Coordination of LiH Molecules to Mo≡Mo Bonds: Experimental and Computational Studies on Mo₂LiH₂, Mo₂Li₂H₄, and Mo₆Li₉H₁₈ Clusters

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ABSTRACT: The reactions of LiAlH₄ as the source of LiH with complexes that contain (H)Mo≡Mo and (H)Mo≡Mo(Mo(H) cores stabilized by the coordination of bulky AdDipp₂ ligands result in the respective coordination of one and two molecules of (thf)LiH, with the generation of complexes exhibiting one and two HLi(thf)H ligands extending across the Mo≡Mo bond (AdDipp₂ = HC(NDipp)₂; Dipp = 2,6-[Mo₂{HLi(thf)H}₃(AdDipp₂)] molecular architecture led to spontaneous trimerization and the supplemented by the coordination of the Mo bond (AdDipp₂ = HC(NDipp)₂; Dipp = 2,6-[Mo₂{HLi(thf)H}₃(AdDipp₂)] molecular architecture led to spontaneous trimerization and the supplemented by the coordination of the Mo bond to the Li ion. Attempts to construct a [Mo₂{HLi(thf)H}₃(AdDipp₂)] molecular architecture led to spontaneous trimerization and the formation of a chiral, hydride-rich Mo₆Li₉H₁₈ supramolecular organization that is robust enough to withstand the substitution of lithium-solvating molecules of tetrahydrofuran by pyridine or 4-dimethylaminopyridine.

INTRODUCTION

Along with noble gas helium, hydrogen and lithium are the simplest, lightest elements and the only ones that existed in the young universe. Helium hydride, HeH⁺, is a molecule of astrophysical importance, whereas LiH is the lightest metal hydride and arouses considerable interest due to its many applications. In the gas phase, molecules of LiH exist as a result of the overlap of the singly occupied H 1s and Li 2s atomic orbitals, with an experimentally determined interatomic distance of ca. 1.60 Å. In the solid state, LiH adopts a cubic NaCl-type structure, characterized by long Li–H contacts of approximately 2.04 Å. Molecular hydrides of the s-block elements have been intensively investigated in recent years. For group 2 metals, new, uncommon structures and a diversity of useful applications in hydrometalation, hydrogenation, and other reactions have been uncovered, thanks in no small part to the great efforts of Mulvey and co-workers of hexamethyldisilane and its derivatives.

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LiO'Bu agglomerate Li₃H₁₇(O'Bu)₁₆ and the synthesis of a (LiH)₄ cube coordinated to three bis(amido)alane units. Transition-metal complexes allegedly containing coordinated monomeric molecules of LiH are sparse. There are, however, some reports describing M–H–Li systems where a degree of covalent bonding within the bridging bond can be proposed on the basis of the observation of one-bond ¹H–⁷Li NMR coupling constants. Despite the scarcity of complexes of this type, it is conceivable that, like other main-group metal–hydrogen bonds (e.g., Mg–H, Al–H, and Zn–H), a molecule of lithium hydride might bind to a transition-metal fragment through its Li–H bond, assisted by an interaction with an adjoining ligand that could compensate for the unsaturation of the lithium coordination shell and further heighten the σ-donor strength of the polar Li–H bond.

In this context, we envisioned that quadruply bonded hydride central units [Mo₅(H)₁₃] (n = 1, 2) could be utilized to build the target molecular architectures. As represented in structure A of Figure 1, such dimolybdenum dihydride units possess strong hydride character and feature Mo–Mo separations of close to 2.10 Å, with Mo–H vectors nearly perpendicular to the Mo–Mo bond. Here, we discuss the...
synthesis and structure of complexes 3·thf and 4·thf (Figure 1) that contain one and two formally monoanionic, bridging H−Li(thf)−H ligands, respectively, spanning the Mo≣Mo bond. We also study the unexpected formation of a unique, hydrocarbon-soluble, hydride-rich Mo₆Li₉H₁₈ cluster, 5·thf, formally resulting from the trimerization of an unobserved monomer [Mo₂(μ-HLi(thf)H)₃(μ-AdDipp₂)], with the loss of a molecule of tetrahydrofuran. Throughout this article, three-center–two-electron (3c−2e) interactions implicating Mo−H and Li−H bonds are represented with the aid of the half-arrow formalism proposed by Green, Green, and Parkin.46

RESULTS AND DISCUSSION

In recent work, we showed that tetrahydrofuran adduct [Mo₂(H)₂(μ-AdDipp₂)₂(thf)₂] (1·thf, where AdDipp₂ = HC-(NDipp)₂) and Dipp = 2,6-Pr₂C₆H₃ is a convenient source of unsaturated dihydride [Mo₂(H)₂(μ-AdDipp₂)₂] containing a trans-(H)Mo≡Mo(H) core (structure A in Figure 1).55 The Mo₂(H)₂ functionality of this complex was engendered by hydrogenolysis of the Mo−C bonds of the [(Me)Mo≡Mo(Me)] homologue,47 a method that continues to be a main vehicle for the synthesis of transition-metal hydrides. Searching for a related monohydride [(H)Mo≡Mo] core, we carried out the two-step transformation shown in Scheme 1a. Low-temperature alkylation of [Mo₂(μ-O₂CH)₂(μ-AdDipp₂)₂] with equimolar amounts of LiEt yielded an ethyl-formate intermediate that was reacted in situ with H₂ and converted to the hydride-formate product, 2·thf (Scheme 1), in good isolated yields (ca. 70%). The coordinated tetrahydrofuran molecule of 2·thf is highly labile, and it was readily replaced by Lewis bases such as 4-dimethylaminopyridine (dmap), 1,3,4,5-tetramethylimidazol-2-ylidene (IMe₄), and PMe₃, giving complexes 2·L (Scheme 1a, top). Similarly, the use of LiAlH₄ as a source of LiH permitted the isolation of complex 3·thf that was obtained as a yellow solid in yields of around 60%. This reaction was not, however, simple and also produced related derivative 4·thf, along with minute amounts of a tetrahydroaluminate complex to be described elsewhere. Complex 3·thf possesses a H−Mo≡Mo−H−Li(thf) chelate moiety resulting from the substitution of the coordinated tetrahydrofuran of 2·thf by a molecule of (thf)LiH, with the formation of a σ-Li−H complex, that becomes stabilized by the concomitant formation of a 3c−2e Mo−H→Li bond involving the adjacent Mo−H terminus.

Next, 1·thf was utilized as a source of the [Mo₂(H)₂] center (Scheme 1b). Mixing a tetrahydrofuran solution of this complex with a solution of LiAlH₄ in the same solvent caused the immediate precipitation of a bright-yellow solid that was

Figure 1. Simplified representations of the structures of complexes 3·thf-5·thf. The three structural types originate from [Mo₂(H)ₙ] cores by the incorporation of one, two, or three molecules of (thf)LiH (n = 1, complex 3·thf; n = 2, A and complex 4·thf; when n = 3, the unobserved monomer trimerizes to complex 5·thf with the loss of a molecule of tetrahydrofuran). In the structure of 5·thf, symmetry-related lithium atoms share the same color.
identified as dilithium tetrahydride dimolybdenum complex $[\text{Mo}_2\{\mu\text{-HLi(thf)}\text{H}\}_2\{\mu\text{-AdDipp}^2\}_2]$ (4-thf), that is, as a Mo$_2$Li$_2$H$_4$ cluster. As drawn in Scheme 1b, the compound contains two trans-$\mu$-HLi(thf)H ligands that extend across the Mo≣Mo bond. Thus, it can be related to 3·thf by means of formal replacement of the bridging formate of the latter by a second $\mu$-Li(thf)H$_2$−three-atom chelating ligand. In agreement with this rationale, complexes 3·thf and 4·thf were generated in high yields (70−85%) by the more direct method summarized in Scheme 1c, based on the reaction of readily available $[\text{Mo}_2\{\mu\text{-O}_2\text{CH}\}_2\{\mu\text{-AdDipp}^2\}_2]$ with LiAlH$_4$. The $^7\text{Li}[^1\text{H}]$ NMR spectrum is a somewhat broad singlet at 3.6 ppm that transforms into a 1:2:1 triplet in the proton-coupled $^7\text{Li}$ NMR experiment, with a one-bond $^7\text{Li}$−$^1\text{H}$ coupling constant of 16 Hz.

Complex 4·thf is only scarcely soluble in common solvents such as benzene, toluene, and tetrahydrofuran, but it is just sufficienty soluble in C$_6$H$_5$F for NMR studies. Pertinent NMR data are also included in Figure 2. In particular, the Mo$_2$LiH$_2$ moieties exhibit comparable $^1J(^7\text{Li}−^1\text{H})$ couplings of 17 Hz.

These observations categorically demonstrate the existence of HLiH entities coordinated to the Mo≣Mo quadruple bond in the 3·thf and 4·thf molecules. Besides, they attest without a doubt to the fact that, although probably mainly Coulombic in nature (vide infra), the Mo−H−Li−H−Mo bonding interactions involve a considerable degree of covalency, that is, of substantial electron density shared among the molybdenum, hydrogen, and lithium valence orbitals. It is pertinent to remark that the observation of scalar coupling in lithium hydride complexes is rare, to the point that few $^1J(^6,^7\text{Li}−^1\text{H})$ values can be found in the literature.\(^{31,32}−35\) Previously observed couplings range from approximately 6 to 15 Hz such that the 16 to 17 Hz values found for 3·thf and 4·thf are among the highest thus far reported. For the LiH molecule, a $^1J(^6\text{Li}−^1\text{H})$ coupling constant of 159 Hz has been calculated.\(^{49}\)
Complexes $3\cdot$thf and $4\cdot$thf possess good thermal stability. Their C$_6$D$_6$ and C$_6$D$_5$F solutions appear to be stable for 1 day at room temperature, though decomposition occurs upon heating at 70 °C for 3 to 4 h. In the solid state, decomposition is apparent only at $T \geq 150$ °C. The two compounds behave as soluble LiH carriers, particularly $4\cdot$thf, which is the more reactive of the two. For instance, complex $4\cdot$thf reacted with Ph$_2$C(O) to give the expected alkoxide Ph$_2$C(H)(OLi).$20,22

Their molecular structures were investigated by X-ray crystallography and optimized by means of DFT calculations. Owing to poor crystal properties, the data collected for the former do not permit a rigorous structural discussion, particularly with respect to what concerns the geometric parameters of H atoms. Nonetheless, they allow us to define beyond any doubt the connectivity represented in Figure S2.

**Figure 3.** Solid-state structure of $4\cdot$thf. Some atoms have been omitted for clarity. Thermal ellipsoids are shown at 50%. Selected bond distances (Å) and a bond angle (deg): Mo1–Li1, 2.91(2) and 2.97(2); Mo1–Mo1, 2.106(7); Mo1–N1, 2.10(1); Mo1–N2, 2.20(1); Li1–O1, 1.86(2) Å; and N1–Mo1–Li1, 92.1(5).
The NBO approach results in limited participation of the lithium atomic orbitals in occupied MOs. However, this does not mean that its interactions with the hydrides and the molybdenum atoms are strictly ionic, since the calculated reduced charge of the lithium ion is +0.67, indicative of a non-negligible covalent contribution. The reduced charge of the lithium "ion" is thus associated, in addition to thf → Li donation, with two sets of donor–acceptor interactions: (i) donation from σ(Mo−H) to Li and (ii) donation from the components of the Mo=Mo bond to Li (Figure 4c).

From the energy point of view, there are two sets of dominant interactions (Figure 5a) that imply donations from the σ(Mo−H) and σ(Mo−H) bonds to both s(Li) and p_x(Li) and from the σ component of the Mo=Mo bond to the atomic orbitals of Li. In the first set, we find donation from σ(Mo−H) to both s(Li) and p_x(Li), which are responsible for 84% of the interaction energy. Among the second set of interactions, donation from σ(Mo=Mo) to s(Li) (Figure 4c) makes a significant contribution of 12%; smaller contributions come from the donations of δ(Mo−Mo) to p_y(Li) and of σ(Mo−Mo) to p_x(Li), while almost negligible contributions appear for π(Mo−Mo) and for p_y and s(Li).

As a result of all of these donor–acceptor interactions from the Mo_H_2 moiety to the lithium ion, the distribution of the 0.33 valence electron held by the Li atomic orbitals (Figure 5b) reflects the major role played by the 2s and 2p_x Li AOs as acceptors. The high population of the lithium p_x orbital compared to its minor acceptor role toward the Mo=Mo group is undoubtedly due to the donation from its thf ligand. Finally, the lowest atomic orbital population in p_y results from the interesting donation from the δ(Mo=Mo) bonding orbital (Figure 4c).

We can therefore conclude that the stability of the Mo−H–Li=H−Mo ring results mainly from the formation of two 3c–2e Mo−H–Li bonds, supplemented by σ coordination of the Mo=Mo bond to the Li atom. The latter bonding component is consistent with a short distance between Li and the Mo=Mo centroid of 2.77 Å (Mo−Li = 2.97 Å), to be compared with a
covalent radii sum of 2.82 Å. Although of lesser quantitative importance, the existence of non-negligible electron donation from the bonding π and δ(Mo—Mo) orbitals is worth being stressed. The fact that the calculated dissociation energy of 4-thf into (thf)Li—H and dihydride [Mo2(H)2(μ-AdDipp2)] is 27.9 kcal/mol, smaller than the sum of NBO interaction energies shown in Figure 5a (98.7 kcal/mol), is explained by the high energy required to deform the (thf)Li group from linear in the free molecule to a highly bent (120°) geometry in 4-thf as well as to modify the second coordination sphere of the Mo atoms to make room for the Li—thf moiety.

Having successfully built Mo2LiH4 and Mo2Li2H4 platforms based on Mo—Mo bonds coordinated to one and two H—Li(thf)—H units, respectively, our next goal was to explore the possibility of reaching a Mo2Li3H6 organization in a purported Li(thf) based on Mo2LiH6 complex. To this end and taking into account the successful synthesis of complexes 3-thf and 4-thf by the procedure shown in Scheme 1c, we prepared tris(acetate) precursor [Mo3(μ-O2CMe)3(μ-AdDipp2)] and performed its reaction with an excess of LiAlH4. Although the above Mo2LiH6 complex could not be observed, the transformation led to complex 5-thf, identified as a polymetallic hydride cluster Mo2Li2H18 (Scheme 2), that probably results from spontaneous trimerization of the targeted Mo2Li1H6 monomer, with the loss of a molecule of tetrahydrofuran. The reaction was, however, complex and gave in addition compound [Mo2(μ-O2CMe)2(μ-AdDipp2)] through an undisclosed reaction path. Like the bis(formate) analogue (Scheme 1c), the latter may react further with LiAlH4, justifying that isolated yields of 5-thf are about 25%. Complex 5-thf is very air-sensitive and decomposes instantly in the solid state. Under strict anaerobic conditions, solutions of 5-thf decomposed gradually upon stirring at room temperature under an atmosphere of H2, generating LiAdDipp2 as a byproduct. Dideuterium acted similarly and showed that H/D exchange took place, as attested to by NMR detection of HD along with H2. The H2-promoted cluster breakup was not investigated any further. Nevertheless, it seems plausible that H2 may disrupt the cluster structure by displacing LiH molecules from the [Li9H18]− linker, eliminating LiAdDipp2. As an extension of these studies, various attempts were made to produce an alleged {Mo2(H)₈[Li(thf)]₄} complex (i.e., the hydride analogue of known methyl compound {Mo2(CH₃)₆[Li(OEt)₂]₃}). As detailed in the SI, all essayed trials were unsuccessful.

The room-temperature ¹H NMR spectra of complexes 5-L in C₆D₆ or thf-d₅ solution show two septets and four doublets for the 12 isopropyl groups of the amidinate spectator ligands, in accordance with the proposed D₃ molecular symmetry (details in Supporting Information). The 18 H atoms that make up the [Li₉H₁₈]⁻ linker are expected to give rise to three resonances of equal relative intensity. Whereas for 5-thf one of these signals seems to be hidden underneath other resonances, the three are clearly observed for complex 5-py with chemical shifts of 2.04, 5.21, and 5.41 ppm. They appear as broad multiplets, but while the 2.04 peak becomes a singlet in the ¹H¹Li NMR spectrum, the other two are converted to doublets with J₁H₁Li = 4 Hz. The ¹Li NMR spectrum contains three resonances centered at 5.4, 4.7, and 2.7 ppm, with relative intensities approaching roughly 6:2:1, once more in agreement with the proposed structure.

The molecular structure of complex 5-thf was determined by X-ray crystallography (Figure 6) and computational studies. Since the calculated and experimental structures are very

**Scheme 2. Formation of Hexamolybdenum Nonlithium Dodecaoctahydride Cluster 5-thf**

![Image](https://doi.org/10.1021/jacs.1c01602)

Figure 6. Solid-state structure of 5-thf as determined by X-ray diffraction. Thermal ellipsoids are shown at 30%. Hydrogen atoms (except the hydride ligands) are omitted for clarity, as are thf molecules. Selected bond lengths (Å) and a bond angle (deg): Mo—Mo, 2.10 av.; Mo—Li9, 2.30 av.; Mo—N, 2.13 av.; Li9—Li7, 2.45(2); Li9—Li8, 2.50(2); Li7—Li9—Li8, 176.3(9).
similar (Table 1), all of the features that are discussed here based on the X-ray data also apply to the optimized geometry. The whole cluster is built up by successive concentric groups around a central Li₁ unit (Figure 7, left) formed by Li₇, Li₉, and Li₈ with a nearly linear arrangement (176(1)°) and distances of 2.50(2) and 2.45(2) Å, which are slightly shorter than twice the lithium covalent radius (2.56 Å).55 We have been unable to locate a solid-state or gas-phase structure in which such a Li₃ rod is present. The only Li₃ group whose structure we are aware of appears in the crystal structure of Li₃[IrD₅], with Li–Li distances of 2.58 and 2.76 Å and a Li–Li–Li angle of 75.7°.60 The first concentric group around the central axis is composed of six H₆⁰ atoms that provide a nearly octahedral coordination sphere to the central Li₉ atom (Figure 7, right) and act as bridging atoms with the terminal atoms of the Li₃ rod, with Li–H separations in the 1.70–2.20 Å interval. These hydrides are connected to the molybdenum atoms of the three Mo₂ units that constitute the second concentric ring, with the shape of a slightly twisted trigonal prism and Mo–H distances in the range of 1.67–2.05 Å. The Mo–Mo bond length of 2.1020(7) Å is coherent with 4-fold bonding.51

Leaving aside the Li atoms, an ionic description of the cluster leaves us with three [Mo₂{μ-AdDipp₂}H₆]³⁻ blocks, in which each Mo atom bears two cis hydrides and one trans hydride relative to the N atoms of the μ-AdDipp₂ ligand. The latter have just been described as forming an H₆⁰ octahedron around the inner Li₃ rod and being bonded to the three Mo₂ units as well. The 12 cis hydrides can be described as distorted trigonal prisms, one with the trigonal faces roughly at the height of the external atoms of the central Li₉ rod, or H₆⁰ group, and the other with the trigonal faces very close to the central Li₉ atom, or H₆⁰⁺. Finally, the six peripheral Li atoms form another trigonal prism (Figure 7, left) with one of the triangular faces (Li₁, Li₃, and Li₅) rotated ca. 13° relative to the other (Li₂, Li₄, and Li₆). Those Li atoms form three Li₃ dumbbells with Li–Li distances of 2.83–2.90 Å and are supported by hydrides bridges to neighboring Li and Mo atoms, with Li–H separations in the range of 1.74–2.29 Å (section 5 in the Supporting Information).

**CONCLUSIONS**

We have demonstrated that a monomeric molecule of LiH can bind to the unsaturated molybdenum atom of [(H)Mo≡Mo] entities by means of a 3c−2e Mo→Li interaction combined with a σ-Li−H→Mo bond. [Mo₃{μ-HLi(thf)H}_₃]₂ skeletons containing five-membered H→Mo≡Mo→H−Li rings have been constructed in this manner for n = 1 and 2. When n = 3, trimerization of the purported [Mo₃{μ-HLi(thf)H}_₃(μ-AdDipp₂)] monomer occurs spontaneously, leading to a hydride-rich Mo₆Li₉H₁₈ supramolecular organization that features an uncommon linear Li₉ group around which are organized Mo₉ Li₁₉ and two H₆ polyhedra with shapes intermediate between an octahedron and compressed trigonal prisms.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01602. Relevant experimental and calculated bonding parameters for 3-thf, 4-thf and 5-thf; computational details; and atomic coordinates for the optimized geometries of the same compounds; synthesis and characterization of compounds (PDF)

Olex2 1.3 data (PDF)

**Accession Codes**

CCDC 2059184–2059187 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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DEDICATION
This paper is dedicated to the memory of our esteemed colleague and friend Professor Malcolm L. H. Green, in recognition of his monumental contributions to inorganic chemistry, organometallic chemistry, and catalysis.

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