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Synthesis and Characterization of Thermally Robust Amidinato Group 13 Hydride Complexes

Marcus L. Cole,[b] Cameron Jones,*[a] Peter C. Junk,[b] Marc Kloth,[a] and Andreas Stasch[a]

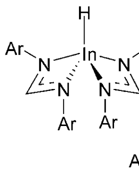
Abstract: The reactivity of two sterically bulky amidines, ArNC(R)N(H)Ar (Ar = 2,6-diisopropylphenyl; R = H (HFiso); *t*Bu, (HPiso)) towards $LiMH_4$, M = Al or Ga, $[AlH_3(NMe_3)]$, and $[GaH_3(quin)]$ (quin = quinuclidine) has been examined. This has given rise to a variety of very thermally stable aluminum and gallium hydride complexes. The structural motif adopted by the prepared complexes has been found to be dependent upon both the amidinate ligand and the metal involved. The 1:1 reaction of HFiso with $LiAlH_4$ yielded dimeric $[\{AlH_3(\mu\text{-Fiso})Li(OEt_2)\}_2]$. Amidine HFiso reacts in a 1:1 ratio with $[AlH_3(NMe_3)]$ to give the unusual hydride-bridging dimeric complex, $[\{AlH_2(Fiso)\}_2]$, in which the $Fiso^-$ ligand is nonchelating. The equivalent reaction with the bulkier amidine, HPiso, yielded a related hydride-bridging complex, $[\{AlH_2(Piso)\}_2]$, in which the $Piso^-$ ligand is chelating. In contrast, the treatment of $[GaH_3(quin)]$ with one equivalent of HFiso afforded the four-coordinate complex $[GaH_2(quin)(Fiso)]$, in which the $Fiso^-$ ligand acts as a localized monodentate amido–imine ligand. The 2:1 reactions of HFiso with $[AlH_3(NMe_3)]$ or $[GaH_3(quin)]$ gave the monomeric complexes $[MH(Fiso)_2]$, which are thermally robust and which exhibit chelating amidinate ligands. In contrast, HPiso did not give 2:1 complexes in its reactions with either of the Group 13 trihydride precursors. For sake of comparison, the reactions of $[AlH_3(NMe_3)]$ and $[GaH_3(quin)]$ with the bulky carbodiimide ArN=C=NAr and the thiourea Ar(H)NC(=S)N(H)Ar were examined. These last reactions afforded the five-coordinate thioureido complexes, $[MH\{N(Ar)C[N(H)(Ar)]S\}_2]$, M = Al or Ga.

Keywords: aluminum · amidinates · gallium · hydrides · structure elucidation

Introduction

The coordination chemistry of the amidinate class of ligand, $[RNC(R')NR]^-$, has been widely studied. The substituents on the nitrogen atoms and backbone carbon centers can be readily varied and a large number of transition-metal, lanthanide, and main-group-metal complexes exhibiting a range of amidinate coordination modes have now been prepared.[1] In Group 13, amidinate complexes of metal alkyl and halide fragments have been extensively investigated[2] over recent years and have found application, for example, as olefin polymerization catalysts[2e–i] and chemical vapor deposition (CVD) precursors.[2j] Surprisingly, however, only one structurally authenticated amidinato Group 13 hydride complex, namely, $[AlH\{(Me_3Si)NC(Ph)N(SiMe_3)\}_2]$,[3] has been reported prior to our involvement in the field.

We recently extended this work by using the bulky formamidinate ligand $[ArNC(H)NAr]^-$ (Ar = 2,6-diisopropylphenyl; $Fiso^-$) to kinetically stabilize the first structurally characterized amido indium hydride complex, $[InH(Fiso)_2]$ (**1**; decomp 160–170 °C).[4] The remarkable thermal stability of this complex arises partly from the protection afforded to the InH fragment by the bulky $Fiso^-$ ligands; this is thought to circumvent associative decomposition pathways involving intermolecular In-H-In bridges. The proposed intermediate



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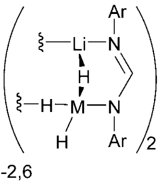

2 M = In
3 M = Ga

Ar = $C_6H_3iPr_2$-2,6

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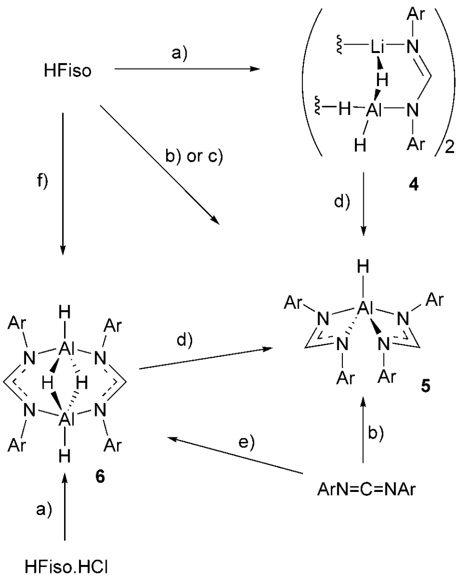
in the formation of **1** from the reaction of $LiInH_4$ with two equivalents of HFiso was isolated in the corresponding 1:1 reaction. This amidotrihydridoindate complex (**2**) has a hydride-bridging dimeric structure. Its gallium analogue (**3**) has also been prepared, but does not react with HFiso to give $[GaH(Fiso)_2]$, that is, the counterpart of **1**.[4] This difference is believed to arise from the aversion of gallium hydride fragments to attain coordination numbers greater than four.[5]

Considering the importance of Group 13 alkyl– and halide–amidinate complexes, and the relative paucity of analogous Group 13 hydride complexes, we saw a systematic extension of our preliminary efforts in this area as being worthwhile. Herein, we report on the synthesis and properties of a variety of aluminum and gallium hydride complexes derived from the $Fiso^-$ ligand and its bulkier pivamidinate counterpart, $[ArNC(tBu)NAr]^-$, $Piso^-$. Differences in the structure and thermal stabilities of these complexes are rationalized in terms of the steric bulk of their amidinate ligands and the electronic properties of the Group 13 metal.

Results and Discussion

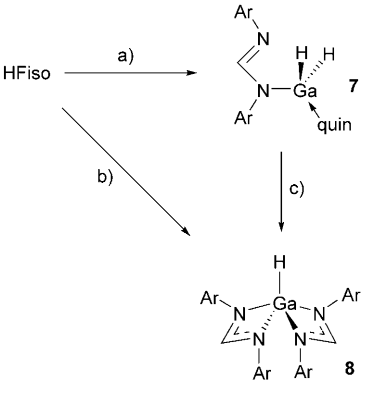
Syntheses: To test the generality of the reaction that gave **2** and **3**, HFiso was treated with one equivalent of $LiAlH_4$ in diethyl ether which led to a good yield (77%) of the expected amidotrihydridoalanate complex (**4**) after recrystallization from hexane (Scheme 1). When **4** was treated with a further equivalent of HFiso in THF, or when $LiAlH_4$ was reacted with HFiso in a 2:1 stoichiometry, the monomeric complex $[AlH(Fiso)_2]$ (**5**) was reproducibly formed in isolated yields of approximately 60% by means of H_2 and LiH elimination processes. This can be compared to the analogous preparation of the indium hydride complex (**1**) and in light of the lack of reactivity of the gallium hydride complex (**3**) towards HFiso, it tends to confirm that the relative polarity of M−H bonds is $M = Al > Ga < In$. Compound **5** can alternatively be prepared through H_2 elimination in the 2:1 reaction between HFiso and $[AlH_3(NMe_3)]$ (87% yield), or by the hydroalumination of two equivalents of the carbodiimide (ArN=C=NAr) with $[AlH_3(NMe_3)]$ in toluene (71% yield). This latter reaction can be compared to previously reported formations of amidinate aluminum methyl complexes from the treatment of carbodiimides with $AlMe_3$.[2h]



Scheme 1. Synthesis of compounds **4**–**6**, (HFiso = ArNC(H)N(H)Ar); a) $LiAlH_4$, Et_2O; b) $0.5[AlH_3(NMe_3)]$, toluene; c) $0.5LiAlH_4$, THF; d) HFiso, THF or toluene; e) $2[AlH_3(NMe_3)]$, toluene; f) $[AlH_3(NMe_3)]$, toluene.

In an attempt to form a neutral mono(amidinato) aluminum hydride complex, a solution of HFiso in toluene was slowly added to one equivalent of $[AlH_3(NMe_3)]$ at −78 °C. Surprisingly, this resulted in a mixture of **5** and the unusual dimeric complex $[\{AlH(\mu\text{-}H)(Fiso)\}_2]$ (**6**), which could be separated by fractional crystallization (Scheme 1). Complex **6** could alternatively be prepared in good yield (69%) by reaction of the hydrochloride salt, HFiso·HCl, with a solution of $LiAlH_4$ in diethyl ether or by heating a 2:1 mixture of $[AlH_3(NMe_3)]$ and the carbodiimide (ArN=C=NAr) at reflux in toluene for 45 minutes (62% yield). When complex **6** was treated with one equivalent of HFiso in toluene, H_2 elimination occurred and the monomeric bis(amidinato) complex **5** was formed cleanly.

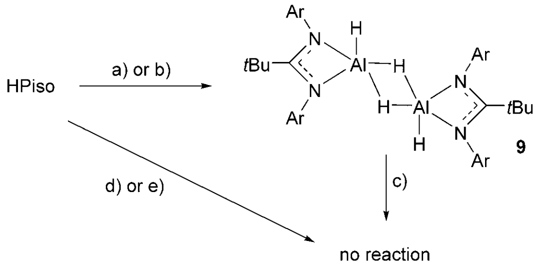
It is interesting that an effort to prepare the gallium counterpart of **6** by treating $[GaH_3(quin)]$ (quin = quinuclidine) with one equivalent of HFiso in diethyl ether led instead to the monomeric amido–gallane complex (**7**) in low-to-moderate yield (38%; Scheme 2). Presumably, the different outcome here results partly from the relatively strong Lewis basicity of quinuclidine (cf. Brønsted pK_a 10.95[6]), which makes it more difficult to displace from the gallium center of **7** by the imine arm of the $Fiso^-$ ligand than it is to displace NMe_3 (pK_a 9.81[6]) from the aluminum center of any intermediate in the formation of **6**. Another contributing factor is likely to be the well-documented preference for gallium hydride fragments to prefer a coordination number of four (as in **7**) as opposed to more Lewis acidic aluminum



Scheme 2. Synthesis of compounds **7** and **8** (HFiso = ArNC(H)N(H)Ar); a) $[GaH_3(quin)]$, Et_2O; b) $0.5[GaH_3(quin)]$, Et_2O; c) HFiso, Et_2O.

hydride fragments, which favor five- or six-coordination (as in **6**).[5] This being said, the reaction of **7** with a second equivalent of HFiso did lead to displacement of the quinuclidine ligand and the formation of the five-coordinate complex **8**, which can also be formed in the one pot reaction of [GaH_3(quin)] with two equivalents of HFiso. This contrasts to the lack of reactivity of **3** towards HFiso, which must be due to the reluctance of this complex to eliminate LiH in the presence of excess amidine.

It was reasoned that increasing the steric bulk of the amidinate ligand should lead to more thermally stable complexes and perhaps different structural motifs. To this end, a derivative of HFiso with a *tert*-butyl substituent on the amidine backbone, namely, ArN(H)C(*t*Bu)NAr (HPiso), was treated with one equivalent of [$AlH_3(NMe_3)$] in toluene to give [{AlH(μ-H)(Piso)}$_2$] (**9**) in good yield (83%; Scheme 3).

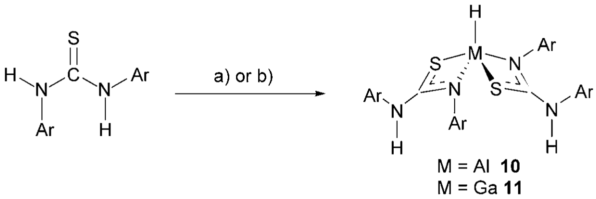


Scheme 3. Reactions of HPiso with Group 13 hydride complexes (HPiso = ArNC(*t*Bu)N(H)Ar); a) [$AlH_3(NMe_3)$], toluene; b) $LiAlH_4$, Et_2O; c) HPiso, toluene, reflux; d) [GaH_3(quin)], toluene; e) $LiGaH_4$, Et_2O.

Like **6**, this is a dimeric compound, but its amidinate ligands each chelate one aluminum center rather than bridging the two metals, as is the situation for **6**. This difference presumably stems from the greater bulk of the Piso$^-$ ligand over that of Fiso$^-$ which favors aluminum chelation for the former. Indeed, this ligand has previously demonstrated aluminum chelation in mono(amidinato) complexes, for example, [$AlMe_2$(Piso)].[2h] The corresponding reaction of [$AlH_3(NMe_3)$] in toluene with two equivalents of HPiso at room temperature or even in boiling toluene did not lead to a second hydrogen elimination and the formation of [AlH(Piso)$_2$], but instead returned only **9** and unreacted HPiso. Again, this can be explained by the considerable steric bulk of the Piso$^-$ ligand. It is also noteworthy that the 1:1 reaction of HPiso with $LiAlH_4$ in diethyl ether did not lead to an analogue of **4**, but instead gave **9** as the major product. In contrast to the reactions with aluminum hydrides, HPiso did not react with [GaH_3(quin)] in toluene at room temperature or even at 60°C. Heating a solution of the reactants in toluene at reflux for one hour led only to the decomposition of the gallane complex and deposition of gallium metal. Similarly, treating HPiso with either $LiInH_4$ or [$InH_3(NMe_3)$] under a variety of stoichiometries led only to decomposition of the indium hydride species present upon workup, evidenced by the precipitation of significant quantities of indium metal from the reaction mixtures.

Jordan[2e] and Arnold[2b] have shown that bulky amidinato–$AlMe_2$ complexes can undergo methyl abstraction reactions to give the corresponding cationic species. These have considerable potential, for example, in olefin polymerization processes due to the enhanced electrophilicity of their metal centers. Cationic aluminum hydride complexes are rare, but if examples could be accessed with low coordination numbers at the metal center they may well find similar applications. We believed the Piso$^-$ ligand might stabilize such complexes and thus investigated the reactions of **9** with one equivalent of either Brookhart's acid, [$H(OEt_2)_2$][BAr_F],[7] or [CPh_3][BAr_F], $[BAr_F]^- = [B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$. The IR spectra of the intractable product mixtures from both reactions were identical, but did not include Al–H stretching absorptions, which normally occur in the region 1750–1850 cm^{-1} for cationic aluminum hydride complexes.[5] As a result, our efforts in this direction were abandoned.

Considering that the thiourea ArN(H)C(=S)N(H)Ar is a precursor in the synthesis of the carbodiimide ArN=C=NAr and HPiso, and that the reactivity of similar thioureas towards aluminum alkyls have been investigated,[2h] we thought it worthwhile to investigate reactions of ArN(H)C(=S)N(H)Ar with Group 13 hydride complexes. Treating the thiourea with [$AlH_3(NMe_3)$] under any stoichiometry in toluene afforded complex **10** in moderate yield (Scheme 4). Interestingly, no hydroalumination of the thiocarbonyl function was observed and the resulting secondary amine functionalities were not deprotonated, even in the presence of an excess of the aluminum hydride starting material. In a similar fashion, treatment of [GaH_3(quin)] with two equivalents of the thiourea gave good yields of the gallium hydride complex **11**. Unfortunately, all attempts to prepare an indium analogue of **10** and **11** by treating ArN(H)C(=S)N(H)Ar with [InH_3(quin)] led to decomposition upon workup and the deposition of indium metal.



Scheme 4. Synthesis of compounds **10** and **11**, a) 0.5[$AlH_3(NMe_3)$], toluene; b) 0.5[GaH_3(quin)], toluene.

Crystallographic studies: All the aluminum hydride complexes that incorporate the Fiso$^-$ ligand (**4**–**6**) have been characterized by crystallography and their molecular structures are depicted in Figures 1–3 (see also Table 1). The hydride ligands in **4** and **6** were located from difference maps and refined isotropically. Efforts to accurately refine the hy-

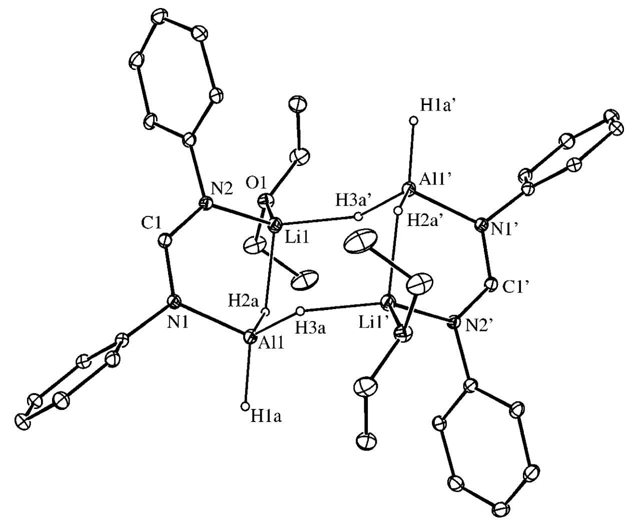


Figure 1. Molecular structure of **4** (ORTEP, thermal ellipsoids shown at 30 % probability level). Isopropyl groups and non-hydride hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.892(2), Al1–H1a 1.52(2), Al1–H2a 1.51(3), Al1–H3a 1.56(3), Al1–N1 1.892(2), Li1–H2a 1.97(3), Li1–H3a′ 1.93(3), O1–Li1 1.938(5), N2–Li1 2.038(4), N1–C1 1.343(3), N2–C1 1.297(3); N1-Al1-H1a 108.7(9), N1-Al1-H2a 105.6(10), H1a-Al1-H2a 114.8(14), N1-Al1-H3a 108.7(9), H1a-Al1-H3a 112.0(14), H2a-Al1-H3a 106.7(14), N2-C1-N1 122.9(2), Al1-H2a-Li1 111.5(3), Al1-H3a-Li1′ 144.0(3). Symmetry transformation used to generate equivalent atoms: $-x$, $-y$, $1-z$.

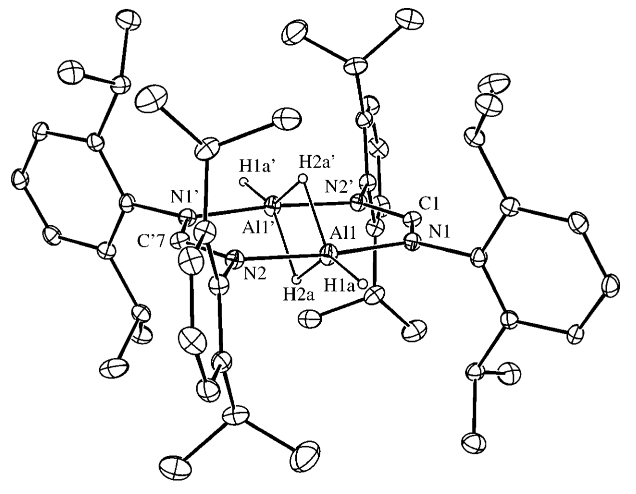


Figure 3. Molecular structure of **6** (ORTEP, thermal ellipsoids shown at 30 % probability level). Non-hydride hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.966(4), Al1–N2 1.955(4), Al1–H1a 1.52(5), Al1–H2a 1.73(4), N1–C1 1.330(6), N2–C1′ 1.335(6); N2′-C1-N1 122.0(5), N2-Al1-N1 171.67(18), N1-Al1-H1a 95.8(17), N2-Al1-H1a 92.4(17), N2-Al1-H2a 89.7(13), N1-Al1-H2a 85.1(13), Al1-H2a-Al1′ 100.0(3). Symmetry transformation used to generate equivalent atoms: $-x+1/2$, $-y+3/2$, $-z+1$.

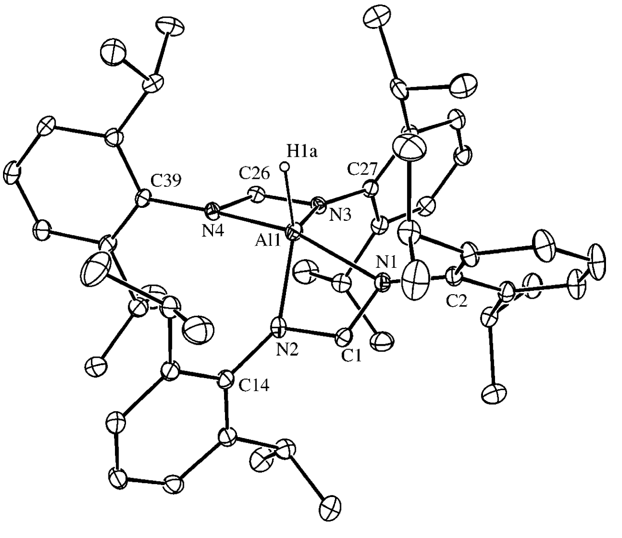


Figure 2. Molecular structure of **5** (ORTEP, thermal ellipsoids shown at 30 % probability level). Non-hydride hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 2.071(3), Al1–N2 1.910(3), Al1–N3 1.927(3), Al1–N4 2.085(3), N1–C1 1.300(4), N2–C1 1.335(4), N3–C26 1.340(4), N4–C26 1.295(4); N1-C1-N2 112.1(3), N4-C26-N3 114.3(3), N2-Al1-N1 66.49(12), N3-Al1-N1 102.40(13), N2-Al1-N3 123.45(14), N1-Al1-N4 158.23(14), N3-Al1-N4 66.88(12).

dride ligand in the structure of **5** failed due to the relatively poor quality of the data and consequently this was placed in a calculated position. The asymmetric units for the structures of both **4** and **6** contain two crystallographically independent monomeric units. In the case of **4** there are no significant geometric differences between the two and so comment on the symmetry generated dimer of only one of these will be made here. In the structure of **6**, one of the monomeric units is affected by a significant level of disorder, which, although satisfactorily modeled, has decreased the accuracy of its geometric parameters relative to the other ordered monomeric unit. As a result comment will be made only on the symmetry generated dimer of the ordered unit.

The structure of **4** is isomorphous to that of its gallium analogue (**3**) and is dimeric with inter- and intramolecular Al-H-Li bridges that give rise to an eight-membered $Li_2Al_2H_4$ ring. This ring has a pseudo-chair conformation with the hydrogen atoms H2a and H2a′ *trans* to each other. In contrast, the indium hydride complex **2** adopts a pseudo-boat conformation in which these hydrides are *cis* to each other. Both the Al and Li atoms possess distorted tetrahedral environments with Al–N and Li–N distances in the normal range for such interactions.[8] Although of low accuracy, both the bridging and terminal Al–H bonds in **4** (1.53 Å av) are consistent with other examples reported in the literature.[5] The NCN angle of the amidinate unit is quite open at 122.9(2)° (cf. **3** 123.4(2)°, **2** 124.8(3)°) relative to the angles in related chelating amidinate complexes (e.g., 113.2° av in **5** vide infra). In addition, the bond lengths within the NCN fragments of **4** suggest a considerably lower degree of delocalization than in complexes in which amidinate ligands chelate to heavier Group 13 metal centers, for example, **1**.

Complex **5** is isomorphous with both **1** and **8** and possesses a heavily distorted trigonal bipyramidal geometry at the metal center with N1 and N4 in axial positions. This geometry is similar to that of the only previously reported amidinate aluminum hydride complex, [AlH{(Me$_3$Si)NC(Ph)N(SiMe$_3$)}$_2$].[3] The distances from N1 and N4 to the metal

Table 1. Crystal data and refinement details for **4**–**6**.

	4	**5**	**6**
formula	$C_{58}H_{96}Al_2Li_2N_4O_2$	$C_{50}H_{71}AlN_4$	$C_{50}H_{74}Al_2N_4$
M_r	949.23	755.09	785.10
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$
a [Å]	11.103(2)	14.685(3)	47.691(10)
b [Å]	13.166(3)	16.001(3)	10.490(2)
c [Å]	21.211(4)	21.161(4)	21.747(4)
α [°]	92.95(3)	90	90
β [°]	91.12(3)	110.64(3)	115.95(3)
γ [°]	93.83(3)	90	90
V [Å^3]	3088.8(11)	4653.2(16)	9783(3)
Z	2	4	8
ρ_{calcd} [Mg m^{-3}]	1.021	1.078	1.067
μ [mm^{-1}]	0.086	0.080	0.095
$F(000)$	1040	1648	3424
crystal size [mm]	0.30 × 0.25 × 0.25	0.15 × 0.10 × 0.12	0.35 × 0.25 × 0.25
reflections collected/unique	31 331/12 053	33 403/8179	19 800/6341
R_{int}	0.0794	0.1089	0.0910
goodness-of-fit on F^2	1.026	1.009	1.214
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0634$, $wR_2 = 0.1526$	$R_1 = 0.0833$, $wR_2 = 0.1907$	$R_1 = 0.0970$, $wR_2 = 0.1926$
largest diff peak hole [e Å^{-3}]	0.524/−0.411	0.806/−0.235	0.323/−0.237

(2.078 Å av) are significantly greater than the Al−N(equatorial) interactions (1.919 Å av). It is of note that the bond lengths within the NCN fragment of the amidinate ligands differ significantly, which indicates less delocalization over that fragment than in the analogous indium complex (**1**). In the structure of complex **6** the amidinate ligands display a different bonding mode in which they bridge two distorted trigonal bipyramidal aluminum centers to form a near planar eight-membered $Al_2N_4C_2$ ring. Each aluminum center is additionally coordinated by one terminal and one bridging hydride ligand with Al−H distances of 1.52(5) and 1.73(4) Å respectively. The Al−N distances within the complex (1.960 Å av) are in the normal range,[8] whilst all the N−C distances within the amidinate backbones are equal within experimental error (1.333 Å av). Not surprisingly, the NCN angles in these backbones (122.0(5)°) are considerably more obtuse than in **5**, but similar to those in **4**.

The molecular structures of the gallium hydride complexes **7** and **8** are depicted in Figures 4 and 5, respectively (see also Table 2). The data for **8** were weak, especially at theta angles greater than 22°, giving rise to the relatively high R factor for this structure. Despite this, the hydride ligand in this complex and those in **7** were located from difference maps and refined isotropically without restraints. Complex **7** is monomeric and only one N center of the amidinate ligand coordinates the gallium center (Ga−N 1.948(3) Å). This ligand appears to have a localized NCN fragment (N1−C1: 1.354(4), N2−C1: 1.285(4) Å), the angle of which, 123.3(3) Å, is comparable to those in **4** and **6**. The slightly distorted tetrahedral gallium center is also coordinated by a molecule of quinuclidine and two hydride ligands, the latter of which display Ga−H bond lengths (1.52 Å av) in the normal range.[5,8] In **8**, the amidinate ligands chelate the gallium center which has a heavily distorted trigonal bipyramidal geometry with N1 and N4 in apical positions. All the metrical parameters for this complex are similar to those in isomorphous **1** and **5**, though the bond lengths within the NCN fragments of the ligands indicate a degree of delocalization over these fragments intermediate between those in its aluminum and gallium counterparts.

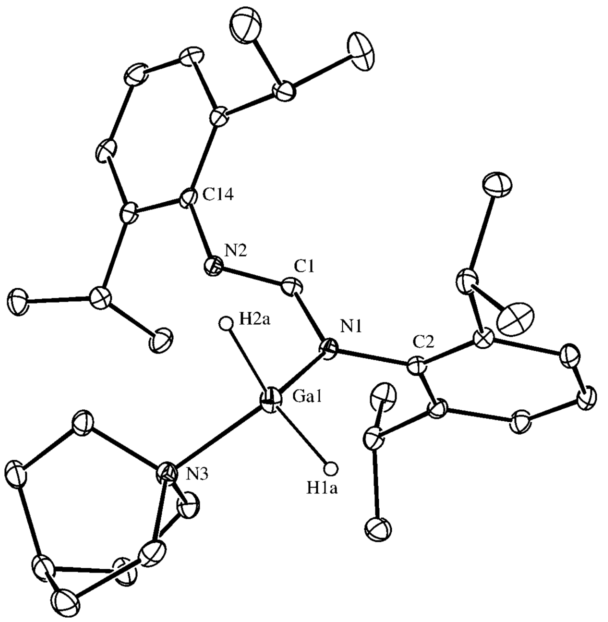


Figure 4. Molecular structure of **7** (ORTEP, thermal ellipsoids shown at 30 % probability level). Non-hydride hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1−N1 1.948(3), Ga1−N3 2.063(3), Ga1−H1a 1.505(18), Ga1−H2a 1.529(19), N1−C1 1.354(4), N2−C1 1.285(4); N2-C1-N1 123.3(3), N1-Ga1-N3 108.41(12), N1-Ga1-H1a 111.4(16), N1-Ga1-H2a 108(2), N3-Ga1-H2a 104(2), N3-Ga1-H1a 103.2(16).

The molecular structure of **9** is depicted in Figure 6 (see also Table 2); it exists as a centrosymmetric hydride-bridged dimer. In contrast to the structure of **6**, and presumably because of the extra steric bulk of the amidinate ligands in **9**, each of its aluminum centers is chelated by one amidinate. In addition, they are ligated by two bridging and one terminal hydride to give them distorted square based pyramidal geometries with H2a in the apical position. The Al−N distances (1.945 Å av) are consistent with those in the previously discussed complexes and, as in **6**, the bridging Al−H distances, 1.64(2) Å, are longer than

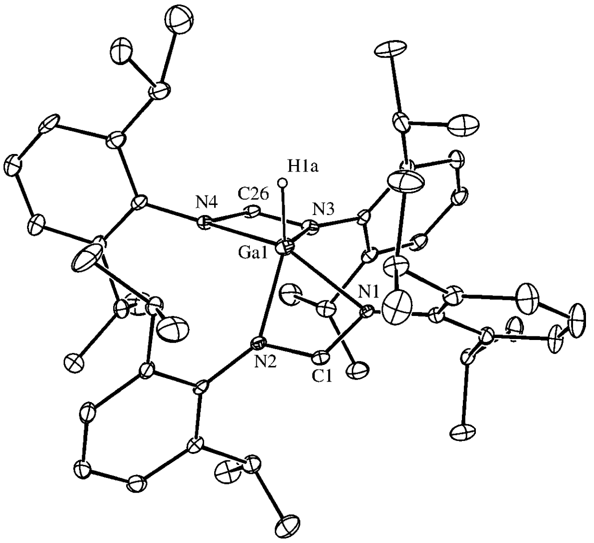


Figure 5. Molecular structure of **8** (ORTEP, thermal ellipsoids shown at 30 % probability level). Non-hydride hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1–H1a 1.65(6), Ga1–N1 2.137(4), Ga1–N2 2.001(4), Ga1–N3 1.977(4), Ga1–N4 2.173(4), N1–C1 1.297(7), N2–C1 1.313(7); N2-C1-N1 116.3(4), N1-Ga1-N4 152.67(16), N2-Ga1-N3 119.60(17), N3-Ga1-N1 102.09(17), N2-Ga1-N4 99.96(16), N1-Ga1-N4 64.68(16), N3-Ga1-H1a 120(2), N2-Ga1-H1a 120(2), N1-Ga1-H1a 104(2), N4-Ga1-H1a 103(2).

the terminal Al–H bonds, 1.51(3) Å. The *tert*-butyl group in the backbone of the amidinate leads to more steric repulsion of the aryl groups than in the Fiso$^-$ ligand and gives rise to a more acute NCN angle, 107.3(2)° (cf. 107.4(2)° in [AlMe$_2$(Piso)][2h]), than in, for example, **5** (113.2° av).

The scattering intensities for **10** were also weak at high theta angles and this led to the relatively poor quality of its crystal structure (Figure 7, see also Table 2). Despite this,

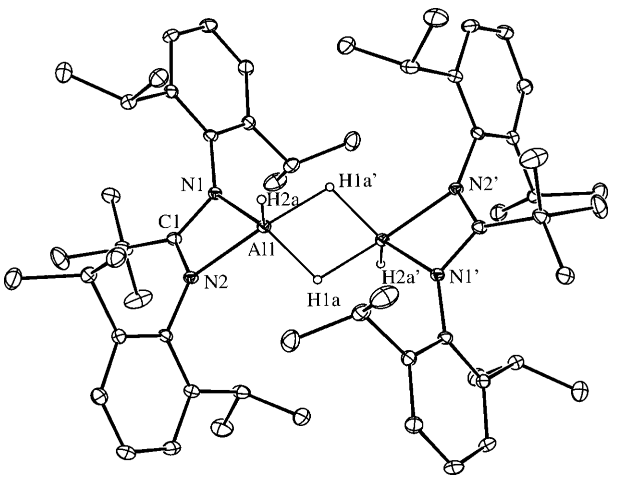


Figure 6. Molecular structure of **9** (ORTEP, thermal ellipsoids shown at 30 % probability level). Non-hydride hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.920(2), Al1–N2 1.970(2), Al1–H1a 1.64(2), Al1–H2a 1.51(3), N1–C1 1.355(3), N2–C1 1.334(3); N2-C1-N1 107.3(2), N1-Al1-N2 67.64(8), N1-Al1-H1a 126.0(8), N1-Al1-H2a 121.4(10), N2-Al1-H1a 98.4(8), N2-Al1-H2a 111.3(10), H1a-Al1-H2a 112.3(13), Al1-H1a-Al1′ 105.2(3) Symmetry transformation used to generate equivalent atoms: 1−*x*, 1−*y*, −*z*.

the hydride ligand was located from difference maps and refined isotropically without restraints (Al–H 1.54(3) Å). This showed the aluminum center in the complex to have a heavily distorted trigonal bipyramidal geometry with both sulfur atoms in the apical positions (S-Al-S 156.20(6)° compared to N-Al-N 127.09(14)°). The thioureido ligands chelate the aluminum center with average Al–N distances of 1.912 Å, similar to those in the related aluminum alkyl complex, [AlMe$_2${η^2-SC[N(H)Ad]N(Ad)}] (Ad = adamantyl), 1.910(3) Å.[2h] Interestingly, however, the Al–S distances in

Table 2. Crystal data and refinement details for **7**–**10**.

	7	**8**	**9**·(C$_7$H$_8$)$_2$	**10**
formula	$C_{32}H_{50}GaN_3$	$C_{50}H_{71}GaN_4$	$C_{72}H_{106}Al_2N_4$	$C_{50}H_{71}AlN_4S_2$
M_r	546.47	797.83	1081.57	819.21
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	12.279(3)	14.800(3)	12.890(3)	10.451(2)
b [Å]	18.533(4)	16.073(3)	14.686(3)	19.262(4)
c [Å]	14.239(3)	21.031(4)	17.611(4)	24.154(5)
α [°]	90	90	90	90
β [°]	105.15(3)	110.60(3)	93.08(3)	91.02(3)
γ [°]	90	90	90	90
V [Å^3]	3127.7(11)	4683.0(16)	3329.1(11)	4861.5(17)
Z	4	4	2	4
ρ_{calcd} [Mg m^{-3}]	1.161	1.132	1.079	1.119
μ [mm^{-1}]	0.903	0.623	0.086	0.164
$F(000)$	1176	1720	1184	1776
crystal size [mm]	0.30 × 0.25 × 0.15	0.15 × 0.15 × 0.12	0.20 × 0.20 × 0.20	0.25 × 0.10 × 0.05
reflections collected/unique	21793/6107	22196/7927	19812/5838	47744/8432
R_{int}	0.0539	0.0602	0.0877	0.2523
goodness-of-fit on F^2	1.041	1.028	1.014	1.042
final R indices	$R_1 = 0.0593$,	$R_1 = 0.0940$,	$R_1 = 0.0613$,	$R_1 = 0.0822$,
[$I > 2\sigma(I)$]	$wR_2 = 0.1382$	$wR_2 = 0.2714$	$wR_2 = 0.1298$	$wR_2 = 0.1305$
largest diff peak hole [e Å^{-3}]	1.737 (near Ga1)/−0.434	1.422 (near Ga1)/−1.238	0.554/−0.237	0.240/−0.244

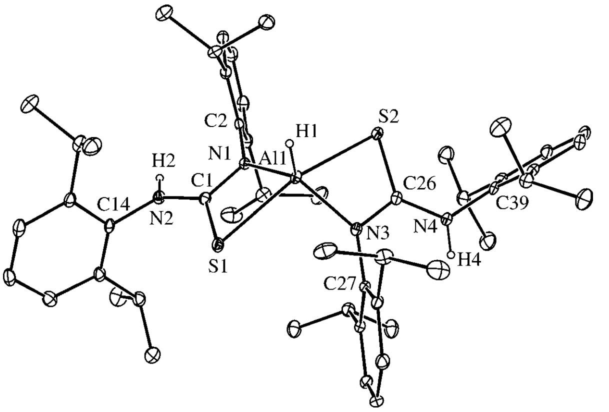


Figure 7. Molecular structure of **10** (ORTEP, thermal ellipsoids shown at 30 % probability level). Non-hydride hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.913(3), Al1–N3 1.912(3), Al1–S1 2.4796(19), Al1–S2 2.4814(18), Al1–H1 1.54(3), N1–C1 1.332(5), N2–C1 1.352(5), N3–C26 1.336(5), N4–C26 1.342(5), S1–C1 1.706(4), S2–C26 1.711(4); N1-Al1-N3 127.09(14), S1-Al1-S2 156.20(6), N1-Al1-S2 99.22(11), N3-Al1-S1 98.50(12), N1-Al1-H1 117.7(12), H1-Al1-S1 101.6(12), N3-Al1-H1 115.2(12), S2-Al1-H1 102.2(12), N1-C1-N2 121.2(4), N1-C1-S1 114.7(3), N3-C26-N4 120.9(4), N3-C26-S2 114.8(3).

10 (2.480 Å av) are significantly longer than in the adamantyl-substituted complex (2.342(2) Å), in which the negative charge was proposed to be centered largely on the sulfur center. This does not appear to be the case for **10**, because of its relatively long Al–S bonds, and also because its C–S bonds (1.708 Å av) are markedly shorter than in [AlMe$_2${η^2-SC[N(H)Ad]N(Ad)}] (1.758(3) Å) and hence presumably have more double bond character. Despite this, the N–C distances in the N_2CS fragments of both complexes are similar and reminiscent of partially delocalized NCN systems.

Spectroscopic data and thermal stability: The ^{1}H NMR spectrum of the amidotrihydridoalanate complex **4** differs significantly to that of its gallium analogue (**3**) in that it exhibits two broad isopropyl methyl signals that integrate in a 1:1 ratio, and only one methine signal, which is broad and unresolved. In the corresponding ^{1}H NMR spectrum of **3**, three sharp and well-resolved isopropyl methyl doublet signals (integrating in a 1:1:2 ratio) and two methine septet or virtual septet signals were observed. In the case of **3**, this information was interpreted as arising from a free rotation of the aryl group attached to the gallium coordinated nitrogen atom, but restricted rotation of the other aryl group due to the greater steric bulk of the Li(Et_2O) fragment relative to the GaH_3 fragment. The spectrum for **4** clearly shows that a fluxional process is occurring at room temperature, though all efforts to resolve the spectra by using variable temperature NMR experiments met with failure due to significant precipitation of the complex from [D$_8$]toluene below 0 °C. It seems reasonable, however, that this fluxional process involves an exchange of the amidinate nitrogen centers between the coordinated Li and Al fragments. This could occur by decomplexation of one nitrogen atom from Li and re-coordination at the Al-center to give a five-coordinate Al-chelated intermediate from which the other nitrogen atom is decomplexed and subsequently re-coordinates the Li center. That a similar process is not favored for **3** is not surprising considering the well-known preference of gallium for four-coordination, especially in anionic systems.[5] Indeed, the closely related indium hydride complex **2** displays a similar fluxionality to **4**, which is as would be expected considering indium's preference for five or six coordination.

The ^{1}H NMR spectrum of **4** also exhibits a broad hydride resonance at $\delta = 4.35$ ppm that is at higher field than those of its gallium and indium analogues (cf. **3** $\delta = 4.68$ ppm, **2** $\delta = 6.02$ ppm). The relative positionings of these signals has been observed before in homologous series of Group 13 hydride complexes[9] and can now be considered the norm. Conversely, the IR spectrum (Nujol mull) of **4** revealed two Al–H stretching bands at 1821 (sharp, terminal Al–H) and 1756 cm^{-1} (broad, bridging Al–H), which are intermediate between those of the related indium and gallium complexes **2** (1719, 1632 cm^{-1}) and **3** (1879, 1769 cm^{-1}), respectively. Again, this relative ordering has recently been established[5a,9] and reflects the polarities of the M–H bonds in the complexes. Complex **4** is thermally stable and melts without decomposition at 126 °C, which can be compared to its thermally more labile indium and gallium counterparts which decompose at 42–44 °C (**2**) and 84–86 °C (**3**), respectively.

The spectroscopic data and thermal stability properties of another homologous series of complexes, namely the bis(amidinato) complexes [MH(Fiso)$_2$] (M = Al **5**, Ga **8**, and In **1**) can also be compared. Their NMR spectroscopic data are all similar though the hydride resonance could not be observed in the ^{1}H NMR spectra of any complex. This is not unusual and results from broadening of these signals by the respective quadrupolar Group 13 metal. Relatively sharp and strong M–H stretching absorptions were observed in the IR spectra of the complexes, the positions of which show the same ordering as for the previously mentioned complexes (**5**: 1823, **8**: 1911, **1**: 1719 cm^{-1}). These absorptions are, however, significantly shifted to higher wavenumbers than the previous series and indeed most neutral Group 13 hydride complexes.[5] This probably arises from a negative inductive effect from the two anionic amidinate ligands that decreases the polarity of the M–H bonds. All three compounds display excellent thermal stability, but do decompose in the solid state at temperatures that follow the order normally seen for Group 13 hydride complexes, for example, **1** 160, **8** 211, and **5** 231 °C. The stability of these complexes can be ascribed to the steric protection afforded their M–H fragments by the bulky amidinate phenyl substituents; which prevent any opportunity for the formation of intermolecular M-H-M bridges. Indeed, it has been suggested that such bridges could lower the energy barrier to homolytic decomposition processes and subsequent dihydrogen elimination from gallium and indium hydride species.[5b,e] In this respect, there is some evidence that **1**, **5** and **8** decompose by means of intramolecular processes, as in the solid state or in solution no metal deposition is seen when they are heated past their decomposition temperatures. Instead, the only products are free HFiso and brown, insoluble organometallic materials of indeterminate composition. This suggests the decomposition process involves hydrogen transfer to one of the complex's Fiso$^-$ ligands and metallation of the other. It should be noted that similar metallation decomposition processes have been reported for N-heterocyclic carbene adducts of Group 13 trihydrides, for example, $[InH_3\{C[N(iPr)C(H)]_2\}]$.[9]

None of the mono(amidinato) Group 13 complexes, **6**, **7**, or **9**, are isostructural with each other, and so it is difficult to make comment on NMR spectroscopic trends. However, some comparisons can be made between their IR spectra, which in the case of **6** (Nujol mull) exhibits terminal and bridging Al–H stretching absorptions at 1868 and 1835 cm^{-1}, respectively, whilst, surprisingly, only one broad and strong Al–H stretching band (1845 cm^{-1}) was observed in the IR spectrum of dimeric **9**. These values are in the normal range for amido aluminum hydride complexes that contain terminal and/or symmetrically bridging hydrides, for example, $[\{Al(\mu\text{-}H)[N(SiMe_3)_2]_2\}_2]$ $\nu(Al{-}H) = 1880$ cm^{-1};[10] $[\{AlH(\mu\text{-}H)(TMP)\}_3]$ TMP = 2,2′,6,6′-tetramethylpiperidine, $\nu(Al{-}H) = 1863$ and 1834 (terminal), 1778 cm^{-1} (bridging).[11] Similarly, compound **7** showed one Ga–H stretching band (1872 cm^{-1}) in its IR spectrum. It is noteworthy that the M–H stretching absorptions for **6** and **7** occur at lower wavenumbers than those for the corresponding bis(amidinate) complexes **5** and **8**, due to a lesser negative inductive effect of one amidinate ligand as opposed to two. In addition, both the 1:1 complexes are less thermally stable (**6** 205 °C decomp, **7** 148 °C decomp) than their more sterically protected 2:1 counterparts, and in contrast to those complexes, they decompose to give the Group 13 metal, HFiso and H_2 gas. The bulkier Piso$^-$ ligand of **9** and its chelating coordination mode seemingly afford this complex considerably greater thermal stability than any of the Fiso$^-$ substituted complexes. In fact, this complex melts at 190 °C and no decomposition was observed in the melt, even when it was heated to 300 °C. Moreover, the compound can be cleanly sublimed in vacuo at temperatures in excess of 280 °C.

The spectroscopic data for the thioureido complexes **10** and **11** are similar and consistent with them being isostructural. Their ^1H and ^{13}C NMR spectra both show eight methyl and four methine signals in line with the fact that the isopropyl groups on each thioureido ligand are diastereotopic. The IR spectra of the complexes both show N–H and M–H stretching absorptions, the latter of which were found at 1849 (**10**) and 1929 cm^{-1} (**11**), that is, at higher wavenumbers than those of the related bis(amidinato) complexes **5** and **8**. Complexes **10** and **11** are also more thermally stable than **5** and **8** in the solid state and do not decompose until 240 (**10**) and 226 °C (**11**). This is perhaps unusual as the steric protection afforded the metal centers in the former should be less than in the latter.

Conclusion

In conclusion, we have used two bulky amidinate ligands, Fiso$^-$ and Piso$^-$, to prepare a variety of very thermally stable aluminum and gallium hydride complexes. The structural motifs adopted by the prepared complexes have been found to be dependent upon both the amidinate ligand and the metal involved. In this respect, the prepared gallium hydride complexes displayed a tendency to possess four-coordinate metal centers, whereas all the neutral aluminum hydride complexes were shown to have five-coordinate metal centers. This difference is derived from the greater electronegativity of gallium relative to aluminum. The bulk of the amidinate ligand has an effect on its solid-state coordination mode in the mono(amidinato) complexes, as evidenced by the fact that the Fiso$^-$ ligand was not shown to chelate the metal center in any of its 1:1 complexes, whereas Piso$^-$ chelates aluminum in complex **9**. This difference presumably arises from the *tert*-butyl substituent in the latter which narrows its NCN angle relative to that of Fiso$^-$, thus making it more amenable to chelation. The greater steric bulk of Piso$^-$ also appears to be the reason behind the increased thermal stability of **9** over **6**. This can also be used to explain why no bis(Piso) complexes could be prepared.

Other trends in thermal stabilities that have been noted in this study include the general and lower stability of gallium hydride complexes relative to their aluminum hydride analogues, and the greater stability of the more sterically protected bis(Fiso) complexes relative to their mono(Fiso) counterparts. The former trend is also seen in the two thioureido complexes, **10** and **11**.

Considering the emerging importance of amidinato Group 13 alkyl and halide complexes to a number of areas, it seems unusual that very few studies have centered on related Group 13 hydride complexes. This study and our preliminary investigations on amidinato indium and gallium hydride complexes have proved that a variety of stable complexes displaying novel structural features can be readily prepared. In future publications we will chronicle our efforts to develop further this understudied field, which has significant potential to be applied to areas such as organic synthesis and homogeneous catalysis.

Experimental Section

General: All manipulations were carried out by using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Hexane, toluene, THF, and [D$_6$]benzene were distilled over potassium, whilst diethyl ether was distilled over Na/K alloy. IR spectra were obtained as Nujol mulls using a Perkin–Elmer 1600 series FTIR spectrometer with NaCl plates. NMR spectroscopy was carried out using either Jeol Eclipse 300 or Bruker DPX 400 spectrometers. Mass spectra were recorded using a VG Fisons Platform II instrument operating under APCI conditions, or were obtained from the EPSRC Mass Spectrometry Service, Swansea. Microanalyses were carried out by Medac Ltd. UK. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. $[AlH_3(NMe_3)]$,[12] $[GaH_3(quin)]$,[13] HFiso,[14] ArN(H)C(=S)-N(H)Ar,[15] and ArN=C=NAr[16] were synthesized by literature procedures. HPiso was prepared by treating ArN=C=NAr with one equivalent of *t*BuLi in Et_2O followed by aqueous workup. Its spectroscopic data were checked against the literature values.[17] HFiso·HCl was obtained by treatment of HFiso with concentrated hydrochloric acid in THF, removing all volatiles in vacuum and drying the residue for 1 h at 100 °C under vacuum.

$[\{AlH_3(\mu\text{-Fiso})Li(OEt_2)\}_2]$ (4): A solution of HFiso (1.92 g, 5.27 mmol) in Et_2O (40 mL) was added to a solution of $LiAlH_4$ (0.20 g, 5.27 mmol) in Et_2O (10 mL) at −78 °C over a period of 5 min. The resultant suspension was allowed to warm to 25 °C and volatiles were removed under vacuum. The residue was extracted into hexane (25 mL) and the extract slowly cooled to −35 °C to yield colourless crystals of **4** (1.91 g, 77 %). M.p.: 126–127 °C; ^1H NMR (400 MHz, C_6D_6, 298 K): $\delta=0.86$ (t, $^3J_{HH}=7.0$ Hz, 12H; CH_2CH_3), 1.35 (br d, $^3J_{HH}=6.9$ Hz, 24H; $CHCH_3$), 1.60 (br d, $^3J_{HH}=6.9$ Hz, 24H; $CHCH_3$), 3.06 (q, $^3J_{HH}=7.0$ Hz, 8H; OCH_2), 3.74 (br, 8H; $CHCH_3$), 4.25 (br, 6H; AlH_3), 7.23–7.48 (m, 12H; ArH), 7.68 ppm (s, 2H; NC(H)N); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=14.3$ (CH_2CH_3), 24.2 ($CHCH_3$), 24.9 ($CHCH_3$), 28.1 (CH), 65.8 (CH_2), 123.3 (*p*-ArC), 124.0 (*m*-ArC), 144.4 (*o*-ArC), 145.1 (*ipso*-ArC), 165.1 ppm (NCN); ^7Li NMR (300 MHz, C_6D_6, 298 K): $\delta=0.70$ ppm (br s); IR (Nujol): $\tilde{\nu}=1821$ (sharp s, terminal Al−H), 1756 cm^{-1} (br s, bridging Al−H); MS/APCI: *m*/*z* (%): 366 (100) $[HFiso]^+$; elemental analysis calcd (%) for $C_{58}H_{96}Al_2Li_2N_4O_2$: C 73.39, H 10.19, N 5.90; found: C 72.94, H 10.27, N 6.12.

$[AlH(Fiso)_2]$ (5)

Method A: $[AlH_3(NMe_3)]$ (5.0 mL of a 0.58 M solution in toluene, 2.89 mmol) was added to a slurry of HFiso (2.11 g, 5.79 mmol) in toluene (50 mL) at −78 °C over a period of 5 min. The mixture was slowly warmed to room temperature and stirred for 4 h. The resultant solution was concentrated under reduced pressure to 25 mL and placed at −30 °C overnight to yield **5** as colourless crystals. Two further crops were obtained. (1.91 g, 87 %);

Method B: $[AlH_3(NMe_3)]$ (1.0 mL of a 0.58 M solution in toluene, 0.58 mmol) was added at to a solution of $(ArN)_2C$ (0.42 g, 1.16 mmol) in toluene (50 mL) −78 °C over a period of 5 min. The mixture was slowly warmed to room temperature and stirred for 3 h. Workup as for method A afforded **5** (0.31 g, 71 %);

Method C: A solution of HFiso (0.50 g, 1.37 mmol) in THF (10 mL) was added to a solution of $LiAlH_4$ (0.026 g, 0.70 mmol) in THF (10 mL) at −78 °C over a period of 5 min. The resultant suspension was allowed to warm to 25 °C, filtered and solvents were removed under vacuum. The residue was extracted into toluene (5 mL) and slowly cooled to −35 °C yielding colourless crystals of **5** (0.31 g, 60 %).

Data for **5**: M.p.: 231–233 °C (decomp); ^1H NMR (300 MHz, C_6D_6, 298 K): $\delta=1.14$ (br d, $^3J_{HH}=6.6$ Hz, 24H; CH_3), 1.20 (br d, $^3J_{HH}=6.7$ Hz, 24H; CH_3), 3.87 (br virtual sept, $^3J_{HH}=6.7$ Hz, 8H; CH), 7.19–7.34 (m, 12H; ArH), 7.62 ppm (s, 2H; NC(H)N); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=24.1$ (CH_3), 24.7 (CH_3), 27.3 (CH), 122.5 (*p*-ArC), 124.6 (*m*-ArC), 138.0 (*o*-ArC), 143.4 (*ipso*-ArC), 166.4 ppm (NCN); IR (Nujol): $\tilde{\nu}=1823$ cm^{-1} (sharp s, AlH); MS/APCI: *m*/*z* (%): 366 (100) $[HFiso]^+$, 756 (24) $[M]^+$; elemental analysis calcd (%) for $C_{50}H_{71}AlN_4$: C 79.53, H 9.48, N 7.42; found: C 78.69, H 9.42, N 7.66.

$[\{AlH_2(Fiso)\}_2]$ (6)

Method A: A solution of $LiAlH_4$ (0.245 g, 6.46 mmol) in Et_2O (25 mL) was added to a frozen (−196 °C) mixture of HFiso·HCl (1.94 g, 4.84 mmol) and Et_2O (70 mL). The mixture was brought to −78 °C, then slowly warmed to room temperature and stirred overnight. Gas evolution was noticed at about −25 °C. The solvent was removed under reduced pressure and the residue extracted with hexane/toluene (1:1, 40 mL). Placement of the extract at −30 °C gave **6** as colourless crystals overnight (1.31 g, 69 %).

Method B: A solution of $(ArN)_2C$ (0.84 g, 2.32 mmol) in toluene (15 mL) was added to $[AlH_3(NMe_3)]$ (8.8 mL of a 0.58 M solution in toluene, 5.10 mmol), and the mixture heated at reflux for 45 min. The resultant solution was concentrated to about 8 mL and stored at −30 °C to give **6** (0.56 g, 62 %).

Data for **6**: M.p.: 205–207 °C (decomp); ^1H NMR (400 MHz, C_6D_6, 298 K): $\delta=1.28$ (d, $^3J_{HH}=6.8$ Hz, 24H; CH_3), 1.36 (d, $^3J_{HH}=6.8$ Hz, 24H; CH_3), 3.51 (virtual sept, $^3J_{HH}=6.8$ Hz, 8H; CH), 4.60 (br s, 4H; Al-H), 7.10–7.35 (m, 12H; Ar-H), 7.62 ppm (s, 2H; NC(H)N); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=24.7$ (CH_3), 24.8 (CH_3), 29.0 (CH), 123.6 (*p*-ArC), 125.9 (*m*-ArC), 142.8 (*o*-ArC), 145.3 (*ipso*-ArC), 162.0 ppm (NCN); IR (Nujol): $\tilde{\nu}=1868$ (Al-H terminal), 1835 cm^{-1} (Al-H bridging); MS/APCI: *m*/*z* (%): 366 (100) $[HFiso]^+$; elemental analysis calcd (%) for $C_{50}H_{74}Al_2N_4$: C 76.39, H 9.62, N 7.13; found: C 76.79, H 9.52, N 7.28.

$[GaH_2(Fiso)(quin)]$ (7): A solution of HFiso (0.63 g, 1.74 mmol) in Et_2O (40 mL) was added to a solution of $[GaH_3(quin)]$ (0.32 g, 1.74 mmol) in Et_2O (10 mL) at −78 °C over a period of 5 min. The resultant suspension was allowed to warm to 25 °C, after which time solvents were removed under vacuum. The residue was extracted into hexane (15 mL) and slow cooled to −35 °C, yielding colourless crystals of **7** (0.36 g, 38 %). M.p.: 148–150 °C (decomp); ^1H NMR (300 MHz, C_6D_6, 298 K): $\delta=1.16$ (br s, 6H; CH_2), 1.43 (br, 24H; CH_3), 1.52 (br, 1H; CH), 3.06 (br, 6H; CH_2N), 3.85 (br, 4H; $CHCH_3$), 5.12 (br s, 2H; GaH_2), 7.08–7.26 (m, 6H; ArH), 7.55 ppm (s, 1H; NC(H)N); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=20.1$ (CH), 24.4 (br, CH_3), 25.6 (CH_2), 28.2 ($CHCH_3$), 48.1 (NCH_2), 123.2 (*p*-ArC), 125.3 (*m*-ArC), 143.8 (*o*-ArC), 145.9 (*ipso*-ArC), 163.7 ppm (NCN); IR (Nujol): $\tilde{\nu}=1872$ cm^{-1} (br s, GaH_2); MS/APCI: *m*/*z* (%): 366 (100) $[HFiso]^+$, 547 (7) $[M]^+$; elemental analysis calcd (%) for $C_{32}H_{50}GaN_3$: C 70.33, H 9.22, N 7.69; found: C 69.50, H 9.26, N 7.80.

$[GaH(Fiso)_2]$ (8): A solution of HFiso (0.99 g, 2.72 mmol) in Et_2O (40 mL) was added to a solution of $[GaH_3(quin)]$ (0.25 g, 1.36 mmol) in Et_2O (10 mL) at −78 °C over a period of 5 min. The resultant suspension was allowed to warm to 25 °C, after which volatiles were removed under vacuum. The residue was extracted into hexane (15 mL) and slow cooled to −35 °C, yielding colourless crystals of **8** (0.22 g, 21 %). M.p.: 211–213 °C (decomp); ^1H NMR (250 MHz, C_6D_6, 298 K): $\delta=1.19$ (br d, $^3J_{HH}=7.9$ Hz, 24H; CH_3), 1.32 (br d, $^3J_{HH}=7.8$ Hz, 24H; CH_3), 3.55 (br, poorly resolved signal, 8H; CH), 7.03–7.28 (m, 12H; ArH), 7.55 ppm (s, 2H; NC(H)N); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=23.6$ (CH_3), 23.9 (CH_3), 28.3 (CH), 123.2 (*p*-ArC), 125.4 (*m*-ArC), 140.2 (*o*-ArC), 143.8 (*ipso*-ArC), 163.8 ppm (NCN); IR (Nujol): $\tilde{\nu}=1911$ cm^{-1} (sharp, s, GaH); MS/APCI: *m*/*z* (%): 366 (100) $[HFiso]^+$; elemental analysis calcd (%) for $C_{50}H_{71}GaN_4$: C 75.27, H 8.97, N 7.02; found: C 74.31, C 8.78, N 7.36.

$[\{AlH_2(Piso)\}_2]$ (9): $[AlH_3(NMe_3)]$ (3.25 mL of a 0.58 M solution in toluene, 1.89 mmol) was added at to slurry of HPiso (0.72 g, 1.71 mmol) in toluene (15 mL) −78 °C over a period of 5 min. The resultant solution was warmed to room temperature and stirred overnight, whereupon it was concentrated under reduced pressure to 10 mL, filtered, and stored at −30 °C to give colourless crystals of $\mathbf{9}\cdot(C_7H_8)_2$. (0.77 g, 83 %). M.p.: 190–191 °C (no decomp observed until 300 °C); ^1H NMR (300 MHz, C_6D_6, 298 K; toluene NMR resonances are not given): $\delta=1.03$ (s, 18H; $C(CH_3)_3$), 1.38, 1.42 (2d, $^3J_{HH}=6.8$ Hz, 48H; CH_3), 3.70 (sept, $^3J_{HH}=6.8$ Hz, 8H; CH), 4.87 (br s, 4H; AlH), 7.10–7.40 ppm (m, 12H; Ar-H); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=22.6$ ($C(CH_3)_3$), 27.0 (CH), 29.0 (CH_3), 29.2 (CH_3), 41.9 ($C(CH_3)_3$), 123.7 (*p*-ArC), 125.7 (*m*-ArC), 139.2 (*o*-ArC), 144.4 (*ipso*-ArC), 181.4 ppm (NCN); IR (Nujol): $\tilde{\nu}=1845$ cm^{-1} (s, AlH); MS/APCI: *m*/*z* (%): 366 (100) $[HFiso]^+$, 547 (7) $[M/2]^+$; elemental analysis calcd (%) for $C_{72}H_{106}Al_2N_4$: C 79.95, H 9.88, N 5.18; found: C 79.26, C 9.86, N 5.53.

$[AlH\{N(Ar)C[N(H)(Ar)]S\}_2]$ (10): $[AlH_3(NMe_3)]$ (1.1 mL of a 0.58 M solution in toluene, 0.638 mmol) was added to slurry of ArN(H)C(=S)N(H)Ar (0.46 g, 1.16 mmol) in toluene (20 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred for 2 h. The resulting solution was concentrated and placed at 4 °C to yield colourless crystals of **10** (0.28 g, 53 %). M.p.: 240–242 °C (decomp); ^1H NMR (400 MHz, C_6D_6, 298 K): $\delta=1.03$ (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.12 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.38 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.40 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.48 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.51 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.58 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.72 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 3.07 (sept, $^3J_{HH}=6.8$ Hz, 2H; CH), 3.33 (sept, $^3J_{HH}=6.8$ Hz, 2H; CH), 3.66 (sept, $^3J_{HH}=6.8$ Hz, 2H; CH), 3.93 (sept, $^3J_{HH}=6.8$ Hz, 2H; CH), 5.60 (br s, 1H; AlH), 6.30 (s, 2H; NH), 7.04–7.30 ppm (m, 12H; ArH); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=24.1$ (CH_3), 24.2 (CH_3), 24.3 (CH_3), 24.7 (CH_3), 25.0 (CH_3), 25.6 (CH_3), 26.6 (CH_3), 27.7 (CH_3), 28.7 (CH), 28.9 (CH), 29.1 (CH), 29.3 (CH), 124.2, 124.3, 124.6, 125.2, 129.5, 130.3, 133.4, 136.5, 146.1, 146.7, 147.3, 147.5, (ArC), 182.1 ppm (NCS); IR (Nujol): $\tilde{\nu}=3341$ (NH), 1849 cm^{-1} (AlH); MS/EI: m/z (%): 817.4 (100) $[M-H]^+$; EI accurate MS: $[M-H]^+$ calcd for $C_{50}H_{70}AlN_4S_2$: 817.4852; found: 817.4835.

[GaH{N(Ar)C[N(H)(Ar)]S}$_2$] (11): A solution of [GaH_3(quin)] (0.146 g, 0.794 mmol) in toluene (20 mL) was added to a solution of ArN(H)C(=S)-N(H)Ar (0.60 g, 1.51 mmol) in toluene (20 mL) at −80 °C. The mixture was slowly warmed to room temperature and stirred for 3 h. The resultant solution was then concentrated in vacuo to 20 mL and stored at −28 °C for 20 h to yield **11** as a colourless crystalline material. (0.37 g, 57 %). M.p.: 226–228 °C (decomp to yellow solid); ^1H NMR (400 MHz, C_6D_6, 298 K): $\delta=1.02$ (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.14 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.44 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.46 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.55 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.59 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.60 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 1.77 (d, $^3J_{HH}=6.8$ Hz, 6H; CH_3), 3.07 (sept, $^3J_{HH}=6.8$ Hz, 2H; CH), 3.41 (sept, $^3J_{HH}=6.8$ Hz, 2H; CH), 3.80 (unresolved overlapping signals, 4H; CH), 6.17 (s, 2H; NH), 7.04–7.30 ppm (m, 12H; ArH), ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): $\delta=23.9$ (CH_3), 24.2 (CH_3), 24.5 (CH_3), 24.6 (CH_3), 25.0 (CH_3), 25.8 (CH_3), 26.8 (CH_3), 27.9 (CH_3), 28.7 (CH), 29.0 (CH), 29.1 (CH), 29.3 (CH), 124.1, 124.3, 124.7, 125.0, 129.4, 130.2, 134.2, 136.8, 146.5, 146.6, 147.1, 147.5, (ArC), 181.6 ppm (NCS); IR (Nujol): $\tilde{\nu}=3342$ (NH), 1929 (GaH); MS/EI: m/z (%): 860.4 (100) $[M]^+$; EI accurate MS: $[M^+]$ calcd for $C_{50}H_{71}{}^{69}GaN_4S_2$: 860.4370, found: 860.4397.

X-ray single-crystal structural analyses: Crystals of **4**–**10** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made by using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares (SHELX97)[18] using all unique data. All non-hydrogen atoms are anisotropic with non-hydrides included in calculated positions (riding model). Hydride ligands in the structures of all complexes except **5** were located from difference maps and refined isotropically without restraints. The hydride ligand of **5** was included in a calculated position. The crystal structure refinements of **5**, **6**, **8**, and **10** converged with relatively high R factors due to weakness of higher angle data. In the case of **6**, the weakness of the data at θ angles greater than 22.5° prompted their exclusion from the structural refinement process. Despite the relatively poor quality of the structures of **5**, **6**, **8**, and **10**, their gross molecular connectivities are unambiguous and fully supported by their spectroscopic and analytical data. Crystal data, details of data collections and refinement are given in Tables 1 and 2.

CCDC CCDC-265825 (**4**), CCDC-265826 (**5**), CCDC-265827 (**6**), CCDC-265828 (**7**), CCDC-265829 (**8**), CCDC-265830 (**9**), and CCDC-265831 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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