaction with an *in situ* generated ammonia molecule, led to the formation of an *N, N'*-di substituted guanidine, which further reacts with another molecule of an *N, N'*-diaryl carbodiimide leads to a conjugated bis-guanidine (CBG). Formation of a compound **4a** can be proposed in three steps: First, nucleophilic addition of an *in situ* generated acetonitrile N-oxide (which is the decomposition product of acetamidoxime) Second, an abstraction of a proton thereby generation of a carbon nucleophile. Third, the attack of carbon nucleophile to an oxygen atom and simultaneous cleavage of O-N bond thereby the elimination of acetonitrile. It is noticed that sp^3 C-H bond activation and insertion of oxygen atom into sp carbon and sp^3 C-H bond.

Formation of **4b**

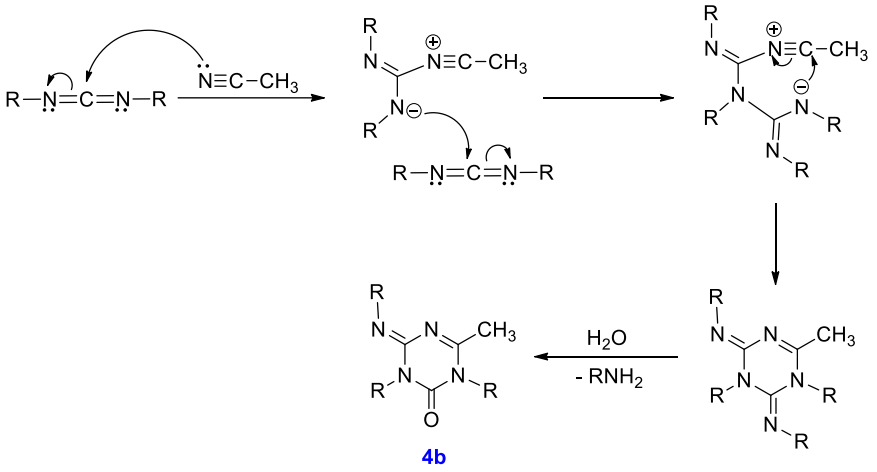
N, N'-diaryl carbodiimide reacts with acetonitrile leads to the formation of a zwitterion. Next, nucleoplilic addition of the anionic nitrogen to a carbon atom of another CDI molecule and followed by ring closure occurs. Further, elimination of RNH_2 upon reaction with water affords compound **4b.**

Conjugated bis-guanidine reacts with water at harsh reaction conditions which allow the formation of a tri-N-substituted guanylurea (**4c**).

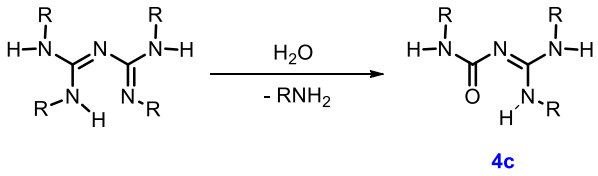
Figure 4.6: Proposed mechanism for the formation of byproducts 4a, 4b and 4c from method A (Scheme **4.2).**



Mechanism for byproduct 4b



Mechanism for byproduct 4c



In the ^{1}H NMR of CBG ligands two sets of magnetically non equivalent N–*H* protons were observed. The 'N–*H*' proton resonates as a broad singlet in the downfield region in the range 12.83–13.04 ppm for compounds L^{1-4} (3H) (**1-4**) in C_6D_6 is due to the N–*H*–N intramolecular hydrogen bonding.

Another well resolved singlet featured at 4.63– 4.96 ppm is due to the 'N–*H*' resonance of the 'Ar–N*H*' for the compounds L^{1-4} (3H) in C_6D_6. The carbon resonance of 'N_3C' observed at 154.7 – 156.9 ppm for the compounds L^{1-4} (3H) in C_6D_6**.** These values are well in agreement with previously reported 150.8 ppm for the substituted guanidines $\{ArNCN(H)Ar\}_2\{\mu\text{-}N(C_2H_4)_2N\}$ (Ar = 2,6 $^{i}Pr_2$-C_6H_3) [75]. In IR spectroscopy stretching frequencies ranging from 3080 to 3400 cm^{-1}, which are characteristic for the '*N–H*' protons in the compounds L^{1-4} (3H) were observed These values are well in agreement with previously reported 3391 cm^{-1} for the substituted guanidines $\{ArNCN(H)Ar\}_2\{\mu\text{-}N(C_2H_4)_2N\}$ (Ar = 2,6 $^{i}Pr_2$-C_6H_3) (75). Furthermore, compounds **1-4** were characterized by melting point, HRMS & HPLC analysis determined the purity of these compounds.

Although the NMR spectra of these compounds **1–4** have given evidence of their formation, single–crystal X–ray structures for **1-4** were obtained for further confirmation. The composition and connectivity in all these compounds **1–4** was established clearly by the X–ray studies. Single crystals suitable for X–ray analysis of compounds **1–4** were grown from ethyl acetate. Compound **1** was crystallized in the triclinic space group $P\bar{1}$, compounds **2, 3** were crystallized in the monoclinic space group $P2_1/n$ and compound **4** was crystallized in the orthorhombic space group Pbca. Only one molecule exists in the asymmetric unit of all the compounds **1–4.** The molecular structure revealed the CBG frame as a conjugated structure incorporating five nitrogen atoms with a C_2N_3 ring for compounds **1-4** displayed in (Figures **4.8, 4.9, 4.10** and **4.11** respectively) and terminal nitrogen atoms held together by intramolecular hydrogen bonding in compounds **1-3**. The intra molecular hydrogen bond between amine and imine nitrogens appears to be inappreciably weaker, the amine imine N-*H* distances are in the range of 1.77–1.97 Å for compounds **1-3** and the amine N-*H* distances are in the range of 0.86 – 0.998 Å for compounds

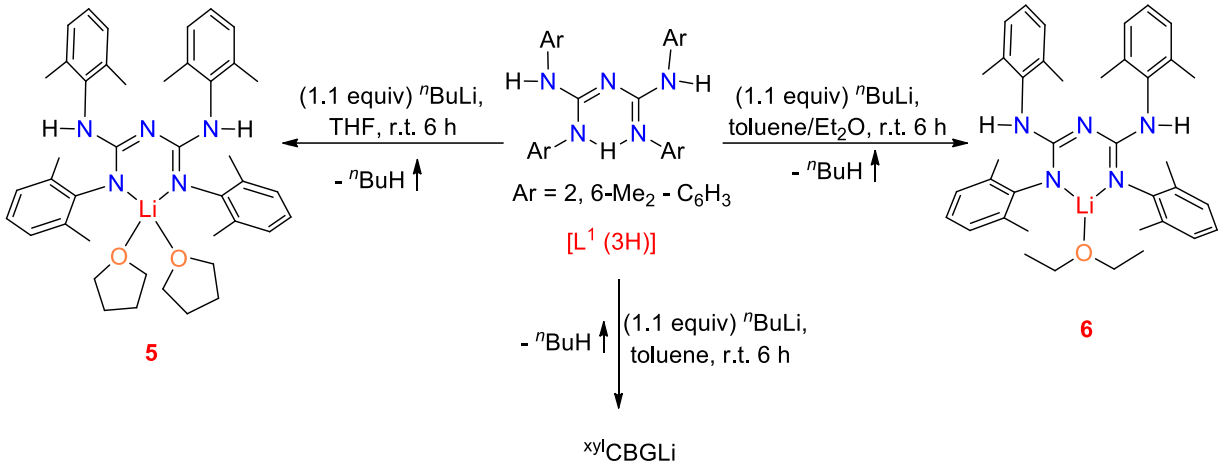
1-4. However, in the compound **4** absence of intra molecular hydrogen bond is noticed which is attributed to the steric nature of the ligand. In compound **4,** the same hydrogen atom is attached to the central nitrogen atom of the CBG, which is flanked by two CDI units. In all cases other two hydrogen atoms are attached to two side-arm nitrogen atoms.

These nitrogen rich molecules are anticipated as ideal ancillary ligands for the construction of a wide range of metal complexes. Accordingly, we investigated the coordination of chemistry of tetra-aryl substituted conjugated bis-guanidines with lithium element. To the best of our knowledge there have been no reports on the coordination chemistry of tetra-aryl substituted conjugated bis-guanidines. CBGs are analogues of *β*-diketiminate and 1, 3, 5-triazapentadienyl ligands. Therefore, we can presume that both free CBG ligands and their lithium salts are ideal precursors for the construction of metal complexes of all blocks of the periodic table. Less and more bulky free ligands such as **1** and **4** have been utilized for the coordination chemistry of lithium to understand the structure and bonding aspects.

Compounds **5-8** are highly air and moisture sensitive. All compounds **5-8** were confirmed by multinuclear (^{1}H, ^{13}C and ^{7}Li) magnetic resonance spectroscopy. Moreover, compounds **5, 6** and **8** were confirmed by single crystal X-ray structural analysis.

The lithium compounds can be obtained through the treatment of the free ligand with *n*-BuLi in tetrahydrofuran, diethyl ether or in hydrocarbon solvents. The addition of *n*-BuLi to the solution of **1** in THF and Et_2O in a 1:1 stoichiometric ratio at room temperature followed by stirring the reaction mixture for 8 h provided the lithium salts **5** (Fig.**4.15**) and **6** (Fig.**4.16**) respectively as their solvent adducts. The colorless crystals of compounds **5, 6** were obtained from *n*-hexane and THF, toluene and diethyl ether mixture respectively in moderate yields 55% (Scheme **4.3**).

Scheme 4.3. Coordination of CBG with Lithium element



The reaction of *n*-BuLi with **1** in toluene solution in a 1:1 stoichiometric ratio at room temperature followed by stirring the reaction mixture for 8 h yielded the lithium salt **7** (Scheme **4.3**) in the un solvated form. Woefully, the attempts to produce the crystal structure of **7** were unsuccessful but the compound was isolated as a colorless solid in good yield 61%. Compound 8 (Fig. **4.17**) was synthesized by stirring the reaction mixture of **4** and *n*-BuLi in toluene in a 1:1 stoichiometric ratio at room temperature for 8 h. Colorless crystals for **8** were acquired from toluene in good yield 60% (Scheme **4.4**)

Scheme 4.4. Metal-arene interaction of Lithium ion with adjacent aryl groups

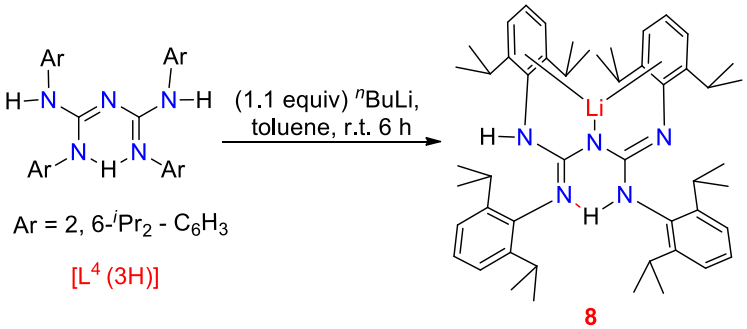
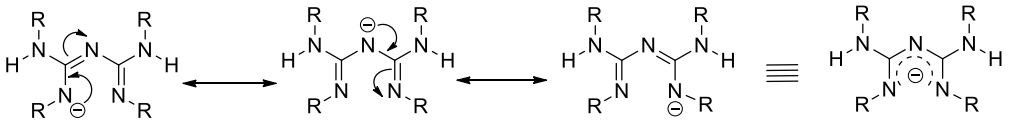
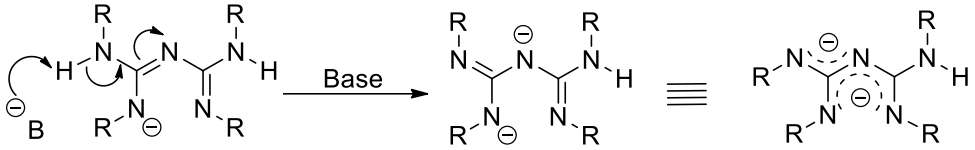


Figure 4.7. Some plausible resonating structures of mono anionic and di anionic CBG

Mono anionic CBG



Di anionic CBG



The ^{1}H NMR spectrum revealed the complete disappearance of a broad singlet in the down field region at 12.90 ppm, corresponding to *N–H–N* in the free ligand **1,** which evidenced the formation of compounds **5, 6** and **7.** Further, two broad singlets exhibiting at 0.92 and 2.86 ppm in C_6D_6 for eight protons each are indicative for the coordination of two THF molecules to the central lithium ion in **5**, which are distinguished by uncoordinated THF molecules appear in C_6D_6 as broad singlets at 3.54 and 1.47 ppm. Similarly in the ^{1}H NMR spectrum of compound **6** in C_6D_6 one triplet for six hydrogens and one quartet for four hydrogens situating at 0.82 and 2.96 ppm. Thus the NMR spectrum confirmed the survival of two coordinated thf molecules in **5** and one coordinated ether molecule in **6** the isolation procedure. In case of the compound **7** no solvation of lithium ion was noticed, this was interpreted by the ^{1}H NMR spectrum in THF-d_8 in which there is no change in the position of the solvent residual signals appearing as a broad singlet at 3.54 and 1.73 ppm. The NMR spectrum of compound **8** is little equivocal, featuring one hydrogen at 13.01 ppm instead of two hydrogen atoms around 5 ppm, however this can be

explained by proposed tautomeric structures of the compound **8** which are authenticated by its X-ray crystal structure. The ^{7}Li NMR signals at 2.06, 0.79, –0.77 and 2.17 ppm for compounds **5-8** respectively, confirms the presence of lithium atom in all the compounds.

Single crystals suitable for X–ray analysis of compounds **5**, **6** and **8** were grown from hexane/thf, toluene/diethyl ether, and toluene respectively. Compounds **5, 6** were crystallized in the triclinic space group $P\bar{1}$ and **8** was crystallized in the orthorhombic space group Pbca. Only one molecule exists in the unit cell of all the compounds **5, 6** and **8** displayed in figures **4.15, 4.16** and **4.17** respectively except for complex **6** in which a co–crystallized toluene molecule was observed in the asymmetric unit**.** The single crystal XRD experiments revealed the molecular structures of **5, 6** displaying the four and three coordinated 'Li' center containing a six–membered C_2N_3Li rings respectively. In the complexes **5** and **6** the metal atom was deviated from the plane of the atoms C_2N_3Li resembling boat conformation. The lithium atom was surrounded by the nitrogen atoms of chelating conjugated bis-guanidine and two oxygen atoms of THF molecules in case of compounds **5** and one oxygen atom of diethyl ether molecule in compound **6**. The Li–O and Li–N bond lengths for the compounds **5** are Li1−O1 2.001(6), Li1−O2 2.029(6), N1−Li1 1.963(6) and N2− Li1 1.958(6), which close to the reported Li–O and Li–N bond distances of tetra coordinated lithium complex [{(2,6-^{i}Pr$_2$C$_6$H$_3$)N(CH$_3$)C}$_2$CH]Li(THF)$_2$ Li1−O1 1.994(3), Li1−O2 1.947(3) and N1−Li1 1.955(2).[76] The geometry at lithium has been well described as distorted tetrahedral in **5**. The N−Li−O bond angles for **5** are N2−Li1−O2 113.8(3), N1−Li1−O2 123.1(3) which are grossly deviated from the idealized value 109.5° and bite angles of the conjugated bis-guanidine is N2−Li1−N1 92.3(2) all these values are falling in the range of those previously reported for tetra coordinated complex [{(2,6-^{i}Pr$_2$C$_6$H$_3$)N(CH$_3$)C}$_2$CH]Li(THF)$_2$.[76] The Li–O and Li–N bond lengths for the compounds **6** are Li1−O1 1.930(4), N1−Li1 1.903(4) and N2−Li1

1.902(4), which are resembling the reported values of tri coordinated lithium complex [{(2,6-$^{i}Pr_2C_6H_3$)N(CH_3)C}$_2$CH]Li(Et_2O), Li1−O1 1.911(4), N1−Li1 1.917(4), N2−Li1 1.912(4). The geometry at lithium has been well described as distorted trigonal planar in **6,** N−Li−O bond angles for **6** are N1−Li1−O1 124.6(2), N2−Li1−O1 137.2(2), which have shown the deviation from the idealized value 120°. The bite angles of the conjugated bis-guanidine is N2−Li1−N1 98.15(17), all these values are lying in the range of reported values for the tri coordinated lithium complex [{(2,6-$^{i}Pr_2C_6H_3$)N(CH_3)C}$_2$CH]Li(Et_2O).[77] Surprisingly in case of complex **8**, mono coordinated lithium was observed (Figure **4.17**). The conjugated bis-guanidine ligand acts as an amide that is coordinating the Li atom through N1 and there is an approximately η^4-interaction of the Li-centre with the Ar–substituent's of both N2 and N5 atoms. The N1–Li1 bond distance in compound **8** is 1.979(5) and is shorter than the N1–Li1 bond of a reported LiN_3H_4 mono coordinated lithium which is 2.113(3) (78). The Li…..C interactions have the values: Li1–C40 2.313(5), Li1–C45 2.624(5), Li1–C33 2.466(5), Li1–C32 2.771(5), Li1–C28 2.323(5), Li1–C29 2.617(5), Li1–C41 2.454(5), Li1–C42 2.787(5) Å. The C–N bond lengths of compound **8**, N1–C2 1.364(3), N1−C1 1.380(3), N2–C1 1.333(3), N3–C1 1.345 (3), N4–C2 1.318(3) supporting the structure **8** (Scheme **4.4**).

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Table 4.1. Crystal and refinement data for **1– 6** and **8**

	1	2	3	4	5	6	8
Chemical formula	$C_{34}H_{39}N_5$	$C_{38}H_{47}N_5$	$C_{42}H_{55}N_5$	$C_{50}H_{71}N_5$	$C_{42}H_{54}LiN_5O_2$	$C_{45}H_{54}LiN_5O$	$C_{50}H_{70}LiN_5$
Formula weight	517.70	573.81	629.91	742.11	667.84	687.87	748.05
Temperature (K)	293(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71069	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	*P2(1)/n*	$P2_1/n$	*Pbca*	$P\bar{1}$	$P\bar{1}$	*Pbca*
a (Å)	8.1985(5)	8.341(5)	10.3436(9)	20.6500(16)	11.866(3)	11.7001(4)	20.6026(13)
b (Å)	13.3253(8)	26.858(5)	23.4343(19)	20.2437(12)	12.354(3)	13.8696(5)	19.9482(12)
c (Å)	14.2747(8)	15.054(5)	15.9008(12)	21.7941(17)	15.263(7)	14.2063(5)	21.8897(15)
α (deg)°	74.538(3)	90.000(5)	90	90	92.892(19)	110.725(2)	90
β (deg)°	87.169(3)	102.563(5)	105.047(2)	90	103.96(2)	107.048(2)	90
γ (deg)°	79.508(3)	90.000(5)	90	90	118.084(13)	94.671(2)	90
Volume ($Å^3$)	1477.90(15)	3292(2)	3722.1(5)	9110.6(11)	1880.2(11)	2016.72(13)	8996.3(10)
Z	2	4	6	8	2	2	8
Density (g/ cm^{-3})	1.163	1.158	1.124	1.082	1.180	1.133	1.105
μ (Mo Kα) mm^{-1}	0.069	0.069	0.066	0.063	0.073	0.068	0.064
F(000)	556.0	1240	1368.0	3248.0	720.0	740.0	3264.0
□□ max (°)	61.248	27.95	55.894	50.956	51.22	53.68	51.822
Reflections collected	27450	47506	28712	48688	20641	24623	103345
Independent reflections	8969	7838	8672	8401	6915	8537	8631
GOOF	1.040	1.050	1.048	0.965	1.016	1.052	1.002
Final R indices [I > 2σ (I)]	R_1 = 0.0800, wR_2 = 0.2569	R1 = 0.0735, wR2 = 0.2082	R_1 = 0.0534, wR_2 = 0.1283	R_1 = 0.0595, wR_2 = 0.1450	R_1 = 0.0645, wR_2 = 0.1568	R_1 = 0.0560, wR_2 = 0.1418	R_1 = 0.0599, wR_2 = 0.1362

Table 4.2. Crystal and refinement data for **4a**, **4b** and **4c**

	4a	**4b**	**4c**
CCDC number			
Empirical formula	$C_{25}H_{34}N_2O$	$C_{40}H_{54}N_4O$	$C_{76}H_{108}N_8O_2$
Formula weight	378.54	606.87	1165.70
Temperature	296(2) K	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073Å	0.71073Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2₁/c*	*P2(1)/n*	*P2₁/n*
a (Å)	12.1764(13)	10.609(5)	19.9029(15)
b (Å)	17.495(2)	15.958(5)	16.6851(12)
c (Å)	21.066(3)	21.356(5)	23.7486(18)
α (deg)°	90	90.000(5)	90
β (deg)°	90.917(7)	91.552(5)	114.333(4)
γ (deg)°	90	90.000(5)	90
Volume ($Å^3$)	4486.9(9)	3614(2)	7185.9(9)
Z	8	4	4
Density (calculated) g cm^{-3}	1.121	1.115	1.077
Absorption coefficient μ (Mo Kα) mm^{-1}	0.068	0.067	0.065
F(000)	1648.0	1320	2544.0
□ max	51.482	26.12	52.94
Reflections collected	23873	43374	103353
Independent reflections	8457	7129	14743
GOOF	0.977	1.007	1.026
Final R indices [I > 2σ (I)]	R_1 = 0.0967, wR_2 = 0.2282	R1 = 0.0596, wR2 = 0.1298	R_1 = 0.0643, wR_2 = 0.1415

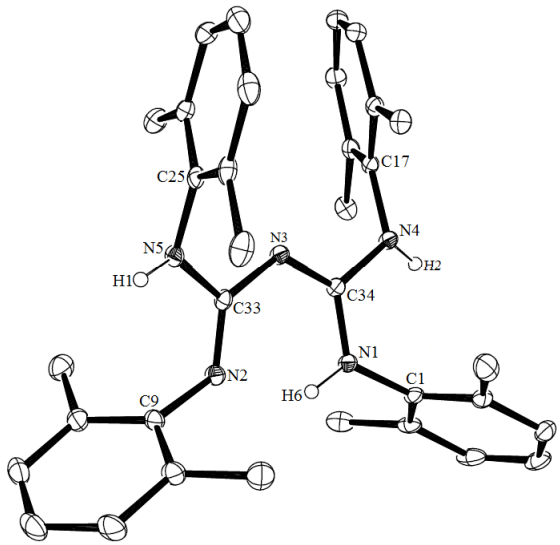


Figure 4.8. Molecular structure of **1.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): N2−C33 1.305(2), N3−C33 1.3740(19), N3−C34 1.312(2), N1−C34 1.353(2), N5−C33 1.381(2), N4−C34 1.3778(19), N1−C1 1.424(2), N5− H1 0.828, N1− H6 0.892, N4− H2 0.892; N2−C33−N3 124.25(14), C34−N3−C33 120.80(14), N3−C34−N1 125.31(14), N3−C33−N5 113.04(14), N3−C34−N4 117.63(14).

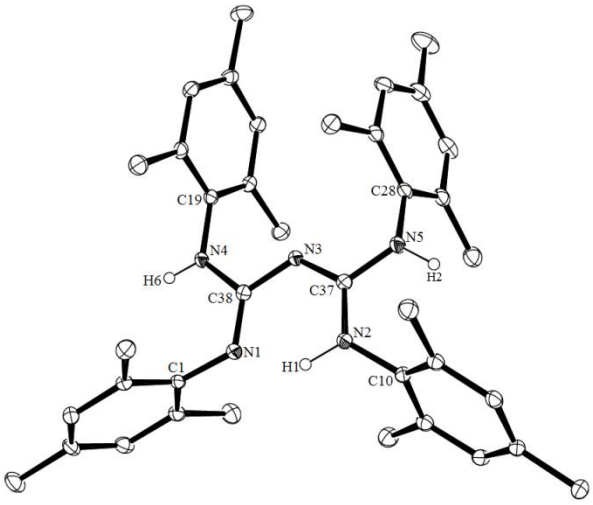


Figure 4.9. Molecular structure of **2.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å)and bond angles (deg): C38− N1 1.308(3), C38− N3 1.369(3), C37− N3 1.317(3), C37−N2 1.356(3), C38−N4 1.372(3), C37−N5 1.365(3), N4−H6 0.844, N5− H2 0.882, N2−H1 0.998;N1–C38–N3 125.1(2), C37−N3−C38 121.9(2). N3–C37–N2 124.5(2), N3−C38−N4 112.3(2), N3–C37–N5 117.2(2).

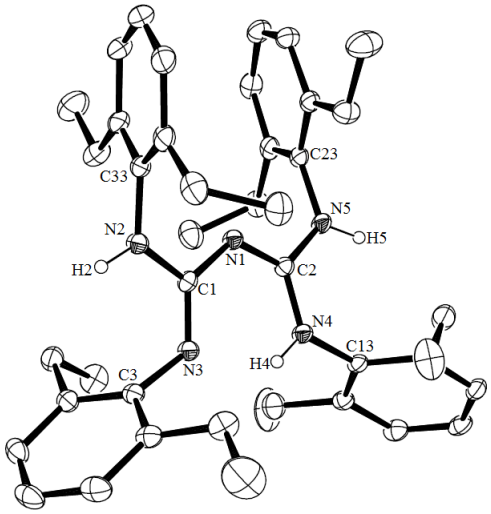


Figure 4.10. Molecular structure of **3.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): N3–C1 1.344(2), N1 – C1 1.3680(18), N1 – C2 1.3181(18), N4 – C2 1.344(2), N2–C1 1.3775(18), N5 – C2 1.3660(19), N4 – H4 0.860, N5 – H5 0.860, N2–H2 0.860; N3–C1–N1 124.75(13),C2–N1–C1 121.24(13), N1–C2–N4 124.51(13), N1–C1–N2 113.42(13), N1–C2–N5 117.42 (14).

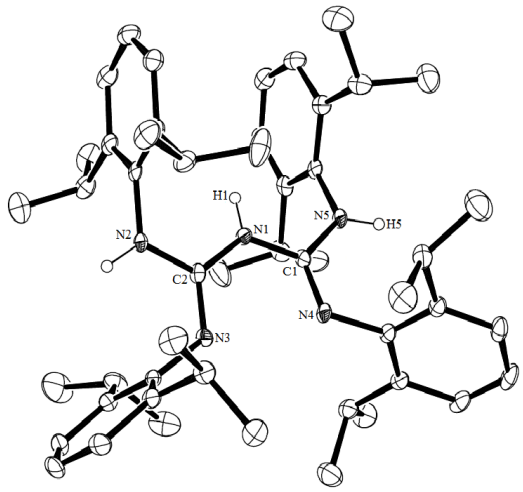


Figure 4.11. Molecular structure of **4.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity.

Selected bond distances (Å) and bond angles (deg): N3−C2 1.324(3), N1−C2 1.343(2), N1−C1 1.348(2), N4−C1 1.306(3), N2−C2 1.360(2), N5−C1 1.369(2), N1−H1 0.8600, N2−H2 0.8600, and N5−H5 0.8600; N3−C2−N1 123.05(18), C2−N1−C1 122.27 (17), N4−C1−N1123.62(18), N1−C2−N2 116.18(18), N1−C1−N5 114.49(18).

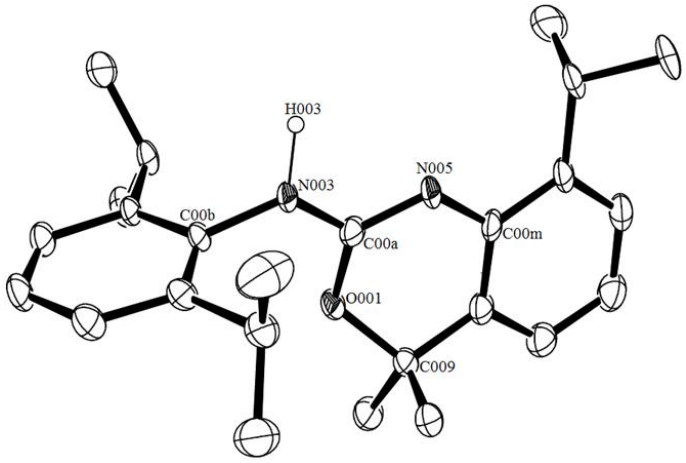


Figure 4.12. Molecular structure of **4a.**

The thermal ellipsoids are shown at 30% probability, and all the Hydrogen atoms except those bound to Nitrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg):

N003−H003 1.10(6), N003−C00A 1.305(5), N003−C00B 1.441(5), O001−C00A 1.352(5), O001−C009 1.477(4), N005−C00A 1.327(5). N005−C00M 1.396(5); C00A−N003−H003 116(3), C00A−N003−C00B 126.4(3), N003−C00A−N005 120.9(4), N003−C00A−O001 116.8(4), C00A−O001−C009 117.1(3), N005−C00A−O001 122.2(4).

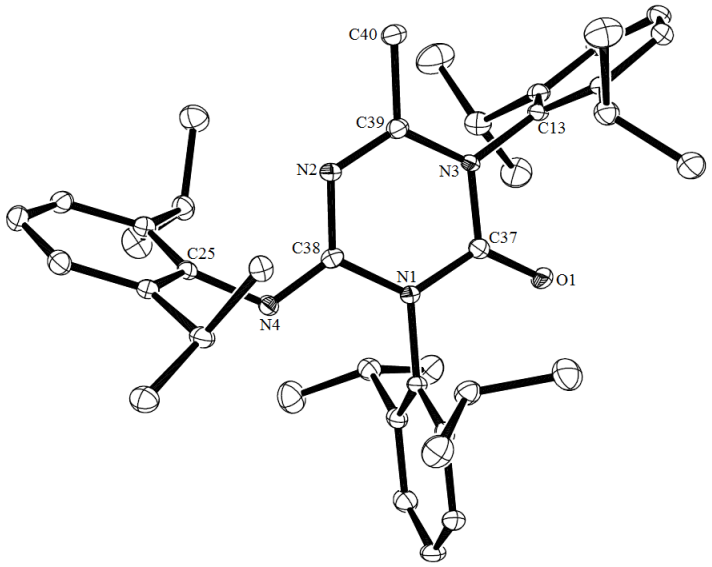


Figure 4.13. Molecular structure of compound **4b.** The thermal **e**llipsoids are shown at 30% probability, and all the Hydrogen atoms except those bound to Nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C37−O1 1.209(3), C39−C40 1.491(4) , C37−N1 1.383(3), C37−N3 1.399(3), C38−N4 1.267(3), C38−N2 1.385(3), C38−N1 1.411(3), C39−N2 1.295(3), C39−N3 1.380(3); O1−C37−N1 123.7(2), N1−C37−N3 114.7(2), N4−C38−N1 118.1(2), N2−C38−N1 117.8(2), N2−C39−N3 123.4(2), C37−N1−C38 122.8(2), C37−N1−C1 117.3(2), C39−N2−C38 119.4(2), C39−N3−C37 121.0(2).

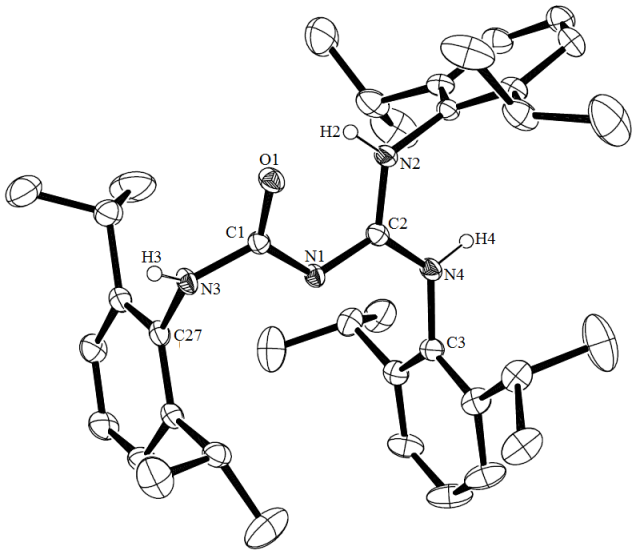


Figure 4.14. Molecular structure of compound **4c.** The thermal **e**llipsoids are shown at 30% probability, and all the Hydrogen atoms except those bound to Nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): O1−C1 1.256(2), N1−C2 1.335(3), N1−C1 1.369(3), N2−C2 1.354(3), N2−H (2) 0.8600, N3−C1 1.343(3), N 3−H 3 0.8600 Å, N4−C2 1.324(3), N4−C3 1.431(3), N4−H4 0.8600; C2−N1−C1 120.81(18), C2−N2−H2 117.7, C1−N3−H3 117.8, C2−N4−C3 124.86(18), C2−N4−H4 117.6, O1−C1−N3 119.77(19), O1−C1−N1 124.59(19), N3−C1−N1 115.59(18), N4−C2−N1 119.75(19), N4−C2−N2 118.07 (19), N1−C2−N2 122.1 (2).

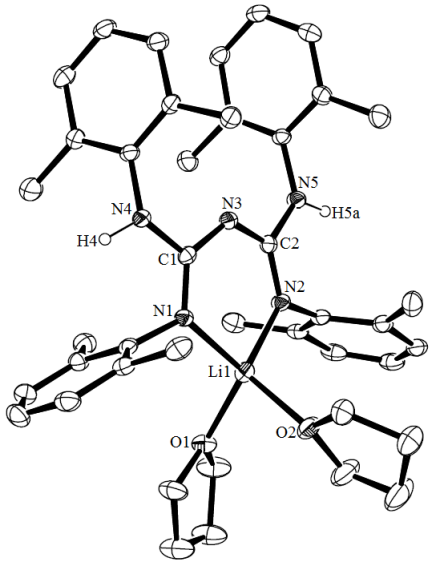


Figure 4.15. Molecular structure of **5.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Li1−O1 2.001(6), Li1−O2 2.029(6), N1−Li1 1.963(6), N2−Li1 1.958(6), C1−N1 1.322(4), N3−C1 1.339(4), N3−C2 1.348(4), N2−C2 1.323(3), N4−C1 1.404(4), C2−N5 1.380(4), N5−H5A 0.8800, N4−H4 0.879; N2− Li1−N1 92.3(2), N1−Li1−O1 112.4(3), N2−Li1−O2 113.8(3), N1−Li1−O2 123.1(3), O1−Li1−O2 92.6(2), N1−C1−N3 128.6(3), C1−N3−C2 123.5(2), N2−C2−N3 127.2(3), N3−C1−N4 112.5(2), N3−C2−N5 112.4(2).

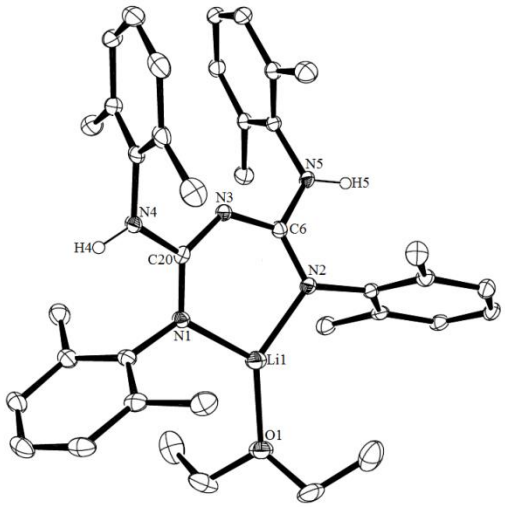


Figure 4.16. Molecular structure of **6.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Li1−O1 1.930(4), N1−Li1 1.903(4), N2−Li1 1.902(4), C20−N1 1.326(2), C20−N3 1.340(2), C6−N3 1.341(2), C6−N2 1.321(2), C20−N4 1.381(2), C6−N5 1.381(2), N4−H4 0.8600, N5−H5 0.8600; N2−Li1−N1 98.15(17), N1−Li1−O1 124.6(2), N2−Li1−O1 137.2(2), N1−C20−N3 126.95(18), C20−N3−C6 124.39(16), N2−C6−N3 127.50(17), N3−C20−N4 112.88(16), N3−C6−N5 112.59(16).

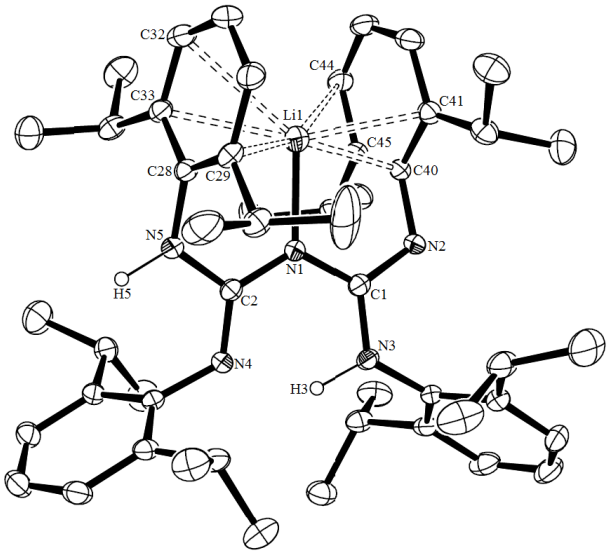


Figure 4.17. Molecular structure of **8.** The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): N1–Li1 1.979(5), N4–C2 1.318(3), N1–C21.364(3), N1− C1 1.380(3), N3–C1 1.345 (3), N5–C2 1.367(3), N2–C11.333(3), N5–H5 1.053, N3–H31.050; C2− N1 –Li1 120.8(2), C1− N1–Li1 117.47(19), N4–C2–N1 124.5(2), C2− N1–C1 121.76(19), N3–C1–N1 121.5(2), N1–C2–N5 115.1(2), N2–C1–N1 119.05(19), Li(1)–C(40) 2.313(5), Li(1)–C(45) 2.624(5), Li(1)–C(33) 2.466(5), Li(1)–C(32) 2.771(5), Li(1)–C(28) 2.323(5), Li(1)–C(29) 2.617(5), Li(1)–C(41) 2.454(5), Li(1)–C(42) 2.787(5)

Experimental section

General Methods.

All the reactions dealing with air and moisture–sensitive compounds were carried out in standard Schlenk line and nitrogen filled glove box. Unless otherwise noted, all the reagents and solvents required were purchased from commercial suppliers and used without further purification. Solvents toluene, benzene & hexane were collected from mBraun solvent purification system and used as such. THF was dried over sodium wire and distilled before use. Starting materials aryl carbodiimides and acetamidoxime were prepared by following the recent literature procedures [15], [16] respectively. NMR spectra were {^{1}H (400 MHz), ^{13}C {^{1}H} (101 MHz), & ^{7}Li {^{1}H} (155.5 MHz)} were recorded on Bruker AV 400 MHz instrument. The chemical shift values are reported in parts per million (ppm) and are reference to the residual solvent (7.16, 7.26 & (3.58, 1.73) for ^{1}H; 128.09, 77.16 & (67.2, 24.9) for ^{13}C; for C_6D_6, $CDCl_3$ and (THF-$d_8$respectively). The ^{7}Li NMR are reported with referenced to the standard ^{7}Li NMR of LiCl in D_2O. High-resolution mass spectra (HRMS) were recorded on Bruker micrOTOF–Q II spectrometer. IR spectra were recorded on Perkin–Elmer FTIR spectrometer. Melting points were recorded on digital melting point apparatus and are uncorrected. The purity of the conjugated bis-guanidines has been determined by high-pressure liquid chromatography (HPLC) using a C18 Agilent ZORBAX GF-450 Eclipse XDB column. Analytical HPLC was performed on an Agilent Technologies 1200 Series (Quaternary Pump) system equipped with a UV detector set at 254 nm. The compounds were dissolved in acetonitrile. 5 % *n*-hexane/95 % isopropanol mixture has been used as an eluent system. HPLC retention times (HPLC t_R) were obtained at flow rates of 1 mL min^{-1} using an isocratic run.

Crystallographic data.

The single crystals of the compounds **1–6**, **4a**, **4b**, **4c** and **8** suitable for X-ray diffraction have been grown at room temperature. Compounds **1**, **2**, **3, 4a** and **4c** were crystallized as colorless needles, **4** and **4b** as colorless blocks from ethyl acetate. Single crystals of **5** were obtained from hexane/thf mixture as colorless blocks and the compound **6** was crystallized from toluene/diethyl ether mixture as colorless small needles. The crystals for compound **8** were obtained as colorless needles from toluene at 27 ^{o}C. Paraffin liquid heavy oil was used to immerse the crystals and the crystals were mounted on a glass fiber. Data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector. Mo Kα radiation (λ = 0.71073 Å) was used to collect the diffraction data, a curved graphite monochromator was used to focus and to make the diffraction data monochromatic. An Oxford Cryostream 700 instrument was used to control the temperature. Crystals of the compounds **2–6** and **8** were cooled at 100 K under a cold nitrogen flow during the measurements. The scaling and integration of data were performed by using SAINT+ [SAINT+, Bruker AXSInc. Madison, Wisconsin, USA, 1999 (Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer V.6.02.)] Absorption corrections were done by using SADABS (SADABS, Bruker AXS, Madison, Wisconsin, USA, 2004). The structure was solved by direct methods and refined on F2 with SHELXL-97 (G.M. Sheldrick, Acta Crystallography. Sect. A 64 (2008)112–122).Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non hydrogen atoms were refined with anisotropic displacement parameters. The crystal data for all compounds along with the final residuals and other pertaining details are provided in the tables.

Synthetic Procedures.

Synthesis of (1). [L^1(3H)]

Method A: To a mixture of 2, 6–dimethylphenyl carbodiimide (6.0 g, 24 mmol, 2.1 equiv) and acetamidoxime (0.845 g, 0.0114 mmol, 1.0 equiv) toluene (30 mL) was added and the reaction mixture was refluxed for two days, the reaction was monitored by TLC. The crude reaction mixture was subjected to column chromatography and pure compound was isolated in 5:95 % ethyl acetate /*n*–Hexane mixture solvents. The compound was crystallized from ethyl acetate. These crystals were characterized by single crystal X-ray diffractometer. (Yield: 1.42 g, 2.74 mmol, 46 %).

Method B: To a solution of 2, 6–dimethylphenyl carbodiimide (1 g, 4 mmol, 1.0 equiv) in acetonitrile, aqueous ammonia (25%) (0.272 g, 0.068 mL, 68 μL, 16 mmol, 4.0 equiv). was added at room temperature, and the reaction mixture was stirred at room temperature for 15 hours. Formation of colorless precipitate was observed, this was filtered, dried and crystallized from dichloromethane to give the compound **1** as a colorless solid (Yield: 1.11 g, 2.16 mmol, 54 %): Mp 210–212 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 1.89 (s, 12H, CH_3), 2.37 (s, 12H, CH_3), 4.63 (s, 2H, N*H*), 6.68 (d, *J* = 8.0Hz, 4H, Ar*H*), 6.84 (t, *J* = 8.0Hz, 2H, Ar*H*), 6.96 – 6.99 (m, 2H, Ar*H*), 7.05 (d, *J* = 8.0Hz, 4H, Ar*H*), 12.90 (s, 1H, N*H*N); ^{13}C NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 18.6 (Ar-*C*H_3), 18.6 (Ar-*C*H_3), 125.2 (Ar-*C*), 125.8 (Ar-*C*), 127.5 (Ar-*C*), 128.8 (Ar-*C*), 134.2 (Ar-*C*), 136.1(Ar-*C*), 137.0 (Ar-*C*), 141.2 (Ar-*C*), 154.7 (N_3*C*). IR (KBr pellet, cm^{-1}) 3380s, 3019m, 2920m, 1618s, 1586m, 1567s, 1499m, 1468m, 1399s, 1356s, 1295m, 1251m, 1225s, 890s, 768s. HRMS (ESI-TOF-Q) *m/z*: [M+H] $^{+}$calcd. for $C_{34}H_{39}N_5$ 518.3278, found: 518.3294. HPLC: P_{HPLC}98%, t_R2.11.

Synthesis of compound (2). [L^2 (3H)] To a mixture of 2, 4, 6–trimethylphenyl carbodiimide (6 g, 21.55 mmol, 2.1equiv) and acetamidoxime (0.759 g, 10.26 mmol, 1.0 equiv). toluene (30 mL) was added and the reaction mixture was refluxed for two days, the reaction was monitored by TLC. The crude reaction mixture was subjected to column chromatography and pure compound was isolated in 5:95 % ethyl acetate /*n*–Hexane mixture solvents. The crude product was crystallized from dichloromethane to give **2** as a colorless solid (Yield: 1.36 g, 2.37 mmol, 44 %).

Method B: Using 2, 4, 6–trimethylphenyl carbodiimide (1 g, 3.592 mmol, 1.0 equiv) and aqueous ammonia (25%) (0.244 g, 0.061 mL, 61 μL, 14.368 mmol, 4.0 equiv). The crude product was crystallized from dichloromethane to give **2**as a colorless solid (Yield: 1.07 g, 1.867 mmol, 52 %): Mp 229–231 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 1.94 (s, 12H, CH_3), 2.21 (s, 12H, CH_3), 2.40 (s, 12H, CH_3), 4.71 (s, 2H, N*H*), 6.51 (s, 4H, Ar*H*), 6.86 (s, 4H, Ar*H*), 12.83 (s, 1H, N*H*N); ^{13}C NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 18.6 (Ar-*C*H_3), 18.7 (Ar-*C*H_3), 21.0 (Ar-*C*H_3), 21.1 (Ar-*C*H_3), 129.5 (Ar-*C*), 133.9 (Ar-*C*), 134.0 (Ar-*C*), 134.4 (Ar-*C*), 134.6 (Ar-*C*), 135.9 (Ar-*C*), 138.7 (Ar-*C*), 155.1(N_3*C*). IR (KBr pellet, cm^{-1}) 3665m, 3383s, 2915m, 2854m, 1621m, 1601m, 1567s, 1474m, 1396m, 1356m, 1233s, 1030m, 1010m, 874m, 845s, 785m. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{38}H_{47}N_5$574.3904, found: 574.3932. HPLC: P_{HPLC} 100%, t_R 13.28.

Synthesis of compound (3). [L^3 (3H)] To a mixture 2, 6–diethylphenyl carbodiimide (6.0 g, 19.57 mmol, 2.1 equiv) and acetamidoxime (0.69 g, 9.32 mmol, 1.0 equiv) toluene (30 mL) was added and the reaction mixture was refluxed for two days, the reaction was monitored by TLC. The crude reaction mixture was subjected to column chromatography and pure compound was isolated in 5:95 % ethyl acetate /*n*–Hexane mixture solvents. The crude product was crystallized

from dichloromethane to give **3** as a colorless solid (Yield: 1.11 g, 1.76 mmol, 36 %): Mp 160 – 167 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 1.02 (t, J = 8.0 Hz, 12H, CH_2CH_3), 1.28 (t, J = 8.0Hz, 12H, CH_2CH_3), 2.20 – 2.27 (m, 4H, CH_2CH_3), 2.30 – 2.37 (m, 4H, CH_2CH_3), 2.64 – 2.73 (sept, 4H, CH_2CH_3), 3.03 – 3.12 (sept, 4H, CH_2CH_3), 4.87 (s, 2H, NH), 6.78 (d, J = 8.0Hz, 4H, ArH), 6.98 – 7.01 (m, 2H, ArH), 7.05 – 7.13 (m, 6H, ArH), 12.96 (s, 1H, NHN); ^{13}C NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 14.7 (Ar-CH_2CH_3), 15.1 (Ar-CH_2CH_3), 25.2 (Ar-CH_2CH_3), 25.3 (Ar-CH_2CH_3), 125.6 (Ar-C), 125.8 (Ar-C), 126.5 (Ar-C), 127.0 (Ar-C), 135.6 (Ar-C), 139.8 (Ar-C), 140.0 (Ar-C), 142.1(Ar-C), 155.4 (N_3C). KBr pellet, cm^{-1}) 3378s, 3048m, 3066m, 2962s, 2933s, 2349s, 2340s, 2361s, 1609m, 1568m, 1514m, 1507m, 1457m, 1423m, 1291s, 1265s, 1222s, 897s, 868s, 789s, 717s. HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{42}H_{56}N_5$630.4530, found: 630.4519. HPLC: P_{HPLC} 100%, t_R2.29.

Synthesis of compound (4) [L^4 (3H)]

Method A: To a mixture of 2, 6-diisopropylphenyl carbodiimide (6.0 g, 16.55 mmol, 2.1 equiv) and acetamidoxime (0.583 g, 7.88 mmol, 1.0 equiv) toluene (30 mL) was added and the reaction mixture was refluxed for two days, the reaction was monitored by TLC. The crude reaction mixture was subjected to column chromatography and pure compound was isolated in 5:95 % ethyl acetate /*n*–Hexane mixture solvents. The crude product was crystallized from dichloromethane to give **4** as a colorless solid (Yield: 2.456 g, 3.311 mmol, 80 %).

Method B: using 2, 6–diisopropylphenyl carbodiimide (1.0 g, 2.759 mmol, 1.0 equiv) in acetonitrile aqueous ammonia (25%) (0.187 g, 0.0467 mL, 46.75 μL, 11.03mmol, 4.0 equiv).The crude product was crystallized from dichloromethane to give **4** as colorless crystals (Yield: 0.819 g, 1.103 mmol, 50 %): Mp 212–214 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 0.96 (d, J = 8.0 Hz, 12H, $CH(CH_3)_2$), 1.01 (d, J = 8.0 Hz, 12H, $CH(CH_3)_2$), 1.27 (d, J = 8.0Hz, 12H, $CH(CH_3)_2$),

1.34 (d, *J* = 4.0 Hz, 12H, CH(C*H*$_3$)$_2$), 3.08 – 3.15 (sept, 4H, C*H*(CH$_3$)$_2$), 3.61 – 3.68 (sept, 4H, C*H*(CH$_3$)$_2$), 4.96 (s, 2H, N*H*), 6.92 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.06 – 7.13 (m, 3H, Ar*H*), 7.17 (s, 3H, Ar*H*), 7.19 (d, *J* = 4.0 Hz, 1H, Ar*H*), 13.04 (s, 1H, N*H*N); ^{13}C NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 22.1 (CH (*C*H$_3$)$_2$), 23.6 (CH (*C*H$_3$)$_2$), 24.0 (CH (*C*H$_3$)$_2$), 25.7 (CH (*C*H$_3$)$_2$), 28.5 (*C*H (C*H*$_3$)$_2$), 28.8 (*C*H (C*H*$_3$)$_2$), 123.0 (Ar-*C*), 123.8 (Ar-*C*), 126.4 (Ar-*C*), 134.0 (Ar-*C*), 138.3 (Ar-*C*), 144.3 (Ar-*C*), 147.3 (Ar-*C*), 156.9 (N$_3$*C*). IR (KBr pellet, cm^{-1}) 3399s, 2958s, 2867m, 1607m, 1586m, 1566m, 1460m, 1395m, 1358m, 1326m, 1256s, 792m, 757m. HRMS (ESI-TOF-Q) *m/z*: [M+H] $^{+}$ calcd. for $C_{50}H_{72}N_5$742.5782, found: 742.5772. HPLC: P_{HPLC} 100%, t_R2.23.

Synthesis of compound (4a). Followed the mentioned synthetic procedure Method A, using (6 g, 16.55 mmol) 2, 6−diisopropylphenyl carbodiimide, and acetamidoxime (0.583 g, 7.88 mmol). The pure compound was obtained from column chromatography as a 2nd spot (from top of TLC plate) in 5:95 % ethyl acetate/hexane mixture solvents. The compound was crystallized from ethyl acetate to give **4a** as colorless solid (0.1565 g, 0.413 mmol, 2.5 %): Mp 145 – 155 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, 25 ^{o}C) δ 1.01 (d, *J* = 8.0 Hz, 2H, CH(*C*H$_3$)$_2$), 1.19 (d, *J* = 8.0 Hz, 12H, CH(*C*H$_3$)$_2$), 1.26 (d, *J* = 8.0 Hz, 2H, CH(*C*H$_3$)$_2$), 1.59 (s, 6H, C(C*H*$_3$)$_2$O), 2.17 (s, 2H, CH(*C*H$_3$)$_2$), 3.22 – 3.29 (m, 2H, C*H*(CH$_3$)$_2$), 3.39 (br.s, 1H C*H*(CH$_3$)$_2$), 6.91 – 6.96 (m, 2H, Ar*H*), 7.13 – 7.20 (m, 4H, Ar*H*); ^{13}C NMR (101MHz, $CDCl_3$, 25 ^{o}C) δ 22.1 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 26.9 (*C*H(*C*H$_3$)$_2$), 27.7 (*C*H(C*H*$_3$)$_2$), 28.5 (*C*H(C*H*$_3$)$_2$), 29.8 (*C*H(C*H*$_3$)$_2$), 31.0 (*C*H(C*H*$_3$)$_2$), 113.0 (Ar *C*), 116.0 (Ar *C*), 120.9 (Ar *C*), 122.1 (Ar *C*), 123.1 (Ar *C*), 123.6 (Ar *C*), 124.4 (Ar *C*), 125.0 (Ar *C*). IR (KBr pellet, cm^{-1}) 3193, 3110, 3062, 2964, 2927, 2866, 1677, 166, 1643, 1624, 1609, 1583, 1508, 1459, 1442, 1280, 1255, 1160, 1103, 963, 923, 887, 872, 827, 810, 767, 752. HRMS (ESI−TOF−Q) *m/z*: [M+H] $^{+}$calcd. for $C_{25}H_{36}N_2O$ 379.2744, found: 379.2742. HPLC: P_{HPLC} 100%, t_R2.28.

Synthesis of compound (4b). Followed the mentioned synthetic procedure Method A, using (6.0 g, 16.55 mmol) 2, 6-diisopropylphenyl carbodiimide, and acetamidoxime (0.583 g, 7.88 mmol). Pure compound was obtained from column chromatography as a 3rd spot (from top of TLC plate) in 5:95 % ethyl acetate/hexane mixture solvents. The compound was crystallized from ethyl acetate to give **4b** as colorless solid (0.302 g, 0.495 mmol, 3 %): Mp 255 − 265 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 1.08 (d, J = 8.0 Hz, 6H, CH(CH_3)$_2$), 1.17 – 1.22 (m, 18H, CH(CH_3)$_2$), 1.28 (d, J = 4 Hz, 6H, CH(CH_3)$_2$), 1.35 (d, J = 8.0Hz, 6H, CH(CH_3)$_2$), 1.84 (s, 3H, CH_3), 2.83 – 2.91 (sept, 4H, CH(CH$_3$)$_2$), 3.04 – 3.11 (sept, 2H, CH(CH$_3$)$_2$), 6.98 – 7.06 (m, 3H, ArH), 7.26 (d, J = 8.0 Hz, 4H, ArH), 7.36 – 7.45 (m, 2H, ArH), ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C) δ 22.6 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 25.4 (*C*H(CH$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 29.5 (*C*H(CH$_3$)$_2$), 122.5 (Ar *C*), 122.9 (Ar *C*), 124.1 (Ar *C*), 124.7 (Ar *C*), 129.4 (Ar *C*), 130.5 (Ar *C*), 131.0 (Ar *C*), 131.3 (Ar *C*), 138.8 (Ar *C*), 143.6 (Ar *C*), 145.8 (Ar *C*), 145.9 (Ar *C*),146.1 (N_2C-CH_3), 150.2 (N_2C=O), 160.0 (N_3C). IR (KBr pellet, cm^{-1}) 3409, 3057, 2960, 2943, 2930, 2869, 2885, 1729, 1704, 1598, 1587, 1508, 1464, 1447, 1385, 1330, 1092, 1057, 987, 936, 823, 803, 709. HRMS (ESI–TOF-Q) *m/z*: [M+H] $^{+}$ calcd. for $C_{40}H_{55}N_4O$ (607.4370), found: 607.4360. HPLC: P_{HPLC} 100%, t_R2.34.

Synthesis of compound (4c). Followed the mentioned synthetic procedure method A (6 g, 16.55 mmol) 2, 6 diisoprpoyl phenyl carbodiimide and acetamidoxime (0.583 g, 7.88 mmol) pure compound was obtained from column chromatography as a 4th spot (from top of TLC plate) in 5:95 % ethyl acetate/hexane mixture solvents. The compound was crystallized from ethyl acetate to give **4c** as a colorless solid (0.145 g, 0.25 mmol, 1.5 %): Mp 115 −125 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 0.95 (d, J = 8.0 Hz, 2H, CH (CH_3)$_2$), 1.10 (d, J = 8.0 Hz, 5H, CH (CH_3)$_2$),

1.21 (d, *J* = 8.0 Hz, 11H, CH (CH_3)$_2$), 1.25 (d, *J* = 4.0 Hz, 11H, CH (CH_3)$_2$), 1.37 (d, *J* = 8.0 Hz, 4H, CH (CH_3)$_2$), 1.50 (d, *J* = 4.0 Hz, 3H, CH(CH_3)$_2$), 3.25 – 3.34 (m, 4H, C*H* (CH_3)$_2$), 3.36 – 3.57 (m, 2H, C*H* (CH_3)$_2$), 5.12 (s, 1H, N*H*), 6.06 (s, 1H, N*H*), 6.89 – 6.91 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.06 – 7.09 (m, 5H, Ar*H*), 7.18 – 7.23 (m, 3H, Ar*H*), 12.06 (s, 1H, N*H*), 12.92 (s, 1H, N=CO*H*); ^{13}C NMR (101MHz, C_6D_6, 25 ^{o}C) δ 22.2 (CH(CH_3)$_2$), 23.9 (CH(CH_3)$_2$), 25.4 (CH(CH_3)$_2$), 29.0 (CH(CH_3)$_2$), 29.1 (CH(CH_3)$_2$), 29.4 (CH(CH_3)$_2$), 123.2 (Ar *C*), 123.6 (Ar *C*), 124.0 (Ar *C*), 124.3 (Ar *C*), 124.5 (Ar *C*), 133.4 (Ar *C*), 136.4 (Ar *C*), 141.5 (N_2C=O), 147.2 (N_3C). IR (KBr pellet, cm^{-1}) 3460, 3359, 3164, 3065, 2963, 2883, 2868, 1681, 1645, 1609, 1586, 1521, 1256, 1197, 1107, 1059, 936, 905, 883, 825, 802, 810, 769, 753, 728. HRMS (ESI-TOF-Q) *m/z*: [M+H]$^+$ calcd. For $C_{38}H_{55}N_4O$, 583.4370 found: 583.4481. HPLC: P_{HPLC}96.8%, t_R2.26.

Synthesis of compound (5). To a solution of (0.25 g, 0.482 mmol, 1.0 equiv) compound **(1)** in THF (10 mL) ^{n}BuLi (1.6 M in *n*-hexane, 0.31 mL, 0.507 mmol, 1.1 equiv) was added at 0 ^{o}C and then the reaction mixture was stirred at room temperature for 8 hours. The compound was crystallized from hexane and thf mixture to give **5** as a colorless sold (Yield: 0.177 g, 0.265 mmol, 55 %): Mp 177 – 186 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 0.92 (br., 8H, OCH_2CH_2), 2.06 (s, 12H, CH_3), 2.46 (s, 12H, CH_3), 2.86 (br.s, 8H, OCH_2CH_2), 4.63 (s, 2H, N*H*), 6.74 (d, *J* = 8.0 Hz, 5H, Ar *H*), 6.86 – 6.89 (m, 3H, Ar *H*), 6.93 – 6.96 (m, 2H, Ar *H*), 7.13 (s, 2H, Ar *H*); ^{13}C NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 18.8 (Ar-CH_3), 19.1 (Ar-CH_3), 25.0 (OCH_2CH_2), 67.7 (OCH_2CH_2), 122.6 (Ar-*C*), 125.0 (Ar-*C*), 127.5 (Ar-*C*), 128.6 (Ar-*C*), 132.6 (Ar-*C*), 136.1 (Ar-*C*), 139.2 (Ar-*C*), 149.1 (Ar-*C*), 155.1 (N_3C). ^{7}Li NMR (155.5 MHz, C_6D_6, 25 ^{o}C) δ 2.06.

Synthesis of compound (6). To a solution of (0.25 g, 0.482 mmol, 1.0 equiv) compound **(1)** in diethyl ether (10 mL) ^{n}BuLi (1.6 M in *n*-hexane, 0.31 mL, 0.507 mmol, 1.1 equiv) was added at 0 ^{o}C and then the reaction mixture was stirred at room temperature for 8 hours. The compound

was crystallized from toluene to give **6** as a colorless sold (Yield: 0.170 g, 0.285 mmol, 59 %): Mp 177 – 186 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 0.82 (t, J = 8.0 Hz, 6H, OCH_2CH_3), 2.01 (s, 12H, CH_3), 2.36 (s, 12H, CH_3), 2.96 (q, J = 8.0 Hz, 4H, OCH_2CH_3), 4.55 (s, 2H, NH), 6.71 (d, J = 8.0 Hz, 5H, Ar *H*), 6.83 – 6.86 (m, 2H, Ar *H*), 6.96 (t, J = 8.0 Hz, 2H, Ar *H*), 7.05 (d, J = 8.0 Hz, 1H, Ar *H*), 7.13 (s, 2H, Ar *H*); ^{13}C NMR (101 MHz, C_6D_6, 25 °C) δ 14.8 (OCH_2CH_3), 18.8 (Ar-CH_3), 19.1 (Ar-CH_3), 65.9 (OCH_2CH_3), 122.7 (Ar-*C*), 125.1 (Ar-*C*), 127.5 (Ar-*C*), 128.6 (Ar-*C*), 132.6 (Ar-*C*), 136.0 (Ar-*C*), 139.0 (Ar-*C*), 148.9 (Ar-*C*), 154.9 (N_3C). ^{7}Li NMR (155.5 MHz, C_6D_6, 25 °C) δ 0.79.

Synthesis of compound (7). To a solution of (0.2 g, 0.386 mmol, 1.0 equiv) of **(1)** in toluene (10 mL) ^{n}BuLi (1.6 M in *n*-hexane, 0.253 mL, 0.406 mmol, 1.1 equiv) was added at room temperature, during addition of ^{n}BuLi immediate formation of colorless precipitate was observed. The compound was dried to give **8** colorless solid (Yield: 0.123 g, 0.235 mmol, 61 %): Mp 180 – 187 °C. ^{1}H NMR (400MHz, THF-d_8, 25 °C) δ 1.92 (s, 12H, CH_3), 2.38 (s, 12H, CH_3), 4.79 (s, 3H, NH), 6.51 (d, J = 8.0 Hz, 4H, ArH), 6.59 – 6.62 (m, 3H, ArH), 6.70 – 6.73 (m, 3H, ArH), 6.97 (d, J = 8.0 Hz, 4H, ArH); ^{13}C NMR (101 MHz, THF-d_8, 25 °C) δ 19.0 (Ar-CH_3), 19.1(Ar-CH_3), 121.8 (Ar-*C*), 124.6 (Ar-*C*), 127.5 (Ar-*C*), 128.4 (Ar-*C*), 132.9 (Ar-*C*), 136.1 (Ar-*C*), 140.2 (Ar-*C*), 150.5 (Ar-*C*), 155.0 (N_3C). ^{7}Li NMR (155.5 MHz, THF-d_8, 25 °C) δ − 0.77.

Synthesis of compound (8). To a solution of (0.20 g, 0.27 mmol, 1.0 equiv) of compound **(4)** toluene (10 mL) ^{n}BuLi (1.6 M in *n*-hexane, 0.185 mL, 0.296 mmol, 1.1equiv) was added at room temperature and stirred at room temperature for overnight the compound was crystallized from toluene to give **7** as a colorless solid (Yield: 0.121 g, 0.16 mmol, 60 %): Mp 206 – 214 °C. ^{1}H NMR (400 MHz, Toluene-d_8, 25 °C) δ 0.92 (d, J = 8.0 Hz, 12H, CH (CH_3)$_2$), 0.98 (d, J = 4.0 Hz, 12H, CH (CH_3)$_2$), 1.24 (d, J = 8.0 Hz, 12H, CH (CH_3)$_2$), 1.33 (d, J = 4.0 Hz, 12H, CH

(C*H*$_3$)$_2$)), 3.06 – 3.13 (sept, 4H, C*H* (CH$_3$)$_2$), 3.59 – 3.65 (sept, 4H, C*H* (CH$_3$)$_2$), 4.95 (s, 1H, N*H*), 6.88 (d, *J*= 8.0 Hz, 3H, Ar*H*), 7.02 – 7.06 (m, 3H, Ar*H*), 7.12 – 7.20 (m, 6H, Ar*H*), 13.04 (s, 1H, N*H*N); ^{13}C NMR (101 MHz, Toluene-d$_8$, 25 ^{o}C) δ 22.1 (CH (*C*H$_3$)$_2$), 23.6 (CH (*C*H$_3$)$_2$), 23.9 (CH (*C*H$_3$)$_2$), 25.6 (CH (*C*H$_3$)$_2$), 28.3 (*C*H (CH$_3$)$_2$), 28.5 (*C*H (CH$_3$)$_2$), 28.6 (*C*H (CH$_3$)$_2$), 28.8 (*C*H (CH$_3$)$_2$), 122.5 (Ar-*C*), 123.0 (Ar-*C*), 123.7 (Ar-*C*), 123.8 (Ar-*C*), 126.3 (Ar-*C*), 134.0 (Ar-*C*), 138.2 (Ar-*C*), 142.8 (Ar-*C*), 144.2 (Ar-*C*), 146.0 (Ar-*C*), 147.3 (Ar-*C*), 156.9 (N$_3$*C*). ^{7}Li NMR (155.5 MHz, Toluene-d$_8$, 25 ^{o}C) δ 2.17.

Conclusion

A series of a structurally characterized a new class of guanidines, conjugated bis–guanidines have been reported. More importantly, these can be synthesized in the absence of metal. In addition, we have shown the coordination chemistry of these ligands with the lithium element. We reported the solvated and un solvated lithium salts bearing the ligands **1** and **4**. Some exciting features of these ligands while coordinating with the lithium metal have been observed. In case of ligand **1**, solvated lithium salts were obtained when the lithiation was done in the presence of ethereal solvents such as 'THF 'and 'Et$_2$O' and un solvated lithium salts were observed when lithiation was carried out in toluene. The ligand '**4**' showed peculiar behavior during lithiation with ^{n}BuLi, forming lithium salt in which the 'Li' metal is mono coordinated and having interaction with carbon atoms of the aromatic part of the ligand. Finally, during lithiation of **1** with ^{n}BuLi formation six membered heterocycle was observed in both the cases *i.e* solvated and unsolvated. Whereas lithiation of **4** in toluene with ^{n}BuLi led to the formation of mono coordinated lithium complex with metal–arene interaction.

References

1 R. Bonnett, D. C. Bradley and K. J. Fisher, *Chem. Commun.*, 1968, 886–887.

2 R. Bonnett, D. C. Bradley, K. J. Fisher and I. F. Rendall, *J. Chem. Soc. A*, 1971, 1622–1627.

3 J. E. Parks and R. H. Holm, *Inorg. Chem.*, 1968, **7,** 1408–1416.

4 L. B. Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102,** 3031–3066.

5 Y. C. Tsai, *Coord. Chem. Rev.*, 2012, **256**, 722–758.

6 S. P. Sarish, S. Nembenna, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2011, **44**, 157–170.

7 M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396.

8 P. W. Roesky, *Molecular Catalysis of Rare-Earth Elements*, Springer Berlin, Heidelberg, 2010;

9 F. T. Edelmann, *Coord. Chem. Rev.*, 2015, **284**, 124–205.

10 F. T. Edelmann, *Coord. Chem. Rev.*, 2016, **318**, 29–130.

11 W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233**, 131–155.

12 A. A. Mohamed, *Coord. Chem. Rev.*, 2010, **254**, 1918–1947.

13 V. T. Annibale and D. Song, *RSC Adv.*, 2013, **3**, 11432–11449.

14 D. Zhu and P. H. M. Budzelaar, *Dalton Trans.*, 2013, **42**, 11343–11354.

15 S. J. Malthus, S. A. Cameron and S. Brooker, *Coord. Chem. Rev.*, 2016, **316**, 125–161.

16 O. D. Cabaret, B. M. Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176.

17 J. Wu, T.L. Yu, C.T. Chen and C.C. Lin, *Coord.Chem. Rev.*, 2006, **250**, 602–626.

18 R. H. Platel, L. M. Hodgsonand C. K. Williams, *Polym. Rev.*, 2008, **48**, 11–63.

19 G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618–6639.

20 M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163.

21 S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479.

22 V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283–316.

23 S. Arndt and J. Okuda, *Adv. Synth. Catal.*, 2005, **347**, 339–354.

24 P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, *Chem. Rev.*, 2006, **106**, 2404–2433.

25 N. Heße, R. Fröhlich, I. Humelnicu and E. U. Würthwein, *Eur. J. Inorg. Chem.*, 2005, 2189−2197.

26 N. Heße, R. Fröhlich, B. Wibbeling and E. U. Würthwein, *Eur. J. Org. Chem.*, 2006, 3923−3937.

27 I. Häger, R. Fröhlich and E. U. Würthwein, *Eur. J. Inorg. Chem.*, 2009, 2415−2428.

28 H. V. R Dias and S. Singh, *Dalton Trans.*, 2006, **16**, 1995−2000.

29 H. V. R Dias, S. Singh and T. R. Cundari, *Angew. Chem., Int. Ed.* 2005, 44, 4907−4910.

30 A. R. Siedle, R. J. Webb, F. E. Behr, R. A. Newmark, D. A. Weil, K. Erickson, R. Naujok, M. Brostrom, M. Mueller, S. H. Chou and V. G. Young, *Inorg. Chem.* 2003, **42**, 932−934.

31 H. V. R. Dias and S. Singh, *Inorg. Chem.*, 2004, **43**, 5786− 5788.

32 H. V. R. Dias and S. Singh, *Inorg. Chem.*, 2004, **43**, 7396−7402.

33 H. V. R. Dias, S. Singh and J. A. Flores, *Inorg. Chem.*, 2006, **45**, 8859− 8861.

34 J. A. Flores and H. V. R. Dias, *Inorg. Chem.*, 2008, **47**, 4448−4450.

35 M. Pfeiffer, A. Murso, L. Mahalakshmi, D. Moigno, W. Kiefer and D. Stalke, *Eur. J. Inorg. Chem.*, 2002, **12**, 3222−3234.

36 H. Gornitzka and D. Stalke, *Eur. J. Inorg. Chem.*, 1998, **3**, 311−317.

37 J. Ashenhurst, *Organometallics*, 2013, **32**, 3174−3184.

38 X. B. Lu, H. Wang and R. J. He, *Mol. Catal. A: Chem.*, 2002, **186**, 33−42.

39 G. Rajagopal, S. S. Kim and J. M. Kwak, *Bull. Korean Chem. Soc.*, 2006, **27**, 1907.

40 K. Bakthavachalam and N. D. Reddy, *Organometallics*, 2013, **32**, 3174-3184.

41 E. R. King and T. A. Betley, *Inorg. Chem.*, 2009, **48**, 2361−2363.

42 E. R. King, E. T. Hennessy and T. A. Betley, *J. Am. Chem. Soc.*, 2011, **133**, 4917−4923.

43 E. R. King, G. T. Sazama and T. A. Betley, *J. Am. Chem. Soc.*, 2012, **134**, 17858−17861.

44 A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891−1932.

45 G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Ed.*, 2008, **47**, 1184−1201.

46 C. G. Gianopoulos, K. Kirschbaum and M. R. Mason, *Organometallics*, 2014, ***33***, 4503.

47 Z. Zhang and D. Dolphin, *Inorg. Chem.*, 2010, **49**, 11550−11555.

48 Z. Zhang, Y. Chen and D. Dolphin, *Dalton Trans.*, 2012, **41**, 4751−4753.

49 V. S. Thoi, J. R. Stork, D. Magde and S. M. Cohen, *Inorg. Chem.*, 2006, **45**, 10688−10697.

50 J. R. Stork, V. S. Thoi and S. M. Cohen, *Inorg. Chem.*, 2007, **46**, 11213−11223.

51 A. T. T. Hsieh, C. A. Rogers and B. O. West, *Aust. J. Chem.*, 1976, **29**, 49−54.

52 S. Kusaka, R. Sakamoto and H. Nishihara, *Inorg. Chem.*, 2014, 53, 3275−3277.

53 E. Rumyantsev, S. N. Aleshin and E. V. Antina, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 2011, **54**, 30−33.

54 C. Ikeda, S. Ueda and T. Nabeshima, *Chem. Commun.*, 2009, 2544−2546.

55 A. A. Trifonov, *Coord. Chem. Rev.*, 2010, **254**, 1327−1347.

56 F. T. Edelmann, *Adv. Organomet. Chem.*, 2008, **57**, 183−352.

57 T. Chlupatý and A. Růžička, *Coord. Chem. Rev.*, 2016, **314**, 103−113.

58 T. Elkin and M. S. Eisen, *Catal. Sci. Technol.*, 2015, **5**, 82−95.

59 S. T. Barry, *Coord. Chem. Rev.*, 2013, **257**, 3192−3201.

60 F. T. Edelmann, *Chem. Soc. Rev.*, 2009, **38**, 2253−2268.

61 F. T. Edelmann, *Chem. Soc. Rev.*, 2012, **41**, 7657.

62 C. Jones, *Coord. Chem. Rev.*, 2010, **254**, 1273–1289.

63 P.J. Bailey and S. Pace, *Coord. Chem. Rev.*, 2001, **214**, 91-141.

64 M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354-396.

65 S.P. Green, C. Jones and A. Stasch, *Science.*, 2007**, *318***, 1754-1757.

66 C. Jones, P.C. Junk, J.A. Platts and A. Stasch, *J. Am. Chem. Soc.*, 2006**, 128**, 2206-2207.

67 US 8,530,544 B2.

68 B. Kovačević and Z. B. Maksić, *Chem. Eur. J.*, 2002**, 8**, 1694-1702.

69 V. Raab, J. Kipke, R. M. Gschwind and J. Sundermeyer, *Chem. Eur. J.*, 2002**, 8**, 1682-1693.

70 V. Raab, K. Harms, J. Sundermeyer, B. Kovačević and Z. B. Maksić, *J. Org. Chem.*, 2003**, 68**, 8790-8797.

71 V. Raab, E. Gauchenova, A. Merkoulov, K. Harms, J. Sundermeyer, B. Kovačević and Z. B. Maksić, *J. Am. Chem. Soc.*, 2005**, 127**, 15738-15743.

72 J. Alsarraf, Y.A. Ammar, F. Robert, E. Cloutet, H. Cramail and Y. Y. Landais, *Macromolecules.*, 2012, **45**, 2249−2256.

73 A. K. Maity, J. Alejandro, M. Magana and S. Fortier, *Inorg. Chem.*, 2015, ***54***, 10030−10041.

74 P. V. Gushchin, M. R. Tyan, N. A. Bokach, M. D. Revenco, M. Haukka, M.J. Wang, C.H. Lai, P.T. Chou and V. Y. Kukushkin, *Inorg. Chem.*, 2008**, 47**, 11487-11500.

75 G. Jin, C. Jones, P. C. Junk, K.-A. Lippert, R. P. Rose and A. Stasch, *New. J. Chem.*, 2009, **33**, 64–75.

76 D. T. Carey, E. K. C. Eatough, E. V. Mafé, F. S. Mair, R. G. Pritchard, J. E. Warren and R. J. Woods, *Dalton Trans.*, 2003, 1083–1093.

77 M. Stender, R. J. Wright, B. E. Eichler, J. Prust, M. M. Olmstead, H. W. Roesky and P. P. Power, *J. chem. Soc., Dalton Trans.*, 2001, 3465-3469.

78 P. K. Sawinski, V. L. Deringera and R. Dronskowski., *Dalton Trans.*, 2013, **42**, 15080–15087.

Chapter 5: Mono and Bimetallic Aluminum Alkyls, Mono Metallic Aluminum Halide, Hydride, Alkoxide and Gallium Diiodide Complexes stabilized by a Bulky Conjugated Bis-Guanidinate Ligand

Abstract

A new class of conjugated bis-guanidine ligands such as L(3H) [L = {$(ArN)_2C$=N-C= N(Ar)(NAr)}; Ar = 2, 6-Me_2 - C_6H_3] and L^1(3H) [L^1 = {$(ArN)_2C$=N-C= N(Ar)(NAr)}; Ar = 2, 6-$^iPr_2$ - C_6H_3] have been employed to synthesize a series of four- and six-membered aluminum heterocycles. Generally, aluminum complexes bearing *N*, *N*'- chelated *β*-diketiminate or dipyrromethane and guanidinate or amidinate ligand systems form six-and four-membered heterocycles, respectively. However, the conjugated bis-guanidine ligand has the capability of forming both four- and six-membered heterocycles possessing multi-metal centers within the same molecule; this is due to the presence of three acidic protons, which can be easily deprotonated (two protons) upon treatment with metal reagents. Mono and dinuclear aluminum alkyls, mononuclear aluminum halide, hydride, alkoxide, and gallium diiodide complexes have been structurally characterized.

Introduction

In 1970, Lappert & coworkers reported the first guanidinate stabilized transition metal complex.[1] Since then the guanidinate anions have been found their great utility as supporting ligands for the main group as well as a transition or lanthanide metal complexes in organometallic chemistry. The chemistry of low oxidation state metal complexes stabilized by bulky guanidinate ligands is a crucial area receiving at most attention of main group chemists in recent years. The steric and/or electronic properties provided by bulky guanidine ligand systems are the key factors, in controlling the processes such as disproportionation, oligomerization etc. Guanidinate ligands supported aluminum (III) metal complexes have received increased attention, in the late 1990s.

However, the aluminum (III) complexes of the related *β*-diketaminate, triaza framework, guanidinate and amidinate ligands have been well demonstrated

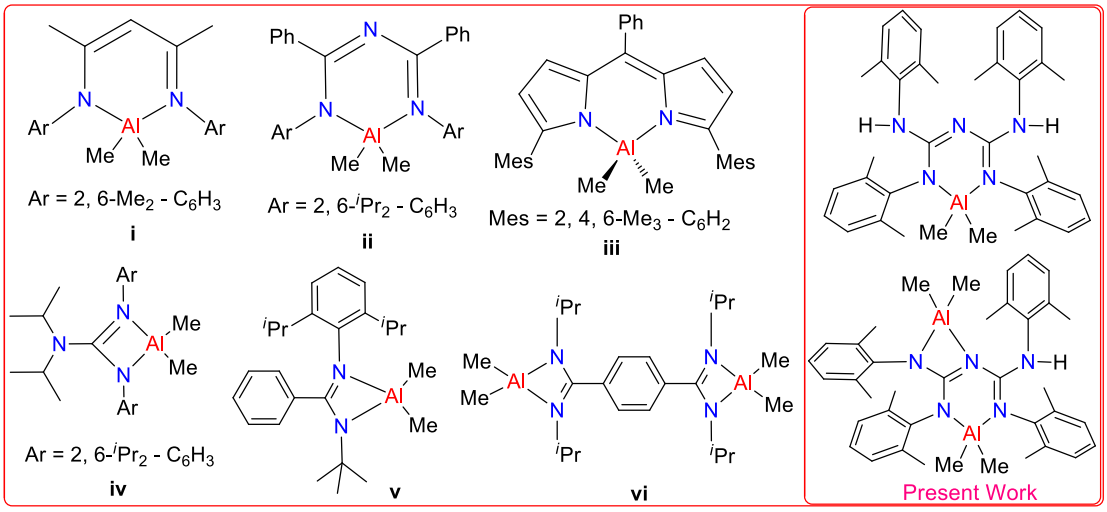


Figure 5.1. Selected representative examples of four- and six-membered aluminum alkyls (early reported work (left) and present work (right).

Apart from these ligand systems, a triaza ligand known as 1, 5- bis (2, 6-diisopropylphenyl)-2, 4-diphenyl-1, 3, 5-triazapenta-1, 3- diene and aluminum complexes of its anion have been known. Aluminum complexes bearing *β*-diketiminate ligands have been extensively reported[2–23]. The chemistry of triazapentadienate ligands, which resemble the β-diketiminates closely, has been less explored.[25-33] A decent number of aluminum complexes of triaza framework ligands such as bis (2-pyridyl) amine[34-36] and phthalocyanin[37-38] have been documented in the literature. Cationic aluminum complexes of a quaternary 1, 3, 5-triazapenta-1, 3-diene has also been noticed[39]. Aluminum complexes supported by a tertiary 1, 3, 5-triazapenta-1, 3-diene ligand, have been developed by Bakthavachalam et.al.[40] Jordan and co-workers have utilized aluminum complexes stabilized by an *N, N*'chelated monoanionic bidentate amidinate ligand for the polymerization of ethylene at atmospheric pressure.[41] Bergman group reported aluminum complexes stabilized by

guanidinate ligands and their catalytical activity for the hydroamination of carbodiimides[42]. Aluminum alkyl, iodide, hydride complexes of a bulky dipyrromethene ligand have been shown by Gianopoulos et.al.[43-44] The aluminum hydride chemistry is well-established for the reduction of various unsaturated and polar functional groups.[45-48] The activation of nonpolar sulfur-sulfur bonds can be demonstrated by the characteristic reactivity of [$LAlH_2$] (L= HC ($CMeNAr)_2$, Ar=2,6-$^{i}Pr_2C_6H_3$).[49-50] Driess and co-workers shown the C-H and C-O bonds activation mediated by the hydrido-Al(I)-Fe complex.[51] The possible replacement to transition-metal compounds for catalysis is functionalized [$LAlH_2$], and the more relevant example is aluminum hydride which can function similar to a transition-metal catalyst reported by Yang, Parameswaran, Roesky and co-workers[52]. Compounds containing an Al or Ga center in the +1 oxidation state and their coordination, redox chemistry is a rapidly growing and engrossing field. The chemistry of group 13 metal (I) heterocycles has begun to be explored recently. Aluminum diiodide complexes stabilized by bulky *N, N'*- chelated ligands are ideal precursors for isolating the Al (I) heterocycle and it can be achieved by the reduction of these aluminum diiodide complexes with potassium in toluene at room temperature. The best example is neutral six-membered *β*-diketiminato supported room-temperature stable monomeric Al (I) species [:M{[N(Ar)C(Me)]$_2$CH}], Ar) C_6H_3 $^{i}Pr_2$-2,6 (M = Al, Tl)[53-56]. Similarly the gallium diiodide complexes stabilized by *N,N'*- chelated ligands are also ideal precursors for isolating the Ga(I) heterocycle. The synthesis and characterization of sterically encumbered *β*-diketiminate stabilized gallium diiodide complexes was reported by Stender and Power[57] and the same research group shown the synthesis of Ga (I) heterocycles from gallium diiodide complexes[58]. Generally, *N, N*'-chelated *β*-diketiminate forms C_3N_2Al and triaza (1,5-bis(2,6-diisopropylphenyl)-2,4-diphenyl-1,3,5-triazapenta-1,3-diene forms C_2N_3Al six-membered

heterocycles. Guanidinate and amidinate ligands form CN_2Al four-membered heterocycle as shown in the (figure **5.1)**. Ligands coordinate with *N,N'*- chelated fashion, which can bind two aluminum dialkyls forming both four and six-memberd heterocycles containing C_2N_3Al and CN_2Al core, respectively within the single moiety possessing multi metal centers so far not reported in the literature. The interesting and unique coordination feature of this new type of motifs is attributed to the novelty in the construction of the ligand, *i.e.* the arrangement of five nitrogen atoms in conjugation and three of them are having protons attached, more over the three protons are not in the same chemical environment. Among the three acidic protons, one involves in hydrogen bonding with nearby nitrogen, which is the only available coordination site to form six-membered metallocycle. Herein, we report a well-defined mono-and dinuclear aluminum alkyls, mononuclear aluminum halide, hydride, alkoxide and gallium diiodide complexes bearing a new class of bulky conjugated bis-guanidine ligands for the first time.

Results and discussion

Synthesis and spectroscopic characterization of aluminum complexes

A new type of conjugated bis-guanidine (CBG) ligands such as L(3H) [L = $\{(ArN)_2C{=}N{-}C{=}N(Ar)(NAr)\}$; Ar = 2, 6-$Me_2$ - C_6H_3] and L^1(3H) [L^1 = $\{(ArN)_2C{=}N{-}C{=}N(Ar)(NAr)\}$; Ar = 2, 6-$^iPr_2$ - C_6H_3] have been synthesized in reasonable yields by a new synthetic procedure developed in our laboratory and are shown in (figure **5.2)** along with N–*H*and N_3C resonances.

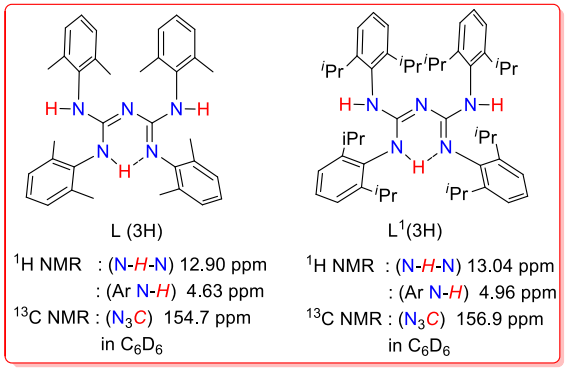
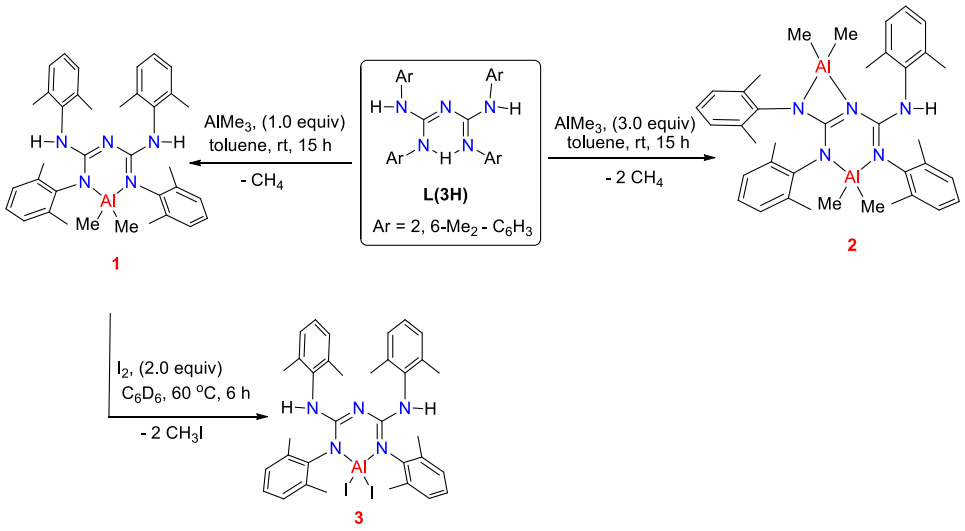


Figure 5.2. N–*H* and N_3C resonances of CBG ligands.

The synthesis compound **1** [L(2H)$AlMe_2$] and **2**[L(H)($AlMe_2$)$_2$] was accomplished by the reaction of L(3H) with trimethylaluminum in toluene at room temperature. The formation of mono- or di-nuclear Al(III) dialkyl complexes of L(3H) was found to be dependent on stoichiometric ratio of limiting reagent, as it leads to different products with different molar ratios of trimethylaluminum solution (Scheme **5.1**). When the reaction mixture of L(3H) and trimethyl aluminum in a 1:1 molar ratio was stirred at room temperature for 15 h formation of compound **1** (Scheme **5.1**) was observed as a colorless compound in good yield (65 %). On the other hand, in the 1:3 molar ratio of L(3H) and trimethyl aluminum solution at room temperature for 15 h led to the formation of an interesting compound **2** (Scheme **5.1**). Further a reaction of **1** with two equivalents of iodine in C_6D_6 at 60 ^oC for 6 h affords the compound **3** [L(2H)AlI_2] (Scheme **5.1**).

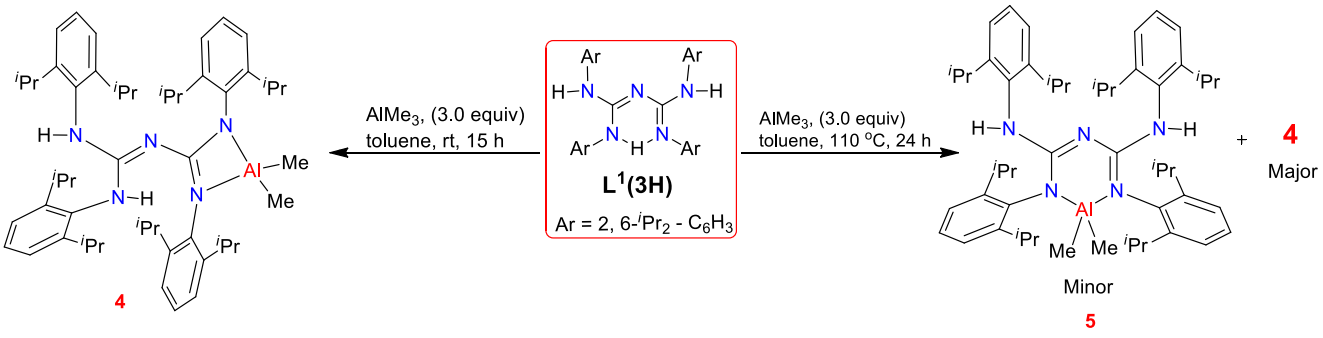
Scheme 5.1. Synthesis of conjugated bis-guanidinate supported Al (III) alkyl and halide complexes.



Compounds **1–3** have been spectroscopically characterized. ^1H NMR spectroscopic analysis (C_6D_6) revealed that the N–*H*–N resonance at 12.90 ppm as a singlet in L(3H) has completely

vanished in compound **1.** A singlet for six protons at −0.48 ppm confirms the presence of one $Al(CH_3)_2$ in compound **1.** The N–H resonances of two ArN–*H* shifts from 4.63 ppm for L(3H) to 4.83 ppm for **1**. NMR data establishes that **2** is a di-nuclear aluminum alkyl complex, so apart from the N-*H*-N resonance at 12.90 ppm in L(3H), one of the two N–*H* resonances of ArN–*H* at 4.63 ppm was disappeared entirely in **2**, the only one N–*H* resonance in compound **2** was observed at 5.0 ppm. Moreover, the presence of two singlets at − 0.54, and − 0.77 corresponding to six protons of each evidences the existence two different $Al(CH_3)_2$ groups in the compound **2**, this is expected due to two different chemically equivalent protons of $Al(CH_3)_2$groups**.** The imine carbon (N_3C) resonance of L(3H) in C_6D_6 is 154.7 ppm and it was to 157.6 and 164.0 ppm for compounds **1** and **2** respectively. The $Al(CH_3)_2$ carbon resonances, were observed at – 7.59 ppm for compound **1,** two resonances at − 7.51 and − 7.91 ppm for the compound **2.** These results are consistent with the conversion of the ligand L(3H) to the compounds **1** and **2**. The methyl proton resonance of $Al(CH_3)_2$ at + 0.48 ppm in **1** were completely consumed in **3**. The two N− *H* resonances of ArN−*H* at 4.83 ppm in **1** were shifted to 5.04 ppm in **3.** The carbon resonances of $Al(CH_3)_2$, in the upfield region at – 7.59 ppm for compound **1** were disappeared in the compound **3.** These results are providing an evidence for the conversion of the **1** to **3.** The presence of two iodide ligands which are attached to aluminum atom was further confirmed by single crystal X-ray structural analysis (*vide infra*).

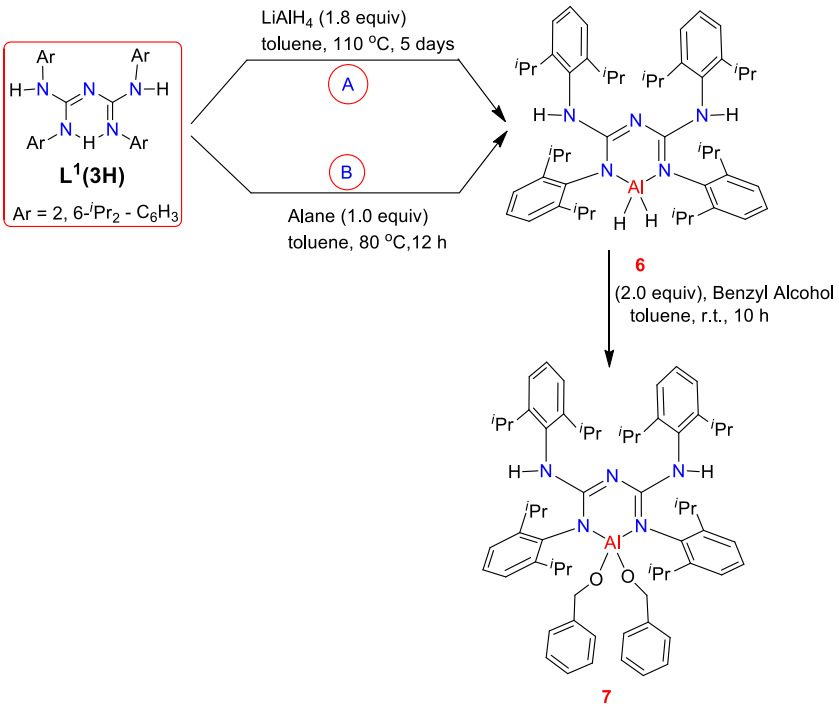
Scheme 5.2. Synthesis of conjugated bis-guanidinate supported Al (III) alkyl complexes



In case of less bulky CBG *i.e* .L(3H) the formation of Al(III) dialkyl complexes was controlled by stoichiometric ratio of a reagent. In contrast, the formation of more bulky CBG ligand *i.e* .L^1(3H) supported Al(III) dialkyl complexes was monitored by reaction temperatures. Overall the reactions of conjugated bis-guanidines can be tuned by the bulky nature of the ligand and reagent, stoichiometric ratios and the temperature conditions. Reaction temperatures play a key role in the formation of products for more bulky ligands and stoichiometric ratios are important reaction conditions for less bulky ligands. This can be evidenced by the formation of compounds **4** & **5**. When the reaction mixture of 1:3 molar ratios of L^1(3H) and trimethyl aluminum in toluene was stirred at room temperature for 16 h, generates an unsymmetrical or complex bearing a four-membered metallocycle [L^1(2H)$AlMe_2$] (**4),** which is sterically favored. The crude product was crystallized from toluene to give **4** as colorless crystals in an isolated yield of 65.4 %. When the same reaction mixture was heated at 110 ^oC for 24 h, the formation of a mixture of compounds **4** & **5** (Scheme **5.2**) was observed by ^1H NMR spectroscopy. Further, pure compound of **5** *i.e*. symmetrical [L^1(2H)($AlMe_2$)] was isolated as colorless compounds by crystallization of the mixture of **4** & **5** in *n*-hexane, to give **5** in 37.3% yield. The N–*H*–N resonance at 13.04 ppm in L^1(3H) was completely disappeared in both compounds **4** and **5**. The two equivalent ArN–*H* resonances at 4.96 ppm in L^1(3H) became chemically unequivalent and resonate at different chemical shift positions as singlet (1H) at 4.86 and 6.51 ppm in compound **4,** this is because of unsymmetric structure of **4** (Scheme **5.2**). However, in case of compound **5** the two equivalents ArN-*H* resonances retain the chemical equivalency with significant change (approximately 1 ppm) in the chemical shift position suggesting the symmetric structure for the compound **5**. Methyl protons of Al (CH_3)$_2$resonate at − 0.16 and − 0.30 ppm in compounds **4** and **5** respectively. Carbon resonance of 'N_3C' at 156.9 ppm in L^1(3H) was shifted to 168.03 ppm in

4. Carbon resonance of Al (CH_3)$_2$were noticed at – 8.34 ppm for compound **4**. It is noteworthy to mention that less bulky L(3H) ligand at the same reaction conditions led to the formation of a di-nuclear aluminum dialkyl complex in contrast to mono nuclear in the case of aluminum complex bearing more bulky ligand L^1(3H) (*vide infra*). This is attributed to the steric nature of the ligand. Next, we targeted to prepare well-defined molecular aluminum dihydride complex, because recent report suggests that such molecules act as catalysts for the hydroboration of carbonyl compounds.

Scheme 5.3. Synthesis of conjugated bis-guanidine supported Al (III) hydride and alkoxide complexes

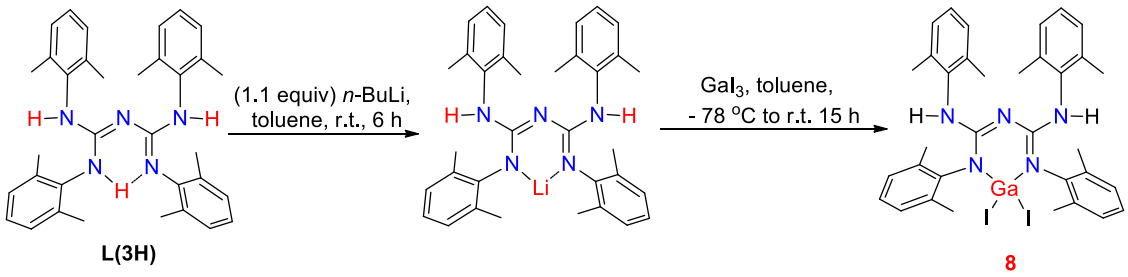


Accordingly, the first well–defined aluminum dihydride complex bearing a *N,N'*– chelated conjugated bis-guanidinate ligand has been reported. CBG supported aluminum dihydride can be synthesized by two synthetic methods (Method **A** and **B**) (Scheme **5.3**). In the first method, the reaction between L^1(3H) and $LiAlH_4$ in 1:1.8 ratio at reflux temperature in toluene for 5 d led to

the formation of [L^1(2H)AlH_2] **(6)** in 43.4 % yield. However, compound **6** can also be synthesized in better yield by the reaction of L^1(3H) with alane. The reaction mixture of 1:1 molar ratio of L^1(3H) and alane in toluene was stirred at 80 ^oC for 12 h, followed by crystallization from toluene to give **6** as colorless crystals in good yield (65 %). The N–*H*–N resonance at 13.04 ppm in L^1(3H) was completely vanished. The ArN–*H* resonances at 4.96 ppm in L^1(3H) were shifted to 5.75 ppm in **6**. The resonances of Al–H were not detected in ^{1}H NMR spectroscopy of compound **6** in C_6D_6 because of the quadrupolar broadening on the ^{27}Al center (nuclear spin = 5/2). In the IR spectrum of **6** two strong bands at 1809 and 1841 cm^{-1} were noticed, attributing to the asymmetric and symmetric stretch of the Al–H bonds, respectively and thus confirming the presence of Al–H bonds. Carbon resonance 'N_3C' at 156.9 ppm in L^1(3H) was shifted to 159.8 ppm in **6**. The reaction between the compound **6** and benzyl alcohol was shown in (Scheme **5.3**). When the reaction mixture of **6** and benzyl alcohol in 1:2 molar ratios was stirred at room temperature in toluene for 12 h, the alkoxide molecule [L^1(2H)Al($OCH_2Ph)_2$] **7** was produced and the crude product was crystallized from toluene to give **7** as colorless crystals in good yield (60 %). The two ArN–*H* resonances at 5.75 ppm in **6** were shifted to 6.05 ppm in **7**. The methylene (–C*H*$_2$–) protons of ($C_6H_5CH_2O$) in **7** resonate at 5.04 ppm. The imine carbon resonance was noticed at 159.6 ppm of **7** in C_6D_6. CBG supported gallium diiodide can be synthesized by treating the lithium salt of CBG with freshly prepared GaI_3 which is obtained by the sonication of 2 equiv gallium and 3 equiv of iodine in toluene. The detailed procedure follows two steps in the first step to a solution of L(3H) (1.0 equiv) in toluene (10 mL), ^{n}BuLi (1.6 M in hexanes,1.0 equiv) was added at room temperature and continued stirring for 6 h. In the second step this lithium salt of CBG was transferred to *in-situ* generated GaI_3 suspension (1.23 equiv) at – 78 ^oC and the reaction mixture slowly warmed to room temp

and continued stirring for 15 h to yield the compound **8** [L^1(2H)GaI_2] in 48% yield (Scheme **5.4**). The N–*H*–N resonance at 12.90 ppm as singlet in L (3H) was completely vanished in compound **8.** The N–H resonances of two ArN–*H* shifts from 4.63 ppm for L (3H) to 5.01 ppm for compound **8**. Finally the molecular composition was confirmed by X-ray analysis and mass spectrometry

Scheme 5.4 Synthesis of conjugated bis-guanidinate supported Ga (III) iodide complex.



Thus the (N–*H*–N) resonances at 12.90 & 13.04 ppm, the two N–*H* resonances of ArN–*H* at 4.63, 4.96 ppm and carbon resonance of 'N$_3$*C*' at 154.7, 156.9 ppm in ligands L(3H) and L^1(3H) respectively in C_6D_6 have been utilized as an useful indicators for evaluating the metal complexes purity from NMR spectroscopy.

Crystallographic information:

Although the NMR spectra of these complexes **1**–**8** are giving conclusive evidence for their formation, for further confirmation, single-crystal X-ray structures were also obtained. The composition and connectivity in all these complexes **1**–**8** was established clearly by the X-ray studies. The single crystal XRD experiments revealed the molecular structures of **1**–**7** displaying the four coordinated 'Al' center containing a six-membered C_2N_3Al ring in all the complexes **1–7** except in **4** which contains the CN_2Al four-membered ring. Interestingly, in case of complex **2**, apart from the six-membered C_2N_3Al ring there is a CN_2Al four membered ring, displaying four

coordinated ‘Al’ center in both the cases. In compound **8** a four coordinated gallium with C_2N_3Ga ring was noticed. Single crystals suitable for X-ray diffraction of all the compounds **1**–**8** except **5** were grown from concentrated toluene solution. For compound **5** the crystals were grown from *n*-hexane solution. Compound **1, 3** and **6** were crystallized in the monoclinic system in Pc, P2(1)/c and C2/c respectively, with four molecules of **1**, two molecules of **3** and one molecule of compound **6** in the respective asymmetric unit. Compounds **2**, **4**, **5** and **7** were crystallized in triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. Compound **8** was crystallized in monoclinic, space group P2(1)/c, with two molecules of **8**, in the asymmetric unit. These compounds are divided into two groups containing isomorphic species. The first group contains complexes **1, 2, 4** and **5** (two similar substituent’s are attached to the metal center), the second include compounds **3**, **6**, **7** and **8** (two small atoms ‘H’, two big atoms ‘I’ and two alkoxide groups bound to the metal center). Molecular structures of these complexes are shown in (Figures **2–9**) respectively. The crystal data and structure refinement details of complexes (**1–8)** are summarized in (table **5.1** and table **5.2)**. In compounds **1**, **3**, **4**, **5** and **7** C_2N_3Al ring was observed, in the compound **2** both C_2N_3Al and CN_2Al rings were observed but in the compound **4** only CN_2Al was observed, In compound **8** C_2N_3Ga ring was observed. In all the cases the metal has deviated from the plane of respective atoms constituting the metallocycle. This boat conformation of the C_2N_3Al ring can be found in compounds **1**, **2**, **3**, **5** and **7**. In case of compound **7** the metal atom much more deviated from the plane of C1, C2, N1 and N2. The aluminum atom was surrounded by the nitrogen atoms of chelating conjugated bisguanidine and two alkyl groups in case of compounds **1**, **2**, **4** and **5** (Figures **5.3, 5.4, 5.6** and **5.7** respectively). The Al-C bond lengths for the compounds **1**, **2**, **4** and **5** lie between 1.949 Å and 1.985 Å, these values are similar to the reported values of Al–C bond lengths 1.962(2) Å of aluminum

complexes stabilized dipyrromethene ligand[43]. The aluminum atom was surrounded by the nitrogen atoms of chelating conjugated bisguanidine and two iodine groups in case of compound **3**, two hydrogen atoms in compound **6**, two alkoxide groups in compound **7** (Figures **5.5, 5.8** and **5.9**). The Al−I bond distances in **3** Al1−I1 is 2.507(2) Å and Al1−I2 is 2.521(2) Å which are very close to the reported values 2.506 Å and 2.524 Å of aluminum iodide complexes supported by a bulky dipyrromethene ligand[44]. The Al1−H bond distances in **6** (Figure **5.8**) is 1.51(3) Å and this value is falling in the range of reported bond lengths Al1−H1 1.51(4) and Al1−H2 1.54(4) Å of (*N*,*N*)AlH_2 where (*N*,*N*) is deprotonated dipyrromethene[43]. The Al−O bond distances in **7** (Figure **5.9**) Al1− O8 is 1.721(13) Å, and Al1− O24 is 1.707(15) Å which are matching with the similar reported Al−O bond distances of aluminum alkoxide complexes Al1–O1 1.706(2) Å supported by dipyrromethene ligand.[44] The Ga−I bond distances in **8** Ga1−I1 is 2.5374(12) Å and Ga1−I2 is 2.5324(11) Å which are very close to the reported value of gallium iodide complexes Ga1−I1 is 2.552(2) Å supported by *β*-diketaminate ligand.[56] The geometry at aluminum in compounds **1–7** and at gallium in compound **8** has been described as distorted tetrahedral. The bite angles of the conjugated bisguanidine ligands N1− Al1− N2, which are 94.0(3), 97.4(3), 68.49(7), 93.93(8), 94.40(11), 94.82(7)° for **1**, **3**, **4**, **5**, **6** and **7** respectively. The bite angles in compound **2** for C_2N_3Al ring 93.18(10)° and for CN_2Al ring is 67.80(10)°. In compound **8** the N1-Ga1-N2 bond angle is 96.9(3). In all the compounds the bite angles of the conjugated bisguanidines are smaller than the regular tetrahedral bond angles (109.28°).

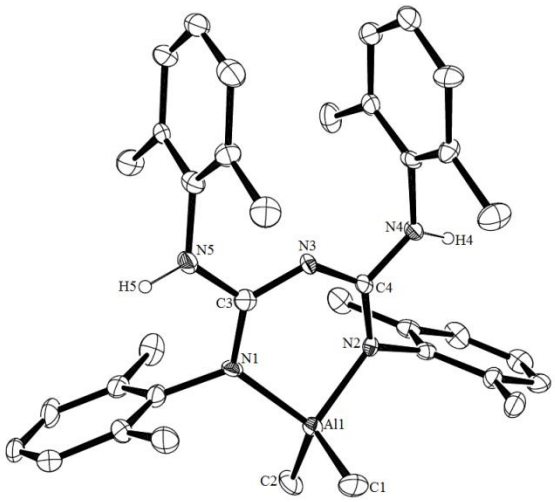


Figure 5.3. Molecular structure of **1**. The thermal ellipsoids are shown at 30% probability and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al1−C1 1.969(11), Al1−C2 1.985(9), Al1−N1 1.915(8), Al1−N2 1.895(7), N1−C3 1.354(10), N3−C3 1.317(11), N3−C4 1.353(11), N2−C4 1.317(10), N5−C3 1.354(12), N4−C4 1.371(10), N4−H4 0.880, N5−H5 0.880; N2−Al1−N1 94.0(3), N2−Al1−C1 111.6(4), N1−Al1−C1 108.4(4), N2−Al1−C2 112.3(4), N1−Al1−C2 114.0(4), C1−Al1−C2 114.85, N3−C3−N1 126.1(8), C3−N3−C4 124.6(7), N2−C4−N3 126.3(7), N3−C3−N5 115.4(8), N3−C4−N4 113.0(7).

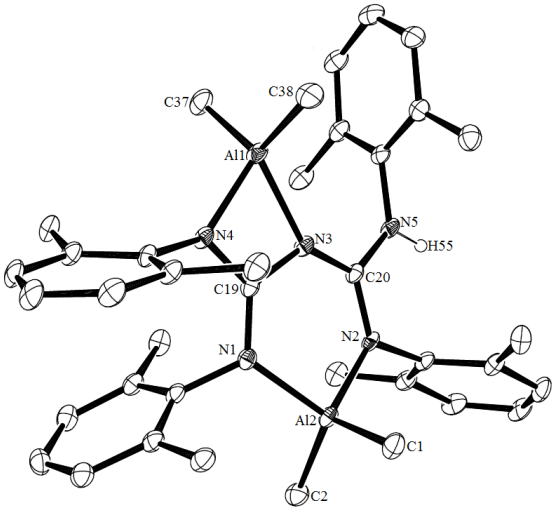


Figure 5.4. Molecular structure of **2**. The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al1−C37 1.958(3), Al1−C38 1.953(3), Al2−C1 1.963(3), Al2−C2 1.957(3), Al1−N3 1.995(2), Al1−N4 1.926(2)**,** Al2−N1 1.902(2), Al2−N2 1.920(2), N1−C19 1.336(3), N3−C19 1.404(3), N3−C20 1.352(3), N2−C20 1.336(3), N4−C19 1.329(3), N5−C20 1.346(3); N1−Al2−N2 93.18(10), N4−Al1−N3 67.80(10), N4−Al1−C37 111.17(12), C38−Al1− C37 118.87(16), C38− Al1− N3 114.43(12), N1− Al2− C2 109.95(12), N2− Al2− C1 113.09(12), C2−Al2−C1 115.42(14), N1−C19−N3 124.0(2), C20−N3−C19 125.6(2), N2−C20−N3 123.4(2), N4−C19−N3 106.3(2), N5−C20−N3 117.1(2).

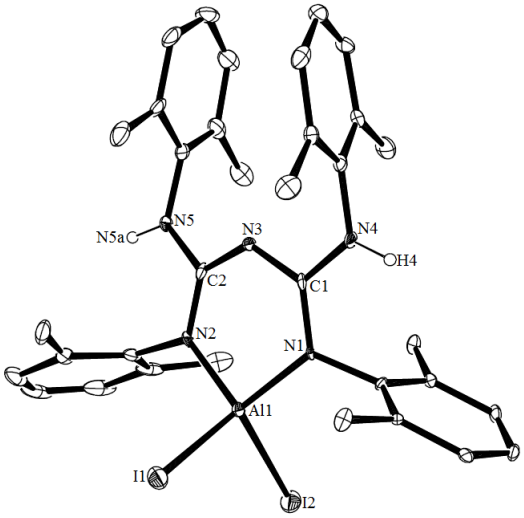


Figure 5.5. Molecular structure of **3**. The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Al1−I1 2.507(2), Al1−I2 2.521(2), Al1−N1 1.853(6), Al1−N2 1.855(6), C2−N2 1.351(9), C2−N3 1.342(9), C1−N3 1.341(9), C1−N1 1.347(9), C2−N5 1.348(9), C1−N4 1.360(9), N4−H4 0.860, N5−H5a 0.860; N1−Al1−N2 97.4(3), N2−Al1−I1 108.8(2), N1−Al1−I2 109.1(2), I1−Al1−I2 104.51(8), N3−C2−N2 126.3(6), C1−N3−C2 124.2(6), N3−C1−N1 126.1(6), N3−C2−N5 113.7(6), N3−C1−N4 112.9(6).

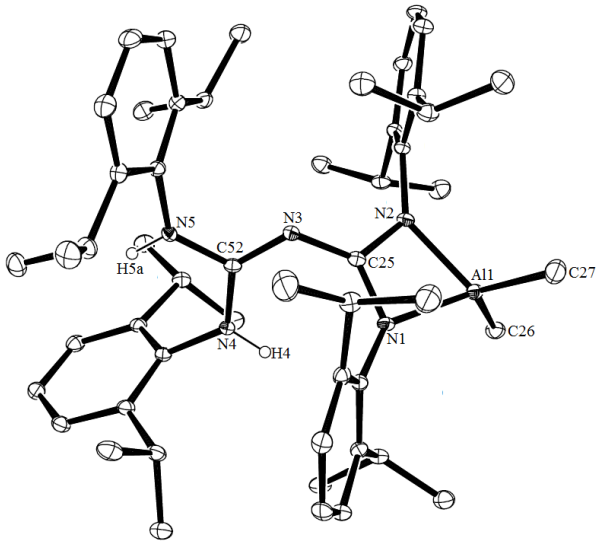


Figure 5.6. Molecular structure of **4**. The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al1−C26 1.965(2), Al1−C27 1.949(3), Al1−N1 1.9487(19), Al1−N2 1.9145(17), N4−C52 1.367(3), N3−C52 1.303(3), N3−C25 1.363(2), N1−C25 1.364(2), N5−C52 1.364(2), N2−C25 1.338(3); N2−Al1−N1 68.49(7), N2−Al1−C27 112.54(9), N1−Al1−C26 115.52(9), C27−Al1−C26 117.57(10), N3−C52−N4 126.45(17), C52−N3−C25 124.32(17), N3−C25−N1 130.47(18), N3−C52−N5 119.24(18), N2−C25−N3 122.30(17).

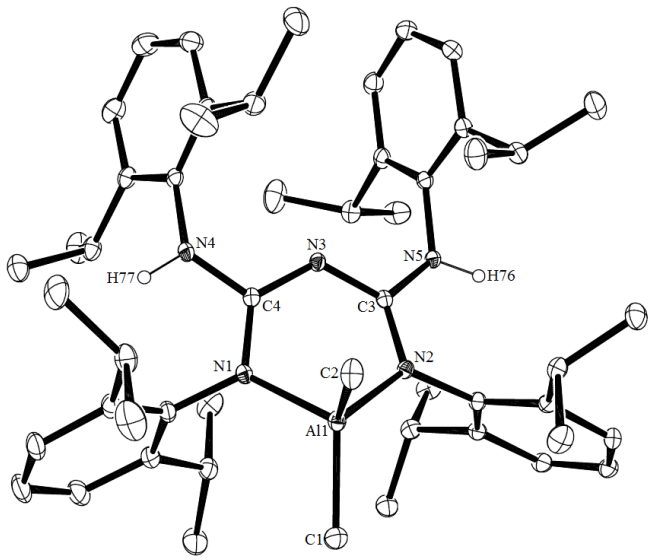


Figure 5.7. Molecular structure of **5**. The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to Nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al1−C1 1.961(3), Al1−C2 1.976(3), N1−Al1 1.912(2), N2−Al1 1.9208(18), C4−N1 1.353(3), C4−N3 1.337(3), C3−N3 1.348(3), C3−N2 1.340(3), C4−N4 1.367(3), C3−N5 1.366(3), N4−H77 0.860(3), N5−H76 0.870(3); N1−Al1−N2 93.94(8), N1−Al1−C1 111.56(10), N2−Al1−C1 113.67(10), N1−Al1−C2 107.28(10), N2−Al1−C2 110.00(10), C(1)−Al1−C2 117.69(12), N3−C4−N1 125.62(19), C4−N3−C3 123.94(19), N2−C3−N3 126.86(18), N3−C4−N4 116.28(19), N3−C3−N5 113.78(19).

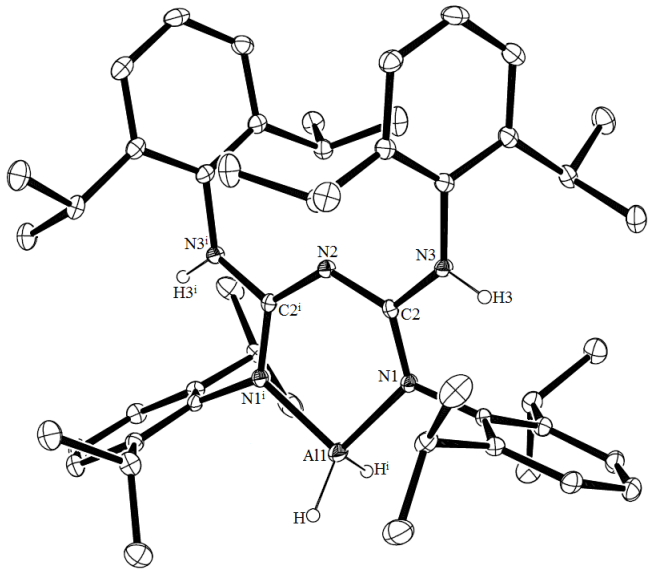


Figure 5.8. Molecular structure of **6**. The thermal ellipsoids are shown at 30% probability, and all the Hydrogen atoms except those bound to Nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al1−H 1.510(3), Al1−N1 1.8834(18), N3−H3 0.8800, N2−C2 1.344(2), N1−C2 1.341(3), N3−C2 1.364(3); $N1^{i}$−Al1−N1 94.40(11), $N1^{i}$−Al1−H 109.5(11), $C2^{i}$−N2−C2 122.8(2), N2−C2−N1 126.6(19), N2−C2−N3 116.17(18).

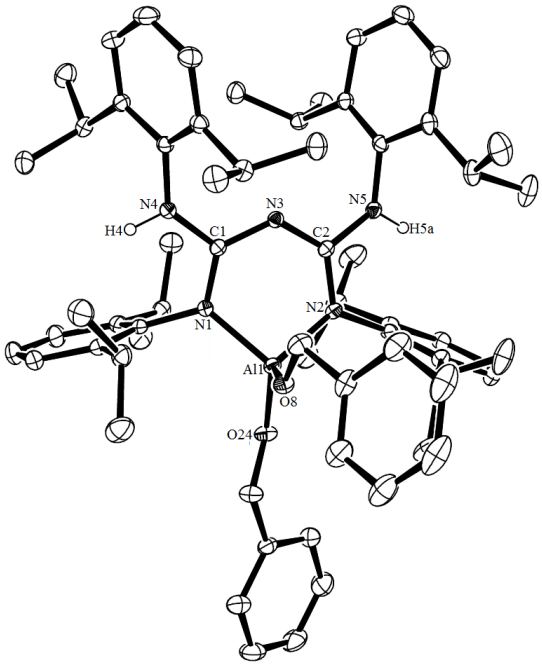


Figure 5.9. Molecular structure of **7**. The thermal ellipsoids are shown at 30% probability, and all the Hydrogen atoms except those bound to Nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al1− O8 1.7214(13), Al1− O24 1.7079(15), Al1− N1 1.8698(15), Al1−N2 1.8761(15), C1−N1 1.355(2), C1−N3 1.3419(19), C2−N3 1.348(2), C2−N2 1.345(2), C1− N4 1.363(2), C2− N5 1.364(2), N4− H4 0.860, N5− H5a 0.860; N1− Al1− N2 94.82(7), N1−Al1−O8 110.28(7), N1−Al1−O24 115.33(7), N2−Al1−O8 113.16(6), N2−Al1−O24 113.06(7), O8−Al1−O24 109.59(7), N1−C1−N3 118.29(13), C1−N3−C2 122.76(15), N3−C2−N2 126.85(14), N3−C1−N4 116.83(15), N3−C2−N5 115.29(15).

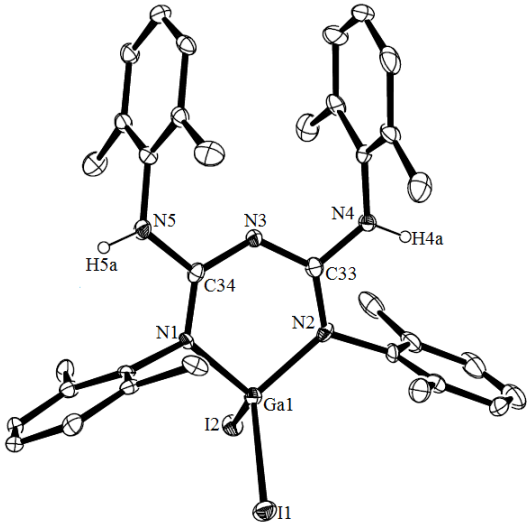


Figure 5.10. Molecular structure of **8**. The thermal ellipsoids are shown at 30% probability, and all the Hydrogen atoms except those bound to Nitrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1-I1 2.5374(12), Ga1-I2 2.5324(11), N1-Ga1 1.902(7), N2-Ga1 1.908(8), N4-H4a 0.860, N5-H5a 0.860, C34-N1 1.334(11), C34-N3 1.350(11), C33-N3 1.334(11), C33-N2 1.341(12), C34-N5 1.385(11), C33-N4 1.367(11), C34-N1-C1 119.4(7), C(34)-N1-Ga1 119.8(6), C33-N3-C34 124.8(8), N1-Ga1-N2 96.9(3), N1-Ga1-I2 117.6(2), N2-Ga1-I2 108.3(2), N1-Ga1-I1 109.0(2), N2-Ga1-I1 119.3(2), I2-Ga1-I1 106.23(4).

Table 5.1. Crystal and refinement data for **1**-**4.**

	1	**2**	**3**	**4**
Empirical formula	C_{36} H_{44} Al N_5	C_{38} H_{49} Al_2 N_5	C_{68} H_{76} Al2 I_4 N_{10}	C_{52} H_{76} Al N_5
Formula weight	573.74	629.78	1594.95	798.16
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71069	0.71069	0.71069
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	*Pc*	$P\bar{1}$	*P2(1)/c*	$P\bar{1}$
a (Å)	14.6955(18)	8.479(6)	16.155(4)	12.710(7)
b (Å)	21.642(3)	14.233(10)	13.828(4)	12.925(6)
c (Å)	20.796(2)	17.132(12)	30.453(9)	16.045(8)
α (deg)°	90	78.773(4)	90	81.775(3)
β (deg)°	90.077(7)	78.779(4)	96.086(2)	81.144(3)
γ (deg)°	90	74.201(4)	90	67.293(3)
Volume ($Å^3$)	6614.0(14)	1929.3(14)	6765(3)	2392.4(15)
Z	8	2	4	2
ρ (g cm^{-3})	1.152	1.084	1.566	1.108
μ(MoKα)mm^{-1}	0.093	0.106	1.916	0.081
F(000)	2464	676.0	3168	872
Reflections collected	42089	22093	74025	28469
Independent reflections	17829	7137	12605	8850
GOOF	0.912	1.024	1.025	1.039
FinalRindices [I>2□(I)]	R1 = 0.0821, wR2 = 0.2144	R1 = 0.0735, wR2 = 0.1995	R1 = 0.0582, wR2 = 0.1518	R1 = 0.0480, wR2 = 0.1202

Table 5.2. Crystal and refinement data for **4**-8**.**

	5	**6**	**7**	**8**
Empirical formula	C_{52} $H_{76}Al$ N_5	C_{50} H_{72} Al N_5	$C_{64}H_{84}AlN_5O_2$	C_{34} $H_{38}GaI_2N_5$
Formula weight	798.16	770.10	982.34	840.21
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71069	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	*C2/c*	$P\bar{1}$	*P2(1)/c*
a (Å)	10.511(6)	27.526(2)	12.137(3)	16.230(10)
b (Å)	11.876(6)	10.6897(7)	12.524(3)	13.803(8)
c (Å)	20.994(11)	19.8704(17)	21.3556	30.483(2)
α (deg)°	94.895(3)	90	73.976(16)	90
β (deg)°	92.249(3)	127.991(9)	85.870(18)	95.754(4)
γ (deg)°	113.447(3)	90	67.853(15)	90
Volume ($Å^3$)	2387.8(16)	4607.8(8)	2887.9(14)	6795.3(8)
Z	2	4	2	8
ρ (g cm^{-3})	1.109	1.110	1.130	1.643
μ(MoKα)mm^{-1}	0.081	0.082	0.082	2.657
F(000)	870	1680.0	1064.0	
Reflections collected	42652	28878	49800	14398
Independent reflections	13225	4763	15478	7528
GOOF	1.005	1.057	1.047	0.946.
FinalRindices [I>2□(I)]	R1 = 0.0751, wR2 = 0.2081	R_1 = 0.0692, wR_2 = 0.1904	R_1 = 0.0579, wR_2 = 0.1323	R_1 = 0.0566, wR_2 = 0.1769

Experimental section

General methods.

All the reactions dealing with air and moisture sensitive compounds were carried out in standard Schlenk line and nitrogen filled glove-box, unless otherwise noted. The precursors L(3H) [L = {$(ArN)_2C=N-$ C=N(Ar)(NAr)}; Ar = 2, 6-Me_2 - C_6H_3] and L^1(3H)[L^1 = [{$(ArN)_2C=N-$C=N(Ar)(NAr)}; Ar = 2, 6-$^iPr_2$ - C_6H_3] were prepared in our laboratory by using a new synthetic procedure. $AlMe_3$ (2.0 M in toluene) and Alane-N, N-dimethylethylamine complex (0.5 M) in toluene were purchased from Sigma-Aldrich and used as received. Anhydrous solvents toluene, benzene, and *n*- hexane were collected from MBraun solvent purification system and used as such. Deuterated benzene (C_6D_6) was dried over a sodium mirror in vacuum prior to use. NMR spectra were {^{1}H (400 MHz), &^{13}C (101 MHz) were recorded on Bruker AV 400 MHz instrument. The chemical shift values are reported in parts per million (ppm) and are referenced to the residual solvent (7.16, & 7.26 for ^{1}H; 128.09 & 77.16 for ^{13}C; for C_6D_6, $CDCl_3$ respectively). High resolution mass spectra (HRMS) were recorded on Bruker micrOTOF-Q II spectrometer. IR spectra were recorded on Perkin-Elmer FTIR spectrometer. Elemental analysis for compounds **6** and **7** was performed by *EuroEA3000-CHNS-Analyzer*.

Crystallographic Data.

The single crystals suitable for X-ray diffraction were obtained from toluene for **1**, **2**, **3** and **4** as colorless needles, **5** as colorless blocks from n-hexane, **6**, and **7** as colorless needles from toluene. Paraffin liquid heavy oil was used to immerse the crystals and the crystals were mounted on a glass fiber. Single-crystal X-ray structural study was performed on a Bruker-APEX-II CCD X-ray diffractometer equipped with an Oxford cryosystem 700 Instruments low-temperature attachment. Data were collected at 100(2) K by using graphite-monochromated Mo Kα radiation

(λ_α = 0.71073 Å). The indexing of frames, integration, and scaling was done by using the SMART and SAINT software package[59] and the absorption correction for data was performed by using the SADABS program[60]. The structures were solved with ShelXT programme by using direct methods[61] and refined by using the ShellXL with least square minimisation[62] in the olex2[63] software. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non hydrogen atoms were refined with anisotropic displacement parameters. The crystal data for all compounds along with the final residuals and other pertaining details are provided in the tables.

Synthesis of [L(2H)AlMe$_2$] (1). Trimethyl aluminum (2.0 M in toluene, 0.25 mL, and 0.504 mmol, 1.0 equiv) was added to a solution of L(3H) (0.25 g, 0.482 mmol, 1.0 equiv) in toluene (~10 mL) at 0 ^{o}C further reaction mixture was allowed to warm to room temperature and continued stirring at room temperature for 12 h. The volatiles were removed under reduced pressure; the solid residue so obtained was then washed with *n*-hexane (~5 mL) and recrystallized from toluene to give compound **1** as colorless crystals. (Yield: 0.180 g, 0.314 mmol, 65%): Mp 290 – 300 ^{o}C. ^{1}H NMR (400 MHz,C_6D_6, 25 ^{o}C): δ – 0.48 (s, 6H, Al(C*H*$_3$)$_2$), 1.85 (s, 12H, C*H*$_3$), 2.48 (s, 12H, C*H*$_3$), 4.83 (s, 2H, Ar N*H*), 6.55 (d, *J* = 4 Hz, 4H, Ar*H*), 6.74 (t, *J* = 8 Hz, 2H, Ar*H*), 6.94 – 6.98 (m, 2H, Ar*H*), 7.02 (d, *J* = 8 Hz, 4H, Ar*H*); ^{13}C{^{1}H}NMR (400 MHz ,C_6D_6, 25 ^{o}C): δ – 7.5 (Al(*C*H$_3$)$_2$), 18.8 (Ar-*C*H$_3$), 18.9 (Ar-*C*H$_3$), 126.4 (Ar*C*), 126.7 (Ar*C*), 127.5 (Ar*C*), 129.5 (Ar*C*), 135.8 (Ar*C*), 135.9 (Ar*C*), 136.1 (Ar*C*), 140.0 (Ar*C*), 157.5 (N$_3$*C*). ESI-TOF: *m/z* 574.3522.

Synthesis of [L(H)(AlMe$_2$)$_2$] (2): Trimethyl aluminum (2.0 M in toluene, 0.72 mL, 1.44 mmol, 3.0 equiv**)** was added to the solution of L(3H) (0.25 g, 0.482 mmol, 1.0 equiv) in toluene (~10 mL) at 0 ^{o}C and the reaction mixture was continued stirring at room temperature for 15 h. The

volatiles were removed under reduced pressure; the solid residue so obtained was then washed with *n*-hexane (~5 mL) and recrystallized from toluene at 5 ^{o}C to give compound **2** as colorless crystals. (0.168 g, 0.267 mmol, 55.4 %). Mp 205-210 ^{o}C. ^{1}H NMR (101 MHz, C_6D_6, 25 ^{o}C) δ – 0.54 (s, 6H, (Al(CH_3)$_2$)), – 0.77 (s, 6H, Al(CH_3)$_2$), 2.03 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 2.43 (s, 6H, CH_3), 5.00 (s, 1H, N*H*), 6.63 – 6.69 (m, 5H, Ar*H*), 6.77 (d, *J* = 8 Hz, 2H, Ar*H*), 6.85 (dd, *J* = 8, 8 Hz, 1H, Ar*H*), 6.95 – 7.03 (m, 4H, Ar*H*); ^{13}C{^{1}H}NMR (400 MHz, C_6D_6, 25 ^{o}C) δ – 7.5 (Al(*C*H$_3$)$_2$), – 7.9 (Al(*C*H$_3$)$_2$), 18.8 (Ar-*C*H$_3$), 18.9 (Ar-*C*H$_3$), 19.3 (Ar-*C*H$_3$), 19.4 (Ar-*C*H$_3$), 20.0 (Ar-*C*H$_3$), 124.5 (Ar-*C*), 124.9 (Ar-*C*), 128.7 (Ar-*C*), 129.3 (Ar-*C*), 129.4 (Ar-*C*), 129.5 (Ar-*C*), 129.9 (Ar-*C*), 132.0 (Ar-*C*), 133.6 (Ar-*C*), 134.1 (Ar-*C*), 136.1 (Ar-*C*), 138.0 (Ar-*C*), 138.7 (Ar-*C*), 140.5 (Ar-*C*), 142.4 (Ar-*C*), 154.9 (N$_3$*C*), 164.0 (N$_3$*C*). ESI-TOF: *m/z* 630.2511.

Synthesis of [L(2H)AlI$_2$] (3): The reaction mixture of compound **1** [L(2H)AlMe$_2$] (0.020 g, 0.0348 mmol, 1.0 equiv) (~0.6 mL) and iodine (0.018 g, 0.0697 mmol, 2.0 equiv**)** in C_6D_6 was heated at 80 ^{o}C for 12 h in the NMR tube. The compound was recrystallized from toluene to give compound **3** as colorless crystals (0.0194 g, 0.0244 mmol, 70 %). ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 1.79 (s, 12H, CH_3), 2.66 (s, 12H, CH_3), 5.11 (s, 2H, Ar N*H*), 6.49 (d, *J* = 8.0 Hz, 4H, Ar*H*), 6.70 (t, *J* = 8 Hz, 2H, Ar*H*), 6.96 (d, *J* = 4 Hz, 6H, Ar*H*); ^{13}C{^{1}H}NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 18.7 (Ar-*C*H$_3$), 21.4 (Ar-*C*H$_3$), 125.7 (Ar*C*), 127.0 (Ar*C*), 129.3 (Ar*C*), 130.1 (Ar*C*), 134.9 (Ar*C*), 135.6 (Ar*C*), 136.2 (Ar*C*), 137.2 (Ar*C*), 158.0 (N$_3$*C*).

Synthesis of [L^{1}(2H)AlMe$_2$] (4): Trimethyl aluminum (2.0 M in toluene, 0.51 mL, 1.02 mmol, 3.0 equiv) was added to the solution of L^{1}(3H) (0.25 g, 0.337 mmol, 1.0 equiv) in toluene (~10 mL) at 0 ^{o}C and the reaction mixture was continued stirring at room temperature for 16 h. The volatiles were removed under reduced pressure; the solid residue so obtained was then washed

with *n*-hexane (~5 mL) and recrystallized from toluene at 5 ^{o}C to give compound **4** as colorless crystals. (0.175 g, 0.219 mmol, 65 %): Mp 190 - 195 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ – 0.16 (s, 6H, Al(*CH*$_3$)$_2$), 0.73 (d, *J* = 8 Hz, 12H, CH(*CH*$_3$)$_2$), 1.07 (d, *J* = 8 Hz, 6H, CH(*CH*$_3$)$_2$), 1.11 (d, *J* = 8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, *J* = 8 Hz, 12H, CH(C*H*$_3$)$_2$), 2.62 (sept, 2H, C*H*(CH$_3$)$_2$), 2.87 – 2.93 (m, 2H, C*H*(CH$_3$)$_2$), 3.77 (sept, 4H, C*H*(CH$_3$)$_2$), 4.86 (s, 1H, N*H*), 6.51 (s, 1H, N*H*), 6.87 (d, *J* = 8 Hz, 2H, Ar*H*), 6.96 (d, *J* = 8 Hz, 2H, Ar*H*), 7.01 (d, *J* = 8 Hz, 2H, Ar*H*), 7.09 (s, 6H, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 ^{o}C) δ – 8.3 (Al(*C*H$_3$)$_2$), 23.0 (Ar-*i*Pr*C*), 24.0 (Ar-*i*Pr*C*), 26.1 (Ar-*i*Pr*C*), 26.7 (Ar-*i*Pr*C*), 28.2 (Ar-*i*Pr*C*), 28.4 (Ar-*i*Pr*C*), 28.8 (Ar-*i*Pr*C*), 123.1 (Ar*C*), 124.4 (Ar*C*), 124.7(Ar*C*), 125.2 (Ar*C*), 130.0 (Ar*C*), 130.5 (Ar*C*), 132.0 (Ar*C*), 138.8 (Ar*C*), 144.3 (Ar*C*), 146.5 (Ar*C*), 148.8 (Ar*C*), 150.0 (Ar*C*), 168.0 (N$_3$*C*). ESI-TOF: *m/z* 798.6163.

Synthesis of [L^{1}(2H)(AlMe$_2$)] (5): Trimethyl aluminum (2.0 M in toluene, 0.595 mL, 1.19 mmol, 3.0 equiv) was added to the solution L^{1}(3H) (0.25 g, 0.337 mmol, 1.0 equiv) in toluene (~15 mL) at 0 ^{o}C and then the reaction mixture was continued stirring at 110 ^{o}C for 24 h. Formation of mixture of products was observed. The volatiles were removed under reduced pressure; the solid residue so obtained was recrystallized from *n*-hexane at 0 ^{o}C to give **5** as colorless crystals (0.1 g, 0.125 mmol, 37.3 %). Mp 235 – 240 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ – 0.30 (s, 6H, Al(*C*H$_3$)$_2$) 0.89 – 1.02 (m, 24H, CH(*C*H$_3$)$_2$), 1.34 (d, *J* = 4 Hz, 12H, CH(*C*H$_3$)$_2$), 1.39 (d, 8 Hz, 12H, CH(*C*H$_3$)$_2$), 3.08 – 3.01 (sept, 4H, C*H*(*C*H$_3$)$_2$), 3.90 – 3.83 (m, 4H, C*H*(*C*H$_3$)$_2$), 5.91 (s, 2H, N*H*), 6.80 (d, *J* = 8 Hz, 4H, Ar*H*), 6.95 – 6.98 (m, 2H, Ar*H*), 7.1 – 7.22 (m, 4H, Ar*H*); ^{13}C{^{1}H}NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 24.9 (Ar-*i*Pr*C*), 27.1 (Ar-*i*Pr*C*), 28.5 (Ar-*i*Pr*C*), 123.0 (Ar*C*), 125.4 (Ar*C*), 127.07 (Ar*C*), 132.8 (Ar*C*), 137.8 (Ar*C*), 145.2 (Ar*C*), 146.7 (Ar*C*), 159.5 (N$_3$*C*). ESI-TOF: *m/z* 798.6150.

Synthesis of [L^1(2H)AlH_2] (6): Method A: The reaction mixture of L^1(3H) (2.0 g, 2.694 mmol, 1.0 equiv) and $LiAlH_4$ (0.184 g, 4.850 mmol, 1.8 equiv) toluene (~15 mL) was stirred at 110 ^oC for 5 days. The volatiles were removed under reduced pressure; then the compound was crystallized from toluene to get compound **6** as colorless crystals (0.9 g, 1.169 mmol, 43.4 %). **Method B:** The reaction mixture of L^1(3H) (0.25 g, 0.336 mmol, 1.0 equiv) and alane-*N*,*N*-dimethylethylamine complex solution (0.5 M in toluene, 0.7 mL, 0.353 mmol, 1.0 equiv) in toluene (~10 mL) was stirred heated at 80 ^oC for 12 h. The volatiles were removed under reduced pressure; the solid residue so obtained was recrystallized from toluene, to give compound **6** as colorless crystals (0.168 g, 0.219 mmol, 65 %): Mp 220-230 ^oC. ^1H NMR (400 MHz, C_6D_6, 25 ^oC) δ 0.81 (d, J = 8.0 Hz, 11H, CH(CH_3)$_2$), 1.08 (d, J = 8.0 Hz, 12H, CH(CH_3)$_2$), 1.33 (d, J = 8.0 Hz, 12H, CH(CH_3)$_2$), 1.51 (d, J = 4.0 Hz, 12H, CH(CH_3)$_2$), 3.05 – 3.12 (m, 4H, C*H*(CH_3)$_2$), 3.78 – 3.85 (m, 4H, C*H*(CH_3)$_2$), 5.75 (s, 2H, N*H*), 6.81 (d, J = 8.0 Hz, 4H Ar*H*), 6.96 (t, J = 8.0 Hz, 2H Ar*H*), 7.18 (s, 4H, Ar*H*); $^{13}C\{^1H\}$NMR (101 MHz, C_6D_6, 25 ^oC) δ 22.7 (Ar-*i*Pr*C*), 24.7 (Ar-*i*Pr*C*), 25.3 (Ar-*i*Pr*C*), 26.8 (Ar-*i*Pr*C*), 28.7 (Ar-*i*Pr*C*), 123.1 (Ar*C*) 125.4 (Ar*C*), 127.5 (Ar*C*), 132.6 (Ar*C*), 136.2 (Ar*C*), 145.8 (Ar*C*), 147.1 (Ar*C*), 159.8 (N_3C). IR (KBr pellet, cm^{-1}) 3793 (br), 3392(s), 2921, 2726, 2672, 1841s (Al-*H*), 1809s (Al-*H*), 1453, 1376, 1311, 1260, 1094, 1020, 797, 721, 559, 520.

Synthesis of [L^1(2H)Al (OCH_2Ph)$_2$] (7). The reaction mixture of compound **6** [L^1(2H)AlH_2] (0.15 g, 0.194 mmol, 1.0 equiv) and benzyl alcohol (0.044 g, 43 µL, 0.409 mmol, 2.0 equiv) in toluene (~10 mL) was stirred at room temperature for 12 h. The volatiles were removed under reduced pressure; the solid residue so obtained was recrystallized from toluene, to give compound **7** as colorless crystals (0.115 g, 0.116 mmol, 60 %): Mp 190 - 200 ^oC. ^1H NMR (400 MHz, C_6D_6, 25 ^oC) δ 0.76 (s, 11H, CH(CH_3)$_2$), 1.07 (s, 12H, CH(CH_3)$_2$), 1.28 (t, J = 4 Hz, 25H,

CH(CH_3)$_2$), 3.02 – 3.09 (sept, 4H, C*H*(CH_3)$_2$), 3.86 – 3.93 (sept, 4H, C*H*(CH_3)$_2$), 5.04 (s, 4H, OCH_2Ph), 6.05 (s, 2H, N*H*), 6.79 (d, *J* = 8.0 Hz, 4H, Ar*H*), 6.94 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.05 (m, 2H, Ar*H*), 7.12 – 7.14 (m, 10H, Ar*H*), 7.19 (d, 4H, Ar*H*); ^{13}C{^{1}H}NMR (101 MHz, C_6D_6, 25 ^{o}C) δ 24.8 (Ar-*i*Pr*C*), 26.3 (Ar-*i*Pr*C*), 28.7 (Ar-*i*Pr*C*), 28.8 (Ar-*i*Pr*C*), 65.1 (O-*C*H_2Ph), 123.0 (Ar*C*), 125.4 (Ar*C*), 125.6 (Ar*C*), 126.0 (Ar*C*), 127.2 (Ar*C*), 132.2 (Ar*C*), 136.7 (Ar*C*), 145.1 (Ar*C*), 145.8 (Ar*C*), 147.2 (Ar*C*), 159.6 (N3*C*).

Synthesis of [L2H(GaI_2)] (8) ^{n}BuLi (1.6 M in hexanes, 1.0 mL, 1.617 mmol) was added to a solution of L(3H) (0.759 g, 1.47 mmol) in toluene (~20 mL) and the reaction mixture was continued stirring at room temperature 6 h, the prepared lithium salt [L(2H) Li] was transferred to the *in situ* generated GaI_3 (1.23 equiv) suspension at – 70 ^{o}C, the reaction mixture was slowly warmed to room temp and continued the stirring for 15 h. The volatiles were removed under reduced pressure; the solid residue so obtained was recrystallized from toluene at 0 ^{o}C to give compound **8** as a colorless crystals. (0.591 g, 0.703 mmol, 48%); Mp >300 ^{o}C; ^{1}H NMR (C_6D_6) δ 1.79 (s, 6H, CH_3), 2.69 (s, 6H, CH_3), 5.01 (s, 2H, N*H*), 6.49 (d, *J* = 8 Hz, 4H, Ar*H*), 6.71 – 6.68 (m, 2H, Ar*H*), 6.99 – 6.91 (m, 6H, Ar*H*); ^{13}C NMR (C_6D_6) δ 18.7. 21.2, 127.0, 130.0, 135.4, 135.9, 136.1, 138.3, 147.73, 157.10. ESI-TOF: m/z 840.

Conclusion

Structurally characterized both mono and bimetallic aluminum alkyls and mono metallic aluminum alkoxide, halide and hydride complexes bearing *N*,*N* chelated conjugated bis−guanidinate ligand have been reported for the first time. Besides, we have shown the synthesis of CBG stabilized six-membered gallium heterocycle. We have investigated the difference in reactivity and coordination properties of ligands L(3H) and L^{1}(3H) toward the reagent trimethylaluminum depending upon reaction conditions. We noticed the formation of mono

[L(2H)$AlMe_2$] and dinuclear [L(H)($AlMe_2$)$_2$] compounds in the case of ligand L(3H) when treated with trimethyl aluminum (1.0 equiv) and (3.0 equiv), respectively at room temperature. Where as in the case of L^1(3H) formation of only mono nuclear symmetrical or unsymmetrical [L^1(2H)$AlMe_2$] was observed when treated with trimethyl aluminum (3.0 equiv) at 100 ^oC temperature. Compound **1** upon treatment with 2 equivalents of iodine in C_6D_6 led to the formation of compound **3**, in which alkyl-halide exchange was occurred. Deprotonation of L^1(3H) upon treatment with alane led to the formation of aluminum dihydride complex, L(2H)AlH_2] **6**. Compound **6** was further treated with two equiv benzyl alcohol, which allowed the formation of aluminum dialkoxide complex, L^1(2H)Al(OR)$_2$ **7**. Lithiation of L(3H) followed by the reaction with *in situ* generated gallium tri iodide suspension resulted in the formation of compound **8**. We presume that both compounds **6** and **7** can act as catalysts for various organic transformations. Both compounds **3** and **6** are ideal precursors for the preparation of six-membered low valent aluminum (I) heterocycles. Currently, such studies are underway in our laboratory.

References

1 G. Chandra, A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *J. Chem. Soc.*, 1970, 2550-2558.

2 S. Gong and H. Ma, *Dalton Trans.*, 2008, 3345–3357.

3 C. E. Radzewich, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1998, **120**, 9384–9385.

4 H. Zhu, Z. Yang, J. Magull, H. W. Roesky, H. G. Schmidt and M.`Noltemeyer, *Organometallics.*, 2005, **24**, 6420–6425.

5 X. Li, L. Duan, H. Song, C. Ni and C. Cui, *Organometallics*., 2006, **25**, 5665–5667.

6 H. Zhu, J. Chai, V. Chandrasekhar, H. W. Roesky, J. D. Magull, H.`Vidovic, G. Schmidt, M. Noltemeyer, P. P. Power and W. A. Merrill, *J. Am. Chem. Soc.*, 2004, **126**, 9472–9473.

7 H. Zhu, J. Chai, H. Fan, H. W. Roesky, U. N. Nehete, H. G. Schmidt and M. Noltemeyer, *Eur. J. Inorg. Chem.*, 2005, 2147–2150.

8 C. E. Radzewich, I. A. Guzei and R. F. Jordan, *J. Am. Chem. Soc.*, 1999, **121**, 8673–8674.

9 H. Zhu, J. Chai, V. Jancik, H. W. Roesky, W. A. Merrill and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 10170–10171.

10 S. Singh, S. S. Kumar, V. Chandrasekhar, H. J. Ahn, M. Biadene, H. W. Roesky, N. S. Hosmane, M. Noltemeyer and H. G. Schmidt, *Angew. Chem., Int. Ed.* 2004, **43**, 4940–4943.

11 H. Zhu, J. Chai, C. He, G. Bai, H. W. Roesky, V. Jancik, H. G. Schmidt and M. Noltemeyer, *Organometallics.*, 2005, **24**, 380–384.

12 B. Qian, D. L. Ward and M. R. Smith, *Organometallics.*, 1998, **17**, 3070–3076.

13 C. Cui, S. J. Ko1pke, H. I. Regine, H. W. Roesky, M. Noltemeyer, H. G. Schmidt and B. Wrac kmeyer, *J. Am. Chem. Soc.*, 2001, **123**, 9091– 9098.

14 H. Zhu, J. Chai, H. Fan, H. W. Roesky, C. He, V. Jancik, H. G. Schmidt, M. Noltemeyer, W. A. Merrill and P. P. Power, *Angew. Chem., Int. Ed.*, 2005, **44**, 5090–5093.

15 M. Stender, B. E. Eichler, N. J. Hardman and P. P. Power, *Inorg. Chem.*, 2001, **40**, 2794–2799.

16 V. Jancik, L. W. Pineda, J. Pinkas, H. W. Roesky, D. A. Neculai, M. Neculai and R. H. Irmer, *Angew. Chem., Int. Ed.* 2004, **116**, 2194–2197.

17 Y. Peng, H. Fan, V. Jancik, H. W. Roesky and R. H. Irmer, *Angew. Chem., Int. Ed.* 2004, **43**, 6190–6192.

18 V. Jancik, H. W. Roesky, D. Neculai, A. M. Neculai and R. H. Irmer, *Angew. Chem., Int. Ed.* 2004, **43**, 6192–6196.

19 Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull and C. E. Hughes, *Angew. Chem., Int. Ed.*, 2004, **43**, 3443–3445.

20 H. W. Roesky and S. S. Kumar, *Chem. Commun.*, 2005, 4027–4038.

21 Z. Yang, H. Zhu, X. Ma, J. Chai, H. W. Roesky, C. He, J. Magull, H. G. Schmidt and M. Noltemeyer, *Inorg. Chem.*, 2006, **45**, 1823– 1827.

22 S. Singh, H. J. Ahn, A. Stasch, V. Jancik, H. W. Roesky, A. Pal, M. Biadene,H. I.Regine, M. Noltemeyer and H.G. Schmidt, *Inorg. Chem.*, 2006, **45**, 1853–1860.

23 G. G. Sandra, J. Vojtech, C. Raymundo, T. Ruben and M. Monica, *Angew. Chem., Int. Ed.* 2007, **46**, 2895–2898**.**

24 N. Heße, R. Fröhlich, I. Humelnicu and E. U. Würthwein, *Eur. J. Inorg. Chem.*, 2005, 2189−2197.

25 N. Heße, R. Fröhlich, B. Wibbeling and E. U. Würthwein, *Eur. J. Org. Chem.*, 2006, 3923−3937.

26 I. Häger, R. Fröhlich and E. U. Würthwein, *Eur. J. Inorg. Chem.*, 2009, 2415−2428.

27 H. V. R. Dias and S. Singh, *Dalton Trans.*, 2006, **16**, 1995−2000.

28 H. V. R. Dias, S. Singh and T. R. Cundari, *Angew. Chem., Int. Ed.* 2005, **44**, 4907−4910.

29 A. R. Siedle, R. J. Webb, F. E. Behr, R. A. Newmark, D. A. Weil, K. Erickson, R. Naujok, M. Brostrom, M. Mueller, S. H. Chou and V. G. Young, *Inorg. Chem.*, 2003, **42**, 932−934.

30 H. V. R. Dias and S. Singh, *Inorg. Chem.*, 2004, **43**, 5786−5788.

31 H. V. R. Dias and S. Singh, *Inorg. Chem.*, 2004, **43**, 7396−7402.

32 H. V. R. Dias, S. Singh and J. A. Flores, *Inorg. Chem.*, 2006, **45**, 8859− 8861.

33 J. A. Flores and H. V. R. Dias, *Inorg. Chem.*, 2008, **47**, 4448− 4450.

34 M. Pfeiffer, A. Murso, L. Mahalakshmi, D. Moigno, W. Kiefer and D. Stalke, *Eur. J. Inorg. Chem.*, 2002, **12**, 3222−3234.

35 H. Gornitzka and D. Stalke, *Eur. J. Inorg. Chem.*, 1998, **3**, 311−317.

36 J. Ashenhurst, L. Brancaleon, S. Gao, W. Liu, H. Schmider, S. Wang, G. Wu and Q. G. Wu, *Organometallics.*, 1998, **17**, 5334−5341.

37 X. B. Lu, H. Wang and R. J. He, *Mol. Catal. A: Chem.*, 2002, **186**, 33−42.

38 G. Rajagopal, S. Kim and J. M. Kwak, *Bull. Korean Chem. Soc.*, 2006, **27**, 1907.

39 J. D. Masuda and D. W. Stephan, *Dalton Trans.*, 2006, **17**, 2089−2097.

40 K. Bakthavachalam and N. D. Reddy, *Organometallics.*, 2013, **32**, 3174−3184.

41 M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125−8126.

42 J. Koller and R. G. Bergman, *Organometallics.*, 2010, **29**, 5946−5952.

43 C. G. Gianopoulos, K. Kirschbaum and M. R. Mason, *Organometallics.*, 2014, **33**, 4503−4511.

44 C. G. Gianopoulos, N. Kumar, Y. Zhao, L. Jia, K. Kirschbauma and M. R. Mason, *Dalton Trans.*, 2016, **45**, 13787–13797

45 J. C. Fettinger, P. A. Gray, C. E. Melton and P. P. Power, *Organometallics.*, 2014, **33**, 6232–6240.

46 W. Uhl, C. Appelt, J. Backs, H. Westenberg, A. Wollschl.ger and J. Tannert, *Organometallics.*, 2014, **33**, 1212–1217.

47 W. Uhl, J. Grunenberg, A. Hepp, M. Matar and A. Vinogradov, *Angew. Chem., Int. Ed.* 2006, **45**, 4358–4361.

48 C. Y. Lin, C. F. Tsai, H. J. Chen, C. H. Hung, R. C. Yu, P. C. Kuo, H. M. Lee and J. H. Huang, *Chem. Eur. J.*, 2006, **12**, 3067 –3073.

49 V. Jancik, Y. Peng, H. W. Roesky, J. Li, D. Neculai, A. M. Neculai and R. Herbst-Irmer, *J. Am. Chem. Soc.*, 2003, 125, 1452 –1453.

50 V. Jancik, M. M. M. Cabrera, H. W. Roesky, R. H. Irmer, D. Neculai, A. M. Neculai, M. Noltemeyer and H.G. Schmidt, *Eur. J. Inorg. Chem.*, 2004, 3508–3512.

51 G. Tan, T. Szilvasi, S. Inoue, B. Blom and M. Driess, *J. Am. Chem. Soc.*, 2014, 136, 9732–9742.

52 Z. Yang, M. Zhong, X. Ma, S. De, C. Anusha, P. Parameswaran and H. W. Roesky, *Angew. Chem., Int. Ed.* 2015, **54**, 10225 –10229.

53 C. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem., Int. Ed.* 2000, **39**, 4274.

54 N. J. Hardman, B. E. Eichler and P. P. Power, *Chem. Commun.*, 2000, 1991.

55 M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, *Dalton Trans.*, 2005, 273.

56 Y. Cheng, P. B. Hitchcock, M. F. Lappert and M. Zhou, *Chem. Commun.*, 2005, 752.

57 M. Stender, B. E. Eichler, N. J. Hardman and P. P. Power, *Inorg. Chem.*, 2001**, 40**, 2794-2799.

58 SAINT+ Software for CCD Diffractometers, Bruker AXS, Madison, WI, 2000.

59 G. M. Sheldrick, SADABS Program for Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1999.

60 G. M. Sheldrick, Acta Cryst. 2015, A71, 3.

61 G. M. Sheldrick, Acta Cryst., 2015, C71, 3.

62 O.V. Dolomanov, L.J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program *J. Appl. Cryst.*, 2009, **42**, 339-341.