

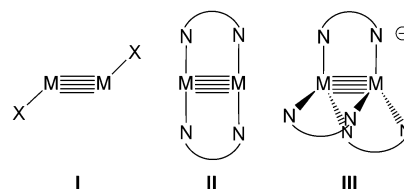
Metal–Metal Multiple Bonds

An Electron-Rich Molybdenum–Molybdenum Quintuple Bond Spanned by One Lithium Atom**

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In the field of metal–metal multiple bonding, there are many factors that affect the metal–metal bond lengths. The most determinant cause is the structural configuration of complexes,^[1] and this has been illustrated by the Group 6 metal–metal quadruple bonds. In the large number of tetragonal quadruply bonded complexes $[M_2X_8]$,^[1] the increase in the internal twist angle between two MX_4 fragments leads to elongation of the metal–metal quadruple bond.^[1,2] For example, those quadruply bonded dimolybdenum complexes with the torsion angles about the Mo–Mo bond of 26–40° possess long Mo–Mo bonds in the range of 2.18–2.19 Å, which is because a major part of the δ bonding has been abolished.

In contrast to the relatively mature metal–metal triple- and quadruple-bond chemistry,^[1,3] quintuple bonding is in its infancy. In contrast to the trigonal triply bonded and tetragonal quadruply bonded dinuclear complexes, the geometry of a quintuply bonded compound has been controversial. Theoretically, the most accepted configuration of a quintuple bonded complex is the type I *trans-bent* geometry (Scheme 1).^[4] On the experimental side, the first quintuple bond, in $[Cr_2Ar'_2]$ ($Ar' = 2,6-[2,6-(iPr)_2C_6H_3]_2C_6H_3$)^[5a] and derivatives,^[5b] was reported by Power et al. It is worthy noting these remarkable complexes in fact adopt the type II geometry, although the central Cr_2 unit is stabilized by two monoanionic terphenyl ligands. Since then, many efforts have been dedicated to isolating dinuclear species featuring quintuple-bond character. For example, the groups of Theopold,^[6] Tsai,^[7] and Kempe^[8] reported several type II quintuply bonded Cr_2 and Mo_2 complexes with extremely short



Scheme 1. Three possible geometries for quintuply bonded complexes.

metal–metal quintuple bonds spanned by two bidentate nitrogen-based ligands. The existence of the Cr–Cr quintuple bond of the type II complex was recently corroborated by charge-density studies.^[9] Preliminary reactivity studies on the type II complexes indicate these univalent and low-coordinate dinuclear species are reactive towards unsaturated organic functionalities and small molecules.^[10,11] Compared to the many type II complexes, only one example of the type III complex, $[Cr_2\{\mu-HC(N-2,6-Me_2C_6H_3)_2\}_3]^-$ (**1**), was recently reported, although such type of species was proposed by Hoffmann et al. in 1979.^[12] Unexpectedly, compound **1** possesses an ultrashort Cr–Cr quintuple bond (1.74 Å),^[7a] which has also been supported by theoretical calculations.^[7a,13]

The quintuply bonded Group 6 M_2 ($M = Cr, Mo$) complexes reported to date have very short M–M bond distances. Theoretical analysis on the type II Cr_2 complexes^[6–8] implied that these short Cr–Cr distances are associated with the steric bulk of the ligands.^[13] Furthermore, computations on the quintuply bonded Group 6 model compounds M_2X_2 ($M = Cr, Mo, W$; $X = H, F, Cl, Br, CN, Me$) revealed the M–M bond distances vary with the structural conformation.^[44] Since the recognition of the structure of **1**, we became interested in characterizing the type III and its related compounds, because we wish to have a better understanding of the nature of the bonding and correlation between the metal–metal distance and structural configuration. Herein we describe the synthesis, characterization, and preliminary studies of the unique, formally Mo–Mo quintuply bonded species $[Mo_2(\mu-Li)\{\mu-HC(N-2,6-Et_2C_6H_3)_2\}_3]$ (**5**), whereby the Mo atoms are connected by a new type of Mo–Mo interaction, and its preliminary reactivity.

Unlike the synthesis of the quintuply bonded dimolybdenum complexes $[Mo_2\{\mu-\eta^2-RC(N-2,6-iPr_2C_6H_3)_2\}_2]$ ($R = H, Ph$) starting from the quadruply bonded species $K_4[Mo_2Cl_8]$,^[7c] we develop a different method to prepare a new type quintuply bonded dimolybdenum compound. As illustrated in Scheme 2, two equiv of the lithium amidinate, $Li[HC(N-2,6-Et_2C_6H_3)]$, was added to a mixture of $[Mo_2Cl_6(thf)_3]$ and 5 equiv of Zn powder in THF at $-35^\circ C$.^[14] After

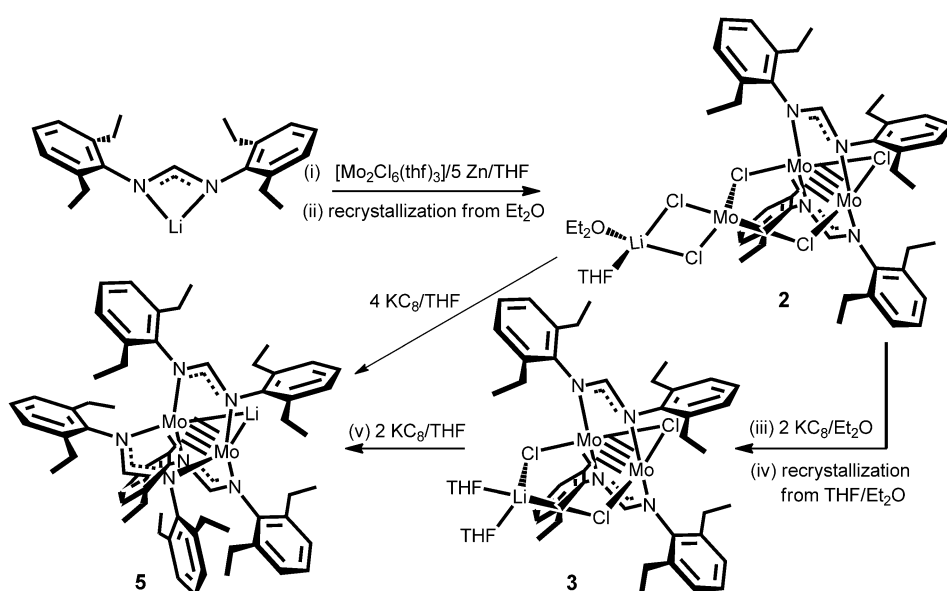
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[**] We are grateful to the National Science Council, Taiwan for financial support under Grants NSC 99-2113-M-007-012-MY3 (Y.C.T.), and NSC98-2113-M-009-010-MY2 and 100-2627-B-009-001 (J.S.K.Y.). We also thank Prof. R. Bruce King and Prof. Yu Wang for suggestions.

Supporting information for this article, including experimental details for the synthesis, X-ray crystallographic data of complexes **2**, **3**, **5**, and **6**, and computations and frontier orbitals of **5**, is available on the WWW under <http://dx.doi.org/10.1002/anie.201200122>.



Scheme 2. Formation of complex **5**.

workup and recrystallization from diethyl ether, the orange diamagnetic trimolybdenum complex $[\text{Mo}_2\{\mu\text{-HC}(\text{N-2,6-Et}_2\text{C}_6\text{H}_3)_2(\mu\text{-Cl})\}\{\mu\text{-Cl}\}_2\text{Mo}(\mu\text{-Cl})_2\text{Li}(\text{thf})(\text{OEt}_2)]$ (**2**) was isolated in 22% yield. The formulation of **2** was corroborated by single-crystal X-ray diffraction analysis,^[15] and its molecular structure is depicted in the Supporting Information, Figure S1. The core structure of **2** adopts a paddle-wheel configuration, whereby the Mo_2 unit is spanned by two amidinato, one chloro, and one unusual bidentate tetrahedral $\{\text{MoCl}_4\}^{2-}$ ligands to give an “ate” complex. The Mo–Mo bond length is 2.0789(12) Å, a typical Mo–Mo quadruple bond.^[1,2]

Subsequent treatment of an ethereal solution of **2** with 2 equiv of KC_8 and recrystallization from THF/diethyl ether led unexpectedly to the isolation of the diamagnetic orange “ate” complex $[\text{Mo}_2\{\mu\text{-HC}(\text{N-2,6-Et}_2\text{C}_6\text{H}_3)_2(\mu\text{-Cl})\}\{\mu\text{-Cl}\}_2\text{Li}(\text{thf})_2]$ (**3**; 32% yield). The fate of the extruded “ MoCl_2 ” fragment is not clear. The molecular structure of **3** was elucidated by X-ray crystallography (Supporting Information, Figure S2). The structure of **3** resembles that of our recently reported quadruply bonded dimolybdenum complexes $[\text{Mo}_2(\mu\text{-Cl})\{\mu\text{-Cl}\}_2\text{Li}(\text{OEt}_2)]\{\mu\text{-}\eta^2\text{-RC}(\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\}_2$,^[7c] except that the lithium ion in **3** is four-coordinate owing to the less-bulky amidinates. Interestingly, the Mo–Mo bond length (2.0817(10) Å) is slightly longer than that in **2**.

In light of the isolation of **1** from KC_8 reduction of $[\text{Cr}(\text{thf})(\mu\text{-Cl})_2]\{\mu\text{-}\eta^2\text{-HC}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)_2\}_2$ by ligand redistribution, we wondered whether the dimolybdenum derivative, $[\text{Mo}_2(\mu\text{-HC}(\text{N-2,6-Et}_2\text{C}_6\text{H}_3)_2)_3]^-$ (**4**), which is analogous to **1**, could be generated from the reduction of **3**. To our delight, this is indeed the case. Unexpectedly, treatment of **3** with 2 equiv of KC_8 afforded the lithiated diamagnetic orange complex $[\text{Mo}_2(\mu\text{-Li})\{\mu\text{-HC}(\text{N-2,6-Et}_2\text{C}_6\text{H}_3)_2\}_3]$ (**5**) in low yield of isolated product (17%). Alternatively, complex **5** (11% yield) can be obtained from the reaction of **2** and four equiv of KC_8 . The formulation of **5** indicates its formation is also by

a complicated ligand redistribution process, which explains its low yield. Spectroscopic properties of **5** support its formulation. In the ^1H NMR spectrum, two ligand environments in a ratio of 2:1 were observed. The signal in the ^7Li NMR spectrum corresponding to the Li atom is found at $\delta = 2.61$ ppm. X-ray crystallography was also used to establish the formulation of **5**. The molecular structure presented in Figure 1 demonstrates a paddle-wheel configuration, whereby the Mo_2 unit is bridged by three amidinates and a lithium ion. The three adjacent aryl paddles on each Mo atom are arranged in a propeller-like edge-to-face orientation,^[16] similar to that in the

pseudo D_{3h} symmetry complex **1**.^[7a] All of the Mo–N bond lengths (ca. 2.155 Å) are comparable to those in the quadruply bonded complexes $[\text{Mo}_2\{\mu\text{-HC}(\text{NAr})_2\}_4]$.^[1] The separation between Li1 and Mo1 is 2.640(8) Å, which is shorter than those (2.70 Å in average) in the square tetramolybdenum $[\text{Cp}_2\text{MoH}(\mu\text{-Li})_4]$ ^[17] and the trigonal trimolybdenum species $[\text{Cp}_2\text{MoH}(\mu\text{-Lithf})_3]$ (2.844(7) and 2.830(6) Å).^[18]

As is usually the case for a multiply bonded dinuclear complex, the most intriguing metric parameter is the metal–

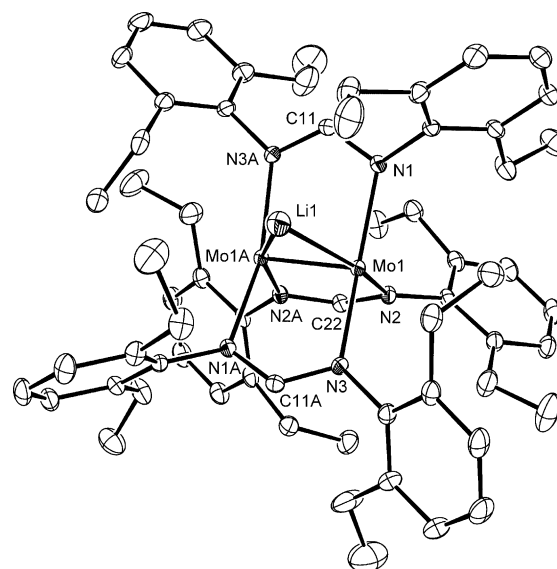


Figure 1. ORTEP of **5**. Ellipsoids are set at 35% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–Mo1A 2.0612(4), Mo1–N1 2.142(2), Mo1–N2 2.171(2), Mo1–N3 2.171(2), Mo1–N3 2.154(2), Mo1–Li1 2.640(8), C11–N1 1.325(3), C22–N2 1.330(3); N1–Mo1–Mo1A 94.17(6), N2–Mo1–Mo1A 93.80(5), N3–Mo1–Mo1A 92.36(6), N1–Mo1–N2 99.31(8), N2–Mo1–N3 101.56(8), N1–Mo1–N3 157.65(8), Mo1–Li1–Mo1A 45.96(14).

metal bond distance. The bond length of Mo1–Mo1A of **5** is 2.0612(4) Å, which is longer than those (2.02 Å) of the only reported type II quintuply bonded dimolybdenum compounds [Mo₂{μ-η²-RC(N-2,6-*i*Pr₂C₆H₃)₂}]₂ (R = H, Ph),^[7c] but slightly shorter than the shortest Mo–Mo quadruple bonds (2.063(1) Å) in the tetrakisamidato dimolybdenum species [Mo₂{*t*BuNC(Me)O}₄].^[19] To achieve the preparation of anionic complex **4** and then determine the Mo–Mo bond length, efforts to remove Li⁺ ion from **5** by the addition of two equiv of [12]crown-4 ether were not successful. In fact, the lack of oxygen donors at the Li atom implies that it is well-protected by the four neighboring ethyl groups of the supporting amidinates. In the presence of 2 equiv of [12]crown-4 ether, K⁺ reduction of **3** led to unidentified products as assayed by NMR spectroscopy. To gain a better understanding of the influence of the bound Li⁺ ion on the Mo–Mo bond length, we performed DFT calculations at RI-BP86/def2-TZVP to acquire the structural parameters of **4**. The optimized structure of **4** (Supporting Information, Figure S3) resembles **1** significantly. The computed Mo–Mo bond length is 2.070 Å, which surprisingly is longer than that of **5**. Furthermore, as shown in Figure 2, more complex ions

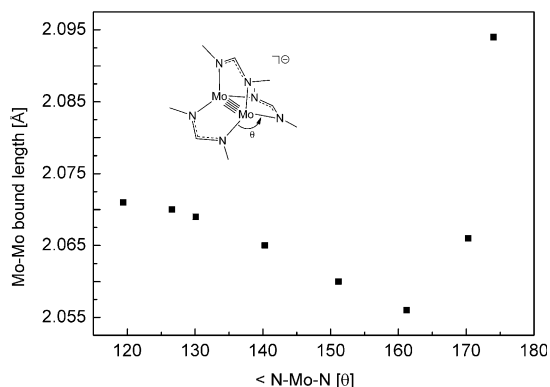


Figure 2. Variation of the Mo–Mo bond length [Å] versus the corresponding complex conformation based on the formulation of **4**.

based on the formulation of **4** were calculated by varying the N–Mo–N angles from 120 to 175°, and the constraint-optimized Mo–Mo separations slightly fluctuate from 2.056 to 2.094 Å. That is, the bound Li⁺ ion does not perturb the length of the Mo–Mo bond.

Hoffmann proposed the metal–metal quintuple bond could exist in a *D*_{3h} symmetry dinuclear complex.^[12] In view of *C*_{2v} symmetry complex **5**, one question immediately arises: Does the Mo–Mo quintuple bond exist in **5**? To gain deeper insight into the nature of the bonding, computational studies were then performed. The DFT calculations at the BP86 level with basis sets of triple-zeta quality afforded a gas-phase structure for **5** that is in good agreement with the X-ray data (Supporting Information, Table S10). For example, the computed Mo–Mo bond length is 2.069 Å (BP86/def2-TZVP) or 2.060 Å (BP86/def2-TZVPP). The MO studies at BP86/def2-TZVP indicate no significant N–Mo π-bonding interactions. Attention was next drawn to the nine highest-energy occupied MOs, namely the HOMO down to HOMO–8 (Support-

ing Information, Figure S5). Of these nine MOs, HOMO, HOMO–1, HOMO–3, HOMO–7, and HOMO–8 have their electron densities concentrated on the metals rather than the ligands, and thus may be assumed to be responsible for the metal–metal bonding. On the other hand, HOMO–2, HOMO–4, HOMO–5, and HOMO–6 have most of their electron density on the ligands and thus may be associated with metal–ligand bonding. Among these five occupied Mo–Mo bonding MOs, HOMO–7 (*d*_{xz} + *d*_{xz}) and HOMO–8 (*d*_{yz} + *d*_{yz}) represent two Mo–Mo π bonds, while the Mo–Mo σ character is found at HOMO–3 (*d*_z² + *d*_z²). As shown in Figure 3, the contour plots of the HOMO (*s**d*_{x²–y²} + *s**d*_{x²–y²}) and

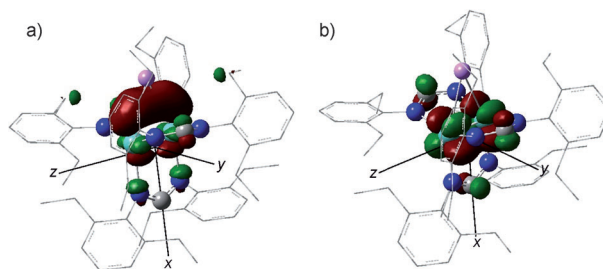


Figure 3. Representation of a) the HOMO and b) HOMO–1 of **5** from DFT calculations.

HOMO–1 (*d*_{xy} + *d*_{xy}) unambiguously indicate a pair of Mo–Mo δ bonds. Considerable electron density in the region between Li⁺ ion and the molybdenum atoms is observed in HOMO, but the interaction between the Li⁺ ion and Mo atoms is mainly ionic, considering that HOMO is composed of Li (11.63%) and two Mo (44.18% from each) atoms based on NBO calculations (Supporting Information, Table S11). Overall, the pattern of these five occupied metal–metal bonding MOs leads to an effective bond order (eBO) of 3.67,^[20] which is less than five mainly because of the large occupation of the antibonding δ orbitals and the slight bonding interaction between Li and two Mo atoms (eBO of the Mo–Li–Mo is 0.57). For comparison, the calculated eBO of Power's quintuple bonded species [Cr₂Ar₂] is 3.52.^[4d,g] Although the calculated bond order is less than five, the Mo–Mo bond in **5** is formally quintuple, because five orbitals and five electrons on each Mo atom are involved in the bonding (Supporting Information, Figure S5).

Unlike the redox couple of **1/1**⁺, one-electron oxidation of **5** by AgCl or [Cp₂Fe][CF₃SO₃] does not afford the neutral mixed-valent species [Mo₂{μ-HC(N-2,6-Et₂C₆H₃)₂}]₃. Treatment of **4** in THF with 2 equiv of AgCl does not lead to **3**, but rather to the isolation of the quadruply bonded complex [Mo₂(μ-Cl){μ-HC(N-2,6-Et₂C₆H₃)₂}]₃ (**6**; Supporting Information, Figure S6).

In summary, a new method has been developed to synthesize a new quintuple bonded dimolybdenum complex [Mo₂(μ-Li){μ-HC(N-2,6-Et₂C₆H₃)₂}]₃ (**5**) that is supported by bidentate bridging ligands. The quintuply bonded Mo₂ unit in such configuration is so electron-rich that it strongly binds a lithium ion and undergoes facile two-electron oxidation. DFT calculations and structure parameters indicate a new

type of metal–metal quintuple bond in **5**. Future work will be directed towards investigating the Mo–Mo bond in compound **5**.

Received: January 6, 2012

Revised: April 24, 2012

Published online: May 29, 2012

Keywords: amidinato ligands · bond theory · lithium · molybdenum · multiple bonds

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- [15] Crystallographic data for **2**: C₅H₁₂, C₅₀H₇₂N₄Cl₅LiMo₃O₂, $M_r = 1233.13$, $T = 200(2)$ K, monoclinic, space group $P2_1/m$, $a = 11.2471(2)$, $b = 23.2133(4)$, $c = 11.6527(2)$ Å, $\beta = 95.8800(10)^\circ$, $V = 3026.31(9)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.353$ Mg m⁻³, $\mu = 0.869$ mm⁻¹, reflections collected: 29236, independent reflections: 5474 ($R_{\text{int}} = 0.0593$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0831$, $wR_2 = 0.2564$, R indices (all data): $R_1 = 0.0988$, $wR_2 = 0.2722$. **3**: C₅₄H₈₀N₄Cl₃LiMo₂O₃, $M_r = 1138.39$, $T = 200(2)$ K, triclinic, space group $P\bar{1}$, $a = 12.8489(8)$, $b = 14.8293(10)$, $c = 15.7277(10)$ Å, $\alpha = 78.092(2)^\circ$, $\beta = 77.167(3)^\circ$, $\gamma = 78.233(2)^\circ$, $V = 2819.5(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.341$ Mg m⁻³, $\mu = 0.630$ mm⁻¹, reflections collected: 18407, independent reflections: 9714 ($R_{\text{int}} = 0.0757$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0772$, $wR_2 = 0.1362$, R indices (all data): $R_1 = 0.1680$, $wR_2 = 0.1723$. **5**: C₆₃H₈₁N₆LiMo₂, $M_r = 1121.16$, $T = 200(2)$ K, monoclinic, space group $C2/c$, $a = 14.2716(3)$ Å, $b = 19.0562(4)$ Å, $c = 20.4389(4)$ Å, $\beta = 95.0020(10)^\circ$, $V = 5537.4(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.345$ Mg m⁻³, $\mu = 0.498$ mm⁻¹, reflections collected: 18499, independent reflections: 4885 ($R_{\text{int}} = 0.0285$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0316$, $wR_2 = 0.0777$, R indices (all data): $R_1 = 0.0394$, $wR_2 = 0.0932$. **6**: C₇H₈, C₇₀H₈₉ClMo₂N₆, $M_r = 1241.80$, $T = 200(2)$ K, monoclinic, space group $C2/c$, $a = 19.9867(3)$ Å, $b = 15.8678(3)$ Å, $c = 22.7923(4)$ Å, $\beta = 108.8470(10)^\circ$, $V = 6840.9(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.206$ Mg m⁻³, $\mu = 0.448$ mm⁻¹, reflections collected: 28006, independent reflections: 6008 ($R_{\text{int}} = 0.0917$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0743$, $wR_2 = 0.2007$, R indices (all data): $R_1 = 0.1178$, $wR_2 = 0.2423$. CCDC 798802 (**2**: C₅H₁₂), CCDC 798803 (**3**), CCDC 798804 (**5**), CCDC 830534 (**6**: C₇H₈) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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