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Chemistry of the Mo–Mo Triple Bond in the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_{12}H_{20})$ Metallacycle

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The reaction mechanisms for the acetylene exchange and the catalytic acetylene hydrogenation reactions based on $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC_2R)$ are based on an initial step of carbon monoxide dissociation to give an $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(RC_2R)$ intermediate.[1] In attempts to promote these reactions by photodissociation of the CO ligand, we found that irradiation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$ solutions in the presence of hydrogen and 3-hexyne generated $(C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$.[1] We describe here the thermal synthesis of this compound, its characterization and spectroscopic properties, and its chemistry derived from the formal Mo–Mo triple bond.

Experimental Section

Reagents and Procedures. See ref 1.

Preparation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$ (2.0212 g, 3.917×10^{-3} mol) and 3-hexyne (44 mL, 4.1×10^{-1} mol) were dissolved in 250 mL of mesitylene. The resulting solution was refluxed for 3 h, and then the volatile products were removed under vacuum. The resulting residue was dissolved in toluene and placed on top of a silica gel chromatography column. Elution with toluene developed a red band (starting material); continued elution with toluene developed and removed a green band. This last fraction was freed of solvent under vacuum. Recrystallization of the residue from hexane afforded air-sensitive crystals (yield 25%). Anal. Calcd for $C_{23}H_{30}Mo_2O$: C, 53.70; H, 5.84. Found: C, 53.18; H, 6.04. ^1H NMR (benzene-d_6): $\delta = 0.55$ (t, $J = 6.4$ Hz, 6 H), 1.45 (t, $J = 6.4$ Hz, 6 H), 1.8, 2.0, 2.35, and 2.65 (sextets of relative intensity 2 (2 H) with each sextet an overlapping doublet, $J \cong 13$ Hz, of quartets, $J = 6.4$ Hz), 4.75 (s, 5 H), ~5.2 (s, 5 H). IR (hexane solution): $\nu(CO)$ 1747.5 cm^{-1} (s).

Reaction of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$ with Donor Ligands and with Acid. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$ (0.1100 g, 2.14×10^{-4} mol) was dissolved in 20 mL of pentane. The resulting solution was placed in a reaction tube and then was subsequently cooled to −196 °C. The tube was evacuated and then filled to 1 atm with carbon monoxide. The tube and contents were allowed to warm to room temperature. On stirring at room temperature, the color of the solution changed; and, after 1 h, the color was red. At this point, the pentane solution was vacuum concentrated, filtered, and then cooled to −30 °C. Crystals formed, and these were collected (yield 70%) (air sensitive). Anal. Calcd for $C_{25}H_{30}Mo_2O_3$: C, 52.63; H, 5.32. Found: C, 52.86; H, 5.96. ^1H NMR (benzene-d_6): $\delta = 0.95$ (t, $J = 6.4$ Hz, 6 H), 1.10 (t, $J = 6.4$ Hz, 6 H), 2.2 (apparent decet, 4 H), 2.4 (apparent doublet of quartets, 4 H), 4.15 (s, 5 H), 4.85 (s, 5 H). CO ^{13}C NMR (toluene-d_8 + toluene) (20 °C): $\delta = 246.9$ (2 CO), 236.0 (1 CO). IR (hexane solution): $\nu(CO)$ 1965 (m), 1947.5 (m), 1920 (s), 1882.5 cm^{-1} (w).

$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$ (0.100 g, 1.95×10^{-4} mol) was dissolved in 20 mL of hexane. To this solution was added triethylphosphine (0.12 mL, 8.2×10^{-4} mol). The solution was stirred for 2 h at room temperature. After this period of time, the solvent was removed and the residue analyzed by infrared spectroscopy. No reaction had occurred. The reaction was repeated with trimethyl phosphite. No reaction took place.

$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$ (0.100 g, 1.95×10^{-4} mol) and *tert*-butyl isocyanide (0.33 g, 8.5×10^{-4} mol) were dissolved in 20 mL of hexane. The resulting solution was stirred at room temperature. After 1 h, the solution had changed from green to red. The solution was concentrated, filtered, and cooled to −30 °C. The slightly air-sensitive crystals that separated were collected (yield ~70%). Anal. Calcd for $C_{31}H_{48}N_2Mo_2O$: C, 58.24; H, 7.06; N, 4.12. Found: C, 58.50; H, 7.40; N, 4.16. ^1H NMR (benzene-d_6): $\delta \cong 1.15$ (s, 9 H), 1.20 (s, 9 H), 1.3 (complex mult), 1.45 (t, $J \cong 6$ Hz, 3 H), 4.35 (s, 5 H), 5.2 (s, 5 H). IR (hexane solution): $\nu(CO)$ and $\nu(CN)$ 1970, 1950, 1920 cm^{-1}.

$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$ (0.100 g, 1.95×10^{-4} mol) was dissolved in ether, and trifluoromethanesulfonic acid (5.84×10^{-2} g, 3.89×10^{-4} mol) was added. The mixture was stirred for 1 h at room temperature after which time there was an orange precipitate. The precipitate was collected by filtration. Anal. Calcd for $C_{25}H_{32}Mo_2F_6O_7S_2$: C, 36.86; H, 3.93; S, 7.86. Found: C, 37.12; H, 4.02; S, 7.59. ^1H NMR (dichloromethane-d_2): −8.93 (s) for the hydride resonance. The protonation reaction was not consistently reproducible and studies of this reaction continue.

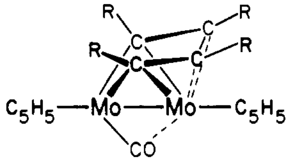
Reactions of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$ (0.050 g, 8.8×10^{-5} mol) were dissolved in heptane, and triethylphosphine (0.07 mL, 8.8×10^{-4} mol) was added. The resulting mixture was heated at reflux for 45 min. At the end of this time span, the volatile products were removed under vacuum, and the residue was analyzed by infrared spectroscopy. Analysis showed the presence of both $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$.

$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$ (0.050 g, 8.8×10^{-5} mol) was dissolved in heptane. The resulting solution was refluxed for 45 min. After this period of time, the solvent was removed. The residue was analyzed by infrared spectroscopy which showed the presence of both $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$.

Reaction with Alkynes. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$ (0.050 g, 8.8×10^{-5} mol) was dissolved in pentane, and 3-hexyne (0.07 mL, 8.8×10^{-4} mol) was added. The resulting solution was refluxed for 4 h. After this period of time, the volatile portions were removed. The residue was analyzed by infrared spectroscopy. Analysis showed the presence of both $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$.

Results and Discussion

The metallacycle derived from the coupling of two 3-hexyne ligands, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_{12}H_{20})$, was first obtained by irradiation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(3-hexyne) in the presence of hydrogen and 3-hexyne.[1] We showed that this complex can be readily generated by a thermal reaction at 160 °C—some 40 °C above the range at which acetylene ligand-exchange was reported[1] to be measurably fast for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC_2R)$ complexes and a free acetylene. There are two structurally established precedents for this metallacycle, namely, $(\eta^5\text{-}C_5H_5)_2Cr(CO)(C_6H_5C_2C_6H_5)_2$[2] and $(\eta^5\text{-}C_5H_5)_2Cr(CO)(C_6H_5C_2H)_2$[3] which have structure **1**.[4] Our hexyne-derived metallacycle had spectroscopic properties fully consistent with structure **1**. There was a single, low-energy CO stretching vibration at 1747.5 cm^{-1} due to a bridging (or semibridging) carbonyl ligand. The proton NMR spectrum of the hexyne-derived metallacycle had two sets of methylene resonances, and in each of these the methylene hydrogen atoms were diastereotopic, as is required of structure **1**.



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(1) S. Slater and E. L. Muetterties, *Inorg. Chem.*, **19**, 3337 (1980).

(2) S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, J. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 221 (1978).

(3) J. S. Bradley, *J. Organomet. Chem.*, **150**, C1 (1978).

(4) The C_5 centroids of the two cyclopentadienyl ligands are not collinear with the Cr–Cr bond vector presumably because of steric factors. In $(C_5H_5)_2Mo_2(CO)_4$ and another molybdenum metallacycle (derived from an acetylene and $(C_5H_5)_2Mo_2(CO)_4$), both of which have a formal triple Mo–Mo bond, the C_5 centroids are nearly colinear with the Mo–Mo bond vector. Hence, we expect our molybdenum species to have near colinearity of the two C_5 centroids and the two molybdenum atoms.

(5) The Cr–Cr distances in the two crystallographically determined structures are identical within experimental error, 2.337 (2) and 2.337 (3) Å.[2,3]

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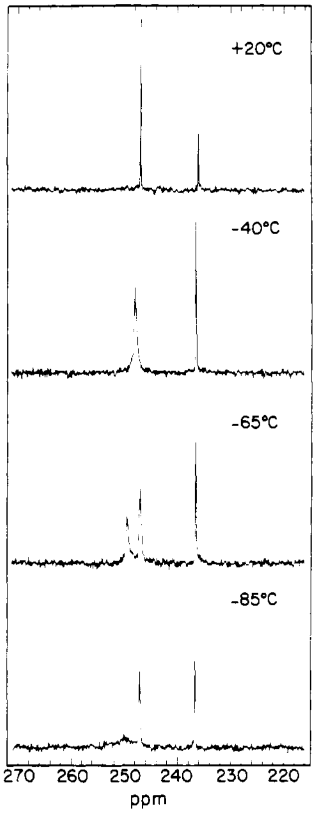
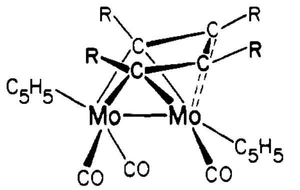


Figure 1. CO ^{13}C DNMR spectra for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_{12}H_{20})$ in a toluene solution.

Metallacycles of structural form **1** have a metal–metal bond of formal bond order 3; crystallographic data,[2,3] which established short metal–metal bond distances, support this characterization. We have explored the reactivity of this type of multiple bond for the metallacycle derived from 3-hexyne. Carbon monoxide rapidly converted the bridged monocarbonyl to the metal–metal singly bonded species $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_{12}H_{20})$, with two terminal carbonyl groups on one molybdenum atom and one terminal carbonyl on the other (see below); this reaction was thermally reversible. Analogous was the facile addition of two *tert*-butyl isocyanide ligands at 25 °C to give $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)[CNC(CH_3)_3]_2(C_{12}H_{20})$. In sharp contrast, neither triethylphosphine nor trimethyl phosphite reacted with the metallacycle. Molecular models clearly suggest that this lack of reaction is steric in origin. There is insufficient room to allow addition of bulky ligands without a large increase in the molybdenum–molybdenum separation. Protonation of the metal–metal triply bonded metallacycle did proceed rapidly to give the dimer $(\eta^5\text{-}C_5H_5)(H)_2Mo(\eta^5\text{-}C_5H_5)Mo(CO)(C_{12}H_{20})^{2+}$.

The tricarbonyl derived from **1** should have structure **2** with essentially a Mo–Mo formal bond order of 1. The infrared spectrum of a solution of **2** showed that all the carbonyls were terminal. All three CO environments should be differentiable by NMR barring dynamic processes that equilibrate CO sites. At ~-65 °C, the ^{13}C spectrum of **2** consisted of a three-line pattern consistent with the proposed structure (Figure 1). At higher temperatures, two of the three CO ligands underwent selective site exchange. These are assigned to CO ligands bonded to the same molybdenum atom.[6] Below -65 °C, one of the terminal CO resonances underwent extensive broadening; we propose no specific explanation for the broadening (either another dynamic process or a selective relaxation effect may be extant).



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The proton NMR spectrum of the isocyanide derivative, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)[CNC(CH_3)_3]_2(C_{12}H_{20})$, which should be isostructural with **2**, showed the presence of two $(CH_3)_3C$ proton resonances of nearly equal intensity. Irrespective of whether the isocyanide ligands are on the same or different molybdenum atoms, there would be two isocyanide ligand environments; hence, the NMR data do not establish which isomer predominates in solution. Because of overlap of some methylene and methyl (metallacycle) resonances, there was no obvious and unique interpretation of all the ^1H NMR resonances; note that all ethyl groups should be inequivalent and the protons in each CH_2 group should be diastereotopic, irregardless of the isocyanide ligand placement. The structure of the hydride derived from **1** by protonation was not defined by the spectroscopic data.

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Registry No. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$, 76136-86-2; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$, 76136-87-3; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)[CNC(CH_3)_3]_2(C_{12}H_{20})$, 76282-00-3; $(\eta^5\text{-}C_5H_5)(H)_2Mo(\eta^5\text{-}C_5H_5)Mo(CO)(C_{12}H_{20})^{2+}(F_3CSO_3^-)_2$, 76282-02-5; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$, 61373-51-1.

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(6) These assignments are based on several considerations. First, the ^{13}C chemical shift of the two CO ligands involved in the low-temperature exchange have very similar chemical shifts—a feature that might be expected for the two CO ligands on the same molybdenum atom (in a formal sense, the oxidation states of the two molybdenum atoms are different). Second, an intermetal (intramolecular) exchange should tend to involve all three CO ligands. CO exchange localized at a single metal site is a fairly common low-energy process in polynuclear complexes.[7]

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One-Electron Oxidations of Quadruply Bonded Molybdenum Dimers[1]

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The molybdenum(II) dimers $Mo_2(O_2CR)_4$ (R = alkyl or aryl) and $[Mo_2(SO_4)_4]^{4-}$ may be oxidized reversibly, both chemically and electrochemically, to $[Mo_2(O_2CR)_4]^+$ and $[Mo_2(SO_4)_4]^{3-}$.[4-9] These oxidations correspond to a change

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(1) Part 28 of the series entitled "Complex Halides of the Transition Metals".

(2) Undergraduate research participant from Kalamazoo College, Kalamazoo, Mich. 49001.

(3) Postdoctoral research associate, 1977–1978.

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(5) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 399.

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