Cluster Compounds

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A Hydrocarbon-Soluble Lithium Hydride Complex**

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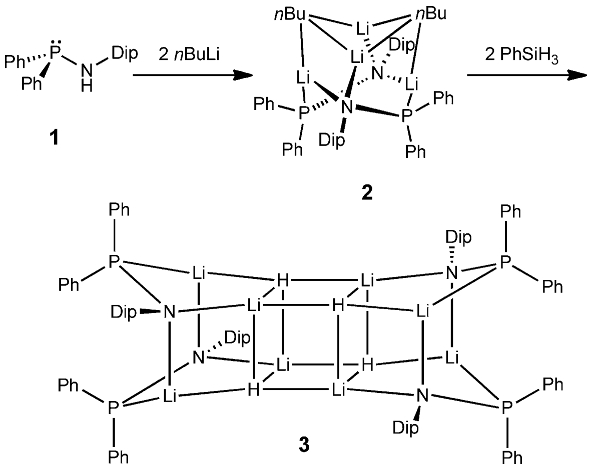
Lithium hydride is the lightest metal hydride and is considered to be the simplest ionic compound.[1,2] With a low molecular weight of just under 8 $\mathrm{g\,mol^{-1}}$ and a relatively high hydrogen content of 12.7 % it is of interest for numerous applications including hydrogen storage technologies[3] and uses in organic and inorganic synthesis.[4] LiH crystallizes with a rock salt structure and shows a high lattice energy of approximately 220 $\mathrm{kcal\,mol^{-1}}$.[1] This renders the material stable and relatively easy to handle, but also makes it too insoluble and unreactive for many applications.

In recent years, a number of well-defined and structurally characterized molecular s-block metal hydride complexes have been forthcoming and show significant differences to the properties of the parent bulk metal hydride, that is, MH for the group 1 metals and MH_2 for the group 2 metals. The majority of these achievements concentrate on the molecular compounds of the group 2 metals Be,[5] Mg,[6] and Ca.[7] Some of these hydride complexes have already been employed in hydrometalation reactions[8] and have even been successfully used as a hydrogenation catalyst on alkenes.[9]

The majority of hydride complexes involving group 1 metals are mixed metal systems, and can be considered ate complexes, for example $LiAlH_4$ and its derivatives.[2,10] Some remarkable examples include mixed metal systems such as $[[\{(Me_3Si)_2N\}AlH_2Li]_3(LiH)]$ having a central distorted $(LiH)_4$ cube featuring one hydride moiety solely bound to Li cations.[11] There are also a number of complexes having an interstitial hydride surrounded by seven or eight lithium ions, as in cationic $[L_6HLi_8]^+$ (L = a chelating monoanionic N-ligand) and the related neutral complex $[L_6HLi_7]$.[12,13] Active forms of alkali metal hydrides MH (M = Li, Na, K) have been obtained from mixtures of metal alkoxides and alkyl metal compounds in the presence or absence of dihydrogen or from alkyl metal compounds and silanes.[4,14] Mixed lithium alkoxide/lithium hydride aggregates have been generated thermally or photolytically in solution,[15] and the remarkable 'superaggregate' $[(t\mathrm{BuOLi})_{16}(\mathrm{LiH})_{17}]$ was, in one instance, obtained in an undetermined yield and structurally characterized.[16]



Scheme 1. Preparation of **2** and **3**.

Reaction of the new phosphinoamine $DipNHPPh_2$ (**1**; Dip = 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$; Scheme 1), prepared from DipNHLi and $ClPPh_2$,[17] with two equivalents of *n*BuLi in *n*-hexane afforded the mixed alkyl phosphinoamido lithium complex $[(\mathrm{DipNPPh}_2)_2\mathrm{Li}_4n\mathrm{Bu}_2]$ (**2**).[17] For comparison, the reaction of equimolar amounts of $DipNHPPh_2$ and *n*BuLi in a hydrocarbon solvent affords the poorly soluble phosphinoamido lithium salt $[(DipNPPh_2)Li]$, which is presumably oligo- or polymeric in structure. Addition of donor solvents to $[(DipNPPh_2)Li]$ afford the soluble complexes $[(DipNPPh_2)Li(Do)_2]$ $[(Do)_2 = (THF)_2$ or (TMEDA)], which have three-coordinate lithium cations showing N,O,O and N,N,N coordination modes, respectively, and no Li···P contacts.[17,18]

A single-crystal X-ray structure analysis of compound **2**[17] revealed a mixed dialkyl bisphosphinoamido lithium complex composition (Figure 1). Compound **2** crystallizes with a full molecule in the asymmetric unit and features a severely distorted Li_4 tetrahedron (dashed lines in Figure 1) with interatomic Li···Li distances ranging from 2.407(4) Å (Li1-Li3) to 3.218(4) Å (Li1-Li2).[19] The P–N bond lengths in the phosphinoamide moiety are only marginally shorter than the comparable bond length in the parent phosphinoamine **1** (1.699(5) Å).[17] Two *n*-butyl groups in **2** cap two of the four Li_3 faces with Li-C distances ranging from 2.202(3) Å to 2.270(3) Å. Both *n*-butyl groups in **2** are disordered and have been modeled with two positions for the outer three carbon atoms, and only the major butyl components are shown in Figure 1. Two Li cations (Li1, Li2) each coordinate to one N and one P atom from different phosphinoamide ligands and have one contact each to one *n*Bu carbon atom. In addition, each of those two Li cations show Li···H contacts to alkyl groups of one *i*Pr group of the Dip moiety; the shortest Li···H distances being approximately 2.06–2.09 Å. The other two Li cations (Li3, Li4) bind to one N atom each and to two *n*Bu

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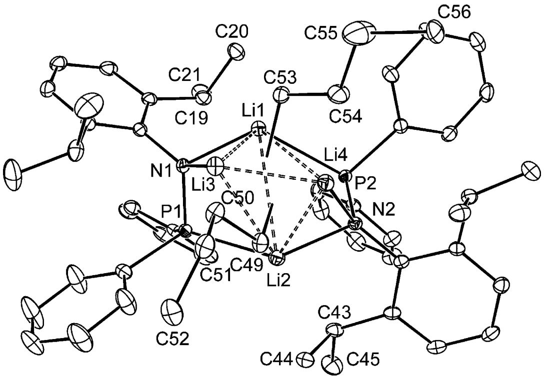


Figure 1. Crystal structure of $[(\mathrm{DipNPPh_2})_2\mathrm{Li_4}n\mathrm{Bu_2}]$ (**2**). The thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity. Only the main components of the disordered *n*-butyl groups are shown. Selected bond lengths [Å] and angles [°]: P1–N1 1.6786(13), P2–N2 1.6785(13), Li1–N1 2.034(3), Li1–P2 2.560(3), Li2–N2 2.072(3), Li2–P1 2.591(3), Li3–N1 2.023(2), Li3···P1 2.962(3), Li4–N2 2.018(3), Li4–P2 2.884(3), Li2–C49 2.256(3), Li3–C49 2.218(3), Li4–C49 2.202(3), Li1–C53 2.270(3), Li3–C53 2.217(3), Li4–C53 2.245(3), Li1···Li2 3.218(4), Li1···Li3 2.407(4), Li1···Li4 2.856(4); N1-P1-Li2 94.89(7), P1-N1-Li1 112.26(10), P1-N1-Li3 105.92(10), Li3···Li1···Li4 57.04(10), Li3···Li1···Li2 58.67(10), Li4···Li1···Li2 46.57(8), Li4···Li2···Li3 57.07(10), Li4···Li2···Li1 58.84(10), Li3···Li2···Li1 46.29(8), Li1···Li3···Li4 70.40(12), Li1···Li3···Li2 75.04(11), Li4···Li3···Li2 53.11(10), Li2···Li4···Li1 74.58(11), Li3···Li4···Li1 52.56(10).

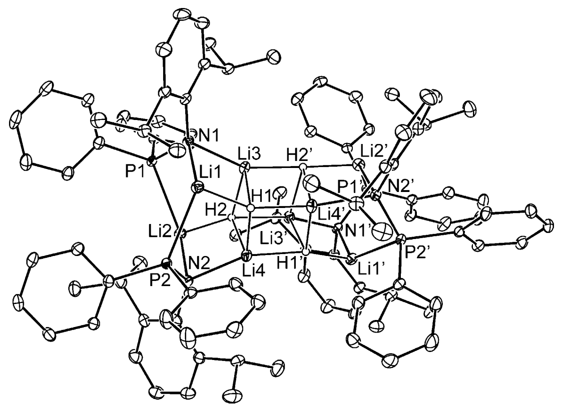


Figure 2. Crystal structure of $[\{(\mathrm{DipNPPh_2})\mathrm{Li}\}_4(\mathrm{LiH})_4]\cdot\mathrm{C_6H_6}$, ($\mathbf{3}\cdot\mathrm{C_6H_6}$). The thermal ellipsoids are shown at 30% probability. The solvent molecule and hydrogen atoms except hydride ligands have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N1 1.666(2), P2–N2 1.673(2), P1–Li2 2.530(4), N1–Li3 2.037(4), N1–Li1 2.042(4), Li1–P2 2.530(4), N2–Li4 2.032(4), N2–Li2 2.038(4), Li1–H1 1.83(4), Li2–H2 1.81(4), Li3–H2 1.98(4), Li3–H1 1.96(4), Li4–H1 1.99(4), Li4–H2 1.97(4), Li1···Li2 3.131(6), Li1···Li3 2.509(5), Li1···Li4 3.051(6), Li2···Li3 3.061(6), Li3···Li3′ 2.668(8), Li3···Li4 2.821(6), Li3′···Li4 2.691(5), Li4···Li4′ 2.682(8); H2-Li4-H1 88.3(18), Li3-H2-Li4 ca. 91.0, Li4-H1-Li4′ ca. 87.8, Li4-H1′-Li3′ ca. 89.2. Symmetry operation: #1 $-x, y, -z+{}^{1}/_{2}$; #2 $-x, -y+1, -z$.

carbon atoms. In addition, they show short Li···H contacts to one β-methylene unit in each of the *n*-butyl groups (Li3 to C50 and Li4 to C54); the shortest contacts being around 2.0 Å. Some related complexes having the general formula $\mathrm{L_2Li_4}n\mathrm{Bu_2}$ (L = anionic ligand) and featuring a distorted $\mathrm{Li_4}$ tetrahedron have been structurally characterized and show similar overall features compared with those of **2**.[20]

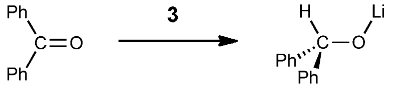
The ^{1}H NMR spectrum of compound **2** in deuterated benzene at 30 °C displays one broadened septet resonance and two very broad doublets corresponding to the protons of the *i*Pr substituents. At elevated temperatures of approximately 60–70 °C, only one sharp septet and one broadened doublet resonance is found for those protons. Cooling a sample of **2** in deuterated toluene leads to splitting of the broad septet resonance at a coalescence temperature of approximately 19 °C (equates to a $\Delta G^{\neq}$ of ca. 13 kcal mol^{-1}), and at low temperatures of approximately −30 to −50 °C two sharp septet and four doublet resonances are found. This situation remains largely unchanged down to −85 °C, albeit with significantly broadened resonances. At room temperature, one major singlet is observed in the ^{7}Li NMR spectrum and the ^{31}P{^{1}H} NMR spectrum shows one broad resonance, which resolves to a multiplet at low temperatures.[17] This behavior suggests an exchange of ligands around the $\mathrm{Li_4}$ core in **2**, which is rapid on the NMR timescale at elevated temperatures. Similar fluxional processes have been observed, especially at elevated temperatures for several of the related $\mathrm{L_2Li_4}n\mathrm{Bu_2}$ molecules.[20]

Treating $[(\mathrm{DipNPPh_2})_2\mathrm{Li_4}n\mathrm{Bu_2}]$ (**2**) with two equivalents of phenylsilane at room temperature in benzene or toluene affords the crystalline complex $[\{(\mathrm{DipNPPh_2})\mathrm{Li}\}_4(\mathrm{LiH})_4]$ (**3**; see Figure 2 for the molecular structure from a single-crystal structural determination), a hydrocarbon-soluble compound having a central distorted $(\mathrm{LiH})_4$ cube. As with other s-block metal precursor complexes,[6a,c–e,7,8a–c] phenylsilane readily substitutes alkyl groups with hydride ligands. When the reaction is carried out in deuterated benzene and monitored by multinuclear (^{1}H, ^{7}Li and ^{31}P{^{1}H}) NMR spectroscopy it is evident that compound **2** is formed in a rapid reaction in approximately 90 % yield with $\mathrm{PhSiH_2}n\mathrm{Bu}$ as the by-product.

$[\{(\mathrm{DipNPPh_2})\mathrm{Li}\}_4(\mathrm{LiH})_4]\cdot\mathrm{C_6H_6}$ ($\mathbf{3}\cdot\mathrm{C_6H_6}$) crystallizes with half a molecule in the asymmetric unit. During the course of this study, we characterized two additional solvates,[17] each with two full molecules of **3** in the asymmetric unit, which have very comparable metrical features. Only the structure of $\mathbf{3}\cdot\mathrm{C_6H_6}$ will be discussed herein. The structure of **3** derives from that of **2** by retaining the overall geometry, substituting the *n*Bu groups with hydride ligands, and dimerization of the fragments through the newly formed hydride ligands. This process leads to an $\mathrm{Li_8}$ cluster compound with a central distorted $(\mathrm{LiH})_4$ cube. The hydride ligands have been located from difference maps and refined in all solvates. The Li cations form an array of three connected edge-sharing tetrahedrons,[21] with the middle one containing the $(\mathrm{LiH})_4$ cube. All Li···Li distances fall into the range found for those of **2**. The lengths of the determined Li–H bonds within the central $(\mathrm{LiH})_4$ cube (1.96(4)–1.99(4) Å) are close to the shortest Li-H distances in cubic LiH (ca. 2.03-2.04 Å),[1] close to those of $[[\{(\mathrm{Me_3Si})_2\mathrm{N}\}\mathrm{AlH_2Li}]_3(\mathrm{LiH})]$,[11] and comparable to those of the interstitial Li-H compounds $[\mathrm{L_6HLi_8}]^+$ and $[\mathrm{L_6HLi_7}]$.[12,13] In addition, comparable short Li···H$_{\mathrm{aliphatic}}$ contacts are found in **3**, the shortest one being around 2.0 Å, and similar interactions are observed in **2**. Four shorter Li-H contacts of 1.81(4)–1.83(4) Å are measured to Li1 and Li2 of the outer tetrahedra. The hydrides, like the *n*Bu groups in **2**, can be considered capping two of the four Li_3 faces of the outer two Li_4 tetrahedra.

In solution, the ^{1}H NMR spectrum of **3** in deuterated benzene or toluene at 30 °C shows two septets and three doublets, having the relative intensities of 1:1:2, for the protons of the isopropyl groups, and one broad resonance at $\delta = 4.18$ ppm with an integration of four for the hydride ligands. This chemical shift represents a typical value for main-group hydride compounds including most of the characterized s-block metal hydride complexes.[2,5–7] Previously, IGLO calculations for LiH containing cluster compounds have suggested an ^{1}H NMR chemical shift range of approximately 3.5–4.0 ppm.[15] The $^{31}P\{^1H\}$ NMR spectrum displays a multiplet centered at $\delta = 33.7$ ppm,[17] and the ^{7}Li NMR spectrum shows two broad resonances at $\delta = 3.0$ and 2.6 ppm. The former resonance appears considerably sharper in the ^{1}H decoupled ^{7}Li NMR spectrum and it is therefore likely associated with the central $(LiH)_4$ core. The NMR spectra are consistent with an idealized D_2 symmetry as obtained from the crystals structure. At elevated temperatures, the septets and doublets broaden (ca. 40 °C) and the two broadened septets merge into one at around 55 °C ($\Delta G^{\ddagger}$ of ca. 16 kcal mol^{-1}). Above this temperature, one broad resonance is observed for the methine septets, and sharpens at approximately 90–100 °C, and one broad doublet is found for the isopropyl methyl groups. The broad resonance assigned to the LiH moieties remains essentially unchanged across the investigated temperature range. The high-temperature NMR spectra are consistent with fluxional behavior of the anionic ligands around the $Li_8H_4^{4+}$ core and suggest a rapid exchange processes. This heating experiment was accompanied by significant decomposition of **3** (approximately above 60 °C), thus irreversibly forming poorly soluble [(DipNPPh$_2$)Li], and by implication LiH. The decomposition is rapid at 90–100 °C and compound **3** decomposes within several minutes, a process presumably induced by the structural changes at higher temperatures.

To demonstrate that the hydrocarbon-soluble LiH complex **3** can be a suitable reagent for hydrometallation reactivity,[6g,8] we investigated its reaction with benzophenone (Scheme 2). When this reaction is carried out in deuterated benzene at room temperature and monitored by ^{1}H, ^{7}Li, and $^{31}P\{^1H\}$ NMR spectroscopy, a rapid reaction is observed. The broad singlet assigned to the LiH moieties in the ^{1}H NMR spectrum of **3** disappeared upon treatment with benzophenone and new sharp resonances at $\delta = 5.41$ ppm emerged. After the reaction, crystallization of the known hexameric cage compound $[\{(Ph_2CHO)Li\}_6]$[22] was observed, and the compound was characterized by single-crystal X-ray structure analysis and ^{1}H NMR spectroscopy. After precipitation, $[\{(Ph_2CHO)Li\}_6]$ shows a very low solubility in noncoordinating solvents, and in deuterated benzene/THF (ca. 5:1) the Ph$_2$C*H* resonance shifts to $\delta = 6.08$ ppm, which compares well with the reported resonance in deuterated THF ($\delta = 6.03$ ppm).[22] On a preparative scale, $[\{(Ph_2CHO)Li\}_6]$ could be obtained from **3** and benzophenone in good yield.[17]



Scheme 2. Schematic hydrolithiation of benzophenone using **3**.

In summary, we have prepared and structurally characterized a hydrocarbon-soluble LiH complex having a central $(LiH)_4$ cube, and it is a promising reagent for synthesis as has been demonstrated by a hydrolithiation reaction with benzophenone.

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