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Invited review

New developments in the chemistry of organoaluminum and organogallium hydrides

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Abstract

A survey of our recent work on organoaluminum and organogallium hydrides is presented. Three types of ligand system have been employed for the stabilization of monomeric aluminum and gallium mono- and dihydrides. The "two-armed" 2,6-bis (dimethylaminomethyl) phenyl ligand is effective when intramolecular bis(base) stabilization is necessary; its use has permitted the isolation of the first examples of monomeric aluminum and gallium dihydrides. The use of the corresponding "one-armed" 2-(dimethylaminomethyl) phenyl ligand resulted in the formation of gallium mono- and dihydride monomers and an aluminum dihydride dimer. The first base-free aluminum and gallium monohydrides and gallium dihydride have been stabilized by employing the bulky 2, 4, 6, -tris(*t*-butyl) phenyl ligand.

Keywords: Aluminium; Gallium; Hydrides

Neutral organoaluminum hydrides, $RA1H_2$ and R_2AlH, constitute well-known classes of compound [1]. However, owing to the coordinative unsaturation at the metal center, previous examples of base-free organoaluminum hydrides were confined to dimers or higher oligomers. Considerably less is known about the structures and chemical properties of analogous molecules featuring Ga–H bonds. As in the case of the organoaluminum hydrides, there is a pronounced tendency toward oligomerization and, prior to 1993, the structurally authenticated examples (electron diffraction) comprised the dimers $[Me_2Ga(\mu\text{-}H)]_2$, $[H_2Ga(\mu\text{-}X)]_2$ ($X = Cl$ or NMe_2), and $[H_2Ga(\mu\text{-}H)_2BH_2]$ and the unusual trinuclear species $[HGa(BH_4)_2]$ with a pentacoordinate gallium atom [1,2]. Stable indium hydrides are very rare and restricted to a handful of anionic species [1,3]. A neutral ether adduct of composition $((InH_3)_x \cdot nEt_2O)$ is unstable and decomposes to a polymeric indium (I) hydride of unknown structure.

One of our motivations for developing the chemistry of monomeric Group 13 hydrides related to the fact that AlH_n and GaH_n moieties have been detected on surfaces during film growth from organoaluminum [4] and organogallium [5] sources. In principle, therefore, organohydrides of Group 13 elements could serve as useful models for enhanced understanding of the reaction chemistry of surface-bound MH_n entities. A second motivation for developing these classes of compound concerned the possibility that, because of the order of bond strengths H–H > M–H, thermal or photochemical reductive elimination of H_2 might occur, thus providing a convenient new route to M(II) dimers and M(I) clusters. Finally, and somewhat optimistically, we were interested in the feasibility of preparing neutral organoindium hydrides.

In the initial approach to the synthesis of monomeric Group 13 dihydrides, we opted to employ the intramolecular Lewis base stabilization provided by the 2,6-bis(dimethylaminomethyl)phenyl ligand which is conveniently available as the lithium salt [6]. The first task, synthesis of the precursor dihalides, was readily accomplished [7–9] by use of the following metathetical reactions (Eq. 1)

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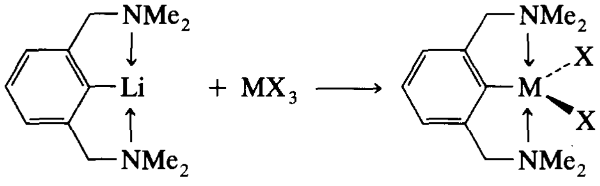


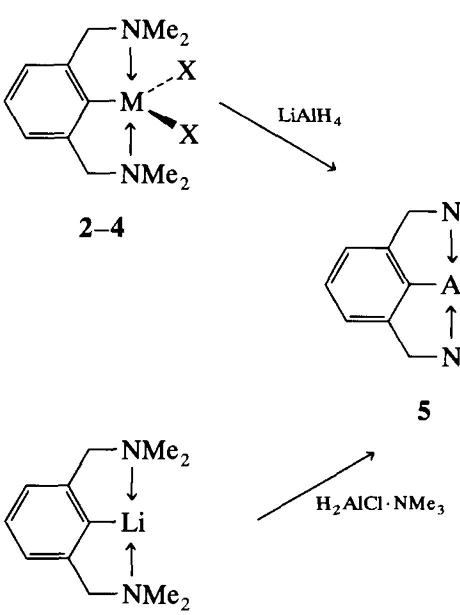
(1)

1

2: M = Al; X = Cl
3: M = Ga; X = Cl
4: M = In; X = I

Compounds **2**–**4** have been characterized by single-crystal X-ray diffraction. Both amine "arms" are coordinated in each compound and the geometry at the Group 13 atom is approximately trigonal bipyramidal. As expected, the N–M–N bond angles are somewhat less than 180° owing to the constraints of the ligand system.

The reaction of **2** with $LiAlH_4$ in Et_2O solution afforded a virtually quantitative yield of **5**, the first base-stabilized monomeric aluminum hydride (Scheme 1) [7].



2–4

5

1

Scheme 1.

Interestingly, the same aluminum hydride was obtained in high yields by treatment of the heavier Group 13 halides **3** and **4** with $LiAlH_4$. Moreover, **5** can also be produced, albeit in lower yields, via the metathetical reaction of lithium reagent **1** with $H_2AlCl \cdot NMe_2$ [7]. An X-ray diffraction study confirmed the monomeric nature of **5** (Fig. 1) and revealed that both amine "arms" are coordinated. Both hydrides were located in the final difference map and the overall geometry at the pentacoordinate aluminum center is trigonal bipyramidal. However, while the H_2AlC moiety is planar within experimental error (sum of angles at Al = 360.0(21)°), the axial ligands are distinctly nonlinear (N(1)–Al(1)–N(2) = 157.8(2)°) owing to the constraints of the ligand system. The latter factor also explains why the N–Al bond lengths in **5** (av. 2.255(5) Å) are longer than those in typical amine–alane adducts, e.g. 2.063(8) Å in Me_3NAlH_3. The average Al–H bond length is **5** (1.50(4) Å) is comparable to those reported for other terminal Al–H bonds [1].

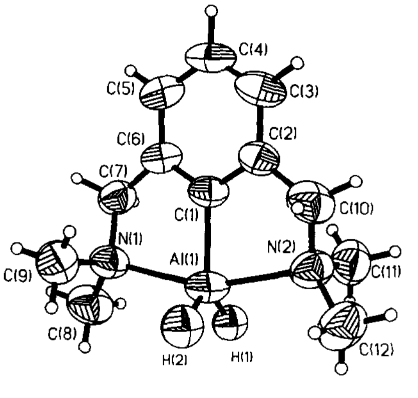
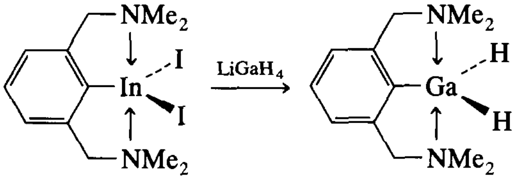


Fig. 1. Thermal ellipsoid plot of **5** showing atom labeling scheme.

Because of the facile transmetalation reactions noted above, it was recognized that the synthesis of the corresponding gallium dihydride (**6**) would have to be approached by treatment of **3** with $LiGaH_4$ [10]. As expected, the reaction of the indium iodide **4** with $LiGaH_4$ also affords **6** (Eq. 2) [10]

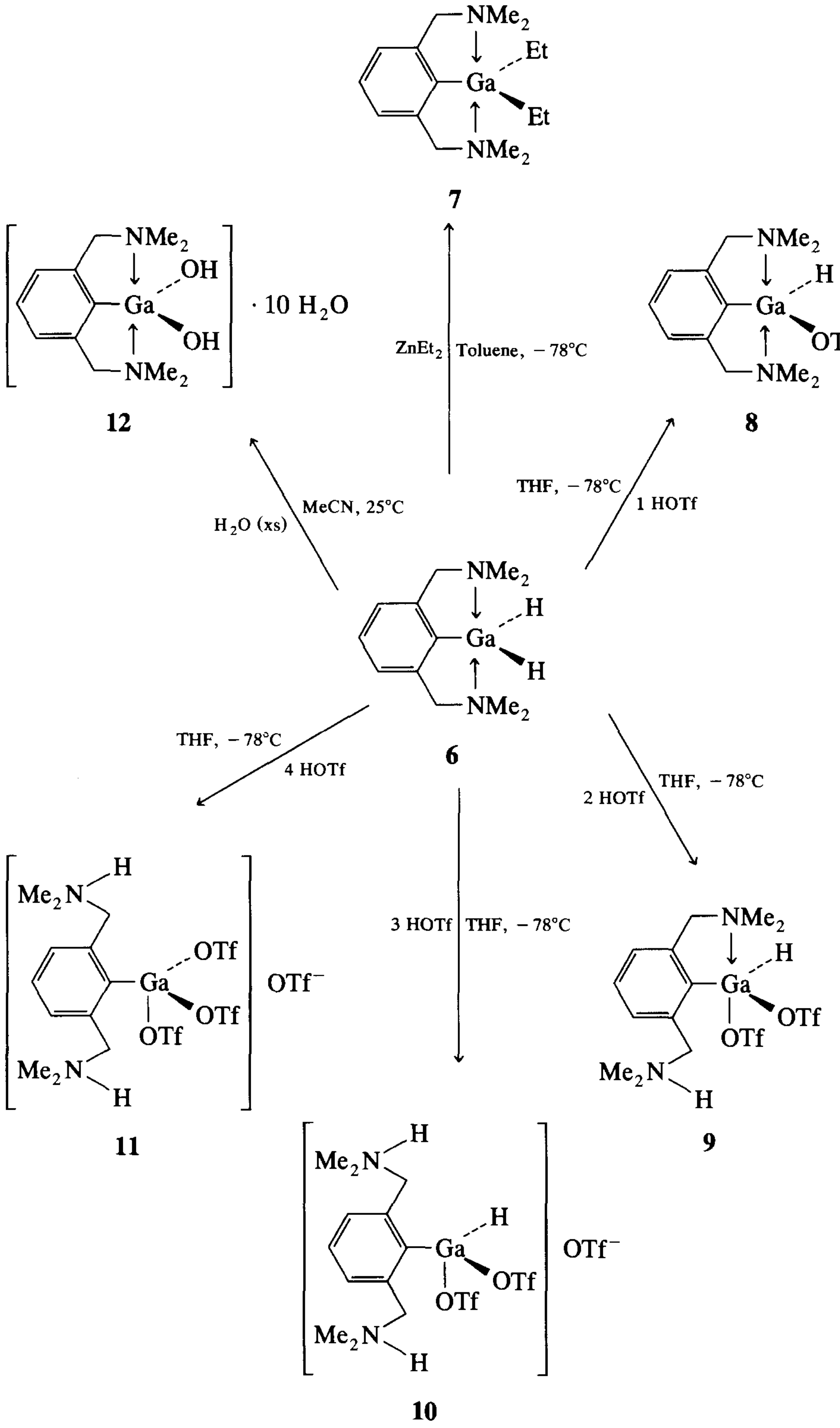


(2)

4 **6**

An X-ray diffraction study showed that the crystalline state of **6** comprises monomers and that there are no unusually short intermolecular contacts. Both hydrides were located, and the average Ga–H bond length of 1.41(9) Å is in the same range reported for terminal Ga–H bonds (see below). As expected, the geometry at the pentacoordinate gallium center is very similar to that in the analogous aluminum hydride **5** and the distorted trigonal bypyramid comprises a $CGaH_2$ plane and an N–Ga–N axis with a bond angle of 155.4(2)°.

Preliminary studies reveal that **6** exhibits a diverse reactivity [10]. As indicated in Scheme 2, treatment of **6** with $ZnEt_2$ results in quantitative conversion to the $GaEt_2$ derivative **7**. This is an interesting result because previous Ga–H to Ga-alkyl transformations had been effected by olefin hydrogallation rather than by hydride/alkyl exchange. Further manifestations of the hydride reactivity were evident when **6** was treated with successive equivalents of triflic acid (HOTf). Interestingly, the first equivalent of HOTf attacks a Ga–H bond



Scheme 2.

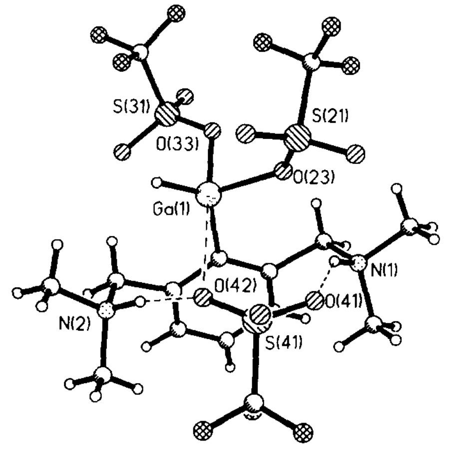
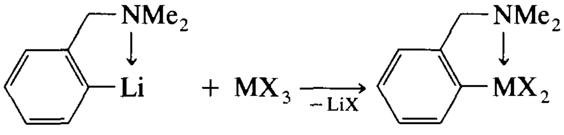


Fig. 2. Perspective of **10** and atom labeling scheme.

to afford **8** rather than quaternizing one of the Me_2N groups. Note, however, that the second equivalent of HOTf does, in fact, quaternize one of the Me_2N groups. Undoubtedly this is due to the significantly reduced hydridic character of the remaining Ga–H moiety in **8**. Such a view is consistent with the downfield shift of the Ga–H ^1H NMR resonance in proceeding from **6** to **8**. As anticipated on the basis of the latter argument, the third equivalent of HOTf also quaternizes a Me_2N group to form **10** in preference to attacking the Ga–H bond. It is, in fact, only the fourth equivalent of HOTf that protonates the final Ga–H bond to produce the tetra(triflato) species **11**. Compounds **8**, **9**, and **10** have been characterized by X-ray crystallography [10,11]. The solid-state structure of **10** is of particular interest because the external triflate anion is hydrogen-bonded to two NH^+ groups (Fig. 2). The overall geometry at gallium is approximately trigonal due to the proximity (3.166 Å) of one of the triflate oxygen atoms (O(42)). The monomeric gallium hydride is also reactive toward hydroxide ions. Thus aqueous hydrolysis of **6** affords **12**, the first example of a bis(hydroxide) of gallium. The solid state of **12** is intriguing since, as a consequence of extensive hydrogen bonding, it involves a layer-type structure wherein $Ga(OH)_2$ moieties point toward the water layers (Fig. 3). Hydrogen bonding is also responsible for the cohesion of the gallium-containing organometallic layers since half of the GaOH groups are linked to the GaOH groups of neighboring molecules.

Unfortunately, the "two-armed" hydrides **5** and **6** proved to be surprisingly stable to vapor-phase heating or to irradiation with 254 nm light, thus frustrating our plan to employ these compounds as sources of Al(I) and Ga(I). We therefore turned our attention to the synthesis of aluminum and gallium dihydrides bearing the corresponding "one-armed" ligand system in the hope that they might prove to be more amenable to reductive elimination of molecular hydrogen. As in the case of the "two-armed" derivatives described above, the first step involved the synthesis of the requisite Group 13 dihalides. This was accomplished [9,12] by means of metathetical reactions using the appropriate lithium aryl (Eq. 3) [13]



(3)

13: M = Al; X = Br
14: M = Ga; X = Cl
15: M = In; X = I

All three compounds were amenable to study by X-ray crystallography. Compounds **13** (Fig. 4) and **14** are monomeric and the aluminum and gallium atoms are both four-coordinate due to a donor–acceptor interaction with the amine "arm" [12]. There is, however, considerable departure of bond angles from the ideal tetrahedral angle. Moreover, the N–metal-C-C-C rings

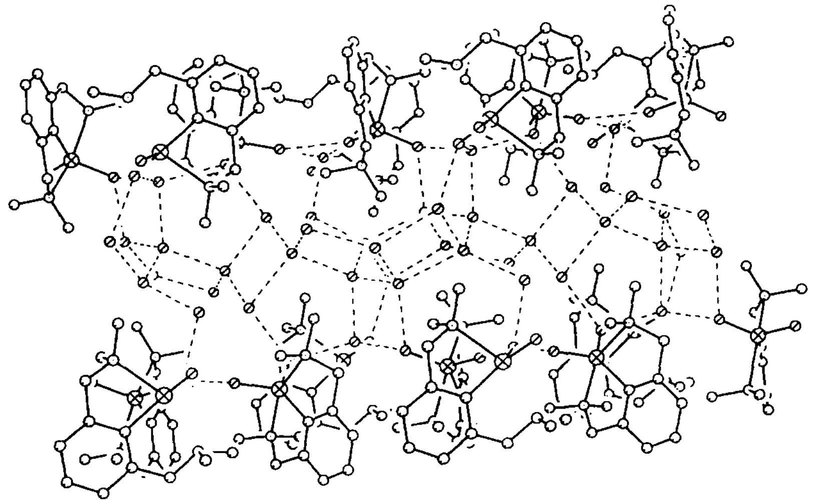


Fig. 3. Crystal packing diagram of **12** showing water layer.

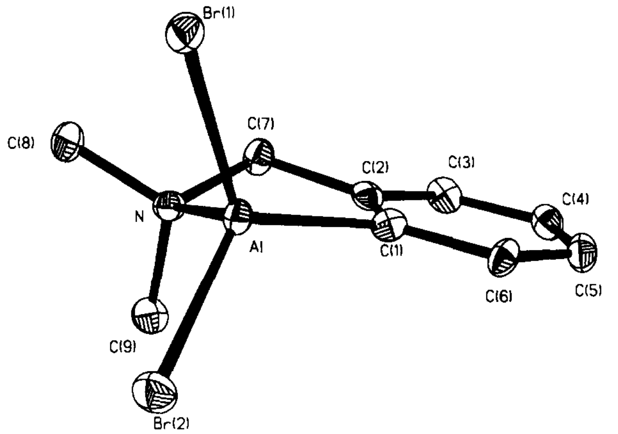


Fig. 4. Thermal ellipsoid plot of **13** with atom numbering.

are distinctly nonplanar due to the protrusion of the N atom from the least-squares aryl plane. The metal–N bond lengths in **13** (2.003(5) Å) and **14** (2.071(2) Å) are appreciably shorter than those in the corresponding "two-armed" systems **2** (2.261(3) Å) [7] and **3** (2.355(4) Å) [8] owing presumably to the fact that the latter compounds involve an intramolecular base competition. The indium iodide **15** adopts a dimeric structure (Fig. 5) in the solid state [9]. The dimeric unit comprises two unsymmetrical In–I–In bridges and, since the In_2I_2 moiety lies on a crystallographic center of symmetry, it is necessarily planar. Since the amine "arm" is coordinated, each indium atom is pentacoordinate in what is best described as a trigonal bipyramidal array. The average In–N bond length in **15** is ca. 0.1 Å shorter than that in the corresponding "two-armed" compound **4** [9].

Treatment of **13** with $LiAlH_4$ afforded an 85% yield of the corresponding hydride **16** [12]. Compound **16** also resulted from the transmetalation reaction of **14** or **15** with $LiAlH_4$ (Eq. 4)

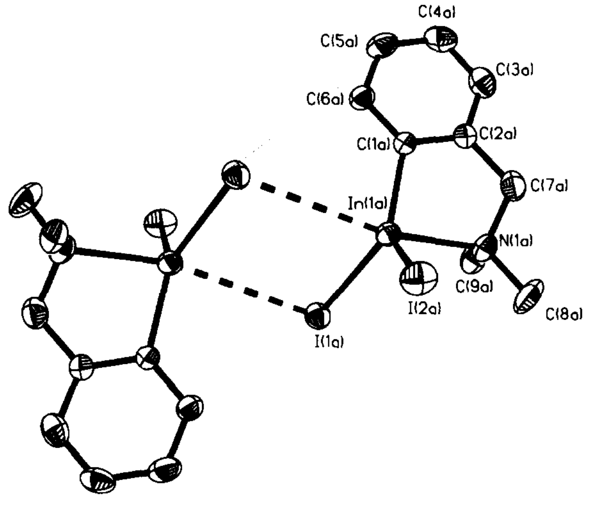


Fig. 5. Thermal ellipsoid plot of **15** showing atom numbering scheme.

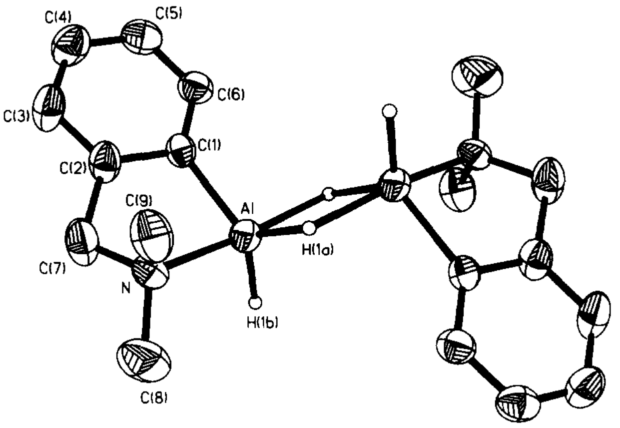
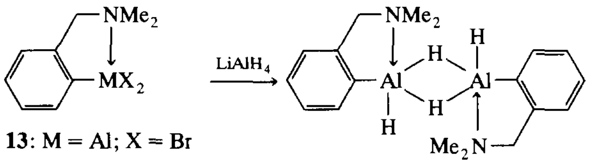


Fig. 6. Thermal ellipsoid plot of **16** showing atom labeling scheme.



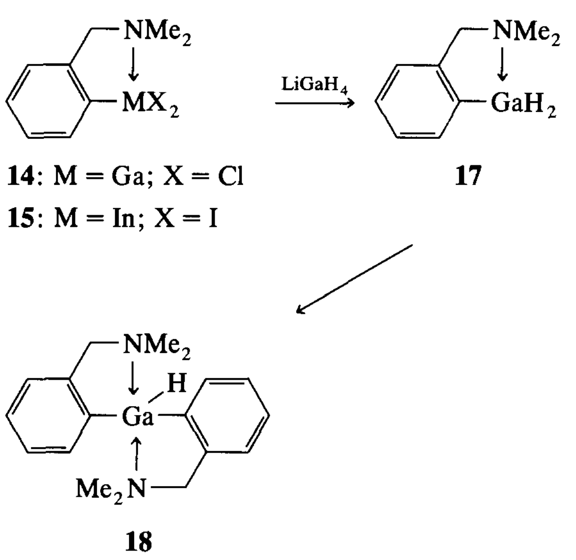
(4)

13: M = Al; X = Br
14: M = Ga; X = Cl
15: M = In; X = I

16

The dimeric nature of **16** was suggested both by the detection of a dimer-Me peak in the CI mass spectrum and also by the presence of terminal and bridging Al–H stretching frequencies in the IR spectrum. Confirmation of this structural assignment was provided by an X-ray crystal structure analysis [12]. Since the dimer resides on a crystallographic center of symmetry, the Al_2H_2 unit is necessarily planar (Fig. 6). It is worth noting, however, that the Al–H–Al bridges are somewhat asymmetrical and the two bonds differ in length by 0.24 Å. The terminal Al–H bond is shorter than either of the bridge bonds and is similar in length to that in **5** [7]. The overall geometry at aluminum is close to trigonal bipyramidal and comprises a C(1)–H(1b)–H(1a)–Al plane with a sum of bond angles of 359.1(1) Å and a N–Al–H(1aa) axis with an angle of 170.4(2)°. The Al–N bond length (2.102(4) Å) is approximately 0.1 Å longer than that in the precursor bromide **13** [12]. The observation that **16** is a dimer, rather than a monomer like **5**, is clearly a consequence of the coordination of two amine "arms" in the latter.

The removal of an amine "arm" also has a consequence on the outcome of the reaction of **14** or **15** with $LiGaH_4$. As shown in Scheme 3, the gallium dihydride **17** formed initially undergoes a redistribution reaction to form **18** over a period of several days at −20°C [12]. The structures of both **17** and **18** were established by X-ray diffraction. Unfortunately, the crystals of **17** were only of mediocre quality and it was not possible to locate the hydride ligands. Nevertheless, the presence of a terminal GaH_2 group was established by the detection of a hydride resonance of relative intensity 2 at δ 5.12 in the ^1H NMR spectrum and by the presence of



Scheme 3.

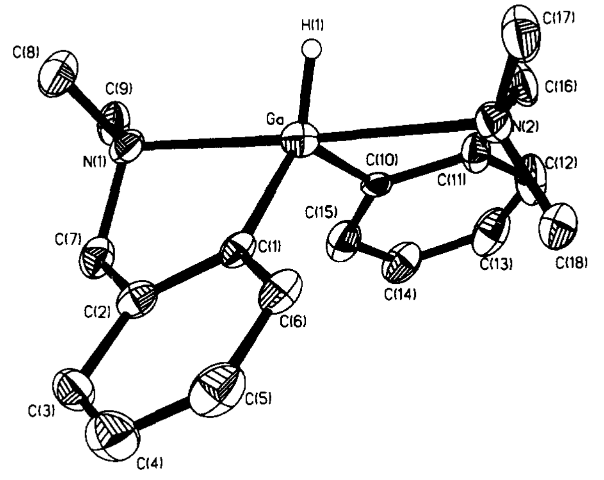
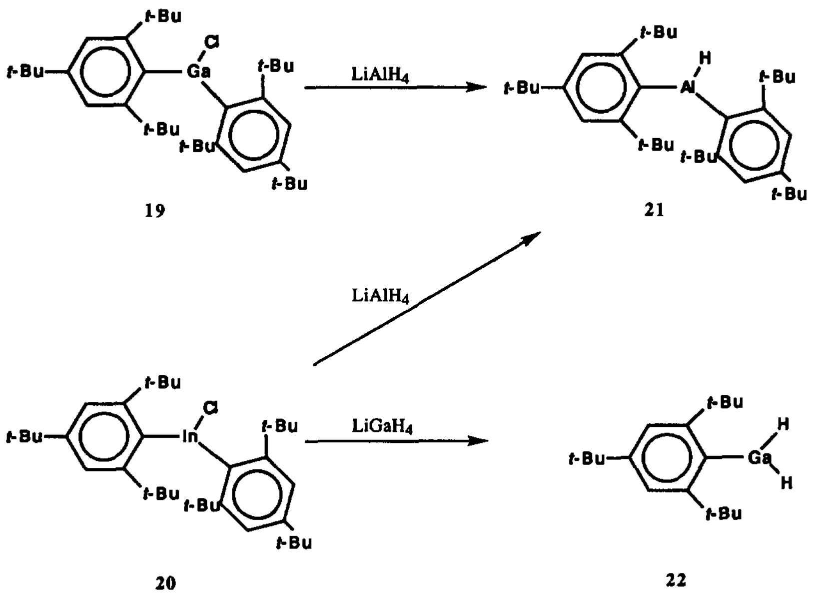


Fig. 7. Thermal ellipsoid plot of **18** with atom numbering scheme.

symmetric and asymmetric Ga–H stretching frequencies in the IR spectrum. Moreover, the Ga–N bond length in **17** (2.087(7) Å) is very similar to that in the precursor chloride **14** (2.071(2) Å) thus indicating a four-coordinate gallium center. The overall geometry of **18** (Fig. 7) resembles that of the corresponding chloride complex $[2\text{-}(Me_2NCH_2]C_6H_4]_2GaCl$ reported by two other groups [14]. The amine "arms" of both ligands are coordinated to gallium thereby rendering the geometry at this center close to trigonal bipyramidal. The sum of bond angles in the H–Ga–C(1)–C(10) plane is 357.3(4)° and the angle of the N(1)–Ga–N(2) axis is 177.0(3)°. The hydride ligand in **18** was located and the Ga–H bond length of 1.150 Å is slightly longer than that in the "two-armed" gallium dihydride **6** [10]. As expected from the standpoint a intramolecular Lewis base competition, the Ga–N bond distances in **18**, which average 2.390(8) Å, are somewhat longer than that in **17** (2.087(7) Å) [12]. The "one-armed" aluminum and gallium hydrides **16**, **17**, and **18** were found to be as robust as the "two-armed" hydrides. Each compound sublimes without decomposition and survives prolonged irradiation with 254 nm light.

Given that both the "one-armed and "two-armed" aluminum and gallium hydrides proved to be unusually thermally and photochemically stable, we turned our attention next to the synthesis and structural assay of base-free aluminum and gallium hydrides. In order to obtain monomeric derivatives it was important to maximize the steric blockade and accordingly our work in this area started with the very bulky halides $(Ar^*)_2GaCl$ [15] and $(Ar^*)_2InCl$ [16]; ($Ar^* = 2,4,6\text{-}{}^tBu_3C_6H_2$). (The bromo analogue of the latter was reported indepen-



Scheme 4.

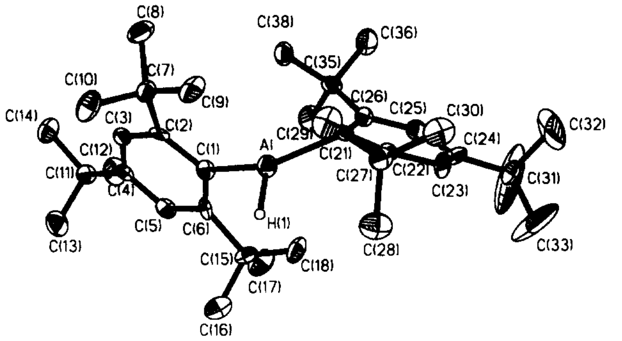


Fig. 8. Thermal ellipsoid plot of **21** showing atom labeling scheme.

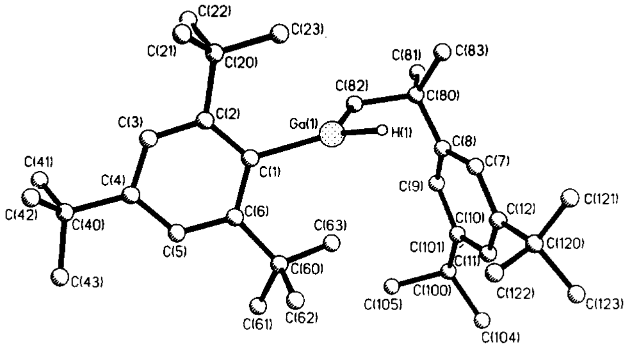


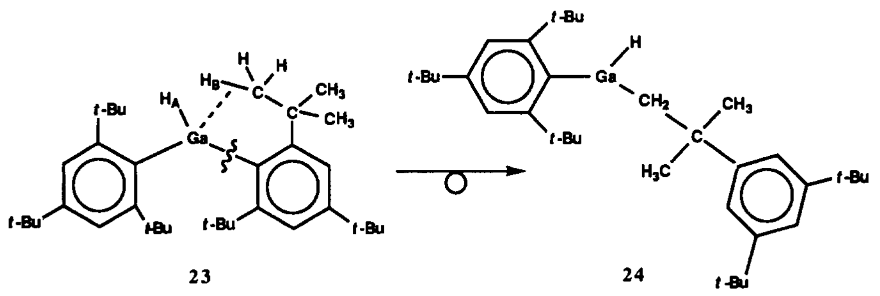
Fig. 9. Perspective of **24** showing atom numbering scheme.

dently by Oliver et al. [17]). As indicated in Scheme 4, the reaction of $(Ar^*)_2GaCl$ (**19**) or $(Ar^*)_2InCl$ (**20**) with $LiAlH_4$ results in transmetalation and formation of $(Ar^*)_2AlH$ (**21**), the first example of a base-free monomeric organoaluminum hydride [18]. By means of X-ray crystallography it was demonstrated that the cause of the monomeric nature of **21** (Fig. 8 resides in the fact that two of the *ortho*-^{t}Bu groups at C(2) and C(22) partially shield the terminal Al–H functionality thereby preventing the formation of Al–H–Al bridges. Although the geometry at aluminum is trigonal planar within experimental error, the C–Al–C bond angle is unusually wide (132.1(4)°) thus bearing witness to the existence of strain in this molecule. The Al–H bond length in **21** is the same as that in the "two-armed" aluminum hydride **5** [7] within experimental error.

Transmetalation was also observed in the reaction of $(Ar^*)_2InCl$ (**20**) with $LiGaH_4$; however, in this case it was accompanied by cleavage of an aryl group and formation of the gallium dihydride **22** [18]. We have also prepared **22** by treatment of $(Ar^*)_2GaCl$ [19] with $LiGaH_4$ [16]. The X-ray analysis of **22** was complicated by disorder of the *ortho*-^{t}Bu groups and by the weakly diffracting nature of the crystals. Nevertheless, and as in the case of the "one-armed" gallium dihydride **17**, it was possible to demonstrate the presence of the GaH_2 moiety by ^{1}H NMR (δ 6.41) and IR spectroscopy (νGaH) 1887 and 1908 cm^{-1}).

The anticipated product of the ambient temperature reaction of $(Ar^*)_2GaCl$ with $LiGaH_4$ was the monohydride $(Ar^*)_2GaH$ (**23**). It came as somewhat of a surprise therefore to discover that the product of this reaction is in fact the "aryl-rotated" isomer **24** [16]. It is surmised that, due to an agostic interaction between one of the C–H bonds of an *ortho*-^{t}Bu group, transfer of H_B to gallium occurs in concert with cleavage of the Ga–C(*ipso*) bond, formation of a new Ga–C bond and 1,2 transfer of H_A to the aryl ring (Scheme 5).

It should be pointed out that $(Ar^*)_2GaCl$ is converted to a benzo(b)gallolane and $[Ga(CH_2CMe_2C_6H_3\{3,5^tBu_2\}(Ar^*)Cl]$, the chloro analogue of **24**, upon heating in high vacuum at 140–160°C [15]. On the basis of the available evidence, we believe that the two rearrangement mechanisms are different. Firstly, we do not observe gallolane formation, and secondly, the rearrangement of **23** to **24** takes place under markedly milder conditions. An X-ray crystallographic study of **24** confirmed the monomeric nature and connectivity (Fig. 9) and revealed that the environment of the gallium atom is trigonal planar [16]. Within experimental error the Ga–H bond length in **24** is (1.43(10) Å) is identical to that in the "two-armed" gallium hydride **6** (1.41(9) Å) [10]. A final point of structural interest concerns the short contacts between the gallium atom and one of the hydrogen atoms on each of the two *ortho*-^{t}Bu groups. The Ga(1) ··· H(63c) contact (2.03(2) Å) is shorter than the Ga(1)–H(23A) contact (2.28(2) Å). However, the arrangement of the latter is such that mid-point of the C(23)–H(23A) bond is located near the quasi-threefold rotation axis of the gallium atom, thus suggesting an agostic interaction. As



Scheme 5.

indicated above, an agostic interaction may be involved in the rearrangement of **23** to **24**.

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