Coordination of LiH Molecules to Mo≡Mo Bonds. Experimental and Computational Studies on Mo_2LiH_2, $Mo_2Li_2H_4$ and $Mo_6Li_9H_{18}$ Clusters.

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ABSTRACT: The reactions of $LiAlH_4$ as source of LiH with complexes that contain (H)Mo≡Mo and (H)Mo≡Mo(H) cores stabilized by coordination of bulky Ad^{Dipp2} ligands, result in the respective coordination of one and two molecules of (thf)LiH, with generation of complexes exhibiting one and two HLi(thf)H ligands extending across the Mo≡Mo bond (Ad^{Dipp2} = $HC(NDipp)_2$; Dipp = $2,6-{}^iPr_2C_6H_3$; thf = tetrahydrofuran, C_4H_8O). A theoretical study reveals the formation of Mo–H–Li three center-two electron bonds, supplemented by the coordination of the Mo≡Mo bond to the Li ion. Attempts to construct a $[Mo_2\{HLi(thf)H\}_3(Ad^{Dipp2})]$ molecular architecture led to spontaneous trimerization and formation of a chiral, hydride-rich $Mo_6Li_9H_{18}$ supramolecular organization, that is robust enough to withstand substitution of the 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.[1] Helium hydride, HeH^+, is a molecule of astrophysical importance,[2] whereas LiH is the lightest metal hydride and arises considerable interest due to its many applications.[3-5] In the gas phase, molecules of LiH exist as a result of overlap of the singly occupied H 1s and Li 2s atomic orbitals,[6] with an experimentally determined interatomic distance of *ca.* 1.60 Å.[7] In the solid state, LiH adopts a cubic NaCl-type structure, characterized by long Li⋯H contacts of approximately 2.04 Å.[3]

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 use of sterically encumbered auxiliary ligands.[3,8-19] Progress for the alkali metals has been more limited although with notable exceptions. These include Stasch's hydrocarbon-soluble lithium hydride cluster $[\{(DippNPPh_2)Li\}_4(LiH)_4]$, containing a $(LiH)_4$ central cube (Dipp = $2,6-{}^iPr_2C_6H_3$),[20] as well as the generation by Mulvey and coworkers of hexane-soluble, lithium hydride transfer reagents.[21,22] Of particular relevance is the synthesis of the dilithiozincate hydride $[(tmed)Li]_2[\{^iPrNCH_2CH_2N(^iPr)\}Zn(^tBu)H]$ that retains the Li–H bond in solution and undergoes dynamic association and dissociation of (tmed)LiH.[21] Also noteworthy are reports on hydride encapsulation by molecular alkali metal clusters,[23] the structural characterization of the LiH and LiO^tBu agglomerate $Li_{33}H_{17}(O^tBu)_{16}$,[24] and the synthesis of a $(LiH)_4$ cube coordinated to three bis(amido)alane units.[25]

A **3·thf** **4·thf** $[Mo_6(\mu\text{-Li})_9(\mu\text{-H})_{18}(\mu\text{-Ad}^{Dipp2})_3(thf)_8]$
5·thf

$[Mo\equiv Mo] \equiv Mo_2(\mu\text{-Ad}^{Dipp2})_2 \equiv$

$Ad^{Dipp2} = HC(NDipp)_2$; $Dipp = 2,6\text{-}^iPr_2C_6H_3$
thf = tetrahydrofuran
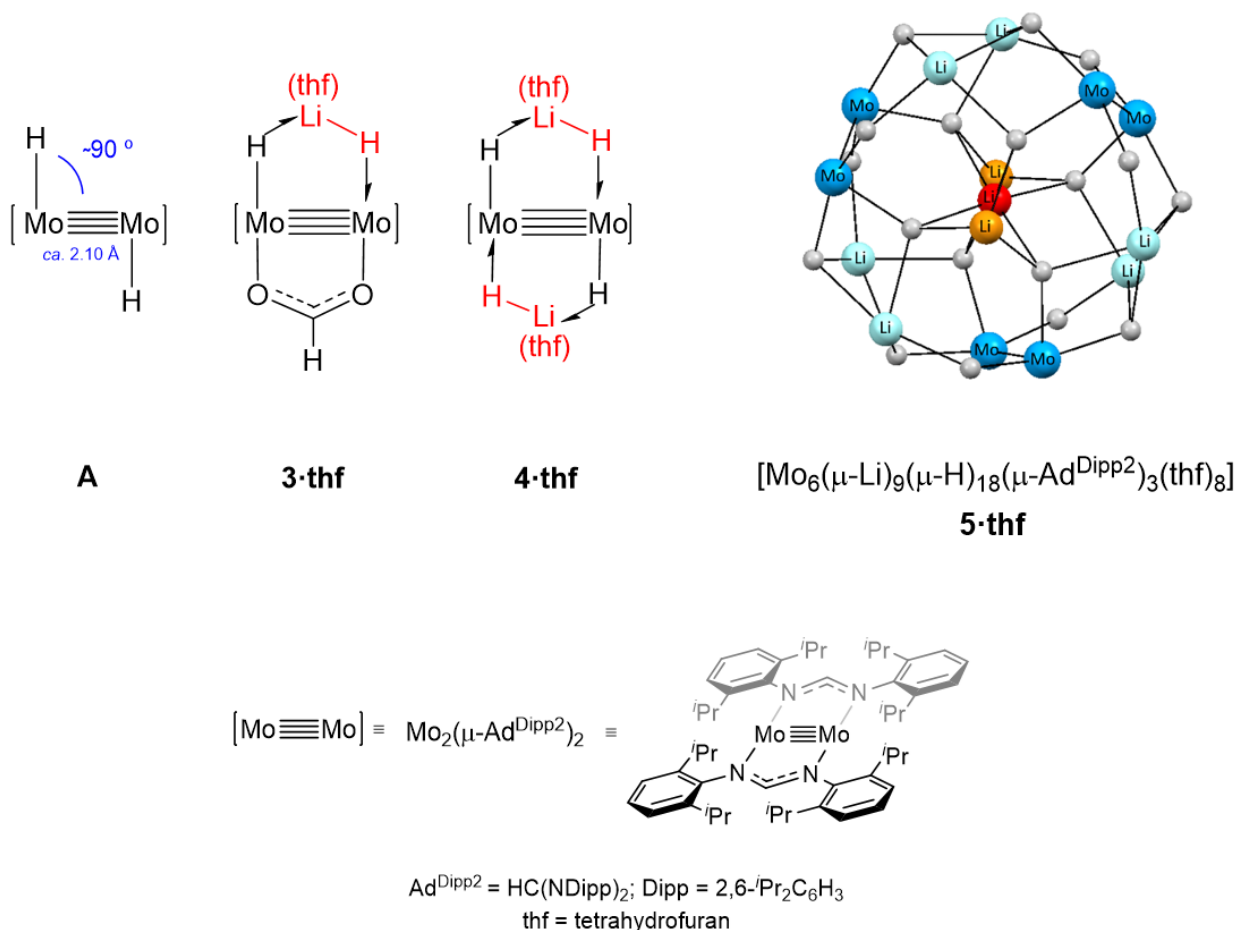
Figure 1. Simplified representations of the structures of complexes **3 thf**-**5 thf**. The three structural types derive from $[Mo_2(H)_n]$ cores by incorporation of one, two or three molecules of (thf)LiH; n = 1, complex **3 thf**; n = 2, **A** and complex **4 thf**; when n = 3, the unobserved monomer trimerizes to complex **5 thf** with loss of a molecule of tetrahydrofuran. In the structure of **5 thf**, symmetry-related lithium atoms share the same color .

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 bridge bond can be proposed based on the observation of one-bond ^1H–$^{6,7}Li$ NMR coupling constants.[21,26-35] Despite the scarcity of complexes of this type, it is conceivable that, alike other main-group metal-hydrogen bonds e.g. Mg–H, Al–H or Zn–H,[36-44] 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 heighten farther the σ-donor strength of the polar Li–H bond.

In this context, we envisioned that quadruply bonded dinuclear molybdenum hydride central units $[Mo_2(H)_n]$ (n = 1, 2) could be utilized to build the target molecular architectures. As represented in structure **A** of Figure 1, such dimolybdenum dihydride units, that possess strong hydride character[45] and feature Mo–Mo separations close to 2.10 Å, with Mo–H vectors nearly perpendicular to the Mo–Mo bond.[45] Here, we discuss the synthesis and structure of complexes **3 thf** and **4 thf** (Figure 1), that contain, respectively, one and two, for-

mally monoanionic, bridging H–Li(thf)–H ligands spanning the Mo≡Mo bond. We also study the unexpected formation of a unique, hydrocarbon soluble, hydride-rich $Mo_6Li_9H_{18}$ cluster, **5 thf**, formally resulting from trimerization of unobserved monomer $[Mo_2\{\mu\text{-HLi(thf)H}\}_3(\mu\text{-Ad}^{Dipp2})]$, with loss of a molecule of tetrahydrofuran. Throughout this paper, 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 the tetrahydrofuran adduct $[Mo_2(H)_2(\mu\text{-Ad}^{Dipp2})_2(thf)_2]$ (**1 thf**, where $Ad^{Dipp2} = HC(NDipp)_2$ and $Dipp = 2,6\text{-}^iPrC_6H_3$) is a convenient source of the unsaturated dihydride $[Mo_2(H)_2(\mu\text{-Ad}^{Dipp2})_2]$ containing a *trans*-(H)Mo≡Mo(H) core (**A** in Figure 1).[45] The $Mo_2(H)_2$ functionality of this complex was engendered by hydrogenolysis of the Mo–C bonds of $[(Me)Mo\equiv Mo(Me)]$ homologue,[47] a method that continues to be a main vehicle for the synthesis of transition-metal hydrides.

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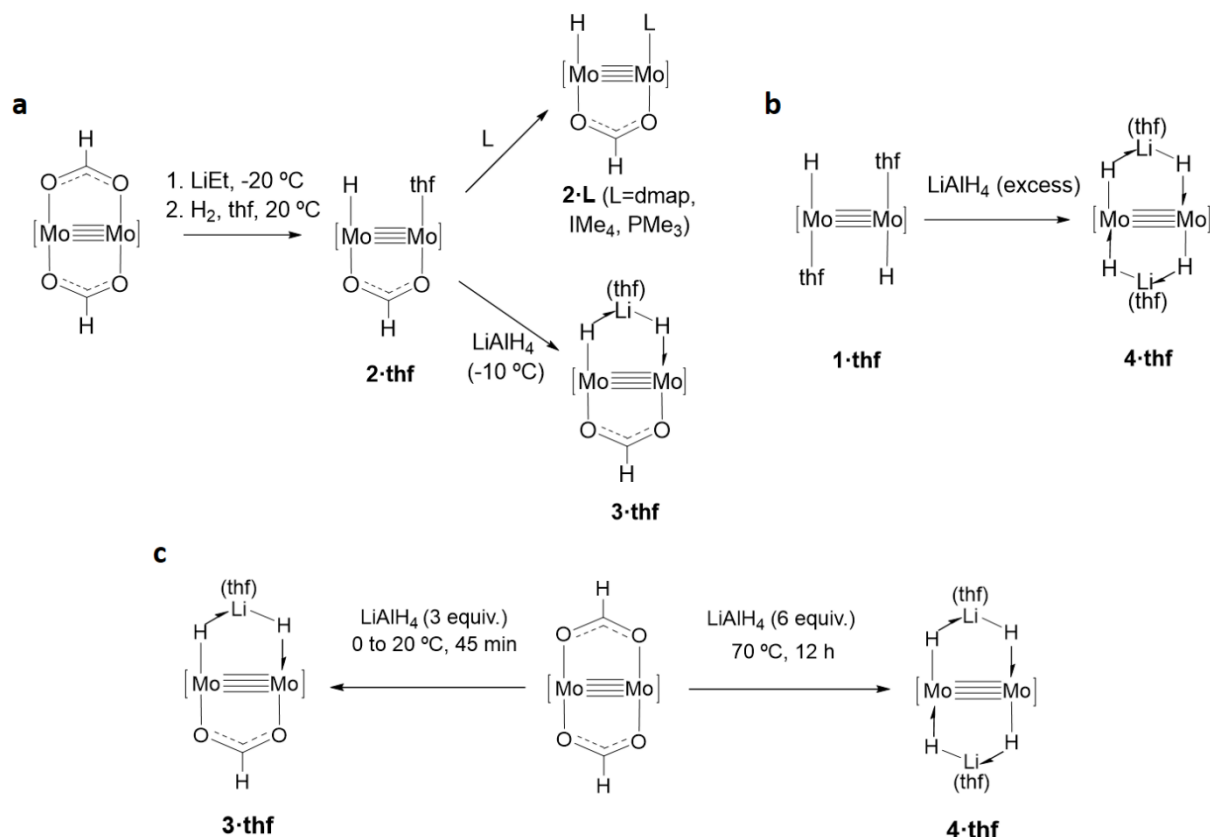
Scheme 1. Synthesis of hydride complexes with Mo≡Mo bonds. a) Compounds **2 thf**, **2 L** and **3 thf**. b) and c) Direct synthesis of complexes **3 thf** and **4 thf**. [Mo≡Mo] is an abbreviation for $Mo_2(\mu\text{-Ad}^{Dipp2})_2$, L = 4-dimethylaminopyridine (dmap), 1,3,4,5-tetramethylimidazol-2-ylidene (IMe4) and PMe3.

Searching for a related monohydride [(H)Mo≡Mo] core, we carried out the two-step transformation shown in Scheme 1a. Low temperature alkylation of $[Mo_2(\mu\text{-O}_2CH)_2(\mu\text{-Ad}^{Dipp2})_2]$ with equimolar amounts of LiEt yielded an ethyl-formate intermediate that was *in situ* reacted with H_2 and converted into the hydride-formate product, **2 thf**, 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 around 60%. This reaction was not, however, simple and produced in addition the 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 formation of a σ-Li–H complex, that becomes stabilized by 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 a $[Mo_2(H)_2]$ center (Scheme 1b). Mixing a tetrahydrofuran solution of this complex with a solution of LiAlH4 in the same solvent, caused immediate precipitation of a bright yellow solid that was identified as the dilithium tetrahydride dimolybdenum complex

$[Mo_2\{\mu\text{-HLi(thf)H}\}_2(\mu\text{-Ad}^{Dipp2})_2]$ (**4 thf**), that is, as a $Mo_2Li_2H_4$ cluster. As drawn in Scheme 1b, the compound contains two *trans*-[μ-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 μ-Li(thf)H2- 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 $[Mo_2(\mu\text{-O}_2CH)_2(\mu\text{-Ad}^{Dipp2})_2]$ with LiAlH4, under appropriate conditions.

Complexes **2 L**, **3 thf** and **4 thf** were characterized with the aid of microanalytical, spectroscopic and X-ray data, and were additionally studied by computational methods. For the molecules of **2 L**, the structure proposed is based on IR and NMR data and was unmistakably confirmed by X-ray crystallography for **2 IMe4** (see Figure S1). Regarding complexes **3 thf** and **4 thf**, their hydride signals were not readily apparent in the IR spectra, possibly because of the Mo–H–Li bridging character, so that the unambiguous identification of the three-atom HLiH chains in **3 thf** and **4 thf** owes much to the ^{1}H and ^{7}Li NMR experiments developed. Surprisingly more soluble in benzene and toluene than in tetrahydrofuran, the H atoms of the HLi(thf)H ligand in **3 thf**, resonate at δ 4.33 (C_6D_6), appearing as a partially resolved multiplet due to coupling to the [7]Li (92.6%; $I = 3/2$) and [6]Li (7.4%; $I = 1$) nuclei. As can be seen in Figure 2, this signal becomes a singlet in the

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$^1H\{^7Li\}$ NMR spectrum. Moreover, the 4.33 multiplet is absent in the ^1H NMR spectrum of the DLiD isotopologue of **3 thf**, prepared by reaction of $[Mo_2(\mu-O_2CH)_2(\mu-Ad^{Dipp2})_2]$[48] with $LiAlD_4$. The $^7Li\{^1H\}$ NMR spectrum is a somewhat broad singlet at 3.6 ppm that transforms into a 1:2:1 triplet in the proton-coupled ^7Li NMR experiment, with a one-bond $^7Li-^1H$ coupling constant of 16 Hz.

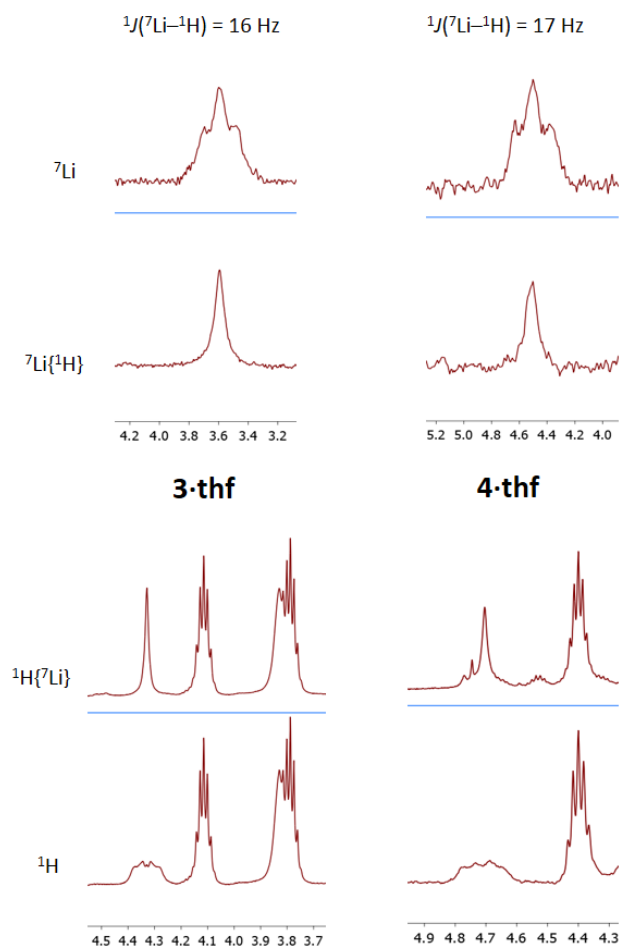Figure 2. From bottom to top, ^1H, $^1H\{^7Li\}$, $^7Li\{^1H\}$ and ^7Li NMR spectra of the HLiH moieties of complexes **3 thf** (left) and **4 thf** (right). ^1H resonances at lower frequency relative to Mo−H−Li are due to methane protons of the Ad^{Dipp2} ligands or to tetrahydrofuran.

Complex **4 thf** is only scarcely soluble in common solvents like benzene, toluene and tetrahydrofuran, but it is just sufficiently soluble in C_6H_5F for NMR studies. Pertinent NMR data are also included in Figure 2. In particular, the Mo_2LiH_2 moieties exhibit comparable $^1J(^7Li-^1H)$ couplings of 17 Hz. These observations categorically demonstrate the existence of HLiH entities coordinated to Mo–Mo quadruple bond in the molecules of **3 thf** and **4 thf**. Besides, they attest without a doubt 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 sharing among the molybdenum, hydrogen and lithium valence orbitals. It is pertinent to remark that observation of scalar coupling in lithium hydride complexes is rare, to

the point that few $^1J(^{6,7}Li-^1H)$ values can be found in the literature.[21, 29-35] Previously observed couplings range from 6 to 15 Hz, approximately, such that the 16-17 Hz values found for **3 thf** and **4 thf** are among the highest thus far reported. For the LiH molecule, a $^1J(^7Li-^1H)$ coupling constant of 159 Hz has been calculated.[49]

Complexes **3 thf** and **4 thf** possess good thermal stability. Their C_6D_6 and C_6D_5F solutions appear to be stable for one day at room temperature, though decomposition occurs upon heating at 70 °C for 3-4 hours. In the solid state, decomposition is apparent only at T ≥ 150 °C. The two compounds behave as soluble LiH carriers, particularly **4 thf**, which is the more reactive of the two. For instance, complex **4 thf** reacted with $Ph_2C(O)$, to give the expected alkoxide $Ph_2C(H)(OLi)$.[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 in what concerns the geometric parameters of H atoms. Nonetheless, they allow to define beyond any doubt the connectivity represented in Figure S2. Figure 3 contains an ORTEP representation of the molecules of **4 thf**, along with selected metrics. A more complete set of bond distances is collected in Table 1, that contains both experimental and computational data. At the time this manuscript was in preparation, there was no precedent for a structural motif of this kind in the Cambridge Structural Database (CSD).[50] The two bridging H–Li(thf)–H and Ad^{Dipp2} ligands of complex **4 thf** occupy mutually *trans* positions, originating a typical paddle-wheel structure[51-53] around a Mo–Mo quadruple bond of length 2.1006(7) Å. The discrepancy observed between the experimental and calculated Mo–H and Li–H distances collected in Table 1 is most likely due to the incertitude in the localization by X-ray diffraction of hydride ligands bound to a heavy atom such as molybdenum. The computed distances are 1.85 and 1.78 Å, respectively. The first is almost coincident with the average Mo–H–Mo bond lengths determined by neutron diffraction,[54] while the second is somewhat longer than the 1.60 Å value measured for the molecule of LiH in the gas phase but significantly shorter than the interatomic separation of 2.04 Å found for this hydride in the solid state.[3] Regarding the Mo–Li distances, the experimental values of 2.91(2) and 2.97(2) Å are indistinguishable within experimental error, whereas in the optimized structure this slight asymmetry vanishes leading to a separation of *ca.* 2.97 Å. For comparison, the sum of the covalent radii of the atoms is 2.82 Å.[55]
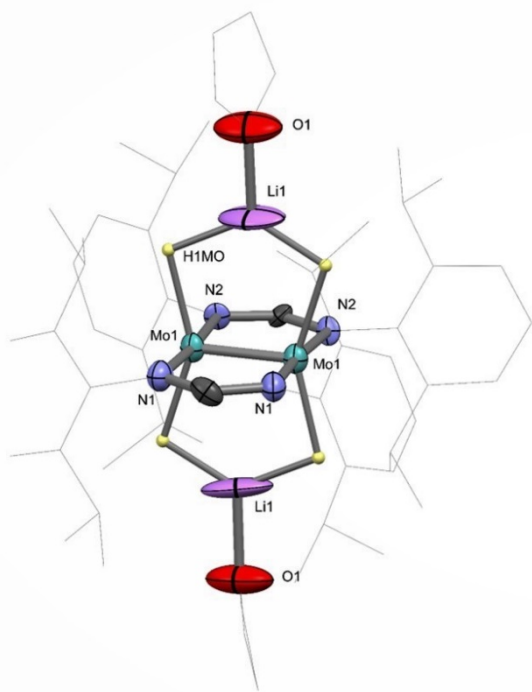
Figure 3. The solid-state structure of **4 thf**, some atoms have been omitted for clarity. Thermal ellipsoids are shown in 50 %. Selected bond distances (Å) and angles (°): Mo1–Li1, 2.91(2) and 2.97(2); Mo1–Mo1, 2.1006(7); Mo1–N1, 2.10(1); Mo1–N2, 2.20(1); Li1–O1, 1.86(2) Å; N1–Mo1–Li1 92.1(5).

	4 thf		5 thf	
	Calcd.	Exp.	Calcd.	Exp.
Mo–Mo	2.134	2.1006(7)	2.14-2.15	2.10 (av.)
Mo–H	1.852	2.05	1.83-1.84 (Mo–H^{cent})	1.67-2.04
Mo–Li	1.787 1.784	1.74 1.85	3.21-3.25 (Mo–Li9)	3.15-3.24
Li–H	2.971 2.968	2.97(2) 2.91(2)	1.97-2.07 (Li9–H^{cent})	1.81-2.09
		Li7/8–Li9	2.44-2.46	2.45-2.50
		Li7–Li9–Li8	176.5	176.3

Table 1. Selected experimental and computational structural parameters for complexes **4 thf** and **5 thf**.

We have carried out geometry optimization and an NBO analysis of chemical bonding within the Mo–H–Li–H–Mo rings of **4 thf**. For simplicity, we describe here the comparable results obtained for the monolithiated species **4 thf '**, whose structure (Figure 4b) finds precedent in that of the methyl complex analog [Mo$_2$\{µ-MeLi(thf)Me\}(µ-Me)(µ-Ad^{Dipp2})$_2$].[47,56] The energy for the dissociation of **4 thf '** into (thf)Li–H and the dihydride [Mo$_2$(H)$_2$(µ-Ad^{Dipp2})$_2$] given by our calculations is 27.9 kcal/mol, while the dissociation of two molecules of (thf)Li–H from **4 thf** is 55.1 kcal/mol. The NBO analysis discloses four orbitals that are responsible for the σ, two π and one δ components of the quadruple Mo–Mo bond (Figure 4a). In addition, we find that the dx^2-y^2 orbitals, not involved in Mo–Mo bonding, form spd hybrids directed towards the hydrides[47] and combine with s(H) orbitals to form the two Mo–H bonds (one of them is shown in Figure 4a).

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 charge at Li 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, to two sets of donor-acceptor interactions, (i) donation from σ(Mo–H) to Li and (ii) donation from the components of Mo≡Mo to Li (Figure 4c).

From the energetic 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$_z$(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$_z$(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) has significant contribution of 12%; smaller contributions come from donation of δ(Mo–Mo) to p$_x$(Li) and of σ(Mo–Mo) to p$_y$(Li), while almost negligible contributions appear among π(Mo–Mo) and p$_y$ and s(Li).

As a result of all these donor-acceptor interactions from the Mo$_2$H$_2$ moiety to the lithium ion, the distribution of the 0.33 valence electrons held by the Li atomic orbitals (Figure 5b) reflects the major role played by the 2s and 2p$_z$ Li AOs, as acceptors. The high population of the lithium p$_y$ 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 at p$_x$ results from the interesting donation from the δ(Mo≡Mo) bonding orbital (Figure 4c).

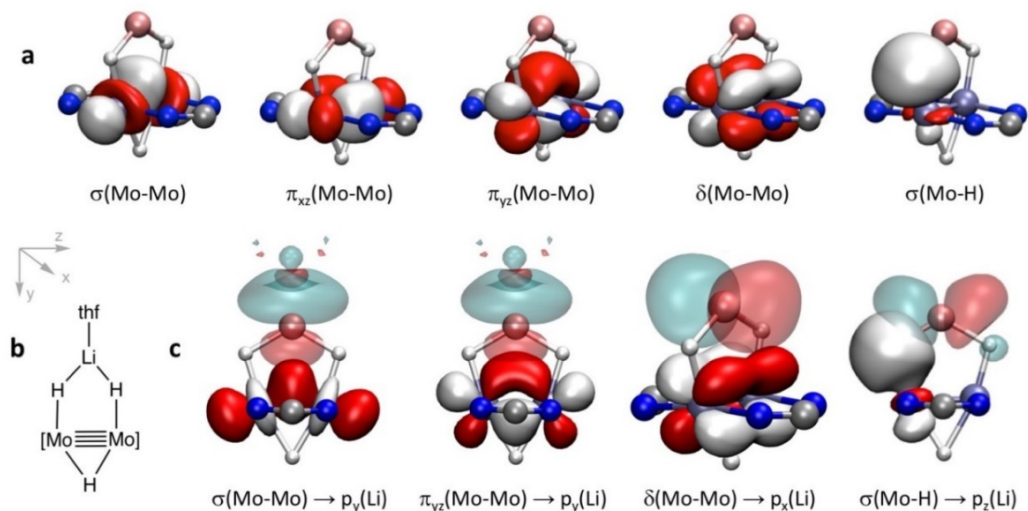Figure 4. (a) The four NBO orbitals corresponding to the σ, two π and one δ components of the quadruple Mo≡Mo bond in **4 thf**', and one of the Mo–H σ bonding orbitals composed by the δ (Mo–Mo)-type x^2-y^2 and the hydride 1s orbitals. (b) Coordinates orientation and composition of the central fragment of the molecule shown in the orbital plots. (c) Some representative interactions between donor (white and red) and acceptor (light blue and pink) natural orbitals in **4 thf**'.

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 Mo≡Mo centroid of 2.77 Å (Mo–Li = 2.97 Å), to be compared with a covalent radii sum of 2.82 Å.[55] 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 the dihydride $[Mo_2(H)_2(\mu\text{-}Ad^{Dipp2})_2]$ is of 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–H 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 Mo_2LiH_2 and $Mo_2Li_2H_4$ 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 $Mo_2Li_3H_6$ organization in a purported $[Mo_2\{HLi(thf)H\}_3(\mu\text{-}Ad^{Dipp2})]$ 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 the tris(acetate) precursor $[Mo_2(\mu\text{-}O_2CMe)_3(\mu\text{-}Ad^{Dipp2})]$ and performed its reaction with an excess of LiAlH_4. Although the above $Mo_2Li_3H_6$ complex could not be observed, the transformation led to complex **5 thf**, identified as a polymetallic hydride cluster $Mo_6Li_9H_{18}$ (Scheme 2), that probably results from spontaneous trimerization of the targeted $Mo_2Li_3H_6$ monomer, with loss of a molecule of tetrahydrofuran. The reaction was, however, complex and gave in addition compound $[Mo_2(\mu\text{-}O_2CMe)_2(\mu\text{-}Ad^{Dipp2})_2]$ through an undisclosed reaction path. Alike the bis(formate) analogue (Scheme 1c), the latter may react further with LiAlH_4, justifying that isolated

yields of **5 thf** are of about 25%. Complex **5 thf** is very air sensitive and decomposes instantly in the presence of oxygen and water, both in solution and in the solid state. Under strict anaerobic conditions, solutions in tetrahydrofuran or aromatic hydrocarbons remain unchanged at 25 °C for at least 24 hours, although decomposition is fast above 50 °C.
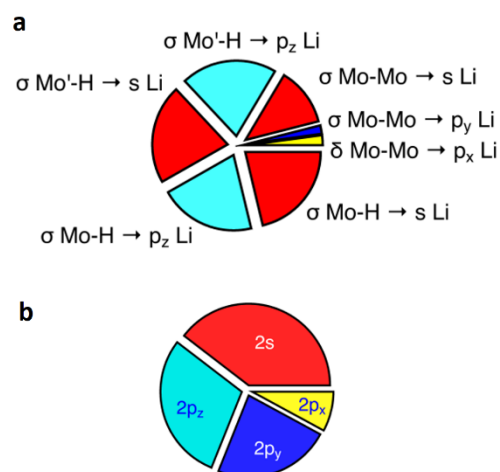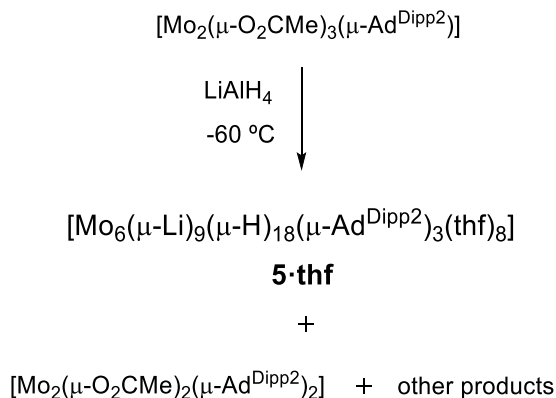

Figure 5. (a) Relative energy contributions of natural orbital donor-acceptor interactions between $[Mo_2(H)_2(\mu\text{-}H)(\mu\text{-}Ad^{Dipp2})_2]^-$ and (thf)Li$^+$ fragments in **4 thf**'. (b) Share of the Li valence electron density at each of its atomic orbitals, resulting from σ(Mo–H)→Li, Mo≡Mo→Li and thf→Li donor-acceptor interactions.

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$[Mo_2(\mu\text{-}O_2CMe)_3(\mu\text{-}Ad^{Dipp2})]$

$\downarrow$ LiAlH$_4$, -60 °C

$[Mo_6(\mu\text{-}Li)_9(\mu\text{-}H)_{18}(\mu\text{-}Ad^{Dipp2})_3(thf)_8]$

5·thf

+

$[Mo_2(\mu\text{-}O_2CMe)_2(\mu\text{-}Ad^{Dipp2})_2]$ + other products

Scheme 2. Formation of the hexamolybdenum nonalithium dodecaoctahydride cluster **5 thf**.

The new supramolecular entity can be understood as a triangular array of $[Mo_2(\mu\text{-}Ad^{Dipp2})]^{3+}$ components[51,57,58] connected by a $[Li_9H_{18}]^{9-}$ linker in a fairly robust manner. The Li-coordinated molecules of tetrahydrofuran were readily substituted by pyridine and 4-dimethylaminopyridine, giving complexes **5 py** and **5 dmap** without alteration of the molecular skeleton. Notwithstanding the foregoing, complex **5 thf** acted as an efficient source of LiH in the hydrolithiation of Ph$_2$C(O) to give Ph$_2$C(H)(OLi).[20,22] Somewhat unexpectedly, solutions of **5 thf** decomposed gradually upon stirring at room temperature under an atmosphere of H$_2$, generating LiAd^{Dipp2} as a byproduct. Dideuterium acted similarly and evidenced that H/D exchange took place, as attested by NMR detection of HD along with H$_2$. The H$_2$-promoted cluster breakup was not investigated any further. Nevertheless, it seems plausible that H$_2$ may disrupt the cluster structure by displacing LiH molecules from the $[Li_9H_{18}]^{9-}$ linker, eliminating LiAd^{Dipp2}. As an extension of these studies, various attempts were made to produce an alleged $\{Mo_2(H)_8[Li(thf)]_4\}$ complex, i.e. the hydride analogue of the known methyl compound $\{Mo_2(CH_3)_8[Li(OEt_2)]_4\}$.[59] As detailed in the SI all essayed trials were unsuccessful.

The room-temperature ¹H NMR spectra of complexes **5 L** in C$_6$D$_6$ or thf-d_8 solutions, show two septets and four doublets for the twelve isopropyl groups of the amidinate spectator ligands, in accordance with the proposed D_3 molecular symmetry (see Supporting Information for details). The 18 H atoms that make up the $[Li_9H_{18}]$ linker are expected to originate 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 2.04, 5.21 and 5.41 ppm. They appear as broad multiplets, but while the 2.04 peak becomes a singlet in the ¹H{⁷Li} NMR spectrum, the other two convert into doublets with $^2J_{HH}$ = 4 Hz. The ⁷Li 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 similar (Table 1), all the features that are discussed here based on the X-ray data apply also to the optimized geometry. The

whole cluster is built up by successive concentric groups around a central Li$_3$ 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, 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 Li$_3$ rod is present. The only Li$_3$ group whose structure we are aware of appears in the crystal structure of Li$_3$[IrD$_6$], 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 by six H^{cent} 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 Li$_3$ rod, with Li–H separations in the interval 1.70 - 2.20 Å. These hydrides are connected to the molybdenum atoms of the three Mo$_2$ units, that constitute the second concentric ring, with the shape of a slightly twisted trigonal prism and Mo–H distances in the range 1.67 - 2.05 Å. The Mo–Mo bond lengths of 2.1020(7) Å are coherent with four-fold bonding.[51]
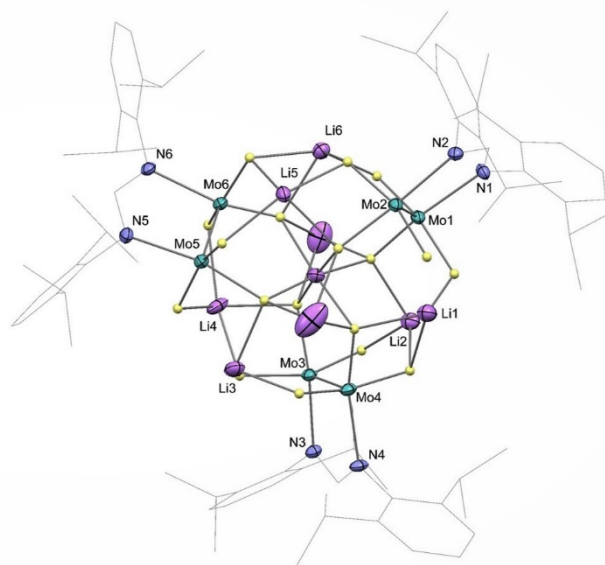

Figure 6. Solid-state structure of **5 thf** right as determined by X-ray diffraction. Thermal ellipsoids are shown at 30%, Hydrogen atoms (except the hydride ligands) are omitted for clarity, as well as thf molecules. Selected bond lengths [Å] and angles [°]: Mo–Mo, 2.10 av.; Mo–Li9, 3.20 av.; Mo–N, 2.13 av.; Li9–Li7, 2.45(2); Li9–Li8, 2.50(2); Li7–Li9–Li8, 176.3(9).
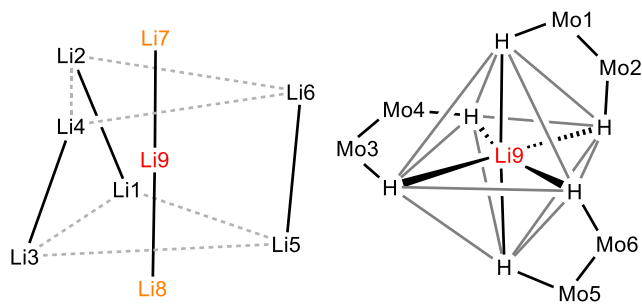
Figure 7. The Li_9 polyhedron present in the molecules of complex **5 thf** (left) and the distribution of H and Li atoms in the proximity of the central lithium atom Li9 (right).

Leaving aside the Li atoms, an ionic description of the cluster leaves us with three $[Mo_2(\mu\text{-}Ad^{Dipp2})H_6]^{3-}$ blocks, in which each Mo atom bears two *cis* and one *trans* hydride relative to the N atoms of the $\mu\text{-}Ad^{Dipp2}$ ligand. The latter have just been described as forming an H_6 octahedron around the inner Li_3 rod and being bonded to the three Mo_2 units as well. The twelve *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 Li_3 rod, or H_6^{ext} group, or the other with the trigonal faces very close to the central Li9 atom, or H_6^{int}. Finally, the six peripheral Li atoms form another trigonal prism (Figure 7, left) with one of the triangular faces (Li1, Li3, Li5) rotated *ca.* 13° relative to the other (Li2, Li4, Li6). Those Li atoms form three Li_2 dumbbells with Li···Li distances of 2.83 - 2.90 Å and are supported by hydride bridges to neighboring Li and Mo atoms, with Li–H separations in the range 1.74 - 2.29 Å. (See section 5 in the Supporting Information).

Conclusion

In conclusion, we have demonstrated that a monomeric molecule of LiH can bind to the unsaturated molybdenum atom of $[(H)Mo\equiv Mo]$ entities, by means of a 3c-2e Mo–H→Li interaction combined with a σ-Li–H→Mo bond. $[Mo_2\{\mu\text{-}HLi(thf)H\}_n]$ 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 $[Mo_2\{\mu\text{-}HLi(thf)H\}_3(\mu\text{-}Ad^{Dipp2})]$ monomer occurs spontaneously, leading to a hydride-rich $Mo_6Li_9H_{18}$ supramolecular organization that features an uncommon linear Li_3 group around which are organized Mo_6, Li_6, and two H_6 polyhedra with shapes intermediate between the octahedron and compressed trigonal prisms.

ASSOCIATED CONTENT

Supporting Information. Relevant experimental and calculated bonding parameters for **3 thf**, **4 thf** and **5 thf** (tables S1 and S2), computational details, and atomic coordinates for the optimized geometries of the same compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Coordination of LiH Molecules to Mo≡Mo Bonds