Inorganic Chemistry
Article
pubs.acs.org/IC

Monomeric Group 13 Metal(I) Amides: Enforcing One-Coordination Through Extreme Ligand Steric Bulk

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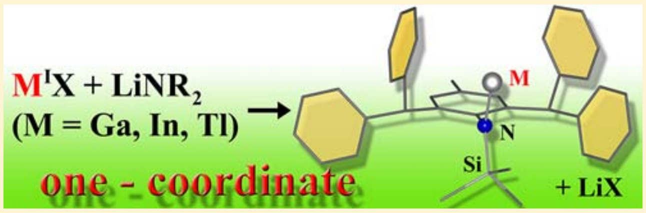
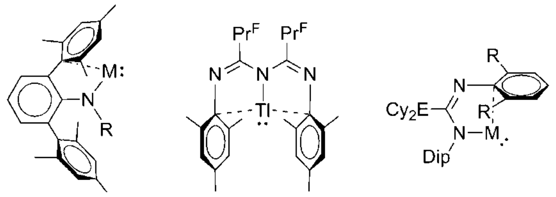
S *Supporting Information*



ABSTRACT: Reactions of the extremely bulky amido alkali metal complexes, [KL′(η^6-toluene)], or in situ generated [LiL′] or [LiL″] {L′/ L″ = N(Ar*)(SiR_3), where Ar* = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4 and R = Me (L′) or Ph (L″)} with group 13 metal(I) halides have yielded a series of monomeric metal(I) amide complexes, [ML′] (M = Ga, In, or Tl) and [ML″] (M = Ga or Tl), all but one of which have been crystallographically characterized. The results of the crystallographic studies, in combination with computational analyses, reveal that the metal centers in these compounds are one coordinate and do not exhibit any significant intra- or intermolecular interactions, other than their N-M linkages. One of the complexes, [InL′], represents the first example of a one-coordinate indium(I) amide. Attempts to extend this study to the preparation of the analogous aluminum(I) amide, [AlL′], were not successful. Despite this, a range of novel and potentially synthetically useful aluminum(III) halide and hydride complexes were prepared en route to [AlL′], the majority of which were crystallographically characterized. These include the alkali metal aluminate complexes, [L′AlH_2(μ-H)Li(OEt_2)$_2$(THF)] and [{L′Al(μ-H)$_3$K}$_2$], the neutral amido-aluminum hydride complex, [{L′AlH(μ-H)}$_2$], and the aluminum halide complexes, [L′$AlBr_2$(THF)] and [L′AlI_2]. Reaction of the latter two systems with a variety of reducing agents led only to intractable product mixtures.

■ INTRODUCTION

Considerable progress has been made in the field of molecular group 13 metal(I) complex chemistry over the past decade.[1] These systems are often very reactive and have found a variety of applications in areas which include coordination chemistry (use as metal-donor Lewis bases),[2] organic synthesis,[3] materials chemistry,[4] and the activation of small molecules,[5] etc. Generally, sterically bulky ligands are required to kinetically stabilize group 13 metal(I) complexes from participating in the disproportionation processes and/or other decomposition pathways. While most work in this area has involved the use of bulky aryl, alkyl, or silyl ligands, anionic N-donor ligands have also played a significant role.[1] Of the latter, bi- and tridentate ligand systems (e.g., β-diketiminates,[6] doubly reduced 1,4-diazabutadienes,[7] guanidinates,[8] tris(pyrazolyl)-borates,[9] etc.) are especially important due to the extra stabilization they offer metal(I) centers through "the chelate effect". With that said, a handful of bulky monodentate amides have been successfully utilized in the preparation of examples of complexes of all the group 13 metals in the +1 oxidation state. These typically aggregate into oligomers through M−M bonding (e.g., as in tetrahedral [{ML}$_4$], where M = Al[10] or Ga[11] and L = −N($SiMe_3$)(Dip); Dip = $C_6H_3Pr^i_2$-2,6 or 2,2′,6,6′-tetramethylpiperidino),[12] weak M···M interactions (e.g., as in [{TlN($SiMe_3$)(Dip)}$_4$][13]), or bridging ligands (e.g., as in [{Tl[μ-N($SiMe_3$)$_2$]}$_2$][14] and [{In(μ-Carb)}$_\infty$], Carb = bulky carbazolyl[15]). Monomeric examples of Ga^I and Tl^I amides and imino-amides (**1**[16,17] and **2**,[18] Figure 1) have been reported, and these can be considered as having quasi one-coordinate metal centers, that also exhibit weak intramolecular arene interactions in the solid state. Related to these compounds are monomeric amidinato, guanidinato and phosphaguanidinato In^I and Tl^I complexes (e.g., **3**,[8,19]) that



1a M = Ga, R = $SiMe_3$
(2.685 Å)
1b M = Tl, R = Me
(2.980 Å)

2
(3.022 Å)

3a M = In, E = P, R = Pr^i
(2.799 Å)
3b M = Tl, E = N, R = Pr^i
(2.928 Å)

Figure 1. Previously reported examples of structurally characterized, monomeric group 13 metal(I) amides (Pr^F = C_3F_7, Dip = $C_6H_3Pr^i_2$-2,6). The shortest M···C_{ipso} interaction is defined with a dotted line (distances given in parentheses).

Received: October 16, 2012
Published: November 16, 2012

display apparently slightly stronger M···arene interactions in the solid state.

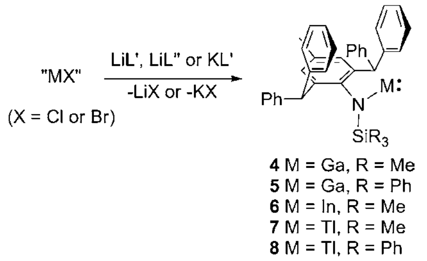
If truly one-coordinate group 13 metal(I) amides were accessible, they could display interesting ambiphilic behavior in their further reactivity (cf. the known chemistry of metal diyls, :MR, where M = group 13 metal and R = alkyl, aryl, etc.[1]). This would result from them possessing only four valence electrons at their metal centers (making them potentially electrophilic), including a metal-based lone pair of electrons (making them potentially nucleophilic). We have recently developed an extremely bulky class of amido ligands [e.g., $-N(Ar^*)(SiR_3)$, where Ar* = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4 and R = Me (L′) or Ph (L″)[20]] which we have shown to have similar stabilizing properties to the very bulky terphenyl ligand class developed by the group of Power.[3c] These ligands have allowed us access to a range of unprecedented low-coordinate group 14 metal amide complexes (e.g., monomeric [L′ECl] (E = Ge or Sn),[20] a singly bonded amido-digermyne [L′Ge-GeL′],[21] the weak intramolecularly arene-stabilized cations $[L'E:]^+$ (E = Ge or Sn),[22] and the acyclic boryl-germylene [L′Ge{B(DAB)}] (DAB = $\{DipNCH\}_2$).[23] It seemed reasonable that these bulky amides could also prove useful for the stabilization of low-coordinate/low-oxidation state group 13 metal complexes. Here, we show that this is the case and report the preparation and characterization of a series of monomeric, essentially one-coordinate amido Ga^I, In^I, or Tl^I complexes. In addition, we detail our unsuccessful attempts to access the corresponding monomeric Al^I amides.

■ RESULTS AND DISCUSSION

(i). Monomeric Gallium(I), Indium(I), and Thallium(I) Amides.

Lithium or potassium complexes of the bulky amide ligands, L′ and L″, were reacted with group 13 metal(I) halides affording the metal(I) amide complexes, **4**–**8**, in moderate to good yields (Scheme 1). It is of note that in these reactions, [LiL′] and [LiL″] were generated in situ prior to use, whereas [KL′] was prepared via the reaction of L′H with $[KN(SiMe_3)_2]$ in toluene and purified as the toluene complex [KL′(η^6-toluene)] prior to use. The spectroscopic and crystallographic characterization of this compound {and the related compound $[KL'(OEt_2)]$} can be found in the Supporting Information. It is also noteworthy that the gallium(I) amides, **4** and **5**, could only be prepared in reasonable yields using $[\{Ga^ICl(THF)\}_n]$ as the gallium source. This metastable complex was synthesized using a specialized reactor for the co-condensation of GaCl and THF in a toluene matrix,[4a] as detailed in the Supporting Information. Attempts to prepare **4** and **5** using the more accessible and thermally stable reagent, "GaI",[24] gave only very low yields of the complexes. Similarly, the indium(I) amide, **6**, could not be prepared in either toluene or THF using poorly soluble InBr as the indium source. Instead, a metastable solution of $[InBr(tmeda)_n]$ was generated by dissolving InBr in a 10% v/v tmeda/toluene mixture at −30 °C.[25] This was then reacted with [KL′(η^6-toluene)] to give **6** in a good isolated yield.

Scheme 1. Preparation of Compounds 4–8 (L′ = N(Ar*)($SiMe_3$) and L″ = N(Ar*)($SiPh_3$); Ar* = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4)



Compounds **4**–**8** are all colorless to pale yellow crystalline solids which are extremely air and moisture sensitive, though thermally stable at room temperature. Their ^1H and ^{13}C NMR spectra are consistent with the molecules possessing C_s symmetry in solution, while the EI mass spectrum of each compound exhibits a molecular ion peak of moderate intensity. The ^{71}Ga and ^{115}In NMR spectra were acquired for concentrated solutions of the gallium and indium amides, though no signals were observed in each case. This is presumably due to the quadrupolar nature of these nuclei (^{71}Ga: $I = 3/2$, natural abundance = 39.6%; ^{115}In: $I = 9/2$, natural abundance = 95.7%) and their unsymmetrical coordination environments, giving rise to significant line broadening. In contrast, the ^{205}Tl NMR spectra (^{205}Tl: $I = 1/2$, natural abundance = 70.5%) of **7** and **8** displayed resonances at $\delta = 3325$ ppm (peak width at half height = 760 Hz) and $\delta = 3029$ ppm (peak width at half height = 820 Hz), respectively. No ^{29}Si satellites were observed about the resonance of either compound. While ^{205}Tl NMR spectroscopic data for Tl^I amides are sparse, these values are comparable to the chemical shift of $\delta = 3229$ ppm reported for the monomeric, three-coordinate complex, $[TlN\{C_6H_3(PMe_2)Me\text{-}2,4\}_2]$.[26]

The crystallographic characterization of **4**, **6**, and **7** revealed the compounds to be isostructural. As a result, only the molecular structure of **4** is depicted in Figure 2 (see Supporting Information for the molecular structures of **6** and **7**), while the structure of the more hindered compound, **5**, is also shown in Figure 2 (see Table 1 for selected metrical parameters of **4**–**7**). All the compounds are monomeric and exhibit no M···M separations closer than 5.4 Å. Their N-centers have trigonal planar geometries, which in the cases of **4**, **5**, and **7** include M–N distances close to those reported for related complexes [e.g., **1a**: Ga–N 1.980(2) Å and **1b**: Tl–N 2.348(3) Å].[17] There are no examples of one-coordinate In^I amides to compare to **6**, but it is of note that its In–N distance is only marginally shorter than that in **3a**, viz. 2.283(2) Å.[8a] It is apparent that the metal centers in **4**–**7** are all essentially one-coordinate. The closest metal–arene interactions involving the flanking $C(H)Ph_2$ groups are to the *ipso*-carbon centers, C(15) and C(28), while the interactions with the *o*-, *m*-, and *p*-carbons of those phenyl groups are substantially longer. It is of note that in the more bulky gallium amide, **5**, the shortest Ga-arene contact involving the $SiPh_3$ group is also very long, at 3.194(4) Å. The lengths of these contacts in the Ga^I and Tl^I amides can be put into context when they are compared with the substantially shorter $M\cdots C_{ipso}$ distances in the quasi-one-coordinate systems, **1** and **2**,[16,17] depicted in Figure 1. Similarly, the contacts in the In^I amide, **6**, are markedly shorter than those in **3a**.[8] While it is likely that there is some interaction between the metal centers of **4**–**7** and their flanking phenyl groups, this must be considered as very weak in each case.

Quantum-chemical calculations (BP86/RI-DFT/def2-TZVPP/def2-SVP) were carried out on **4**, **6**, and **7** in the gas phase. In all cases, their geometries optimized to be very close to those in the experimental solid state structures, including similar arrangements of the phenyl groups about the metal centers (see Table 1 for selected metrical parameters). Analyses

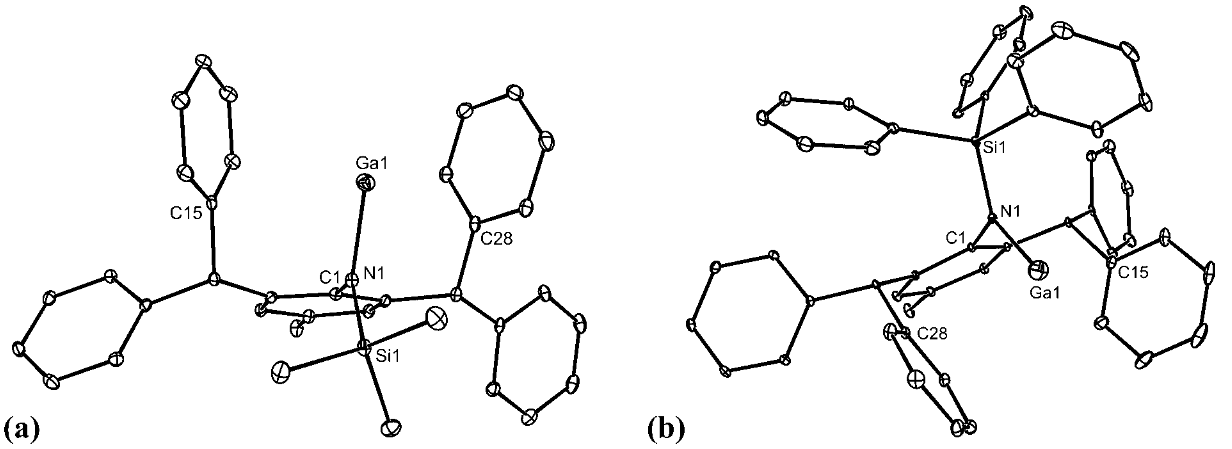


Figure 2. Thermal ellipsoid plot (25% probability surface) of the molecular structures of (a) **4** and (b) **5**. Hydrogen atoms of both structures are omitted. Selected metrical parameters for these compounds and for **6** and **7** are given in Table 1.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 4–7.[a]

	4	5	6	7[b]
M(1)-N(1)	1.954(2) (1.988)	1.985(4)	2.188(2) (2.232)	2.356(13) (2.348)
C(1)–N(1)	1.425(3)	1.435(5)	1.413(3)	1.414(19)
N(1)–Si(1)	1.729(2)	1.726(4)	1.713(2)	1.690(14)
M(1)-C(15)	3.245(2) (3.245)	3.302(4)	3.287(3) (3.322)	3.233(12) (3.334)
M(1)-C(28)	3.120(2) (3.225)	3.122(4)	3.201(3) (3.310)	3.226(15) (3.321)
M(1)-N(1)–Si(1)	121.77(11)	120.7(2)	121.65(12)	118.7(7)
M(1)-N(1)–C(1)	116.60(15)	118.7(3)	116.15(16)	119.0(10)
C(1)–N(1)–Si(1)	121.55(15)	120.5(3)	122.16(18)	122.3(11)

[a] Selected metrical parameters for the calculated (BP86/RI-DFT/def2-TZVPP/def2-SVP) gas phase structures of **4**, **6**, and **7** are given in parentheses. [b] The asymmetric unit of the crystal structure of **7** contains two crystallographically independent molecules. Metrical parameters for only one are given.

of the frontier orbitals of the calculated molecules revealed similar electronic structures. Accordingly, only that for the gallium amide, **4**, will be presented here. The LUMO of the compound essentially comprises an empty Ga-based p-orbital coplanar with the CNSiGa fragment, while the empty p-orbital orthogonal to that fragment is associated with LUMO + 9 (Figure 3). This is directed toward a phenyl ring on each side of the gallium center. However, there does not appear to be any significant Ga-arene bonding interaction taking place in that orbital, or any of the filled MOs near the frontier. The HOMO has character consistent with the N–Ga σ-bond, while the HOMO-4 largely comprises the Ga lone pair, which appears to possess a high s-orbital component. Moreover, there appears to be negligible overlap between the N p-orbital of **4** (HOMO-1) and either empty p-orbital at Ga. Therefore, it seems likely that the degree of N–Ga π-bonding in the compound is not substantial. This picture of the electronic structure of **4** is similar to that arising from computational studies we recently reported for the isoelectronic germanium(II) monocation, $[L'Ge:]^+$.[22] Interestingly, the experimentally determined structure for the cation differs from that of **4**, in that it is unsymmetrical and one phenyl substituent of the ligand displays a weak η^2-arene interaction with the germanium center (Ge···C_{ipso}: 2.642(2) Å; Ge···C_{ortho}: 2.661(2) Å). This difference likely arises from the higher electrophilicity of the cationic germanium center, relative to the gallium center in neutral **4**.

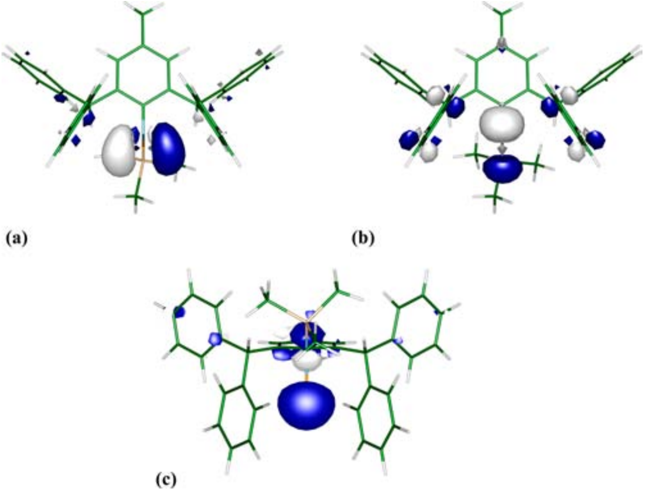


Figure 3. (a) LUMO + 9, (b) LUMO, and (c) HOMO − 4 of **4**.

An NBO charge analysis of **4** revealed that the Ga–N bond is heavily polarized (Ga: +0.88, N: −1.37), as might be expected given the relative electronegativities of the two elements. Consistent with this polarization is the low calculated Wiberg Bond Index (WBI) for the interaction (0.352) and the fact that the lone pair at Ga is almost exclusively of s-character (99.9%). As an indication of the weakness of the Ga–arene interactions in **4**, the calculated WBIs for the two closest Ga···C_{ipso} interactions involving the flanking phenyl groups are both negligible at 0.016.

(ii). Attempted Preparations of Monomeric Aluminum(I) Amides. Although a handful of oligomeric amido aluminum(I) species are known (vide supra), there are no examples of monomeric, one-coordinate systems that have been reported in the literature. Indeed, to the best of our knowledge, there are no reports of any structurally authenticated one-coordinate aluminum(I) complexes.[27] Accordingly, given our success with the preparation of the heavier group 13 amides, **4–8**, we investigated the preparation of the analogous aluminum(I) complex, [AlL′].

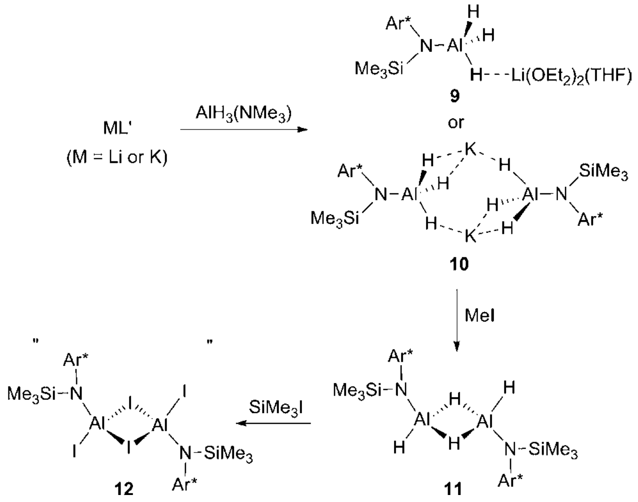
Our initial strategy was to react either [LiL′] or [KL′(η^6-toluene)] with a toluene/THF solution of the metastable aluminum(I) species, [{$Al^ICl(THF)$}$_n$].[4a] Surprisingly, in both cases, no salt elimination reaction was observed, and the alkali metal amide was recovered from the reaction mixture. This contrasts with the successful preparation of the gallium(I) amide, **4**, and reactions of less bulky amide complexes (e.g., [LiN(Dip)($SiMe_3$)]) with aluminum(I) chloride solutions. The latter are known to give large mixed valence, metalloid cluster compounds (e.g., [$Si@Al_{56}${N($SiMe_3$)(Dip)}$_{12}$]).[28] We cannot be certain why no reactions were observed in this study, but the considerable steric bulk of the amide ligand, L′, and the presumably stronger metal−metal bonds in [{$Al^ICl(THF)$}$_n$] relative to those in [{$Ga^ICl(THF)$}$_n$] are most likely contributing factors.

We turned our attention then to the preparation of aluminum(III) halide precursors, [$L'AlX_2$] (X = Br or I), the reduction of which could potentially yield the target complex, [AlL′] (cf. the preparation of [{Al[N($SiMe_3$)(Dip)]}$_4$] via the reduction of [AlI_2{N($SiMe_3$)(Dip)}][10]). To this end, the 1:1 reaction of [KL′(η^6-toluene)] with $AlBr_3$ in THF was carried out, and this afforded a good yield of the crystalline compound, [$L'AlBr_2$(THF)]. This complex was spectroscopically characterized and shown by an X-ray crystallographic study (see Supporting Information) to be monomeric with a distorted tetrahedral aluminum center. Attempts were made to reduce the compound using a number of reagents, viz. KC_8, [Na(naphthalide)], or [{Mg^I(^{Mes}Nacnac)}$_2$] (^{Mes}Nacnac = [$(MesNCMe)_2CH]^-$, where Mes = mesityl[29]), though in all cases intractable mixtures of products were obtained, the NMR spectroscopic analyses of which revealed L′H as a significant component.

It is well-known that p-block metal iodide complexes are typically more easily reduced than their bromide counterparts. As a result, the preparation of [$L'AlI_2$] was attempted via the reaction of [KL′(η^6-toluene)] with AlI_3. Again, this led to an intractable mixture of products and was not pursued further. To overcome this problem, it seemed reasonable, based on the results of previous studies of Roesky[10] and Cui,[30] that either [$L'AlMe_2$] or [$L'AlH_2$] could be iodinated to give [$L'AlI_2$]. However, attempts to prepare those complexes by treatment of L′H with either $AlMe_3$ or [$AlH_3(NMe_3)$] led to no reaction, even at elevated temperatures (*ca.* 70 °C). In light of this, the synthesis of [$L'AlH_2$] was explored using a less direct route. To this end, the reactions of [LiL′] and [KL′(η^6-toluene)] with [$AlH_3(NMe_3)$] were carried out, and these gave moderate and high yields, respectively, of the alkali metal amido−aluminate complexes, **9** and **10** (Scheme 2). Subsequent treatment of either of these with one equivalent of MeI afforded high yields of the neutral amido−aluminum hydride, **11**, the reaction of which with $SiMe_3I$ gave the target aluminum iodide complex, **12**, in excellent yield. Unfortunately, all efforts to reduce **12** to the aluminum(I) amide, [AlL′], by its reaction with KC_8, [Na(naphthalide)], or [{Mg^I(^{Mes}Nacnac)}$_2$] proved fruitless and instead led to unidentifiable product mixtures. That said, **12** and [$L'AlBr_2$(THF)] hold considerable potential for use by synthetic inorganic chemists as precursors for other low oxidation state and/or low coordination number aluminum complexes.

Despite the lack of success in obtaining an aluminum(I) amide complex, the aluminum hydride precursor complexes, **9**−**11**, are of significant novelty in their own right, and as such, a brief discussion of their structural features is worthwhile. The molecular structures of the compounds are depicted in Figure 4. In all compounds, the hydride ligands were located from difference maps and their positional parameters freely refined. Compounds **9** and **10** represent rare examples of alkali metal amido−hydrido−aluminate complexes, while to the best of our knowledge, compound **10** is the first structurally characterized potassium salt of such an aluminate. The lithium aluminate, **9**, is a monomeric contact ion pair which exhibits a single hydride bridge between the Al and Li centers of the salt. This contrasts to analogous systems incorporating less bulky amide ligands, which typically form cyclic dimeric structures (e.g., [{$(SiMe_3)_2NAlH(\mu\text{-}H)_2Li(OEt_2)_2$}$_2$][31] and [{(Dip)[$(Me_3Si)_2HC$]$NAlH(\mu\text{-}H)_2Li(THF)_2$}$_2$]),[30] through two bridging hydrides per Al center. The reluctance of **9** to form a similar dimeric structure is most likely a result of the imposing sterics of its amide ligand. It is noteworthy that the Li center of **9** is coordinated by both THF and diethyl ether molecules because both these solvents were used in the synthesis of the compound. In contrast, no coordinating solvents were utilized in the preparation of **10**, and as a result, this complex crystallizes as an unusual and congested dimer in which each potassium center is connected to both Al centers through three hydride bridges. Furthermore, both potassium centers enhance their electronic satisfaction through η^6- and η^2-interactions with a phenyl group from each amide ligand.

Scheme 2. Syntheses of Compounds 9−12



The steric bulk of the amide ligand can also be used to account for the nature of the structure of **11**. That is, although unsolvated monodentate amido−aluminum dihydride complexes have been previously described, they typically form dimeric or higher nuclearity systems with terminal hydride and bridging amide ligands (e.g., [{$H_2Al(\mu\text{-}NMeEt)$}$_2$][32] and [{$H_2Al(\mu\text{-}NMe_2)$}$_3$].[33] Such an amide bridging motif is disfavored for **11**, and hence, it dimerizes through unsymmetrical hydride bridges. While hydride-bridged structures are unknown for four-coordinate, monodentate amido-aluminum dihydride complexes, they have been reported for five-coordinate systems which incorporate bulky, bidentate anionic N-donor ligands (e.g., as in [{(Piso)AlH(μ-H)}$_2$] (Piso = [$(DipN)_2CBu^t]^-$).[34] Although the crystal structure of the iodide analogue of **11** (viz. **12**) could not be obtained, it seems likely that it has a similar structure to the aluminum hydride complex in the solid state.

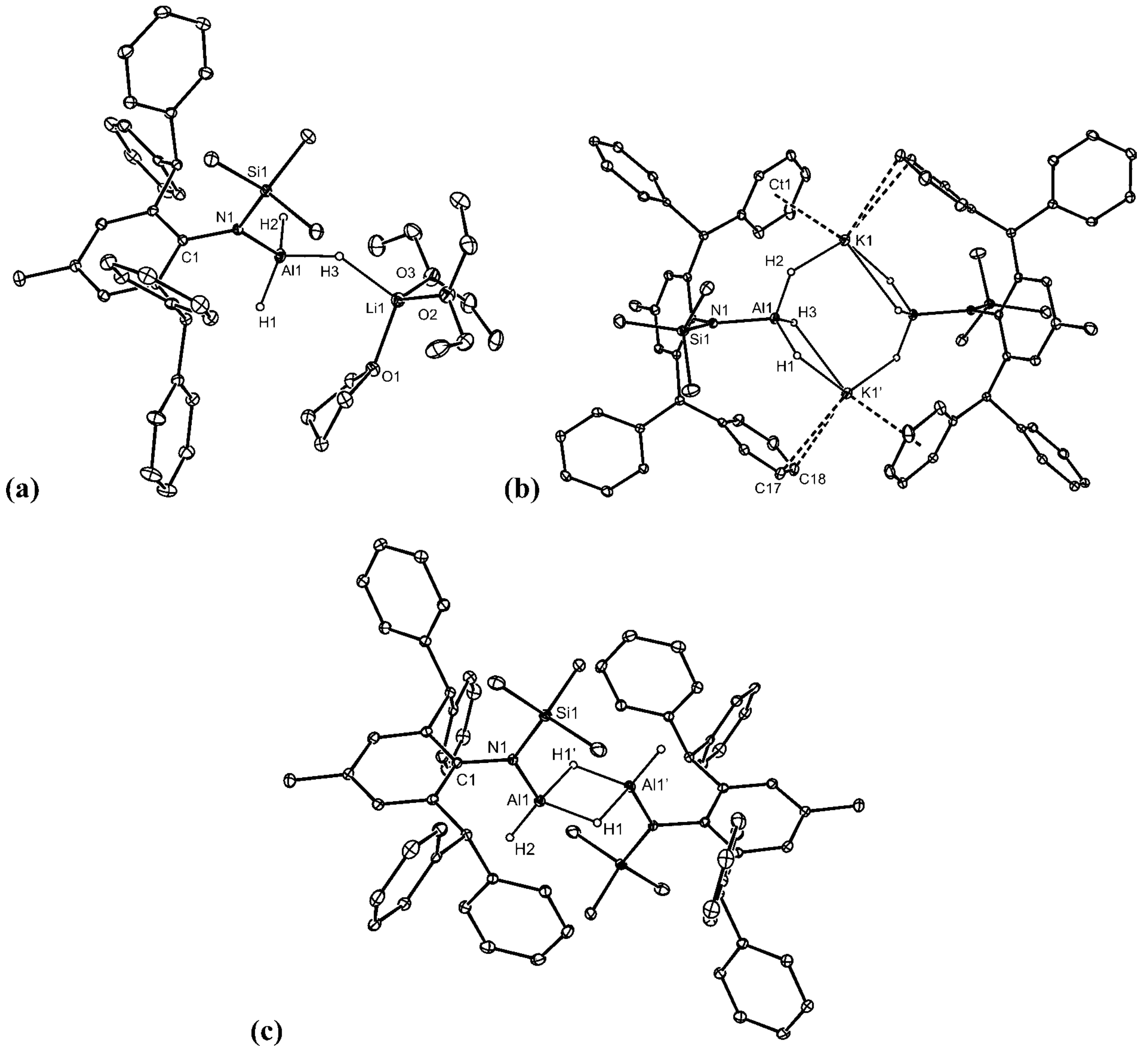


Figure 4. Thermal ellipsoid plot (25% probability surface) of the molecular structures of (a) **9**, (b) **10**, and (c) **11**. Selected bond lengths (Å) and angles (°) for **9**: Al(1)−N(1) 1.8767(18), Al(1)−H(1) 1.48(3), Al(1)−H(2) 1.59(3), Al(1)−H(3) 1.56(3), Li(1)−H(3) 1.88(3), N(1)−Al(1)−H(1) 109.0(11), N(1)−Al(1)−H(2) 112.5(11), N(1)−Al(1)−H(3) 112.9(10). **10**: Al(1)−N(1) 1.8531(17), Al(1)−H(1) 1.53(2), Al(1)−H(2) 1.55(2), Al(1)−H(3) 1.56(2), K(1)−H(2) 2.67(2), K(1)′-H(1) 2.73(2), K(1)′-H(3) 2.74(2), K(1)-Ct(1) 2.950(1), K(1)′-C(17) 3.198(3), K(1)′-C(18), 3.254(3), N(1)−Al(1)−H(1) 111.3(9), N(1)−Al(1)−H(2) 112.0(8), N(1)−Al(1)−H(3) 112.2(9); symmetry operation (′) = −x + 1, −y + 2, −z + 1. **11**: Al(1)−N(1) 1.8050(18), Al(1)−H(1) 1.66(2), Al(1)−H(2) 1.48(2), Al(1)′-H(1) 1.79(2), N(1)−Al(1)−H(2) 123.4(8), H(1)−Al(1)−H(1)′ 81(1); symmetry operation (′) = 1/2 − x, 3/2 − y, 1 − z.

■ CONCLUSIONS

In summary, reactions of alkali metal complexes of extremely bulky amide ligands with heavier group 13 metal(I) halide salts or complexes have afforded a series of monomeric, one-coordinate group 13 metal(I) amides. These include a one-coordinate indium(I) amide, which has no precedent in the literature. The results of computational studies on one of the prepared gallium(I) amides imply that there are negligible interactions between the phenyl groups of the amide ligand and the gallium center, which was also shown to possess a lone pair of essentially s-character. Although attempts to prepare aluminum(I) amides were not successful, several novel bulky amido−aluminum(III) hydride complexes were synthesized and crystallographically characterized en route to the low oxidation state target complex. We are currently further examining the chemistry of the metal(I) amides reported here, including their use as soluble sources of the monovalent metals in metathesis reactions. Our efforts in this direction will be reported in due course.

■ EXPERIMENTAL SECTION

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high purity dinitrogen. THF, hexane, and toluene were distilled over potassium; diethyl ether was distilled over Na/K alloy, while tmeda was distilled over sodium. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AvanceIII 400 spectrometer and were referenced to the resonances of the solvent used. ^{7}Li, ^{27}Al, ^{29}Si{^{1}H}, and ^{205}Tl NMR spectra were recorded on a Bruker AvanceIII 400 spectrometer and were referenced to external 9.7 M aqueous LiCl, 1 M aqueous $[Al(OH_2)_6]^{3+}$, $SiMe_4$, and 0.1 M aqueous $Tl(NO_3)$, respectively. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Perkin-Elmer RX1 FT-IR spectrometer as Nujol mulls between NaCl plates. Microanalyses were carried out by the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. The compounds L′H,[20] L″H[20], and $[AlH_3(NMe_3)]$[35] were prepared by literature procedures, while a 3:1 toluene/THF solution of $[\{Ga^{I}Cl(THF)\}_n]$ (0.34 M) was prepared by a variation of the co-condensation technique developed by Schnöckel[4a] (see Supporting Information for further details). All other reagents were used as received.

Preparation of [KL′(η^6-toluene)]. To a stirred solution of L′H (1.50 g, 2.93 mmol) in THF (30 mL) at −78 °C was added a solution of $[KN(SiMe_3)_2]$ (0.61 g, 3.08 mmol) in THF (10 mL). The reaction mixture was warmed to room temperature and was stirred for 3 h, whereupon volatiles were removed in vacuo, the resulting solid extracted with toluene (40 mL) and the extract filtered. The filtrate was concentrated to *ca.* 20 mL and stored at −30 °C overnight to give colorless crystals of the title compound (1.32 g, 71%.). M.p.: 214–216 °C (dec). ^1H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.42 (s, 9H, Si*Me*$_3$), 2.10 (br s, 6H, overlapping, Ar–C*H*$_3$/toluene-C*H*$_3$), 6.55 (s, 2H, C*H*Ph$_2$), 6.65–7.33 (m, 27H, Ar-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 296 K) δ = 5.4 (Si*Me*$_3$), 21.4 (br, overlapping Ar-CH_3/toluene-CH_3), 53.3 ($CHPh_2$), 125.6, 130.0, 129.2, 137.8, 124.5, 125.7, 127.3, 127.7, 128.5, 128.6, 130.2, 130.6, 139.4, 141.9, 146.5, 151.0 (toluene-*C* and Ar-*C*). $^{29}Si\{^1H\}$NMR (C_6D_6, 80 MHz, 296 K): No signal observed, even for a concentrated sample and long acquisition time. IR (Nujol) ν/cm^{-1} 1596 (m), 1484 (m), 1456 (m), 1373 (m), 1246 (w), 1029 (s), 921 (m), 695 (s). MS (EI 70 eV) *m*/*z* (%): 549.2 (M-$C_7H_8^+$, 42), 512.3 [$(SiMe_3)Ar^*NH_2^+$, 100], 439.2 ($Ar^*NH_2^+$, 50), 167.0 ($CHPh_2^+$, 21). Anal. Calc. for $C_{43}H_{44}KNSi$: 80.45% C, 6.91% H, 2.18% N. Found: 80.37% C, 6.85% H, 2.26% N.

*Preparation of [GaL′] (**4**).* $LiBu^n$ (1.8 mL of a 1.6 M solution in hexane) was added to a solution of L′H (1.40 g, 2.73 mmol) in THF (40 mL) at −78 °C over a period of 2 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon it was concentrated to *ca.* 10 mL. Toluene (40 mL) was then added to the solution and the mixture cooled to −78 °C. $[\{Ga^{I}Cl(THF)\}_n]$ (10.1 mL of a 0.34 M solution in 3:1 toluene/THF) at −80 °C was added to this solution, and the mixture was warmed to room temperature over a period of 12 h, whereupon volatiles were removed in vacuo. The resultant solid was extracted with toluene (40 mL) and filtered. The filtrate was concentrated to ca. 20 mL and stored at −30 °C overnight, yielding a colorless precipitate. This was recrystallized from a minimum volume of diethyl ether to give colorless crystals of **4** (0.98 g, 62%). M.p.: 230–240 °C (decomp to a black solid). ^1H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.42 (s, 9H, Si*Me*$_3$), 1.92 (s, 3H, Ar–C*H*$_3$), 6.13 (s, 2H, C*H*Ph$_2$), 6.85 (s, 2H, *m*-Ar-*H*), 7.02–7.26 (m, 20H, Ar-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 296 K) δ = 3.9 (Si*Me*$_3$), 21.2 (Ar-CH_3), 53.3 ($CHPh_2$), 126.4, 126.5, 128.6, 129.7, 129.9, 130.0, 130.3, 130.4, 142.4, 144.8, 145.0, 147.6 (Ar-*C*). $^{29}Si\{^1H\}$ NMR (C_6D_6, 80 MHz, 296 K) δ = 0.1 (br s). IR (Nujol) ν/cm^{-1}: 1597 (s), 1454 (s), 1378 (s), 1240 (s), 1030 (m), 903 (w). MS (EI 70 eV) *m*/*z* (%) 579.2 (M^+, 55), 512.3 [$(SiMe_3)Ar^*NH_2^+$, 100], 167.0 ($CHPh_2^+$, 26). Anal. Calc. for $C_{36}H_{36}GaNSi$: 74.49% C, 6.25% H, 2.41% N. Found: 74.38% C, 6.20% H, 2.38% N.

N.B.: Compound **4** was alternatively prepared by the 1:1 reaction of [LiL′] and “GaI” (prepared by sonication of a solution of I_2 over a large excess of Ga metal). However, this led only to a low yield (7%) of the compound.

*Preparation of [GaL″] (**5**).* $LiBu^n$ (2.16 mL of a 1.6 M solution in hexane) was added to a solution of L″H (2.30 g, 3.29 mmol) in toluene (40 mL) at −78 °C over 2 min. The reaction mixture was warmed to room temperature and stirred for 2 h, before being cooled back to −78 °C. $[\{Ga^{I}Cl(THF)\}_n]$ (12.1 mL of a 0.34 M solution in 3:1 toluene/THF) was added to this solution, and the mixture was warmed to room temperature over a period of 12 h, whereupon volatiles were removed in vacuo. The resultant solid was extracted with toluene (40 mL) and filtered. The solution was concentrated to ca. 20 mL and stored at −30 °C overnight, yielding an off-white precipitate. This was recrystallized from a minimum volume of hexane to give **5** as colorless crystals (0.86 g, 34%). M.p.: 278–283 °C (dec). ^1H NMR (C_6D_6, 400 MHz, 296 K) δ = 1.92 (br s, 3H, Ar–C*H*$_3$), 6.15 (br s, 2H, C*H*Ph$_2$), 6.49–7.70 (m, 37H, Ar-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 296 K) δ = 21.2 (Ar-CH_3), 52.7 ($CHPh_2$), 126.1, 127.5, 128.4, 129.6, 129.8, 129.9, 130.1, 130.2, 130.3, 136.3, 137.0, 137.8, 141.6, 144.0, 144.9, 148.3 (Ar-*C*). $^{29}Si\{^1H\}$NMR (C_6D_6, 80 MHz, 296 K): δ = −23.5 (br s). IR (Nujol) ν/cm^{-1} 1596 (m), 1493 (m), 1454 (m), 1375 (m), 1252 (w), 1029 (s), 895 (m), 695 (s). MS (EI 70 eV) *m*/*z* (%) 765.2 (M^+, 8), 698.3 [$(SiPh_3)Ar^*NH_2^+$, 45]. Anal. Calc. for $C_{51}H_{42}GaNSi$: 79.89% C, 5.52% H, 1.83% N. Found: 80.06% C, 5.50% H, 1.83% N.

*Preparation of [InL′] (**6**).* A solution of [KL′(η^6-toluene)] (0.50 g, 0.78 mmol) in toluene (40 mL) was added to a solution of InBr (0.154 g, 0.79 mmol) in a 10% tmeda/toluene mixture at −30 °C. The resultant solution was warmed to 0 °C over a period of 5 h. Volatiles were then removed in vacuo and the residue extracted with diethyl ether. The extract was filtered, and the filtrate concentrated to ca. 10 mL, then stored at −30 °C overnight to give colorless crystals of **6** (0.27 g, 56%). M.p.: 210–218 °C (decomp to a black solid). ^1H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.44 (s, 9H, Si*Me*$_3$), 1.98 (s, 3H, Ar–C*H*$_3$), 6.29 (s, 2H, C*H*Ph$_2$), 6.85–7.26 (m, 22H, ArH); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 296 K) δ = 4.7 (Si*Me*$_3$), 21.2 (Ar-CH_3), 53.2 ($CHPh_2$), 126.4, 126.6, 128.6, 128.7, 129.5, 130.0, 130.1, 130.4, 130.6, 141.9, 145.5, 148.4 (Ar-*C*). $^{29}Si\{^1H\}$NMR (C_6D_6, 80 MHz, 296 K) δ = −9.2 (s). IR (Nujol) ν/cm^{-1} 1597 (m), 1462 (s), 1455 (m), 1377 (s), 1260 (m), 1031 (w), 919 (m), 697 (m). MS (EI 70 eV) *m*/*z* (%) 625.2 (M^+, 20), 512.3 [$(SiMe_3)Ar^*NH_2^+$, 100], 167.0 ($CHPh_2^+$, 20); Anal. Calc. for $C_{36}H_{36}InNSi$: 69.12% C, 5.80% H, 2.24% N. Found: 69.21% C, 5.74% H, 2.30% N.

*Preparation of [TlL′] (**7**).* $LiBu^n$ (0.64 mL of a 1.6 M solution in hexane) was added to a solution of L′H (0.50 g, 0.97 mmol) in THF (30 mL) at −78 °C over a period of 2 min. The reaction mixture was warmed to room temperature and stirred for 2 h. The resultant solution was then added to a suspension of TlBr (0.28 g, 0.99 mmol) in THF (10 mL) at −78 °C, and the mixture was warmed to room temperature over a period of 12 h. Volatiles were then removed in vacuo and the residue extracted with diethyl ether. The extract was filtered and the filtrate concentrated to ca. 10 mL and stored at −30 °C overnight to give pale yellow crystals of **7** (0.42 g, 60%). M.p.: 163–168 °C (decomp to a black solid). ^1H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.46 (s, 9H, Si*Me*$_3$), 2.16 (s, 3H, Ar–C*H*$_3$), 6.59 (s, 2H, C*H*Ph$_2$), 6.77 (m, 2H *m*-Ar-*H*), 6.86–7.27 (m, 20H, Ar-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 296 K) δ = 4.6 (Si*Me*$_3$), 21.1 (Ar-CH_3), 52.8 ($CHPh_2$), 126.1, 126.4, 128.4, 128.5, 128.6, 129.9, 130.2, 141.7, 141.8, 144.2, 145.7, 150.0 (Ar-*C*). $^{29}Si\{^1H\}$ NMR (C_6D_6, 80 MHz, 296 K): δ = −12.4 (s); ^{205}Tl NMR (C_6D_6, 230.8 MHz, 296 K) δ = 3325 (peak width at half height = 760 Hz). IR (Nujol) ν/cm^{-1} 1597 (m), 1492 (m), 1455 (m), 1377 (s), 1262 (s), 1074 (w), 1028 (w), 937 (m), 697 (s). MS (EI 70 eV) *m*/*z* (%) 715.2 (M^+, 5), 512.3 [$(SiMe_3)Ar^*NH_2^+$, 100], 439.2 ($Ar^*NH_2^+$, 25), 167.0 ($CHPh_2^+$, 22). Anal. Calc. for $C_{36}H_{36}NSiTl$: 60.46% C, 5.07% H, 1.96% N. Found: 60.37% C, 4.94% H, 1.87% N.

*Preparation of [TlL″] (**8**).* $LiBu^n$ (0.56 mL of a 1.6 M solution in hexane) was added to a solution of L″H (0.60 g, 0.85 mmol) in THF (30 mL) at −78 °C over a period of 2 min. The reaction mixture was warmed to room temperature and stirred for 2 h. The resultant solution was then added to a suspension of TlBr (0.25 g, 0.87 mmol) in THF (10 mL) at −78 °C, whereupon it was warmed to room temperature over a period of 12 h. Volatiles were then removed in vacuo and the residue extracted with toluene (20 mL). The extract was filtered and the filtrate concentrated to ca. 10 mL and placed at −30 °C overnight to give **8** as a yellow crystalline solid (0.56 g, 73%). M.p.: 235–242 °C (decomp to a black solid). ^1H NMR (C_6D_6, 400 MHz, 296 K) δ = 2.16 (s, 3H, Ar–C*H*$_3$), 6.49 (s, 2H, C*H*Ph$_2$), 6.66–7.73 (m, 37H, Ar-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 296 K) δ = 20.9 (Ar-CH_3), 52.1 ($CHPh_2$), 125.9, 126.3, 128.1, 128.2, 128.8, 129.3, 130.1, 130.5, 135.2, 136.3, 136.8, 140.1, 141.0, 144.6, 145.6, 150.7 (Ar-*C*). $^{29}Si\{^1H\}$NMR (C_6D_6, 80 MHz, 296 K) δ = −27.4 (s); ^{205}Tl NMR (C_6D_6, 230.8 MHz, 296 K) δ= 3029 (peak width at half height = 820 Hz). IR (Nujol) ν/cm^{-1} 1596 (m), 1493 (m), 1376 (s), 1260 (s), 1104 (s), 1028 (w), 936 (m), 699 (s). MS (EI 70 eV) *m*/*z* (%) 901.3

Table 2. Summary of Crystallographic Data for 4–7, 9–11, [L′AlBr$_2$(THF)], [KL′(η^6-toluene)], and [KL′(OEt$_2$)]

	4	**5**	**6**	**7**	**9**	**10**•(toluene)$_2$	**11**	[L′AlBr$_2$(THF)]•(toluene)	[KL′(η^6-toluene)]	[KL′(OEt$_2$)]
empirical formula	$C_{36}H_{36}GaNSi$	$C_{51}H_{42}GaNSi$	$C_{36}H_{36}InNSi$	$C_{36}H_{36}NSiTl$	$C_{48}H_{67}AlLiNO_3Si$	$C_{86}H_{94}Al_2K_2N_2Si_2$	$C_{72}H_{76}Al_2N_2Si_2$	$C_{47}H_{52}AlBr_2NOSi$	$C_{43}H_{44}KNSi$	$C_{40}H_{46}KNOSi$
formula weight	580.47	766.67	625.57	715.12	768.04	1343.97	1079.49	861.79	641.98	623.97
crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	*P*-1	*P*-1	$P2_1/n$	*P*-1	$C2/c$	*P*-1	*P*-1	$C2/c$
a (Å)	9.9435(5)	10.5031(4)	9.228(4)	10.3441(4)	12.9536(3)	10.2955(5)	28.906(2)	10.8455(4)	10.1389(3)	16.9915(6)
b (Å)	10.4360(4)	10.7024(4)	10.4818(4)	10.3596(4)	25.9791(6)	12.6163(7)	9.7641(5)	11.0069(5)	10.2967(4)	11.2798(4)
c (Å)	15.0534(8)	19.9408(8)	15.0271(6)	31.3869(11)	13.7056(4)	15.1988(7)	23.958(2)	18.8926(8)	19.1038(7)	36.4772(13)
α (deg)	90.098(4)	94.447(3)	90.361(3)	88.429(3)	90	100.176(4)	90	82.820(4)	102.997(3)	90
β (deg)	107.111(4)	90.037(3)	106.816(3)	89.341(3)	97.686(2)	99.877(4)	116.129(10)	73.508(3)	92.524(3)	95.084(4)
γ (deg)	92.642(3)	118.298(4)	92.706(3)	64.926(4)	90	91.641(4)	90	76.903(3)	110.950(3)	90
vol (Å^3)	1491.17(12)	1965.91(13)	1494.12(10)	3045.3(2)	4570.8(2)	1910.79(17)	6070.8(8)	2101.83(15)	1797.77(11)	6963.7(4)
Z	2	2	2	4	4	1	4	2	2	8
ρ (calcd) (g.cm^{-3})	1.293	1.295	1.390	1.560	1.116	1.168	1.181	1.362	1.186	1.190
μ (mm^{-1})	0.988	0.767	0.856	5.368	0.110	0.223	0.131	2.014	0.212	0.218
F(000)	608	800	644	1416	1664	716	2304	892	684	2672
reflections collected	10601	31344	23709	21146	20815	12561	18415	13816	27427	21382
unique reflections	6455	8569	6461	13191	9904	7451	5464	8210	7837	6831
R_{int}	0.0260	0.0324	0.0440	0.0503	0.0276	0.0413	0.0644	0.0335	0.0341	0.0328
R1 indices [$I > 2\sigma(I)$]	0.0418	0.0857	0.0369	0.1081	0.0583	0.0479	0.0466	0.0536	0.0394	0.0449
*w*R2 indices (all data)	0.1073	0.2837	0.0906	0.2471	0.1644	0.1253	0.1092	0.1329	0.1003	0.1074
CCDC No.	903988	903989	903990	903991	903992	903986	903987	903983	903985	903984

(M^+, 25), 698.3 [$(SiPh_3)Ar^*NH_2^+$, 47]. A reproducible microanalysis for this compound could not be obtained.

Preparation of [L′AlBr$_2$(THF)]. To a solution of $AlBr_3$ (0.20 g, 0.78 mmol) in toluene (10 mL) at −78 °C was added a solution of [KL′(η^6-toluene)] (0.50 g, 0.78 mmol) in toluene (30 mL) over 5 min. The resultant solution was warmed to room temperature over 12 h, whereupon volatiles were removed in vacuo to give an off-white solid. This residue was dissolved in toluene and layered with hexane to give colorless crystals of the title compound (0.473 g, 79%.). M.p.: 119−121 °C. ^{1}H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.24 (s, 9H, Si*Me*$_3$), 0.74 (m, 4H, THF-C*H*$_2$), 1.95 (s, 3H, Ar−C*H*$_3$), 3.36 (m, 4H, THF-OC*H*$_2$), 6.82 (s, 2H, C*H*Ph$_2$), 6.94−7.60 (m, 22H, Ar-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 296 K) δ = 4.0 (Si*Me*$_3$), 21.3 (Ar-CH$_3$), 24.3 (THF-CH$_2$), 51.4 (CHPh$_2$), 75.0 (THF-OCH$_2$), 126.2, 126.4, 128.3, 128.5, 129.2, 129.9, 130.4, 130.9, 133.7, 141.6, 145.1, 145.6 (Ar-C). ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 296 K) δ = 4.1 (s). ^{27}Al NMR (C_6D_6, 104.2 MHz, 296K) δ = 97.4 (br s). IR (Nujol) ν/cm^{-1} 1598 (s), 1377 (s), 1247 (s), 1123 (m), 1078 (m), 1032 (w), 899 (s), 704 (s), 605 (m). MS (EI 70 eV) *m*/*z* (%) 697.1 (M^+-THF, 7), 512.3 [$(SiMe_3)Ar^*NH_2^+$, 30], 439.3 ($Ar^*NH_2^+$, 100), 167.0 ($CHPh_2^+$, 35). Anal. Calc. for $C_{40}H_{44}AlBr_2NOSi$: 62.42% C, 5.76% H, 1.82% N. Found: 62.27% C, 5.88% H, 1.93% N.

Preparation of [L′AlH$_2$(μ-H)Li(OEt$_2$)$_2$(THF)] (9). LiBu^n (0.65 mL of a 1.6 M solution in hexane) was added to a solution of L′H (0.50 g, 0.97 mmol) in THF (30 mL) at −78 °C over 2 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was dissolved in diethyl ether and cooled to −78 °C, after which [$AlH_3(NMe_3)$] (1.53 mL of a 0.67 M solution in toluene) was added, and the mixture was warmed to room temperature over 12 h. The reaction solution was then filtered and the filtrate concentrated to ca. 10 mL and stored at −30 °C overnight to give colorless crystals of **9** (0.37 g, 49%). M.p.: 192 °C (dec). ^{1}H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.12 (s, 9H, Si*Me*$_3$), 1.04 (t, 12H, OCH$_2$C*H*$_3$), 1.23 (m, 4H, THF-C*H*$_2$), 2.00 (s, 3H, Ar−C*H*$_3$), 3.21 (q, 8H, OC*H*$_2$CH$_3$), 3.42 (m, 4H, THF-OC*H*$_2$), 6.82 (s, 2H, C*H*Ph$_2$), 7.06−7.59 (m, 22H, Ar-*H*), Al*H* resonance not observed. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 296 K) δ = 3.0 (Si*Me*$_3$), 15.2 (OCH$_2$CH$_3$), 21.1 (Ar-CH$_3$), 25.2 (THF-CH$_2$), 51.7 (CHPh$_2$), 65.8 (OCH$_2$CH$_3$), 68.7 (THF-OCH$_2$), 125.7, 126.2, 128.1, 128.2, 129.3, 130.8, 130.9, 131.0, 141.5, 144.9, 148.4, 150.0 (Ar-C). ^{7}Li NMR (C_6D_6, 155 MHz, 296K) δ = −0.45 (s). ^{27}Al NMR (C_6D_6, 104.2 MHz, 296K) δ = 115.0 (br s). IR (Nujol) ν/cm^{-1} 1645 (Al−H, br s), 1595 (m), 1493 (m), 1247 (s), 1257 (s), 1131 (m), 1076 (m), 930 (s), 786 (s). MS (EI 70 eV) *m*/*z* (%): 512.3 [$(SiMe_3)Ar^*NH_2^+$, 100], 439.2 ($Ar^*NH_2^+$, 22), 167.0 ($CHPh_2^+$, 20). Anal. Calc. for $C_{48}H_{67}AlLiNO_3Si$: 75.06% C, 8.79% H, 1.82% N. Found: 74.95% C, 8.81% H, 1.85% N.

Preparation of [{L′Al(μ-H)$_3$K}$_2$] (10). To a solution of [KL′(η^6-toluene)] (0.85 g, 1.32 mmol) in toluene (30 mL) at −78 °C was added [$AlH_3(NMe_3)$] (1.33 mL of a 1.04 M solution in toluene) over 2 min. The resultant solution was warmed to room temperature over 12 h, whereupon volatiles were removed in vacuo to give an off-white solid. This residue was dissolved in toluene and layered with hexane to give colorless crystals of **10** (0.69 g, 91%). Mp: 115−118 °C (decomp). ^{1}H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.37 (s, 18H, Si*Me*$_3$), 1.99 (s, 6H, Ar−C*H*$_3$), 6.82 (s, 4H, C*H*Ph$_2$), 6.85 (m, 4H *m*-Ar-*H*), 6.97−7.42 (m, 40H, Ar-*H*), no Al*H* resonance observed. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 296 K) δ = 3.0 (Si*Me*$_3$), 21.3 (Ar-CH$_3$), 51.3 (CHPh$_2$), 125.7, 126.4, 128.4, 128.4, 129.0, 129.2, 130.3, 130.4, 130.7, 141.6, 145.4, 148.1 (Ar-C). ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 296 K): No signal observed, even for a concentrated sample and long acquisition time. ^{27}Al NMR (C_6D_6, 104.2 MHz, 296K) δ = 117.9 (br s). IR (Nujol) ν/cm^{-1} 1640 (Al−H, br s), 1493 (m), 1377 (s), 1261 (s), 1098 (s), 1029 (w), 922 (m), 795 (s), 761 (s), 722 (s). MS (EI 70 eV) *m*/*z* (%) 1119.4 (M^+−K, 15), 540.2 [$(SiMe_3)Ar^*NAlH_3^+$, 72], 512.2 [$(SiMe_3)Ar^*NH_2^+$, 100], 167.0 ($CHPh_2^+$, 8). Anal. Calc. for $C_{72}H_{78}Al_2K_2N_2Si_2$: 74.57% C, 6.78% H, 2.42% N. Found: 74.62% C, 6.74% H, 2.49% N.

Preparation of [{L′AlH(μ-H)}$_2$] (11). To a solution **10** (0.50 g, 0.86 mmol) in toluene (30 mL) at −78 °C was added CH_3I (0.147 g, 1.03 mmol). The resultant solution was warmed to room temperature over 12 h, whereupon volatiles were removed in vacuo to give an off-white solid. This residue was dissolved in toluene and layered with hexane to give colorless crystals of **11** (0.40 g, 86%). M.p.: 264−268 °C. ^{1}H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.21 (s, 18H, Si*Me*$_3$), 1.91 (s, 6H, Ar−C*H*$_3$), 3.15 (br s, 4H, Al*H*), 6.14 (s, 4H, C*H*Ph$_2$), 6.96 (m, 4H *m*-Ar-*H*), 7.00−7.29 (m, 40H, Ar-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 296 K) δ = 3.1 (Si*Me*$_3$), 21.3 (Ar-CH$_3$), 52.7 (CHPh$_2$), 125.6, 126.5, 128.5, 128.57, 129.1, 129.2, 130.1, 130.4, 130.8, 142.5, 142.6, 145.5 (Ar-C). ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 296 K) δ = 5.0 (s). IR (Nujol) ν/cm^{-1} 1890 (Al−H, br s), 1493 (s), 1376 (s), 1250 (s), 1076 (m), 1031 (w), 909 (m), 728 (m), 698 (s). MS (EI 70 eV) *m*/*z* (%): 512.3 [$(SiMe_3)Ar^*NH_2^+$, 100], 439.3 ($Ar^*NH_2^+$, 25), 167.0 ($CHPh_2^+$, 24). Anal. Calc. for $C_{72}H_{76}Al_2N_2Si_2$: 80.11% C, 7.10% H, 2.59% N. Found: 79.99% C, 7.17% H, 2.61% N.

N.B. Compound **11** can be similarly prepared in high yield via the reaction of **9** with CH_3I.

Preparation of [L′AlI$_2$] (12). To a solution of **11** (0.30 g, 0.55 mmol) in toluene (20 mL) at −78 °C was added Me_3SiI (0.22 g, 1.11 mmol). The resultant solution was warmed to room temperature over 12 h, whereupon volatiles were removed in vacuo to give an off-white solid. This residue was dissolved in toluene and layered with hexane to give colorless crystals of **12** (0.37 g, 84%). Mp: 180−186 °C (decomp). ^{1}H NMR (C_6D_6, 400 MHz, 296 K) δ = 0.42 (s, 9H, Si*Me*$_3$), 1.88 (s, 3H, Ar−C*H*$_3$), 6.19 (s, 2H, C*H*Ph$_2$), 6.95−7.51 (m, 22H, Ar-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 296 K) δ = 4.8 (Si*Me*$_3$), 21.1 (Ar-CH$_3$), 52.5 (CHPh$_2$), 126.7, 128.6, 128.7, 129.2, 129.8, 130.1, 130.3, 132.8, 133.2, 141.3, 143.4, 146.4 (Ar-C). ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 296 K) δ = 7.1 (s). IR (Nujol) ν/cm^{-1} 1598 (w), 1493 (m), 1250 (m), 1077 (m), 1031 (w), 903 (m), 699 (s). MS (EI 70 eV) *m*/*z* (%) 790.9 (M^+, 12), 679.1 (M^+−I, 100). Anal. Calc. for $C_{36}H_{32}AlI_2NSi$: 54.62% C, 4.58% H, 1.77% N. Found: 54.52% C, 4.69% H, 1.80% N.

X-ray Crystallography. Crystals of **4**−**7**, **9**−**11**, [L′AlBr$_2$(THF)], [KL′(η^6-toluene)] and [KL′(OEt$_2$)] suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were carried out at 123 K with an Oxford Gemini Ultra diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 by full matrix least-squares (SHELX97),[36] using all unique data. All non-hydrogen atoms are anisotropic with non-hydride hydrogen atoms included in calculated positions (riding model). The positional parameters of the hydride ligands of **9**−**11** were freely refined. The high *r*-factors for the crystal structures of **5** and **7** are due to the samples used in the diffraction experiments being non-merohedral twins. In both cases, the diffraction pattern arising from the minor twin component could not be deconvoluted from the diffraction pattern of the major component. Despite this, the molecular connectivity of the structures are unambiguous, and their metrical parameters should be considered as reliable, within the estimated standard deviations (ESDs) of the parameters. In addition, there are two crystallographically independent molecules of **7** in the asymmetric unit of its crystal structure. There are no significant geometric differences between them. Crystal data, details of data collections, and refinement are given in Table 2.

Computational Studies. For quantum-chemical calculations, Turbomole[37] (version 5.9) was used, employing the Becke−Perdew 86-functional[38] at RI-DFT[39] level with the def2-SVP basis set[40] for Si, N, C, and H atoms and the def2-TZVPP basis set for Ga, In, and Tl atoms.[41] The molecular orbitals of the global minimum energy structure of each compound (showing zero imaginary frequencies) were visualized with the aid of molden.[42] NBO orbital and Wiberg Bond Index analyses were performed for [GaL′] using Gaussian09[43] and NBO 3.0[44] at the very same combination of functional and basis sets as above.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data as CIF files for all crystal structures; ORTEP diagrams for **6**, **7**, [L′AlBr$_2$(THF)], [KL′(η^6-toluene)], and [KL′(OEt$_2$)]; selected metrical parameters for [L′AlBr$_2$(THF)], [KL′(η^6-toluene)], and [KL′(OEt$_2$)], and further details of the synthetic and computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Australian Research Council (grant to C.J.) and the U.S. Air Force Asian Office of Aerospace Research and Development (Grant FA2386-11-1-4110 to C.J.). The EPSRC is also thanked for access to the U.K. National Mass Spectrometry Facility.

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