

Interconversion of Quadruply and Quintuply Bonded Molybdenum Complexes by Reductive Elimination and Oxidative Addition of Dihydrogen*

Mario Carrasco, Natalia Curado, Celia Maya, Riccardo Peloso, Amor Rodríguez, Eliseo Ruiz, Santiago Alvarez,* and Ernesto Carmona*

Transition metal complexes that exhibit multiple metal–metal bonding are of fundamental importance in chemistry.^[1a] Following decades of intense scrutiny of double, triple, and quadruple metal–metal bonds, in 2005 Power and co-workers made an outstanding discovery with the characterization of the first stable molecule with fivefold bonding between two chromium atoms.^[2] This report encouraged the search for further examples of quintuply bonded dimetal compounds^[1b] and was followed by numerous experimental^[3–11] and computational studies.^[12–18] By and large, these studies have focused on chromium compounds.^[1b,2–8,11] However, Tsai and co-workers have extended their investigation of the Cr–Cr quintuple bond^[6,7,11] to analogous molybdenum complexes and have isolated two closely related compounds supported by monoanionic amidinate ligands, *N,N'*-disubstituted with 2,6-diisopropylphenyl groups.^[9] Recently, another compound with the Mo^I₂ central unit reinforced by three amidinate ligands and a bridging lithium cation has also been reported by the same group of researchers.^[10]

Identification of the above complexes with fivefold metal–metal bonding has prompted research directed toward under-

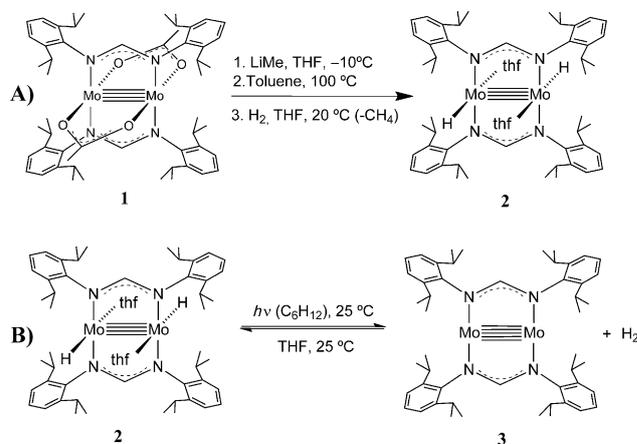
standing their bonding characteristics^[12–18] and the chemical reactivity of their central M–M quintuple bond. So far, only a few reports have appeared in the literature concerning mainly the chemical properties of the Cr–Cr quintuple bond. Thus, these complexes feature interesting reactivity toward unsaturated molecules like N₂O,^[19] alkenes, and alkynes,^[20,21] and are able to activate white phosphorous, yellow arsenic, and AsP₃.^[22] Similar to carbon–carbon double and triple bonds, the Cr–Cr quintuple bond of an aminopyridinate complex undergoes facile carboalumination, to generate the corresponding Cr–Cr quadruple-bond derivative with formally monoanionic bridging CH₃ and AlMe₂ groups.^[23] Disproportionation of Cr^I to Cr⁰ and Cr^{II} induced by the addition of [18]crown-6-ether to a Cr–Cr quintuply bonded complex has also been demonstrated.^[11] During the preparation of this manuscript the reactivity of Mo–Mo quintuply bonded compounds with alkynes has been shown.^[24]

The above results illustrate the potential of quintuply bonded electron-rich M^I₂ centers for bimetallic activation. Herein we describe that the quadruply bonded dimolybdenum dihydride complex [Mo₂(H)₂{HC(N-2,6-*i*Pr₂C₆H₃)₂}(thf)₂] **2** undergoes reductive elimination of H₂ from its [(H)Mo≡Mo(H)] core under UV irradiation (365 nm) to afford the known [Mo₂{HC(N-2,6-*i*Pr₂C₆H₃)₂}]₂, **3**,^[9] with fivefold Mo–Mo bonding (Scheme 1B). Because a tetrahydrofuran (THF) solution of the latter reacts readily with H₂ to reform **2**, our results demonstrate that quadruply and quintuply bonded dimolybdenum complexes may interconvert by means of reductive elimination and oxidative

[*] M. Carrasco, N. Curado, Dr. C. Maya, Dr. R. Peloso, Dr. A. Rodríguez, Prof. E. Carmona
 Instituto de Investigaciones Químicas-Departamento de Química Inorgánica, Universidad de Sevilla-Consejo Superior de Investigaciones Científicas
 Avenida Américo Vespucio 49, 41092 Sevilla (Spain)
 E-mail: guzman@us.es
 Prof. E. Ruiz, Prof. S. Alvarez
 Departament de Química Inorgànica and Institut de Química Teòrica i Computacional, Universitat de Barcelona
 Martí i Franquès 1–11, 08028 Barcelona (Spain)

[**] Financial support (FEDER contribution and Subprogramas Juan de la Cierva) from the Spanish Ministry of Science and Innovation (Projects CTQ2010-15833, CTQ2011-23862-C02-01 and Consolider-Ingenio 2010 CSD2007-00006), the Generalitat de Catalunya (Project 2009SGR-1459), and the Junta de Andalucía (Grant FQM-119 and Project P09-FQM-5117) is gratefully acknowledged. M.C. and N.C. thank the Spanish Ministry of Education (AP-4193) and the Spanish Ministry of Science and Innovation (BES-2011-047643) for research grants. We also thank Prof. M. L. Poveda for helpful discussions and advice, Dr. J. López-Serrano for assistance and discussions on NMR analyses, and the Centre de Supercomputació de Catalunya (CESCA) for the allocation of computational resources.

Supporting information for this article (experimental details) is available on the WWW under <http://dx.doi.org/10.1002/anie.201209064>.



Scheme 1. A) Synthesis of the bis(hydride) complex **2** and B) its interconversion with the quintuply bonded complex **3**.

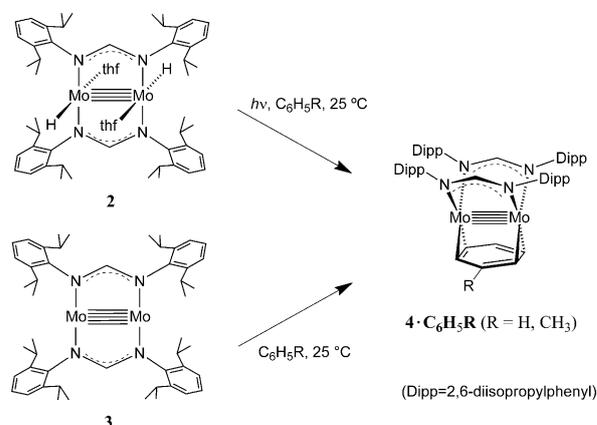
addition of dihydrogen, two ubiquitous reactions in transition metal chemistry.^[25] We also show in Scheme 2 that compound **3** reacts reversibly (thermally or with light irradiation) with aromatic solvents like benzene and toluene, to yield the corresponding adducts, $[\text{Mo}_2\{\text{HC}(\text{N}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\}_2(\text{C}_6\text{H}_5\text{R})]$ (**4**; where $\text{R} = \text{H}$, **4-C₆H₆** or $\text{R} = \text{CH}_3$, **4-C₆H₅CH₃**). The electronic structure of the new complexes is discussed with the help of density functional calculations.

Reaction of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and the lithium amidinate, $\text{Li}[\text{HC}(\text{N}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2]$, in THF in a 1:2 molar ratio, resulted in the formation of the complex $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2\{\text{HC}(\text{N}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\}_2]$, **1**, whose structural formula is depicted in Scheme 1 A. Solid-state magnetic susceptibility data revealed that **1** is diamagnetic. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data (see Supporting Information) were in agreement with a *trans* distribution of the ligands, which is otherwise expected on steric grounds.^[26] Methylation of **1** by LiMe gave rise to an interesting set of methyl complexes of the quadruply bonded $[\text{Mo}_2(\text{amidinate})_2]$ unit that will be discussed in a separate publication. As shown in Scheme 1 A and described in the Supporting Information, a three-step, one-flask procedure that involved LiMe and H_2 as key reagents converted **1** into the bis(hydride) complex **2**, with the last hydrogenation step liberating CH_4 . Hydride species with multiply bonded Mo atoms are scarce.^[27–29] Spectroscopic data were in agreement with the hydride formulation proposed for **2**, which feature a Mo–H IR stretching band at 1525 cm^{-1} and a ^1H NMR hydride resonance with $\delta = 5.67\text{ ppm}$. These assignments have been corroborated by deuteration experiments and, in the case of the ^1H NMR hydride signal, by a reaction in an NMR tube with a slight excess of CHCl_3 (Supporting Information). Further corroboration was provided by a single-crystal X-ray experiment. The analysis of the structure of **2** confirmed the existence of two terminal hydride ligands, with a Mo–H distance of approximately 1.71 \AA and a Mo–Mo separation of $2.089(1)\text{ \AA}$. The latter is in accord with a quadruply bonded Mo–Mo compound, which is further supported by computational studies (Supporting Information). Complex **2** is stable toward loss of H_2 at temperatures up to 60°C , and upon heating at higher temperatures, it undergoes extensive decomposition. Nevertheless, UV irradiation (365 nm) of its solutions in cyclohexane led to an approximately 1:1 mixture of **2** and **3** (Scheme 1 B).

To generate **3** cleanly, stirred solutions of **2** in cyclohexane were irradiated for approximately 24 hours, with intermittent vacuum/argon cycles to remove the liberated H_2 , permitting the isolation of **3** in approximately 75% yield. **3** was characterized by comparison of the NMR spectra with those in the literature^[9] and by X-ray analysis of a cyclohexane solvate (Supporting Information). Complex **3** reacted readily at 25°C with H_2 (1 bar, approximately 30 min, reacted in an NMR tube) in $[\text{D}_8]\text{THF}$ to reform the bis(hydride) complex **2**. To our knowledge, this reactivity, whereby dinuclear oxidative addition and reductive elimination of H_2 interconvert complexes with quintuple and quadruple M–M bonds, has no precedent in the literature. Oxidative addition and reductive elimination in doubly and triply bonded M_2 compounds ($\text{M} = \text{Mo}, \text{W}$) are well-known reactions^[30–32] but those involving H_2 are rare.^[33] Indeed, oxidative addition of H_2 to known M–M

quintuple bonds has not been investigated. Experimental and theoretical studies on the mechanism of this reaction are in progress and will be reported in due course.

Originally the photolysis of **3** was performed in benzene, leading to a clean conversion into a new, multiply bonded Mo_2 -arene complex, **4-C₆H₆** (Scheme 2). The corresponding



Scheme 2. Generation of **4-C₆H₆R** from complexes **2** and **3**.

toluene adduct, **4-C₆H₅CH₃**, was prepared similarly. Not unexpectedly, these arene adducts could also be generated by dissolving complex **3** in the corresponding aromatic hydrocarbon (Scheme 2). At 25°C , in the dark, these reactions have half-life times, $t_{1/2}$, of 0.25 hours for benzene and 4.5 hours for toluene. However, exposure of these solutions to sunlight increases significantly the rate of the reaction.

Compounds like **4** that contain arene-bridged multiply bonded M_2 units are very rare, although recently Masuda and co-workers reported the first examples of a quadruply bonded Mo^{II}_2 species of this kind.^[34,35] Solid-state magnetic-susceptibility measurements for **4-C₆H₆** confirmed its diamagnetic nature (Supporting Information). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances owing to the amidinate ligands of **4-C₆H₆** are consistent with C_2 molecular symmetry (Supporting Information). However, only one resonance was observed at 25°C for the coordinated molecule of benzene (3.87 ppm in the ^1H NMR and 71.2 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR), indicating that, at this temperature, the coordinated and non-coordinated C–C bonds undergo fast exchange. Cooling the sample to -85°C only caused broadening of these signals.

Benzene solutions of compound **4-C₆H₆** can be heated at 120°C in the dark without noticeable decomposition. In C_6D_6 , there is no observable reaction at 80°C but at 120°C full conversion into **4-C₆D₆** occurred after stirring for 24 hours. Similarly, a C_6D_{12} solution of **4-C₆H₆** in the dark, at room temperature, showed no evidence for C_6H_6 dissociation and generation of **3**, but at 120°C , a 4:1 mixture of **4-C₆H₆:3** was generated. However, under sunlight for a period of 0.5 hours at ambient temperature, solutions of **4-C₆H₅CH₃** in benzene, and those of **4-C₆H₆** in toluene, transformed completely into **4-C₆H₆** and **4-C₆H₅CH₃**, respectively. In a kinetic competition experiment, arene-free complex **3** reacted in the dark at room temperature with an excess of an equimolar mixture of C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$ to afford mostly (approximately 95%) the

benzene adduct. A thermodynamic preference for $4\text{-C}_6\text{H}_6$ over $4\text{-C}_6\text{H}_5\text{CH}_3$ was also shown, as heating a solution of $4\text{-C}_6\text{H}_6$ in the above mixture of solvents at 120°C in the dark yielded solely $4\text{-C}_6\text{H}_6$. Furthermore, treatment of $4\text{-C}_6\text{H}_5\text{CH}_3$ with an excess of the same mixture of benzene and toluene at 120°C for two days in the dark caused formation of $4\text{-C}_6\text{H}_6$.

The solid-state molecular structure of $4\text{-C}_6\text{H}_6$ presented in Figure 1 features a Mo–Mo quintuple bond length of $2.106(1)\text{ \AA}$ ($2.105(1)\text{ \AA}$ for $4\text{-C}_6\text{H}_5\text{CH}_3$; Supporting Informa-

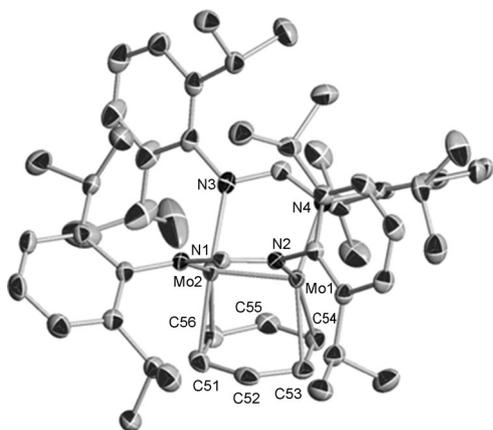


Figure 1. Solid-state molecular structure of $4\text{-C}_6\text{H}_6$, with thermal ellipsoids set at 50% probability.

tion). This bond is longer than that of **3** (approximately 2.02 \AA)^[9] but it is in the upper part of the $2.02\text{--}2.12\text{ \AA}$ range predicted theoretically for Mo–Mo quintuple bonds.^[14] The two Mo atoms are symmetrically bound to their respective carbon atoms, with a Mo–C distance of approximately 2.22 \AA (Figure 2). The Mo–C(52) and Mo–C(55) separation varies between approximately 2.62 \AA and 2.73 \AA (Figure 2) and may therefore be viewed as non-bonding. There is a small arene distortion upon coordination, which is evidenced mainly in the lengthening of the arene C–C bonds, with the coordinated C(53)–C(54) and C(51)–C(56) being the longest at 1.45 \AA (Figure 2). These structural data and the arene substitution chemistry outlined above for complexes **4** are more consistent with their formulation as Mo_2^1 species with a coordinated neutral molecule of $\text{C}_6\text{H}_5\text{R}$ rather than as Mo_2^2 derivatives of an arene dianion,^[36–38] $\text{C}_6\text{H}_5\text{R}^{2-}$. Thus, five pairs of *d* electrons

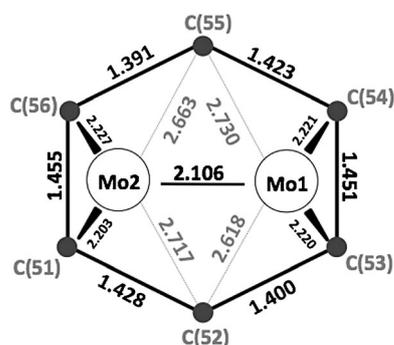


Figure 2. Selected bond lengths taken from Figure 1.

would in principle be available for metal–metal bonding, as in the parent complex **3**. However, the strong electronic interaction of the δ and δ^* orbitals of the $[\text{Mo}_2(\text{amidinate})_2]$ fragment with the π and π^* orbitals of the arene results in a smaller bond order, close to a quadruple bond (see below). For the sake of simplicity, and keeping in mind Cotton's qualitative definition of bond order,^[11a] compounds **4** are represented in Scheme 2 as Mo_2^1 derivatives with fivefold bonding between their metal atoms.

Geometry optimization of complex $4\text{-C}_6\text{H}_6$ yields a structure that is in excellent agreement with the experimental one in the Mo–Mo (2.134 \AA) and Mo–C bond distances, in the C–C bond distance distribution pattern of the benzene ring, and in the N–Mo–N hinge angles. A significant HOMO–LUMO gap attests to the thermodynamic stability of the benzene adduct and indicates the monoconfigurational character of its electronic structure. The coordination of benzene to the dimolybdenum unit brings about a remarkable reorganization of its electronic structure that can be understood with the help of the Dewar–Chatt–Duncanson model and of the symmetry properties of the molecular orbitals of the interacting benzene and Mo_2 fragments in the idealized C_{2v} point group.

Two donor–acceptor interactions involve the occupied π orbitals of benzene belonging to the A_1 and B_1 irreducible representations and the in-phase and out-of-phase combinations of the sp^2 hybrid orbitals of the Mo atoms (not shown). However, the purported back-bonding interactions must involve the $\delta(B_2)$ and $\delta^*(A_2)$ orbitals of the Mo_2 moiety and benzene π orbitals of the same symmetries (Figure 3). Notice that both orbitals of A_2 symmetry are empty in the quintuply bonded Mo_2 and neutral benzene fragments, which in principle, prevents back-bonding. Moreover, the fragment orbitals of B_2 symmetry are both occupied and should produce four-electron repulsion rather than bonding. But the strong overlap between the orbitals of the two fragments stabilizes the A_2 bonding MO below the antibonding B_2 one

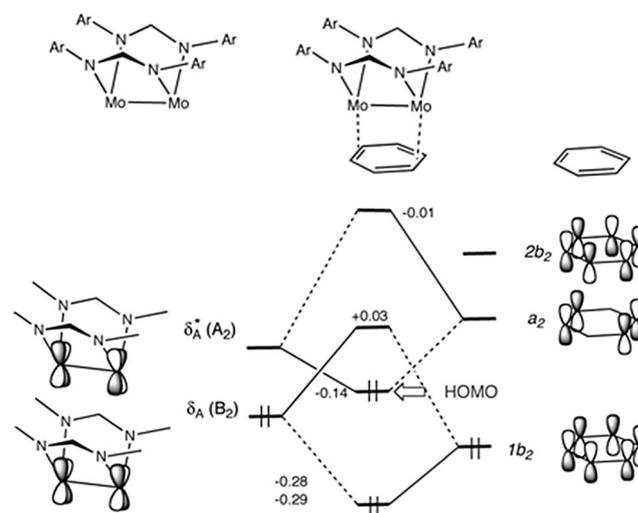


Figure 3. Partial orbital-interaction diagram showing the electronic reorganization associated with back-bonding of the Mo_2L_2 fragment to C_6H_6 .

and induces the transfer of an electron pair from the B_2 to the A_2 set.

Such an electron reshuffling can be simply described in terms of two two-electron donor–acceptor interactions by considering several alternative ways of assigning the four electrons, considering the Mo_2 and benzene fragments. As an example, we may consider an initial electron transfer from $\delta(B_2)$ to $\pi^*(A_2)$ that would allow for two back-bonding interactions and implies a formal oxidation of the Mo atoms to Mo^{II} and the corresponding reduction of benzene to a dianionic form. These canonical Lewis structures of $4 \cdot C_6H_6$ coincidentally predict a decreased Mo–Mo bond order and a partial loss of the aromatic character of benzene, in agreement with the structural data (Figure 2). A small but non-negligible anionic character of the benzene ring is shown by its negative calculated charge (-0.20), as compared to a neutral benzene ring in the analogous Mo^{II}_2 adduct reported by Masuda and co-workers.^[34] In summary, as expected the back-bonding interactions provide Mo–C bonding at the expense of weakening the C–C and Mo–Mo bonds.

Comparison of the Mo–Mo bond distance and calculated Meyer bond order for the benzene adduct reported herein with those of the undisputed quintuple bond of Tsai et al. (3)^[9] and with the related Mo^{II}_2 benzene adduct of Masuda and co-workers (Figure 4),^[34] indicates that compound $4 \cdot C_6H_6$

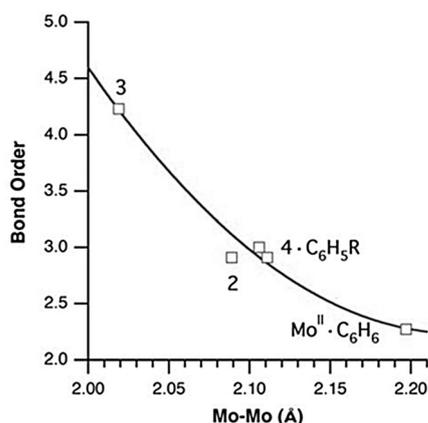


Figure 4. Scatter plot of experimental Mo–Mo bond distances and calculated Meyer bond orders for compounds with quadruple and quintuple bonds discussed in this paper (see Ref. [9] and [34] for **3** and $Mo^{II} \cdot C_6H_6$, respectively).

is somewhere in-between a quintuple and a quadruple bond, albeit closer to a quadruple Mo–Mo bond, in agreement with the description of the electronic structure just discussed. This situation is comparable to that of compound **2**, which should be considered formally as a hydrido- Mo^{II}_2 species, with similar Mo–Mo distances and Meyer bond orders.

Received: November 12, 2012

Revised: December 4, 2012

Published online: February 1, 2013

Keywords: density functional calculations · hydrides · metal arene · molybdenum · multiple bonds

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