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A Rare Dimer of Dimers Having Four Hydride Linkers Joining Two Quadruply Bonded Dimolybdenum Units

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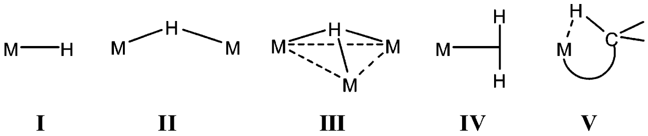
Hydride anions, H^-, have been found to cause the assembly of dimolybdenum units $[Mo_2(cis\text{-DAniF})_2]^{2+}$, DAniF = *N*,*N*′-di(*p*-anisyl)formamidinate, forming a tetranuclear complex $[Mo_2(cis\text{-DAniF})_2]_2(\mu\text{-H})_4$ (**1**) with an Mo_4H_4 core that may be described as an elongated tetrahedron in which the H atoms are along the four long edges of such tetrahedron and the Mo_2 units are along the short edges. The two quadruply bonded dimolybdenum units, separated by only 2.718 Å, are essentially orthogonal. This gives the shortest $[Mo_2]\cdots[Mo_2]$ distance known for complexes with multiple dimolybdenum units. DFT calculations indicate that the energy of a cuboidal isomer is only 3.8 kcal/mol above that of **1**, but such an isomer has not been observed.

Introduction

A major breakthrough in the chemistry of transition-metal hydrides occurred in 1931 when Hieber and co-workers discovered $H_2Fe(CO)_4$.[1] This synthesis was then followed by the preparation of several related metal carbonyl hydrides including $HCo(CO)_4$.[2] Many hydrides are important in industrial processes and catalysis.[3,4] More recently, there has been interest in their use as materials for energy storage,[5] and they have promising applications in the so-called hydrogen economy.[6] Additionally, many hydrides have important uses in organic chemistry as powerful reducing agents.[7] Hydrides have also been invoked in metalloenzymes, especially hydrogenases, and this represents a very active area of research.[8]

Scheme 1



Hydrogen, the simplest element in the periodic table, binds to transition metals in a great variety of modes (Scheme 1)[9] which include terminal,[10] doubly bridging,[11] triply bridging (capping),[12] as an η^2-H_2 ligand in sideways-bound dihydrogen complexes (nonclassical arrangement),[13] and in agostic

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[†] Deceased, February 20, 2007.

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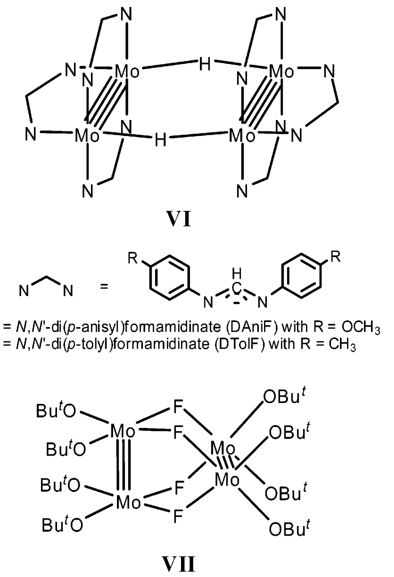
Scheme 2



M$\cdots$H−C interactions forming 3c−2e bonds.[14] Only two types of hydride species with covalently bonded dimolybdenum units have been made, the first compound being $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$.[15] A recent study in this laboratory reported the other species made by reductive substitution reactions of $Mo_2(DArF)_3Cl_2$, DArF = *N,N′*-diarylformamidinate (Ar = *p*-tolyl and *p*-anisyl), with $NaHBEt_3$, which produces the very stable tetranuclear complexes, $[Mo_2(DArF)_3]_2(\mu\text{-}H)_2$ (**VI** in Scheme 2), in which two quadruply bonded $Mo_2(DArF)_3$ units are linked by two hydride groups forming a $\overline{\text{Mo}-\text{Mo}-\text{H}-\text{Mo}-\text{Mo}-\text{H}}$ ring.[16] Here, we describe the assembly of a molecule in which two $[Mo_2(\textit{cis}\text{-}DAniF)_2]^{2+}$ units (DAniF = *N,N′*-di(*p*-anisyl)formamidinate) are linked by four hydride anions. This compound has a distorted-tetrahedral Mo_4 skeleton consisting of four $\overline{\text{Mo}-\text{H}-\text{Mo}-\text{Mo}-\text{H}}$ five-membered rings. The two quadruply bonded dimolybdenum units are essentially orthogonal. The separation between midpoints of the metal−metal bonds of only 2.718 Å represents the shortest $Mo_2\cdots Mo_2$ distance known for complexes with multiple dimolybdenum units. The only other molecule having dimetal units and a similar tetrahedral skeleton is the tetranuclear complex $[Mo_2(OBu^t)_4]_2(\mu\text{-}F)_4$ (**VII** in Scheme 2), which has two triply bonded Mo_2^{6+} units coupled by four fluoride anions.[17]

Experimental Section

Materials and Methods. Solvents were dried and then distilled under N_2 following conventional methods or under argon using a Glass Contour solvent purification system. Solvents were dried once more before use, by placing the solvents over molecular sieves for 12 h. The molecular sieves had been dried overnight at 300 °C. The synthesis was conducted under N_2 using Schlenk-line techniques. The starting materials $[Mo_2(\textit{cis}\text{-}DAniF)_2(NCCH_3)_4](BF_4)_2$[18] and HDAniF[19] were prepared following published methods. The hydride source $Bu^n{}_4NBH_4$, which was obtained from Aldrich, was dried under vacuum overnight.

Physical and Characterization Measurements. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ. ^{1}H NMR spectra were recorded at 25 °C on a Mercury-300 NMR spectrometer with chemical shifts (δ ppm) referenced to protonated solvent residue. Electronic spectra were measured in the range of 200−800 nm on a Shimadzu UV-2501PC spectrophotometer. Cyclic voltammograms (CV) were recorded on a CH Instruments model-CH1620A electrochemical analyzer with Pt working and auxiliary electrodes, a Ag/AgCl reference electrode, a scan rate of 100 mV/sec, and 0.1 M Bu_4NPF_6 as electrolyte.

Preparation of $[Mo_2(\textit{cis}\text{-}DAniF)_2]_2(\mu\text{-}H)_4$, 1. To a suspension of orange $[Mo_2(\textit{cis}\text{-}DAniF)_2(NCCH_3)_4](BF_4)_2$ (0.14 g, 0.13 mmol) and $Bu^n{}_4NBH_4$ (0.080 g, 0.31 mmol) was added 20 mL of ether. At the beginning of the reaction, the dimolybdenum starting material remained at the bottom of the flask. As the mixture was stirred for about 16 h, the color of the solid in the suspension turned to yellowish brown. The solvent was then decanted, and the yellow-brown solid was washed with ether (2 × 15 mL) and dried under vacuum. Crystallization from a 1:3 mixture of toluene and hexane produced a mixture of small dark-red, block-shaped, and star-shaped crystals. Both types of crystals had the same unit-cell parameters and ^{1}H NMR spectra (vide infra). Yield of crystals: 62 mg (34%). ^{1}H NMR (in benzene-d_6, ppm): 8.90 (s, 4H, −NC*H*N−), 6.84 (d, 16H, aromatic), 6.54 (d, 16H, aromatic), 6.23 (s, 4H, Mo*H*Mo), 3.15 (s, 24H, −OC*H*$_3$). ^{1}H NMR (in acetone-d_6, ppm): 8.81 (s, 4H, −NC*H*N−), 6.80 (d, 16H, aromatic), 6.72 (d, 16H, aromatic), 5.38 (s, 4H, Mo*H*Mo), 3.78 (s, 24H, −OC*H*$_3$). ^{1}H NMR (in a 1:1 mixture of acetone-d_6/benzene-d_6, ppm): 8.69 (s, 4H, −NC*H*N−), 6.62 (d, 16H, aromatic), 6.46 (d, 16H, aromatic), 5.67 (s, 4H, Mo*H*Mo), 3.35 (s, 24H, −OC*H*$_3$). UV−vis in benzene-d_6, λ_{max} (nm) (ϵ, $M^{-1}\,cm^{-1}$): 525 (5.4×10^3). Anal. calcd. for $C_{60}H_{64}Mo_4N_8O_8$ (**1**): C, 51.15; H, 4.58; N, 7.95. Found: C, 51.41; H, 4.72; N, 7.67.

X-ray Structure Determination. A single-crystal suitable for X-ray analysis was mounted and centered on the tip of a cryoloop. The crystal was then attached to a goniometer head. Data for **1** were collected at −60 °C on a Bruker SMART 1000 CCD area detector system. Cell parameters were determined using the program *SMART*.[20] Data reduction and integration were performed with the software package *SAINT*,[21] while absorption corrections were applied using the program *SADABS*.[22] The positions of the heavy atoms were found via direct methods using the program *SHELXTL*.[23] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the

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(20) *SMART Software for the CCD Detector System*, version 5.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

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Table 1. X-ray Crystallographic Data

compound	**1**
empirical formula	$C_{60}H_{64}Mo_4N_8O_8$
fw	1408.95
space group	$C2/c$ (No. 15)
a (Å)	27.206(5)
b (Å)	16.046(3)
c (Å)	17.643(3)
α (deg)	90
β (deg)	129.913(2)
γ (deg)	90
V (Å^3)	5907.6(18)
Z	4
T (K)	213
d_{calcd} (g/cm^3)	1.584
μ (mm^{-1})	0.890
R1^a (wR2^b)	0.029 (0.069)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) from X-ray Crystallography and DFT Calculations

	experimental	calculated
Mo1−Mo1A	2.0864(6)	2.128
Mo2−Mo2A	2.0859(6)	2.129
$Mo_2 \cdots Mo_2$^{a}	2.718	2.778
Mo1⋯Mo2	3.0781(6)	3.160
Mo1⋯Mo2A	3.1063(6)	3.159
Mo1−H1	2.03(4)	1.934
Mo1A−H2	2.14(3)	1.943
Mo2−H1	1.90(4)	1.951
Mo2A−H2A	2.15(3)	1.934
Mo1−H1−Mo2	102.9(4)	109.16
Mo1A−H2−Mo2	92.7(4)	108.83
Mo1−Mo1A−Mo2A−Mo2	80.62(2)	82.66

[a] Distance between the midpoints of the two [Mo$_2$] units.

remaining non-hydrogen atoms. The bridging hydride species were clearly defined in the electron density maps, and the positions were refined isotropically without constraints. Other hydrogen atoms were added in idealized positions. Non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data for **1** are given in Table 1, and selected bond distances and angles are given in Table 2.

Computational Details. Density functional theory (DFT)[24] calculations were performed with Becke's[25] hybrid three-parameter exchange functional and the Lee−Yang−Parr[26] nonlocal correlation functional (B3LYP) in the *Gaussian 03* program.[27] Double-ζ quality basis sets (D95)[28] were used on C, N, and H atoms as implemented in *Gaussian*. A small effective core potential (ECP) representing the 1s2s2p3s3p3d core was used for the molybdenum atoms along with its corresponding double-ζ basis set (LANL2DZ).[29] Time-dependent density functional (TD-DFT) calculations[30] were performed to aid in the assignment of the electronic spectrum. All calculations were performed on Origin 3800 64-processor SGI supercomputers located at the Texas A&M supercomputing facility.

Results and Discussion

Synthesis. The first approach to the synthesis of **1** was to employ a procedure similar to that used for cuboidal clusters of the type $[Mo_2(cis\text{-}DAniF)_2]_2(\mu\text{-}X)_4$, $X = Cl^-$, Br^-, and I^-,[31] which are prepared in acetonitrile or ethanol according to the equation

$$2[Mo_2(cis\text{-}DAniF)_2(NCCH_3)_4](BF_4)_2 + 4Bu^n{}_4NX \rightarrow [Mo_2(cis\text{-}DAniF)_2]_2(\mu\text{-}X)_4 + 4Bu^n{}_4NBF_4$$

However, unlike reactions with the halides that produce the product in the polar solvents, reaction of the building block $[Mo_2(cis\text{-}DAniF)_2(NCCH_3)_4]^{2+}$ with a variety of hydride sources, such as KH, LiH, $NaBH_4$, and $NaAlEt_3H$, does not produce the hydride analogue. The only combination of hydride source and solvent that was found to produce the target compound was that of $Bu^n{}_4NBH_4$ and ether. The low solubility of the neutral product in ether appears to provide an additional driving force to the reaction. As the orange building block slowly dissolved in ether, a brown precipitate was produced simultaneously. A long stirring period is essential to obtain a pure product. The use of alcohols such as methanol or ethanol as solvent should be avoided because under such reaction conditions alkoxide anions may form, and these are capable of bridging [Mo$_2$] units,[32] forming alkoxide-bridged compounds.[33] To obtain analytically pure samples in satisfactory yield, it is essential to rigorously dry all solvents and reagents. If trace amounts of H_2O are present, hydroxide groups partially replace the bridging hydride

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(32) The abbreviation [Mo$_2$] represent the $[Mo_2(cis\text{-}DAniF)_2]^{2+}$ unit.

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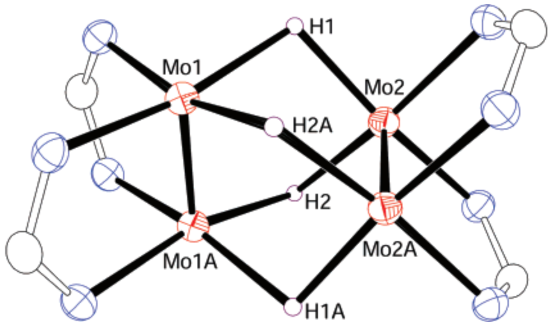
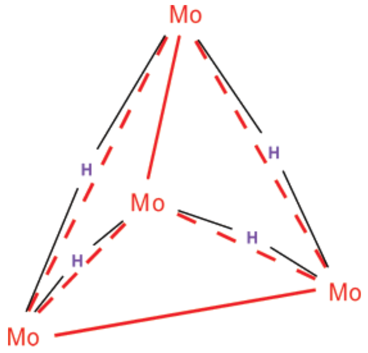


Figure 1. Core structure of **1** with ellipsoids drawn at the 40% probability level for the non-hydrogen atoms. All *p*-anisyl groups and hydrogen atoms of the methine groups have been omitted for clarity.

Scheme 3



groups. Water is also known to promote a side reaction that leads to the formation of the paddle wheel compound $Mo_2(DAniF)_4$.[34]

Unlike the stable complexes $[Mo_2(DArF)_3]_2(\mu\text{-}H)_2$,[16] in which two hydride groups link two dimolybdenum units, compound **1** is extremely air and moisture sensitive (vide infra). This compound also reacts with chlorinated solvents such as CH_2Cl_2, giving $[Mo_2(\textit{cis}\text{-}DAniF)_2]_2(\mu\text{-}Cl)_4$, as shown by the isolation of red block-shaped crystals from solutions of **1** in mixtures of CH_2Cl_2/hexane that were analyzed by X-ray crystallography.

Structural Results. Compound **1** crystallizes in the monoclinic space group $C2/c$ with the molecule residing on a special position ($Z = 4$). The molecule consists of two dimolybdenum units, $[Mo_2(\textit{cis}\text{-}DAniF)_2]^{2+}$, linked by four hydride groups, as shown by the drawing of the core in Figure 1. Unlike the structures of the cuboidal $[Mo_2]_2(\mu\text{-}X)_4$ species, which have essentially parallel Mo_2 units,[31] the two dimetal units in **1** are almost perpendicular to each other, having a torsion angle of 80.62(2)°. The molecule has two $\overline{\mathrm{Mo{-}H{-}Mo{-}Mo{-}H}}$ five-membered rings. If the supporting DAniF ligands are ignored, the Mo_4H_4 core can be described by an elongated tetrahedron, shown in red in Scheme 3, where the solid lines represent Mo−Mo and Mo−H bonds and the broken lines delineate the tetrahedral skeleton. In this tetrahedron, the H atoms are approximately at the midpoints of four long edges, while the Mo_2 units represent the two short edges. In contrast to the hydride linkers in $[Mo_2(DArF)_3]_2(\mu\text{-}H)_2$ compounds where the two hydrides are wrapped by six formamidinate ligands, in **1** the hydrides are unprotected by the DAniF groups. Because of this, the likelihood of the hydrides being attacked by other molecules is greatly enhanced and the reactivity of **1** is much greater than that of the $[Mo_2(DArF)_3]_2(\mu\text{-}H)_2$ compounds.[16] It should be noted that the high reactivity of **1** is reminiscent of that in very reactive dinuclear species having $M(\mu\text{-}H)_4M$ cores.[35] Representative examples of compounds with four bridging, classical hydrides are $H_2(PEt_2Ph)_2Re(\mu\text{-}H)_4Re(PEt_2Ph)_2H_2$[36] and those having formulas $(C_5Me_5)_2M_2H_4$, where $M_2 = Ru_2$,[35a] Os_2,[37] Fe_2[38] and RuOs.[37b]

The metal−metal bond distances for the two crystallographically independent dimolybdenum units are essentially the same (2.0864(6) and 2.0859(6) Å in Table 2), falling in the range of the Mo−Mo quadruply bonded compounds having two bridging ligands.[39] The $\delta \rightarrow \delta^*$ transition is observed at 525 nm in the UV−vis spectrum. The separation between the midpoints of the $[Mo_2]$ units (2.718 Å) is the shortest $Mo_2\cdots Mo_2$ distance known for complexes with multiple dimolybdenum units. The Mo−H distances[40] of ca. 1.90−2.15 Å are longer than those determined by neutron diffraction in terminal Mo−H (1.685(3) Å)[41] and other hydride-bridged complexes (ca. 1.85 Å).[16,42] The bent Mo−H−Mo angles are in the range of 93−103°, smaller than those found in other hydride-bridged complexes.[16,42]

The molecular structure of **1** represents a significant departure from those of the halide-bridged *dimer of dimers* with two parallel quadruply bonded Mo_2^{4+} units[31] but resembles that of $[Mo_2(OBu^t)_4]_2(\mu\text{-}F)_4$, which has two triply bonded Mo_2^{6+} units coupled by four F^- ions, in that the dimetal units are orthogonal to each other.[17] In **1**, there is a two-fold axis that passes through the two midpoints of the Mo−Mo bonds (Mo1−Mo1A and Mo2−Mo2A) and two idealized mirror planes perpendicular to each other that intersect at the C_2 axis. In addition, there are two idealized two-fold axes that pass through the midpoints of each two separated long edges of the distorted-tetrahedral core, namely, Mo1−Mo2 and Mo1A−Mo2A and Mo1A−Mo2 and Mo1−Mo2A, respectively, and the overall structure has idealized D_{2d} symmetry. In the idealized structure, he DAniF ligands are equivalent, as are the hydride anions.

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(40) It should be noted that the positions of hydrogen atoms are not accurately determined by X-ray crystallography.

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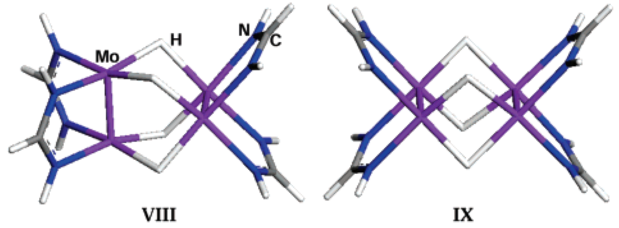
(42) Petersen, J. L.; Dahl, L. F.; Williams, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6610.

Scheme 4



The ^{1}H NMR spectrum of **1** in benzene-d_6 shows the presence of only one highly symmetrical species in solution and is consistent with the solid-state structure. The signal for the four methine protons, one from each of the DAniF ligands, appears as a singlet (8.90 ppm in benzene-d_6). In this solvent, there is also only one singlet at 3.14 ppm, which accounts for the 24 protons of the methoxy groups. The signals for the aromatic groups also support this assignment. Finally, the solvent-dependent singlets at 6.23 ppm (benzene-d_6), 5.38 ppm (acetone-d_6), and 5.67 ppm (1:1 acetone-d_6/benzene-d_6) all integrate as four hydrogen atoms and have been assigned to the hydride linkers.[43] Chemical shifts for hydrides are generally quite variable. For example, this chemical shift in $[Mo_2(DArF)_3]_2(\mu\text{-}H)_2$ (**VI** in Scheme 2) in CD_2Cl_2 is around 1.2 ppm,[16] 7.06 ppm (in benzene-d_6) for $[(Cy_2)N)_2ClTa(\mu\text{-}H)]_2$,[44] and −5.5 ppm for $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$ in benzene-d_6.[15b]

Electrochemistry and DFT Calculations. The CV of **1** (Figure S1, Supporting Information) measured in THF exhibits only one redox process at a potential of 0.20 V vs Ag/AgCl. Although the shape of the wave resembles those for reversible processes, the intensity rapidly decreases with continuing cycling, indicating that this corresponds to an irreversible process. This indicates that with time there is an irreversible oxidation of the hydride groups. When a small amount of a ferrocenium salt was added to **1** in acetone or benzene, there was rapid production of hydrogen gas, and an uncharacterized yellowish brown solution was obtained. Whenever very small amounts of water were added to red solutions of **1** in benzene, gas bubbles were also produced.

A series of DFT calculations were carried out on **1**. Geometry optimization was done using the parameters from the crystal structure as starting point. The model was simplified to $[Mo_2(cis\text{-}NHCHNH)_2]_2(\mu\text{-}H)_4$ (**VIII** in Scheme 4), but no symmetry constraints were imposed. The general agreement between calculated and experimental geometric data, shown in Table 2, suggests that the simplification in which the anisyl groups were replaced by hydrogen atoms is acceptable. The overestimation of the Mo−Mo distances (ca. 0.04 Å) is reasonable and consistent with previous studies because the hydrogen atoms are not as basic as the *p*-anisyl groups.[45]

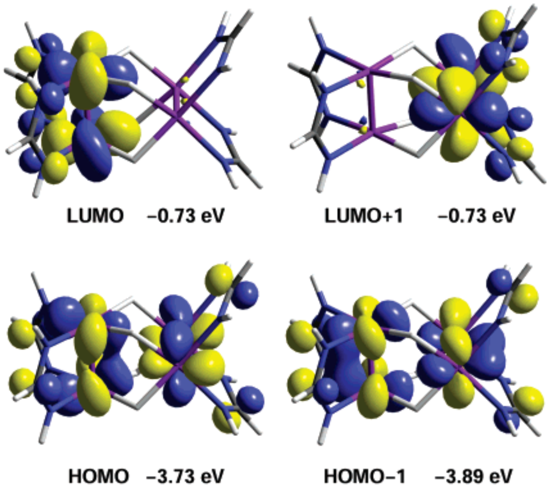


Figure 2. View of 0.04 surface contour diagrams for the frontier orbitals for model of **1**, calculated using DFT.

Geometry optimization was also performed on the isomer **IX** (Scheme 4) having two parallel $[Mo_2]$ units. This species resembles the halide-containing $[Mo_2(cis\text{-}DAniF)_2]_2(\mu\text{-}X)_4$ compounds.[31] This isomer, which was not observed experimentally, has an energy that is higher by only 3.8 kcal/mol than that for the model of **1**. Because the calculated energy difference is relatively small, the existence of the second isomer cannot be ruled out under different experimental conditions. It is possible that **1** may be favored by its insolubility in the reaction media. Heating benzene-d_6 solutions of **1** to 60 °C for at least 1 h, in attempts to interconvert **1** into **IX**, did not show any changes in the ^{1}H NMR spectra.

An analysis of the frontier orbitals from the calculations (Figure 2) indicates that there is a small interaction between the δ orbitals in the dimetal units, which is mainly due to electrostatic repulsion. This contrasts with the cuboidal clusters of the type $[Mo_2(cis\text{-}DAniF)_2]_2(\mu\text{-}X)_4$, for which the parallel disposition of the dimetal units allows orbital overlap through space.[31b] In **1**, the two molecular orbitals, one bonding (a_1, $\delta + \delta$) and one antibonding (b_2, $\delta - \delta$) over the four molybdenum atoms, are slightly different in energy. The two δ^* orbitals as the lowest-unoccupied molecular orbital (LUMO) and LUMO + 1 are degenerate.

TD-DFT calculations were also carried out on the hydride-bridged complex using the optimized geometry of the model $[Mo_2(cis\text{-}NHCHNH)_2]_2(\mu\text{-}H)_4$. Such calculations have been useful in understanding the electronic spectra of compounds having two $[Mo_2]$ units linked by dicarboxylate groups.[45] The neutral species **1** show one weak absorption band in the UV−vis range. The band, observed at 525 nm, is calculated at 561 nm for the symmetry-allowed $\delta \rightarrow \delta^*$ type transition.

Conclusions

The synthesis of a rare compound in which four hydride groups link two quadruply bonded units is reported. Despite the short $[Mo_2]\cdots[Mo_2]$ separation, electronic communication between Mo_2 units is small because of the orthogonal

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(43) Solvent dependency for the hydride signals is not unusual. See for example: Ash, C. E.; Darensbourg, M. Y.; Hall, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 4173.

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arrangement of the dimolybdenum units that limit interactions between δ bonds.

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Supporting Information Available: X-ray crystallographic data for **1** in standard CIF format and a CV of $[Mo_2(cis\text{-}DAniF)_2]_2(\mu\text{-}H)_4$ (**1**) in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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