Metal Hydride Complexes

Kinetic Control over the Thermal Stability of the In–H Bond: Synthesis and Characterization of Amido Indium Hydride Complexes**

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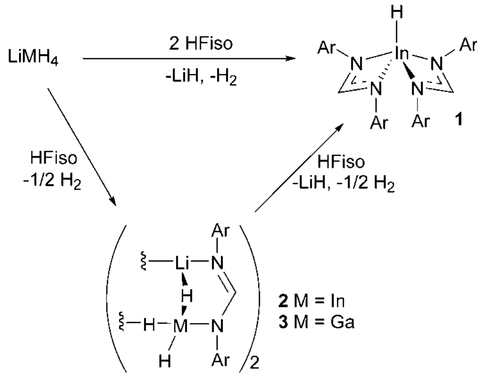
In memory of Colin Eaborn

Aluminium and gallium hydride chemistry is now well developed and complexes that incorporate Al–H and Ga–H bonds have found a wide variety of applications in organic transformations, inorganic synthesis, and materials chemistry.[1] Until recently, this situation was not mirrored by indium hydride complexes as it was generally accepted that the relative weakness of the In–H bond led to their observed thermal instability. In this respect, Downs and co-workers have rightly pointed out that the In–H bond is stronger than the In–C bond and given the thermal stability of indium alkyls, the instability of indium (and gallium) hydride compounds is partly kinetic in origin.[2] It is likely that this instability is derived from the propensity of the metal hydrides to associate through M-H-M bridges, which lower the energy barrier to homolytic decomposition processes that involve dihydrogen elimination. This proposal is in line with the recent first observation of solid $[(InH_3)_n]$, which decomposes above 180 K.[3]

In contrast, we have prepared the first InH_3 complexes that have moderate thermal stability given the right choice of ligand.[4] Most success has been had with highly nucleophilic N-heterocyclic carbenes (NHCs), which form strong C–In dative bonds and discourage the formation of intermolecular In-H-In bridges by providing a degree of steric shielding to the InH_3 fragment.[5] A number of alkyl, halogen, phosphido and gallyl indium hydride complexes[4,6] have also been prepared and are finding applications in inorganic[4] and organic synthesis.[7] For these applications to expand, greater control over the thermal stability of indium hydride complexes is required.

Bulky amide ligands have been widely used to stabilize aluminium and gallium hydride complexes,[8] though amido indium hydride complexes are unknown, except for several matrix-isolated examples, for example, $[H_2InNH_2]$.[9] We wished to prepare such complexes and saw the amidinate class of ligand, $[RNC(R')NR]^-$, as being appropriate to this cause. The stabilizing features this class of ligand offers include an ability to chelate metal centers and the potential to incorporate bulky substituents on the N atom and on the C backbone of the ligand. Both stabilizing features have been previously exploited in a range of Group 13 halide and alkyl complexes.[10] In this preliminary study, we have specifically chosen the bulky formamidinate ligand, $[ArNC(H)NAr]^-$ $Ar = C_6H_3iPr_2$-2,6 (Fiso),[11] which has been utilized to prepare the first amido indium hydride complexes, one of which displays unprecedented thermal stability.

Treatment of an ethereal solution of $LiInH_4$[4] with two equivalents of HFiso led to H_2 and LiH elimination and a moderate yield of **1** after recrystallization from diethyl ether (Scheme 1). In the solid state, **1** does not show any decomposition in air after one week and under argon does not begin to decompose until 160 °C (compare with $[AlH(Fiso)_2]$, decomp 231–233 °C).[12] In toluene solutions it can be heated in a sealed tube at 125 °C for 3 h before complete decomposition occurs. This does not afford indium metal but HFiso and an insoluble, brown organo-indium material, the exact identity of which could not be determined. The decomposition process is presumably intramolecular and involves hydrogen transfer to one Fiso ligand and metallation of the other (compare with NHC metallation in the decomposition of $[InH_3\{C[N(iPr)CH]_2\}]$).[4] The ^1H NMR spectrum of **1** does



Scheme 1. Synthesis of compounds **1**–**3**.

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not exhibit an observable In−H resonance signal, which can be explained by quadrupolar broadening of this signal by the ^{113}In and ^{115}In isotopes ($I = 9/2$). Its infrared spectrum does, however, show a sharp In−H stretching absorption, as would be expected for a terminal hydride ligand. This occurs at significantly higher frequency (1748 cm^{-1}, compared with 1823 cm^{-1} for [AlH(Fiso)$_2$][12]) than the In−H stretching modes of InH_3 complexes (1640–1660 cm^{-1})[4] due to a negative inductive effect from the two anionic Fiso ligands, which decreases the relative polarity of the In−H bond. Consequently, this decrease should lead to a decrease in the predisposition of the indium hydride fragment to be involved in intermolecular hydride bridges. The deuteride analogue of **1**, namely, **1**−D (decomp 165–170 °C), was prepared from $LiInD_4$ and HFiso and its infrared spectrum is essentially identical to that of **1**, though no absorption at 1748 cm^{-1} is present. A corresponding In−D stretch was not discernable at the expected wavenumber (ca. 1240 cm^{-1}) due to strong masking from the fingerprint region.

The molecular structure of **1** (Figure 1 a)[13] shows that the complex is monomeric and has a heavily distorted trigonal bipyramidal indium coordination environment with N(2) and N(4) in axial positions. The hydride ligand was located from difference maps and refined isotropically; the In−H bond length is 1.71(6) Å (av 1.68 Å in [$InH_3(PCy_3)$], Cy = cyclohexyl[4]). The geometry of **1** is similar to that of the related indium chloride complex, [InCl{CyNC(*t*Bu)NCy}$_2$],[14] and the only other example of a structurally characterized amidinate Group 13 hydride complex, [AlH{(Me$_3$Si)NC(Ph)N(SiMe$_3$)}$_2$],[15] though the bulk of the Ar substituents in **1** cause it to be significantly more distorted. We believe that these groups also lead to the remarkable thermal stability of the complex by forming a heavily protected "pocket" in which the hydride ligand sits (Figure 1 b). This pocket prevents the formation of intermolecular In-H-In bridges and hinders chemical attack of the InH moiety.

To examine the mechanism of formation of **1**, the reaction of $LiInH_4$ with HFiso was carried out in a 1:1 stoichiometry, which led to the formation of the amidotrihydrido indate complex, **2**, in moderate yield. The corresponding gallium complex, **3**, was prepared by an analogous procedure. Further treatment of **2** with HFiso led to the formation of **1**, H_2, and LiH, thus confirming that **2** is an intermediate in the aforementioned 2:1 reaction. In contrast, **3** did not react with HFiso, which can be explained by the less hydridic nature of Ga−H compared with In−H bonds[4] and the fact that gallium hydride complexes disfavor coordination numbers greater than 4.[1b] In the solid state, **2** begins to decompose at 42 °C (compare with **3**, m.p. 84–86 °C) and in solution it is unstable above 0 °C deposits indium metal, evolves H_2 gas, and generates a solution of [Li(Fiso)], as determined by ^{7}Li and ^{1}H NMR studies.

The infrared spectrum (Nujol mull) of **2** displays In−H stretching absorptions for the terminal (1719 cm^{-1}; compare with that in **3** 1879 cm^{-1}) and bridging (1632 cm^{-1}; **3** 1769 cm^{-1}) hydride ligands, the assignment of which was confirmed by their absence in the spectrum of the corresponding trideuteride complex, **2**−D_3 (1161 cm^{-1} In−D bridging, In−D terminal-masked). Because of the thermal instability of **2**, solution NMR spectroscopic studies of this compound were carried out at ≤ -30 °C and in the case of the ^{1}H NMR spectrum, a broad In−H resonance was observed at $\delta = 6.02$ ppm (**3**, Ga−H $\delta = 4.68$ ppm) in the normal region.[4] The ^{1}H-coupled and decoupled ^{6}Li and ^{7}Li spectra comprise only singlet resonances in the temperature range, −30 to −80 °C. In contrast, the ^{6}Li NMR spectrum of **3** exhibits a sharp doublet resonance signal at 25 °C ($^1J_{LiH} = 1.2$ Hz), which suggests that this compound exists as a monomer in solution with the intramolecular Li-H-Ga bridge remaining intact.[16] Cooling solutions of **3** led only to loss of resolution of the doublet at about −15 °C and the resultant broad singlet did not resolve to a doublet of doublets, as expected for a hydride bridged dimeric structure, down to −80 °C.

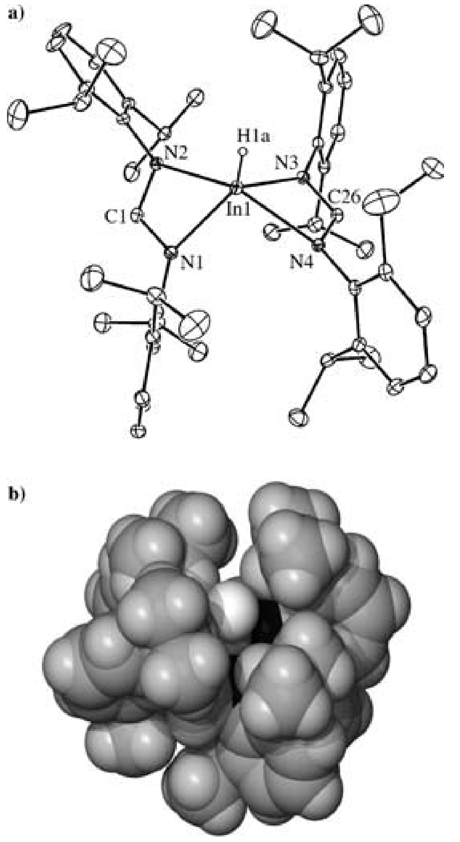

Figure 1. a) Molecular structure of **1** (ORTEP, thermal ellipsoids set at 20 % probability). Selected bond lengths [Å] and angles [°]: In(1)-N(3) 2.177(3), In(1)-N(1) 2.196(3), In(1)-N(2) 2.289(3), In(1)-N(4) 2.301(3), In(1)-H(1a) 1.71(6), N(1)-C(1) 1.320(4), N(2)-C(1) 1.310(4), N(3)-C(26) 1.305(4), N(4)-C(26) 1.307(4); N(1)-In(1)-N(2) 59.64(10), N(3)-In(1)-N(4) 59.38(10), N(2)-In(1)-N(4) 146.08(10), N(1)-In(1)-N(3) 116.26(10), N(1)-In(1)-(H1a) 123.9(17), N(2)-In(1)-(H1a) 113.8(19), N(3)-In(1)-(H1a) 119.1(17), N(4)-In(1)-(H1a) 100.0(19), N(2)-C(1)-N(1) 116.1(3), N(3)-C(26)-N(4) 116.4(3). b) Space filling model of **1**. The hydride ligand is shown in white (at the center).

The solid-state structure of **2** is depicted in Figure 2[13] and represents the first structural characterization of a trihydrido indate complex. The location and isotropic refinement of the hydride ligands confirmed that the complex dimerizes through intermolecular hydride bridges to give a {$Li_2In_2H_4$}

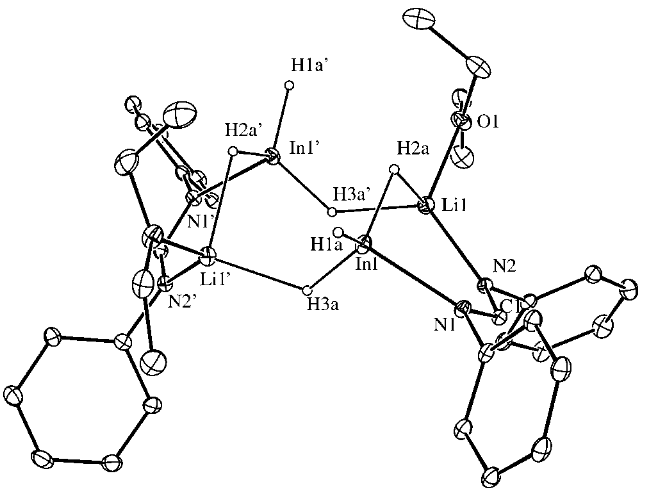

Figure 2. Molecular structure of **2** (isopropyl groups omitted for clarity). Selected bond lengths [Å] and angles [°]: In(1)-N(1) 2.178(3), In(1)-H(1a) 1.64(4), In(1)-H(2a) 1.71(4), In(1)-H(3a) 1.66(4), Li(1)-H(2a) 2.14(5), Li(1)-H(3a') 2.10(5), N(2)-Li(1) 2.002(6), N(1)–C(1) 1.329(4), N(2)–C(1) 1.308(4); N(1)-In(1)-H(1a) 106.9(15), N(1)-In(1)-H(2a) 99.7(15), N(1)-In(1)-H(3a) 104.8(13), H(1a)-In(1)-H(2a) 114.6(19), H(1a)-In(1)-H(3a) 115.3(19), H(2a)-In(1)-H(3a) 113(2), In(1)-H(2a)-Li(1) 106(2), Li(1')-H(3a)-In(1) 124(2), N(1)-C(1)-N(2) 124.8(3). Symmetry transformation: ′ −*x*, *y*, −*z*+1/2.

ring, which adopts what could be described as a boat conformation with the intramolecular hydride bridges, H(2) and H(2′), *cis* to each other. It is noteworthy that the gallium analogue, **3**, has a similar structure[13,16] though these hydride bridges are *trans*, thus giving a pseudochair conformation to the corresponding $\{Li_2Ga_2H_4\}$ ring. There is no difference in the bridging and terminal In–H bond lengths, within experimental error, as is the case for both crystallographically independent Li–H bonds. Not surprisingly, the bridging formamidinate ligand backbones in **2** are more open [N(1)-C(1)-N(2) 124.8(3)°] and significantly more localized than the chelating ligands in **1** [N-C-N, 116.3° av].

In summary, we have prepared and structurally characterized the first examples of amido indium hydride complexes, one of which, **1**, has unprecedented thermal stability. We believe this arises largely from steric shielding of the In–H fragment, which not only protects it from chemical attack but also circumvents the formation of M-H-M bridges, a proposed pathway to Group 13 hydride decomposition. We are currently examining the preparation and reactivity of other amidinate Group 13 hydride complexes. In addition, the characteristics of bulky amidinates may lend them to the eventual stabilization of thallium hydride complexes, a goal we are pursuing.

Experimental Section

1: A solution of HFiso (1.03 g, 2.82 mmol) in Et_2O (40 cm^3) was added over 5 min to an in situ generated solution of $LiInH_4$ (1.41 mmol) in Et_2O (50 cm^3) at −78 °C. The resultant suspension was warmed to 25 °C, concentrated to about 35 cm^3 and filtered. Slow cooling of the filtrate to −35 °C yielded colorless crystals of **1** (0.34 g, 29 %); m.p.: 160–170 °C (decomp); ^1H NMR (250 MHz, C_6D_6, 298 K): $\delta = 1.18$ (d, 24 H, $^3J(H,H) = 6.7$ Hz, CH_3), 1.26 (d, 24 H, $^3J(H,H) = 6.7$ Hz, CH_3), 3.55 (sept, 8 H, $^3J(H,H) = 6.7$ Hz, CH), 7.22–7.35 (m, 12 H, Ar-H), 7.77 ppm (s, 2 H, NC(H)N); $^{13}C\{^1H\}$ NMR (250 MHz, C_6D_6, 298 K): $\delta = 23.7$ (CH_3), 24.4 (CH_3), 28.5 (CH), 123.6 (*p*-ArC), 125.4 (*m*-ArC), 140.9 (*o*-ArC), 143.7 (*ipso*-ArC), 164.3 ppm (NCN); IR (Nujol): $\tilde{\nu} = 1748$ cm^{-1} (s, In-H); MS/APCI *m/z* (%): 366 $[HFiso]^+$ (100), 844 $[MH]^+$ (18); Elemental analysis cald (%) for $C_{50}H_{71}InN_4$: C 71.24, H 8.49, N 6.64 %; found: C 71.12, H 8.57, N 6.94 %.

2: A solution of HFiso (0.51 g, 1.41 mmol) in Et_2O (20 cm^3) was added to an in situ generated solution of $LiInH_4$ (1.41 mmol) in Et_2O (50 cm^3) at −78 °C over 5 min. The resultant suspension was warmed to −20 °C whereupon the volatile products were removed in vacuo. The residue was extracted into hexane (20 cm^3) and the extract cooled to −35 °C yielding colorless crystals of **2** (0.43 g, 27 %); m.p.: 42–44 °C (decomp); ^1H NMR (300 MHz, $[D_8]$toluene, 243 K): $\delta = 0.79$ (br, 12 H, OCH_2CH_3), 1.21–1.46 (br overlapping m, 48 H, CH_3), 2.91 (br, 8 H, OCH_2), 3.54 (br, 4 H, CH), 3.72 (br, 4 H, CH), 6.02 (br, 6 H, InH), 7.10–7.25 (br, 12 H, Ar-H), 7.29 ppm (br, 2 H, NC(H)N); $^{13}C\{^1H\}$ NMR (300 MHz, $[D_8]$toluene, 243 K): $\delta = 14.3$ (OCH_2CH_3), 23.5 (CH_3), 25.2 (CH_3), 28.1 (CH_3), 32.1 (CH), 34.6 (CH), 65.2 (OCH_2), 123.6 (*p*-ArC), 124.2 (*m*-ArC), 143.0 (*o*-ArC), 147.4 (*ipso*-ArC), 167.9 ppm (NCN), all signals broad; $^7Li\{^1H\}$ NMR (300 MHz, $[D_8]$toluene, 243 K): $\delta = 1.45$; $^6Li\{^1H\}$ NMR (300 MHz, $[D_8]$toluene, 243 K): $\delta = 1.51$ ppm; IR (Nujol): $\tilde{\nu} = 1719$ cm^{-1} (s, terminal In-H), 1632 (br s, bridging In-H); MSAPCI *m/z* (%): 366 $[HFiso]^+$ (100). The thermal instability of **2** precluded its elemental analysis.

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[13] Crystal data for **1**: $C_{50}H_{71}InN_4$ $M_r = 842.93$, monoclinic, space group $P2_1/n$, $a = 14.774(3)$, $b = 16.317(3)$, $c = 20.936(4)$ Å, $\beta = 110.24(3)^\circ$, $V = 4735.3(17)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.182\ g\,cm^{-3}$, $F(000) = 1792$, $\mu(Mo_{K\alpha}) = 0.535\ mm^{-1}$, 150(2) K, 9211 unique reflections [R_{int} 0.0707], R (on F) 0.0463, wR (on F^2) 0.1159 ($I > 2\sigma(I)$); **2**.$(Et_2O)_{0.5}$: $C_{60}H_{102}In_2Li_2N_4O_{2.5}$, $M = 1161.97$, monoclinic, space group $C2/c$, $a = 23.916(5)$, $b = 15.999(3)$, $c = 21.368(4)$ Å, $\beta = 111.49(3)^\circ$, $V = 7608(3)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.014\ g\,cm^{-3}$, $F(000) = 2452$, $\mu(Mo_{K\alpha}) = 0.640\ mm^{-1}$, 150(2) K, 8676 unique reflections [R_{int} 0.0679], R (on F) 0.0474, wR (on F^2) 0.1234 ($I > 2\sigma(I)$); **3**: $C_{58}H_{96}Ga_2Li_2N_4O_2$ $M = 1034.71$, triclinic, space group $P\bar{1}$, $a = 11.103(2)$, $b = 13.166(3)$, $c = 21.211(4)$ Å, $\alpha = 92.95(3)$, $\beta = 91.12(3)$, $\gamma = 93.83(3)^\circ$, $V = 3088.8(11)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.113\ g\,cm^{-3}$, $F(000) = 1112$, $\mu(Mo_{K\alpha}) = 0.911\ mm^{-1}$, 150(2) K, 12440 unique reflections [R_{int} 0.0482], R (on F) 0.0434, wR (on F^2) 0.0950 ($I > 2\sigma(I)$). CCDC-235631–235633 (**1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[16] Selected spectroscopic and structural data for **3** have been submitted as Supporting Information.