

COMMUNICATION

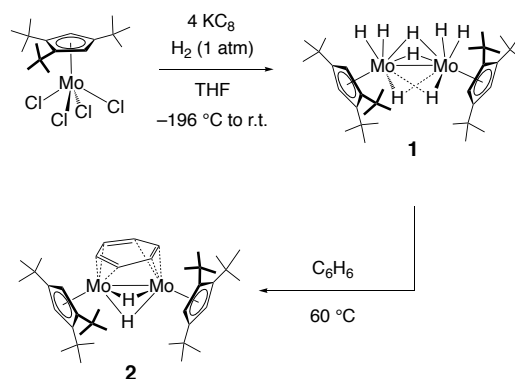
A Dinuclear Mo₂H₈ Complex Supported by Bulky C₅H₂^tBu₃ ligandsYasuhiro Ohki,^{*,a} Kodai Ishihara,^a Moeko Yaoi,^a Mizuki Tada,^{a,b} W. M. C. Sameera,^c and Roger E. Cramer^dReceived 00th January 20xx,
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Hydride-bridged transition metal complexes have been found to serve as suitable precursors for the activation of small molecules without the use of reducing agents. In this study, we synthesized a dinuclear Mo₂H₈ complex supported by bulky C₅H₂^tBu₃ (Cp^t) ligands, Cp^t₂Mo₂H₈ (**1**), from the reaction of Cp^tMoCl₄ with KC₈ under H₂. The hydrides of complex **1** can be replaced with benzene at 60 °C to afford a μ-benzene complex Cp^t₂Mo₂H₂(μ-C₆H₆) (**2**).

Di- and tri-nuclear transition metal complexes, whose cores are supported only by bridging hydrides and metal-metal bonds, have been useful in the activation of small molecules.¹ For instance, a dianionic Nb₂-hydride complex [(*anti*-[O₃])₂Nb₂(μ-H)₄]²⁻ (**a**; [O₃] = HC(C₆H₂-2-O-3,5-^tBu₂)₃) can break the triple bond of N₂,² a Ru₃-hydride complex Cp^{*}₃Ru₃(μ-H)₃(μ₃-H)₂ (**b**, Cp^{*} = C₅Me₅) activates the C-H/C-C bonds of various organic substrates,³ and a Ti₃-hydride complex (C₅Me₄SiMe₃)₃Ti₃(μ-H)₆(μ₃-H) (**c**) can cleave the triple bond of N₂⁴ or a C-C bond of benzene.⁵ A relevant hydride-bridged Mo-Fe-S cluster has also been postulated as a key intermediate in the biological reduction of N₂.⁶ Among these hydride-bridged complexes, only three crystallographically identified examples are known for non-carbonyl molybdenum compounds, in particular (Me₃P)₆Mo₂H₄, [Cp₂Mo₂H₃(μ-η⁵:η⁵-fulvalene)]⁺, and (C₇H₇)₂Mo₂H₃.⁷ In addition, several relevant carbonyl-hydride complexes of molybdenum were reported in the literature.⁸ As the π-acidity and the various bonding modes of CO are often disadvantageous in the activation of small molecules, we were interested in the synthesis of non-carbonyl, di- or tri-nuclear molybdenum complexes where metals are bridged only by hydrides. Among various protocols reported for the synthesis of transition metal hydrides,⁹ three notable classes are (i) salt-metathesis reactions of metal-halides with hydride reagents

(*e.g.* for **a**, **b**, and many others), (ii) hydrogenolysis of metal-alkyls (*e.g.* for **c** and rare-earth complexes¹⁰ *etc.*), and (iii) addition of H₂ to low-valent precursors (*e.g.* for Pt₄(PⁱPr₂Ph)₄H₈,¹¹ [Rh₆(PⁱPr₃)₆H₁₂]⁺,¹² (iPr₃P)₅Ni₅H₆,¹³ and other various examples). We have also recently demonstrated that metal-amides will react with HBpin to produce Fe- and Co-hydride clusters.¹⁴ In this study, we report the formation of a simple dinuclear hydride complex consisting of only Mo, hydrides, and cyclopentadienyl ligands.



Scheme 1. Synthesis of **1** and its reaction with benzene.

The entitled dinuclear molybdenum hydride complex Cp^t₂Mo₂H₈ (**1**, Cp^t = C₅H₂^tBu₃) was obtained in 41% yield (based on Mo) from the reaction of the half-sandwich Mo(V) chloride complex Cp^tMoCl₄¹⁵ with 4 equiv. of KC₈ under a H₂ atmosphere (Scheme 1 top). We reasoned in this reaction that the bulkiness of the ancillary Cp ligand was important. In fact, complex mixtures were obtained from analogous reactions of half-sandwich complexes supported by less bulky Cp ligands, such as Cp^{*}MoCl₄^{16a} or (C₅Me₄H)MoCl₄^{16b}. Although these mixtures remain incompletely characterized, addition of 18-crown-6 enabled us to precipitate small amounts of Cp^{*}K(18-crown-6) (from the reaction of Cp^{*}MoCl₄) and a crystalline dinuclear complex **A** having three Cp-based ligands (from the reaction of (C₅Me₄H)MoCl₄). These crystals were manually selected and characterized only by X-ray crystallographic analysis (Fig. S14-15 and Fig. 1b). Based on their structures, we can speculate that

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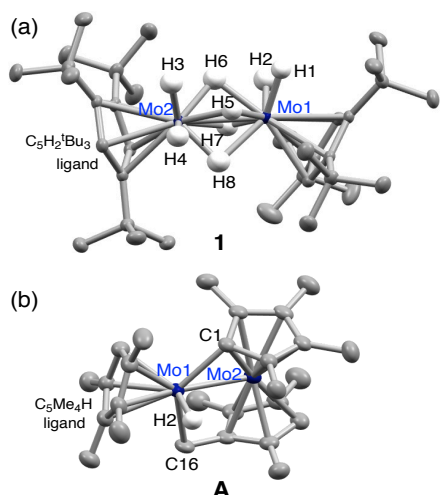


Fig. 1 (a) Molecular structure of **1** with atomic displacement parameters set at 50% probability. Hydrogen atoms except hydrides are omitted for clarity. Selected distances for **1** (Å): Mo-Mo 2.55911(19), Mo1-H1 1.57(2), Mo1-H2 1.59(2), Mo1-H5 1.766(19), Mo1-H6 1.76(2), Mo1-H7 1.664(16), Mo2-H3 1.611(18), Mo2-H4 1.58(2), Mo2-H5 1.78(2), Mo2-H6 1.860(16), Mo2-H7 2.02(2), Mo2-H8 1.59(2).

(b) Structure of the anionic part of **A**, which precipitated from the reaction of (C₅Me₄H)MoCl₄, KC₈, H₂, and 18-crown-6.

interaction between a K ion of KC₈ and a cyclopentadienyl ring of a Cp-Mo species induces dissociation of K-Cp, which can subsequently react with another Cp-Mo to furnish a molybdocene moiety as is found in the structure of **A**. In this regard, the bulky C₅H₂^tBu₃ (Cp[†]) ligand diminishes or eliminates such a pathway by slowing or preventing the interaction between K and the cyclopentadienyl ring. It should be also noted that previously reported synthetic procedures for hydride complexes of Cp-Mo-phosphines include treatment of CpMo-chlorides with phosphines and LiAlH₄ followed by methanolysis.^{15a,17} In the absence of phosphines, however, the sequential reactions of Cp[†]MoCl₄, Cp[†]*MoCl₄, or (C₅Me₄H)MoCl₄ with LiAlH₄ and methanol merely gave complex mixtures, which were difficult to characterize.

Complex **1** is diamagnetic and its ¹H NMR spectrum exhibited four singlet signals at -3.53 (hydride), 1.29 (^tBu), 1.37 (^tBu), and 4.96 (C₅H₂^tBu₃) ppm, and the presence of the eight hydrides was confirmed by the intensity of the hydride signal. Although the molecular structure of **1** shows terminal Mo-H and bridging Mo-H-Mo hydrides (Fig. 1a), the lone hydride signal at -3.53 ppm remained a single signal even at -80 °C in toluene-d₈ (Fig. S6), which indicates facile exchange between Mo-H and Mo-H-Mo. Upon standing in C₆D₆ at ambient temperature, the hydride signal in the NMR gradually disappeared over three days. This is indicative of the H/D exchange between hydrides and C₆D₆ via reversible C-D(H) bond cleavage.

The molecular structure of **1** was unequivocally determined by means of a single-crystal X-ray diffraction analysis (Fig. 1a).⁵ Each molybdenum atom is coordinated by bridging/semi-bridging/terminal hydrides and an ancillary Cp[†] ligand. The Mo-H and Mo-H-Mo distances span the ranges 1.57(2)-1.61(2) and 1.66(2)-2.02(2) Å, respectively. Due to the long H-H contacts

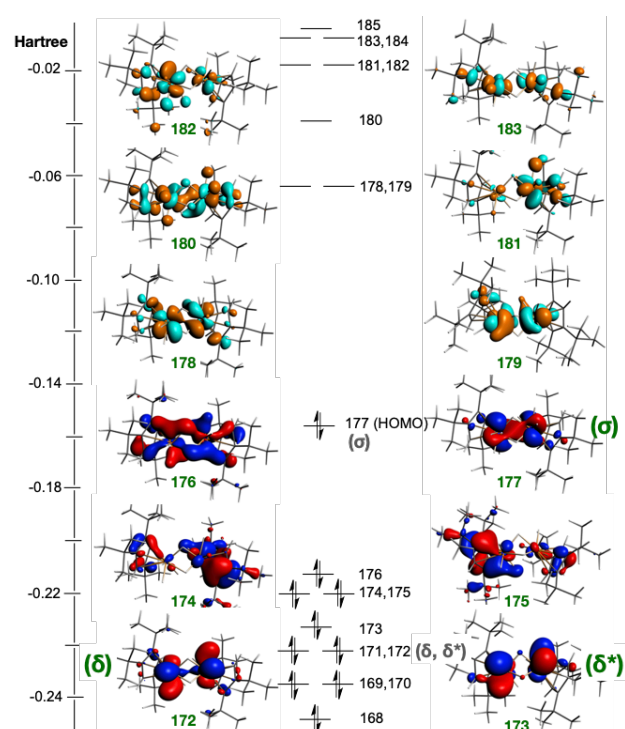


Fig. 2 Kohn-Sham frontier molecular orbitals of the optimized structure of **1**.

among hydrides (1.68(3) Å or longer), direct H-H bonding is unlikely, while hydride complexes with H-H distances in the range of 1.1 to 1.5 Å are termed elongated H₂ complexes.¹⁸ As a 30-electron dinuclear complex, **1** satisfies the effective atomic number (EAN) rule when a Mo-Mo triple bond is included. The Mo-Mo distance of **1** (2.55911(19) Å) is comparable to the previously reported hydride-bridged Mo-Mo triple bonds (2.528(2)-2.5730(6) Å)¹⁹ and is shorter than the hydride-bridged Mo-Mo double bonds (2.6351(5)-2.7901(7) Å)²⁰. We attribute this short Mo-Mo bond to the influence of the bridging hydrides, because DFT analysis of **1** indicated a Mo-Mo single bond as discussed below.

We optimized the structure of **1** in the *S* = 0 and 1 states, using revPBE-D3(BJ)/TZP/ZORA/COSMO(BENZENE) methods in the ADF program.²¹ The ground state of **1** is *S* = 0, which is in agreement with the diamagnetic nature of **1**, and the optimized *S* = 1 state is 23.2 kcal/mol higher than the ground state. Positions of hydrides and the Mo-Mo distance (2.54 Å) in the optimized *S* = 0 state structure are in agreement with the crystallographically determined structure. Kohn-Sham frontier molecular orbitals of **1** are shown in Fig. 2. The HOMO (177) has σ character, while HOMO-4 (173) and HOMO-5 (172) show δ and δ^* characters, respectively. Therefore, the $\sigma^2\delta^2\delta^{*2}$ configuration indicates a Mo-Mo single bond.²² The computed Mayer bond index²³ of 0.92 also suggests a Mo-Mo single bond, which is in agreement with the reported Mayer bond indexes of known dinuclear Mo-Mo complexes.^{22a} We have also performed a quantum theory of atoms in molecules (QTAIM) analysis (Table S4),²⁴ where a bond critical point (BCP) was found between the two Mo atoms.

Complex **1** was found to incorporate a benzene molecule when heated at 60 °C, furnishing Cp[†]₂Mo₂H₂(μ - η^3 : η^3 -C₆H₆) (**2**)

as black crystals in 87% yield (Scheme 1 bottom). The chemical formula of **2** was supported by the signal at $m/z = 737.86$ in the electro-spray ionization mass (ESI-MS) spectrum (Fig. S13). In this reaction, reductive elimination of H_2 from **1** occurs to store electrons at the molybdenum atoms followed by addition of a benzene molecule. Evolved H_2 (1.75 equiv) was detected (see Supporting Information). In a report of an analogous process, UV irradiation (365 nm) of a Mo_2 complex with a quadruple Mo-Mo bond and two terminal hydrides released H_2 and incorporated an arene molecule as a bridging ligand.²⁵ Some relevant dinuclear complexes with a bridging arene ligand have been also reported for different transition metals.²⁶ Inverted-sandwich complexes with a $M(\mu-\eta^6:\eta^6\text{-arene})M$ moiety may be also relevant.²⁷ In the 1H NMR spectrum of **2** in C_6D_6 , singlet signals for hydrides and bridging benzene were observed at -7.56 and 3.82 ppm, respectively. The benzene signal is shifted upfield relative to free benzene due to disruption of its aromaticity through interaction with two molybdenum atoms. After hours at room temperature, no ligand exchange was found between the benzene ligand and solvent C_6D_6 . Appearance of a singlet NMR signal for the benzene ligand indicates its fluxional nature at room temperature. In a variable-temperature 1H NMR experiment in toluene- d_8 , the benzene signal was found to broaden upon lowering the temperatures and split into two signals in a 4:2 ratio at -80 °C (Fig. S7). This observation is indicative of a pseudo- C_{2v} symmetry of the $Mo_2H_2(C_6H_6)$ moiety, which can be explained by a swing behaviour of C_6H_6 between **2** or isomers with a $\mu-\eta^2:\eta^2$ -coordination mode of C_6H_6 using the 1,2- and 4,5-positions of the ring or a $\mu-\eta^3:\eta^3$ -coordination mode of C_6H_6 using the 1,2,3- and 4,5,6-positions. The $\mu-\eta^2:\eta^2$ -coordination mode has precedence in an amidinate-bridged Mo_2 complex,²⁵ and the corresponding isomer derived from **2** is calculated to be only 0.5 kcal/mol higher in energy relative to the lowest energy structure. Despite a number of attempts, we were unable to locate a local minimum for the $\mu-\eta^3:\eta^3$ -coordination mode of C_6H_6 . The structure optimizations converged to an isomer close to the $\mu-\eta^2:\eta^2$ -coordination mode. A relaxed potential energy surface scan for the C_6H_6 rotation indicated that the complete rotation of C_6H_6 has a barrier of 2.1 kcal/mol (Fig. S16). Thus, rotation of the C_6H_6 ligand should be possible at ambient temperature but is difficult at low temperatures. On the other hand, interconversion of **2** with its isomer in the $\mu-\eta^2:\eta^2$ -coordination mode is almost barrierless (Fig. S16). Therefore, we propose that the swing behaviour of the C_6H_6 ligand between **2** and an isomer with a $\mu-\eta^2:\eta^2$ -coordination mode accounts for the low-temperature NMR observations.

In the molecular structure of **2**, the C_6H_6 ligand is intermediate between the $\mu-\eta^2:\eta^2$ - and $\mu-\eta^3:\eta^3$ -modes (Fig. 3). We can alternatively describe a twisted $\mu-\eta^2:\eta^2$ -mode for the benzene ligand, as two Mo-C(benzene) distances are significantly longer (2.534(12) for Mo1-C3 and 2.579(14) Å for Mo2-C6) than the other four Mo-C(benzene) distances (2.191(12)-2.212(12) Å). This unique arene bridge bonding mode has been reported for a Mo_2 complex having a bridging *para*-xylene.²⁵ While the benzene molecule in **2** has not undergone any chemical transformation, it does exhibit

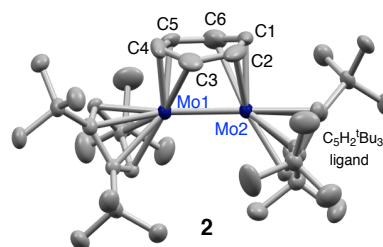


Fig. 3. Molecular structure of **2** with atomic displacement parameters set at 50% probability. One of two independent molecules in the unit cell is shown, and hydrogen atoms are omitted for clarity. Selected distances for **2** (Å): Mo-Mo 2.5906(13), Mo1-C3 2.534(12), Mo1-C4 2.197(13), Mo1-C5 2.194(13), Mo2-C1 2.191(12), Mo1-C2 2.212(12), Mo2-C6 2.579(14), C1-C2 1.43(2), C1-C6 1.38(2), C2-C3 1.434(19), C3-C4 1.37(2), C4-C5 1.45(2), C5-C6 1.43(2).

significant structural changes, which suggest changes in its electronic structure. The benzene ligand in the crystal structure of **2** deviates from planarity and the angle between the C6-C1-C2 and C3-C4-C5 planes is 30° , which is in agreement with that of the DFT-optimized structure (35°). This structural feature is consistent with strong back-donation from the relatively electron-rich Mo(II) centres. The back-donation would result in bond alternation of the benzene ligand, and thus the C-C bond distances of the benzene ligand range from 1.37(2) to 1.45(2) Å with the diagonally arranged C1-C6 and C3-C4 distances shorter than other C-C distances.

According to DFT calculations, the ground state of **2** is a closed-shell singlet ($S = 0$), while the triplet ($S = 1$) state is 15.0 kcal/mol higher in energy. Key structural parameters of the optimized $S = 0$ structure of **2** with two bridging hydrides show good agreement with the X-ray structure (Table S5). The calculated Mo-Mo distance (2.57 Å) is also in agreement with the X-ray structure of **2** (2.5906(13) Å). Kohn-Sham frontier molecular orbitals of the ground state of **2** (Fig. S17) suggests a $\sigma^2\delta^2\delta^{*2}$ configuration, leading to a Mo-Mo single bond. The computed Mayer bond index²² of **2** is 1.17, which also indicates a Mo-Mo single bond and is qualitatively in agreement with the reported Mayer bond indexes of Mo-Mo complexes.^{22a}

In summary, a novel dinuclear molybdenum polyhydride, $Cp^*_2Mo_2H_8$ (**1**), was synthesized and characterized. At elevated temperatures, complex **1** was found to incorporate a benzene molecule via elimination of H_2 . This reaction pattern for generation of vacant metal sites is common to the previously reported di- and tri-nuclear complexes with bridging hydrides, which promote the cleavage of various bonds.²⁻⁵ Thus, we expect **1** as a useful platform for activation of small molecules.

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Conflicts of interest

There are no conflicts to declare.

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