An Unsaturated Four-Coordinate Dimethyl Dimolybdenum Complex with a Molybdenum-Molybdenum Quadruple Bond

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We describe the synthesis, molecular, and electronic structure of the complex \([\text{Mo}_2\text{Me}_2(\mu-HC(NDipp))_2]_2\) (2), that contains a dimeric core with a Mo–Mo quadruple bond and features uncommon four-coordinate geometry and fourteen-electron count at each molybdenum atom (Dipp = 2,6-iPr_2C_6H_3). The coordination polyhedron approaches a square pyramid with one of the molybdenum atoms nearly co-planar with the basal square plane in which the coordination position trans with respect to the Mo–Me bond is empty. The other three sites contain two trans nitrogen atoms of different amide groups and the methyl group. The second Mo atom occupies the apex of the pyramid and forms a Mo–Mo bond of length 2.080 (1) Å, consistent with a quadruple bond. Compound 2 reacts with tetrahydrofuran (THF) and trimethylphosphine to yield the mono-adducts \([\text{Mo}_2\text{Me}_2(\mu-HC(NDipp))_2]_2(L)\) (3-THF and 3-PMe_3, respectively) with one terminal and one bridging methyl groups. In contrast, 4-dimethylaminopyridine (dmap) forms the bis-adduct \([\text{Mo}_2\text{Me}_2(\mu-HC(NDipp))_2(dmap)]_2\) (4), with terminally coordinated methyl groups. Hydrogenolysis of complex 2 leads to the bis(hydride) \([\text{Mo}_2H_2(\mu-HC(NDipp))_2(thf)]_2\) (5-THF) with elimination of CH_3. Computational, kinetic and mechanistic studies, that include the use of D_2, and of complex 2 labelled with ^13C (99%) at the Mo–CH_3 sites, support the intermediacy of a methyl-hydride reactive species. A computational analysis of the terminal and bridging coordination of the methyl group to the Mo-Mo core is also reported.

Introduction

In the course of ongoing studies on binuclear molybdenum compounds with M–M quadruple bonds we became interested in preparing alkyl and aryl complexes of the (Mo_2)_4^4+ core that could be used as precursors for low-coordinate second-row diorganometal(II) species and for related hydride complexes. As a result of these efforts, a series of mono- and bis-terphenyl complexes \([\text{Mo}_2(\mu-Ar')_2(\text{O}_{2}C\text{R})_2]_2\) and \([\text{Mo}_2(\mu-Ar')_2(\text{O}_{2}C\text{R})_2]_2\), were obtained for different terphenyl ligands (Ar') and carboxylate groups. The new compounds displayed a Mo–Mo bond length close to 2.10 Å, typical of a quadruple bond, and a coordinative and electronic unsaturation partially compensated by the existence of weak Mo-C_{terphen} secondary interactions involving η^1 binding of a flanking aryl ring. Latterly, within the same line of research, uncommon lithium di- and trimethyl dimolybdenum(II) ate complexes in which the unprecedented trimetallic agostic bond structure \(S = \text{Et}_2\text{O}, \text{THF}\) is stabilized by metal coordination to auxiliary pyridylamido (also called aminopyridinate) and amidinate ligands were also investigated.

The methyl group is the simplest alkyl function. Be that as it may, it can adopt a variety of coordination modes in its interaction with transition metal centres. Thus, besides common terminal binding, M–Me, it can perform a bridging role, M(μ-Me)M, generating a variety of structures\(^{14-7}\) that encompass the symmetrical pyramidal and the monohapto agostic binding forms depicted in Figure 1.\(^{18,9}\) Even if a large number of methyl complexes of molybdenum is presently...
known, information on compounds of this sort that contain the (Mo$_3$)$^{4+}$ central unit is scarce.$^{[10]}$

![Figure 1](image_url)

**Fig. 1.** Half-arrow representations for non-agostic μ$^\text{Me}^\text{Me}$ – Me (left) and monohapto agostic μ$^\text{Me}^\text{Me}$ – Me (right) bridging methyl groups (see ref. 8).

In 1974 the pyrophoric salt [Li(thf)$_4$][Mo$_2$Me$_6$] was prepared by Cotton, Wilkinson and co-workers and found to exhibit a Mo–Mo bond distance of 2.148(2) Å and Mo–Me bond lengths in the range ca. 2.27-2.31 Å.$^{[11]}$ The structures of neutral complexes of composition [Mo$_2$Me$_6$(PR$_3$)$_4$] (PR$_3$ = PMe$_3$, PMe$_2$Ph) were later ascertained with similar Mo-Mo (ca. 2.15 Å) and Mo–Me (2.25 Å) bond distances.$^{[12]}$ No other methyl (Mo$^{4+}$) complexes seem to have been described with the exception of the mentioned ate complexes recently reported by our group, that were isolated as lithium derivatives with either contact ion pair or solvent-separated ion pair formulations. Some methyl derivatives with Mo–Mo bonds of order lower than four have also been described.$^{[13-16]}$

Transition metal organometallics that possess structures of low coordination number and low electron count are reactive species in a number of catalytic reactions.$^{[17]}$ Furthermore, their unsaturated metal centres can provide active frames for the activation of small molecules such as H$_2$$^{[18]}$ or N$_2$$^{[19]}$. In the field of molecular metal-metal multiple bonds, unusual physical properties and reactivity patterns have been disclosed in unsaturated complexes of chromium, molybdenum and other metals.$^{[20-25]}$ In this article we report the synthesis and structural characterization by NMR, X-ray and computational methods of the four coordinate, fourteen-electron dimethyl complex [Mo$_2$Me$_2$μ-HC(NDipp)$_2$]$_2$ (2) (Dipp = 2,6-i-Pr$_2$C$_6$H$_3$). This compound has a salient solid-state structure (B) with terminal methyl groups and coordinatively and electronically unsaturated metal atoms. In accordance with these features, it reacts readily with tetrahydrofuran and PMe$_3$ to yield the monoadducts [Mo$_2$Me$_2$μ-Me]μ-HC(NDipp)$_2$]$_2$(L)] (3-THF and 3-PMe$_3$), and with 4-dimethylaminopyridine (dmap) to afford the bis-adduct [Mo$_2$Me$_2$μ-HC(NDipp)$_2$]$_2$(dmap)$_2$ (4). As discussed in detail below, while in complex 2 and in the latter complex 4 the two methyl groups form normal 2e-2e Mo–CH$_3$ bonds, in the two complexes 3 one of the methyl groups bridges the two molybdenum atoms and participates in a monohapto agostic interaction.$^{[18-19]}$ Complex 2 reacts with H$_2$ to generate the bis(hydride) derivative [Mo$_2$H$_2$μ-HC(NDipp)$_2$]$_2$(thf)$_2$ (5), previously characterized by our group.$^{[26]}$ Kinetic, mechanistic and computational studies on this reaction, that include the use of samples of 2 and 3-THF labelled with $^{13}$C at the Mo–CH$_3$ sites, support the intermediacy of the methyl-hydride species [Mo$_2$(CH$_3$)$_2$(H)$μ$-HC(NDipp)$_2$]$_2$(THF)$_2$ (6-THF).

**Results and Discussion**

As cited in the introductory comments, we have recently characterized some lithium trimethyl dimolybdenum(II) ate complexes that exhibit an unprecedented Li[μ-Me]Mo[μ-Me]Mo[μ-Me] trinmetallic core (structure A), supported by coordination to two bridging aminopyridinate or amide ligands. Even if the aminate derivative, which has composition [Mo$_2$(μ-Me)[μ-Me]Li(THF)][μ-HC(NDipp)$_2$]$_2$ (1), was obtained by the reaction of the bis(acetate)bis(amine)ate precursor [Mo$_2$(μ-O$_2$CMe)$_2$]μ-HC(NDipp)$_2$]$_2$ Dipp = 2,6-i-Pr$_2$C$_6$H$_3$ with an excess of LiMe, in some instances, NMR analysis of the reaction mixtures suggested the formation of small quantities of a lithium-devoid neutral metal derivative, of the (Mo$_3$)$^{4+}$ central unit. It was assumed that the new species contained a [Mo$_2$Me$_2$] core, and accordingly, we set out to isolate this compound. We found that heating at 100°C for 3-5 hours toluene or toluene-hexane solutions of 1 resulted in the elimination of LiMe and formation of the dimethyl complex 2 (Scheme 1). To avoid contamination by tetrahydrofuran (THF), that reacts instantly with 2 to yield the corresponding adduct 3-THF (vide infra), solid 2 was treated twice with 5 mL of pentane, stirred for 15 min and thoroughly dried in vacuo (see Experimental Section). Crystallization from toluene at -23°C afforded very air sensitive red crystals of the desired product.

![Scheme 1](image_url)

**Scheme 1 Synthesis of unsaturated complex 2.**

Complex 2 did not react with either CO$_2$ (2 bar, 12 h, 25°C) or C$_2$H$_4$ (0.5 bar, 12 h, 60°C). In contrast, its treatment with LiMe at room temperature in a 1:1 molar ratio (Scheme 2) gave cleanly compound 1, that was characterized by comparison of its NMR data with those of an authentic sample.$^{[30]}$ New complexes formed when 2 was reacted with an excess of THF, PMe$_3$ and 4-dimethylaminopyridine (dmap). While THF and PMe$_3$ yielded mono-adducts, 3-THF and 3-PMe$_3$,
respectively, the pyridinic ligand with smaller cone angle (101.1° for pyridine, vs 118° for PMe3)[27] afforded the bis(adduct) 4. Under similar conditions, no observable reaction took place between complex 2 and the bulkier phosphine PMe3Ph (cone angle 122°),[27b] probably as a consequence of steric hinderance.

Complex 3·THF was isolated as an oxygen- and moisture-sensitive red crystalline solid, following crystallization from a toluene:THF solvent mixture. As represented in Scheme 2, it converted back to the solvent free complex 2 by action of vacuum, at room temperature or slightly above (ca. 40°C). The solvated complex has, however, enhanced thermal stability in comparison with the base-free complex 2 and slightly reduced reactivity towards oxygen and water. Since, in addition, the coordinated THF is highly labile (see below), 3·THF was commonly used in place of 2 for many of the reactivity studies that will be discussed in the following paragraphs (see Scheme 2). The new complexes represented in Scheme 2 were characterized by microanalysis, NMR spectroscopy and X-ray crystallography. For the study of the reaction of 2 with H2, to be analysed in a forthcoming section, samples of this complex and of the adducts 3·THF and 3·PMe3 enriched in 13C (99%) at the Mo–CH3 sites were prepared. Their examination by variable temperature NMR spectroscopy proved valuable for structural assignment. The 1H NMR spectrum of complex 2 (C8D8, 25°C) contains two septets (3.54 and 4.25 ppm) and four doublets (in the interval 1.0 – 1.4 ppm) for the eight iso-propyl substituents of the two amidinate ligands, coherent with the molecular symmetry proposed for this complex. In addition, a singlet at δ 1.89 can be attributed to the metal bonded CH3 groups. The corresponding 13C NMR resonance appears at 14.7 ppm and is characterized by a JCH coupling constant of 120 Hz. These data are consistent with terminal coordination of the methyl groups.[10] Low temperature 13C(1H) studies of complex 2 enriched in 13C were undertaken (Figure S1). Upon cooling at -20°C the 14.7 ppm resonance broadens, and it fades into the base line when the temperature drops to -40°C. Then it merges at -60°C with δ 15.5 ppm, to become broader at -70°C, and then disappear again into the base line when the temperature decreases to -85°C. By comparison with the dynamic behaviour of 3·THF (vide infra) the higher energy dynamic process (coalescence temperature -40°C) can be attributed to equilibration of complex 2 with small, undetected amounts of its THF adduct (originated by minor amounts of THF). In turn, the lower energy process (coalescence at -85°C) could tentatively be viewed as involving an isomeric Mo3(µ-Me)3 bridging structure, although the lack of computational support in favour of this formulation (see below) casts doubts on the participation of such an species. An alternative possibility could be the attainment at very low temperatures of a weak e-agostic interaction of the kind hinted by the X-ray data to be discussed in an upcoming section. The 1H NMR spectrum of 3·THF (C8D8, 25°C) shows only one resonance at 1.89 ppm attributable to the metal-bonded methyl protons, which is clearly in disagreement with the formulation presented in Scheme 2 that contains one terminal and one bridging methyl ligands. The corresponding 13C NMR resonance appears with δ 15.9 and has a JCH coupling constant of 118 Hz. Similarly, the iso-propyl substituents of the amidinate ligands of 3·THF give rise to a pattern of signals that resembles that discussed above for the parent complex 2 (i.e. two septets at 3.81 and 4.04 ppm and four doublets in the range 1.0 – 1.4 ppm). All these data are in agreement with fast dissociation of the coordinated molecule of THF, a process that slows down considerably upon cooling at lower temperatures. Thus, only a broad hump centred at 16.1 ppm is observed at -20°C in the 13C(1H) NMR of a sample of 3·THF enriched in 13C (Figure S2) that becomes broader with further cooling, such that cannot be distinguished from the base line between -30 and -40°C. Extra cooling to -60°C causes, however, the appearance of three signals with chemical shifts 13.5, 15.5 and 21.2 ppm. The central one corresponds to complex 2, whereas the other two can be respectively ascribed to the terminal and bridging methyl groups of complex 3·THF by comparison with compound 3·PMe3 (see below) and with other Mo≡Mo complexes that contain terminal and bridging methyl groups.[3]
As depicted in Scheme 2, the reaction of 2 or 3-THF with PMe3 (ca. 1.5 equiv) generated cleanly the analogous adduct 3-PMe3 for which a similar structure containing terminal and bridging methyl groups can also be proposed. Notwithstanding, the room temperature ¹H, ¹³C(¹H) and ³¹P(¹H) NMR spectra feature broad resonances indicating that phosphine dissociation is fast under these conditions. Upon cooling at -45°C (C₆D₆) the broad room temperature ³¹P(¹H) NMR signal of 3-PMe3 centred at -27 ppm converts into a sharp singlet with δ = -23.4. Similarly, two broad ¹H NMR resonances are recorded at -45°C with δ 0.25 and 1.37, due respectively to the terminal and bridging Mo-bonded methyl protons. The corresponding ¹³C NMR signals appear at 17.5 (δJCCH = 115 Hz) and 2.5 ppm (δJCCH = 115 Hz; δJCCH = 40 Hz). In the ¹³C(¹H) NMR spectrum of ¹³C-labelled 3-PMe3 the Mo(μ-1³C₃H₇)Mo resonance appears as a doublet of doublets due to an additional ²JC coupling of 5 Hz, whereas that due to the terminal Mo–¹³CH₃ group (17.5 ppm) becomes somewhat broad, presumably, due to unresolved two-bond ¹³C–¹³C, and three-bond ¹³C–³¹P couplings. These signals coalesce at 25°C (Figure S3; see the Supporting Information) and at 66°C give rise to a broad singlet centred in the proximity of 10.3 ppm. Using the slow-exchange approximation[28] the rate constant at the coalescence temperature (ca. 25°C) was calculated to be k = 13060 s⁻¹, with a corresponding ΔG° value of 11.8 kcal·mol⁻¹. By contrast, the pyridinic adduct 4 contains two coordinated molecules of 4-dimethylaminopyridine and therefore two terminal Mo–Me bonds. This complex was obtained employing either 2 or 3-THF as precursors (Scheme 2). In contrast with the monoadducts 3-THF and 3-PMe3, complex 4 has a rigid structure in solution under ambient conditions, the most distinctive NMR signals being the ¹H and ¹³C resonances due to the equivalent Mo–CH₃ functions that appear respectively at 1.84 and 14.7 ppm. The latter exhibits a one-bond ¹³C–¹H coupling constant of 120 Hz.

As already indicated, the neutral dimethyl complexes 2, 3-THF, 3-PMe3 and 4 were characterized by single-crystal X-ray studies and their molecular structures are represented in Figures 2, 3, 4 and 5, respectively. Figure 2 contains two ORTEP perspective views of the molecules of 2 that emphasize their coordinative unsaturation. For each Mo atom the coordination polyhedron approaches closely a square pyramid in which one of the basal coordination sites (namely that occupied by the apex of the pyramid. The Mo–Mo bond distance of 2.080 (1) Å is consistent with a metal-metal quadruple bond. The Me–Mo–Mo bond angles (ca. 93°) and the Mo–Me bond lengths (ca. 2.19 Å) are in accord with terminal coordination of the methyl groups.

As can also be seen in Figure 2 (bottom view) in the solid state two H atoms that belong to methyl groups of iso-propyl substituents of each amidinate ligand hover over the vacant
coordination site of the molybdenum centres. The Mo···H distance is however long (2.7 Å) and the C–H···Mo angle large (149.5°). The two parameters are well above the range expected for agostic interactions (~ 1.8–2.3 Å and 90–140°).[9] It therefore seems that complex 2 is a genuinely unsaturated, four-coordinate dimolybdenum complex and the marked unsaturation of its metal atoms is only compensated by feeble ε-agostic interactions. This conclusion is in accordance with the solution NMR data already discussed. A three-coordinate quadruply bonded complex [Mo₂(µ-η²-Me₂Si(NDipp)₂]²⁺ has been reported. However, this compound exhibits a long Mo–Mo quadruple bond (2.1784(12) Å) and fairly short Mo–N bonds (1.958(4) Å) that are indicative of σ- and π-donor coordination behaviour of the amido nitrogen atoms.[29] The (Mo₂)⁴⁺ core of adducts 3·THF, 3·PMe₃ and 4 is characterized by a slightly longer Mo–Mo bond of length in the range 2.086–2.110 Å, the longest distance (2.110(1) Å) corresponding to complex 4. The Mo₂(µ-N²N)₂ framework that supports the coordinated methyl and neutral Lewis base ligands in these complexes (N²N represents the amidinate ligand) exhibits in all cases similar structural parameters that are also close to the corresponding metrics in 2. Thus, Mo–N distances range between ca. 2.13 and 2.22 Å, trans N–Mo–N bond angles have values of roughly 170° and Mo–Mo–N angles are of about 92° (both kinds of bond angles are close to the ideal 180 and 90° values).

The two terminal Mo–CH₃ bonds of 4 have normal[12–16] lengths (ca. 2.24 Å) although they are somewhat longer than the terminal Mo–CH₃ unit of 3·THF (2.21 Å) and 3·PMe₃ (2.19 Å), perhaps as a consequence of the superior coordination number of the molybdenum atoms. However, in the latter two complexes there is a bridging methyl group that originates an acute Mo–C–Mo angle (approximately 51°) and Mo–C bonds...
that differ appreciably in length. These Mo–C distances have values of 2.220(3) and 2.573(3) Å in 3-THF and of 2.292(2) and 2.492(2) Å in the PMe₃ complex analogue. In each case the shorter Mo–C bond is approximately trans with respect to the neutral Lewis base (C–Mo–O and C–Mo–P angles of 160.4(1) and 166.1(1)°, respectively), and the difference between the shorter Mo–C bonds in the two complexes is doubtless due to the diverse trans influence exerted by the THF and PMe₃ ligands. The bond angle that at the pertinent Mo atom encompasses the terminal and bridging methyl groups in these complexes amounts 156.7(1) and 175.5(1)° in 3-THF and 3-PMe₃, respectively.

Notwithstanding the uncertainties in defining the positions of hydrogen atoms by X-ray diffraction, the crystallographic data obtained for complexes 3 denote the existence in the solid state of a weak monohapto agostic interaction between the CS₂–HCS₂ bond and the Mo2 atom (Figures 3 and 4). In addition to the already provided Mo2–CS₂ bond distances (2.573(3) and 2.492(2) Å), this three-centre two-electron interaction (3c–2e) is defined by a Mo2–HCS₂ contact of about 2.28 Å and by a C–H–Mo angle of between ca. 96 and 87°, in the expected ranges for these parameters. Notice, however, that the Mo2–HCS₂ separations are in the upper part of the 1.80–2.30 Å range considered for agostic interactions and furthermore that they are much longer than the Mo–H bonds in the bis(hydride) complex [Mo₂(H₂μ-HC(NDipp)₂)₂(THF)₂] (5-THF) that have lengths of 1.71 Å. If one also takes into account that these bridging methyl groups present JCH couplings around 118 Hz, it can only be concluded that these agostic interactions must be weak.

Geometry optimization of the base-free, trans complex 2 gave a structure in good agreement with the experimental one, with a terminal Me group bonded to each Mo atom. The cis isomer was found to correspond also to an energy minimum 5.8 kcal/mol higher in energy than the trans one. The lower stability of the cis isomer is most likely associated to steric repulsion between the two methyl groups, as suggested by Mo–Mo–Me bond angles of 104°, to be compared with 94° in the trans isomer. No energy minimum could be found for an alternative geometry with two bridging Me groups. The special bonding topology of the quadruply bonded Mo₂ Me₂(N= N) preserves the Mo₂(N= N) skeleton of the quintuply bonded precursor while the Mo atoms present an unusual square pyramidal coordination geometry with a vacant basal position. In the Mo₅⁺(N= N) fragment the δ-type orbital that points in the direction of the N-donor ligands becomes the LUMO, which is allowed by symmetry to mix in some metal s orbital contribution (Scheme 3, D₂h(A1g)). Upon symmetry descent to that of the Mo₅Me₂(N= N)₂ complex (from D₅h to C₂h), further hybridization with metal p orbitals is possible, resulting in a fragment orbital with two lobes in the right directions to act as acceptors toward donor fragments. A similar hybridization scheme applies to the corresponding δ* orbital that yields an out-of-phase version of the acceptor orbital shown in Scheme 3, thus accounting for two possible donor-acceptor interactions with incoming ligands.
The calculated in-phase Mo–Me σ–bonding orbital, shown in Figure 6 clearly shows the hybridization expected from Scheme 3. Moreover, one can also observe some mixing-in of the σ-bonding combination of the z^2 orbitals that belongs to the same symmetry representation. A similar mixing of δ and σ metal-metal bonding components has already been detected in Cr–Cr quintuply bonded systems.[32]

**Fig. 6.** dσ molecular orbital incorporating Mo-Mo δ+σ and Mo-Me σ bonding character.

**Reactivity of Complexes 2 and 3-THF toward dihydrogen**

Complexes 2 (plus added THF) and 3-THF reacted cleanly at room temperature with H₂ (1.5 bar) in toluene, with elimination of CH₄, to afford the known bis(hydride) [Mo₂H₂(μ-HC(NDipp)₂)₂(thf)₂] (5·THF), in essentially quantitative yield (by ¹H NMR spectroscopy). In contrast, no reaction was observed between CH₄ and complex 2 enriched in ¹³C (99%) at the Mo–CH₃ sites, at temperatures of 60-80°C, and a pressure of 40 bar of methane.

To investigate the mechanism of the hydrogenolysis reaction, a kinetic study was carried out. Initially, adduct 3-THF containing small amounts of tetrahydrofuran was utilized as a surrogate for 2. Using ¹H NMR spectroscopy, the reaction rate was determined in C₆D₆ at 0°C under the pseudo-first-order conditions created by a dihydrogen pressure of 5 bar. A graphical concentration vs. time representation (Figure 54; see the Supporting Information) indicated not only first-order dependence on the concentration of 3·THF, further confirmed by the straight line plot of the logarithmic function ln[3·THF] vs. time (Figure S5), but also the appearance of an intermediate, 6·THF, that reached maximum concentration approximately upon completion of the first half-life (ca. 40 min) and subsequently decayed into product 5·THF. It was therefore clear that the overall transformation consisted of two consecutive irreversible pseudo-first-order reactions, of which the first was somewhat slower than the second.[32] A computer fit of experimental data to theoretically predicted consecutive rate constants led to approximate k⁰obs1 and k⁰obs2 values of 3x10⁴ and 8x10⁴ s⁻¹, respectively. It seems reasonable to propose that the reactive intermediate 6·THF has a methyl-hydride formulation, [Mo₂(Me)(H)]⁻, and this hypothesis was confirmed by mechanistic studies to be described below (Scheme 4).

To avoid the unnecessary kinetic complications due to coordinated THF in the above study of dihydrogen activation, a kinetic analysis of the analogous transformation of the Lewis base-free complex 2 was undertaken. Once more, reaction rates were measured in C₆D₆ under pseudo-first-order conditions over a H₂ pressure in the interval from 5 to 9 bar. Graphical representations of ln[k] vs. time (Figures S6) yielded straight lines in accordance with first-order dependence on the concentration of 2. Furthermore, a plot of the observed rate constants against the concentration of H₂ was also linear (Figure 7A), indicating that the reaction was also first-order in dihydrogen. The concentration of dihydrogen in the samples was determined using ferrocene as an internal reference. The variation of k as a function of the reaction temperature was ascertained over the temperature range 288 to 318 K. An Eyring representation (Figure 7B) provided values of the activation parameters ΔH* = 12.5 (1.7) kcal·mol⁻¹, ΔS* = -28.0 (5.9) cal·mol⁻¹·K⁻¹, with ΔG* = 20.9 (0.2) kcal·mol⁻¹. Besides, use of D₂ (Figure S7) provided a kinetic isotope effect kD/kH of 2.9, indicating that cleavage of the H-H bond was rate determining.
To gain information on the nature of the reaction intermediate, further experimental work was accomplished. The purported hydride-methyl species was also detected in the reaction of 2 with H₂ although it was more difficult to observe due to faster reaction rates in comparison with 3·THF. Accordingly, the latter complex was utilized for these studies that were performed in an NMR tube with C₂D₈ as the solvent.

Treatment of a C₂D₈ solution of 3·THF with 1.5 bar of H₂ produced after ca. 30 min at 25°C a mixture of unreacted 3·THF, the bis(hydride) product 5·THF and the hydride-methyl complex 6·THF (Scheme 4) in an approximate 2:1:1 ratio. The reaction was quenched by removal of H₂, and a slight excess of PMe₃ (ca. 1.5 equiv. relative to 3·THF) was added at 25°C, to convert the above mixture of products into the corresponding PMe₃ adducts, 3·PMe₃, 5·PMe₃ and 6·PMe₃. The complete experiment was repeated utilizing D₂ instead of H₂, and furthermore the 3·PMe₃: 5·PMe₃: 6·PMe₃ mixture was also engendered starting from 3·THF enriched in ¹³C (99%) at the Mo−CH₃ sites. For experimental convenience, to avoid overlap of signature resonances, ¹H and ³¹P NMR identification of the aforementioned mixtures was effected at −10°C, whereas ¹³C NMR spectra were measured at 0°C.

**Scheme 4** Products of the NMR-tube reaction of 3·THF and H₂ quenched after ca. 50% conversion and generation of the corresponding PMe₃ adducts. The 3c-2e interactions are depicted using the half-arrow notation proposed by Green, Green and Parking.¹⁸ The bridging amidinate ligands have been omitted for the sake of clarity.
Identification of the individual components of the foregoing miscellanies of products by multinuclear NMR spectroscopy was straightforward. Thus complexes 3-THF, 3-PMe$_3$, 5-THF and 5-PMe$_3$ (in the pertinent isotopologue forms) were authenticated by comparison of their NMR parameters with those of authentic samples.\cite{26a,33} Signature NMR data for the pursued intermediates 6-THF and 6-PMe$_3$ provided strong support for the hydride-methyl formulation proposed in Scheme 4. Particularly noteworthy are the following: (i) A $^{13}$P NMR resonance at -10°C for 6-PMe$_3$ characterized by $\delta$ -12.7, $^3$J$_{PH} = 60$ and $^2$J$_{PD} = 9$ Hz. (ii) The Mo–CH$_3$ group of 6-PMe$_3$ is responsible for a $^{13}$C resonance at ca. 17 ppm that exhibits $^3$J$_{CH}$, $^3$J$_{CH}$ and $^3$J$_{CB}$ coupling constants of 116, 18 and 2 Hz, respectively. In 6-THF enriched in $^{13}$C this signal appears at 18.2 ppm although an additional $^3$J$_{CH}$ coupling with the hydride ligand of 17 Hz becomes discernable ($^3$J$_{CH} = 115$ Hz). (iii) The Mo–H resonance of 6-THF appears at 6.23 (ca. 6.1 ppm in the deuterated isotopologue). This chemical shift is very close to that recorded for the bis(hydride) complex 5-THF (5.7 Hz; ca. 5.8 ppm for the bis-deuteride isotopologue).

A detailed mechanism for the hydrogenation reaction of 2 can be obtained from a computational study of stationary points along the potential energy surface along a path that takes from 2 to 6. The species that have been found as stationary points along such path, their relative energies and some relevant bond distances and angles are shown in Scheme 5. The approach of H$_2$ to the dimolybdenum species 2 yields a transition state (TS1) with a side-on orientation relative to a Mo atom. This transition state corresponds to the point at which H$_2$ passes in between three Me groups, two from the aryl groups of the amidinate ligands coordinated to the Mo atom being approached, and the Me group coordinated to the other Mo atom (seven H–H···C distances between 2.31 and 2.59 Å). Then it proceeds to an intermediate (Int) with a σ-bond coordinated H$_2$, with the H–H and Mo-Mo bonds perpendicular to each other. Then, rotation of H$_2$ forms an incipient H–C bond with a methyl group, while the other Me adopts a bridging coordination mode in a transition state (TS2). The next step seems to consist in a concerted bond reorganization that results in the liberation of a methane molecule and the transfer of the other methyl group to the non-hydrogenated Mo atom to give the detected intermediate 6. The free energy change for this whole process is -24.1 kcal/mol. The rate determining step is the formation of the TS2 transition state that involves significant lengthening of the Mo-Me bond to the leaving methyl group, and partial formation of a new H–Me bond. This mechanism is consistent with the kinetic studies that show the rate of the reaction to be dependent of the partial pressure of H$_2$.

**Experimental section**

**General considerations**

All manipulations were carried out using standard Schlenk and glove-box techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. Toluene (C$_6$H$_5$n), n-pentane (C$_5$H$_{12}$) and n-hexane (C$_6$H$_{14}$) were distilled under nitrogen over sodium. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen over...
sodium/benzophenone. [D₆]Benzene and [D₆]THF were distilled under argon over sodium/benzophenone; [D₆]toluene was distilled under argon over sodium. The quadriply bonded complex [{Mo₂(µ-Me)(µ-Me)Li(thf)(µ-HC(NDipp))}_{3}] (1) was prepared as described previously.[3] Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external SiMe₄ (δ: 0 ppm) using the residual proton solvent peaks as internal standards (1H NMR experiments), or the characteristic resonances of the solvent nuclei (13C NMR experiments), while 31P was referenced to H₃PO₄. Spectral assignments were made by routine one- and two-dimensional NMR experiments (1H, 13C, 13C(1H), 31P(1H), COSY, NOESY, HSQC and HMBC) where appropriate. UV–visible spectra were recorded on a Perkin Elmer Lambda 750 spectrometer. For elemental analyses a LECO TruSpec CHN elementary analyzer, was utilized.

**Synthesis of [{Mo₂(µ-Me)(µ-HC(NDipp))}_{3}]** (2)

The complex [{Mo₂(µ-Me)(µ-Me)Li(THF)(µ-HC(NDipp))}_{3}] (1), was generated from [{Mo₂(µ-OC(NDipp))(µ-HC(NDipp))}_{2}] and LiMe as described previously.[3] A solution of 1 in toluene (0.8 g, ca. 0.6 mmol, 15 mL) was heated at 100 °C for 3 hours and it was then cooled down to room temperature, filtered and evaporated to dryness. Pentane (2 x 5 mL) was added and the resulting suspension was stirred at room temperature for 15 min before removal of the solvent. The brown-red solid that was obtained was further dried under vacuum for 1 h and redissolved in toluene (ca. 0.5 g of the complex in 10 mL of the solvent) with warming at around 60 °C. The resulting concentrated solution was kept at -23 °C for two days to give red crystals of complex 2 (0.2 g, 42 %). 1H NMR (400 MHz, CD₂Cl₂, 25 °C): δ = 1.01, 1.16, 1.26, 1.37 (d, 12H each, J_HH = 6.7 Hz, Me₆Dipp), 1.89 (s, 6 H, Mo-Me₆), 3.54, 4.25 (sept, 4H each, J_HH = 6.7 Hz, CHMe₂), 6.92 (dd, 4 H, J_HH = 7.5 Hz, J_HH = 1.2 Hz, m-Dipp), 7.03 (apparent t, 4 H, J_HH = 4.0 Hz, p-Dipp), 7.09 (dd, 4 H, J_HH = 7.5 Hz, J_HH = 1.2 Hz, m'-Dipp), 8.31 (s, 2 H, NC(NH)). The signal ‘designs the groups closer to the methyl group (Mo-CH₃).’ 13C(1H) NMR (100 MHz, CD₂Cl₂, 25 °C): δ = 14.7 (q, J_CC ≈ 120 Hz, Mo–Me₆). Elemental analysis calc. (%) for C₈₅H₇₀Mo₂N₂C₂: C, 65.81; H, 8.07; N, 5.90. Exp.: C, 66.0; H, 8.4; N, 6.1.

**Synthesis of [{Mo₂(µ-Me)(Me)(µ-HC(NDipp))}_{2}(thf)] (3-THF)**

Procedure A. Red crystals of the title complex were obtained from a saturated solution of complex 2 (0.6 g) in a mixture of toluene (7 mL) and THF (0.3 mL) at -23°C for 2 days (310 mg, 48%). Procedure B. A solution of complex 1 (2.0 g, 1.6 mmol) in toluene (30 mL) was heated at 100°C for 3 hours. The reaction mixture was filtered and the red solution was dried under vacuum (340 mg, 67%). 1H NMR (400 MHz, CD₂Cl₂, 25°C): δ = 1.08, 1.15 (d, 12H each, J_HH = 6.8 Hz, Me₆Dipp), 1.26 (m, 4 H, O-CH₂CH₃), 1.33, 1.36 (d, 12H each, J_HH = 6.8 Hz, Me₆Dipp), 1.89 (s, 6 H, Mo-Me₆), 3.39 (m, O-CH₂CH₂), 3.81, 4.04 (sept, 4H each, J_HH = 6.8 Hz, CHMe₂), 6.98-7.06 (m, Me-Dipp, m'-Dipp, p-Dipp), 8.28 (s, 2 H, NC(NH)). 13C(1H) NMR (100 MHz, CD₂Cl₂, 25°C): δ = 15.9 (q, J_CC ≈ 118 Hz, Mo–Me₆). UV-Visible (C₂D₆): λ_max (ε) = 480 nm (2160 mol⁻¹ L⁻¹ cm⁻¹). Elemental analysis calc. (%) for C₆₄H₆₆O₂N₂O₂: C, 65.87; H, 8.29; N, 5.49. Found: C, 66.0; H, 8.4; N, 5.7.

**Synthesis of [{Mo₂(µ-Me)(Me)(µ-HC(NDipp))}_{2}(PMe₆)] (3-PMMe₆)**

About 0.5 mmol of either compound 2 or 3-THF was dissolved in toluene (10 mL) and PMe₆ was added dropwise (1.5 equiv) to the solution mixture. After 2 hours of stirring at room temperature the solution was evaporated in vacuo, and the resulting solid was washed with pentane (5 mL) at 0°C. Crystals were obtained from a saturated solution of the complex in toluene at -23°C for 24 hours (340 mg, 67%). 1H NMR (500 MHz, C₂D₆, -45°C): δ = 0.25 (s, 3 H, Mo-Me₆), 0.45, 0.67 (d, 6 H each, Me₆Dipp), 0.95 (m, 9 H, PMe₆), 0.97, 1.06, 1.17 (s, 6 H each, Me₆Dipp), 1.22 (m, 9 H, Mo-µ-Me y Me₆Dipp), 1.32, 1.37 (s, 6 H each, Me₆Dipp), 3.40 (m, 4 H, CHMe₂), 3.82, 3.93 (m, 2 H each, CHMe₂), 6.8-7.07 (m, 12 H, m-Dipp, m’-Dipp γ p-Dipp), 8.67 (s, 2 H, NC(NH)). The signal ‘designs the groups closer to the methyl group (Mo-CH₃).’ 13C(1H) NMR (125 MHz, C₂D₆, -45°C): δ = 2.5 (d, J_HC = 40 Hz, µ-Me), 14.4 (d, J_HC = 18 Hz, PMe₆), 17.5 (Mo–Me₆), 23.3, 23.5, 24.5, 24.6, 25.7, 26.8, 27.2, 27.4 (Me₆Dipp), 26.7, 28.1, 28.2, 28.3 (CHMe₂), 123.4-125.6 (m-Dipp⁹, m’-Dipp⁹, m’-Dipp⁹ γ p-Dipp⁹), 141.2, 143.2, 143.3, 144.0 (o-Dipp), 145.8, 145.9 (ips-Dipp), 162.5 (NC(NH)). The signal ‘designs the groups closer to the methyl group (Mo-CH₃).’ 13C(1H) NMR (125 MHz, C₂D₆, -45°C): δ = 2.5 (d, J_HC ≈ 115 Hz, J_HC = 40 Hz, µ-Me), 17.5 (q, J_CC ≈ 115 Hz, Mo–Me₆). 13P(1H) NMR (200 MHz, C₂D₆, -45°C): δ = 23.4. The signals are broad due to the low temperature and the fluxionality of the complex. UV-Visible (C₂D₆): λ_max (ε) = 339, 390 (shoulders), 540 nm (1270 mol⁻¹ L⁻¹ cm⁻¹). Elemental analysis calc. (%) for C₆₄H₆₆O₂N₂O₂P: C, 64.44; H, 8.36; N, 5.47. Found: C, 64.5; H, 8.8; N, 5.9.

**Synthesis of [{Mo₂(µ-Me)(µ-HC(NDipp))}_{2}(dmapp)] (4)**

Starting from complex 2 or 3-THF (ca. 0.2 mmol) and 4-dimethylaminopyridine (0.06 g, 0.5 mmol) a toluene solution was prepared (10 mL) and stirred at room temperature for 5 hours. Concentration of the solvent gave a bright red solid that
was crystallized from a saturated toluene solution after cooling at -23°C for 3 days (160 mg, 65%). 1H NMR (500 MHz, CD$_2$D$_6$, 25°C): δ (ppm): 1.03, 1.18, 1.30, 1.46 (d, 12H each, $J_{HH} = 7.1$ Hz, Me$_{Dipp}$), 1.84 (s, 6H, Mo-Me$_2$), 2.1 (s, 12H, pyr-NMe$_2$), 3.91, 4.04 (sept, 4H each, $J_{HH} = 6.2$ Hz, CHMe$_2$), 5.89 (broad s, 4H, 3.5-pyr), 6.99-6.93 (m, 8H, m'-Dipp, p'-Dipp), 7.01 (dd, 4H, $J_{HH} = 7.4$ Hz, m'-Dipp), 8.01 (broad s, 4H, 2.6-pyr), 8.37 (s, 2H, NC(H)N). The signal ‘·’ designates the groups closer to the methyl group (Mo-CH$_3$). $^{13}$C($^1$H) NMR (125 MHz, CD$_2$D$_6$, 25°C): δ (ppm): 14.7 (Mo-Me$_2$), 24.3, 24.4, 26.3, 27.5 (CHMe$_2$), 27.8, 28.0 (CHMe$_2$), 37.9 (pyr-NMe$_2$), 106.4 (3.5-pyr), 123.0 (m'-Dipp), 123.7 (p'-Dipp, p'-Dipp), 124.9 (m'-Dipp), 144.5, 144.7 (p'-Dipp, p'-Dipp), 146.5 (ipso-Dipp), 149.2 (2.4-pyr), 153.7 (ipso-pyr-NMe$_2$), 161.4 (NC(H)N). The signal ‘·’ designs the groups closer to the methyl group (Mo-CH$_3$). $^{13}$C, $^1$H NMR (125 MHz, CD$_2$D$_6$, 25°C): δ (ppm): 14.7 (q, $^1$J$_{CH} \sim 120$ Hz, Mo-Me$_2$). UV-Visible (CD$_2$D$_6$): $\lambda_{max}$ (ε) = 360, 440 (shoulders), 512 nm (3150 mol$^{-1}$ L cm$^{-1}$). Elemental analysis calc(%) for C$_{44}$H$_{82}$Mo$_2$N$_2$: C, 66.42; H, 8.11; N, 9.39. Found: C, 66.0; H, 8.6; N, 9.6.

Reactions of complexes 2 and 3·THF with H$_2$

Complex 2. Complex 2 (2 mg, 2x10$^{-3}$ mmol) was dissolved in 0.45 mL of C$_2$D$_6$. To this solution, 0.1 mL of the standard solution of ferrocene in C$_2$D$_6$ (0.0215 M) was added. Three vacuum/argon cycles were performed at 203 K to remove the argon atmosphere in the Young NMR tube. For the different experiments performed, the tube was then charged with 5, 7, 8 or 9 bar of dihydrogen at 203 K and shaken (Figure S6). The reaction progress was checked by $^1$H NMR spectroscopy at 298 K. Analogous experiments were carried out with a fixed pressure of 8 bar of dihydrogen at 288, 293, 298, 303 and 308 K. To measure the kinetic isotope effect, two identical solutions of complex 2 in C$_2$D$_6$ were prepared (2 mg, 2x10$^{-3}$ mmol). After cooling at 203 K, the argon atmosphere was pumped out and the corresponding NMR tubes were charged with a pressure of 5 bar of H$_2$ and D$_2$, respectively (see Figure S7).

Complex 3·THF. Complex 3·THF (2.5 mg, 2.5 x 10$^{-3}$ mmol) in 0.55 mL of C$_2$D$_6$ was cooled to -70°C. The argon atmosphere was pumped out and replaced by 5, 5 or 6 bars of H$_2$. The reaction progress was checked by $^1$H NMR spectroscopy at 273 K.

Computational Details

The calculations were performed with the Gaussian09 computer code.$^{[38]}$ The hybrid B3LYP functional$^{[39]}$ was employed together with the all-electron triple-$\zeta$ basis set proposed by Schäefer et al.$^{[40]}$ for the light atoms while for the molybdenum atoms an all-electron basis set with a contraction (84211111/641111/51111) was used.$^{[41]}$ This all-electron basis set was used to avoid problems found with common pseudopotentials that provide artifact charge and bond order values for the studied complexes. Transition states and energy minima were corroborated by the calculation of the corresponding frequencies.

Conclusions

The computational, crystallographic and NMR studies described in this paper underscore that although terminal and bridging coordination of methyl groups to a quadruply bonded Mo$_2$ core have comparable energetics, the former is preferred to the latter. This appears to be a common situation that applies widely to other metal-metal bonded transition metal complexes.$^{[14a,34-37]}$ In the context of the work reported herein, it explains the observation in the solid state of the four-coordinate, fourteen-electron structure of complex 2, in spite of its marked unsaturation, clearly manifested in its reactivity toward conventional Lewis bases and against dihydrogen.

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