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

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Abstract. A series of bulky bis-guanidine ligands such as $L^1(2H)$, $L^2(2H)$ and $L^3(2H)$, where $L = \{ArNCNAr\}_2\{\mu-N(C_2H_4)_2N\}$, 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 $L^3(2H)$ ($Ar = 2, 6-iPr_2-C_6H_3$) have been utilized to synthesize four-membered dinuclear aluminum heterocycles. Deprotonation of $L^{1-3}(2H)$ (1.0 equiv.) upon treatment with trimethyl aluminum (2.1 equiv.) in toluene led to the formation of bimetallic aluminum alkyls: $[L^1(AlMe_2)_2]$ (**1**), $[L^2(AlMe_2)_2]$ (**2**) and $[L^3(AlMe_2)_2]$ (**3**). Aluminum halide complex i.e., $[L^3(AlI_2)_2]$ (**4**) was obtained by the reaction of compound **3** with four equivalents of molecular iodine in toluene at 80 °C, in which alkyl-halide exchange occurred. All the compounds (**1–4**) were confirmed by multinuclear (1H and ^{13}C) magnetic resonance spectroscopy. Furthermore, compounds **2–4** were confirmed by single crystal X-ray structural analysis. All the compounds **1–4** display the expected number of signals in the 1H and ^{13}C NMR spectra and are consistent with their compositions. The solid state structures of **1–4** 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.

Keywords. Aluminum; guanidine; group 13 metal; main group metal; N, N' -donor ligand; organoaluminum complex.

1. Introduction

Since the synthesis of first transition metal guanidinate complex by Lappert and coworkers¹ in 1970, coordination chemistry of anionic guanidates has been studied significantly, 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., cyclohexene 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 of our knowledge, there are no reports on dinuclear guanidates of aluminum complexes. Therefore, we targeted to synthesize dinuclear aluminum complexes by utilizing bi-nucleating 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 low toxicity of aluminum. Recently, it has been demonstrated that aluminum based molecular compounds can be utilized as catalysts for

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various organic transformations, including hydroboration of carbonyl compounds, hydroboration of olefins and alkynes, cytosilylation, etc.^{19–23}

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

2. Experimental

2.1 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 (1H (400 MHz), and ^{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 and 7.26 for 1H ; 128.09 and 77.16 for ^{13}C , in C_6D_6 , $CDCl_3$, respectively). Melting points were recorded on digital melting point apparatus and are uncorrected.

2.2 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-K α radiation ($\lambda = 0.71073 \text{ \AA}$) 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.

2.3 Synthesis and characterization of compounds **1–4**

2.3a Synthesis of compound 1: To a stirred solution of $L^1(2H)$ (0.3 g, 0.511 mmol, 1.0 equiv.) in toluene (~10 mL), trimethyl aluminum (2.0 M in toluene, 0.54 mL and 1.073 mmol, 2.1 equiv.) was added at $-78^\circ C$. 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 **1**. (Yield: 0.221 g, 0.316 mmol, 62 %). M.p.: $185\text{--}190^\circ C$; 1H NMR (400 MHz, C_6D_6 , $25^\circ C$): δ – 0.34 (s, 12H, $Al(CH_3)_2$), 2.13 (s, 24H), 2.35 (s, 8H, $N(CH_2)_2N$), 6.82 (s, 12H, ArH). ^{13}C NMR (101 MHz, C_6D_6 , $25^\circ C$): δ – 9.2 $Al(CH_3)_2$, 18.9 (CH_3), 44.8 ($N(CH_2)_2N$), 124.8 (ArC), 128.9 (ArC), 133.1 (ArC), 141.6 (ArC), 163.1 (N_3C).

2.3b Synthesis of compound 2: 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 $-78^\circ C$. 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.: $230\text{--}237^\circ C$; 1H NMR (400 MHz, C_6D_6 , $25^\circ C$): δ – 0.31 (s, 12H, $Al(CH_3)_2$), 2.13 (d, $J = 4.0 \text{ Hz}$, 36H, CH_3), 2.44 (s, 8H, ($N(CH_2)_2N$)), 6.63 (s, 8H, ArH). ^{13}C NMR (101 MHz, C_6D_6 , $25^\circ C$): δ – 9.2 $Al(CH_3)_2$, 18.8 (Ar CH_3), 20.9 (Ar CH_3), 44.8 ($N(CH_2)_2N$), 129.6 (ArC), 132.7 (ArC), 133.6 (ArC), 139.1 (ArC), 163.2 (N_3C).

2.3c Synthesis of compound 3: 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 $80^\circ C$ 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.: $215\text{--}222^\circ C$; 1H NMR (400 MHz, $CDCl_3$, $25^\circ C$): δ – 0.73 (s, 12H, $Al(CH_3)_2$), 1.00 (d, $J = 4.0 \text{ Hz}$, 24H), 1.10 (d, $J = 4.0 \text{ Hz}$, 24H), 2.30 (s, 8H, ($N(CH_2)_2N$)), 3.21–3.27 (sept, 8H), 6.99 (d, $J = 4.0 \text{ Hz}$, 3H), 7.01 (s, 5H, ArH), 7.06 (s, 2H, ArH), 7.07 (d, $J = 4.0 \text{ Hz}$, 2H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$, $25^\circ C$): δ – 9.4 $Al(CH_3)_2$, 23.1, 26.0, 28.0, 44.4 ($N(CH_2)_2N$), 123.5 (ArC), 125.5 (ArC), 138.2 (ArC), 144.6 (ArC), 162.5 (N_3C).

2.3d Synthesis of compound 4: In a Glove box, a J Young valve NMR tube was charged with compound **3** (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 $80^\circ C$ for 15 h in an oil bath. The progress of the reaction was monitored by 1H NMR spectroscopy. Once the 1H NMR spectrum confirms the complete disappearance of $L^3(AlMe_2)_2$ peak, the NMR tube was kept at room temperature for 2 days, which yielded colourless crystals of compound **4**. (Yield: 0.031 g, 0.0227 mmol, 70%). M.p.: $270\text{--}280^\circ C$; 1H NMR (400 MHz, $CDCl_3$, $25^\circ C$): δ 0.97 (d, $J = 8.0 \text{ Hz}$, 24

Scheme 1. Synthesis of bridged bis-guanidine ligands.

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, ArH), 7.15–7.19 (m, 4H, ArH). ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ 23.5, 27.5, 28.3, 44.2 ($N(CH_2)_2N$), 124.3 (ArC), 127.4 (ArC), 134.9 (ArC), 145.3 (ArC), 164.6 (N_3C).

3. Results and Discussion

3.1 Synthesis and spectroscopic characterization

The bridged bis-guanidine molecules such as L¹(2H), L²(2H) and L³(2H), where L = {ArNCNAr}₂{μ-N(C₂H₄)₂N}, for L¹(2H) (Ar = 2, 6-Me₂-C₆H₃), L²(2H) (Ar = 2, 4, 6-Me₃-C₆H₂) and L³(2H) (Ar = 2, 6-ⁱPr₂-C₆H₃), were prepared by previously reported literature procedures by using piperazine (or dilithiated piperazine) and *N,N'*-diaryl carbodiimide as precursors (Scheme 1).^{24,25}

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 guanidates of aluminum metal complexes.⁷ i) Metallation of neutral guanidines with aluminum alkyls; ii) Salt metathesis reaction of alkali guanidates with AlX₃ (X = halide); iii) Addition of Al-N bond of Al₂(NMe₂)₆ to carbodiimide.¹² By employing the first method, guanidates of aluminum complexes were prepared. Metallation of neutral bis-guanidines with AlR₃ (R = alkyl) afforded the guanidates of aluminum alkyl complexes. The less to more bulky bis-guanidine ligands L^{1–3}(2H) have been utilized to prepare aluminum alkyl complexes (**1–3**). The synthesis of organoaluminum compounds **1**[L¹(AlMe₂)₂] and **2**[L²(AlMe₂)₂] was achieved by the reaction of corresponding free ligand with trimethyl aluminum in toluene at room temperature (Scheme 2).

The treatment of L³(2H) with trimethylaluminum at elevated temperature (80 °C) in toluene resulted in compound **3** (Scheme 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

Scheme 2. Synthesis of bimetallic aluminum alkyl complexes **1** and **2**.

Scheme 3. Synthesis of bimetallic aluminum alkyl and iodide complexes **3** and **4**.

N,N'-chelated aluminum diiodide complex. This was achieved by alkyl-halide exchange reaction. Compound **4** was prepared from the reaction of **3** with molecular iodine in C₆D₆ at 80 °C for 15 h. Compounds **1**, **2**, **3** and **4** were isolated as colorless crystalline solids in 62%, 60%, 59% and 70% yields, respectively. All the compounds were found to be thermally stable and melt in the range of 185–280 °C. The metal complexes **1–4** were characterized by multinuclear (¹H and ¹³C) magnetic resonance spectroscopy. Furthermore, structure of compounds **2–4** were confirmed by single crystal X-ray structural analysis. All the compounds **1–4** display the expected number of signals in the ¹H and ¹³C NMR spectra and are consistent with their composition.

The ¹H NMR spectra of compounds **1** and **2** exhibit singlet resonances at –0.34 and –0.31 ppm in C₆D₆, respectively corresponding to 12 protons of the two

AlMe₂ groups, *i.e.*, L^{1–2}(AlMe₂)₂. Similarly, the ¹H spectrum of compound **3** shows a singlet resonance at –0.73 ppm in CDCl₃ corresponding to 12 protons of the two AlMe₂ groups, *i.e.*, L³(AlMe₂)₂. In the ¹H spectrum, a complete disappearance of singlet resonance at –0.73 ppm in CDCl₃, which indicates the formation of compound **4**. ¹³C NMR spectra of compounds **1**, **2**, **3** and **4** show a characteristic peak for the N3C carbon atom of the bis-guanidinate ligand 163.1, 163.2, 162.5 and 164.6 ppm (compound **1–2** in C₆D₆ while **3–4** in CDCl₃) respectively. ¹³C NMR spectra of compounds **1**, **2** and **3** exhibit a characteristic peak for the Al(CH₃)₂ at –9.2, –9.2, and –9.4 ppm respectively, which is absent in the case of compound **4**. However, the presence of two iodide ligands which are attached to aluminum atom in compound **4** was further confirmed by single crystal X-ray structural analysis.

Figure 1. 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–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 2. 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–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. Molecular structure of **4**. 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).

3.2 Crystallographic information

The crystals of **2–4** suitable for single crystal X-ray diffraction analysis were recrystallized from the concentrated toluene solution. The compound **2** crystallizes in triclinic system with $P\bar{1}$ space group, while, both compounds **3** and **4** crystallized in the monoclinic system with $P2_1/n$ space group. Both compounds **2** and **3** are isostructural. Molecular structures of these complexes **2–4** are shown in Figures 1, 2 and 3, respectively. The crystal data and structure refinement details of complexes **2–4** are summarized in Table 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 **4**, the aluminum center is in distorted tetrahedral geometry, which is surrounded by the nitrogen atoms of chelating bridged bis-guanidine and two iodine moieties. The Al–C bond lengths for the compounds **2** and **3** 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 **4** 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 bridged bis-guanidine ligands N1–Al1–N2, which are 68.75(16), 69.33(10) and 71.19(19)° for **2–4**, respectively.

Table 1. Crystallographic and structure refinement data for **2**, **3** and **4**.

	2	3	4
Empirical formula	C ₄₆ H ₆₄ Al ₂ N ₆	C ₅₈ H ₈₈ Al ₂ N ₆	C ₅₄ H ₇₆ N ₆ Al ₂ I ₄
Formula weight	754.99	923.35	1370.83
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	12.1222(19)	12.528(4)	10.5278(12)
<i>b</i> [Å]	12.893(2)	14.416(6)	20.575(2)
<i>c</i> [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)
<i>Z</i>	2	2	2
Calculated density [g cm ^{−3}]	1.097	1.071	1.516
μ (Mo K α)/mm ^{−1}	0.100	0.091	2.142
<i>F</i> (000)	816.0	1008.5	1357.3
Theta range/°	2.40–25.5	2.44–25.5	2.47–26.12
Reflections collected	26359	15753	25353
Independent reflections	8485	5292	5893
GOOF on <i>F</i> ²	1.096	0.995	0.986
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1039/0.2620	0.0580/0.1181	0.0618/0.1872
<i>R</i> ₁ / <i>wR</i> 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
<i>R</i> _{int}	0.1017	0.1120	0.1022
Data/restraints/parameters	8485/0/503	5292/0/309	5893/0/306

4. Conclusions

A series of new examples of dinuclear aluminum heterocycles is reported. Synthesis of aluminum alkyl complexes such as [L¹(AlMe₂)₂] (**1**), [L²(AlMe₂)₂] (**2**) and [L³(AlMe₂)₂] (**3**) was achieved by the deprotonation of a corresponding free ligand upon treatment with two equivalents of AlMe₃ in toluene. The compound **4**[L³(AlI₂)₂] was prepared by the reaction of the compound **3** with four equivalents of molecular iodine in toluene at 80 °C. Solid state structures for compounds **2–3** 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 compound **4**, aluminum centers adopt a distorted tetrahedral geometry, in which Al is four-coordinated by two N atoms of the ligand and two iodine ligands. We presume that compounds **1–4** 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.

Supporting Information (SI)

Crystallographic data for the structural analyses of complexes **2–4** have been deposited with the Cambridge Crystallographic Data Centre bearing the CCDC Nos. 1833108, 1833109 and 1833110, respectively. Copies of this information are available on request free of charge from CCDC, Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>). ¹H and ¹³C{¹H} NMR spectra for compounds **1–4** (PDF) are reported in Supplementary information which is available at www.ias.ac.in/chemsci.

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