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The synthesis and characterization of aluminum, gallium and zinc formamidinates

Leslie A. Lesikar, Anne F. Richards*

Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, United States Department of Chemistry, La Trobe University, Melbourne 3086, Australia

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ABSTRACT

Reactions of the formamidinate ligand, RN(H)C(H)NR, L^H , (R = 2,6-diisopropylphenyl), with AlMe₃, AlMe₂Cl, GaMe₃ and ZnEt₂ were investigated to examine potential coordination modes of the ligand and the effect of hydrolysis on the products. Nine new complexes have been fully characterized by X-ray crystallography and other spectroscopic techniques and highlight the diverse coordination modes of the formamidinate ligand.

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1. Introduction

Amidinate ligands, $[R^1NC(R^2)NR^3]^-$, have been used extensively for an increasingly large number of main group, transition, and lanthanide metal complexes [1]. The steric and electronic properties of the amidine ligands can be easily tailored by modifying the R group attached to the carbon and nitrogen atoms of the ligand backbone [2,3]. More specifically when R² = H the ligands are classed as formamidines [1b]. An advantage of these ligands is the presence of π -bonds which allows the negative charge to be delocalized across the N–C–N backbone [2,4]. As a result of this charge delocalization, a variety of possible coordination modes to metals can exist, including the monodentate (A), bidentate chelating (B), and bimetallic bridging (C), modes, Fig. 1 [1–5]. While relatively few examples of the monodentate binding mode have been reported [6,7], the other two are more commonly observed [8].

Interest in metal amidinate complexes has been fueled by their relative efficacy for a variety of catalytic applications including olefin polymerization and organic transformations [5,9]. Furthermore, amidinate complexes have become useful precursors for chemical vapor deposition (CVD) [9] and atomic layer deposition (ALD) [10]. More specifically aluminum amidinate complexes are significant due to their ability to act as catalysts; for example in olefin polymerization, [5,9a,9c,9d] polymerization of ethylene [9d], and C–H bond activation [9f]. As a result, several monoamidinate and bisamidinate aluminum alkyl and halide complexes have been reported [9a,9c–f,10–14]. Jordan and co-workers [9a–d] performed a study of aluminum amidinate complexes that afforded monoamidinate, bis(amidinate), and dinuclear cationic complexes. They concluded that the different structural outcomes of the amidinate ligand (Fig. 1) were dependent on steric factors, with the idealized amidinate structure (**B**) having 120° angles at the C and N centers allowing the nitrogen sp^2 orbitals to project in parallel directions. Increased steric interactions between the amidinate substituents will tend to decrease the NCN angle and will favor either chelated structures or $\mu^1 \eta^1 \eta^2$ structures. Other related aluminum and zinc amidinate complexes have been reported [9e,11-15] including the acetamidinate aluminum complexes, [{MeC(NⁱPr)₂}₂AlMe] and [{MeC(NPh)₂}₂AlMe] [14]. Bisamidinate aluminum alkyl complexes incorporating the formamidinate ligand, L^H, are less common. To the best of our knowledge only a similar aluminum hydride bisformamidinate complex, [{HC(NDipp)₂}₂AlH], has been reported by Jones and co-workers [7]. In contrast to the numerous reports of aluminum amidinate complexes, relatively few amidinate complexes of zinc(II) have been reported. Examples include mono-oxygenated tetra nuclear zinc clusters [16], mixed Li/Zn amidinate oxide oligomers [17], bisamidinate [1a,18], and polynuclear zinc structures [19]. Among these results, Gibson, Marshall, and co-workers completed a study on zinc amidinate complexes which demonstrated the importance of steric bulk in order to form mono-chelated zinc(II) triazenide and amidinate complexes [20]. The variety of compounds reported included a bisacetamidinate zinc(II) complex, [{MeC(NDipp)₂}₂Zn] (I), a mono-oxygenated tetranuclear zinc complex, [{MeC(NDipp)₂}Zn₂Me₂]₂O (II), and the first reported examples of mono(η^2 -amidinate) zinc(II) complexes including, $[{^{t}BuC(NDipp)_{2}}ZnN(TMS)_{2}]$ (III) where the parent homoleptic ligand was ^tbutylamidinate, Fig. 2.

Zinc amidinate complexes have potential applications as catalysts for polymerization [19], since the related zinc guanidinate complexes have been found to act as catalysts in ring-opening polymerization (ROP) of lactides [19,20]. Additionally, similar zinc





^{*} Corresponding author. Tel.: +1 817 257 6220; fax: +1 817 257 5851. *E-mail address:* a.richards@latrobe.edu.au (A.F. Richards).

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Fig. 1. Coordination bonding modes including: (A) monodentate, (B) bidentate chelating, (C) bridging.



Fig. 2. Examples of recently reported zinc amidinate complexes.

complexes with N,N'-chelating ligands, such as the β -diketiminate ligand, have also shown to act as catalysts in ROP of lactides and the copolymerization of CO₂ with a variety of epoxides [21]. However, the application potential of zinc amidinates is still unexplored due to their fairly recent discovery.

In light of the recent developments of N,N'-chelating ligands supporting low valent metal complexes [22,23], and as a continuation of our earlier work employing chelating N,N'-donor ligands [24], we were interested investigating the coordination preferences of the smaller formamidinate ligand RN(H)C(H)NR (R = Dipp = 2,6diisopropylphenyl), L^H, which lacks a bulky substituent on the carbon atom of the NCN backbone for the preparation of aluminum, gallium and zinc complexes that are potential catalysts and as precursors to low valent zinc and aluminum complexes. In addition, given the continued interest in the effect of water on organometallic compounds [25] and oxide and hydroxide incorporated organometallic complexes we were interested in examining the effect of hydrolysis on aluminum and gallium alkyls supported by the formamidinate ligand. To this end we investigated the reactions of L^H with AlMe₃, AlMe₂Cl, GaMe₃ and ZnEt₂. Our goal was to specifically focus on the stoichiometric ratio of L^H to metal alkyl in an attempt to obtain varied ligand coordination modes and to examine the effect of water/oxygen contamination using the same reaction conditions, with the aim being the isolation of metal oxide/hydroxide complexes. Herein we report our results.

2. Results and discussion

The formamidinate ligand DippN(H)C(H)NDipp, L^H, was prepared according to literature procedures [26].

2.1. Discussion of 1, [{HC(NDipp)₂}₂AlMe]

The room temperature, 2:1 reaction of L^H with AlMe₃ in toluene afforded colorless crystals of an Al(III) bisformamidinate complex, **1**, that crystallized in the monoclinic space group $P2_1/n$, Scheme 1.

Structural analysis revealed that the aluminum atom adopts distorted trigonal biypyramidal geometry, Fig. 3.

The equatorial positions of the trigonal bypyramid are occupied by the nitrogen and carbon atoms N1, N3, and C51 and, as expected, result in shorter Al-N bond distances as compared to the Al-N distances from the N2 and N4 atoms in the axial positions. These distances are comparable to 1.925(12) Å and 2.096(12) Å reported for Neg-Al and Nax-Al, respectively, in the related complex $[{MeC(N^{i}Pr)_{2}}_{2}AlCH_{3}]$ [14], as well as 1.914(2) Å and 2.041(2) Å observed in [{MeC(NⁱPr)₂}₂AlCl] [9c]. The bond angles N3-Al1-C51, N1-Al1-C51, and N3-Al1-N1 are close to the 120° expected for trigonal bipyramidal geometry. Similarly to the related aluminum systems [{MeC(NⁱPr)₂}₂AlCl] [9c], [{MeC(NⁱPr)₂}₂AlCH₃] [14], [{PhC(NSiMe₃)₂}₂AlH] [9f], and [{HC(NDipp)₂}₂AlH] [7], the N2-Al1-N4 bond angle of 156.46(10)°, shows a distortion from the expected 180° which can be attributed to the rather acute bite angles of 65.89(10)° and 66.29(10)° for N1-Al1-N2 and N3-Al1-N4 respectively. Spectroscopic data confirmed the solid state analysis with distinct Al–Me resonances at -0.36 ppm and 12.9 ppm in the ¹H and ¹³C NMR spectra [9a-c,12,14].

Repeating the reaction of $AIMe_3$ with L^H under similar conditions as were employed for the synthesis of complex **1** (Scheme 1) but using solvents directly from the bottle, resulted in the formation of **2**, Scheme 2, Fig. 4.

X-ray crystallographic analysis on complex **2**, revealed an aluminum dimer, with each Al center supported by a deprotonated ligand. A terminal methyl group can be observed on each aluminum center and methoxy groups bridge the metal centers. The presence of oxygen can be traced to moisture from the undried solvent, as no methanol was used in the synthesis of **2**. We postulate that the methoxy group was produced by the reaction of a methyl ligand with a trace amount of oxygen in the reaction medium. As the methoxy group has a stronger tendency than a methyl group to act as a bridging ligand the dimeric structure of **2**, is not too unexpected [27]. Each aluminum center is five-coordinate and can be described as a distorted trigonal bypyramid in which the nitrogen atoms occupy the axial positions.

As in complex **1**, the negative charge of the ligand is delocalized over the NCN backbone, which is reinforced by N–C bond lengths of 1.311(4) and 1.320(4) Å and similar Al–N bonds of 1.973(3)



Scheme 1. Aluminum product from the reaction of AlMe₃ with L^H.



Fig. 3. Molecular structure of **1**. Thermal ellipsoids drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.928(3), Al1–N2 2.093(3), Al1–N3 1.923(3), Al1–N4 2.113(3), N1–C38 1.325(3), N2–C38 1.300(4), N3–C13 1.336(4), N4–C13 1.294(4), Al1–C51 1.963(3), N2–C38–N1 111.7(3), N4–C13–N3 113.1(3), N1–Al1–N2 65.89(10), N3–Al1–N4 66.29(10), N3–Al1–N2 102.79(11), N3–Al1–N1 121.11(11), N2–Al1–N4 156.46(10), N3–Al1–C51 119.17(14), N1–Al1–C51 119.71(14).

and 2.071(3) Å. The bridged oxygen from the methoxy group has a typical bond length of 1.875(3) Å, and angle of 76.02(11)°. The N–Al–N bond angle of 65.84(11) is similar to the values of 65.89(10)° for N3–Al1–N4 as seen in **1**. The Al–Al separation of 2.919(2) Å is considerably shorter than that of 3.460(3) Å in the related methoxy bridged, $Al_4(\mu 3-8-quinolylimide)_2(CH_3)_7(\mu-OCH_3)$] [28]. In the ¹H NMR a chemical shift associated with the terminal Al–Me groups is observed at -0.45 ppm while the methoxy group can be assigned to the signal at 0.79 ppm. It is noteworthy to mention that our attempts to add stoichiometric quantities of water or oxygen to anhydrous reactions were unsuccessful.

2.2. Discussion of **3**, [{HC(NDipp)₂H}AlMeCl₂], and **4**, [{HC(NDipp)₂H}AlCl_{1.4}I_{1.6}]

Continuing with the reactions of L^H with aluminum alkyls, L^H was reacted with dimethyl aluminum chloride. In contrast to the formation of the bisamidinate complex **1**, the room temperature



Fig. 4. X-ray crystal structure of **2.** Thermal ellipsoids drawn at 30% probability, hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (°): Al1–O1 1.875(3), Al1–O1# 1.830(3), Al1–C26 1.965(4), Al1–N1 2.071(3), Al1–N2 1.973(3), Al1–Al1a 2.919(2), N1–C13 1.311(4), Al1–N2 1.973(3), N1–Al1–C26 108.94(15), N2–Al1–N1 65.84(11), O1–Al1–O1# 76.02(11).

reaction of L^H with a 1.2 equiv. of AlMe₂Cl afforded the monodentate complex **3** in moderate yield, Scheme 3, Fig. 5.

Complex **3** is interesting as despite numerous literature reports of amidinate complexes, only a handful exhibit the monodentate coordination mode, with examples of aluminum fairly rare [29]. The crystal structure of **3** indicates that the metal complex crystallizes preferentially as the *E* isomer with respect to the N1–C13 bond, Fig. 5. The formation of the geometric isomer is predicted to be a result of the hydrogen attached to the NCN backbone, rather than a more bulky alkyl group. For example, the formamidinate gallium complex, [{HC(NDipp)₂H}GaCl₃], crystallizes as the E isomer, [29] whereas the acetamidinate aluminum [29] and molybdenum [30] complexes, [{MeC(NDipp)₂H}All₃] and [{MeC(N- $Dipp_{2}HMO(CO)_{5}$, crystallize in the Z form. The aluminum center in 3 has distorted tetrahedral geometry with the Al1-N1 bond length of 1.915(4) Å in the normal range [1]. A methyl group and a chlorine atom occupy two of the four tetrahedral coordination sites and are refined at full occupancy, while the remaining sites consist of a dative nitrogen bond and a chlorine atom which is disordered over 3 positions, each at 1/3 occupancy. The attachment of



Scheme 2. The effect of water on the formation of 1 affording complex 2.



Scheme 3. Synthesis of [{HC(NDipp)₂H}AlMeCl₂].



Fig. 5. X-ray crystal structure of L^HAlMeCl₂, complex **3.** Thermal ellipsoids drawn at 30% probability level, hydrogen atoms and have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–Cl2 2.137(2), Al1–C26 1.960(4), Al1–N1 1.915(4), N1–C13 1.304(5), N2–C13 1.316(5), C26–Al1–Cl2 116.17(17), N1–Al1–Cl2 104.86(13), N1–Al1–C26 111.21(18), N1–C13–N2 128.7(4).

the second chlorine, rather than a methyl group, is most likely as a result from the reaction conditions, employing a slight excess of Al-Me₂Cl to L^H at room temperature and given that [Me₂AlCl]₂ can disproportionate to provide Me₃Al and [MeAlCl₂]. Such disproportionation of aluminum alkyls in the presence of base has been previously noted, and was initially suggested by Ziegler in the 1950's [31]. Comparison of the N1-C13 and N2-C13 bond lengths: 1.304(5) Å and 1.316(5) Å, respectively, suggest delocalization of the double bond. The hydrogen atom on N2 was located from the electron density difference map and confirmed by ¹H NMR spectroscopy with a resonance peak at 8.46 ppm which corresponds well with chemical shifts of 8.98 and 8.67 ppm reported for the aluminum acetamidinate and gallium formamidinate examples [{MeC(NDipp)₂H}All₃] and [{HC(NDipp)₂H}GaCl₃], respectively [29]. Similarly, the ¹H NMR and ¹³C NMR confirm the presence of only one methyl group attached to the aluminum metal center which is additionally confirmed by mass spectral analysis.



Fig. 6. Crystal structure of the monodentate complex, **4.** Thermal ellipsoids drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cl1–Al1 2.146(4), Al1–Cl2 2.050(12), I1–Al1 2.550(4), I2–Al1 2.506(3), Al1–N1 1.908(7), N1–Cl3 1.316(9), N2–Cl3 1.306(10), Cl2–Al1–Cl1 117.1(5), Cl1–Al1–I1 116.06(17), Cl1–Al1–I2 111.97(15), Cl2–Al1–I2 104.5(5), I1–Al1–I2 110.73(14), N1–Al1–Cl1 109.6(2), N1–Al1–Cl2 109.3(5), N1–Al1–I1 104.0(2), N1–Al1–I2 103.4(2), N2–Cl3–N1 127.0(7).

In an attempt to examine the chemistry of this system, we wished to synthesize [{HC(NDipp)₂H}AlClI₂] for further reactions. To this end, the reaction of [{HC(NDipp)₂H}AlClMe₂] with I₂ was performed, Scheme 4 [32]. Colorless crystals of **4** were isolated in 58% yield and found to crystallize in the monoclinic space group $P2_1/c$, Fig. 6.

Similarly to complex **3**, the Al atom has distorted tetrahedral geometry. The Al1–N1 bond length of 1.908(7) Å and Al–X (X = halide) bond lengths are within the range for normal values [1,9c,13,29]. X-ray crystallographic analysis revealed that complex **4** has an iodine and chlorine ion sharing a position with partial occupancy at 60/40 (I:Cl), which is probably the result of the in situ reaction of L^H with AlMe₂Cl to form the desired LAIMe₂Cl



with subsequent treatment with one equivalent of I₂. Therefore, it is likely the reaction mixture contains a mixture of LAIMe₂Cl and LAICl₂Me [31]. The neutral adduct, **4**, shows delocalization across the NCN backbone (N1–C13 is 1.316(9) Å and N2–C13 is 1.306(10) Å). The solid state analysis is confirmed by solution NMR and IR spectroscopy with indicative N–H and C–H peaks from the NCN backbone observed. Additionally, the N–H stretch at 3302 cm⁻¹ is observed in the infrared spectra. The positive-mode mass spectrum of the aluminum adduct complex **4** gave the parent ion peak at m/z = 644.1 as compared to the calculated m/z = 644.2.

2.3. Synthesis and discussion of [{DippNCHDipp}_2Al_3\mu_3O(OH)_2(Cl/OH)ClMe], **5**

The reaction of AlMe₂Cl with L^H was repeated with the goal of isolating an alumoxane or aluminum hydroxide complex; therefore, solvents were used directly from the bottle, Scheme 5.

Complex **5** was crystallized from hexane in the monoclinic space group, $P2_1/c$. Structural determination revealed a bridged amidinate structure in which two deprotonated ligands support three aluminum centers, Fig. 7.

The aluminum atom, Al1, is coordinated to one nitrogen atom, N1, and is connected to Al2 and Al3 through a μ_3 oxygen atom O1 that links the three aluminum centers. The second aluminum center, Al2, is coordinated to two nitrogen atoms from two different ligands, N2 and N3. The structure can be best described as two 6 membered rings, that share Al2 and O1. Each Al center has slightly distorted tetrahedral geometry, and Al–N distances and NCN angles that are similar to those in neutral chelated amidinate complexes [9c]. As observed in complexes 1–4 the bond lengths of the ligand: N3–C38, N4–C38 and N1–C13, N2–C13 are intermediate between that of single and double bond distances, indicating significant π delocalization within the NCN unit.

Comparing complex **5** with dimeric **1**, [{HC(NDipp)₂}₂AlMe] and monomeric AlMeCl₂ L^{H} , **3**, it can be observed that each Al center is coordinated to at least one nitrogen atom, therefore it seems likely that the presence of moisture and/or oxygen promoted hydrolysis of a chloride or methyl groups and promoted further reactions to occur. The overall cationic charge of +9, from 3 Al³⁺ ions is balanced by two ligands, a terminal methyl groups, two terminal hydroxide groups, a chloride atom, bridged oxygen atom and a mixed occupancy site (Cl2/O3) comprising of a chloride and hydroxide which was successfully refined as 1/3Cl, 2/3 O. The terminal methyl and hydroxyl groups are confirmed by ¹H NMR with an AlMe resonance observed at -0.11 ppm and 3 signals between 0.39-0.91 for the hydroxide groups, which are in the range for other reported Al-OH signals [33]. In the infrared spectra of 5, an OH stretch can be found at 3349 cm⁻¹ which is similar to that observed in related complexes [33].



Fig. 7. Structure of Complex **5.** Selected bond lengths and angles: Al1–01 1.782(4), Al1–N1 1.928(5), Al1–C51 1.954(6), Al1–Cl1 2.125(3), Al2–O1 1.772(4), Al2–N3 1.916(4), Al3–N4 1.926(4), Al3–O3 1.96(2), Al3–O4 2.035(4), Al3–Cl2 2.17(3), N1–Cl3 1.311(7), N2–Cl3 1.334(6), N3–C38 1.333(6), N4–C38 1.319(6), O1–Al1–N1 99.15(19), O1–Al1–C51 118.8(2), N1–Al1–C51 109.3(2), O1–Al1–Cl1 107.51(15), N1–Al1–Cl1 105.30(17), C51–Al1–Cl1 114.9(2), O1–Al2–N3 101.72(19), N3–Al2–N2 120.5(2), N2–Al2–O2 109.99(17), C13–N1–Al1 124.2(4), C13–N2–Al2 120.5(3), C39–N4–Al3 113.0(3).

2.4. Synthesis and discussion of complex **6**, [{DippNCHDipp}₂ $Ga_3(\mu O)_2(Me)_7AlLi$]

Gallium amidinate complexes have previously been synthesized by the reaction of gallium halides with preformed amidinate reagents [11,13,29]. Typically the reactions with bulky amidinates favor a chelating bonding mode because of the steric crowding [11,13,29,34]. Given the limited numbers of gallium amidinate complexes [35] and their potential as volatile precursors to nitride materials [36] we were interested in studying the reactions of GaMe₃ with L^H. To this end, GaMe₃ was prepared from the reaction of GaCl₃ and 3MeLi. The *in situ* generated GaMe₃ was reacted with L^H at room temperature in toluene. Despite numerous attempts and various reaction conditions, we were unable to obtain crystals from this particular reaction. However, our attempts to yield an Al/ Ga, bimetallic complex through the reaction of GaMe₃ with L^H with sequential addition of 1 equivalent of AlMe₃, (Scheme 6) afforded complex **6**, Fig. 8.

The crystal structure of **6** was found to consist of two bridging ligands that support three gallium atoms and one aluminum atom. The N1–C13–N2 backbone bridges the gallium atoms Ga1 and Ga2



Scheme 5. Synthesis of Complex 5.



Scheme 6. Synthesis of complex 6.

while Ga3 is coordinated to the second amidinate ligand through N3. The three gallium atoms and the aluminum atom show slightly distorted tetrahedral geometry. The tetrahedral sites around Ga1 are occupied by a nitrogen atom, N1, two terminal methyl groups and a bridged oxygen atom O2 which bridges all three gallium atoms. Ga3 also has a terminal methyl group and is further coordinated to a second oxygen atom O1 to which there is an AlMe₃ fragment attached. Ga2 is coordinated to the second formamidinate ligand and two methyl groups. The second nitrogen atom of this ligand, N4, has a lithium atom coordinated, which in turn has coordination to the oxygen atoms O1, O2 and Ga3. One can notice a distinct difference in the Ga-N bond lengths. The Ga3-N3 distance of 2.003(3) is comparable to that observed in neutral Ga imine complexes (2.007(2)Å) (e.g., N-methylsalicylaldiminate gallium dimethyl [37] while the N1–Ga1 distance (2.026(3) Å) is comparable to those in bulky gallium amide complexes [38], e.g. $\{Me_2Ga(NHPh)\}_2$ (2.03(7)Å) [27a]. Other bond distances and angles are unexceptional, for example, the average Ga-C(Me) distance of ~1.95 Å in 6 is comparable to 1.957(8) Å observed in hydroxyl(methyl)gallium bis(pyrazolyl)dimethylboron [39a] and in [(2,6-Mes₂C₆H₃Ga(Me)(µ₂-OH)]₂ (average 1.947 Å) [39b]. Similarly the Ga–O distances ~1.96 Å are comparable to reported literature values [40].



Fig. 8. Solid state structure of the bimetallic amidinate cluster, **6.** Selected bond lengths (Å) and angles (°): N1–Ga1 2.026(3), Ga1–C26 1.959(4), Ga1–O1 1.937(3), Ga1–C27 1.973(4), N2–Ga2 1.985(3), Ga2–C28 1.955(5), Ga2–Li1 2.678(8), Li1–O1 2.026(8), Li1–O2 1.923(9), Al1–O2 1.641(3), Al1–C61 1.860(6), O1–Ga3 1.990(2), Ga3–N3 2.003(3), Ga3–C58 1.983(5), N1–C13 1.315(5) C13–N2 1.329(5), N3–C44 1.338(5), N4–C44 1.302(5), Ga3–O1 1.990(2), N1–Ga1–C26 102.32(16), N2–Ga2–C28 113.78(17), N3–Ga3–C57 110.29(18), C13–N2–Ga2 119.1(3), C59–Al1–C60 109.9(3).

If one considers the structure of **6** but without the lithium atom and AlMe₃ fragment present then **6** is structurally very similar to the Al₃ cluster, **5**. Therefore, it is possible that a similar product is formed that but does not crystallize out. As with complex **2**, the synthesis of **5** and **6** was attempted using stoichiometric amounts of water and oxygen but were unsuccessful.

For charge balance, the +13 charge from three Ga atoms, one Al atom and one Li⁺ is offset by eight terminal methyl groups, two anionic ligands, an oxygen atom (O1). Presumably the oxygen atom. O2, is protonated although the hydrogen atom could not be located from the difference map. The solid state structure of **6** is confirmed by NMR and mass spectral analysis. The ¹H NMR spectra of **6** shows three resonances at -0.46, -0.48-0.52 ppm associated with the methyl groups located on the aluminum atom. The methyl groups from the gallium atoms are observed at similar values of 0.41 ppm and 0.39 ppm and overlapping single signals at 0.5–0.6 ppm. These values are similar to those reported for {^tBuC(NⁱPr)₂}GaMe[·]{^tBuC- $(N^{i}Pr)_{2}$ GaMe₂⁺ that displays Ga–Me resonances at 0.55, 0.45, 0.35 [9a] and the related [LGaOH(Me)], $(L = [HC{(CMe)(2,6-)}]$ ${}^{i}Pr_{2}C_{6}H_{3}N)$]²]) that shows two resonances (δ +0.08 and -0.57 ppm), which can be attributed to the protons of OH and GaMe groups, respectively [41a]. The mechanism for the formation of 6 is unclear but work is underway to elucidate a pathway and to prepare a series of bimetallic complexes.

2.5. Discussion of 7, [{HC(NDipp)₂}₂Zn]

In order to compare the coordination preferences and products obtained from the aluminum alkyl reactions with L^H, the reactions with ZnEt₂ were performed under varying conditions.

Colorless crystals of complex **7** were obtained by reacting 1 equiv. of $ZnEt_2$ with 2 equiv. of L^H at room temperature, Scheme 7.

As was previously observed in complex **1**, a homoleptic zinc complex was isolated through elimination of both ethyl groups, Fig. 9. Similar bisformamidinate zinc complexes have been reported, examples including [{PhC(NSiMe₃)₂}₂Zn] and [{MeC(N-Dipp)₂}₂Zn] [17–20].

Structural analysis of complex **7** shows the zinc atom achieves a coordination number of four with N–Zn–N bond angles between 123.77(12)° and 150.08(17)° which can be attributed to the rather acute bite angle 65.97(12)° of the formamidinate ligand. The bond lengths within the ligand backbone N1–C13 and N2–C13 are similar at 1.326(5) Å and 1.306(4) Å and are indicative of delocalization over the NCN backbone. The Zn–N bond distances of 2.013(3) Å and 2.036(3) Å are similar to the Zn–N bond distances that have been reported for similar structures, for example; the acetamidinate zinc(II) complex [{MeC(NDipp)₂}₂Zn] [20] has Zn–N bond distances of 2.031(5) Å and 2.038(4) Å. The ¹H and ¹³C



Scheme 7. Synthesis of the zinc bisformamidinate 7.



Fig. 9. Molecular structure of **7**. Thermal ellipsoids drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–N1 2.013(3), Zn1–N2 2.036(3), N1–C13 1.326(5), N2–C13 1.306(4), N1–Zn1–N2 65.97(12), N1–Zn1–N2#1 123.77(12), N2–C13–N1 113.8(3).

spectra are consistent with the solid state structures. Mass spectra analysis of crystalline **7** displayed the parent ion peak at m/z = 793.4, while infrared analysis displayed the characteristic peaks of 1667, 1634 (C=N), 1557 (C=C), and 1319 cm⁻¹ (C-N).

2.6. Discussion of **8**, [{HC(NDipp)₂}Zn₂Et₂]₂(O), and **9**, [{HC(NDipp)₂}₂Zn₃Et₂](OEt)₂

Continuing with the reactions of L^{H} and $ZnEt_{2}$ with the aim of isolating a heteroleptic Zn(II) complex, the reaction stoichiometery was altered. From the 1:1 reaction of L^{H} with $ZnEt_{2}$ colorless crystals of complexes **8** and **9** were isolated in low yield. Both were found to crystallize in the triclinic space group $P\bar{1}$, Scheme 8.

Single crystal X-ray analysis of complex **8** revealed a $[L_2Zn_4-(Et_4)O]$ complex that has a Zn_4O core in which there is a four-coordinate central oxygen atom surrounded by four zinc atoms, Fig. 10. The formamidinate ligand, L^H , exhibits a bimetallic bridging coordination mode with each nitrogen atom coordinated to a zinc atom. The overall +8 charge of the zinc cations is balanced by a -1 charge observed for each NCN ligand, (-2), as well as a -2 charge on the central oxygen atom and a -1 charge for each ethyl group, (-4). The central oxygen atom O1 adopts distorted tetrahedral geometry with O–Zn bond angles ranging from 98.74(9)° to





Scheme 8. Preparation of the zinc-oxygen cluster formamidinates: 8 and 9.



Fig. 10. Molecular structure of complex **8**. On the left hand side is the asymmetric unit and on the right hand side is the central Zn_4O core of the molecule. Thermal ellipsoids drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1-N2 1.965(2), Zn2-N4 1.966(2), Zn3-N3 1.988(2), Zn4-N1 1.969(2), Zn1-O1 1.966(2), Zn2-O1 1.965(2), Zn3-O1 1.948(2), Zn4-O1 1.960(2), Zn1-Zn2 2.9835(5), Zn2-Zn4 3.1083(6), N1-C13 1.317(4), N2-C13 1.323(4), Zn2-O1-Zn1 98.74(9), Zn3-O1-Zn4 109.72(10), Zn4-O1-Zn1 114.41(9), Zn3-O1-Zn2 114.69(10), O1-Zn1-C28 119.11(13), O1-Zn2-C57 119.34(16), O1-Zn3-C55 123.44(14), C26-Zn4-O1 118.20(16).

114.69(10)° and bond lengths in the range of 1.948(2) Å (Zn3–O1)– 1.966(2) Å (O1–Zn1) and 1.965(2) Å (Zn1–N2) to 1.988(2) Å (Zn3– N3) for N–Zn. These bond lengths compare well to three related tetrahedral Zn₄O cluster amidinate compounds which exhibit bond lengths in the range of 1.912(4)–1.927(3) Å (O–Zn) and 2.023(5)– 2.045(4) Å (N–Zn) for [{HC(NPh₂)₆Zn₄](O) [16a], 1.923(15) Å (O– Zn) and 2.015(6) Å (N–Zn) for [{HC(Np-Tol)₂)₆Zn₄](O) [17], and 1.948(13)–1.953(14) Å (O–Zn) and 1.962(17)–1.974(18) Å (N–Zn) for [{MeC(NDipp)₂}Zn₂R₂]₂(O) (R = Me, Et) [20]. Complex **8** exhibits Zn1???Zn2 and Zn2–Zn4 distances of 2.9835(5) Å and 3.1083(6) Å, respectively, which correspond closely to the [{HC(NPh)₂}₆Zn₄](O) and [{HC(Np-Tol)₂}₆Zn₄](O) complexes with distances at 3.135 Å (mean average) and 3.145(25) Å respectively, [16] and are slightly longer than the sum of van der Waals radii for Zn–Zn, 2.78 Å [42].

In an attempt to eliminate oxygen contamination, the reaction was performed numerous times and it was found that complex **8** is reproducibly isolated. However, on one attempt complex **9** was isolated as colorless needles, Fig. 11. The asymmetric unit of 9 contains two crystallographically independent units. There are no significant geometric differences between the two units, however no higher symmetry space group could be determined by PLATON [43]. Similarly to 8, the crystal structure of 9 reveals a bimetallic bridging binding mode, however, in contrast 9 contains two fourcoordinate oxygen atoms within the central core each with a distorted tetrahedral geometry. The coordination sites around each oxygen atom are occupied by 3 zinc atoms and 1 ethyl group. Examples of a four-coordinate oxygen center with bonds to three zinc atoms and one ethyl group are rare but not unprecedented [44]. The ethyl group attached to the oxygen (O-Et) is likely a result from the elimination of ethane and subsequent coordination to the oxygen atom; indeed the reactions of ZnMe₂ with N,N'diphenyl benzamidine are found to react with molecular oxygen [18]. Each zinc atom in 9 displays distorted tetrahedral geometry. The Zn-Zn separation falls within the range of



Fig. 11. Molecular structure of **9**. On the left hand side is the asymmetric unit and on the right hand side is the Zn₃O₂ core of the molecule. Thermal ellipsoids drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–N1 1.986(3), Zn1–N3 1.984(3), Zn2–N2 2.010(3), Zn3–N4 2.026(3), Zn1–O2 2.036(3), Zn1–O2 2.036(3), Zn2–O1 2.112(3), Zn2–O2 2.179(3), Zn3–O1 2.177(3), Zn3–O2 2.111(3), Zn1–Zn2 2.9905(7), Zn1–Zn3 2.9990(7), Zn2–Zn3 2.9454(8), N1–C13 1.331(5), N4–C38 1.305(5), Zn2–O1–Zn3 86.73(11), C51–O1–Zn1 126.0(3), C53–O2–Zn2 128.4(3), N3–Zn1–O2 110.85(13), N1–Zn1–O1 113.10(13), N2–Zn2–O1 103.29(13), C57–Zn2–O1 119.9(2), N4–Zn3–O1 101.28(12), C55–Zn3–O2 122.56(17).

2.9454(8)–2.9990(7) Å, which correspond closely to the Zn–Zn distances of complex 8 and other previously mentioned examples [42]. However, only three zinc atoms are present in complex 9 with one zinc atom attached to both formamidinate ligands via N,N'chelation. Additionally, the Zn-N, Zn-O and N-C-N bond lengths for complexes 8 and 9 are similar to those observed for related amidinate analogs, such as [{HC(NPh)₂}₆Zn₄]O, [16a] [{HC(N-p- $CH_3C_6H_4)_2_6Zn_4]O$, [16b] and [{MeC(NDipp)_2_2Zn_4]O [20]. The source of the oxygen contamination in both complexes 8 and 9 is not confirmed, but likely from atmospheric oxygen/water moisture during the reaction. Tetranuclear zinc amidinate clusters containing oxygen have been previously reported and are known to be highly oxophilic [17,20]. Spectroscopic data confirmed the structures of 8 and 9. Specifically, distinctive peaks for CN, C=C, and C-N were observed in the infrared spectroscopy with stretching bands at 1667, 1597, 1557, and 1320 cm⁻¹, respectively, for complex **8**, and 1665, 1597, 1561, 1287 cm⁻¹ for complex **9**.

3. Conclusion

The reactions of the neutral formamidinate, DippN(H)C (H)NDipp, with aluminum, gallium and zinc alkyls have produced nine complexes featuring different coordination modes. These nine compounds expand on the large volume of amidinate group 13 complexes. The chelating binding mode is observed which is in accordance with the sterically large 'Dipp' substituents attached to the nitrogen atoms of the NCN backbone. Yet, X-ray crystallographic analysis revealed that steric constraints do not govern coordination modes entirely. Through manipulation of reaction stoichiometry a variety of coordination compounds that feature monodentate and η^2 -bridging coordination as well as cluster complexes were observed. The monomeric complexes and aluminum are adducts, as previously seen with AlX₃ due to their vacant orbital. However, the η^2 -bridging and cluster type zinc complexes are likely the result of the lack of steric protection on the carbon of the NCN backbone. Future work will focus on the further chemistry of the reported structures and will investigate the steric influence of the formamidinate ligand and reaction conditions in metal complex formation.

Table 1

Crystal data for compounds 1-5.

4. Experimental

All manipulations were performed under anaerobic conditions using standard Schlenk techniques. Hexane and Toluene were dried using an MBraun-SPS solvent purification system. The amidinate ligand, L^H = (Dipp)N(H)C(H)N(Dipp), was prepared according to published procedures [26]. All other reagents were purchased from Aldrich and used as received. Crystal data were collected with a Bruker SMART 1000 diffractometer, molybdenum radiation $(\lambda = 0.7107 \text{ Å})$ at $-60 \circ \text{C}$. Crystals were mounted on glass fibers using paratone oil. The data were corrected for absorption. Structures were solved by direct methods [45] and refined [45] via full-matrix least squares. Hydrogen atoms were placed in idealized positions except those for M-CH₃ groups (M = Al, Ga, Zn) and OH groups that were localized from the electron density map and refined isotropically with distant restraints. Crystal data for 1–9 is given in Tables 1 and 2. The ¹H and ¹³C NMR spectra were recorded at 300.05 MHz and 75.45 MHz respectively on a Varian XL-300, IR analysis was conducted as Nujol Mulls with NaCl plates on a MID-AC M4000 Fourier transform infrared (FT IR) spectrometer, and mass spectrometry analysis was carried out using a Bruker Esquire 6000 Mass Spectrometer. Melting points were determined in capillaries under a nitrogen atmosphere and are uncorrected.

4.1. Synthesis of 1, [{HC(NDipp)₂}₂AlMe]

 L^{H} 0.35 g (0.96 mmol) was dissolved in ~20 mL of toluene. At room temperature 0.24 mL of AlMe₃ (2.0 M solution) was added by syringe. The evolution of gas could be observed by small bubbles within the reaction mixture. Stirring was maintained for 2 h, after which time, all volatiles were removed in vacuo. The remaining white sold was extracted into hexanes and stirred. The solution was filtered and stored at room temperature overnight yielding colorless crystals of **1**.

Yield: 0.13 g, 25%. M.p. >250 °C. ¹H NMR (C₆D₆, 25 °C): δ (ppm) −0.36 (s, 3H, AlCH₃), 0.57−1.15 (m, 48H, CH(CH₃)₂), 2.33 (septet, 8H, ¹J_{H−H} = 6.9 Hz, CH(CH₃)₂), 6.58−6.98 (m, 12H, H_{aryl}), 7.33 (s, 2H, NCHN); ¹³C NMR (C₆D₆, 25 °C): δ (ppm) 12.9 (AlCH₃), 21.1 (CH(CH₃)₂), 22.3 (CH(CH₃)₂), 26.9 (CH(CH₃)₂), 117.5 (m-ArC),

Compound name	1	2	3	4	5
Chemical formula	C ₅₁ H ₇₃ AlN ₄	$C_{54}H_{82}Al_2N_4O_2$	C ₂₆ H ₃₉ N ₂ AlCl ₂	C ₂₅ H ₃₆ N ₂ AlCl _{1.4} I _{1.6}	C ₅₁ H ₇₅ Al ₃ Cl _{1.33} N ₄ O _{3.67}
Formula weight	769.11	873.20	477.47	644.21	930.91
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
T (K)	213(2)	223(2)	213(2)	213(2)	213(2)
a (Å)	14.6183(11)	12.641(3)	10.4346(12)	10.8346(12)	18.885(3)
b (Å)	16.3071(13)	16.579(4)	20.253(2)	14.7019(16)	12.3056(19)
c (Å)	21.2633(18)	14.282(4)	14.0541(16)	21.1937(18)	29.332(4)
α (°)	90	90	90	90	90
β(°)	110.087(2)	114.804(4)	108.602(2)	118.063(4)	127.304(7)
γ(°)	90	90	90	90	90
$V(Å^3)$	4760.5(7)	2717.0(12)	2814.9(6)	2979.0(5)	5422.1(14)
Ζ	4	2	4	4	4
Reflections collected	22909	18353	14010	24781	41773
Independent reflections	8591	4876	5057	5363	9790
Data/restraints/parameter ratio	8591/0/522	4876/0/293	5057/1/288	5363/1/302	9790/0/577
R _{int}	0.0847	0.1149	0.0490	0.0622	0.0915
D_{calc} (Mg/m ³)	1.073	1.067	1.127	1.436	1.140
Absorption coefficient (mm ⁻¹)	0.079	0.094	0.277	1.866	0.178
F(000)	1680	952	1024	1286	2000
R indices (all data)	$R_1 = 0.1568$	$R_1 = 0.1673$	$R_1 = 0.1309$	$R_1 = 0.1365$	$R_1 = 0.1753$
	$wR_2 = 0.1761$	$wR_2 = 0.2109$	$wR_2 = 0.2317$	$wR_2 = 0.2096$	$wR_2 = 0.2186$
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0610$,	$R_1 = 0.0828$,	$R_1 = 0.0746$,	$R_1 = 0.0598$,	$R_1 = 0.0835$
	$wR_2 = 0.1321$	$wR_2 = 0.1753$	$wR_2 = 0.1954$	$wR_2 = 0.1462$	$wR_2 = 0.2186$
Largest difference in peak and hole $(e \text{ Å}^{-3})$	0.210 and -0.271	0.477 and -0.309	1.146 and -0.893	0.666 and -0.929	1.002 and -0.562

Table 2				
Crystal	data	for	compounds	6-9

Compound name	6	7	8	9
Chemical formula	C ₅₈ H ₉₄ AlGa ₃ LiNO ₂	$C_{50}H_{70}N_4Zn$	$C_{58}H_{90}N_4OZn_4$	$C_{58}H_{90}N_4O_2Zn_3^{a}$
Formula weight	1122.45	792.47	1120.82	1071.45 ^a
Crystal system	triclinic	orthorhombic	triclinic	triclinic
Space group	ΡĪ	C222 ₁ [46]	ΡĪ	ΡĪ
T (K)	223(2)	213(2)	213(2)	213(2)
a (Å)	10.7199(9)	14.4081(18)	12.1524(6)	10.6164(8)
b (Å)	15.3561(14)	20.4135(18)	13.9272(7)	22.9140(17)
c (Å)	19.2095(17)	16.0402(17)	19.6143(10)	23.9395(19)
α (°)	95.399(2)	90	70.5200(10)	97.0060(10)
β (°)	93.933(2)	90	83.7430(10)	96.0100(10)
γ (°)	100.289(2)	90	71.4230(10)	90.703(2)
V (Å ³)	3085.7(5)	4717.7(9)	2966.6(3)	5746.5(8)
Ζ	2	4	2	2
Reflections collected	25026	10204	17076	45775
Independent reflections	11067	4500	12818	20620
Data/restraints/parameter ratio	11067/0/626	4500/0/258	12818/0/604	20620/4/1215
R _{int}	0.0501	0.0589	0.0221	0.0499
D_{calc} (Mg/m ³)	1.208	1.116	1.255	1.235
Absorption Coefficient (mm ⁻¹)	1.355	0.556	1.636	1.284
F(000)	1190	1712	1188	2276
R indices (all data)	$R_1 = 0.0941$	$R_1 = 0.1067$	$R_1 = 0.0719$	$R_1 = 0.1016$
	$wR_2 = 0.1157$	$wR_2 = 0.1102$	$wR_2 = 0.1097$	$wR_2 = 0.1352$
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0457, wR_2 = 0.0950$	R_1 =0.0507, wR_2 = 0.0948	$R_1 = 0.0410, wR_2 = 0.0914$	R_1 =0.0519, wR_2 = 0.1117
Largest difference in peak and hole (e $Å^{-3}$)	0.523 and -0.460	0.413 and -0.617	0.530 and -0.485	0.968 and –1.150

^a Formula based on one molecule in the asymmetric unit.

121.7 (*m*-ArC), 122.0 (*p*-ArC), 122.3 (*p*-ArC), 124.5 (*o*-ArC), 130.8 (*o*-ArC), 139.1 (ArC-N), 143.0 (ArC-N), 166.4 (NCN); IR (υ cm⁻¹, Nujol mull): 1666 (m), 1635 (w), 1553 (m), 1324 (w), 1292 (w), 1179 (m), 966 (m), 934 (m), 755 (m), 664 (w), 636 (w); MS (*m*/*z*; found (calc.)): 769.4 (769.1) M⁺, 365.3 (364.5) L^H, 176.1 (176.2) L^H-(Dipp)NC(H), 160.3 (159.4) M-AIMe-(DippN)₂C(H)-Dipp-ⁱPr.

4.2. Synthesis of 2, [{HC(NDipp)₂}AlMe(µOMe)]₂

L^H 0.35 g (0.96 mmol) was dissolved in toluene. AlMe₃ (0.6 mL of a 2.0 M solution) was added by neat with stirring. Stirring was maintained for 1 h. the toluene was removed under vacuum and the product extracted into hexane (direct from the bottle). The pale vellow solution was concentrated and stored at room temperature over night affording colorless crystals of 2. Yield: 0.26 g, 30%. M.p. 248–252 °C (decomp). ¹H NMR (C_6D_6 , 25 °C): δ (ppm) –0.45 (s, 6H, AlCH₃), 0.79 (s, 6H, OCH₃), 1.55 (d, 12H, CH(CH₃)₂, ${}^{1}J_{H-H} = 6.90$ Hz), 1.69 (d, 36H, CH(CH₃)₂, ${}^{1}J_{H-H} = 6.90$ Hz), 3.97–4.11 (m, 8H, CH(CH₃)₂, ${}^{1}J_{H-H} = 6.90$ Hz), 7.52–7.62 (m, 12H, Ar–H), 8.06 (s, 2H, NC(H)N). ${}^{13}C$ NMR (C₆D₆, 25 °C): δ (ppm) 1.7 (OCH₃), 12.9 (AlCH₃), 21.9 (CH(CH₃)₂), 22.0 (CH(CH₃)₂), 23.0 (CH(CH₃)₂), 23.3 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 26.6 (CH(CH₃)₂), 27.0 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 30.5 (CH(CH₃)₂), 122.3 (m-ArC), 122.9 (m-ArC), 125.0 (p-ArC), 126.3 (p-ArC), 126.6 (ipso-ArC), 126.9 (ipso-ArC), 143.1 (o-ArC), 144.2 (o-ArC), 165.6 (NCN), 168.5 (NCN). MS (m/z; found (calc.)): 435.1 (436.5), M⁺, 420.5 (421) M-Me, 365.2 (364.5) L^{H} , IR ($v \text{ cm}^{-1}$, Nujol mull): 3348 (w), 1667 (m), 1588 (m). 1538 (w), 1287 (w), 936 (w), 753 (w).

4.3. Synthesis of 3, [{HC(NDipp)₂H}AlMeCl₂]

 L^{H} 0.5 g (1.37 mmol) was dissolved in ~20 mL of toluene. At room temperature, one equivalent of a 1.0 M solution of AlMe₂Cl (1.4 mL) was added drop-wise. The reaction was stirred at ambient temperature for 2–3 h after which time the toluene was removed under reduced pressure and the remaining white solid was extracted into hexanes. After 14 h at room temperature colorless crystals of **3** were isolated. Yield: 0.15 g, 46%. M.p. 243–249 °C (decomp). ¹H NMR (C_6D_6 , 25 °C): δ (ppm) –0.85 (s, 3H, AlCH₃), 1.15–1.28 (m, 24H, CH(CH₃)₂), 2.82–3.23 (m, 4H, CH(CH₃)₂), 7.09–7.25 (m, 6H, H_{aryl}), 7.33 (s, 1H, NCHN), 8.46 (s, 1H, NH); ¹³C NMR (C_6D_6 , 25 °C): δ (ppm) –2.0 (AlCH₃), 19.1 (CH(CH₃)₂), 19.6 (CH(CH₃)₂), 20.7 (CH(CH₃)₂), 21.1 (CH(CH₃)₂), 22.8 (CH(CH₃)₂), 27.3 (CH(CH₃)₂), 120.5 (*m*-ArC), 121.2 (*m*-ArC), 121.8 (*p*-ArC), 123.5 (*p*-ArC), 133.8 (*o*-ArC), 135.8 (*o*-ArC), 141.4 (ArC-N), 143.3 (ArC-N), 166.5 (NCN); IR (νcm^{-1} , Nujol mull): 3067 (shoulder, N–H stretch), 1680 (m), 1639 (m), 1596 (m), 1556 (s), 1528 (m), 1335 (m), 1199 (m), 934 (m), 854 (m), 776 (m), 682 (m); MS (*m*/*z*; found (calc.)): 478.5 (477.5) M⁺, 365.3 (364.5) M–AlCl₂Me, 176.2 (176.3) M–AlCl₂Me–(Dipp)NC(H).

4.4. Synthesis of **4**, [{HC(NDipp)₂H}AlCl_{1.4}I_{1.6}]

To a 25 °C toluene solution (\sim 20 mL) of L^H (0.35 g, 0.96 mmol) was added 1.2 equiv. of AlMe₂Cl (1.2 mL, 1.2 mmol) drop-wise. Evolution of gas was observed. Stirring was maintained for 3 h, after which time freshly sublimed I_2 (0.24 g, 0.96 mmol) was added quickly to the reaction mixture. The dark purple reaction was then allowed to stir for 4 days until the reaction mixture became a clear pale tan color. The toluene was then removed in vacuo and the pale tan solid was extracted into hexane, concentrated, and filtered. Overnight storage of the hexane solution at room temperature afforded colorless crystalline plates of **4**. Yield (based on ligand): 0.36 g, 58%. M.p. 231–235 °C (decomp). ¹H NMR (C₆D₆, 25 °C): δ (ppm) 0.80 (d, 24H, ${}^{1}J_{H-H}$ = 7.2 Hz, CH(CH₃)₂), 2.87 (septet, 4H, ${}^{1}J_{H-H} = 6.8 \text{ Hz}, CH(CH_{3})_{2}), 6.60 (d, 4H, {}^{1}J_{H-H} = 7.5 \text{ Hz}, m-H_{aryl}), 6.78$ (t, 2H, ${}^{1}J_{H-H} = 7.8$ Hz, $p-H_{aryl}$), 6.86 (s, 1H, NCHN), 12.05 (s, 1H, NH); ¹³C NMR (C_6D_6 , 25 °C): δ (ppm) 22.2 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 122.9 (m-ArC), 128.8 (p-ArC), 130.0 (o-ArC), 144.4 (ArC-N), 157.7 (NCN); IR (v cm⁻¹, Nujol mull): 3302 (shoulder, N-H stretch), 1682 (m), 1638 (m), 1595 (m), 1557 (m), 1337 (m), 935 (s), 670 (m); MS (*m/z*; found (calc.)): 644.1 (644.2) M⁺, 422.3 (422.6) M^+ -I-Cl-Cl-iPr, 365.4 (364.5) L^H , 144.2 (144.1) L^H -(Dipp)NH-ⁱPr-H, 130.2 (130.1) L^H-(Dipp)NHC(H)-ⁱPr-2H, 117.2 (117.1) L^H-Dipp-ⁱPr-ⁱPr. The positive-mode mass spectrum of complex **3** gave the parent ion peak at m/z = 644.1 as compared to the calculated m/z = 644.2, which confirms the iodine and chlorine at 60:40 partial occupancy. The parent peak is followed by sequential loss of an ⁱPr, I and Cl (at full occupancy), and Cl (at partial occupancy) to give a peak at m/z = 422.3.

4.5. Synthesis of **5**, [{DippNCHDipp}₂Al₃µ₃O(OH)₂(Cl/OH)ClMe]

To a \sim 20 mL hexane solution of L^H (0.35 g, 0.96 mmol), AlMe₂Cl was added neat (1.2 mL, 1.2 mmol). The reaction mixture was stirred at room temperature for 1 h. The pale yellow solution was filtered from the white solid and stored at room temperature over night to yield crystals of **5**.

Yield: 0.15 g, 46%. M.p. 268–274 M.p. 243–249 °C (decomp). ¹H NMR (C₆D₆, 25 °C): δ (ppm) -0.11 (s, Al-CH₃), 0.39 (s), 0.76 (s), 0.91 (s, Al–OH), 1.40 (d, 6H, CH(CH₃)₂, ${}^{1}J_{H-H}$ = 6.90 Hz), 1.73 (d, 6H, $CH(CH_3)_2$, ${}^{1}J_{H-H} = 6.60 \text{ Hz}$), 1.83–1.87 (overlapping d, CH (CH₃)₂), 4.17-4.35 (overlapping multiplets, 4H, CH(CH₃)₂), 7.48-7.57 (m, 12H, Ar-H), 8.02 (s, 1H, NC(H)N) 8.03 (s, 1H, NC(H)N). ¹³C NMR (C_6D_6 , 25 °C): δ (ppm) 22.3 (CH(CH₃)₂), 22.8 (CH(CH₃)₂), 22.9 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 26.2 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 28.1 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 28.3 (CH(CH₃)₂), 28.5 (CH(CH₃)₂), 29.2 (CH(CH₃)₂), 29.6 (CH(CH₃)₂), 30.0 (CH(CH₃)₂), 31.5 (CH(CH₃)₂), 31.8 (CH(CH₃)₂), 32.1 (CH(CH₃)₂), 34.8 (CH(CH₃)₂), 38.4 (CH(CH₃)₂), 123.9 (m-ArC), 125.1 (p-ArC), 137.9 (ipso-ArC), 144.8 (o-ArC), 146.9 (o-ArC), 170.3 (NCN). IR (v cm⁻¹, Nujol mull): 3349 (m), 1683 (m), 1604 (m), 1593 (m), 1544 (s), 1350 (s), 917 (w), 902 (m), 835 (m), 749 (w), 732 (m), 691 (w), 660 (w). MS (*m/z*; found (calc.)): 365.1 (364.5) L^H, 765.3 (765.1) M⁻ⁱPr, -O-CH₃, -Cl, -2OH, -Cl/O, (= 2L^H(-ⁱPr)₂Al)).

4.6. Synthesis of 6, [{DippNCHDipp}₂Ga₃(μ O₂)AlLiMe₇]

GaCl₃ (0.5 g, 2.83 mmol) in 10 mL of toluene was cooled to -60 °C. Three equivalents of 1.6 M MeLi (5.3 mL) were added drop-wise. The resultant reaction mixture was allowed to stir for 2 h, after which time a toluene solution of L^{H} was added drop-wise. The reaction mixture was warmed to room temperature and stirred for 1 h after which time, 1.4 mL of AlMe₃ was added by syringe. Stirring was maintained for a further 2 h after which time the solution was filtered and extracted into hexanes (direct from the bottle), storage of the colorless solution at 5 °C overnight, yielded colorless crystals of 6. Yield: 0.18 g, 33%. M.p. 209–211 °C. ¹H NMR (C_6D_6 , 25 °C): δ (ppm) -0.52, -0.48, -0.46, (Al-CH₃) 0.39, 0.41, 0.5–0.6 (overlapping), (s, Ga–Me), 1.19 (d, 12H, CH(CH₃)₂, ${}^{1}J_{H-H}$ = 6.90 Hz), 1.33 (d, 12H, CH(CH₃)₂, ${}^{1}J_{H-H}$ = 6.90 Hz), 1.42 (d, 12H, CH(CH₃)₂, ${}^{1}J_{H-H}$ = 6.60 Hz), 1.51 (d, 12H, CH(CH₃)₂, ${}^{1}J_{H-H}$ _H = 6.60 Hz), 3.61–3.73 (septet, 4H, $CH(CH_3)_2$, ${}^{1}J_{H-H}$ = 6.60 Hz), 3.76–3.90 (septet, 4H, $CH(CH_3)_2$, ${}^{1}J_{H-H} = 6.90 \text{ Hz}$), 7.16–7.28 (m, 12H, Ar-H), 7.73 (s, 1H, NC(H)N), 7.75 (s, 1H, NC(H)N). ¹³C NMR $(C_6D_6, 25 \circ C): \delta$ (ppm) -8.9, -7.8, -7.3, -4.9, -4.2, 0.78, 1.28, (Al/Ga CH₃), 21.6 (CH(CH₃)₂), 22.1 (CH(CH₃)₂), 23.0 (CH(CH₃)₂), 23.2 (CH(CH₃)₂), 23.6 (CH(CH₃)₂), 24.2 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 26.5 (CH(CH₃)₂), 30.5 (CH(CH₃)₂), 121.9 (m-ArC), 122.2 (m-ArC), 122.7 (p-ArC), 125.9 (p-ArC), 139.5 (ipso-ArC), 141.4 (ipso-ArC), 142.4 (ipso-ArC), 143.2 (ipso-ArC), 144.1 (o-ArC), 144.9 (o-ArC), 162.8 (NCN), 166.3 (NCN).

MS (*m*/*z*; found (calc.)): 1121.3 (1122.45), M⁺, 1023.5 (1023.7), M–6Me, –Li, 990.0 (991.6), M–8Me, –Li, –2H, 929.7, 856.9, 600.3, 547.8 (548) M–DippNC(H)NDipp–8Me, –Li, –Ga, –Al 463.2 (462) M–DippNCHNDipp, –8Me, –Li, –Ga, –Al, –2ⁱPr, 300.9 (299), M–DippNCHNDipp, –8Me, –Li, –Ga, –Al, –Dipp, O– O(1.83).

4.7. Synthesis of **7**, [{HC(NDipp)₂}₂Zn]

 L^{H} 0.35 g (0.96 mmol) was dissolved in toluene and at room temperature 0.48 mL of ZnEt₂ (1.0 M solution) was added by syringe. The colorless reaction mixture was stirred at room temperature for 2 h after which time the volatiles were removed and the white solid extracted into hexanes. Overnight storage of the reaction mixture at room temperature yielded colorless crystals of **7**.

Yield: 0.18 g, 33%. M.p. 209–211 °C. ¹H NMR (C₆D₆, 25 °C): *δ* (ppm) 0.75 (d, ¹J_{H-H} = 6.9 Hz, 12H, CH(CH₃)₂), 0.84 (d, ¹J_{H-H} = 6.6 Hz, 36H, CH(CH₃)₂), 3.12 (br, 8H, CH(CH₃)₂), 6.60–6.90 (m, 12H, H_{aryl}), 6.96 (s, 2H, NCHN); ¹³C NMR (C₆D₆, 25 °C): *δ* (ppm) 21.1 (CH(CH₃)₂), 22.2 (CH(CH₃)₂), 27.2 (CH(CH₃)₂), 121.8 (*m*-ArC), 123.7 (*p*-ArC), 140.0 (*o*-ArC), 142.3 (ArC-N), 165.9 (NCN); IR (*v* cm⁻¹, Nujol mull): 1667 (w), 1634 (w), 1597 (m), 1557 (m), 1319 (m), 1177 (m), 934 (m), 865 (m), 756 (m), 722 (m); MS (*m*/*z*; found (calc.)): 793.4 (792.5) M⁺, 365.3 (364.5) L^H, 176.1 (176.2) L^H–(Dipp)NC(H).

4.8. Synthesis of **8**, [{HC(NDipp)₂}Zn₂Et₂]₂(O)

 L^{H} 0.35 g (0.96 mmol) was dissolved in toluene and at room temperature 0.96 mL of ZnEt₂ (1.0 M solution) was added by syringe. The colorless reaction mixture was stirred at room temperature for 2 h after which time the volatiles were removed and the white solid extracted into hexanes. The reaction mixture was stored at room temperature overnight and yielded colorless crystals of **8**.

Yield: 0.18 g, 23%. M.p. 210–213 °C. ¹H NMR (C_6D_6 , 25 °C): δ (ppm) 0.52–0.57 (m, 8H, ZnCH₂CH₃), 0.74–0.96 (m, 48H, CH(CH₃)₂), 1.06 (t, ¹J_{H-H} = 6.5 Hz, 12H, ZnCH₂CH₃), 3.03–3.23 (br. m, 8H, CH(CH₃)₂), 6.60–6.86 (m, 12H, H_{aryl}), 7.02 (s, 2H, NCHN); ¹³C NMR (C_6D_6 , 25 °C): δ (ppm) 9.7 (ZnCH₂CH₃), 22.3 (CH(CH₃)₂), 26.9 (ZnCH₂CH₃), 37.7 (CH(CH₃)₂), 122.0 (*m*-ArC), 122.3 (*p*-ArC), 141.9 (*o*-ArC), 144.6 (ArC-N), 153.9 (NCN); IR (υ cm⁻¹, Nujol mull): 1667 (m), 1597 (m), 1557 (m), 1320 (w), 934 (m); MS (*m*/*z*; found (calc.)): M⁺ not observed, 1004.8 (1005.1) M–4Et, 365.3 (364.5) L^H.

4.9. Synthesis of **9**, [{HC(NDipp)₂}₂Zn₃Et₂](OEt)₂

Complex **9** was isolated using the same procedure as described for complex **8**, however the reaction was stirred at room temperature for ~ 16 h.

Yield: 0.25 g, 35%. M.p. 232–235 °C. ¹H NMR (C₆D₆, 25 °C): δ (ppm) 0.23 (q, ¹J_{H-H} = 8.1 Hz, 4H, ZnCH₂CH₃), 0.62 (d, ${}^{1}J_{H-H} = 6.6$ Hz, 12H, CH(CH₃)₂), 0.72 (d, ${}^{1}J_{H-H} = 7.2$ Hz, 12H, CH(CH₃)₂), 0.83 (t, ${}^{1}J_{H-H}$ = 6.3 Hz, 6H, OCH₂CH₃), 0.89 (d, ${}^{1}J_{H-H}$ = 7.2 Hz, 12H, $CH(CH_3)_2$), 1.11 (d, ${}^{1}J_{H-H} = 6.9 \text{ Hz}$, 12H, $CH(CH_3)_2$), 1.32 (t, ${}^{1}J_{H-H}$ = 6.9 Hz, 6H, ZnCH₂CH₃), 2.82–2.98 (m, 4H, CH(CH₃)₂), 3.20– 3.33 (m, 4H, CH(CH₃)₂), 4.16 (q, ${}^{1}J_{H-H}$ = 6.8 Hz, 4H, OCH₂CH₃), 6.60-6.86 (m, 12H, H_{aryl}), 7.00 (s, 2H, NCHN); ¹³C NMR (C₆D₆, 25 °C): δ (ppm) 5.5 (ZnCH₂CH₃), 9.7 (ZnCH₂CH₃), 12.8 (OCH₂CH₃), 21.1 (CH(CH₃)₂), 21.5 (CH(CH₃)₂), 22.3 (CH(CH₃)₂), 23.2 (CH(CH₃)₂), 26.9 (ZnCH₂CH₃), 27.8 (ZnCH₂CH₃), 28.8 (CH(CH₃)₂), 29.4 (CH(CH₃)₂), 33.3 (CH(CH₃)₂), 37.7 (CH(CH₃)₂), 66.6 (OCH₂CH₃), 121.7 (m-ArC), 122.0 (m-ArC), 122.3 (p-ArC), 122.6 (p-ArC), 129.3 (o-ArC), 137.5 (o-ArC), 144.6 (ArC-N), 145.4 (ArC-N), 166.1 (NCN); IR (v cm⁻¹, Nujol mull): 1665 (m), 1597 (m), 1561 (m), 1287 (m), 1180 (m), 756 (m); MS (*m/z*; found (calc.)): M⁺ not observed, 1042.6 (1042.4) M-Et, 447.2 (447.1) M-20Et-2Et-Zn-2Dipp-2ⁱPr-2H, 365.3 (364.5) L^H.

Supplementary Material

The crystal structure data has been deposited with the CCDC. reference numbers 754580-754588 and is available free of charge at http://www.ccdc.cam.ac.uk.

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