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Aromaticity

Reactions of Metal–Metal Quintuple Bonds with Alkynes: [2+2+2] and [2+2] Cycloadditions**

Hong-Zhang Chen, Shih-Cheng Liu, Chun-Hsu Yen, Jen-Shiang K. Yu, Yun-Jen Shieh, Ting-Shen Kuo, and Yi-Chou Tsai**

Benzene, C_6H_6, is one of the most important molecules in organic chemistry. The term aromaticity[1] was developed from the study of benzene and has become an important and fundamental concept in contemporary chemistry since Kekulé proposed a ringlike structure for benzene in 1865.[2] Today, aromatic compounds are not only limited to carbocycles, but also extended to heterocycles containing main-group elements. For example, one or two CH groups of benzene can be replaced by group 14 and 15 elements, such as silicon, nitrogen, and phosphorus, to give heterocyclic aromatics.[3] Furthermore, an aromatic compound can be a transition-metal-containing organometallic species. Hoffmann et al. predicted that a metallabenzene could be possible by replacing one CH group with a transition-metal fragment.[4] On the experimental side, since the recognition of the first metallabenzene, osmabenzene, in 1982,[5] many metallabenzenes have been subsequently synthesized and structurally characterized.[6]

There are many ways to synthesize aromatic compounds. Among the methods, the [2+2+2] cycloaddition reaction of alkynes is a powerful tool to construct highly substituted homo- and heterocyclic aromatic molecules. Such a reaction is thermally allowed,[7] but it does not proceed at ambient temperature without transition-metal catalysts.[8] It is however worth noting that Sekiguchi et al. have demonstrated a catalyst-free [2+2+2] cycloaddition reaction for the synthesis of 1,2-disilabenzene by reacting a kinetically stable disilyne $RSi{\equiv}SiR$ ($R = Si\textit{i}Pr[CH(SiMe_3)_2]_2$) and phenylacetylene at room temperature.[9]

The chemistry of transition-metal multiple bonding was recently reawakened by the recognition the first isolable quintuply bonded dimeric chromium complex $Cr_2Ar'_2$ ($Ar' = C_6H_3$-2,6-$(C_6H_3$-2,6-$\textit{i}Pr_2)_2$ by Power and co-workers.[10] Since then, several quintuply bonded dinuclear group VI metal[11,12] complexes stabilized by nitrogen donors have been reported.[13] Besides interesting bonding, the chromium derivatives have recently been shown to display novel reactions with $AlMe_3$,[11f] N_2O, RN_3,[14] and P_4.[15] Reactions of the chromium dimers with alkynes through a [2+2] cycloaddition process to give 1:1 adducts were recently explored as well.[16] In light of the bonding analogy between the C–C π components of alkynes and metal–metal δ components in the quintuply bonded species (Figure 1), we became interested in exploring reactions between them. Herein, we present the characterization of the first two complexes containing a cyclically delocalized six-membered C_4Mo_2 aromatic ring incorporating a quadruple Mo–Mo bond, and the aromaticity involves δ electrons. These aromatics were obtained by reacting the quintuply bonded dimolybdenum amidinates $[Mo_2\{\mu\text{-}\kappa^2\text{-}RC(N\text{-}2,6\text{-}\textit{i}Pr_2C_6H_3)_2\}_2]$ [R = H (**1**), Ph (**2**)][12a] with two equivalents of a terminal alkyne through a [2+2+2] cycloaddition pathway.

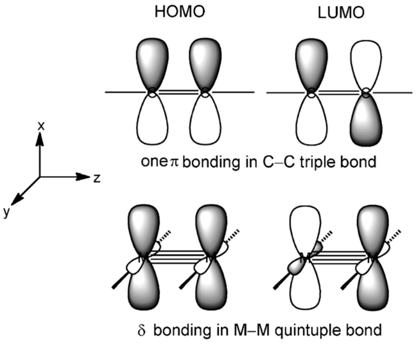

Figure 1. Frontier orbitals of the M–M quintuple bond and C–C triple bond.

As illustrated in Scheme 1, reaction of a THF solution of **1** and an ethereal solution of **2** with two equivalents of 1-pentyne at room temperature yielded the diamagnetic [2+2+2] cycloaddition products $[Mo_2(\mu\text{-}\kappa^1{:}\kappa^1\text{-}1,3\text{-}\textit{n}Pr_2C_4H_2)\{\mu\text{-}\kappa^2\text{-}RC(N\text{-}2,6\text{-}\textit{i}Pr_2C_6H_3)_2\}_2]$ (**3** and **4**, respectively), which were isolated as green crystalline solids in 59.8 % and 66.8 % yield, respectively. Both **3** and **4** are air and moisture sensitive. It is worth pointing out that monitoring these two reactions by ^1H NMR spectroscopy indicated that **3** and **4** (head-to-tail C–

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[*] Dr. H.-Z. Chen, S.-C. Liu, C.-H. Yen, Y.-J. Shieh, Prof. Dr. Y.-C. Tsai
Department of Chemistry and Frontier Research Center
on Fundamental and Applied Sciences of Matters
National Tsing Hua University, Hsinchu 30013 (Taiwan)
E-mail: yictsai@mx.nthu.edu.tw

Prof. Dr. J.-S. K. Yu
Institute of Bioinformatics and Systems Biology and
Department of Biological Science and Technology
National Chiao Tung University, Hsinchu, 30010 (Taiwan)
E-mail: jsyu@mail.nctu.edu.tw

T.-S. Kuo
Department of Chemistry, National Taiwan Normal University
Taipei 11677 (Taiwan)

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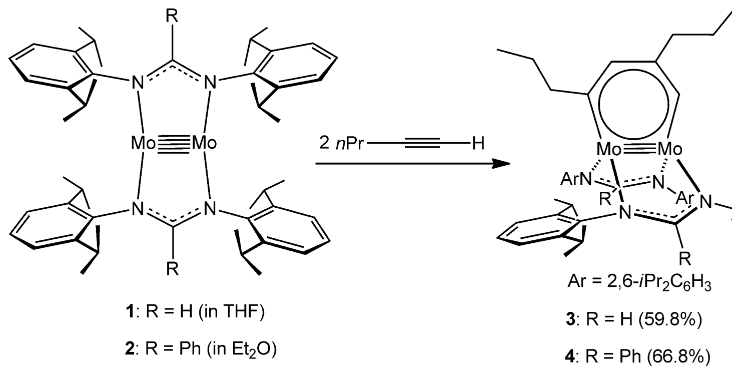


1: R = H (in THF)

2: R = Ph (in Et$_2$O)

3: R = H (59.8%)

4: R = Ph (66.8%)

Scheme 1. Synthesis of complexes **3** and **4**. THF = tetrahydrofuran.

C coupling regioisomer) were the sole products as evidenced by signals for only one amidinato ligand environment and two sets of *n*Pr groups.

Recrystallization of **3** from a diethyl ether/*n*-hexane (1:1) solution at room temperature and **4** from *n*-hexane at −35 °C furnished green crystals suitable for X-ray diffraction studies.[17] Both molecular structures of **3** and **4** are presented in Figure 2. In principle, both **3** and **4** display a lantern-type structure, whereby each Mo$_2$ unit is spanned by the newly formed 1,3-butadienyl group and two amindinato ligands, and is therefore three-coordinate with respect to the ligands. The structural arrangement at each Mo center is better described as a distorted T-shaped geometry, which results from the steric interactions between the 1,3-butadienyl group and the bulky amidinato ligands. The average Mo−N bond length (2.142 Å for **3** and 2.144 Å for **4**) is only slightly longer than that of **1** and **2** (2.117 Å for both).

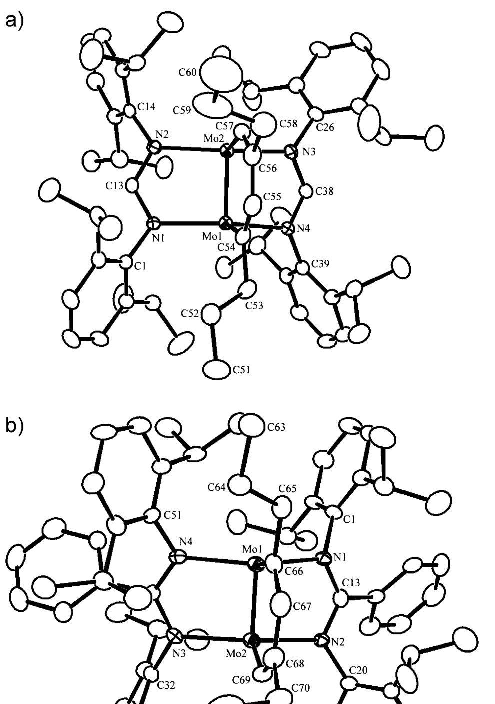


Figure 2. Molecular structures of a) **3** and b) **4** with thermal ellipsoids at 35 % probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **3**: Mo1–Mo2 2.1525(6), Mo1–C54 1.988(5), Mo2–C57 1.982(5), C54–C55 1.391(7), C55–C56 1.396(7), C56–C57 1.387(7); N1-Mo1-N4 155.40(14), N2-Mo2-N3 152.40(14); **4**: Mo1–Mo2 2.1339(7), Mo1–C66 1.999(5), Mo2-C69 1.988(5), C66–C67, 1.400(7), C67–C68 1.402(8), C68–C69 1.375(7); N1-Mo1-N4 147.59(16), N2-Mo2-N3 148.62(16).

The most salient structural feature of both **3** and **4** is the six-membered C$_4$Mo$_2$ metallacycle. These two rings are almost planar with an average internal torsion angle of 1.65 and 2.65° for **3** and **4**, respectively. It is interesting to note that two *n*Pr substituents in both compounds are on the same face of the six-membered rings. Such an arrangement accounts for the less planar C$_4$Mo$_2$ ring of **4**, and is attributed to the stronger steric repulsion between the two *n*Pr groups and two 2,6-*i*Pr$_2$C$_6$H$_3$ substituents of the amidinates. The bond lengths of Mo1-C54 [1.988(5) Å] and Mo2-C57 [1.982(5) Å] in **3** and Mo1-C66 [1.999(5) Å] and Mo2-C69 [1.988(5) Å] in **4** are approximately the same, and they are intermediate between the lengths of Mo−C single and double bonds.[18] In addition, all C−C bond lengths in these two metallacycles are essentially the same and range from 1.375(7) to 1.402(7) Å, which is consistent with the C−C bond length (1.39–1.40 Å)[19] in benzene. As is usually the case for a dinuclear complex, the most intriguing metric parameter is the metal–metal separation. The Mo−Mo bond length in **3** and **4** is 2.1525(6) and 2.1344(7) Å, respectively. These values are equal to those (2.119–2.164 Å) of the paddlewheel Mo$_2^{5+}$ complexes having the Mo–Mo formal bond order of 3.5.[20–27] For instance, the noncarbon aromatic six-membered dimolybdenum/chalcogen Mo$_2$E$_2$Mo$_2$ clusters in [{Mo$_2$(HC(N-4-MeOC$_6$H$_4$)$_2$)$_3$}$_2$(E)$_2$] (E = O,[25] S,[26] Se[27]) supported by amidinates with a Mo–Mo bond order of 3.5 have Mo−Mo bond lengths which fall within the range of 2.135–2.155 Å.

Besides structural parameters, both **3** and **4** display interesting chemical shifts in their ^{1}H NMR spectra. Most importantly, two distinct resonance signals corresponding to the C$_4$Mo$_2$ ring protons were observed in the low-field aromatic region at $\delta = 12.6$ and 8.3 ppm (**3**) and $\delta = 12.5$ and 8.3 ppm (**4**) as a result of the ring current. It is interesting to note that these spectra show an unusually large NMR displacement for two protons in a ring, $\Delta\delta = 4.2$ ppm. The more downfield shifted signals are assigned to the *meta* protons, whereas the *ortho* protons in the vicinity of Mo$_2$ are more shielded and observed upfield in the NMR spectra. Moreover, the signals of ring carbon atoms resonate in a typical aromatic region as well. Therefore, consistent with the archetype of Hückel-type aromaticity, the C$_4$Mo$_2$ rings in complexes **3** and **4** are aromatic and represent the first example of stable quadruply bonded 1,2-dimolybdabenzene derivatives.

In addition to experimental evidence, the electronic delocalization in the C$_4$Mo$_2$ metallacycles of **3** and **4** can be further realized by theoretical calculations. In this regard, we performed DFT calculations on compound **4** at the BP86/def2-TZVP level of theory to reproduce an optimized structure, whose geometry and structural parameters are in good agreement with the X-ray data (see Table S16 in the Supporting Information). For example, two nPr groups are also on the same side of the C$_4$Mo$_2$ ring in the computed structure, and the Mo–Mo distance is 2.154 Å, and the Mo–C bond lengths are 2.019 and 1.982 Å. The molecular orbitals depicting the bonding schemes of the aromatic C$_4$Mo$_2$ ring are shown in Figure 3. Of particular interest is the HOMO, which unequivocally indicates the participation of the Mo-Mo δ bonding in p$_\pi$(C)-d$_\delta$(Mo) for C66-Mo1-Mo2 conjugation and the p$_\pi$–p$_\pi$ π interaction between C67 and C68. The HOMO−1 is mainly C66-C67 and C68-C69 π bonding with some contribution from the Mo atomic orbitals. A combination of in-phase atomic orbitals of p$_\pi$(C) and d$_\delta$(Mo) from the C$_4$Mo$_2$ ring is observed in HOMO−21. As a result, the C$_4$Mo$_2$ ring is a six-electron six-center π-δ conjugation system, which comprise four π electrons from the 1,3-butadienyl fragment and two electrons from the Mo-Mo δ (d$_{xy}$-d$_{xy}$) bond. In addition, the p$_\pi$(C)-d$_\delta$(Mo) π conjugation within the C$_4$Mo$_2$ ring can be further corroborated by the smaller effective Mo–Mo bond order of 2.66 based on NBO analyses.[28]

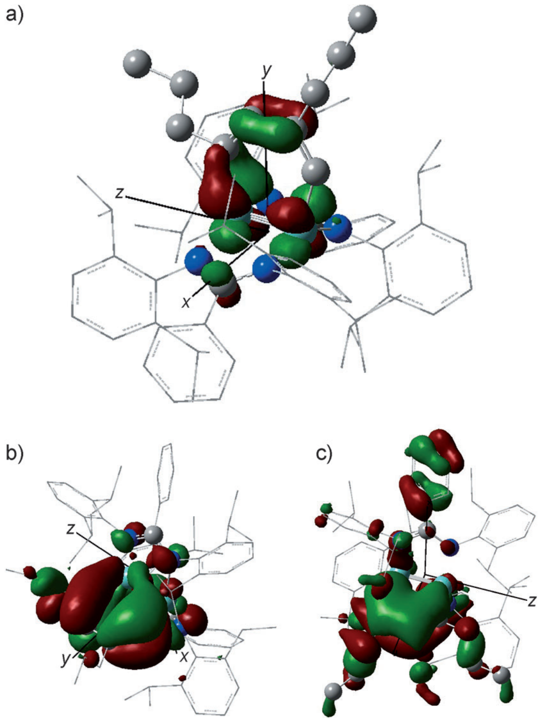
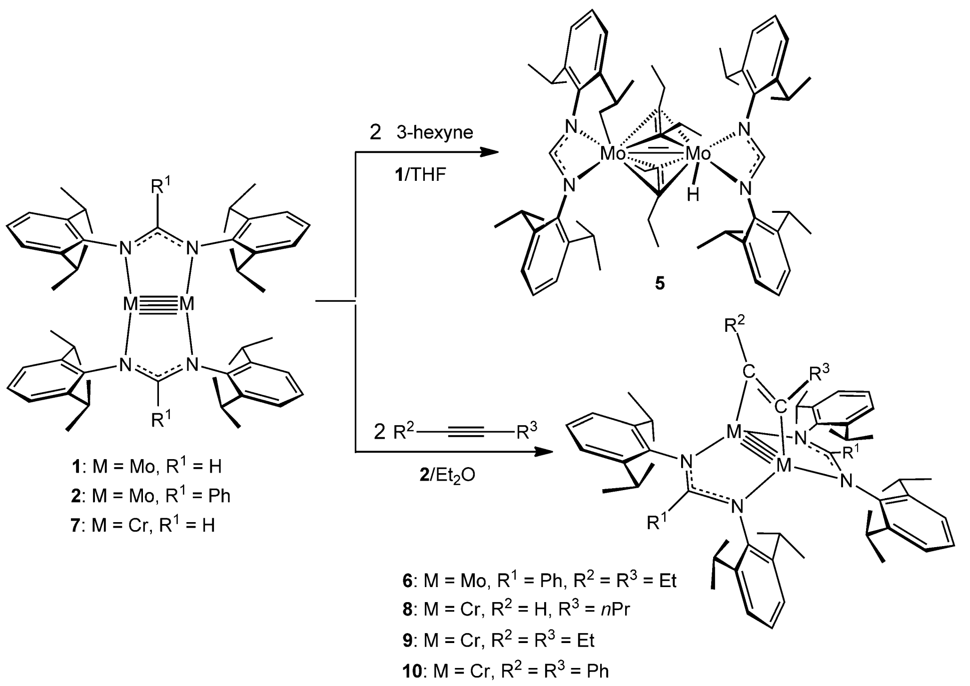


Figure 3. The frontier orbitals of **4**. a) HOMO. b) HOMO−1. c) HOMO−21.

From the mechanistic point of view of the metal-catalyzed alkyne [2+2+2] cycloaddition reactions, two monoynes react with the metal catalyst to engender the formation of an intermediate metallacyclopentadiene system.[7] We then wondered if **3** and **4** could subsequently react with another equivalent of an alkyne to produce a trisubstituted benzene. To our delight, **3** is indeed capable of catalyzing cyclotrimerization of 1-pentyne at ambient temperature, whereas **4** is inactive towards this reaction, presumably because of its more sterically congested ligands. When a diethyl ether solution of **3** was treated with 20 equivalents of 1-pentyne, 1,3,5-nPr$_3$C$_6$H$_3$ was obtained as the sole product in 88 % yield upon isolation. The same product in a high yield was also observed when 20 equivalents of 1-pentyne was added to a THF solution of **1**. The high regioselectivity of alkyne cyclotrimerization is controlled by the bulky amidinato ligands of **3**. A similar effect was also recently demonstrated by a bulky β-diketiminate-supported monovalent vanadium complex.[29]

The reactions of **1** and **2** with an internal alkyne, 3-hexyne, were also performed. In sharp contrast to the reactions of **1** and **2** with 1-pentyne giving the [2+2+2] cycloaddition products **3** and **4**, respectively, treatment of **1** in THF or **2** in diethyl ether with 2 equivalents of 3-hexyne afforded the diamagnetic [2+2] cycloaddition adducts Mo$_2$(H)(μ-κ^2:κ^2-EtCCEt)$_2$[κ^2-HC(N-2,6-iPr$_2$C$_6$H$_3$)$_2$][κ^3-HC(N-2,6-iPr$_2$C$_6$H$_3$)-(N-2-CH(CH$_2$)CH$_3$-6-iPrC$_6$H$_3$)] (**5**) and [Mo$_2$(μ-κ^2-EtCCEt)$_2$-{μ-κ^2-PhC(N-2,6-iPr$_2$C$_6$H$_3$)$_2$}$_2$] (**6**; Scheme 2), respectively. In addition, reactions of the quintuply bonded dimeric chromium amidinate [Cr$_2${μ-κ^2-HC(N-2,6-iPr$_2$C$_6$H$_3$)$_2$}$_2$] (**7**)[11d] with either internal or terminal alkynes exclusively yielded the [2+2] complexation adducts [Cr$_2$(μ-κ^2-R^{2}CCR^3)$_2${μ-κ^2-HC(N-2,6-iPr$_2$C$_6$H$_3$)$_2$}$_2$] (**8**: R^2 = H, R^3 = nPr; **9**: R^2 = R^3 = Et; **10**: R^2 = R^3 = Ph). Their formulations are evidenced by ^{1}H NMR spectroscopy. For example, two distinct ligand environments in **5** are supported by two resonance signals (δ = 7.58 and 7.55 ppm) corresponding to two methine (NCHN) protons of the formamidinate ligands. Two diastereotopic protons of the metalated CH(CH$_3$)CH_2Mo fragment appear at δ = 2.29 (dd) and 0.77 (dd) ppm and the singlet hydride signal is at δ = 2.44 ppm. In the room-temperature ^{1}H NMR spectrum of **6**, four unequivalent isopropyl groups are observed, with CH resonances at δ = 2–4 ppm and diastereotopic Me groups at δ = −0.46–1.59 ppm.

The molecular structures of **5**–**6** and **8**–**10** were determined by single-crystal X-ray diffraction,[17] and are depicted in the Supporting Information (Figures S1–5). The X-ray study of **5** indicates two terminally chelating amidinates and corroborates the presence of a pair of uncoupled and perpendicularly bridged 3-hexyne ligands. The Mo–Mo bond length of 2.4843(11) Å is in the double bond range.[30] The bridging central alkyne C–C bond lengths, 1.297(16) and 1.348(18) Å, are comparable to those in ethylene [1.339(1) Å][31] and the only two examples of bis(alkyne) ditungsten adducts.[32] The C-C-C angles of the coordinated alkynes are in the range of 137.5(12)–142.5(15)°, which are close to that of an sp^2-hybridized carbon atom, thus indicating extensive bonding to the dimolybdenum center. Another prominent structural feature in **5** is the presence of one cyclometalated amidinate ligand resulting from an intramolecular sp^3 C–H oxidative addition to two Mo atoms. The hydrido ligand (located from Fourier difference maps and



Scheme 2. Synthesis of complexes **5**–**6** and **8**–**10**.

refined by least-squares) is terminally bound to Mo1 with a Mo1–H bond length of 1.852(3) Å.

In contrast, all the other [2+2] cycloaddition alkyne adducts **6** and **8**–**10** exhibit a similar molecular structure: a central four-membered C_2Mo_2 metallacycle supported by two bridging amidinates. The most interesting structural feature in these adducts is the bridging alkyne ligands skewed with respect to the metal–metal bond axes. The formation of compounds **6** and **8**–**10** is essentially the result of the oxidative addition of **2** and **7** to the alkynes, which are reduced by two electrons. This reaction is supported by the elongation of the coordinated alkyne C–C bonds [**6**: 1.364(5) Å, **8**: 1.324(4) Å, **9**: 1.341(10) Å, **10**: 1.356(4) Å], and the hybridization around the carbon atoms changes from sp to sp^2, because the C-C-R bond angles decrease from 180° to between 125° and 130°. Furthermore, these complexes have very short metal–metal quadruple bond lengths of 2.0603(4) (**6**), 1.8054(6) (**8**), 1.7981(14) (**9**), and 1.8233(7) Å (**10**). In combination with Kempe and Theopold's analogues,[16] reactions between quintuply bonded dichromium complexes and internal or terminal alkynes solely yield the 1:1 [2+2] cycloaddition products.

In summary, we have demonstrated the recognition of the first two examples of 1,2-quadruply bonded dimolybdenum benzene derivatives **3** and **4** which result from 1-pentyne and quintuply bonded dimolybdenum amidinates reacting through a [2+2+2] cycloaddition reaction. The central aromatic six-membered C_4Mo_2 metallacycles in **3** and **4** comprise six-electron six-center d_δ-p_π conjugation systems, which involve Mo-Mo δ bonding. Mechanistically, in analogy to **6** and **8**–**10**, the [2+2] complexation adducts $[Mo_2(\mu\text{-}\kappa^2\text{-}n\text{PrCCH})\{\mu\text{-}\kappa^2\text{-RC(N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\}_2]$ (R = H, Ph) are intermediates, which subsequently react with another equivalent of a terminal alkyne through the [2+4] cycloaddition reaction to yield the [2+2+2] cycloaddition products **3** and **4**. Reactivity studies of **3** and **4** are currently underway and will be reported in due course.

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Keywords: aromaticity · cycloaddition · electronic structure · multiple bonds · molybdenum

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