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Journey from Mo−Mo Quadruple Bonds to Quintuple Bonds

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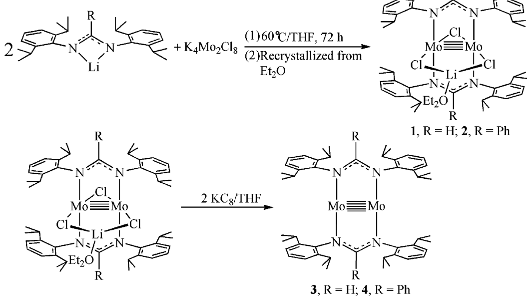
Whereas a large number of compounds containing metal−metal quadruple bonds has been documented over the past four decades[1] since the discovery of $Re_2Cl_8^{2-}$,[2] the quest for complexes containing metal−metal quintuple bonds has just begun. As the existence of the first quintuple Cr−Cr bond in the complex Ar′CrCrAr′ (where Ar′ is the encumbering 2,6-(C_6H_3-2,6-*i*-Pr_2)$_2C_6H_3$ ligand) was recognized by Power et al.,[3] several dichromium complexes featuring ultrashort quintuple bonds have recently been identified by us,[4] Power,[5] Theopold,[6] and Kempe.[7]

Molybdenum is notable for its ability to form strong Mo−Mo multiple bonds. For example, Mo forms the most quadruply bonded compounds and consequently accumulates a wealth of structural and spectroscopic data.[1] Furthermore, it must be noted that the singlet state diatomic Mo_2 molecule containing a true sextuple bond has been observed in the gas phase at low temperatures,[8] and the Mo−Mo bond length was determined to be 1.93 Å.[9] Overall, owing to the success in the recognition of it is homologous Cr−Cr quintuple bonded complexes[4−7] and being sandwiched between Mo−Mo quadruple and sextuple bonded compounds, Mo−Mo quintuple bonded complexes have thus been proposed to be synthesized.[10]

We recently reported a dimolybdenum complex supported by only two diamido ligands, $Mo_2[\mu\text{-}\eta^2\text{-}Me_2Si(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]_2$, obtained from reduction of the triply bonded *syn*-$Mo_2Cl_2[\mu\text{-}\eta^2\text{-}Me_2Si(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]_2$.[11] DFT calculations indicated that this compound features a Mo−Mo quadruple bond. Of particular interest, moreover, is the strong N−Mo(d_{xy}) π interactions, which consequently results in no δ bonding between two d_{xy} orbitals. Inspired by these observations, the Mo−Mo quintuple bond is expected if the said diamido ligands are replaced by the monoanionic amidinates. Herein we report that the encumbering amidinates can indeed stabilize the Mo−Mo quintuple bonds, which are extremely short up to 2.02 Å, the shortest metal−metal bonds beyond the first row transition metals.

Similar to the access of the aforementioned Mo−Mo quadruple bonded compound $Mo_2[\mu\text{-}\eta^2\text{-}Me_2Si(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]_2$, our strategy to accomplish the preparation of complexes containing the Mo−Mo quintuple bonds started from the synthesis of compounds having the Mo−Mo quadruple bonds. As shown in Scheme 1, treatment of the red Mo−Mo quadruply bonded complex $K_4Mo_2Cl_8$[12] with 2 equiv of the sterically hindered amidinates, Li[RC(N-2,6-*i*-$Pr_2C_6H_3$)$_2$] (R = H, Ph), in THF engendered the formation of two Mo−Mo quadruply bonded complexes, $Mo_2(\mu\text{-}Cl)[Cl_2Li(OEt_2)][\mu\text{-}\eta^2\text{-}RC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]_2$ (**1**, R = H; **2**, R = Ph).

Scheme 1



The molecular structures of **1** and **2** were corroborated by X-ray crystallography (Supporting Information (SI) and Figure 1). Both **1** and **2** essentially adopt a paddlewheel structure supported by two encumbering amidinates, one bridging chloro ligand and the Cl−Li−Cl linkage spanning the Mo−Mo bond forming the "-ate" complexes. The Mo−Mo bond length of 2.0875(4) Å of **1** and 2.0756(8) Å of **2** indicates two typical Mo−Mo quadruple bonds.[1] The slightly shorter Mo−Mo bond length in **2** is presumably ascribed to the more encumbering amidinato ligand.[4a]

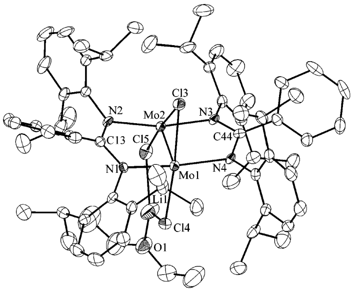


Figure 1. Molecular structure of **2** with thermal ellipsoids shown at the 35% probability level.

Subsequent reduction of **1** and **2** with 2 equiv of KC_8 gave the desired quintuply bonded Mo_2 complexes, $Mo_2[\mu\text{-}\eta^2\text{-}RC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]_2$ (**3**, R = H; **4**, R = Ph). The diamagnetic nature of **3** and **4** are confirmed by measuring their solid (<0.8 B. M.) and solution (Evans method[13]) magnetic moments. The ^1H NMR spectra of **3** in d_8-THF and **4** in C_6D_6 solution showed sharp one ligand set signals in the range δ 0−8 ppm, which are consistent with the high symmetry of **3** and **4**.

The molecular structures of **3** and **4** (Figure 2) were determined by X-ray crystallography. **3** and **4** contain two amidinato ligands spanning the Mo−Mo quintuple bond, and the two Mo atoms, the two N−C−N backbones, and the four *ipso*-carbon atoms of the phenyl rings of **3** are completely coplanar, while the N−Mo−Mo−N torsion angles of **4** are 2° and 172°. Therefore, **3** and **4** display approximately C_{2h} symmetry.[14] The amidinato ligands of the

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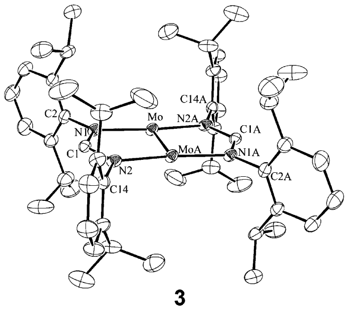

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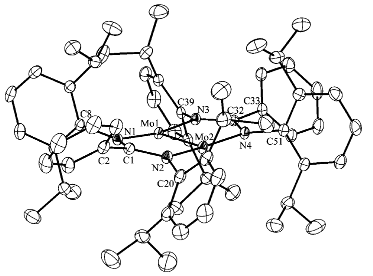

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Figure 2. Molecular structures of **3** (top) and **4** (bottom) with thermal ellipsoids shown at the 35% probability level.

complexes **1**−**4** remain intact due to the C−N bond lengths of their backbones being 1.32−1.35 Å.

Typically for most multiply bonded metal−metal complexes, the most interesting metrical parameter is the metal−metal bond length. The Mo−Mo quintuple bond lengths of **3** and **4** are 2.0187(9) and 2.0157(4) Å, respectively, dramatically shorter than those in **1** and **2**. Though the X-ray determined the shortest Mo−Mo quadruple bond is 2.037(3) Å in the tetragonal dimolybdenum complex, $Mo_2(\mu\text{-}\eta^2\text{-pyNC(O)CH}_3)_4$ (Cotton et al.),[15] this unusually short quadruple bond was suggested to be unreliable. It is interesting to note that these values suggest that the Mo−Mo quintuple bond lengths do not or slightly correlate with the steric bulk of the ancillary ligands. It is also important to note that the Mo−Mo bond lengths in **3** and **4** are substantially shorter than the theoretically predicted Mo−Mo quintuple bond lengths of 2.03−2.10 Å.[10] Conclusively, the ultrashort Mo−Mo quintuple bonds herein are unequivocally a consequence of the formations of 1 σ, 2 π, and 2 δ bonding interactions between two Mo atoms, although a δ bond contributes only slightly to the bond shortening.[1] In comparison, in terms of Cotton's "formal shortness ratio" (FSR), **3** and **4** has an FSR of 0.776 and 0.775, while the FSR of N_2 is 0.786.[1]

To understand the electronic structures and bonding schemes of **3** and **4**, we carried out computations using BP86[16] density functional theory (DFT) with def2-TZVP and def2-TZVPP basis sets.[17] Geometry optimizations on diamagnetic **3** gave metrical parameters (Table S10 in SI) that are in excellent agreement with the X-ray structure. For example, the computed Mo−Mo bond lengths are 2.029 (def2-TZVP) and 2.021 Å (def2-TZVPP). As for the electronic structures, the calculations at BP86/def2-TZVP showed that there is no N−Mo π bonding interactions, and considerable metal−metal bonding characters can be found through HOMO to HOMO-2, HOMO-10, and HOMO-12 as shown in Figure S5 (SI). Those between HOMO-3 and HOMO-9 are primarily contributed from ligands. Of these five Mo−Mo bonding orbitals, HOMO-10 ($d_{xz} + d_{xz}$) and HOMO-12 ($d_{yz} + d_{yz}$) represent two Mo−Mo π bonds, while the Mo−Mo σ character is found at HOMO-2 ($d_{z^2} + d_{z^2}$). HOMO ($d_{xy} + d_{xy}$) and HOMO-1 ($d_{x^2-y^2} + d_{x^2-y^2}$) clearly indicate a pair of Mo−Mo δ bonds. Note that HOMO-1, the side-on sd δ bond, results from hybridization of s (36.7%) and d (63.3%) orbitals, oriented such that the main hybrid orbital axes are parallel to one another. As a result, computations unambiguously support that **3** and **4** possess a Mo−Mo quintuple bond, and these two extremely short Mo−Mo bonds are due to strong interactions between two d^5 Mo(I) centers.

Note also that the Cr−Cr quintuple bond lengths[4] can be successfully predicted by the semiempirical pyramidality effect.[18] However, the estimated Mo−Mo quintuple bond lengths for **3** and **4** by the pyramidality effect are 2.053 and 2.044 Å, respectively, which significantly deviate from the experimental values 2.0187(9) and 2.0157(4) Å, respectively. This discrepancy has also occurred to most of the Mo−Mo quadruply bonded tetragonal complexes.[17]

In summary, we have demonstrated a method to construct the Mo−Mo quintuple bonds. The second Mo−Mo δ bonds of the quintuple bonded dimolybdenum compounds **3** and **4** were developed from reduction of their respective quadruply bonded Mo_2 precursors **1** and **2**. Both **3** and **4** possess an extremely short Mo−Mo quintuple bond of 2.02 Å. The bonding schemes, 2 δ, 2 π, and 1 σ, of the Mo−Mo quintuple bonds of **3** and **4** were corroborated by sophisticated DFT calculations. Owing to the low-coordinate and -valent Mo−Mo centers, **3** and **4** provide a good platform to explore their chemistry. Reactivity studies of **3** and **4** are currently underway.

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Supporting Information Available: Experimental details for synthesis, X-ray crystallographic data of **1**−**4** with tables and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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