

METAL—METAL MULTIPLE BONDS

IV *. THE CHEMISTRY OF BIS(CYCLOPENTADIENYLDICARBONYLMOLYBDENUM) ($Mo \equiv Mo$)

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Summary

The synthesis and chemistry of $Cp_2Mo_2(CO)_4$ (I) a complex containing a reactive $Mo \equiv Mo$ triple bond, are described. The formation of I in refluxing xylene is shown to occur via odd-electron intermediates from homolysis of the $Mo—Mo$ bond in the $Cp_2Mo_2(CO)_6$ precursor. Numerous soft nucleophiles add to I to give complexes, e.g., *trans*- $(CpMo(CO)_2L)_2$ ($L = Ph_3P, P(OMe)_3$), $(\mu-R_2C_2R')Cp_2Mo_2(CO)_4$, and $(\mu-SR)_2Cp_2Mo_2(CO)_4$. $(Et_4N)(Cp_2Mo_2(CO)_4CN)$ may be isolated from the reaction of cyanide ion with I. Iodine and hydrogen chloride react to give $Cp_2Mo_2(CO)_4I_2$ and $(\mu-H)(\mu-Cl)Cp_2Mo_2(CO)_4$, respectively. Silver and mercuric ions are reduced to the metal by I, but Ph_2Hg gives $(CpMo(CO)_3)_2Hg$ in addition to metallic mercury. With tetracyanoethylene, I forms $[CpMo(CO)_4]^+[TCNE]^-$. Complex I mimics the reaction of acetylenes with L_4Pt ($L = Ph_3P$) and forms the triangulo-cluster, $(\mu-L_2Pt)Cp_2Mo_2(CO)_4$. With $Na_2Fe(CO)_4$, $Cp_2Mo_2(CO)_4I_2$ forms the analogous cluster, $(\mu-Fe(CO)_4)Cp_2Mo_2(CO)_4$. By electron counting rules, these clusters should contain $Mo=Mo$ double bonds. Evidence is presented which indicates I and $Co_2(CO)_8$ form an unstable tetrahedrane cluster. At $110^\circ C$ in toluene, I may reversibly dimerize to give a tetrahedrane Mo_4 -cluster, as shown by scrambling experiments. Complex I reacts slowly with $Mn_2(CO)_{10}$ to give $CpMo(CO)_3Mn(CO)_5$ as the only isolable mixed-metal product.

Introduction

The concept of metal—metal multiple bonds dates from 1964 when Cotton proposed a metal—metal quadruple bond to explain the short M—M bond dis-

* For parts I—III see ref. 1.

tance, the eclipsed geometry and diamagnetism of a group of complexes of the general formula, $L_4MML_4^{n-}$ [2]. Since that time, a great deal of work has been done in the areas of preparation and structural and spectroscopic characterization of new complexes with metal-metal multiple bonds [3-18].

The most common reaction type of complexes with M-M quadruple bonds is ligand substitution [3,13,14]. In these reactions, the M_2L_8 unit almost acts as an eight coordinate, mononuclear complex; i.e., the M-M multiple bond does not participate in the reactions. Occasionally, the M-M bond is completely disrupted [3], although in a few cases, the M-M bond order is reduced upon reaction, but the dimeric unit persists [3,16,19-21].

Although less extensive at present, the chemistry of triply-bonded dimers of the type, $L_3M\equiv ML_3$, seems to parallel that of the quadruply-bonded analogs, $L_4MML_4^{n-}$, in that ligand substitution with the $M\equiv M$ bond not participating seems to be the dominant mode of reaction*. Similarly, the complexes, $(C_5Me_5)_2M_2(CO)_4$ (M = Cr, Mo), gave no reactions in which a reagent added to the π -components of the $M\equiv M$ triple bond and maintained the M-M σ -bond [24]. The parent chromium complex, $Cp_2Cr_2(CO)_4$, showed enhanced reactivity toward phosphines as compared to the permethyl complex, but again no products were isolated in which the dimeric Cr_2 unit was maintained [25].

However, we have reported [1a] that the complex, $Cp_2Mo_2(CO)_4$, unlike all the other complexes with M-M multiple bonds reported to date, shows a rich chemistry involving the π -components of the $Mo\equiv Mo$ triple bond. Subsequently, other ligands, viz. allene and dimethylaminocyanamide, have been shown to add to the $Mo\equiv Mo$ triple bond of $Cp_2Mo_2(CO)_4$ [26,27].

The importance of multiple bonds in organic chemistry lies not in the bond order, per se, but in their reactivity. Double and triple bonds are reactive functionalities, capable of many transformations. Such functional group transformations have traditionally been denied to the inorganic chemist due to the unavailability of reactive multiple bonds between heavier elements. Hence, the observation that the multiple bonds in $Cp_2Mo_2(CO)_4$ are capable of undergoing transformations while maintaining the basic structure is of importance. For example, the $Mo\equiv Mo$ unit may in principle be oligomerized to clusters, and the adjacent reactive centers can lead to reactivity not observed with mononuclear or coordinatively saturated dinuclear complexes. In this paper, we report our observations on the reactivity of $Cp_2Mo_2(CO)_4$ (I), and some of the complexes derived from I.

Experimental

All synthetic manipulations were performed under nitrogen or in vacuum using a dual nitrogen/vacuum manifold and standard Schlenck techniques. Ether solvents were dried and deoxygenated by distillation from potassium/benzophenone directly into the reaction flask. IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer, mass spectra on an AEI MS902 spectrometer with a direct inlet. Elemental analyses were performed by Galbraith

* Recently, complexes of the type $M_2(OR)_6$ have been shown to add reversibly phosphines and amines, but the $M\equiv M$ triple bond does not appear to participate directly in these reactions [23].

Laboratories, Knoxville, Tennessee. All melting points were obtained in sealed, evacuated capillaries.

Bis(cyclopentadienyldicarbonylmolybdenum) (Mo≡Mo) (I). A 500 ml side-arm flask was charged with 20.0 g of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ and 200 ml of toluene. The flask was fitted with a reflux condenser and the contents refluxed for 12 h with magnetic stirring, a slow N_2 -purge being maintained through the side-arm. After cooling to room temperature, the solvent was stripped away, leaving a red-brown solid which was transferred to a Soxhlet thimble. The thimble was then placed atop another thimble containing Florisil in a Soxhlet extractor and extracted with 350 ml of methylene chloride until the extracts were nearly colorless. The thimble containing the Florisil adsorbs some dark, sparingly soluble materials which appear to be molybdenum clusters [28]. One hundred ml of 1-octene were added to the methylene chloride extracts and the latter solvent removed under aspirator vacuum to give a well crystallized, maroon solid. (Heptane, etc. may be used in place of 1-octene, but produces poorer quality crystals.) The yields average 87–93%. Small amounts of unreacted $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, best detected by NMR ($\delta(\text{Cp}_2\text{Mo}_2(\text{CO})_6)$ 4.67 ppm vs. δ (I) 4.73 ppm), may be removed with difficulty by careful column chromatography over Florisil using degassed methylene chloride eluant; but it is easier to simply reheat the mixture until all $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ has been converted. Complex I is air-stable as a pure solid, but in solution it is rapidly oxidized to a dark, insoluble powder, releasing CO which reacts with I to give $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ [29].

Bis(methylcyclopentadienyldicarbonylmolybdenum) (Mo≡Mo). A solution of 2.0 g of $(\text{C}_5\text{H}_4\text{Me})_2\text{Mo}_2(\text{CO})_6$ in 30 ml of toluene was refluxed 10 h. The solvent was stripped and the resultant solid dissolved in methylene chloride, the solution filtered, and heptane was then added to the filtrate. The CH_2Cl_2 was pumped off under reduced pressure, giving orange crystals which were washed with petroleum ether and dried (yield 90%).

Exchange reaction between II and III and I and VI. A solution of 0.5 g of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ (III) and 0.5 g of $(\text{C}_5\text{H}_4\text{Me})_2\text{Mo}_2(\text{CO})_6$ (II) in 20 ml of toluene were refluxed for 18 h, and the solvent removed. The resulting solid was analyzed by mass spectrometry (inlet temperature 150°C , ionizing energy 70 eV) by taking the relative peak heights of the respective parent ions to be proportional to the relative amounts of compounds, $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ (I), $\text{Cp}'_2\text{Mo}_2(\text{CO})_4$ (VI, $\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$) and $\text{Cp}'\text{CpMo}_2(\text{CO})_4$ (VII), present in the mixture. Analysis of mixtures of I and VI and II and III verified that no scrambling occurs in the mass spectrometer and established the proportionality constants for the relative intensities of I and VI (i.e., a 50/50 mixture of I and VI gives a slightly higher relative peak height for VI due to its slightly greater volatility). A small complication exists in that the m/e of the $\text{Cp}'_2\text{Mo}_2(\text{CO})_3^+$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$) ion is identical to the m/e of the $\text{Cp}_2\text{Mo}_2(\text{CO})_4^+$ ion. Thus, the m/e 434 peak current is the sum of two ion currents. The spectrum of pure $\text{Cp}'_2\text{Mo}_2(\text{CO})_4$ showed that $I(\text{Cp}'_2\text{Mo}_2(\text{CO})_3^+) = 0.24 I(\text{Cp}'_2\text{Mo}_2(\text{CO})_4^+)$ and this ratio can be used to resolve the m/e 434 peak height into its two components (see discussion).

The scrambling between pure $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ (I) and $(\text{C}_5\text{H}_4\text{Me})_2\text{Mo}_2(\text{CO})_4$ (VI) was determined in a similar fashion: 0.5 g of each complex was dissolved in 20 ml of toluene which was refluxed under N_2 . One ml aliquots were periodically withdrawn, the solvent removed, and the solids analyzed as above.

Addition of triphenylphosphine and trimethyl phosphite to $Cp_2Mo_2(CO)_4$. To 0.35 g (0.8 mmol) of $Cp_2Mo_2(CO)_4$ dissolved in 20 ml of toluene was added 0.52 g (2.0 mmol) of Ph_3P in 10 ml of toluene. The solution turned cherry red and a red solid slowly precipitated. After 30 min, the solid was filtered off and washed with petroleum ether. The IR spectrum of the complex was that reported for the complex prepared from $Cp_2Mo_2(CO)_6$ and triphenylphosphine [30].

A solution of 0.33 g (1.3 mmol) of Ph_3P in 10 ml of toluene was added slowly to 0.55 g (1.3 mmol) of $Cp_2Mo_2(CO)_4$ and the mixture stirred for 30 min, during which time a red solid precipitated. The red solid was filtered off and shown to be identical to the bis-adduct (see above). The yield of $Cp_2Mo_2(CO)_4L_2$ was 0.35 g or 41% of the added $Cp_2Mo_2(CO)_4$. The filtrate was shown by IR to contain unreacted $Cp_2Mo_2(CO)_4$.

The bis(trimethyl phosphite) derivative precipitates as a red solid from solutions of $Cp_2Mo_2(CO)_4$ (0.17 g in 20 ml toluene) when 2/1 molar ratios of $P(OMe)_3$ are added.

Addition of acetylenes to $Cp_2Mo_2(CO)_4$. Acetylene was bubbled through a solution of $Cp_2Mo_2(CO)_4$ (0.3 g) in 20 ml of toluene for 30 min, during which time the color of the solution turned from brown-red to red. The solvent was removed under vacuum and the residue extracted with petroleum ether to give a red solution. Cooling the solution to $-10^\circ C$ gave the crystalline adduct, $Cp_2Mo_2(CO)_4(C_2H_2)$.

The phenylacetylene adduct was prepared by an analogous procedure from 0.5 g (1.2 mmol) of I and an equimolar quantity of phenylacetylene. The work-up procedure was identical to that above. The IR spectra of these acetylene adducts are similar in the carbonyl region to that of $Cp_2Mo_2(CO)_4(Ph_2C_2)$ [31].

Reaction of $Cp_2Mo_2(CO)_4$ and dialkyl disulfides. To 1.0 g (2.3 mmol) of I in 50 ml of toluene was added 0.2 ml (2.3 mmol) of dimethyl disulfide (Me_2S_2) and the mixture was allowed to stir overnight. The toluene was stripped off under reduced pressure and the remaining solid taken up in CH_2Cl_2 and chromatographed over Florisil to give three bands: red, brown, and brown in order of elution. The first band was shown to be $Cp_2Mo_2(CO)_6$. The second band was not characterized due to the very small amounts present. The third band is the major product, and the solid obtained from it was recrystallized twice from CH_2Cl_2 /heptane. The physical properties of the complex are consistent with those reported for $Cp_2Mo_2(CO)_4(SMe)_2$ [32].

The diphenyl disulfide complex [33] was prepared and purified in an entirely analogous fashion.

Tetraethylammonium bis(cyclopentadienyldicarbonyl)cyanodimolybdenum(-I). A suspension of 0.5 g (1.2 mmol) of I and 0.14 g (2.3 mmol) of KCN in 10 ml of methanol was stirred at $-10^\circ C$ for 1 h, during which time the solution became dark green. A solution of 0.6 g of $(Et_4N)Br$ in 5 ml of methanol was then added and the resultant green solid filtered and washed with ether. The solid was recrystallized by dissolving it in a minimum amount of acetone and cooling the acetone to $-78^\circ C$. In solution at room temperature, the green complex rapidly decomposes to $CpMo(CO)_3^-$ and other, unidentified products.

Bis(cyclopentadienyl)tricarbonyl(triphenylphosphine)dimolybdenum ($Mo\equiv Mo$). A suspension of 0.2 g of $Cp_2Mo_2(CO)_4(PPh_3)_2$ in 20 ml of toluene was heated to reflux. The solid slowly dissolved to give a dark solution. After

1.5 h, the solution was allowed to cool and the toluene stripped off. The resultant red oil was chromatographed over a Florisil column with toluene eluant to give two bands, purple and red, in order of elution. The red band was unreacted starting material. The purple eluate afforded a purple solid which was recrystallized from CH_2Cl_2 /heptane. The parent ion of the purple solid was observed at m/e 668 with peaks corresponding to consecutive loss of three carbonyls and a Ph_3P ligand. The purple solid, and especially its solutions, are light sensitive. All manipulations of the solutions during the synthesis and purification were done with exclusion of as much light as possible (all glassware was wrapped with Al-foil).

Reaction of iodine with $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. A solution of 2.9 g (11.3 mmol) of I_2 in 250 ml of toluene was added dropwise over a period of 2 h to a suspension of 4.9 g (11.3 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ in 50 ml of toluene at -24°C . After the addition was complete the mixture was stirred for 30 min at -24°C . Filtration of the cold suspension yielded 5.4 g (70%) of red-brown solid which is pure enough for most preparative purposes. Analytical samples were obtained by recrystallizing the solid from CH_2Cl_2 at -78°C . If the CH_2Cl_2 solutions are never allowed to warm up above 0°C , a red-brown solid is obtained. If allowed to warm to room temperature the color of the solution rapidly changes to violet and a violet solid is then isolated upon cooling to -78°C . Both forms have the same elemental analyses. The parent ion was observed at m/e 688, and fragments corresponding to the loss of four carbonyls and two iodines were also observed. In the solid state, $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{I}_2$ may be handled briefly in air, although solutions are rapidly oxidized. As a solid, the complex appears to be thermally stable, but solutions decompose with half-life of about 4.5 h.

(μ -Chloro)(μ -hydrido)bis(cyclopentadienyldicarbonylmolybdenum) (Mo—Mo). A 110 ml flask was filled to a pressure of 710 Torr with anhydrous hydrogen chloride (4.2 mmol). This flask was connected via a glass stopcock to a second flask charged with 1.8 g (4.2 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ in 30 ml of CH_2Cl_2 . The CH_2Cl_2 solution was degassed by the freeze-thaw method, then allowed to warm to -11°C under vacuum, the connecting stopcock was then opened and the HCl allowed to diffuse into the CH_2Cl_2 solution while the latter was stirred at -11°C . After 1 h, heptane was added to the mixture and some of the CH_2Cl_2 removed under vacuum. The resulting brown solid was isolated by filtration, washed with petroleum ether and dried under vacuum. The parent ion at m/e 470 was observed, as were fragments due to sequential loss of four carbonyls and HCl. The HCl adduct has limited stability in solution, rapidly decomposing to $\text{CpMo}(\text{CO})_3\text{Cl}$, $\text{CpMo}(\text{CO})_3\text{H}$, and other, unidentified solids.

Reactions of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ with Ph_2Hg . A solution of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ (0.8 g, 1.8 mmol) and diphenylmercury (0.6 g, 1.8 mmol) in 30 ml of CH_2Cl_2 was allowed to stir overnight. Filtration yielded some dark solid and very small droplets of mercury; the latter was sublimed off the fritte giving 0.16 g (47%) of metallic mercury. The CH_2Cl_2 -filtrate was concentrated and cooled to -78°C , giving a yellow solid, the IR, NMR, and melting points of which was identical to those of $(\text{CpMo}(\text{CO})_3)_2\text{Hg}$ [33].

Reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ with tetracyanoethylene. A suspension of 0.3 g (0.7 mmol) of I and 0.2 g (0.7 mmol) of TCNE in 50 ml of pentane was stirred overnight to give a dark-brown precipitate. The mixture was filtered and the

solid washed with CH_2Cl_2 until the washings were colorless. The solid was then vacuum dried.

Reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ with tetrakis(triphenylphosphine)platinum(0). To a mixture of 0.30 g (0.24 mmol) of $(\text{Ph}_3\text{P})_4\text{Pt}$ and 0.21 g (0.48 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ was added 60 ml of toluene. The mixture was then stirred for 2 h, during which time the color gradually changed from brown to red. The volume of the toluene was reduced to 20 ml under vacuum and the mixture filtered to remove $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PPh}_3)_2$. The toluene was pumped off the filtrate and the resulting solid extracted with heptane. The extract was cooled to -78°C to yield a red solid which decomposes at room temperature within 24 h.

Reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{I}_2$ with $\text{Na}_2\text{Fe}(\text{CO})_4$. A solution of 0.7 g (1.0 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{I}_2$ in 10 ml of dry THF was added to 0.2 g (1.0 mmol) of $\text{Na}_2\text{Fe}(\text{CO})_4$ suspended in 20 ml of THF. The off-white, iron dianion dissolves as the reaction proceeds to give a red solution. The THF was removed under vacuum to give a red solid which was treated with CH_2Cl_2 . Heptane was added to the filtered CH_2Cl_2 solution and some of the CH_2Cl_2 was pumped off, giving a red solid which was washed with dry, degassed pentane and dried. This solid is extremely reactive to oxygen and thermally decomposes within a day at room temperature. A sample of the solid which had thermally decomposed was chromatographed over Florisil and the two fractions identified as $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Fe}_3(\text{CO})_{12}$ [34].

Reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$. A mixture of 0.8 g of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and 0.6 g of $\text{Co}_2(\text{CO})_8$ in 20 ml of toluene was stirred for 4 h at room temperature. The toluene was then removed under vacuum to give a violet solid which was purified by column chromatography over Florisil. Three bands were obtained: black, red and red, in order of elution. The first band yielded $\text{Co}_4(\text{CO})_{12}$ [34] and the third $\text{Cp}_2\text{Mo}_2(\text{CO})_6$. The spectroscopic properties of the red solid obtained from the second band indicated the composition, $\text{CpMo}(\text{CO})_3\text{Co}(\text{CO})_4$ (parent ion and loss of seven carbonyls in the mass spectrum, IR, and NMR). However, satisfactory elemental analysis could not be obtained, apparently as a result of decomposition in transit. Since this complex has not been prepared previously, we synthesized it by an alternate route.

(Tetracarbonylcobalt)(cyclopentadienyltricarbonylmolybdenum) (Co—Mo). Dicobalt octacarbonyl (0.25 g) was reduced in THF with excess sodium foil (0.5 g). After 30 min, the excess foil was removed by filtration and 0.4 g of $\text{CpMo}(\text{CO})_3\text{Cl}$ in 20 ml THF was added to the pale yellow solution of $\text{Co}(\text{CO})_4^-$. The mixture turned red and was allowed to stir for 30 min. The THF was then pumped off and the remaining solid treated with petroleum ether, and filtered. The filtrate was cooled to -78°C to give a red solid identical to that obtained in the previous experiment.

Reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ with $\text{Mn}_2(\text{CO})_{10}$. A mixture of 0.35 g (0.8 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and 0.3 g (0.8 mmol) of $\text{Mn}_2(\text{CO})_{10}$ in 30 ml of toluene was heated to reflux for 8 h. The solvent was then removed under vacuum and the resultant solid chromatographed over Florisil to give three bands. The first yellow band was eluted with petroleum ether and the resulting solid shown to be unreacted $\text{Mn}_2(\text{CO})_{10}$. The second and third bands, orange and red, respectively, were eluted with CH_2Cl_2 , and shown to be $\text{CpMo}(\text{CO})_3\text{Mn}(\text{CO})_5$ [35] and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, respectively, by comparison of the properties (mass spectrum, IR) with those reported.

TABLE 1
ANALYTICAL DATA FOR COMPLEXES (Found (calcd.) (%))

Compound	C	H	Compound	C	H
$Cp_2Mo_2(CO)_4$ ($C_{14}H_{10}Mo_2O_4$)	38.73 (38.74)	2.33 (2.33)	$Cp_2Mo_2(CO)_4(SMe)_2$ ($C_{16}H_{16}Mo_2O_4S_2$)	36.67 (36.38)	3.02 (3.06)
$Cp'_2Mo_2(CO)_4^a$ ($C_{16}H_{14}Me_2O_4$)	41.48 (41.58)	3.20 (3.06)	$Cp_2Mo_2(CO)_4(SPh)_2$ ($C_{26}H_{20}Mo_2O_4S_2$)	47.58 (47.87)	3.28 (3.09)
$Cp_2Mo_2(CO)_4(PPh_3)_2$ ($C_{50}H_{40}Mo_2O_4P_2$)	61.90 (62.65)	4.20 (4.21)	$Cp_2Mo_2(CO)_3(PPh_3)$ ($C_{31}H_{25}Mo_2O_3P$)	56.69 (55.71)	3.86 (3.78)
$Cp_2Mo_2(CO)_4(P(OMe)_3)_2$ ($C_{20}H_{28}Mo_2O_{10}P_2$)	35.66 (35.21)	4.25 (4.14)	$Cp_2Mo_2(CO)_4(HCl)$ ($C_{14}H_{11}ClMo_2O_4$)	35.45 (35.74)	2.40 (2.36)
$Cp_2Mo_2(CO)_4(C_2H_2)$ ($C_{16}H_{12}Mo_2O_4$)	42.09 (41.77)	2.63 (2.63)			
Compound	C	H	Mo	I/N	O ^b
$Cp_2Mo_2(CO)_4I_2$ $C_{14}H_{10}I_2Mo_2O_4$	24.37 (24.45)	1.50 (1.47)	27.22 (27.90)	37.22 (36.90)	9.69 (9.29)
$[CpMo(CO)_4][TCNE]$ $C_{15}H_5MoN_4O_4$	45.78 (44.92)	1.32 (1.26)	23.44 (23.92)	13.54 (13.97)	15.92 (15.96)

^a $Cp' = (\pi-C_5H_4Me)$. ^b Oxygen by difference.

TABLE 2
SELECTED PHYSICAL CONSTANTS OF THE NEW COMPLEXES PREPARED IN THIS STUDY

Compound	M.p. (°C)	NMR ^a (J, Hz)	IR (cm ⁻¹) ^b
$Cp_2Mo_2(CO)_4$	215–217 dec.	4.67	1900, 1850 (P)
$Cp'_2Mo_2(CO)_4^c$	162–165	Cp: 5.42, Me: 8.30	1890, 1865 (P)
$Cp_2Mo_2(CO)_4(PPh_3)_2$	225–230 dec.		1840 (MC)
$Cp_2Mo_2(CO)_4(P(OMe)_3)_2$	185–186	Cp: 4.98 ^d (1.5); Me: 6.32 ^d (11)	1850 (MC)
$Cp_2Mo_2(CO)_4(C_2H_2)$	147–149	Cp: 4.69; CH: 5.17	2000, 1920, 1850 (P)
$Cp_2Mo_2(CO)_4(PhC_2H)$	134–136	Cp: 4.78; CH: 4.65; Ph: 2.95 ^m	2000, 1930, 1850 (P)
$(Et_4N)(Cp_2Mo_2(CO)_4CN)$	180–185 dec.	Cp: 4.83; CH ₂ : 6.43 ^q ; CH ₃ : 8.56 ^t	1880(sh), 1860, 1810, 1780 (MC)
$Cp_2Mo_2(CO)_3(PPh_3)$	225–230	Cp: 5.42 ^d (2), 5.33; Ph: 2.57 ^m	1875, 1780 (MC)
$Cp_2Mo_2(CO)_4I_2$	129–130 dec.	5.18	1950, 1940, 1860 (P)
$CpMo_2(CO)_4(HCl)$	260–265	Cp: 5.27; H, 19.8	1965, 1895 (P)
$[CpMo(CO)_4]^+[TCNE]^-$	300 dec.		2200, 2120, 2050, 1975 (KBr)
$Cp_2Mo_2(CO)_4Pt(PPh_3)_2$		Cp: 4.80; Ph, 2.90 ^m	1980, 1800 (P)
$Cp_2Mo_2(CO)_4Fe(CO)_4$	280 dec.	5.33	2050, 2020, 2000, 1900, 1875 (P)
$CpMo(CO)_3Co(CO)_4$	65–66	5.48	2080, 2050, 2040, 2010, 1990(sh), 1985, 1950, 1940 (P)

^a τ -values (ppm). All peaks are singlets unless specified otherwise: d, doublet; t, triplet; q, quartet; m, unresolved multiplet. ^b Solvent or phase in parentheses: P = pentane, MC = methylene chloride. ^c $Cp' = \pi-C_5H_4Me$.

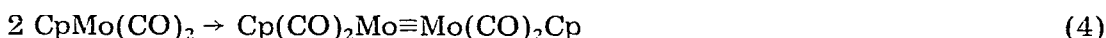
Results

The elemental analyses for the compounds prepared in this study are collected in Table 1. Table 2 gives some selected spectral parameters and the melting points of the new complexes.

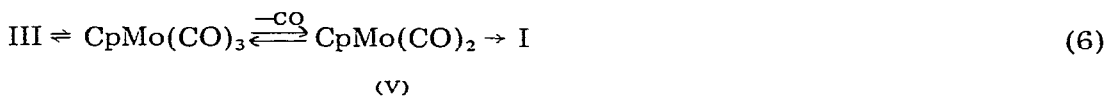
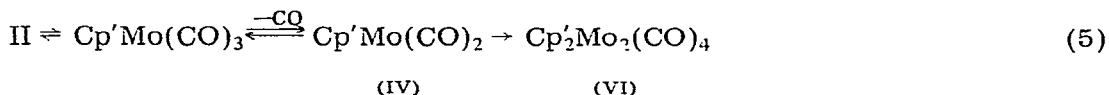
Discussion

A. The formation of $Cp_2Mo_2(CO)_4$ (I)

Complex I was first isolated by Job and Curtis from the photolysis of $CpMo(CO)_3GeMe_2(C_2H_5)$ [36]. Later, Ginley and Wrighton [29] observed the formation of I during the photolysis of $Cp_2Mo_2(CO)_6$; and, simultaneously, we reported that the thermolysis of $Cp_2Mo(CO)_6$ at 100–120°C in toluene or xylene solutions also gives I [1a]. Ginley and Wrighton [29] suggested that the formation of I involved the photodissociation of the Mo—Mo bond of $Cp_2Mo_2(CO)_6$. We had also observed erratic yields of I when reaction 1 was carried out in certain solvents, e.g., 1-octene, and suggested that the thermal reaction might also proceed by radical pathways (eq. 2–4).



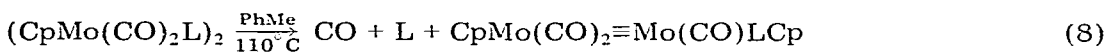
We have now established that the thermal formation of I does in fact proceed simultaneously with the rupture of the Mo—Mo bond of the $Cp_2Mo_2(CO)_6$ precursor. The labelled complex, $Cp'_2Mo_2(CO)_6$ (II, $Cp' = C_5H_4Me$), and $Cp_2Mo_2(CO)_6$ (III) were heated together. No formation of the “mixed” species, $CpCp'Mo_2(CO)_6$, was observed until CO evolution began (eq. 1). Upon completion of the reaction, the three possible complexes: I, VI and VII were present.



The solubilities of the complexes I, VI and VII were so similar that they could not be separated, and their IR and NMR spectra were so nearly identical that the only feasible recourse for analyzing the mixture was by mass spectrometry. Separate experiments showed that the relative peak heights of the parent ions of I and VI were proportional to their relative concentrations, and it seems safe to assume the same holds for the “mixed” complex VII. The degree of scrambling may be expressed as an “equilibrium constant”, $K = [VII]^2/[I][VI]$. The experimental value found for K was 1.7. A completely random scrambling has $K = 4.0$. Separate experiments also showed that there was no detectable

scrambling between II and III or I and VI in the mass spectrometer. We have also demonstrated that I and VI exchange only very slowly under the conditions of reaction 1 (see below). Since Cp dissociation is extremely unlikely, these data show conclusively that Mo—Mo bond homolysis occurs simultaneously with CO evolution and formation of I. There are now several reports dealing with M—M bond homolysis during ligand substitution on dinuclear complexes and the evidence indicates that the carbonyl ligands in the radicals generated by M—M bond scission are much more labile than in the parent dinuclear complex [37—41]. Adams et al. have also shown that the Cr—Cr bond in $\text{Cp}_2\text{Cr}_2(\text{CO})_6$ dissociates in solution [42].

It may be noted here that refluxing a toluene solution of $(\text{CpMo}(\text{CO})_2\text{L})_2$ ($\text{L} = \text{Ph}_3\text{P}$) gives the complex VIII which should contain a Mo≡Mo triple bond (eq. 8).

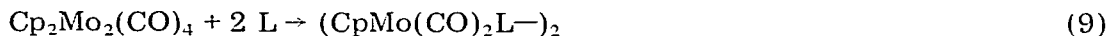


(VIII)

The Cp resonances appear at δ 5.42 and 5.33 ppm in the NMR spectrum of VIII. The former peak is split into a doublet (J 2 Hz) due to coupling with the phosphorus of the ligand. No $\text{Cp}_2\text{Mo}_2(\text{CO})_2\text{L}_2$ could be isolated from the reaction mixture. It may be that recombination of two $\text{CpMo}(\text{CO})\text{L}$ radicals is slow due to steric hindrance.

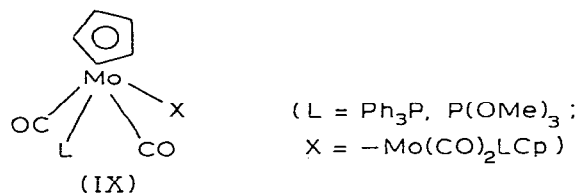
B. Addition of nucleophiles to the Mo≡Mo bond

Soft nucleophiles, e.g. phosphines and phosphites add rapidly to the Mo≡Mo triple bond of I at room temperature (eq. 9).



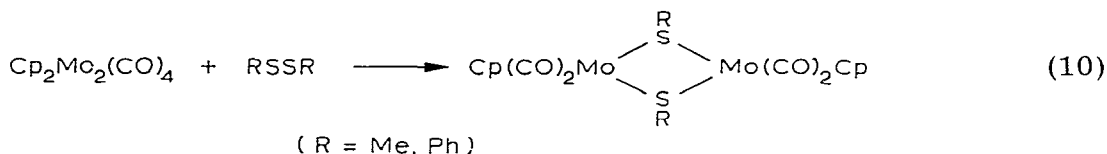
($\text{L} = \text{Ph}_3\text{P}, \text{P}(\text{OMe})_3$)

The phosphine or phosphite ligands displace the semi-bridging carbonyls from the opposite side of the Mo≡Mo bond to give only the *trans*-isomer IX [1c]. The stereo-chemistry was established by the ratio of the intensities of the



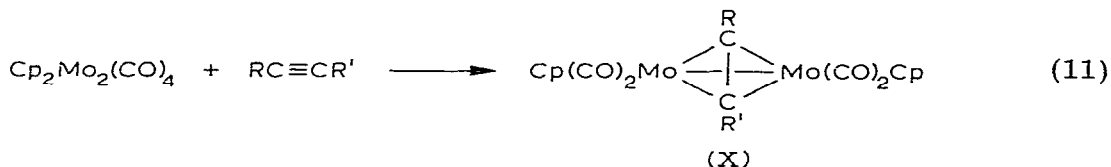
asymmetric and symmetric CO stretches, this ratio being a function of the angle between the carbonyls which is $>100^\circ$ for the *trans*-isomer and ca. 80° for the *cis* [30,43]. The observed ratio, $I(a)/I(s)$, for IX gave OC—M—CO angles of ca. 120° .

Similarly, disulfides add rapidly to I to give sulfido-bridged complexes (eq. 10).



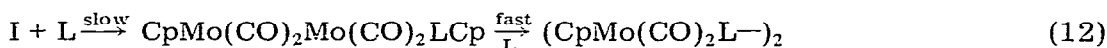
These complexes are identical to those obtained from disulfides and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ at higher temperatures [30,32,44,45]; temperatures at which $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ is converted into I. In fact, it is probably safe to say that all carbonyl substitution reactions on $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ which give neutral adducts have actually involved either I or the 15 electron radical V.

Acetylenes also add to the $\text{Mo}\equiv\text{Mo}$ triple bond to give tetrahedrane complexes X. When $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$, the PMR signals from the Cp groups remained equiva-

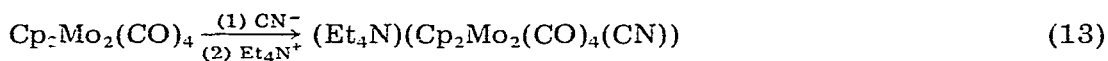


lent, thus establishing the symmetrical, tetrahedrane coordination in X. Since our original report, several other acetylene adducts have been prepared and their molecular structures determined [46,47].

Allowing 1/1 molar ratios of I and triphenylphosphine or trimethylphosphite to react gave only IX and unreacted I. This behavior may be explained by observing that a mono-substituted product has one Mo-atom in a 16-electron configuration which should pick up the second mol of nucleophile very rapidly (eq. 12).



It may also be noted that acetylenes, allene [26], and aminocyanamides [27] act as bidentate ligands in their complexes with I. It was therefore somewhat surprising to find that CN^- reacts with I to give a complex tentatively identified as XI (eq. 13). The ratio of Et_4N^+ to Cp (1/2) is firmly established by NMR. The deep green complex is unstable, decomposing rapidly in solution to $\text{CpMo}(\text{CO})_3^-$ and unidentified insoluble materials. The Cp-resonance of XI appears as a sharp



(XI)

singlet at room temperature, indicating a symmetrical bonding of the cyanide, or a rapid exchange of CO and CN positions on the NMR time scale. We are currently resolving this point and are attempting to determine the crystal structure of XI*.

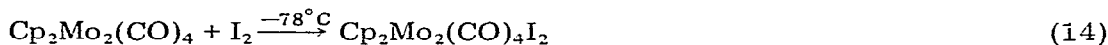
C. Addition of electrophiles to the $\text{Mo}\equiv\text{Mo}$ bond

As shown above, complex I behaves as an electrophilic reagent in its reactions with soft nucleophiles wherein the $\text{Mo}\equiv\text{Mo}$ π -bonds are displaced. However, the presence of π -bond charge density in the complex also allows I to react with many electrophilic reagents.

Thus, in contrast to $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, complex I reacts rapidly with iodine at

* The crystal structure of XI has been solved and supports the formulation. The Cp-resonance splits into two peaks at low temperature [48].

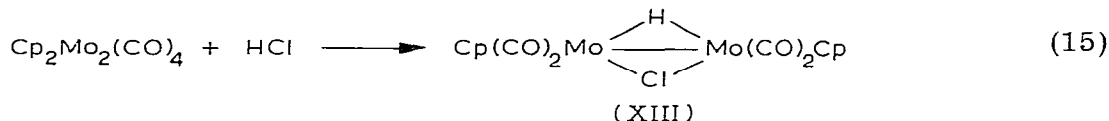
-78°C to give a dimeric iodide XII. Complex XII appears to exist in two dif-



ferent forms, a low temperature red-brown form and a high temperature violet form. The spectroscopic properties in Table 2 are of the violet form. On the basis of partially completed X-ray structure analyses, the low temperature form appears to be iodo-bridged and the high temperature form to have terminal iodine ligands [49].

The red-brown form seems to be somewhat stable at room temperature as a solid, but in solution is converted to the violet form in less than 2 min.

Hydrogen chloride adds to the triple bond of I to give the bridged complex XIII (eq. 15).



Both the Cp and H resonances of XIII appear as sharp singlets at δ 5.27 and 19.8 ppm, respectively. The position of the hydride resonance is consistent with a bridging position for the hydrogen [50]. It is not known at present if the Cp groups are in *cis* or *trans* positions.

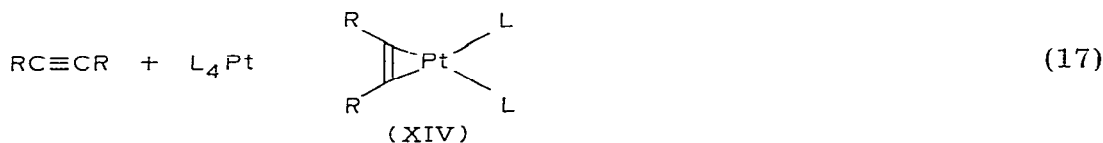
Several attempts were made to prepare metal complexes of I in which the $\text{Mo}\equiv\text{Mo}$ triple bond was to be coordinated to the metal in the fashion of metal olefin complexes, e.g., $\text{Ag}(\text{olefin})^+$, etc. In all cases investigated, the metal (Ag, Hg, etc.) quickly precipitated and I was oxidized to dark insoluble solids with concomitant loss of carbon monoxide. When I and diphenylmercury are allowed to react, about 50% of the mercury is precipitated as metallic mercury and $(\text{CpMo}(\text{CO})_3)_2\text{Hg}$ may be isolated from the solution. Again, some dark, insoluble molybdenum species is produced (eq. 16). The fate of the phenyl groups could not be ascertained.



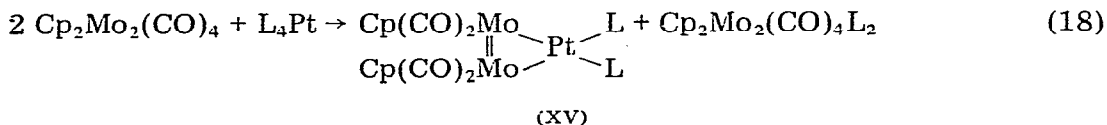
Complex I is also oxidized by TCNE to give a dark, insoluble salt which we formulate as $[\text{CpMo}(\text{CO})_4]^+[\text{TCNE}]^-$ on the basis of its IR spectrum and elemental analyses. The IR spectrum in the $2300\text{--}1950\text{ cm}^{-1}$ region is a superposition of the spectra of $[\text{CpMo}(\text{CO})_4]^+[\text{PF}_6]^-$ and $[\text{K}]^+[\text{TCNE}]^-$ [51,52]. The electrochemistry of complex I is currently under study to more fully understand the redox chemistry of the $\text{Mo}\equiv\text{Mo}$ triple bond in this complex.

D. Metal-cluster formation

Although compound I failed to give simple complexes with metal ions, e.g., Ag^+ and Hg^{2+} (see above), the $\text{Mo}\equiv\text{Mo}$ triple bond in its reaction with L_4Pt ($\text{L} = \text{Ph}_3\text{P}$) does mimic acetylenes. Acetylenes react readily with L_4Pt to displace two mol of triphenylphosphine and form the platinum acetylene complex XIV.

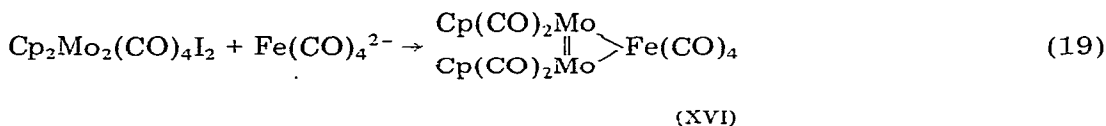


Similarly, the Mo≡Mo triple bond of I displaces phosphine to form complex XV. The displaced triphenylphosphine reacts rapidly with excess I to give the bis(phosphine) adduct IX.



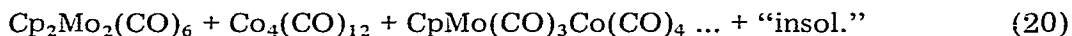
Complex XV is extremely sensitive to oxygen, and even decomposes in the solid state under nitrogen within 24 h. The structure is therefore assigned on the basis of the stoichiometry, the NMR and IR ($\nu(\text{CO})$: 1980, 1800 cm^{-1}) spectra. The latter spectrum still contains the low frequency carbonyl band which suggests the carbonyls may be bridging as 4-electron donors [1c]. The purity of the sample is established by the complete absence of any peaks in the NMR other than Ph and Cp, which are in the correct area ratio (3/1). The Cp peak is a sharp singlet, indicating the equivalence of the Cp groups.

Diiron enneacarbonyl reacts with I to give a host of products. Isolation of the components of this reaction mixture was severely hampered by their apparent instability. However, the tetracarbonyliron dianion reacts smoothly with $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{I}_2$ to produce a red complex formulated as XVI. Complex XVI is also extremely air sensitive and thermolabile, again precluding an elemental analysis.



However, the NMR spectrum consisted only of one sharp singlet for the Cp group. The IR in the carbonyl region is readily resolved into peaks due to the $\text{Mo}(\text{CO})_2$ groups (ν 1900, 1875 cm^{-1}), and to the $\text{Fe}(\text{CO})_4$ group (ν 2050, 2020, and 2000 cm^{-1}). The latter peaks were characteristic of $\text{Fe}(\text{CO})_4$ complexes in number, frequency range, and relative intensities [53]. The thermal decomposition products of solid XVI were shown to be $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Fe}_3(\text{CO})_{12}$.

Acetylenes are known to react with dicobalt octacarbonyl to form acetylene-bridged complexes similar to X [54]. However, the reaction of I with $\text{Co}_2(\text{CO})_8$ failed to give a stable, tetrahedrane-type cluster. Instead, the products in eq. 20 were isolated. The first product, $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, is undoubtedly the result of I scavenging CO from the reaction mixture [29], and the "insol" (insoluble) frac-



tion was similar to the residues produced when I is oxidized and loses carbon monoxide. The third product XVII is rather interesting in that its formation requires the rupture of the Mo≡Mo bond at ambient temperature. $\text{Co}_2(\text{CO})_8$ does not react with $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ under the conditions of eq. 20, and we have no evidence whatever that $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ dissociates up to 90°C*. Hence, some

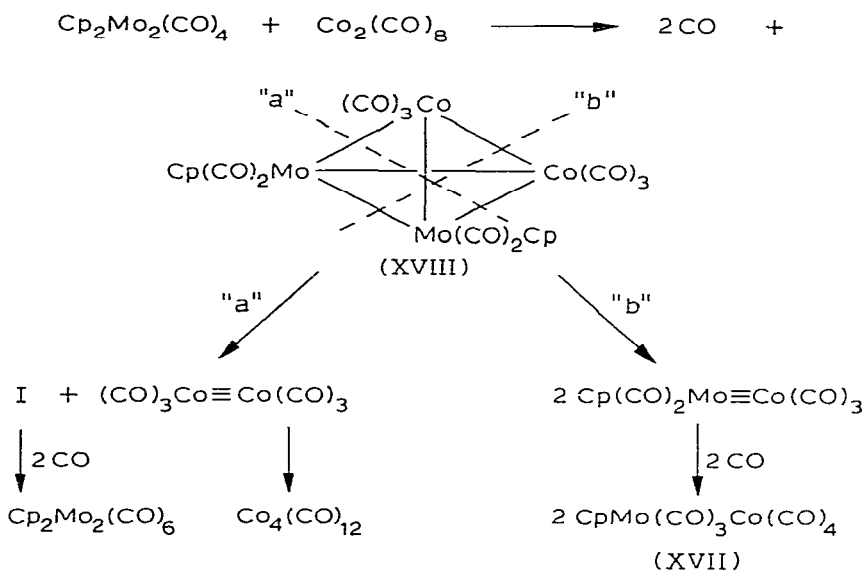
* The PMR spectrum of I is invariant from -90 to +90°C.

low energy pathway must exist for the rupture of the Mo≡Mo triple bond in its reaction with Co₂(CO)₈.

We postulate that this low energy pathway involves the cluster XVIII shown in Scheme 1. In this mechanism, Co₂(CO)₈ reacts with I to give XVIII and CO which is scavenged by I to form Cp₂Mo₂(CO)₆. Cluster XVIII may decompose by either of two paths, path "a" giving I and Co₂(CO)₆ which would have a Co≡Co triple bond on the basis of electron counting. The unstable intermediate, Co₂(CO)₆, may dimerize to give the monometallic, tetrahedrane cluster, Co₄(CO)₁₂. Scission of cluster XVIII along path "b" would give the novel complex, Cp(CO)₂-Mo≡Co(CO)₃, which upon scavenging CO would produce the observed product XVII.

In our experiments on the mechanism of formation of I, it was necessary to show that the products of the reaction do not scramble Cp groups under the conditions of the experiment (see above). To do this we refluxed toluene solutions nearly equimolar in I and VI and periodically analyzed aliquots for scrambling by mass spectrometry. We did observe a very slow exchange reaction between I and VI. The values of *K* (see above) were 0.05, 0.26, and 0.47 after 1, 5 and 8 days, respectively. While these scrambling rates are much too slow to account for the scrambling of Cp and Cp' groups during the synthesis of I (*K* = 1.7), they do show that the triply bonded complexes I and VI do undergo a slow scrambling process. This could be accomplished by the reversible formation of an Mo₄-tetrahedrane structure, which upon dissociation into dimeric units, could break apart along two paths (as in Scheme 1). One path would be the simple reverse of the dimerization step, but the other path would scramble Cp and Cp' groups, i.e., CpCp'Mo₂(CO)₄ would be produced. At this time, however, we cannot rule out some slight decomposition of I or VI to give CO, which

SCHEME 1



would be scavenged by the triple bonds to give $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ and $\text{Cp}'_2\text{Mo}_2(\text{CO})_6$. The latter two complexes could then scramble the Cp and Cp' groups according to eq. 2-4.

$\text{Cp}_2\text{Mo}_2(\text{CO})_4$ does not react with $\text{Mn}_2(\text{CO})_{10}$ at ambient temperature, but after 8 h in refluxing toluene, some $\text{Cp}(\text{CO})_3\text{Mo}-\text{Mn}(\text{CO})_5$ is produced. This behavior parallels the reactivity of $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$ with acetylenes. The former reacts rapidly at 25° C but heating is necessary with the latter [55].

The above results, while not definitive, certainly suggest the possibility of reversible formation of tetradrane-metal clusters and make plausible the notion that triply-bonded dinuclear complexes, e.g., $\text{Co}_2(\text{CO})_6$, $\text{Cp}(\text{CO})\text{Fe}\equiv\text{Fe}(\text{CO})\text{Cp}$, etc., may be intermediates in the formation of tetrahedrane clusters, e.g., $\text{Co}_4(\text{CO})_{12}$ and $\text{Cp}_4\text{Fe}_4(\text{CO})_4$.

In conclusion, the results to date show that the $\text{Mo}\equiv\text{Mo}$ triple bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ possesses both electrophilic and nucleophilic character. The unique reactivity of this complex especially recommends it as a starting point for metal cluster formation and further experiments are in progress on this point.

Acknowledgement

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References

- 1 (a) Part I, R. Klingler, W.M. Butler and M.D. Curtis, *J. Amer. Chem. Soc.*, **97** (1975) 3535; (b) Part II, M.D. Curtis and W.M. Butler, *J. Organometal. Chem.*, **155** (1978) 131; (c) Part III, R.J. Klingler, W.M. Butler and M.D. Curtis, *J. Amer. Chem. Soc.*, **100** (1978) in press.
- 2 F.A. Cotton, N.F. Curtis, C.B. Harris, B.F.G. Johnson, S.J. Lippard, J.T. Mague, W.R. Robinson and J.W. Wood, *Science*, **145** (1964) 1305.
- 3 F.A. Cotton, *Chem. Soc. Revs.*, **4** (1975) 27.
- 4 F.A. Cotton, L.D. Gage, K. Mentis, L.W. Shive and G. Wilkinson, *J. Amer. Chem. Soc.*, **98** (1976) 6922.
- 5 J.G. Norman, Jr. and H.J. Kolari, *J. Amer. Chem. Soc.*, **97** (1975) 33.
- 6 B.I. Swanson, I.J. Rafolko, D.F. Shiver and J. San Filippo, Jr., *Inorg. Chem.*, **14** (1975) 1737.
- 7 F.A. Cotton, D.S. Martin, P.E. Fanwick, T.J. Peters and T.R. Webb, *J. Amer. Chem. Soc.*, **98** (1976) 4681.
- 8 V. Katović, J.L. Templeton, R.J. Hoxmeier and R.E. McCarley, *J. Amer. Chem. Soc.*, **5301** (1975).
- 9 D.J. Brauer and C. Kruger, *Inorg. Chem.*, **15** (1976) 2511.
- 10 N.E. Schore, C.S. Ikenda, and R.G. Bergman, *J. Amer. Chem. Soc.*, **98** (1976) 265.
- 11 I. Fischler, K. Hildenbrand and E.K. von-Gustorf, *Angew. Chem.*, **87** (1975) 35.
- 12 D.J. Salmon and R.A. Walton, *J. Amer. Chem. Soc.*, **100** (1978) 991.
- 13 T. Nimry and R.A. Walton, *Inorg. Chem.*, **17** (1978) 510.
- 14 E. Hochberg and E.H. Abbott, *Inorg. Chem.*, **17** (1978) 506.
- 15 M.H. Chisholm, F.A. Cotton, M.W. Extine and W.W. Reichert, *J. Amer. Chem. Soc.*, **100** (1978) 153.
- 16 S.A. Best, T.J. Smith and R.A. Walton, *Inorg. Chem.*, **17** (1978) 99.
- 17 F.A. Cotton, M. Extine and L.D. Gage, *Inorg. Chem.* **17** (1978) 172.
- 18 F.A. Cotton, W.M. Extine and G.W. Rice, *Inorg. Chem.*, **17** (1978) 176.
- 19 J.R. Ebner and R.A. Walton, *Inorg. Chem.*, **14** (1975) 1987.
- 20 F.A. Cotton and B.J. Kalmbacher, *Inorg. Chem.*, **15** (1976) 522.
- 21 F. Bonati and F.A. Cotton, *Inorg. Chem.*, **6** (1967) 1353.
- 22 M.H. Chisholm, F.A. Cotton, M.W. Extine and R.R. Stults, *Inorg. Chem.*, **16** (1977) 603.
- 23 M.H. Chisholm, F.A. Cotton, M.W. Extine and W.W. Reichert, *J. Amer. Chem. Soc.*, **100** (1978) 153.
- 24 R.B. King, *Coord. Chem. Revs.*, **20** (1976) 155.
- 25 P. Hackett, P.S. O'Neill and A.R. Manning, *J. Chem. Soc. Dalton*, (1974) 1625.

- 26 W.I. Bailey, Jr., M.H. Chisholm, F.A. Cotton, C.A. Murillo and L.A. Rankel, *J. Amer. Chem. Soc.*, 100 (1978) 802.
- 27 M.H. Chisholm, F.A. Cotton, M.W. Extine and L.A. Rankel, *J. Amer. Chem. Soc.*, 100 (1978) 807.
- 28 R.J. Klingler and M.D. Curtis, unpublished results. R.J. Klingler, Ph.D. thesis, The University of Michigan, Ann Arbor, Michigan, 1977.
- 29 D.S. Ginley and M.S. Wrighton, *J. Amer. Chem. Soc.*, 97 (1975) 3533.
- 30 R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, *J. Chem. Soc. A*, 94 (1967).
- 31 A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, 84 (1963) 344.
- 32 P.M. Treichel, J.H. Morris and F.G.A. Stone, *J. Chem. Soc.*, (1963) 720.
- 33 J.M. Burlitch and A. Ferrari, *Inorg. Chem.*, 9 (1970) 563.
- 34 R.B. King, *Organometal. Syn.*, 103 (1965) 95.
- 35 A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and A.S. Beschastnov, *Dokl. Akad. Nauk SSSR*, 159 (1964) 377.
- 36 R.C. Job and M.D. Curtis, *Inorg. Chem.*, 12 (1973) 2510.
- 37 M. Basato, J.P. Fawcett, S.A. Fieldhouse and A.J. Poë, *J. Chem. Soc. Dalton*, (1974) 1856.
- 38 J.P. Fawcett, R.A. Jackson and A.J. Poë, *Chem. Commun.*, (1975) 733.
- 39 B.H. Byers and T.L. Brown, *J. Amer. Chem. Soc.*, 97 (1975) 947.
- 40 H.M. Feder and J. Halpern, *J. Amer. Chem. Soc.*, 97 (1975) 7186.
- 41 D.G. DeWit, J.P. Fawcett and A.J. Poë, *J. Chem. Soc. Dalton*, (1976) 528.
- 42 R.D. Adams, D.E. Collins and F.A. Cotton, *J. Amer. Chem. Soc.*, 96 (1974) 749.
- 43 A.R. Manning, *J. Chem. Soc. A*, (1967) 1984.
- 44 R.T. Haines and C.R. Nolte, *J. Organometal. Chem.*, 24 (1970) 725.
- 45 M.J. Mays and S.M. Pearson, *J. Chem. Soc. A*, (1968) 2291.
- 46 W.I. Bailey, Jr., D.M. Collins and F.A. Cotton, *J. Organometal. Chem.*, 135 (1977) C53.
- 47 W.I. Bailey, Jr., F.A. Cotton, J.D. Jamerson and J.R. Kolb, *J. Organometal. Chem.*, 121 (1976) C23.
- 48 K.R. Im and M.D. Curtis, to be submitted.
- 49 M.D. Curtis and K.R. Im, unpublished results.
- 50 H.D. Kaesz and R.B. Saillant, *Chem. Rev.*, 72 (1972) 231.
- 51 E.O. Fischer, K. Fitchel and K. Oefele, *Chem. Ber.*, 95 (1962) 249.
- 52 D. Demerseman, M. Pankowski, G. Bonquet and M. Bigorgne, *J. Organometal. Chem.*, 117 (1976) C10.
- 53 R. Ugo, G. LaMonica, F. Cariati, S. Cenini and F. Conti, *Inorg. Chim. Acta*, 4 (1970) 390.
- 54 H. Greenfield, H.W. Sternberg, R.A. Friedel, R.A. Wotiz, R. Markby and I. Wender, *J. Amer. Chem. Soc.*, 78 (1956) 120.
- 55 T.H. Coffield, K.G. Ihrman and W. Burns, *J. Amer. Chem. Soc.*, 82 (1960) 4209.