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Mono- and Bimetallic Aluminum Alkyl, Alkoxide, Halide and Hydride Complexes of a Bulky Conjugated Bis-Guanidinate(CBG) Ligand and Aluminum Alkyls as Precatalysts for Carbonyl Hydroboration

Thota Peddarao, Nabin Sarkar, and Sharanappa Nembenna*

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ABSTRACT: Tet (CBG) ligands su	ra-aryl-substituted symmet ch as L^{1-3} (3H) [L(3H)	rical conjugated bis-guanidine = {(ArHN)(ArHN)C=N-C=		Ar Ar H-N N N-H

(CBG) ligands such as L^{1-3} (3H) $[L(3H) = {(ArHN)(ArHN)C=N-C=NAr(NHAr)};$ Ar = 2,6-Me₂-C₆H₃ ($L^{1}(3H)$), 2,6-Et₂-C₆H₃ ($L^{2}(3H)$), and 2,6-ⁱPr₂-C₆H₃ ($L^{3}(3H)$)] have been employed to synthesize a series of four- and six-membered aluminum heterocycles (1-8) for the first time. Generally, aluminum complexes bearing *N*,*N'*- chelated guanidinate and β -diketiminate/dipyrromethene ligand systems form four- and six-membered heterocycles, respectively. However, the conjugated bis-guanidine ligand has the capability of forming both four- and six-membered heterocycles possessing multimetal centers within the same molecule; this is due to the presence of three acidic protons, which can be easily deprotonated (at least two protons) upon treatment with metal reagents. Both mono- and dinuclear aluminum alkyls and mononuclear aluminum alkoxide, halide, and hydride complexes have been structurally characterized. Further, we have demonstrated the potential of mononuclear, six-



membered CBG aluminum dialkyls in catalytic hydroboration of a broad range of aldehydes and ketones with pinacolborane (HBpin).

INTRODUCTION

Lappert and co-workers reported the first guanidinate stabilized transition metal complex in 1970.1 Since then, the N, N', N'', N'''-tetra-substituted guanidinate anions (unsubstituted guanidine core, $N_3C_1H_5$) have found extensive utility as supporting ligands for the main group as well as the transition or lanthanide metal complexes in organometallic chemistry.² However, synthesis and catalytic application of guanidinate aluminum complexes are very limited in the literature.³ On the other hand, the synthesis and coordination chemistry of biguanides, a guanylate derivative of guanidine $(N_5C_2H_7)$, date back to the late 19th century.⁴ As far as coordination chemistry of biguanides with aluminum is concerned, in the year 1964, Nandi et al. reported a complex of Al(III) biguanide, $[C_2N_5H_7)_2Al(OC_2H_5)Cl]Cl$. To our knowledge, this is the only example reported in the literature, which is confirmed by IR and CHN analyses.⁵ Surprisingly, to date, there are no reports on N,N',N'', N'''-tetra-aryl substituted biguanides or conjugated bis- guanidinate (N₅C₂H₃Ar₄ core) metal complexes in the literature. Recently, our group developed a series of tetra-aryl substituted conjugated bisguanidines (CBG);⁶ these are analogues of popular β diketimine or NacNac ligands (see Figure 1).

Generally, N,N'-chelated β -diketiminate⁸/dipyrromethene⁹ and triazapentadienate¹⁰ ligands, upon coordination with any metal (element) center or aluminum, form C_3N_2M or



Figure 1. Selected literature examples of N,N'-chelated aluminum alkyl heterocycles, A–F.⁷

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 $C_3N_2Al^{11}$ and C_2N_3M or C_2N_3Al six-membered heterocycles, respectively. Tetra substituted guanidinate anions¹² form CN_2M or CN_2Al four-membered heterocycles. However, Wei and co-workers reported structurally characterized mononuclear six-membered bis-guanidinate supported aluminum dialkyl complexes, by two synthetic routes: (i) insertion of carbodiimide into a tetra-substituted guanidinate aluminum dialkyl complex and (ii) reaction of the lithium salt of guanidine with $AlMe_2Cl$ followed by the treatment of carbodiimide.^{7e} Very recently, our group reported fourmembered dinuclear aluminum dialkyl complexes bearing a dinucleating tetra-substituted guanidinate anion (see Figure 1).^{7f}

However, guanidine ligands with two monoanionic $N_{,}N'$ chelating sites (ditopic) and, upon coordination with aluminum, that can lead to the formation of both four- and six-membered heterocycles containing CN_2AI and C_2N_3AI core, respectively, so far have not been documented in the literature.

Thus, herein, we report well-defined mono- and dinuclear aluminum alkyls and mononuclear aluminum alkoxide, halide, and hydride complexes bearing a tetra-aryl substituted conjugated bis-guanidinate (CBG) anion for the first time. It is worth mentioning that, compared to the synthesis of Wei's bis-guanidinate aluminum complex, E, we employed a simple deprotonation method, i.e., treatment of CBG with an AlMe₃. More importantly, we have shown that CBG can be used as a dinucleating ligand with two anionic N,N'-chelating sites. Moreover, CBG supported aluminum dialkyls perform as active precatalysts for the reduction of numerous aldehydes and ketones with pinacolborane (HBpin).

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of Aluminum Complexes. A new type of conjugated bisguanidine (CBG) ligand of varying steric bulk such as $L^{1-3}(3H)$ [L(3H) = {(ArHN)(ArHN)C=N-C=NAr-(NHAr)}; Ar = 2,6-Me_2-C_6H_3 (L^1(3H)), 2,6-Et_2-C_6H_3 (L^2(3H)), and 2,6-Pr_2-C_6H_3 (L^3(3H))] have been employed for the preparation of aluminum complexes of CBG (see Figure 2).



Figure 2. N–H and N₃C resonances of $L^{1-3}(3H)$ CBG ligands.

These ligands are synthesized by using the protocol developed in our laboratory. 6

The synthesis of compounds 1 $[L^1(2H)AlMe_2]$, 2 $[L^2(2H)-AlMe_2]$, and 3 $[L^1(H)(AlMe_2)_2]$ was accomplished by the reaction of $L^1(3H)$ or $L^2(3H)$ with trimethylaluminum in toluene at ambient temperature. The construction of mono- or dinuclear Al(III) dialkyl complexes of $L^{1-2}(3H)$ was found to be dependent on the stoichiometric ratio of the metal reagent, as it leads to different products with different molar ratios of

trimethylaluminum solution. When the reaction mixture of $L^{1}(3H)$ and trimethylaluminum in a 1:1 molar ratio was stirred at room temperature for 15 h, formation of compound 1 (Scheme 1) was observed as a colorless compound in good

Scheme 1. Synthesis of Aluminum Alkyl and Halide Complexes of CBG (1-4)



yield (65%). Similarly, the reaction between $L^2(3H)$ and AlMe₃ in toluene in a 1:1 stoichiometric ratio led to the formation of compound **2** in a 70% yield. However, a 1:3 molar ratio of $L^1(3H)$ and trimethylaluminum solution at room temperature for 15 h allowed the formation of compound **3** (Scheme 1). Further, a reaction of aluminum dialkyl complex **1** with two equivalents of molecular I_2 in C_6D_6 at 60 °C for 6 h was performed, which affords compound **4** $[L^1(2H)AII_2]$ (Scheme 1).

Compounds 1–4 have been spectroscopically characterized. Both mono- and dinuclear aluminum alkyl and halide complexes 1–4 exhibit the anticipated resonances in the NMR spectra (¹H and ¹³C{¹H}) and the same with their configuration. The ¹H NMR spectra of aluminum dialkyl complexes 1 and 2 display sharp signals at –0.48 ppm and –0.45 ppm, respectively, assigned to the six hydrogens from the Al(CH₃)₂ group. Moreover, complete disappearance of N– H–N resonances of free ligands L¹(3H) and L²(3H) at 12.91 and 12.97 ppm in C₆D₆, respectively suggests the formation of compounds 1 and 2.

The ¹H NMR spectrum of 3 reveals two singlets at -0.54ppm and -0.77 ppm in C₆D₆ corresponding to six protons of each of the Al(CH_3)₂ groups, which implies that compound 3 is a dinuclear aluminum alkyl complex. And also, there was a complete disappearance of the N-H-N resonance at 12.91 ppm of $L^{1}(3H)$ and one H of the side arm $(ArN-H)_{2}$ resonances at 4.62 ppm. Moreover, the ¹H NMR spectrum of compound 3 shows one singlet at 5.0 ppm, which corresponds to side arm ArN-H. The ¹H NMR spectrum of compound 4 reveals a complete removal of one singlet resonance of $Al(CH_3)_2$ at -0.48 ppm. In ¹³C{¹H} NMR spectra, a distinctive peak for the carbon atom of the N₃C core of the CBG ligand was observed at 157.5, 158.3, and 158.0 ppm in C₆D₆, for compounds 1, 2, and 4, respectively. However, compound 3 shows two peaks for the N_3C at 154.9 (six-membered ring) and 164.0 (four-membered ring) ppm; this is due to the unsymmetrical nature of the dinuclear aluminum complex. The ${}^{13}C{}^{1}H$ NMR spectra of 1 and 2 exhibit a typical signal for $Al(CH_3)_2$ at -7.5 and -8.5 ppm, respectively, while compound 3 displays two peaks at -7.51 and -7.91 ppm. However, the ¹³C{¹H} NMR spectrum of compound 4 reveals a complete disappearance of the $Al(CH_3)_2$ peak, which suggests the alkyl halide exchange in compound 4. Further, $[L^{1}(2H)AII_{2}]$ 4 was confirmed by solid-state structural

analysis, which clearly illustrates the existence of two iodide moieties which are bonded to the Al metal atom (*vide infra*).

In the case of less bulky CBGs, *i.e.*, $L^1(3H)$ and $L^2(3H)$, the formation of Al(III) dialkyl complexes was controlled by the stoichiometric ratio of the reagent. In contrast, the bulkier CBG ligand, *i.e.*, $L^3(3H)$ supported Al(III) dialkyl complexes, was monitored by reaction temperatures. Overall, the reactions of CBGs with an aluminum reagent can be tuned by the bulky nature of the ligand, stoichiometric ratios, and the reaction temperature conditions. The stoichiometric ratios play a crucial role in the formation of products for less bulky ligands, while for reaction temperatures for bulkier ligands, the latter case is evidenced by the formation of compounds **5** and **6**.

Treatment of $L^3(3H)$ with trimethylaluminum in a 1:3 molar ratio in toluene afforded an unsymmetrical aluminum complex bearing a four-membered metallacycle $[L^3(2H)-AlMe_2]$ (5). The crude product was crystallized from toluene to give 5 as colorless crystals in an isolated yield of 65%. When the same reaction was performed at an elevated temperature, 110 °C for 24 h, the formation of a mixture of compounds 5 and 6 (Scheme 2) was observed by ¹H NMR spectroscopy.

Scheme 2. Synthesis of Aluminum Alkyl Complexes of CBG (5 and 6)



Further, a pure compound of **6**, *i.e.*, symmetrical $[L^3(2H)-(AIMe_2)]$, was withdrawn as colorless crystals in 37% yield by crystallization of the *n*-hexane solution containing both **5** and **6**.

The ¹H NMR spectra of **5** and **6** show sharp singlet peaks at -0.16 and -0.30 ppm, respectively, for the six protons of the $Al(CH_3)_2$ group. Complete disappearance of the N-H-N resonance at 13.02 ppm of L³(3H) was noticed in both compounds 5 and 6. The two equivalent ArN-H resonances at 4.94 ppm in $L^{3}(3H)$ became chemically unequivalent and resonated at different chemical shift positions as two singlets at 4.86 ppm (ArN-H) and 6.51 ppm (ArN-H) in compound 5; this is due to the unsymmetric structure of compound 5 (Scheme 2). However, in the case of compound 6, one singlet resonates at 5.91 ppm, which corresponds to the two equivalent ArN-H moieties, suggesting the symmetric structure of compound 6. The ${}^{13}C{}^{1}H{}$ NMR spectra display a diagnostic peak for the N₃C at 168.03 and 159.5 ppm, for compounds 5 and 6, respectively. Another characteristic peak for Al(CH_3)₂ appeared at -0.16 ppm for compound 5, and such an expected peak is silent in compound 6.

Next, the first well-defined aluminum dihydride complex bearing an N,N'-chelated conjugated bis-guanidinate anion has been reported. CBG supported aluminum dihydride can be synthesized by two synthetic methods (methods A and B; Scheme 3).

In the first method, the reaction between $L^3(3H)$ and LiAlH₄ in a 1:1.8 ratio at reflux temperature in toluene for 5 days led to the formation of $[L^3(2H)AlH_2]$ (7) in 43% yield. However, compound 7 can also be synthesized in better yield by the reaction of $L^3(3H)$ with commercially available alane, AlH₃.NMe₂Et. The reaction mixture of a 1:1 molar ratio of $L^3(3H)$ and alane in toluene was stirred at 80 °C for 12 h,

Scheme 3. Synthesis of Aluminum Hydride and Alkoxide Complexes of CBG (7 and 8)

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followed by crystallization from toluene to give 7 as colorless crystals in good yield (65%).

The N-H-N resonance of $L^{3}(3H)$ at 13.02 ppm has completely vanished. The side arm ArN-H resonance at 4.96 ppm, which corresponds to two protons in $L^{3}(3H)$, was shifted to the downfield region at 5.76 ppm in 7. The resonances of Al-H were not detected in TH NMR spectroscopy of compound 7 in C₆D₆ because of the quadrupolar broadening on the ²⁷Al center (nuclear spin = 5/2). In the IR spectrum of 7, two sharp bands at 1809 and 1841 cm^{-1} were noticed, attributed to the symmetric and asymmetric stretching frequencies of the Al-H bonds, respectively, and thus confirming the presence of Al-H bonds. Carbon resonance " N_3C " at 156.5 ppm in L³(3H) was shifted to 159.8 ppm in 7. When the reaction mixture of 7 and benzyl alcohol in a 1:2 molar ratio was stirred at room temperature in toluene for 12 h, the alkoxide molecule $[L^{3}(2H)Al(OCH_{2}Ph)_{2}]$ (8) was produced, and the crude product was crystallized from toluene to give 8 as colorless crystals in good yield (60%). The side arm ArN-H resonance at 5.76 ppm, which corresponds to two protons in 7, was shifted to the downfield region at 6.05 ppm in 8. The methylene $(-CH_2-)$ protons of $(C_6H_5CH_2O)$ in 8 resonate at 5.04 ppm. The N₃C carbon resonance was observed at 159.6 ppm of 8 in C₆D₆.

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 and 3-8 were established clearly by the X-ray studies. Single crystals suitable for X-ray diffraction of all the compounds 1, 3, 4, and 6-8 were grown from concentrated toluene solution, while for compound 5, the crystals were grown from the *n*-hexane solution. Compounds 1, 4, and 7 were crystallized in the monoclinic system with the *Pc*, P2(1)/c, and C2/c, space groups, respectively, whereas compounds 3, 5, 6, and 8 were crystallized in the triclinic with the space group *P*1. Molecular structures of these complexes 1 and 3-8 are shown in Figures 3-5.

The crystal data and structure refinement details of complexes (1 and 3-8) are summarized in (Table S1). In all cases, the aluminum metal center adopts a distorted tetrahedral geometry, connected to a guanidinate anion in N,N'-chelate fashion and two alkyls (1 and 3, 5-6) or two



Figure 3. Molecular structures of 1 (left), 3 (middle) and 4 (right). The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are deleted for clarity. Selected bond lengths (Å) and angles (deg), for 1 (left): 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); N2-Al1-N1 94.0(3), N2-Al1-C1 111.6(4), N1-Al1-C2 114.0(4), C1-Al1-C2 114.85, C3-N3-C4 124.6(7). For 3 (middle): Al1-C37 1.958(3), Al1-C38 1.953(3), Al2-C1 1.963(3), Al2-C2 1.957(3), Al1-N4 1.926(2), Al2-N1 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), C20-N3-C19 125.6(2), N4-C19-N3 106.3(2). For 4 (right): Al1-I1 2.507(2), Al1-I2 2.521(2), Al1-N1 1.853(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); 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).



Figure 4. Molecular structures of 5 (left) and 6 (right). The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are deleted for clarity. Selected bond lengths (Å) and angles (deg), for 5 (left): 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). For 6 (right): 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).

iodides (4) or two hydrides (7) or two alkoxide (8) moieties; thus the aluminum coordination number is four. Further, solidstate structures revealed that all compounds 1, 4, and 6–8 display six-membered metallacycles containing a C_2N_3Al ring, while compound 5 comprises a four-membered metallacycle with CN_2Al ring. Interestingly, compound 3 features both fourand six-membered metallacycles within a single molecule.



Figure 5. Molecular structures of 7 (left) and 8 (right). The thermal ellipsoids are shown at 30% probability, and all the hydrogen atoms except those bound to nitrogen atoms are deleted for clarity. Selected bond lengths (Å) and angles (deg), for 7 (left): Al1–H 1.510(3), Al1–N1 1.8834(18), N2–C2 1.344(2), N1–C2 1.341(3), N3–C2 1.364(3); N1ⁱ–Al1–N1 94.40(11), N1ⁱ–Al1–H 109.5(11), C2ⁱ– N2–C2 122.8(2). For 8 (right): 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).

The Al-C bond lengths in compounds 1, 3, 5, and 6 lie in the range 1.949(3) Å to 1.985(9) Å and are similar to those reported N,N'-chelated aluminum complexes (A-F). A: LAIMe₂ (L = HC[C(Me)N(2,6-Me₂C₆H₃)]₂^{7a} (Al(1)-C(22) 1.959(2) Å, Al(1)-C(23) 1.964(2) Å). B: [L"AlMe₂] $[L'' = {(NArCPh)_2N; Ar = Dipp]^{7b} (Al(1) - C(3) 1.958(2) Å,$ Al(1)-C(4) 1.950(3) Å). C: [L^aAlMe₂; L^a = mesomesityldipyrromethene]^{7c} (Al(1)–C(19) 1.962(2) Å). D: $L^{b}AlMe_{2}$ [$L^{b} = {ArNC(N(^{i}Pr_{2})N(Ar))} (Ar = Dipp)$]^{7d} (Al(1)-C(32) 1.9688(19) Å, Al(1)-C(33) 1.9726(19) Å).E: $[\{N(C_6H_5)C(NAr)-N(C_6H_5)C(NEt_2)N(Ar)\}AlMe_2; Ar =$ $Xyl]^{7e}$ (Al(1)-C(35) 1.956(3) Å, Al(1)-C(33) 1.9950(3) Å). F: $[L'(AlMe_2)_2]$ $[L' = {ArNCNAr}_2{\mu-N(C_2H_4)_2N}; Ar =$ Mes]^{7f} (Al(1)-C(20) 1.949(6) Å, Al(1)-C(21) 1.953(6) Å). And also, Al–N bond distances are similar to those of reported aluminum dialkyl complexes (A-F). The Al-I bond lengths for compound 4, i.e., Al1-I1, are 2.507(2) Å, and Al1-I2 is 2.521(2) Å. These are consistent with the disclosed Al-I bond lengths of N,N'-chelated aluminum diiodide complexes $[L^{a}AII_{2}; L^{a} = meso-mesityl dipyrromethene Al(1)-I(1) 2.506$ (1) Å and Al(1)-I(2) 2.524(1) Å].¹³ The Al1-H bond distance in 7 is 1.51(3) Å, and this value is falling in the range of reported bond lengths Al(1)-H(1) = 1.51(4) and Al(1)-H(1) = 1.51(4)H(2) = 1.54(4) Å of L^aAlH₂; L^a = meso-mesityl dipyrromethene.^{7c} The Al–O bond distances are Al1–O8 = 1.7214(13)Å and Al1– O24 = 1.7079(15) Å in 8 and are consistent with that of compound $L^{a}AlO^{t}Bu_{2}[Al(1)-O(1) = 1.706(2)Å$ and Al(1)-O(2) = 1.701(2)Å].^{9c} The N-Al-N bite angles in compounds 1, 4, and 6-8 in the range of $93.18-97.4^{\circ}$ that are comparable with six-membered aluminum heterocycles [N-Al-N bite angles in compounds A-F: $95.24(7)^{\circ}$ (A), $93.05(8)^{\circ}$ (B), $92.1(1)^{\circ}$ (C), $91.44(9)^{\circ}$ (E), while N-Al-N bite angles in compounds 3 and 5 are 67.80(10) (for fourmembered ring) and $68.49(7)^{\circ}$, respectively, which are close to four-membered guanidinatealuminum dimethyl complexes] [N-A]-N bite angles in compounds D (69.06(6)°) and F $(68.75(16)^\circ)$ and $(69.15(17)^\circ)$].

Three bonding modes (I–III), as illustrated in Chart 1, are observed for aluminum(III) complexes bearing either $L^{1}(3H)$



or $L^{3}(3H)$ ligands. The bonding mode I has been noticed for the mononuclear aluminum dialkyl (1 and 6), dihalide (4), dihydride (7), and dialkoxide (8) complexes, while II is seen for the aluminum dialkyl complex (5). In these bonding modes (I and II), the N,N'- chelating scaffold is characterized as an LX-type ligand comprising both sigma- and pi-donor properties. However, a six-membered metallacycle is noticed in bonding mode I, while a four-membered metallacycle is observed in II, which is attributed to the steric nature of the ligand. Moreover, the bonding mode III type has been observed for the dinuclear aluminum(III) dialkyl complex, in which it exhibits double chelation; the L₂X₂ type ligand consists of two sigma and two pi donor properties. It is worth mentioning that in this bonding type, both four- and sixmembered metallacycles within a single molecule have been detected.

Catalysis: Hydroboration of Aldehydes and Ketones Catalyzed CBG Aluminum Alkyls. The sustainable and environmentally friendly aluminum-based reagents/molecules are ideal for applications in catalysis.¹⁴ Hence, the development of well-defined aluminum-based catalysts is quite attractive.¹⁵ In 2015, Roesky and co-workers reported the β diketiminate supported aluminum hydride as a catalyst for hydroboration of carbonyl compounds.¹⁶ Previously we reported molecular aluminum hydride catalyzed selective reduction of a broad range of aldehydes and ketones.¹⁷ To date, there have been few reports on the aluminum catalyzed reduction of carbonyl compounds.¹⁸ However, the transition metal catalyzed hydroboration of carbonyl compounds has been extensively investigated.¹⁹ Given this, we decided to test the catalytic activity of newly synthesized aluminum alkyls 1 and 2 as precatalysts for hydroboration of several aldehydes and ketones.

We began our investigation by using compound 2 as a catalyst, HBpin as a reducing agent, and benzaldehyde 9a as a model substrate (Table 1).

We noticed the formation of boronate ester in quantitative yield in 12 h at room temperature with a catalyst loading of 5 mol % under neat conditions. Further, the same reaction was carried out by using lower catalyst loadings (3 mol % and 1 mol %). We observed quantitative conversion in both cases; however, an elevated temperature ($60 \, ^\circ$ C) is required for 1 mol % catalyst loading and less time when compared to 3 mol %. Catalyst 1 also gave almost similar results to those of catalyst 2.

With the optimized conditions in hand, we decided to explore the hydroboration of a wide range of aldehydes (Scheme 4).

We were satisfied to see, in all cases, a quantitative conversion of aldehydes (9a-91) into the corresponding

Table 1. Hydroboration of Benzaldehyde with HBpin Catalyzed by 1 and 2^a

entry	cat.	cat. (mol %)	temp	time	conv(%) ^b
1	2	5%	rt	12 h	>99
2	2	3%	rt	12 h	>99
3	2	1%	60 °C	8 h	>99
4	2	1%	60 °C	6 h	88
5	2	1%	60 °C	4 h	76
6	1	3%	rt	12 h	>99
7	1	1%	60 °C	10 h	>99

^{*a*}All reactions were done on 0.3 mmol scales. Benzaldehyde (1 equiv), pinacolborane (1 equiv), $L^{1-2}(2H)AlMe_2$ (*x* mol %), neat. ^{*b*}Conversion was determined by ¹H NMR spectroscopy.





"Reaction conditions: aldehyde (0.3 mmol), pinacolborane (0.3 mmol), catalyst 2 (1 mol %), 8 h at 60 °C under N_2 . Reported numbers are the NMR conversion.

boronate esters (**10a**-**10l**). We noticed the tolerance of halide, nitrile, ester, alkene, and alkyne functionalities.

Further, we explored the catalytic activity of compounds 1 and 2 for the hydroboration of ketones with HBpin. Initially, we chose acetophenone as a model substrate. We observed that 2 mol % of catalyst 1 or 2 at 60 °C afforded the best results (Table 2).

Accordingly, under these optimized reaction conditions, by using catalyst 2, hydroboration of ketones (11a-11l) to yield their corresponding boronate esters (12a-12l) was investigated, which produced at a quantitative yield for all the cases within 12 h (Scheme 5).

The intramolecular chemoselective reduction of ketones in the presence of other functionalities such as halide, nitrile, and ester was noticed.

Furthermore, we have tested the catalytic activity of other newly reported aluminum-based compounds such as dinuclear aluminum alkyl (3), aluminum dihalide (4), mononuclear bulky aluminum dialkyl (6), and aluminum dihydride (7) for the hydroboration of carbonyl compounds with HBpin. Both compounds 3 and 7 exhibit similar catalytic activity to those of

Table 2. Hydroboration of Acetophenone with HBpin Catalyzed by 1 and 2^{a}

entry	cat.	cat. (mol %)	temp	time	$\operatorname{conv}(\%)^{b}$
1	2	6%	rt	12 h	>99
2	2	4%	rt	12 h	>99
3	2	2%	60 °C	12 h	>99
4	2	2%	60 °C	10 h	78
5	2	2%	60 °C	8 h	66
6	1	4%	rt	12h	>99
7	1	2%	60 °C	12 h	>99

^{*a*}All reactions were done on 0.3 mmol scales. Acetophenone (1 equiv), pinacolborane (1 equiv), $L^{1-2}(2H)AlMe_2$ (x mol %), neat. ^{*b*}Conversion was determined by ¹H NMR spectroscopy.

Scheme 5. Hydroboration of Ketones using Al Complex (2) as a Catalyst^a



"Reaction conditions: ketone (0.3 mmol), pinacolborane (0.3 mmol), catalyst 2 (2 mol %), 12 h at 60 $^\circ$ C under N₂. Reported numbers are the NMR conversion.

catalysts 1 and 2 for the hydroboration of benzaldehyde with HBpin, while compounds 4 and 6 are less active when compared to aluminum alkyls or hydride catalysts (see Table S2). Compound 7 shows a similar catalytic activity to those of catalysts 1 and 2 for the hydroboration of acetophenone with HBpin, while catalysts 4 and 6 show low conversion of acetophenone to the corresponding boronate ester (see Table S3). Thus, both aluminum alkyls and hydride-based catalysts are ideal for the hydroboration of carbonyl compounds

The mechanism of aluminum alkyl catalyzed hydroboration of carbonyl compounds was previously reported by other research groups. The aluminum dialkyl reacts with HBpin and generates active catalytic species aluminum alkyl-hydride. Next, the insertion of a carbonyl functionality into the Al–H bond occurs, which leads to the generation of an aluminum alkoxide intermediate.

Finally, the reaction of the aluminum alkoxide with HBpin afforded the boronate ester product and regeneration of aluminum alkyl-hydride catalyst for the further catalytic cycle (Scheme 6).

CONCLUSION

The structurally characterized mono- and dimetallic aluminum alkyls and monometallic aluminum alkoxide, halide, and

Scheme 6. Proposed Mechanism for the Hydroboration of Carbonyl Compounds Catalyzed by Aluminumdialkyl Complex (2)



hydride complexes bearing an N,N'-chelated conjugated bisguanidinate ligand are reported for the first time. We have investigated the difference in reactivity and coordination properties of ligands $L^{1}(3H)$ and $L^{3}(3H)$ toward the reagent trimethylaluminum depending upon reaction conditions. We noticed the formation of mono- $[L^1(2H)AlMe_2]$ (1) and dinuclear $[L^{1}(H)(AlMe_{2})_{2}]$ (3) compounds in the case of ligand $L^{1}(3H)$ when treated with trimethylaluminum (1.0 equiv) and (3.0 equiv), respectively, at room temperature. Whereas, in the case of $L^{3}(3H)$, the formation of only mononuclear unsymmetrical (5) or symmetrical (6) compounds was observed. Compound 1 upon treatment with two equivalents of iodine in C_6D_6 led to the formation of compound 4, in which alkyl-halide interchange took place. Deprotonation of $L^{3}(3H)$ upon treatment with alane afforded the aluminum dihydride complex, $[L^3(2H)AlH_2]$ (7). Compound 7 was further treated with 2 equiv of benzyl alcohol, which allowed the formation of aluminum dialkoxide complex $L^{3}(2H)Al(OCH_{2}Ph)_{2}$ (8). More importantly, compounds 1 and 2 effectively catalyze the reduction of various aldehydes and ketones. Compounds 4 and 7 are suitable starting materials for the preparation of six-membered low valent aluminum(I) heterocycles.²⁰ At present, such investigations are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Methods. All air and moisture sensitive reactions were carried out by using standard Schlenk line and glovebox techniques under an inert atmosphere of dinitrogen. The precursors L^{1-3} (3H) $[L(3H) = \{(ArHN)(ArHN)C=N-C=NAr(NHAr)\}; Ar = 2,6 Me_2 - C_6H_{3,1}(L^1(3H))$, 2,6-Et₂ - C₆H_{3,1}(L²(3H)), and 2,6-ⁱPr₂ - C₆H₃ $(L^{3}(3H))]$ were prepared by using a method developed in our laboratory.⁶ AlMe₃ (2.0 M in toluene) and alane-N,N-dimethyl ethyl amine complex (0.5 M) in toluene were purchased from Sigma-Aldrich and used as received. Anhydrous solvents such as benzene, nhexane, and toluene were collected from the solvent purification system (MBraun), freeze-thawed twice, and stored under an atmosphere of dinitrogen before use. NMR spectra were recorded on a Bruker AV 400 MHz spectrometer {¹H (400 MHz) and ¹³C (100 MHz)} at ambient temperature. Dry deuterated benzene (C_6D_6) and chloroform (CDCl₃) solvents were utilized for NMR analyses. Chemical shifts (δ in ppm) in the ¹H and ¹³C{¹H} NMR spectra were referenced to the residual signals of the deuterated solvents.²¹ Highresolution mass spectra (HRMS) were recorded on Bruker micrO-TOF-Q II spectrometer. IR spectra were recorded on the PerkinElmer FTIR spectrometer.

Synthesis of $[L^{1}(2H)AIMe_{2}]$ (1). To a solution of L(3H) (0.25 g, 0.482 mmol, 1.0 equiv) in toluene (20 mL), trimethylaluminum (2.0 M in toluene, 0.25 mL, and 0.504 mmol, 1.0 equiv) was added at 0 °C. The solution was allowed to attain the room temperature, and the stirring was extended for 15 h. The solvent was removed completely then washed with *n*-hexane and was added to the crude solid toluene (~10 mL), heated to 70 °C, and slowly cooled to room temperature to give 1 as colorless crystals (0.180 g, 0.314 mmol, 65%). Mp: 290-300 °C. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ -0.48 (s, 6H, Al(CH₃)₂), 1.85 (s, 12H, CH₃), 2.48 (s, 12H, CH₃), 4.83 (s, 2H, ArNH), 6.55 (d, J = 4 Hz, 4H, ArH), 6.74 (t, J = 8 Hz, 2H, ArH), 6.94–6.98 (m, 2H, ArH), 7.01 (d, J = 8 Hz, 4H, ArH). ¹³C{¹H} NMR (100 MHz, C_6D_6 , 25 °C): δ 8.0 (Al(CH₃)₂), 18.4 (Ar-CH₃), 18.5 (Ar-CH₃), 126.0 (ArC), 126.3 (ArC), 127.1 (ArC), 129.1 (ArC), 135.4 (ArC), 135.5 (ArC), 135.8 (ArC), 139.6 (ArC), 157.1 (N₃C). ESI-TOF: m/z 574.3522 ([M + H]⁺, calcd. for C₃₆H₄₄AlN₅ + H⁺: 574.3485).

Synthesis of $[L^2(2H)AlMe_2]$ (2). This compound was prepared by the method described for $[L^1(2H)AlMe_2]$ (1) by using $L^2(3H)$ (0.3 g, 0.48 mmol) and trimethylaluminum (2.0 M in toluene, 0.25 mL, and 0.49 mmol). Compound 2 (0.230 g, 0.335 mmol, 70%). Mp: 270– 290 °C. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ –0.45 (s, 6H, $Al(CH_3)_2$), 0.96 (t, J = 8.0 Hz, 12H, CH_3), 1.32 (t, J = 8.0 Hz, 12H, CH_3), 2.16–2.25 (m, 4H, CH_2), 2.30–2.37 (m, 4H, CH_2), 2.83–2.93 (m, 4H, CH_2), 3.18–3.28 (m, 4H, CH_2), 5.08 (s, 2H, ArNH), 6.62– 6.64 (d, J = 8.0 Hz, 4H, ArH), 6.76–6.78 (d, J = 8.0 Hz, 2H, ArH), 6.87–6.91 (m, 2H, ArH), 6.98–7.02 (m, 1H, ArH), 7.05–7.11 (m, 3H, ArH). ¹³C{¹H} NMR (100 MHz, C_6D_6 , 25 °C): δ 8.5 (Al($CH_3)_2$), 13.7 (Ar– CH_2CH_3), 14.0 (Ar– CH_2CH_3), 23.3 (Ar– CH_2CH_3), 24.6 (Ar- CH_2CH_3), 125.0 (ArC), 125.9 (ArC), 126.6 (ArC), 126.5 (ArC), 134.5 (ArC), 138.9 (ArC), 140.5 (ArC), 140.9 (ArC), 158.3 (N₃C).

Synthesis of $[L^1(H)(AIMe_2)_2]$ (3). To a solution of $L^1(3H)$ (0.25 g, 0.482 mmol, 1.0 equiv) in toluene (10 mL), trimethylaluminum (2.0 M in toluene, 0.72 mL, 1.44 mmol, 3.0 equiv) was added at 0 °C. The solution was allowed to warm to room temperature, and the stirring was extended for 15 h. The solvent was removed completely, then washed with n-hexane (5 mL). The crude product was crystallized from toluene (~10 mL) at 5 °C to give 3 as colorless crystals (0.168 g, 0.267 mmol, 55%). Mp: 205–210 °C. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ -0.77 (s, 6H, Al(CH₃)₂), -0.54 (s, 6H, (Al(CH₃)₂)), 2.04 (s, 6H, CH₃), 2.21 (s, 6H, CH₃), 2.33 (s, 6H, CH₃), 2.43 (s, 6H, CH₃), 5.00 (s, 1H, NH), 6.63–6.67 (m, 5H, ArH), 6.76–6.78 (d, J = 8 Hz, 2H, ArH), 6.83-6.87 (m, 1H, ArH), 6.95-7.01 (m, 4H, ArH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ -8.2 (Al(CH₃)₂), -7.9 (Al(CH₃)₂), 18.4 (Ar-CH₃), 18.5 (Ar-CH₃), 18.9 (Ar-CH₃), 19.05 (Ar-CH₃), 19.09 (Ar-CH₃), 19.6 (Ar-CH₃), 124.1 (Ar-C), 124.5 (Ar-C), 129.0 (Ar-C), 129.1 (Ar-C), 129.4 (Ar-C), 129.5 (Ar-C), 131.6 (Ar-C), 133.2 (Ar-C), 133.7 (Ar-C), 135.7 (Ar-C), 137.6 (Ar-C), 138.3 (Ar-C), 140.1 (Ar-C), 142.0 (Ar-C), 154.5 (N₃C), 163.6 (N₃C). ESI-TOF HRMS: m/z 630.2511 ([M + H]⁺, calcd. for C₃₈H₄₉Al₂N₅ + H⁺: 630.5211).

Synthesis of $[L^1(2H)All_2]$ (4). To a solution of $[L^1(2H)AlMe_2]$ (1; 0.020 g, 0.0348 mmol, 1.0 equiv) in C_6D_6 (0.6 mL), iodine (0.018 g, 0.0697 mmol, 2.0 equiv) was added and then the NMR tube was heated at 60 °C for 6 h. The compound was crystallized from toluene at 0 °C to give 4 as colorless crystals (0.0194 g, 0.0244 mmol, 70%). ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ 1.77 (s, 12H, CH₃), 2.68 (s, 12H, CH₃), 5.07 (s, 2H, ArNH), 6.48 (d, *J* = 8.0 Hz, 4H, ArH), 6.68 (t, *J* = 8 Hz, 2H, ArH), 6.93–6.99 (m, 6H, ArH). ¹³C{¹H} NMR (100 MHz, C_6D_6 , 25 °C): δ 18.3 (Ar-CH₃), 21.0 (Ar-CH₃), 126.6 (ArC), 127.2 (ArC), 127.5 (ArC), 129.7 (ArC), 130.1 (ArC), 134.6 (ArC), 135.2 (ArC), 135.8 (ArC), 136.9 (ArC), 157.7 (N₃C).

Synthesis of $[L^3(2H)AlMe_2]$ (5). To a solution of $L^3(3H)$ (0.25 g, 0.337 mmol, 1.0 equiv) in toluene (10 mL), trimethylaluminum (2.0 M in toluene, 0.51 mL, 1.02 mmol, 3.0 equiv) was added at 0 °C, and then the reaction mixture was stirred at room temperature for 15 h.

The solvent was removed completely, then washed with *n*-hexane (10 mL). The crude product was crystallized from toluene at 0 °C to give 5 as colorless crystals (0.175 g, 0.219 mmol, 65%). Mp: 190-195 °C. ¹H NMR (400 MHz, $C_6 D_6$, 25 °C): $\delta - 0.16$ (s, 6H, Al(CH₃)₂), 0.72 $(d, J = 8.0 \text{ Hz}, 12\text{H}, CH(CH_3)_2), 1.06 (d, J = 8.0 \text{ Hz}, 6\text{H}, 6\text{H})$ $CH(CH_3)_2$), 1.10 (d, J = 8.0 Hz, 12H, $CH(CH_3)_2$), 1.14 (d, J = 8.0Hz, 6H, $CH(CH_3)_2$), 1.28 (d, J = 8.0 Hz, 12H, $CH(CH_3)_2$), 2.62 (sept, 2H, CH(CH₃)₂), 2.88-2.93 (m, 2H, CH(CH₃)₂), 3.77 (sept, 4H, $CH(CH_3)_2$), 4.86 (s, 1H, NH), 6.51 (s, 1H, NH), 6.86 (d, J = 8.0Hz, 2H, ArH), 6.95 (d, J = 8.0 Hz, 2H, ArH), 7.00 (d, J = 8.0 Hz, 2H, ArH), 7.09 (s, 6H, ArH). ${}^{13}C{}^{1}H$ NMR (100 MHz, C₆D₆, 25 °C): δ -8.3 (Al(CH₃)₂), 23.0 (Ar-*i*PrC), 24.0 (Ar-*i*PrC), 26.1 (Ar-*i*PrC), 26.7 (Ar-iPrC), 28.2 (Ar-iPrC), 28.4 (Ar-iPrC), 28.8 (Ar-iPrC), 123.1 (ArC), 124.4 (ArC), 124.7(ArC), 125.2 (ArC), 130.0 (ArC), 130.5 (ArC), 132.0 (ArC), 138.8 (ArC), 144.3 (ArC), 146.5 (ArC), 148.8 (ArC), 150.0 (ArC), 168.0 (N₃C). ESI-TOF HRMS: m/z 798.6163 $([M + H]^+, \text{ calcd. for } C_{52}H_{76}AlN_5 + H^+: 798.5989).$

Synthesis of $[L^3(2H)(A|Me_2)]$ (6). To a solution of $L^3(3H)$ (0.25 g, 0.337 mmol, 1.0 equiv) in toluene (15 mL), trimethylaluminum (2.0 M in toluene, 0.595 mL, 1.19 mmol, 3.0 equiv) was added at 0 °C, and then the reaction mixture was stirred at 110 °C for 24 h. Formation of a mixture of products was observed. The crude product was crystallized from *n*-hexane at 0 $^{\circ}$ C to give 6 as colorless crystals (0.1 g, 0.125 mmol, 37%). Mp: 235-240 °C. ¹H NMR (400 MHz, $C_6 D_{61}$ 25 °C): δ -0.30 (s, 6H, Al(CH₃)₂), 0.89-0.90 (m, 24H, $CH(CH_3)_2$, 1.33 (d, J = 4 Hz, 12H, $CH(CH_3)_2$), 1.38 (d, 8 Hz, 12H, $CH(CH_3)_2$, 3.01–3.06 (sept, 4H, $CH(CH_3)_2$), 3.83–3.90 (m, 4H, $CH(CH_3)_2$, 5.91 (s, 2H, NH), 6.79 (d, J = 8 Hz, 4H, ArH), 6.95-6.98 (m, 2H, ArH), 7.16–7.22 (m, 4H, ArH). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz, C₆D₆, 25 °C): δ 24.9 (Ar-*i*PrC), 27.1 (Ar-*i*PrC), 28.5 (AriPrC), 123.0 (ArC), 125.4 (ArC), 127.07 (ArC), 132.8 (ArC), 137.8 (ArC), 145.2 (ArC), 146.7 (ArC), 159.5 (N₃C). ESI-TOF HRMS: m/ z 798.6150 ($[M + H]^+$ calcd. for C₅₂H₇₆AlN₅ + H⁺; 798.5989).

Synthesis of $[L^3(2H)AlH_2]$ (7). Method A. To a mixture of $L^3(3H)$ (2.0 g, 2.694 mmol, 1.0 equiv) and LiAlH₄ (0.184 g, 4.850 mmol, 1.8 equiv), toluene (15 mL) was added, and the reaction mixture was heated at 110 °C for 5 days. Then, the compound was crystallized from toluene to get colorless crystals of compound 7 with a yield of 0.9 g, 1.169 mmol, 43%.

Method B. To a solution of $L^3(3H)$ (0.25 g, 0.336 mmol, 1.0 equiv) in toluene (10 mL), alane-N,N-dimethylethylamine complex solution (0.5 M in toluene, 0.7 mL, 0.353 mmol, 1.0 equiv) was added at room temperature and heated at 80 °C for 12 h. Then, the compound was crystallized from toluene, to give 7 as colorless crystals (0.168 g, 0.219 mmol, 65%). Mp: 220-230 °C. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ 0.81 (d, J = 8.0 Hz, 12H, CH(CH₃)₂), 1.08 (d, J = 8.0 Hz, 12H, $CH(CH_3)_2$, 1.33 (d, J = 8.0 Hz, 12H, $CH(CH_3)_2$), 1.50 (d, J = 4.0 Hz, 12H, CH(CH₃)₂), 3.06–3.13 (m, 4H, CH(CH₃)₂), 3.78-3.84 (m, 4H, CH(CH₃)₂), 5.76 (s, 2H, NH), 6.81 (d, J = 8.0 Hz, 3H ArH), 6.94-6.99 (m, 4H ArH), 7.15-7.19 (m, 5H, ArH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ 22.3 (Ar-*i*PrC), 24.3 (AriPrC), 24.9 (Ar-iPrC), 26.4 (Ar-iPrC), 28.3 (Ar-iPrC), 28.35 (AriPrC), 122.6 (ArC) 125.0 (ArC), 127.1 (ArC), 132.2 (ArC), 135.8 (ArC), 145.4 (ArC), 146.6 (ArC), 159.4 (N₂C). IR (Nujol mull, 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 $[L^{3}(2H)Al$ ($OCH_{2}Ph)_{2}$] (8). To a solution of $[L^{3}(2H)AlH_{2}]$ (7) (0.15 g, 0.194 mmol, 1.0 equiv) in toluene (10 mL), benzyl alcohol (0.044 g, 43 μ L, and 0.409 mmol, 2.0 equiv) was added at room temperature, and the reaction mixture was stirred at room temperature for 12 h. The crude compound was crystallized from toluene to give 8 as colorless crystals (0.115 g, 0.116 mmol, 60%). Mp: 190–200 °C. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 0.76 (s, 12H, CH(CH₃)₂), 1.07 (s, 12H, CH(CH₃)₂), 1.28 (t, J = 4 Hz, 25H, CH(CH₃)₂), 3.02–3.09 (sept, 4H, CH(CH₃)₂), 3.86–3.93 (sept, 4H, CH(CH₃)₂), 5.04 (s, 4H, OCH₂Ph), 6.05 (s, 2H, NH), 6.78 (d, J = 8.0 Hz, 4H, ArH), 6.94 (t, J = 8.0 Hz, 2H, ArH), 7.04–7.07 (m, 2H, ArH), 7.12–7.14 (m, 10H, ArH), 7.19 (d, J = 8.0 Hz, 4H, ArH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ 24.8 (Ar-iPrC), 26.3 (Ar-iPrC), 28.7 (Ar-iPrC), 28.8 (Ar-iPrC), 65.1 (O

 CH_2Ph), 123.0 (ArC), 125.4 (ArC), 125.6 (ArC), 126.0 (ArC), 127.2 (ArC), 132.2 (ArC), 136.7 (ArC), 145.1 (ArC), 145.8 (ArC), 147.2 (ArC), 159.6 (N₃C).

General Procedure for the Catalytic Hydroboration of Aldehydes and Ketones. Aldehyde or ketone (0.3 mmol), pinacolborane (0.3 mmol), and catalyst 1 or 2 (1 mol % or 2 mol %) were charged in a screw cap vial inside the glovebox. Next, the vial was taken out from the glovebox and placed in a preheated oil bath at 60 °C for 8 or 12 h. The course of the reaction was checked by ¹H (in dry CDCl₃) NMR spectroscopy. The ¹H NMR spectrum explains the full conversion of the starting material and the existence of a unique CH_2 or CH peak.

X-ray Crystallography. Crystals of 1 and 3-8 were removed from the Schlenk flask under a stream of dinitrogen and immediately covered with a thin layer hydrocarbon oil. A suitable crystal was selected, attached to the glass fiber, and quickly placed in a lowtemperature stream of dinitrogen. The X-ray diffraction data were collected on a Bruker four-circle Kappa Apex II diffractometer equipped with a charge-coupled detector using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 100 K. Data collection was observed with Apex II software. The data sets were integrated and scaled using Apex II.²² All structures were determined using direct methods employed in ShelXT²³ and OleX,²⁴ and refinement was carried out using least-squares minimization implemented in ShelXL.²⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed geometrically in idealized positions and were refined using a riding model. The crystal data, data collection, and refinement parameters for compounds 1 and 3-8 are summarized in Table S1.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03778.

¹³C{¹H} NMR spectra for compounds **1**, **3–8**, and boronate esters; crystallographic data and structure refinement summary (PDF)

Accession Codes

CCDC 1559771–1559777 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.uk/data_request/ CIF, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:+ 44 1223 336033

AUTHOR INFORMATION

Corresponding Author

Sharanappa Nembenna – School of Chemical Sciences, National Institute of Science Education and Research (NISER), Homi Bhabha National Institute (HBNI), Bhubaneswar 752 050, India; orcid.org/0000-0001-8856-4561; Phone: 0091-6742494174; Email: snembenna@niser.ac.in

Authors

- Thota Peddarao School of Chemical Sciences, National Institute of Science Education and Research (NISER), Homi Bhabha National Institute (HBNI), Bhubaneswar 752 050, India
- Nabin Sarkar School of Chemical Sciences, National Institute of Science Education and Research (NISER), Homi Bhabha National Institute (HBNI), Bhubaneswar 752 050, India

Complete contact information is available at:

https://pubs.acs.org/10.1021/acs.inorgchem.9b03778

Notes

The authors declare no competing financial interest.

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Article

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