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COMMUNICATIONS

A Three-Coordinate and Quadruply Bonded Mo−Mo Complex

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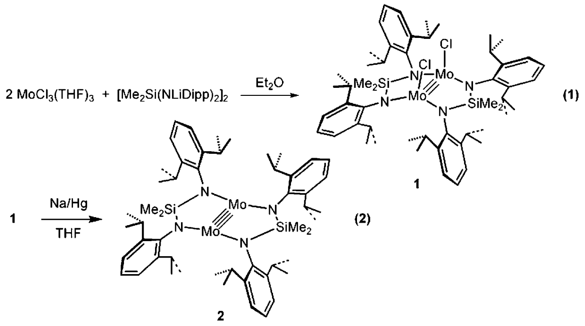
Since Professor Cotton's seminal recognition of the first dirhenium complex $[Re_2Cl_8]^{2-}$ featuring a quadruple bond between two metal atoms in 1964,[1] the field of metal−metal quadruple-bond chemistry has progressed at a dramatic rate in the past decades. Thus far, the paddlewheel motif has been one of the most prevalent structural types observed.[2] It is worth noting that in order to preserve the δ-interaction between two metals, the four ligands coordinating to each metal are restricted to either σ-donors or weak π-donors, such as amines, halides, phosphines, and alkoxides.[2,3]

In addition to the regular quadruply bonded dimetal species, coordination complexes having metal−metal multiple bonds can be stabilized by good π-donor ligands. For instance, Chisholm has pioneered the use of six amide ligands to support group VI metals in discrete "ethane-like" dimeric forms, $M_2(NMe_2)_6$ where M = Mo or W.[4] Moreover, Power's group recently reported the first isolable dichromium complex with a five-fold bond between two Cr atoms, supported by only two bulky monodentate carbyl ligands.[5] Low-coordinate metal complexes are highly attractive due to their unsaturated coordination spheres which can serve as an efficient platform for activating small molecules such as N_2.[6] In this communication, we report a successful synthesis of the first symmetrically bridged[7] and quadruply bonded dinuclear Mo(II) amido complex of the type of M_2X_4.

Metathesis reaction between the dimeric dilithio salts of $[Me_2Si\{NLi(Dipp)\}_2]_2$ (Dipp = 2,6-*i*-$Pr_2C_6H_3$)[8] with 2 equiv of monomeric $MoCl_3(THF)_3$ in diethyl ether at room-temperature resulted in the formation of the corresponding triply bonded dimolybdenum complex *syn*-1,2-$Mo_2Cl_2[\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2]_2$ **1**, (eq 1, Scheme 1) which was isolated by recrystallization from *n*-hexane in 90% yield as air- and moisture-sensitive orange crystals. The proton NMR spectrum of **1** in C_6D_6 showed four doublet resonance signals (δ 0.62, 1.29, 1.47 and 1.69) corresponding to the eight *i*-Pr groups, and two multiplet signals around δ 4.27 and 4.13 ppm which were assigned to the eight methine protons.

Crystals of **1** were analyzed by X-ray crystallography. Interestingly, in contrast to the reported staggered anti rotamers of 1,2-$M_2X_2(NR_2)_4$,[2,9] the structure of **1** adopted the form of the eclipsed syn conformation, featuring two terminal chlorides and two $Me_2Si(NDipp)_2$ ligands spanning a metal−metal triple bond.[10] The ORTEP drawing of **1** is shown in Figure S1 (see Supporting Information). The coordination geometry of each metal center is nearly trigonal pyramidal. A striking structural feature of **1** is the large Cl−Mo−Mo−Cl torsion angle of 30.43(8)°, which is assumed as a consequence of the tetrahedral geometry around Si atoms. The Mo−N distances of 1.977(5) and 1.988(5) Å in **1** are in the range of the documented Mo−N lengths.[2,4,9] Interestingly, despite the structural difference between **1** and complexes *anti*-1,2-$MoX_2(NMe_2)_4$, the Mo−Mo bond length of 2.2016(10) Å for **1** is typical for Mo−Mo triple bonds, which is even slightly shorter than that in the corresponding *anti*-1,2-$MoCl_2(NMe_2)_4$,[9b] due to greater orbital overlap between MX_3 fragments in an eclipsed ligand conformation.[11] Compound **1** thus provides us a good opportunity for the preparation of an unprecedented complex of the type Mo_2X_4.

Scheme 1



In pursuit of an unprecedented three-coordinate and quadruply bonded Mo_2 complex, we sought to chemically reduce **1** by two electrons. The cyclic voltammogram of a solution of **1** (THF/TBAP) shows two reversible reductions at $E_{1/2} = -1.83$ and -2.01 V (relative to Fc/Fc^+) over the course of the cathodic sweep. Accordingly, reduction of an ether solution of **1** with Na/Hg gave the diamagnetic $Mo_2[\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2]_2$ **2** in 43% yield as an extremely air- and moisture-sensitive orange solid. X-ray structure analysis confirmed the dinuclear nature of **2** and the central Mo−Mo bond. The structure revealed a disorder problem, in which two molybdenum atoms were disordered over three positions. (Supporting Information) One orientation of the disordered Mo_2 in **2** depicted in Figure 1 shows a fused bicyclic skeleton containing a central Mo_2^{4+} core spanned by two ligands, and thus exhibiting a virtual C_{2h} symmetry in which the SiC_2 units lie in the horizontal mirror plane. Each Mo atom is three-coordinate by two N atoms of the two amides and one adjacent Mo atom. Atoms of N(1), Mo(1), Mo(1A), and N(1A) are coplanar, and the dihedral angle of N−Mo−Mo−N in both the five-membered SiN_2Mo_2 rings are 12.08(16)°, thus providing effective steric protection for the two Mo atoms. The bond length between Mo(1) and N(1) is 1.967(4) Å and between Mo(1) and N(2A) is 1.958(4) Å which are fairly short, and the sum of the bond angles around N(1), which adopts a trigonal-planar geometry, is 359.4° and that of N(2) is 359.8°, indicating strong π-interactions between Mo and N atoms. As is usually the case for metal−metal dimers, the most intriguing metric is the metal−metal bond length, particularly in such a low-coordinate compound as **2**. Interestingly, the bond length of Mo(1)−Mo(1A) is 2.1784(12) Å and is categorized as a long Mo−Mo quadruple bond.[12]

In addition to crystallographic data, electronic absorption and resonance Raman spectroscopy also provided insight into the existence of metal−metal quadruple bonds.[2] Most quadruply bonded dinuclear complexes are vividly colored due to the small separations in energy between the δ and δ^* orbitals. Indeed, an electronic

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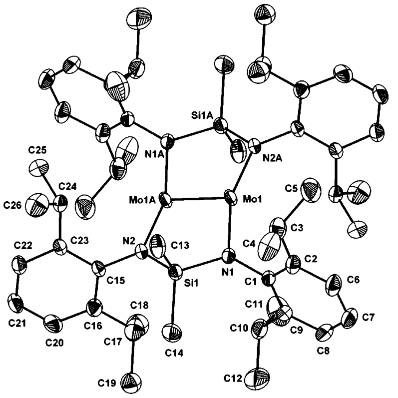
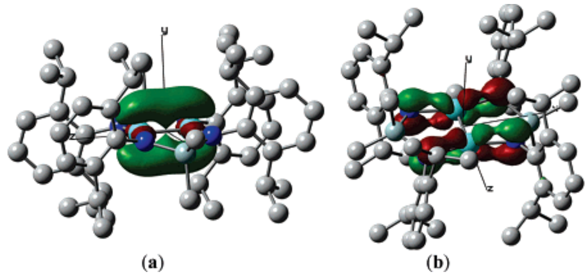


Figure 1. Molecular structure of **2** (thermal ellipsoids at the 30% probability level). Selected bond distances (Å) and angles (deg): Mo(1)−Mo(1A), 2.1784(12); Mo(1)−N(1), 1.967(4); Mo(1)−N(2A), 1.958(4); Si(1)−N(1), 1.747(4); Si(1)−N(2), 1.765(4); N(1)−Mo(1)−Mo(1A), 97.16(11); N(2)−Mo(1A)−Mo(1), 99.37(11); N(1)−Mo(1)−N(2A), 159.56(16); N(1)−Si(1)−N(2), 104.31(19); Si(1)−N(2)−Mo(1), 114.5(2); Si(1)−N(1)−Mo(1), 113.2(2).



(a) **(b)**

Figure 2. Contour plots of HOMO (a) and HOMO−11 (b) of **2**.

absorption band of the orange-colored complex **2** was observed at about 17240 cm^{-1}, which is assigned tentatively to an allowed transition from the molecule's δ^2 (^1A_g) to its $\delta\delta^*$ (^1B_u) electronic state, assuming idealized C_{2h} symmetry for the complex. A time-dependent density functional theory (TDDFT) calculation of the electronic transition gave a value well in accord with the experimentally observed quantity (Table *S*2, Supporting Information). Furthermore, the totally symmetric metal−metal stretch, ν(Mo−Mo), was found at the frequency of 343 cm^{-1} in the resonance Raman spectrum falling in the range of frequencies between 330 and 430 cm^{-1} for the documented quadruply bonded dimolybdenum species.[2]

With the intent of gaining an understanding of the electronic structure and bonding of **2**, we carried out electronic structure computations using density functional theory at the BLYP level. It is noteworthy that sterically encumbered ligand variants are necessary to stabilize **2**. Attempts to model **2** via replacing Dipp groups with H atoms failed due to the crash of the molecular shape. Consequently, calculations on authentic formula were engaged, and the optimized geometry was constrained to C_{2h}. The computed Mo−Mo bond length is 2.168 Å, which agrees very well with the experimental Mo−Mo value of 2.1784(12) Å. As for the electronic structure, attention should be paid to $d_{x^2-y^2}$ and d_{xy} orbitals[13] with two Mo atoms being defined to lie on the z axis. The $d_{x^2-y^2}$ orbitals of Mo atoms in **2** are used for δ-bond formation (HOMO, Figure 2a), although half of each $d_{x^2-y^2}$ orbital is engaged in the formation of two Mo-to-N σ-bonds, while two d_{xy} orbitals are used to form four Mo-to-N π-bonds (HOMO−11, Figure 2b). This is in contrast to the bondings between two metals in conventional paddlewheel structural motifs in which overlap of two d_{xy} orbitals gives rise to a δ-bond in paddlewheel structures while each metal uses $d_{x^2-y^2}$ to form metal-to-ligand σ-bonds. Moreover, not only does the contour plot of HOMO have contribution from $d_{x^2-y^2}$ (69.61%), it also contains 30.30% of s orbital and 0.09% of p orbital on the basis of natural bond orbital (NBO) analysis.[13]

The chemical property of **2** is consistent with the observation made from electrochemical measurements (i.e. the oxidative addition).[14] For example, exposure of **2** to organic chlorides, such as CH_2Cl_2 or 1,2-$C_2H_4Cl_2$, quickly gives **1**, which can then be converted once again to **2** upon reduction. The result provides us the opportunity to further explore the potentially rich chemistry of interconversion between M_2X_6 triple bonds and M_2X_4 quadruple bonds.

In summary, we have prepared an unusual triply bonded dimolybdenum complex, *syn*-1,2-$Mo_2Cl_2[\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2]_2$, **1**, from which the first three-coordinate and quadruply bonded dimolybdenum complex $Mo_2[\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2]_2$ **2** can be isolated upon reduction of **1**. Complex **2** exhibits an electronic structure different from that of the conventional paddlewheel structures. Reactivity studies of **2** are underway.

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Supporting Information Available: Experimental details for the synthesis of **1** and **2**, cyclic voltammetry, UV−vis, X-ray crystallographic data, including tables and CIF files, and details of the computational study (DFT). This material is available free of charge via the Internet at http://pubs.acs.org.

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