

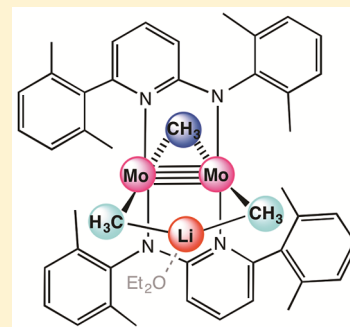
# Lithium Di- and Trimethyl Dimolybdenum(II) Complexes with Mo–Mo Quadruple Bonds and Bridging Methyl Groups

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## Supporting Information

**ABSTRACT:** New dimolybdenum complexes of composition  $[\text{Mo}_2\{\mu\text{-Me}\}_2\text{Li}(\text{S})\{\mu\text{-X}\}(\mu\text{-N}^{\wedge}\text{N})_2]$  (**3a–3c**), where  $\text{S} = \text{THF}$  or  $\text{Et}_2\text{O}$  and  $\text{N}^{\wedge}\text{N}$  represents a bidentate aminopyridinate or amidinate ligand that bridges the quadruply bonded molybdenum atoms, were prepared from the reaction of the appropriate  $[\text{Mo}_2\{\mu\text{-O}_2\text{CMe}\}_2(\mu\text{-N}^{\wedge}\text{N})_2]$  precursors and  $\text{LiMe}$ . For complex **3a**,  $\text{X} = \text{MeCO}_2$ , while in **3b** and **3c**,  $\text{X} = \text{Me}$ . Solution NMR studies in  $\text{C}_6\text{D}_6$  solvent support formulation of the complexes as contact ion pairs with weak agostic  $\text{Mo}\text{--}\text{CH}_3\cdots\text{Li}$  interactions, which were also evidenced by X-ray crystallography in the solid-state structures of the molecules of **3a** and **3b**. Samples of **3c** enriched in  $^{13}\text{C}$  (99%) at the metal-bonded methyl sites were also prepared and investigated by NMR spectroscopy employing  $\text{C}_6\text{D}_6$  and  $\text{THF-}d_8$  solvents. Crystallization of **3c** from toluene:tetrahydrofuran mixtures provided single crystals of the solvent separated ion pair complex  $[\text{Li}(\text{THF})_4][\text{Mo}_2(\text{Me})_2(\mu\text{-Me})\{\mu\text{-HC}(\text{NDipp})_2\}_2]$  (**4c**), where Dipp stands for 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. A computational analysis of the  $\text{Mo}_2(\mu\text{-Me})_2\text{Li}$  core of complexes **3a** and **3b** has been developed, which is consistent with a small but non-negligible electron-density sharing between the C and Li atoms of the mainly ionic  $\text{CH}_3\cdots\text{Li}$  interactions.



## INTRODUCTION

Transition metal alkyl and aryl complexes form a most representative family of metal organic compounds.<sup>1,2</sup> The unique reactivity of the  $\sigma\text{M}\text{--}\text{C}$  bond allows for its participation in elementary reactions, which are the basis of many academic and industrial transformations. In addition, they have furnished unusual molecular and electronic structures,<sup>3</sup> including the synthesis by Wilkinson and co-workers of  $\text{WMe}_6$ ,<sup>4</sup> the first hexamethyl transition metal compound, and the recent discovery by the group of Power of the first stable molecule with quintuple metal–metal bonding, the chromium dimer  $\text{Cr}_2\text{Ar}'_2$ , where  $\text{Ar}'$  represents a terphenyl ligand.<sup>5</sup>

The methyl group is the simplest alkyl function and occupies a conspicuous position among metal alkyls. Leaving aside the fundamental and practical importance of main group methyl compounds, e.g.,  $\text{LiMe}$ ,  $\text{Mg}(\text{Me})\text{X}$ ,  $\text{ZnMe}_2$  or  $\text{AlMe}_3$ ,<sup>1d,2b</sup> transition metal methyl complexes are arguably the most important family of compounds with  $\text{M}\text{--}\text{C}$   $\sigma$  bonds.<sup>6</sup> Moreover, some members of this group have provided the grounds for major breakthroughs in organometallic chemistry such as the isolation of the first methylidene complex<sup>7</sup> or the low temperature NMR characterization of the first  $\sigma\text{-CH}_4$  complex.<sup>8</sup>

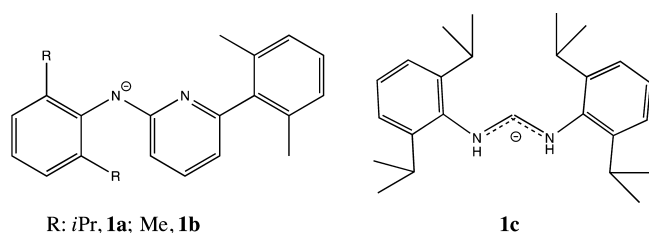
Recent activity in the field of binuclear transition metal compounds that feature metal–metal multiple bonds, sparked by the already cited synthesis of  $\text{Cr}_2\text{Ar}'_2$  compounds, led us to study the utility of the well-known precursor  $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ <sup>9</sup>

for the synthesis of Mo–Mo quadruple bonds.<sup>10</sup> With the use of bridging aminopyridinate<sup>10,11</sup> and amidinate<sup>10,12,13</sup> ligands that possess bulky aryl substituents, we have recently prepared some multiply bonded dimolybdenum species.<sup>14,15</sup> Combining the alluring prospects of this area of research<sup>10–20</sup> with the enticements of the study of  $\text{M}\text{--}\text{C}$   $\sigma$  bonds, we have investigated a series of methyl complexes of the  $\text{Mo}\equiv\text{Mo}$  core, stabilized by coordination of the aminopyridinate and amidinate ligands (**1a–1c**) represented in Figure 1. The new compounds comprise some lithium di- and trimethyl dimolybdenum(II) *ate* complexes (**3a–3c** and **4c**) that are the subject of this paper.

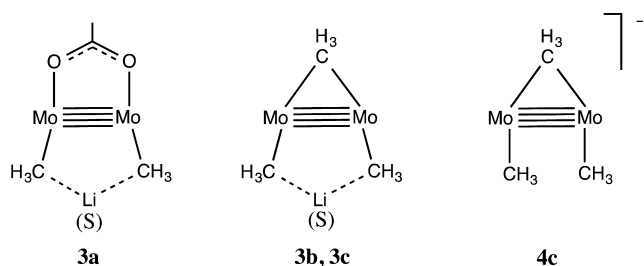
As discussed next, the new complexes **3a–3c** and **4c** feature coordinated methyl groups with three different binding modes, namely terminal  $\text{Mo}\text{--}\text{Me}$ , bridging  $\text{Mo}(\mu\text{-Me})\text{Mo}$  and bridging  $\text{Mo}(\mu\text{-Me})\text{Li}$  units (Figure 2). Moreover they contain an uncommon  $\text{Li}(\mu\text{-Me})\text{Mo}\equiv\text{Mo}(\mu\text{-Me})$  structural motif that finds no precedent among the compounds listed in the Cambridge Structural Database (CSD).<sup>21</sup> X-ray crystallography (complexes **3a** and **3b**) and multinuclear NMR studies ( $\text{C}_6\text{D}_6$  solvent) have unequivocally demonstrated its existence in the molecules of **3a–3b**. Samples of **3c** could not be isolated in the form of single-crystals as crystallization from 1:1 mixtures of toluene and THF yielded instead the related, albeit solvent

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**Figure 1.** Aryl-substituted aminopyridinate (left) and amidinate (right) ligands employed in this work. Throughout this paper, labels **a**, **b**, and **c** in the numbering scheme refer specifically to the above ligands (some authors prefer the term pyridylamido to design ligands of type **1a** and **1b**).



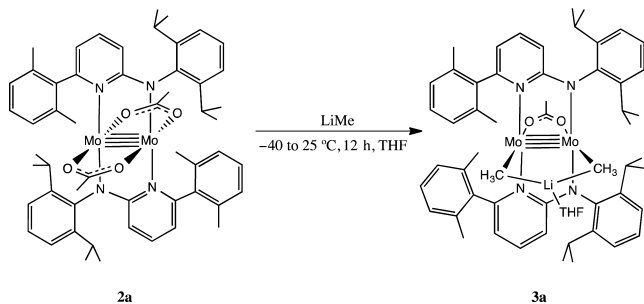
**Figure 2.** Simplified structural representations of the organometallic Mo<sub>2</sub> core of complexes **3a–3c** and **4c**. The bridging aminopyridinate and amidinate ligands have been omitted for clarity. S represents a lithium coordinated molecule of Et<sub>2</sub>O or THF (see text).

separated ion pair complex [Li(THF)<sub>4</sub>][Mo<sub>2</sub>Me<sub>3</sub>(N<sup>^</sup>N)<sub>2</sub>] (**4c**) featuring two terminal Mo–Me bonds and a bridging Mo(μ-Me)Mo linkage (Figure 2).

## RESULTS AND DISCUSSION

The polymethyl dimolybdenum(II) complexes **3a–3c** described in this work were prepared from the corresponding bis(acetate) precursors with paddlewheel structures [Mo<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>(N<sup>^</sup>N)<sub>2</sub>] (**2a–2c**),<sup>15a,d</sup> that contain the aminopyridinate or amidinate ligands **1a–1c** represented in Figure 1. As shown in Scheme 1, treatment of the bis(pyridylamido)

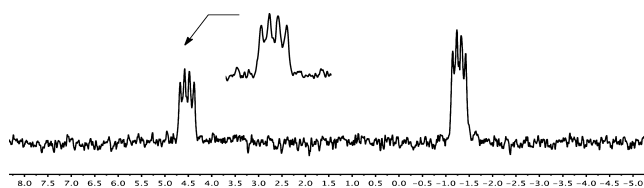
### Scheme 1. Synthesis of Complex 3a



complex **2a**, that has 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> substituents at the amido nitrogen and pyridinic ring, respectively, with ca. 2.5 mol equiv of LiMe occurred with displacement of one of the acetate ligands to form complex **3a**. The complex was obtained as very air sensitive red crystals in ca. 50% yield (after crystallization).

Attempts to replace the remaining acetate employing another mol-equiv of LiMe proved unsuccessful and the use of a large excess of LiMe (~10 equiv) led to the permethylated complex Mo<sub>2</sub>Me<sub>8</sub><sup>4-</sup>, previously isolated as the lithium salt.<sup>22</sup>

The molecular complexity of **3a** was ascertained by X-ray crystallography and will be discussed later together with analogous studies carried out for the related complexes **3b** and **4c**. It was also determined by NMR spectroscopy that demonstrated the presence of a five-membered Mo<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>Li ring. Formation of **3a** implies a change in the coordination of the aminopyridinate ligands in comparison with precursor **2a**, as in the former the two N<sub>amido</sub> and the two N<sub>pyr</sub> donor atoms are placed in mutually *trans* positions whereas in the latter each N<sub>amido</sub> is *trans* with respect to a N<sub>pyr</sub> donor atom. This structural peculiarity is presently being investigated in the parent [Mo<sub>2</sub>(μ-O<sub>2</sub>CR)<sub>2</sub>(μ-Ap')<sub>2</sub>] compounds (Ap' will be utilized as shorthand notation for an aminopyridinate ligand) and will not be discussed further in this paper. With reference to the Li(μ-Me)<sub>2</sub>Mo<sub>2</sub> fragment, only a broad, shielded signal with δ −0.41 ppm appears in the <sup>1</sup>H NMR spectrum (25 °C, C<sub>6</sub>D<sub>6</sub> solvent) due to accidental degeneracy of the nonequivalent methyl resonances. Nevertheless, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 3) features two well-defined resonances with chemical shifts 4.5



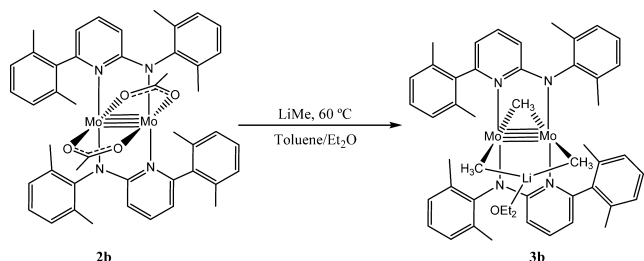
**Figure 3.** <sup>13</sup>C{<sup>1</sup>H} NMR resonances of the bridging methyl groups of the Li(μ-Me)<sub>2</sub>Mo<sub>2</sub> unit of complex **3a**.

and −1.4 ppm that appear as ca. 1:1:1:1 quartets due to coupling to the <sup>7</sup>Li nucleus (*I* = 3/2, 92.5% natural abundance; <sup>1</sup>J<sub>LiC</sub> = 12 Hz). Furthermore, rather low and approximately equal <sup>1</sup>J<sub>CH</sub> couplings of 112 Hz were measured in the <sup>1</sup>H-coupled <sup>13</sup>C NMR experiment. Although additional experimental and theoretical information on this interesting bonding problem will be discussed in posterior sections of this article, the NMR data recorded for **3a**, in particular (i) the observation of shielded <sup>1</sup>H and <sup>13</sup>C resonances for the methyl groups of the Mo<sub>2</sub>Me<sub>2</sub>Li unit; (ii) the <sup>13</sup>C–<sup>7</sup>Li scalar coupling of 12 Hz, comparable to that observed for the tetrameric molecules of [Li<sup>t</sup>Bu]<sub>4</sub> (11 Hz);<sup>23</sup> and (iii) the somewhat reduced <sup>13</sup>C–<sup>1</sup>H coupling of 112 Hz, are in agreement with some electron-density sharing between the two molybdenum-bound CH<sub>3</sub> groups and the lithium cation and therefore with the existence of 3-center 2-electron (3c–2e) agostic bonds.<sup>24,25</sup> Another piece of NMR data that is worth noting is the appearance of a broad singlet centered at 2.15 ppm in the <sup>7</sup>Li spectrum recorded in C<sub>6</sub>D<sub>6</sub>. As discussed later for the related compounds **3b** and **3c**, this observation provides additional support for the formulation of complex **3a** in its solution in C<sub>6</sub>D<sub>6</sub> or other nonsolvating hydrocarbon solvents as a contact ion pair,<sup>26</sup> a structure that persists in the solid state (see below).

We also studied the reaction of the analogous bis(acetate)-bis(aminopyridinate) complex **2b**, that contains the aminopyridinate ligand **1b** of Figure 1. The latter possesses a 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> aryl as substituent of the amido nitrogen atom instead of the 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> aryl of **1a**, causing the steric bulkiness of **2b** to be slightly reduced in comparison with **2a**.<sup>11b,e</sup> Interestingly, the use of **2b** permitted replacement of the two acetate ligands with formation of the trimethyl dimolybdate lithium complex **3b** (vide infra).

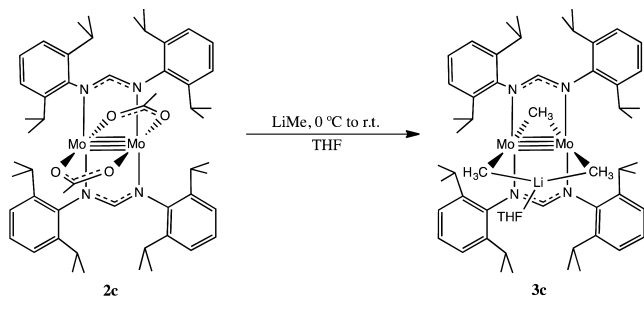
Despite initial expectations, no reaction was observed at room temperature between complex **2b** and a small excess of LiMe (1:3.5 molar ratio). However, after stirring at 60 °C for a total of 18 h the desired product was isolated in ca. 65% yield in the form of dark red crystals (Scheme 2). Possibly, the reduced

**Scheme 2. Synthesis of the Lithium Trimethyldimolybdenum(II) Complex 3b**



steric hindrance of the 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> aryl substituent of the amido nitrogen of **2b** relative to the 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> of **2a** permits displacement at 60 °C of the second acetate ligand with formation of complex **3b**. The related bis(acetate)bis(amidinate) compound **2c** reacted similarly with LiMe, although milder experimental conditions were needed (room temperature; ca. 15% molar excess of LiMe) to yield the expected complex **3c** in ca. 52% isolated yield (Scheme 3). Interestingly, the use of a 1:2 molar ratio of dimolybdenum complex **2c** versus methyl lithium led exclusively to the trimethylated complex **3c** accompanied by unreacted **2c**.

**Scheme 3. Synthesis of the Amidinate Methyl Complex 3c**



Compounds **3b** and **3c** are extremely reactive toward traces of water and oxygen both in solution and in the solid state. For this reason, their solutions degraded rapidly, limiting their manipulation for extended periods of time. Solution NMR data in C<sub>6</sub>D<sub>6</sub> for the new compounds **3b** and **3c** strongly support their formulation as contact ion pairs. Nevertheless, at variance with **3a**, complexes **3b** and **3c** contain a bridging methyl group which behaves as a  $\mu$ -LX ligand and participates in a 3c–2e bond.<sup>25</sup> Besides, the Mo<sub>2</sub> unit forms two  $\sigma$  Mo–C bonds with the methyl groups that interact with the lithium cation through their C–H bonds, in close analogy to the bonding situation described above for complex **3a**. The Li( $\mu$ -Me)Mo( $\mu$ -Me)Mo( $\mu$ -Me) central core of compound **3b** was first characterized by NMR methods and confirmed afterward by X-ray crystallography. However, as briefly mentioned, single crystals of the amidinate complex could only be obtained in the presence of tetrahydrofuran and were shown by NMR studies in this solvent and by X-ray crystallography to correspond to the solvent separated complex **4c** with formulation [Li(THF)<sub>4</sub>]-

[Mo<sub>2</sub>Me<sub>2</sub>( $\mu$ -Me){ $\mu$ -HC(NDipp)<sub>2</sub>}<sub>2</sub>] (Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (vide infra). To authenticate beyond any doubt the central trimethyl heterotrimetallic Li( $\mu$ -Me)Mo( $\mu$ -Me)Mo( $\mu$ -Me) core in complex **3c**, samples of this compound enriched in <sup>13</sup>C in the metal-bonded methyl ligands were obtained and investigated by NMR spectroscopic techniques, both in C<sub>6</sub>D<sub>6</sub> and THF-*d*<sub>8</sub> solvents.

The <sup>1</sup>H NMR spectrum of compound **3b** dissolved in C<sub>6</sub>D<sub>6</sub> hints the presence of a molecule of Et<sub>2</sub>O that completes the coordination of the Li<sup>+</sup> ion. In addition, resonances with chemical shifts 0.71 and –1.35 ppm and relative intensity suitable for three and six hydrogen atoms, respectively, were recorded for the Mo–CH<sub>3</sub> groups. The more shielded one is due to the more polar Mo<sub>2</sub>( $\mu$ -Me)<sub>2</sub>Li methyl protons that, in accordance with the proposed formulation, are related by a C<sub>2</sub> axis of symmetry (Scheme 2), whereas the other can be attributed to the methyl group that bridges the two molybdenum atoms. The corresponding <sup>13</sup>C signals appear at  $\delta$  6.5 and 2.8 ppm and present one-bond <sup>13</sup>C–<sup>1</sup>H couplings of 115 and 110 Hz, respectively. The latter signal is broad as a result of unresolved coupling to the <sup>7</sup>Li nucleus.

The contact ion pair complex **3c** contains a molecule of THF coordinated to lithium, as suggested by <sup>1</sup>H NMR studies. In consequence, it has formulation [Mo<sub>2</sub>( $\mu$ -Me){( $\mu$ -Me)<sub>2</sub>Li(THF)}{ $\mu$ -HC(NDipp)<sub>2</sub>}<sub>2</sub>]. Its characteristic C<sub>2v</sub> molecular symmetry (Scheme 3) causes the appearance of four doublets for the methyl protons of the isopropyl amidinate substituents and hence two septets for the corresponding CHMe<sub>2</sub> methyne protons (data in C<sub>6</sub>D<sub>6</sub>; see Experimental Section for details). The <sup>1</sup>H NMR singlet at  $\delta$  2.21 ppm originated by the acetate groups in the complex precursor **2c** is replaced in **3c** by two signals, one centered at 1.74 (s; 3H) and the other at –0.55 (br s; 6 H) ppm, respectively ascribed to the Mo( $\mu$ -Me)Mo and Mo<sub>2</sub>( $\mu$ -Me)<sub>2</sub>Li hydrogen nuclei. These alkyl groups give rise to <sup>13</sup>C{<sup>1</sup>H} resonances with  $\delta$  7.14 and 4.4 ppm, respectively. Although the latter is poorly resolved, a one-bond <sup>13</sup>C–<sup>7</sup>Li coupling constant of roughly 8 Hz can be estimated. While its magnitude is somewhat lower than corresponding value for **3a** (12 Hz), the observed coupling is once more indicative of some covalency in the CH<sub>3</sub>⋯Li⋯CH<sub>3</sub> interactions. In agreement with the above data, the <sup>7</sup>Li nucleus resonates as a broad singlet with  $\delta$  2.51 ppm (data also in C<sub>6</sub>D<sub>6</sub>), i.e., with chemical shift similar to that of **3a** (2.15 ppm).

As briefly noted, complementary NMR studies were undertaken using also THF-*d*<sub>8</sub> as the solvent and with specimens of **3c** enriched in <sup>13</sup>C (99%) in the metal-bound methyl groups. The labeled samples were prepared as in Scheme 3, but using Li<sup>13</sup>CH<sub>3</sub>, obtained from commercial <sup>13</sup>CH<sub>3</sub>I (99%) and LinBu. Figure S1 (see the Supporting Information) shows the C<sub>6</sub>D<sub>6</sub> <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **3c** with natural abundance and labeled with <sup>13</sup>C, in the  $\delta$  interval from ca. 9 to 2 ppm, along with the fully coupled spectrum. As can be seen, the singlet at  $\delta$  7.4 attributed to Mo( $\mu$ -CH<sub>3</sub>)Mo converts in the spectrum of the <sup>13</sup>C-enriched sample into a triplet (<sup>2</sup>J<sub>CC</sub> = 8 Hz) as a consequence of its coupling with the two equivalent Mo<sub>2</sub>( $\mu$ -<sup>13</sup>CH<sub>3</sub>)<sub>2</sub> Li nuclei.<sup>27</sup> The resonance due to the latter methyl groups (4.4 ppm) does not change appreciably. For the two kinds of bridging methyl groups similar <sup>1</sup>J<sub>CH</sub> couplings of about 112 Hz can be measured.

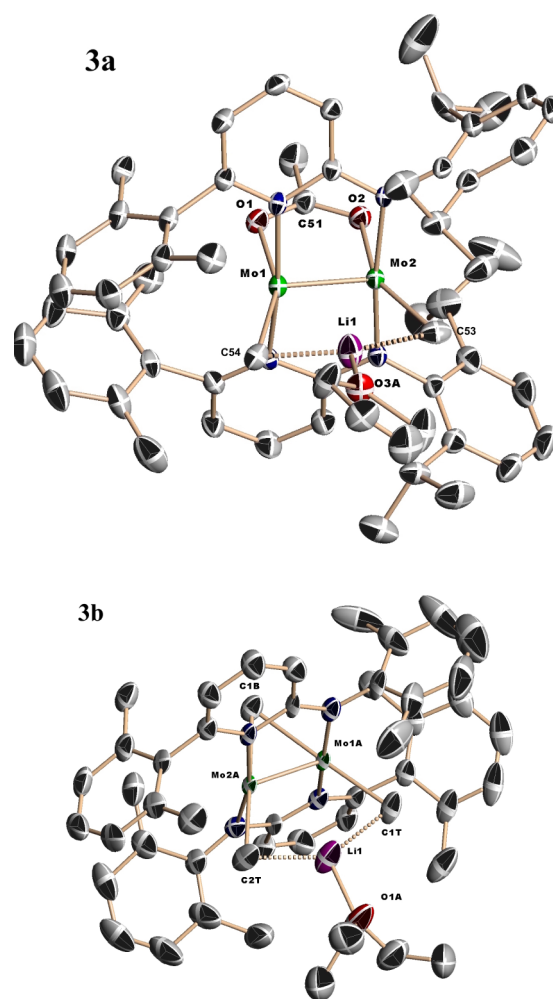
NMR studies of **3c** in THF-*d*<sub>8</sub> revealed some distinct changes. For instance, the <sup>7</sup>Li resonance is now more shielded and appears at –0.1 ppm, thereby shifting by ~2.6 ppm relative to the spectrum recorded in C<sub>6</sub>D<sub>6</sub>. Changes in the <sup>1</sup>H NMR

spectrum are not significant beyond some variations in the chemical shifts of the two types of methyl groups that change from 1.74 and  $-0.55$  in  $C_6D_6$  to 1.25 and  $-0.25$  ppm in THF- $d_8$ . However, the broad  $^{13}C\{^1H\}$  resonance at 4.4 ppm due to the  $Mo(\mu-Me)Li(\mu-Me)Mo$  linkage in  $C_6D_6$  disappears in THF- $d_8$  and converts into a sharp singlet with  $\delta$  14.74, i.e., displaced toward higher frequency by more than 10 ppm. No signs of coupling to  $^7Li$  can be detected. The  $Mo(\mu-Me)Mo$  signal is also deshielded and appears at 10.43 ppm ( $\Delta\delta \sim 3.3$  ppm). In the specimens enriched in  $^{13}C$ , these resonances appear in THF- $d_8$  as a doublet ( $\delta$  14.74) and a triplet (10.43 ppm). A single two-bond coupling constant  $^2J_{CC} = 9$  Hz was measured for **4c** between the two terminal  $Mo-^{13}CH_3$  groups and the single bridging methyl group of the  $Mo(\mu-^{13}CH_3)Mo$  linkage. The magnitude of this coupling lies between typical values for *cis* and *trans* two-bond  $^{13}C-^{13}C$  couplings in other transition metal complexes.<sup>27</sup> All these data unequivocally support the occurrence in THF solutions of an anionic  $[Mo_2Me_3]^-$  organometallic core with the simplified structure represented in Figure 2 (structure **4c**), and therefore with a solvent separated ion pair formulation  $[Li(THF)_4][Mo_2Me_2(\mu-Me)\{\mu-HC(NDipp)_2\}_2]$  for this complex. This proposal has been confirmed by X-ray studies performed with a single-crystal obtained from concentrated toluene/tetrahydrofuran (1:1) solutions of the complex.

As discussed above, the adoption of the contact ion pair formulation **3c** or the solvent separated ion pair structure **4c** is strongly dependent upon the coordination capacity of the solvent. As an additional test, a fresh sample of complex **3c**, prepared as in Scheme 3, was dissolved in  $C_6D_6$ .  $^1H$  and  $^{13}C\{^1H\}$  NMR studies were in accord with the presence of the  $(THF)Li(\mu-Me)Mo(\mu-Me)Mo(\mu-Me)$  core characteristic of the contact ion pair structure. Then, the solvent was evaporated under a vacuum and the solid residue dissolved in THF- $d_8$ . NMR analysis ( $^1H$  and  $^{13}C\{^1H\}$  experiments) revealed the expected features for a monoanionic  $[MeMo(\mu-Me)MoMe]^-$  central unit and the fully solvated  $[Li(THF)_4]^+$  ion characteristic of **4c**. Finally, removal of the solvent under a vacuum with careful drying of the residue and redissolving of the resulting solid in  $C_6D_6$  restored the NMR features of **3c**.

Compounds **3a**, **3b**, and **4c** were characterized by X-ray crystallography and their molecular structures are depicted in Figures 4 (**3a** and **3b**) and 6 (**4c**). Complete details of the crystallographic analyses are collected in Tables S1–3 (see the Supporting Information). Of the three compounds investigated, the two that exhibit a  $Mo(\mu-Me)Mo$   $3c-2e$  bond (i.e., **3b** and **4c**) have almost identical  $Mo-Mo$  bond lengths (ca. 2.084 Å) whereas in the acetate-bridged species **3a** the metal-metal bond is slightly longer at 2.107(6) Å. These values are very close to those reported recently for terphenyl complexes of the  $Mo\equiv Mo$  central unit.<sup>14</sup>

As can be seen in Figure 4, the two  $Ap'$  ligands of complexes **3a** and **3b** (ligands **1a** and **1b** in Figure 1, respectively) adopt different stereochemical distribution upon binding to the respective  $Mo_2$  cores. Thus, in compound **3a** the two  $N_{pyr}$  and the two  $N_{amido}$  nitrogen atoms are mutually *trans* while in complex **3b** they give rise to *trans*- $N_{amido}-Mo-N_{py}$  linkages, as it is commonly observed in dichromium complexes with Cr–Cr multiple bonds.<sup>11</sup> In the two compounds, the dative covalent  $Mo-N_{py}$  bonds are longer than the normal covalent<sup>25</sup>  $Mo-N_{amido}$  bonds. Thus, in **3a** the average  $Mo-N_{py}$  and  $Mo-N_{amido}$  bond lengths are of ca. 2.21 and 2.14 Å, respectively, whereas the similar bonds of **3b** are of about 2.18 and 2.11 Å.

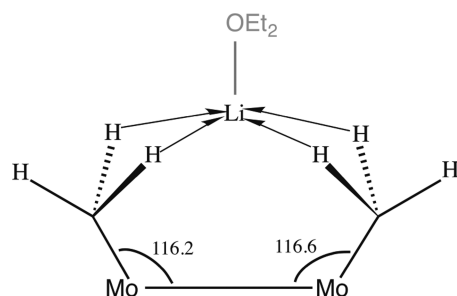


**Figure 4.** Solid-state molecular structures of complexes **3a** (above) and **3b** (below), with thermal ellipsoids set at 30% probability. Selected bond lengths in Å: **3a**: Mo(1)–Mo(2), 2.107(1); Mo(1)–C(54), 2.218(5); Mo(2)–C(53), 2.216(5); C(54)–Li(1), 2.080(1); C(53)–Li(1), 2.143(3). **3b**: Mo(1A)–Mo(2A), 2.084(8); Mo(1A)–C(1T), 2.273(8); Mo(2A)–C(2T), 2.251(7); Mo(2A)–C(1B), 2.411(7); Mo(1A)–C(1B), 2.404(8); C(2T)–Li(1), 2.162(6); C(1T)–Li(1), 2.160(5).

The two complexes contain a  $CH_3\cdots Li(S)\cdots CH_3$  unit that spans over the  $Mo-Mo$  quadruple bond ( $S = THF$  for **3a** and  $Et_2O$  for **3b**). The  $Mo_2C_2Li$  five-membered ring is close to planar, although the lithium atom deviates by 0.428 and 0.249 Å, respectively, from the mean plane of the two molybdenum and the two carbon atoms. Dihedral angles between the  $C-Mo-Mo-C$  and  $C-Li-C$  planes are of  $32^\circ$  for **3a** and  $21^\circ$  for **3b**. The five-membered rings contain comparable  $Mo-C$  bonds with average lengths of ca. 2.21 (**3a**) and 2.26 Å (**3b**). For comparison,  $Mo-CH_3$  distances in the quadruply bonded anionic complex  $Mo_2Me_8^{4-}$  have values<sup>22</sup> in the range 2.27–2.31 Å, while in neutral  $Mo_2Me_4(PR_3)_4$  molecules the  $Mo-CH_3$  bonds have a length of roughly 2.24 Å.<sup>20c,d</sup> Typical  $Mo-Me$  distances in compounds compiled in the CSD are in the 2.10–2.36 Å range.<sup>21</sup>

For complexes **3a** and **3b** the hydrogen atoms of the  $Mo-CH_3$  groups were located on a difference Fourier map. Nevertheless, to ensure a uniform treatment of crystal data they were recalculated into idealized positions. In accordance with the experimental data obtained, it can be proposed that in

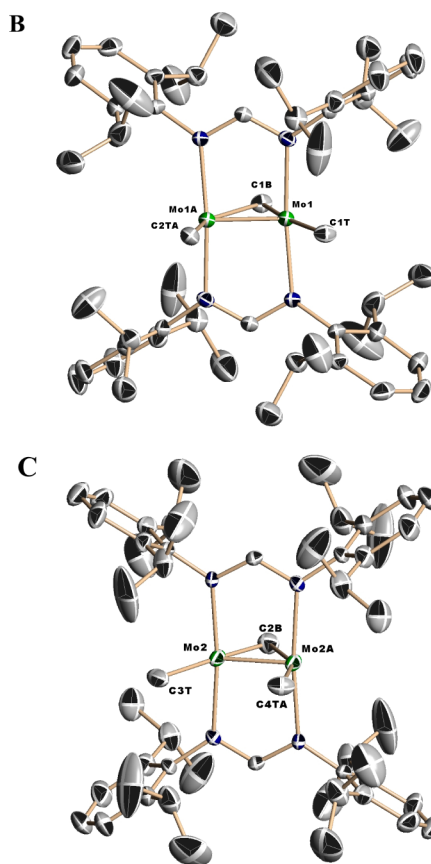
the two complexes the coordination requirements of the lithium ion are partly satisfied by the existence of weak dihapto agostic interactions (Figure 5 and S2; see the Supporting Information) with the molybdenum-bonded methyl groups.



**Figure 5.** Schematic representation of the dihapto agostic  $\text{Mo}_2(\mu\text{-CH}_3)_2\text{Li}$  interactions in complex **3b**. The  $\text{Li}-\text{CH}_3$  distances have a value of ca. 2.16 Å and the  $\text{Li}\cdots\text{H}$  contacts are in the approximate range 1.83–2.11 Å. Angles are in degrees (deg). See also Figure S2 in the Supporting Information for additional details.

Agostic  $\text{M}-\text{CH}_3\cdots\text{Li}$  interactions have been ascertained for different transition metals.<sup>28–31</sup> In complex **3a** the two  $\text{Li}-\text{C}$  bonds of the  $\text{CH}_3\cdots\text{Li}\cdots\text{CH}_3$  portion of the five-membered  $\text{Mo}_2\text{C}_2\text{Li}$  ring are slightly different and distinctly short (2.080(1) and 2.143(3) Å), whereas in **3b** they are practically identical and also short (ca. 2.16 Å). As a reference, the sum of the covalent radii of  $\text{C}_{\text{sp}^3}$  (0.76 Å) and Li (1.28 Å) is 2.04 Å.<sup>32</sup> These metrics denote the existence in the molecules of **3a** and **3b** of non-negligible covalent  $3c-2e$  interactions, as hinted by the solution NMR data already discussed. These interactions seem to be comparable to those found in related complexes. For instance, Gambarotta and co-workers demonstrated that  $[\text{Li}(\text{S})]_4[\text{Cr}_2\text{Me}_8]$  ( $\text{S} = \text{Et}_2\text{O}$ , THF) can be reversibly cleaved by action of tmed (tmed = tetramethylethylenediamine) with formation of  $[\text{Li}(\text{tmed})]_2[\text{CrMe}_4]$ ,<sup>33</sup> and proposed that short  $\text{Li}\cdots\text{CH}_3$  bonding interactions of 2.176 (7) Å were responsible for holding together the two  $\text{CrMe}_4\text{Li}_2$  units of the dimer. The latter, originally characterized by Krause,<sup>34</sup> features a short Cr–Cr distance of 1.968 (2) Å,<sup>33b</sup> but recently, Mulvey et al. have demonstrated that replacing  $\text{Li}^+$  by  $\text{Na}^+$  in  $[\text{Na}(\text{OEt}_2)]_4[\text{Cr}_2\text{Me}_8]$  caused the Cr–Cr separation to increase to 3.263 (2) Å.<sup>35</sup> Interestingly, the isostructural  $[\text{Li}(\text{THF})]_4[\text{Mo}_2\text{Me}_8]$  complex<sup>22</sup> could not be cleaved under reaction conditions similar or harder than those employed for the dichromium complex.<sup>33</sup> In the latter dimolybdenum compound the lithium ions lie at distances of 2.43–2.56 Å from the methyl carbon atoms. It is also worth pointing out that in the two complexes **3a** and **3b** the  $\text{Mo}\cdots\text{Li}$  contacts are long, in the range 2.872(2)–2.962(9) Å, indicating that there are no significant bonding interactions between these atoms. Recently, Tsai et al. have reported studies on a complex with a Mo–Mo quintuple bond spanned by one lithium atom with  $\text{Mo}\cdots\text{Li}$  contacts of 2.640(8) Å that were considered as mainly ionic.<sup>36</sup> It is important to recall that compounds alike **3a** and **3b** that exhibit a bridging hydrocarbyl  $\text{M}(\mu\text{-R})\text{M}'$  structure between transition metal and main group metal atoms are of much current importance, as they are relevant to a number of catalytic reactions, for instance, olefin oligo- and polymerization, cyclizations and additions of carbonyl and alkyl functionalities, and different classes of cross-coupling processes.<sup>29,37–39</sup>

The coordination of the molybdenum atoms of **3a** is completed by a bidentate acetate ligand, while that in **3b** involves instead a bridging methyl group that participates in a  $3c-2e$  interaction. The two kinds of bridging ligands can be viewed as LX ligands thereby yielding a 16-electron count at each molybdenum center, as it is commonly encountered in complexes of this type.<sup>10</sup> Bridging alkyl groups are well-known, although they are much less frequently found than bridging hydride ligands.<sup>25,40–45</sup> Examples in which the bridging alkyls span over multiple M–M bonds are however sparse<sup>11e,46–49</sup> and correspond largely to dichromium complexes. The anionic compound **4c** features also a bridging methyl group (Figure 6).

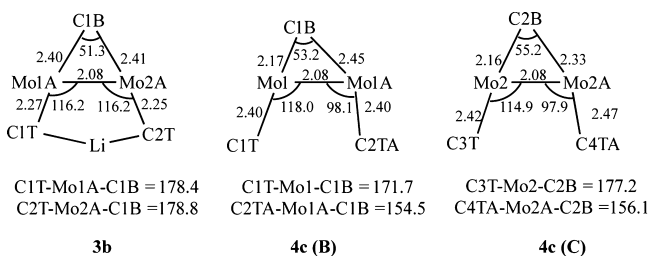


**Figure 6.** Solid-state molecular structure of the anionic  $[\text{Mo}(\text{Me})_2(\mu\text{-Me})\{\mu\text{-HC}(\text{NDipp})_2\}_2]^-$  portion of complex **4c** showing the two independent molecules, **B** (bottom) and **C** (upper structure). The counteranion  $[\text{Li}(\text{THF})_4]^+$  has been omitted for clarity. Thermal ellipsoids are set at 30%. Selected bond lengths in Å **4c** (**B**): Mo(1A)–Mo(1), 2.084(1); Mo(1A)–C(2TA), 2.396(1); Mo(1A)–C(2TA), 2.397(1); Mo(1A)–C(1B), 2.172(1); Mo(1)–C(1B), 2.411(7). (**C**): Mo(2)–Mo(2A), 2.083(1); Mo(2)–C(3T), 2.429(1); Mo(2A)–C(4TA), 2.473(1); Mo(2)–C(2B), 2.328(1); Mo(2A)–C(2B), 2.157(7).

It crystallizes in the  $C_{2/c}$  monoclinic space group with two independent molecules in the asymmetric unit (arbitrarily designated as **B** and **C**). The two display the same geometry and feature similar structural parameters, particularly in what concerns the Mo–Mo and Mo–N bonds. However, their organometallic  $(\mu\text{-Me})\text{Mo}_2\text{Me}_2$  moieties exhibit small differences that merit discussion.

In **3b** the bridging methyl group is appropriately described as symmetric pyramidal with essentially identical Mo–C bond distances (ca. 2.40 Å) and C–Mo–Mo angles (about 64°), and

with a more acute Mo–C–Mo angle of 51.3(2)° (Figure 7). The long Mo–C1B bonds are possibly the consequence of the



**Figure 7.** Bond lengths (Å) and bond angles (deg) for the organometallic [Mo<sub>2</sub>Me<sub>3</sub>] cores of complexes **3b** (left) and **4c** (independent molecules B, center, and C, right). For simplicity, bond distances have been rounded up to the second decimal figure and bond angles to the first.

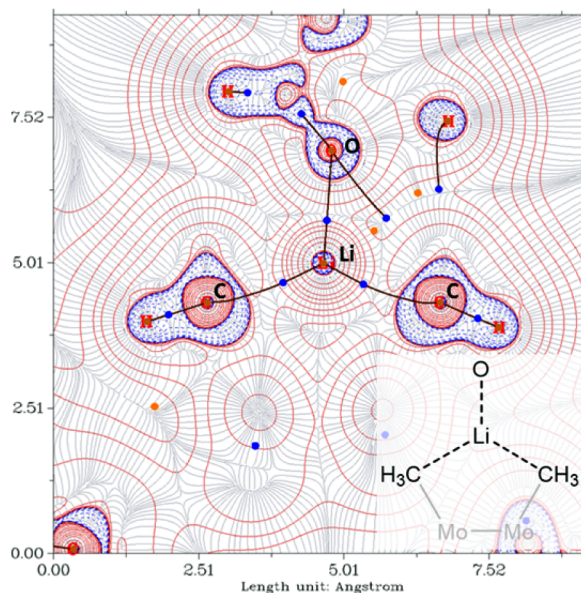
strong *trans* influence<sup>50</sup> exerted by the two molybdenum-bound methyl groups (C1T and C2T) that form regular Mo–C bonds (ca. 2.26 Å) and hold together the lithium ion. The C1T–Mo1A–C1B and C2T–Mo2A–C1B bond angles of 178.4(3) and 178.8(3)°, respectively, are very close to the ideal 180° value.

For the two independent molecules of **4c** (B and C, Figure 7) there are two terminal methyl groups that form long Mo–Me bonds (in the range 2.396(1)–2.473(1) Å). Moreover, they give rise to Mo–Mo–C angles with divergent values, one being of roughly 98° and the other of about 116°. The bridging methyl group generates an acute Mo–C–Mo angle (ca. 53–55°) and two Mo–C bonds that differ appreciably in length. Thus, in molecules B the Mo–C distances are of 2.172(1) and 2.452(1), a situation that therefore approaches terminal coordination to Mo1 (Figure 7),<sup>11e,49c</sup> whereas in C the differences are smaller (2.157(1) and 2.328(1) Å). Although the hydrogen atoms of the bridging methyl groups were not located in the Fourier difference map, they were calculated, these calculations supporting a weak monohapto agostic coordination. Whether the agostic interaction is maintained in solution is unclear since as discussed above, the terminal and bridging methyl groups of complex **4c** exhibit close <sup>1</sup>J<sub>CH</sub> couplings of 115 and 112 Hz, respectively (THF-*d*<sub>8</sub>). We note, however, that similar <sup>13</sup>C–<sup>1</sup>H couplings in Mo–Mo bonded complexes with a bridging methyl group have led to divergent interpretations on the possible existence of agostic interactions.<sup>46</sup>

**Computational Studies on the Mo<sub>2</sub>(μ-Me)<sub>2</sub>Li Linkage of Complexes 3a and 3b.** The gas phase geometries of 3a<sub>C</sub> (with the *i*Pr fragments of 3a replaced by Xyllyl groups) and 3b were optimized at the DFT level with the Gaussian 09<sup>51</sup> package, using the M06<sup>52</sup> and PBE0-D3<sup>53</sup> functionals, which account for dispersion effects. The optimizations were done with the basis set 6-31g(d,p) for *light* atoms and the SDD basis and associated Electron Core Potential for Mo. Both methods reproduce the solid state geometry of 3a and 3b, particularly the short CH<sub>3</sub>⋯Li contacts (Tables S22–S25) of the Mo<sub>2</sub>(μ-Me)<sub>2</sub>Li linkage.

The extent of bonding interaction between the methyl groups and the lithium atoms of 3a and 3b was studied by means of the quantum theory of atoms in molecules (QTAIM).<sup>54</sup> Analysis of the calculated electron densities (ρ) of 3a<sub>C</sub> and 3b with the Multiwfn program<sup>55</sup> reveals bond critical points (bcps) and unique bond paths (bp) between each

carbon and the lithium atoms of their Mo<sub>2</sub>(μ-Me)<sub>2</sub>Li linkages (Figures 8 and S6). Accordingly some level of electron sharing



**Figure 8.** Plot of the laplacian of the electron density ∇<sup>2</sup>ρ of 3a<sub>C</sub> in the C<sub>Mo</sub>C<sub>Mo</sub>Li plane calculated with the M06 functional. The solid and dashed lines correspond to positive and negative values of ∇<sup>2</sup>ρ respectively. In-plane bcps and bond paths of the electron density are superimposed.

between these carbon atoms and their attached hydrogens with the lithium atom becomes apparent by the analysis as discussed below.

The presence of a unique bond path with a bond critical point connecting two atoms is usually invoked as one (but not exclusive)<sup>56</sup> criterion of interacting atoms. Besides, the topological properties of the electron density at the bond critical points have been related to the nature of the interaction between atoms.<sup>57,58</sup> Tables 1 and S4–S8 summarize topological

**Table 1.** QTAIM Analysis of the Electron Density of 3a<sub>C</sub> at Selected bcps<sup>a</sup>

bond	ρ <sup>c</sup>	H <sub>b</sub> <sup>d</sup> = V <sub>b</sub> + G <sub>b</sub>	V <sub>b</sub>  /G <sub>b</sub>	∇ <sup>2</sup> ρ <sup>e</sup>
C–Li <sup>b</sup>	0.0226	0.0033	0.8800	0.1228
Li–O	0.0267	0.0080	0.7933	0.1879
Mo–Mo	0.1796	−0.1094	1.5012	0.4233
Mo–C <sup>b</sup>	0.0840	−0.0250	1.4056	0.1449

<sup>a</sup>Calculations with the M06 functional. <sup>b</sup>Average values of the local total energy density H<sub>b</sub> as the sum of the local potential V<sub>b</sub> and kinetic energies G<sub>b</sub>. <sup>c</sup>e-bohr<sup>−3</sup>. <sup>d</sup>Hartree. <sup>e</sup>e-bohr<sup>−5</sup>.

properties at selected bcps of 3a<sub>C</sub> and 3b. These data are consistent with an important ionic character for the C⋯Li interactions in these molecules, similar to that found in MeLi (see the SI for details and the criteria used). In agreement with this classification the electron density integrated in the basins of the lithium atoms (the AIM or Bader charges) is close to 0.9e as expected for Li<sup>+</sup>. However, this result suggests a small but non-negligible degree of electron sharing between the basins of lithium and the neighboring atoms in agreement with the <sup>1</sup>J<sub>LiC</sub> observed by NMR.

In relation with the above, delocalization indices (δ(A,B)) indicate the number of electron pairs shared (delocalized)

between two atoms A and B, and can be seen as a type of topological order of a bond.<sup>57–59</sup> In our case covalent C–H interactions have  $\delta(\text{C,H})$  close to 1, and  $\delta(\text{Mo,Mo})$  are almost 3 for both molecules considered, whereas the delocalization indices for the C...Li interactions are in the range between 0.05 and 0.06, slightly smaller than the values found for the Li...O interactions (Tables S9–S17), which are in the range between 0.06 and 0.07.

A complementary approach to explain the electron sharing between the methyl carbons and lithium atoms of **3** consists on applying the orbital-based Natural Bonding Orbitals scheme.<sup>60</sup> In this case localized orbitals are derived from molecular orbitals to yield the best Lewis-like bonding description of molecules. Interactions between noncovalently bonded fragments of a molecule are accounted for by delocalizations of two (or three) center populated orbitals into empty antibonding or lone pair (localized on one atom) orbitals.<sup>61</sup> In our case the interaction between the Li atom and the organometallic fragment of complexes **3** is described in terms of delocalizations of Mo–Mo and Mo–C orbitals onto empty orbitals localized on the lithium (see Figures S8–S9 and Tables S18–S19). In addition Wiberg bond indices derived from the NBO analysis support the bonding situation depicted in Figure 5, (Tables S20–21), with values close to 0,1 for the C...Li interaction and around 0.01–0.02 for the four hydrogen atoms of the CH<sub>3</sub> fragments closer to Li, the latter being three- or 4-fold the values found for the hydrogens oriented away from the lithium.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried and degassed prior to use, and stored over 4 Å molecular sieves. Toluene (C<sub>7</sub>H<sub>8</sub>), *n*-pentane (C<sub>5</sub>H<sub>12</sub>), and *n*-hexane (C<sub>6</sub>H<sub>14</sub>) were distilled under nitrogen over sodium. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen over sodium/benzophenone. Benzene-*d*<sub>6</sub> and THF-*d*<sub>8</sub> were distilled under argon over sodium/benzophenone; [D<sub>8</sub>]toluene was distilled under argon over sodium. LiMe was purchased from Sigma-Aldrich as a 1.6 M solution in Et<sub>2</sub>O. The quadruply bonded Mo<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>(N<sup>^</sup>N)<sub>2</sub> complexes **2a–2c** were prepared as described previously.<sup>15a,d</sup> Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external SiMe<sub>4</sub> ( $\delta$ : 0 ppm) using the residual proton solvent peaks as internal standards (<sup>1</sup>H NMR experiments), or the characteristic resonances of the solvent nuclei (<sup>13</sup>C NMR experiments), while <sup>7</sup>Li was referenced to external LiCl. Spectral assignments were made by routine one- and two-dimensional NMR experiments (<sup>1</sup>H, <sup>13</sup>C, <sup>13</sup>C{<sup>1</sup>H}), COSY, NOESY, HSQC and HMBC) where appropriate. UV–visible spectra were recorded on a PerkinElmer Lambda 750 spectrometer. For elemental analyses a LECO TruSpec CHN elementary analyzer, was utilized.

**Synthesis and Characterization of Compound 3a.** To a suspension of the corresponding [Mo<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>(Ap')<sub>2</sub>] complex, **2a**, (600 mg, 0.58 mmol) in THF (ca. 12 mL) cooled to –40 °C, LiMe (2.5 equiv) was added slowly. The low temperature was kept for about 3 h and then the reaction mixture was allowed to reach room temperature with continuous stirring during 3 h giving a red solution that was evaporated in vacuo. The solid residue was extracted with pentane (ca. 35 mL) and was centrifuged. The filtrate was transferred to a Schlenk tube, concentrated and stored at –23 °C during 2 days. Dark red crystals of complex **3a** separated out and were isolated by filtration and dried under a vacuum for 2 h. Yield: 320 mg (50%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = –0.41 (br. s, 6 H, {Mo<sub>2</sub>Me<sub>2</sub>Li-THF}), 0.97 (d, 6 H, Me<sub>Dipp</sub>(endo)), 1.12 (d, 6 H, Me'<sub>Dipp</sub>(endo)), 1.19 (m, 4 H, O–CH<sub>2</sub>CH<sub>2</sub>), 1.27 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Me<sub>Dipp</sub>(exo)), 1.28 (d, 6 H, Me'<sub>Dipp</sub>(exo)), 2.05 (s, 6 H, Me'<sub>Xyl</sub>),

2.21 (s, 3 H, CH<sub>3</sub>CO<sub>2</sub>), 2.31 (s, 6 H, Me<sub>Xyl</sub>), 3.23 (sept, 2 H, CH'Me<sub>2</sub>), 3.39 (m, 4 H, O–CH<sub>2</sub>CH<sub>2</sub>), 3.44 (sept, 2 H, CHMe<sub>2</sub>), 5.76 (dd, 2 H, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 5-py), 6.47 (dd, 2 H, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 3-py), 6.67 (dd, 2 H, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>4</sup>J<sub>HH</sub> = 6.7 Hz, 4-py), 6.71 (virtual t, 4 H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, *m*-Xyl and *m'*-Xyl), 6.85 (t, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, *p*-Xyl), 7.17–7.22 (m, 6 H, *m'*-Dipp, *m*-Dipp, and *p*-Dipp) ppm. The coupling constants <sup>3</sup>J<sub>HH</sub> for all CHMe<sub>2</sub> groups are approximately of 7 Hz. <sup>1</sup>H signals with ' refer to the group located in the same region as the MeLiMe unit. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = –1.4, 4.5 (q, 1 C each, <sup>1</sup>J(<sup>13</sup>C,<sup>7</sup>Li) = 12 Hz, {Mo<sub>2</sub>Me<sub>2</sub>Li-THF}), 20.3 (Me'<sub>Xyl</sub>), 21.0 (Me<sub>Xyl</sub>), 22.9 (CH<sub>3</sub>CO<sub>2</sub>), 24.5 (Me<sub>Dipp</sub>(endo)), 24.8 (O–CH<sub>2</sub>CH<sub>2</sub>), 25.3, 25.5 (Me'<sub>Dipp</sub>(exo) and Me<sub>Dipp</sub>(exo)), 25.8 (Me'<sub>Dipp</sub>(endo)), 27.9 (CHMe<sub>2</sub>), 28.4 (CH'Me<sub>2</sub>), 68.2 (O–CH<sub>2</sub>CH<sub>2</sub>), 108.2 (5-py), 112.5 (3-py), 124.2 (*m*-Dipp), 124.5 (*m'*-Dipp), 125.0 (*p*-Dipp), 126.4 (*m'*-Xyl), 128.2 (*p*-Xyl), 128.5 (*m*-Xyl), 130.9 (4-py), 135.9, 136.0 (*o*-Xyl), 139.7 (*ipso*-Xyl), 144.1 (*o'*-Dipp), 145.8 (*o*-Dipp), 146.9 (*ipso*-Dipp), 157.7, 169.5 (6-py and 2-py), 177.3 (O<sub>2</sub>CCH<sub>3</sub>). The signals with ' refer to the group located in the same region as the MeLiMe unit. <sup>7</sup>Li NMR (194 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = 2.15 (br. s) ppm. UV–visible (C<sub>6</sub>H<sub>14</sub>)  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 255 and 340, 420, and 505 nm (3100, 6000 M<sup>–1</sup> cm<sup>–1</sup>, respectively). Elemental analysis calcd. (%) for C<sub>58</sub>H<sub>75</sub>LiMo<sub>2</sub>N<sub>4</sub>O<sub>3</sub>: C, 64.80; H, 7.03; N, 5.21. Found: C, 64.9; H, 6.9; N, 5.0.

**Synthesis and Characterization of Compound 3b.** The appropriate [Mo<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>(Ap')<sub>2</sub>] complex (**2b**) (1.0 g, 1.1 mmol) was dissolved in a toluene/Et<sub>2</sub>O (2:1) mixture and LiMe (3 equiv) was added. The solution was heated at 60 °C for 6 h. Then, another 3 equiv of LiMe were added and the resulting mixture was heated for a further period of 12 h at 60 °C. The suspension was centrifuged, the filtrate was transferred to a Schlenk tube and the solvent was removed under a vacuum. Diethyl ether (ca. 10 mL) was added and the solution was kept in the fridge for 3 days to obtain dark red crystals of complex **3b** in 65% yield. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = –1.35 (s, 6 H, {Me<sub>2</sub>Li-Et<sub>2</sub>O}), 0.77 (s, 3 H,  $\mu$ -Me), 2.02 (s, 6 H, Me'<sub>Xyl</sub>), 2.05 (s, 6 H, Me'<sub>Xyl</sub>(amino)), 2.20 (s, 6 H, Me<sub>Xyl</sub>(amino)), 2.24 (s, 6 H, Me<sub>Xyl</sub>), 6.06 (d, 2 H, <sup>4</sup>J<sub>HH</sub> = 6.5 Hz, 5-py), 6.46 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, *m'*-Xyl), 6.49 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, *m*-Xyl), 6.57 (t, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, *p*-Xyl), 6.73 (d, 2 H, <sup>4</sup>J<sub>HH</sub> = 8.9 Hz, 3-py), 6.92–7.02 (m, 6 H, *m*-Xyl(amino), *p*-Xyl(amino), and 4-py), 7.07 (m, 2 H, *m'*-Xyl(amino)) ppm. <sup>1</sup>H signals with ' refer to the group located in the same region as the MeLiMe unit. Signals corresponding to aryl (ArN-) are marked with *amino*. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = 2.8 (br. s, {Me<sub>2</sub>Li-Et<sub>2</sub>O}), 6.5 ( $\mu$ -Me), 20.2 (Me'<sub>Xyl</sub>(amino)), 21.7, 21.8 (Me<sub>Xyl</sub>(amino) and Me<sub>Xyl</sub>), 22.4 (Me'<sub>Xyl</sub>), 107.9 (5-py), 110.7 (3-py), 124.6 (*p*-Xyl(amino)), 127.6 (*m'*-Xyl), 128.6 (under signal C<sub>6</sub>D<sub>6</sub>, *m*-Xyl, *p*-Xyl), 129.0, 129.2 (*m'*-Xyl(amino) and *m*-Xyl(amino)), 132.4 (4-py), 133.2 (*o'*-Xyl(amino)), 135.2 (*o*-Xyl(amino)), 135.4 (*o*-Xyl), 137.3 (*o'*-Xyl), 140.4 (*ipso*-Xyl), 148.9 (*ipso*-Xyl(amino)), 156.2 (6-py), 165.5 (2-py) ppm. The signals with ' refer to the group located in the same region as the MeLiMe unit. Signals corresponding to aryl (ArN-) are marked with *amino*. <sup>7</sup>Li NMR (C<sub>6</sub>D<sub>6</sub>, 194 MHz)  $\delta$  = 1.72 ppm. UV–visible (C<sub>7</sub>H<sub>8</sub>)  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 460, 575 (12535, 4685 M<sup>–1</sup> cm<sup>–1</sup>, respectively). Elemental analysis calcd. (%) for C<sub>49</sub>H<sub>61</sub>LiMo<sub>2</sub>N<sub>4</sub>O: C, 63.91; H, 6.68; N, 6.08. Found: C, 63.9; H, 6.6; N, 5.7.

**Synthesis and Characterization of Compound 3c.** Complex [Mo<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>] $\{\mu$ -HC(NDipp)<sub>2</sub>\}<sub>2</sub> (**2c**) (4.0 g, 3.86 mmol) was dissolved in THF (60 mL). The mixture was cooled at 0 °C and LiMe (3.5 equiv) was added slowly. The reaction mixture was allowed to reach room temperature over a period of 12 h. The resulting red suspension was centrifuged, the filtrate was transferred to a Schlenk flask and the solvent was removed under a vacuum. Pentane was added (10 mL), the suspension was stirred for 5–10 min and the solvent was removed in vacuo. This process was repeated one more time and the resulting solid was dried under a vacuum for 4 h to obtain a red solid (2.5 g, ca. 60%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = –0.55 (br. s, 6 H, {Mo<sub>2</sub>Me<sub>2</sub>Li-THF}), 0.98 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Me<sub>Dipp</sub>(endo)), 1.27 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Me'<sub>Dipp</sub>(endo)), 1.32 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Me'<sub>Dipp</sub>(exo)), 1.35 (m, 4 H, O–CH<sub>2</sub>CH<sub>2</sub>), 1.38 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Me<sub>Dipp</sub>(exo)), 1.74 (s, 3 H,  $\mu$ -Me), 3.55 (m, 4 H, O–CH<sub>2</sub>CH<sub>2</sub>), 3.76 (sept, 4 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH'Me<sub>2</sub>), 4.11 (sept, 4 H,

$^3J_{\text{HH}} = 6.8$  Hz,  $\text{CHMe}_2$ ), 7.02 (dd, 4 H,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz,  $m$ -Dipp), 7.06 (t, 4 H,  $^3J_{\text{HH}} = 7.6$  Hz,  $p$ -Dipp), 7.11 (dd, 4 H,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.7$  Hz,  $m'$ -Dipp), 8.59 (s, 2 H, NC(H)N) ppm.  $^1\text{H}$  signals with ' refer to the group located in the same region as the MeLiMe unit.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta = 4.4$  (m,  $^1J(^{13}\text{C}, ^7\text{Li}) \sim 8$  Hz,  $\{\text{Mo}_2\text{Me}_2\text{Li}\cdot\text{THF}\}$ ), 7.14 (s,  $\mu$ -Me), 24.5 ( $\text{Me}_{\text{Dipp}}(\text{endo})$ ), 25.0 ( $\text{Me}'_{\text{Dipp}}(\text{endo})$ ), 25.6 ( $\text{O}-\text{CH}_2\text{CH}_2$ ), 26.6 ( $\text{Me}_{\text{Dipp}}(\text{exo})$ ), 28.4 ( $\text{CH}'\text{Me}_2$ ), 28.5 ( $\text{CHMe}_2$ ), 28.7 ( $\text{Me}'_{\text{Dipp}}(\text{exo})$ ), 124.1, 124.2 ( $m$ -Dipp and  $m'$ -Dipp), 125.7 ( $p$ -Dipp), 143.9 ( $o'$ -Dipp), 145.4 ( $o$ -Dipp), 143.3 ( $ipso$ -Dipp), 161.3 (NC(H)N) ppm. The signals with ' refer to the group located in the same region as the MeLiMe unit.  $^7\text{Li}$  NMR (194 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta = 2.51$  (br. s,  $\{\text{Mo}_2\text{Me}_2\text{Li}\cdot\text{THF}\}$ ) ppm. UV-visible ( $\text{C}_4\text{H}_8\text{O}$ )  $\lambda_{\text{max}}(\epsilon) = 420$  nm ( $2200 \text{ M}^{-1} \text{ cm}^{-1}$ ). Elemental analysis calcd. (%) for  $\text{C}_{57}\text{H}_{87}\text{LiMo}_2\text{N}_4\text{O}$  (3c): C, 65.63; H, 8.41; N, 5.37. Found: C, 65.2; H, 8.1; N, 5.0.

**Synthesis and Characterization of Compound 4c.** This complex was prepared as indicated above for the contact ion pair complex 3c. After removal of the reaction solvent under a vacuum, the obtained crude red solid was crystallized from a saturated THF:toluene solution (1:1) at  $-23$  °C for 3 days. Red crystals of the solvent-separated ion pair complex  $[\text{Li}(\text{THF})_4][\text{Mo}_2\text{Me}_2(\mu\text{-Me})\{\mu\text{-HC}(\text{NDipp})_2\}_2]$  (4c) were isolated by filtration and dried under a vacuum for 2 h. Selected signals for complex 4c:  $^1\text{H}$  NMR (500 MHz,  $\text{THF}-d_6$ , 25 °C)  $\delta = -0.25$  (br. s, 6 H,  $\{\text{Me}-\text{MoMo}-\text{Me}\}$ ), 1.25 (s, 3 H,  $\mu$ -Me) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{THF}-d_6$ , 25 °C)  $\delta = 10.43$  (s,  $\{\text{Mo}_2\text{Me}_2\text{Li}\cdot\text{THF}\}$ ), 14.74 (s,  $\mu$ -Me).  $^7\text{Li}$  NMR (194 MHz,  $\text{THF}-d_6$ , 25 °C)  $\delta = -0.10$  (br. s,  $\{\text{Mo}_2\text{Me}_2\text{Li}\cdot\text{THF}\}$ ) ppm. Elemental analysis calcd. (%) for  $\text{C}_{69}\text{H}_{111}\text{LiMo}_2\text{N}_4\text{O}_4$  (4c): C, 65.80; H, 8.88; N, 4.45. Found: C, 66.5; H, 9.6; N, 4.9.

## CONCLUSIONS

We have prepared and structurally characterized newly designed metal–metal bonded complexes that contain a  $\text{Mo}_2$  core spanned by a  $-\text{CH}_3\cdots\text{Li}\cdots\text{CH}_3-$  fragment. This structural motif is present in compounds 3a–3c and is made up of two  $\text{Mo}-\text{CH}_3$  units that are bonded to a solvated lithium cation ( $\text{S})\text{Li}^+$  ( $\text{S} = \text{Et}_2\text{O}$  or THF) by means of 3c–2e agostic interactions. The resulting  $\text{Mo}_2\text{Me}_2\text{Li}$  central assembly has a Mo–Mo bond length that is consistent with a Mo–Mo quadruple bond. Each metal atom binds additionally to two nitrogen atoms of two bridging aminopyridinate or amidinate ligands, and their coordination is completed by a third bridging ligand, namely, acetate for 3a or methyl in complexes 3b and 3c. Computational studies on the dimethyl heterotrinnuclear  $\text{Mo}_2\text{Me}_2\text{Li}$  framework reveal that the  $\text{CH}_3\cdots\text{Li}$  interactions are mainly ionic with a non-negligible covalent character, which is in agreement with NMR observations.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07899.

Experimental procedures and characterization data for other new compounds described herein, additional tables and figures with computational details and xyz coordinates of calculated species. (PDF)

Crystal data. (CIF)

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### Notes

The authors declare no competing financial interest.

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