Since Professor Cotton’s seminal recognition of the first dirhenium complex [Re₂Cl₆]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 (δ) to be stabilized by good π-donor ligands. 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.⁶ 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 N₂.⁶ In this communication, we report a successful synthesis of the first symmetrically bridged⁷ and quadruply bonded dinuclear Mo(II) amido complex of the type Mₓ₂N₄.

Metathesis reaction between the dimeric dithiolato salts of [Me₂−Si(NLi(Dipp))₂]²⁻ (Dipp = 2.6-i-Pr₂C₆H₃)⁸ with 2 equiv of monomeric MoCl₃(THF) in diethyl ether at room-temperature resulted in the formation of the corresponding triply bonded dimolybdenum complex syn-1,2-Mo₂Cl₂[μ-η²-Me₂Si(NLi(Dipp))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 CD₂O 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-M₂X₂(NR₃)₆,²⁹ the structure of 1 adopted the form of the eclipsed syn conformation, featuring two terminal chlorides and two Me₂Si(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.²⁴,²⁵ Interestingly, despite the structural difference between 1 and complexes anti-1,2-MoX₂(NMe₂)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-MoCl₃(NMe₂)₂⁹ due to greater orbital overlap between MX₃ 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 Mo₂X₄.

In pursuit of an unprecedented three-coordinate and quadruply bonded Mo₂ 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 E₁/₂ = −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 Mo₂[μ-η³-Me₂Si(NDipp)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 Mo₁ of 2 depicted in Figure 1 shows a fused bicyclic skeleton containing a central Mo₂⁺⁺ core spanned by two ligands, and thus exhibiting a virtual C₃ᵥ symmetry in which the SiC₂ 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), Mo₁, Mo₂, N(1A) and N(1A) are coplanar, and the dihedral angle of N—Mo—Mo—N in both the five-membered SiN₂Mo₂ rings is 12.08(16)°, thus providing effective steric protection for the two Mo atoms. The bond length between Mo₁ and N(1) is 1.967(4) Å and between Mo₁ 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 Mo₁–Mo₁A 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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¹ National Tsing Hua University.
² National Chiao Tung University.
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 \(\Delta t^2 (\Lambda_d)\) to its \(\delta h^2 (\Lambda_b)\) 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 S2, Supporting Information).

Furthermore, the totally symmetric metal–metal stretch, \(v(\text{Mo–Mo})\), 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 bound 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 \(\text{H}\) atoms failed due to the crash of the molecular shape. Consequently, calculations on authentic formula were engaged, and groups with \(\text{H}\) atoms failed due to the crash of the molecular shape.

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

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.\(^1\)

The chemical property of 2 is consistent with the observation made from electrochemical measurements (i.e. the oxidative addition).\(^4\) For example, exposure of 2 to organic chlorides, such as \(\text{CH}_2\text{Cl}_2\) or 1,2-\(\text{C}_2\text{H}_4\text{Cl}_2\), quickly gives 1, which can then be converted once again to 2 upon reduction. The result provides us the opportunity further to explore the potentially rich chemistry of interconversion between \(\text{M}_2\text{X}_6\), triple bonds and \(\text{M}_2\text{X}_4\) quadruple bonds.

In summary, we have prepared an unusual triply bonded dimolybdenum complex, \(\text{syn-1,2-Mo}_2\text{Cl}_2(\mu-\eta^2-\text{Me}_2\text{Si}(\text{NDipp}))_2\), 1, from which the first three-coordinate and quadruply bonded dimolybdenum complex \(\text{Mo}_2(\mu-\eta^2-\text{Me}_2\text{Si}(\text{NDipp}))_2\) 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.

Acknowledgment. We are grateful to the National Science Council of Taiwan (Grant NSC 93-2113-M-007-020) for financial support, Mr. Ting-Shen Kuo (National Taiwan Normal University), Professor Ju-Chun Wang (Soochow University, Taiwan, R.O.C.) for help with crystallographic details, and the National Center for High-performance Computing for computer time and facilities. We also thank Professors Christopher C. Cummins (MIT) and Ching-Han Hu (National Changhua University of Education, Taiwan, R.O.C.) for insightful discussions.

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.

References


JA0635884