search Fund, administered by the American Chemical Society, and to the Alfred P. Sloan Foundation, for generous support of this work. Dartmouth's Varian XL-300 NMR spectrometer was purchased with funds from the National Science Foundation.

Registry No. **4a**, 97689-54-8; **4b**, 82665-10-9; **4c**, 97689-55-9; **4d**, 92144-97-3; **5a**, 97689-56-0; **5b**, 97689-57-1; **5c**, 97689-58-2; **5d**, 97689-59-3; **5e**, 97689-60-6; **6**, 97689-61-7; $[MoCp(CO)_3]_2$, 12091-64-4; $[MoCp(CO)_3]^-Na^+$, 12107-35-6; $[WCp(CO)_3]^-Na^+$, 12107-36-7; $[WCp(CO)_3]_2$, 12091-65-5; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-Na^+$, 70850-86-1; $[Mo(C_5Me_5)(CO)_3]_2$, 56200-14-7; $[W(C_5Me_5)(CO)_3]_2$, 70605-19-5; $[C_3Ph_3]PF_6$, 42134-08-7; C_5Me_5H, 41539-64-4; $[C_3Me_3]BF_4$, 12306-61-5; $[C_3Ph_3]BF_4$, 741-16-2; diphenylcyclopropenyl perchlorate, 37647-36-2; *tert*-butyldiphenylcyclopropenyl hexafluorophosphate, 97674-31-2; methyldiphenylcyclopropenyl tetrafluoroborate, 65102-02-5.

Reaction of Bis(cyclopentadienyldicarbonylmolybdenum) with Carbon Monoxide. Evidence against Facile Ligand Dissociation from the Cyclopentadienyltricarbonylmolybdenum Radical

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The reactions of $(MeCp)_2Mo_2(CO)_4$ and $(Cp)_2Mo_2(CO)_4$ mixtures, as well as $MeCpMo(CO)_2{\equiv}Mo(CO)_2Cp$, with carbon monoxide were studied. The products were invariably the corresponding hexacarbonyl dimers $(RC_5H_4)_2Mo_2(CO)_6$ (R = H, CH_3) with no evidence for the respective crossover products. The absence of crossover was verified under a variety of conditions of solvent and temperature. These results are interpreted as excluding a mechanism involving metal–metal bond homolysis. Arguments are presented for direct CO dissociation in the formation of $Cp_2Mo_2(CO)_4$ from $Cp_2Mo_2(CO)_6$ for both the thermal and photochemical pathways.

Introduction

The ligand substitution behavior of dinuclear metal carbonyl complexes with metal–metal single bonds has been a topic of considerable recent interest.[1] Attention has been drawn to these reactions by earlier studies[2] suggesting that the thermal and photochemical substitution reactions of the $M_2(CO)_{10}$ dimers (M = Mn, Re) occur by ligand substitution at the 17-electron intermediates formed by metal–metal bond homolysis. It is now clear from a series of elegant crossover experiments by Muetterties, Atwood and co-workers that the thermal substitution reactions of these dimers occur by a CO-dissociative mechanism that does not involve metal-metal bond cleavage.[3] Furthermore, a number of flash photolysis and low-temperature matrix photolysis experiments have established that CO dissociation and metal-metal bond homolysis are competitive primary photoprocesses and that both pathways can lead to substitution.[4] On the other hand, a number of other studies clearly indicate that 17-electron radicals, when formed, show exceptional ligand lability.[1,5–7] Indeed associative substitution has been demonstrated for the isolable complexes $V(CO)_6$ and $Mn(CO)_3(PBu_3)_2$ as well as some transient radicals.[5,6,7a,b] In this context the formation of $[CpMo(CO)_2]_2$ (**2**) from $[CpMo(CO)_3]_2$ (**1**), eq 1,[8,9] represents a unique example of

Table I. Dimer Ratios for the Decarbonylation of an Equimolar Mixture of 1a and 1c in Refluxing Toluene[a]

time, min	$[\mathbf{1b}]^2/[\mathbf{1a}][\mathbf{1c}]$	% **2a–c**
3	0.43	2.1
6	1.33	4.1
9	2.44	6.1
12	3.26	7.0
15	3.39	12.7
30	3.73	31.9

[a] The dimer ratios were calculated from the relative peak areas of the UV-detector (254 nm) output from the HPLC system correcting for differences in molar absorptivity.

1a, R_1 = H,
R_2 = H
b, R_1 = H,
R_2 = CH_3
c, R_1 = CH_3,
R_2 = CH_3

2a, R_1 = H,
R_2 = H
b, R_1 = H,
R_2 = CH_3
c, R_1 = CH_3,
R_2 = CH_3

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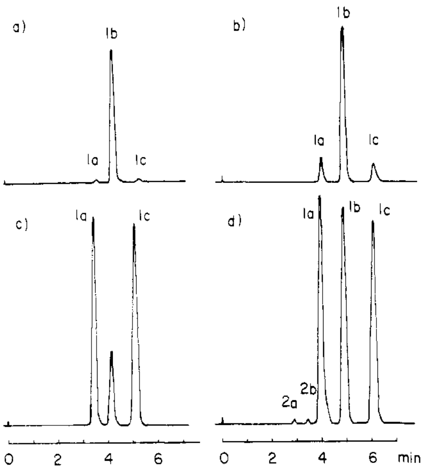


Figure 1. HPLC chromatograms of the products of (a) reaction of **2b** with CO at 23 °C, (b) reaction of **2b** with CO at 110 °C for 5 min, (c) reaction of **2a** + **2c** with CO at 110 °C for 5 min, and (d) heating a mixture of **1a** + **1c** to 110 °C for 5 min under N_2 purge.

a reaction which if it occurs by a metal–metal bond homolysis pathway *must* involve CO ligand dissociation from a 17-electron intermediate. In this paper we report our study of the reverse reaction, addition of carbon monoxide to 2, which is inconsistent with any mechanism for the interconversion of 1 and 2 which involves cleavage of the metal–metal bond.

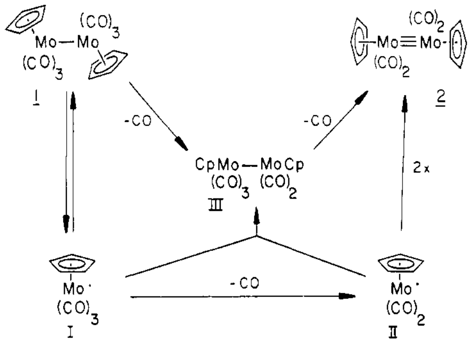
Results

Decarbonylation of 1. First it was necessary to confirm that metal–metal bond homolysis in 1 is faster than decarbonylation. A solution of an equal mixture of **1a** and **1c** in toluene was added to refluxing toluene under a vigorous nitrogen purge. Aliquots were taken at intervals and analyzed for the ratios of **1a–c** and **2a–c**. These data are summarized in Table I. Equilibration of the **1a–c** dimers was observed to proceed much faster than formation of 2. It was also observed that **1c** reacted faster than **1a**. Analysis of these mixtures was achieved by using reversed-phase HPLC eluting with CH_3CN/H_2O (5:1) under an inert atmosphere.[10] This method gave clean base-line separation of all six dimers with the exception of the **2a**/**1c** pair which overlapped slightly.

Contrary to reports in the literature[11] room-temperature solutions of the dimers 1 and 2 are stable to exchange reactions in the dark. However, even room lights are sufficient to affect significant amounts of exchange in minutes. It should also be noted that mass spectrometry is an unreliable method for determining the ratios of the dimers **1a–c**.

Preparation of 2b. To avoid the problem of differential reactivity in our experiments we needed the mixed dimer **2b**. It was known that the reaction of $MeCpMo(CO)_3H$ and $CpMo(CO)_3CH_2CH_3$ gives an equal mixture of **1b** and **2b**.[12] This mixture was prepared and separated by column chromatography. The recrystallized dimer **2b** obtained in this way was only contaminated by traces of **2a** and **2c** as determined by ^1H NMR, IR, MS, and HPLC.

Scheme I



Crossover Experiments. Treatment of solutions of $MeCpMo(CO)_2{\equiv}Mo(CO)_2Cp$ (**2b**) with CO at ambient temperature in the dark gave a quantitative yield of **1b** (eq 2). Only traces of **1a** and **1c** could be observed by

$$MeCpMo(CO)_2{\equiv}Mo(CO)_2Cp + CO \rightarrow MeCpMo(CO)_3{-}Mo(CO)_3Cp \quad (2)$$

HPLC, Figure 1a, and even these small amounts can be attributed to **2a** and **2c** impurities in **2b**. Comparable results were obtained with mixtures of **2a** and **2c**. No crossover could be observed under any conditions. This included changes in solvent (toluene, pentane, THF), concentration of the metal complex (10^{-2}–10^{-5} M), or CO partial pressure. Indeed introduction of CO by diffusion through a needle valve into a nitrogen-filled reaction vessel also gave no crossover.

Under an atmosphere of CO the equilibrium position for eq 1 was found to lie entirely to the left, even at 110 °C. Efficient conversion of 1 into 2 could only be achieved if CO is removed from the reaction vessel. Thus, **1a** could be recovered quantitatively when heated to 110 °C in xylenes under an atmosphere of CO. At this temperature **1a** and **1c** are converted to a nearly statistical mixture of **1a–c** in about 15 min, Table I. The dimers **2a–c** are stable to exchange at this same temperature.[8b] Significantly, when a degassed solution of **2b** in xylenes was preheated to 110 ± 2 °C, and then treated with CO (1 atm) for 5 min, followed by evacuation to remove CO and cooling, **1b** contaminated by only small amounts of **1a** and **1c** was obtained, Figure 1b. A nonequilibrium mixture of dimers was also obtained upon treatment of a mixture of **2a** and **2c** with CO (1 atm) at 110 °C, Figure 1c. The mixture of dimers obtained upon heating **1a** and **1c** to 110 °C for 5 min is shown in Figure 1d for comparison. In both experiments the observed crossover products can be attributed to reversible metal–metal bond cleavage in 1 after it is formed.

Discussion

The metal–metal bonded dimer 1 can be converted to the triply bonded dimer 2 in good yield either by heating solutions to 110 °C (or above) or by photolysis in aromatic or hydrocarbon solvents, provided CO is removed by purging with an inert gas.[8,9] This reaction is entirely reversible; addition of 2 equiv of CO leads to quantitative recovery of 1.[9] The metal–metal bond homolysis mecha-

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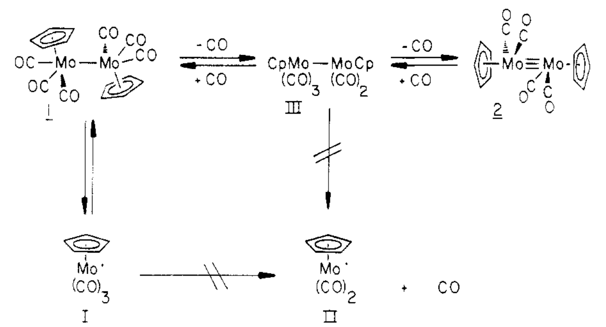
nism involving the intermediates I and II as shown in Scheme I has been proposed for both the thermal and photochemical reactions.[8,9] In both cases simple dimerization of II was postulated; however it is more reasonable to assume combination of I and II will give $Cp_2Mo_2(CO)_5$ (III), followed by loss of another CO ligand to give the product. Indeed, Rest and co-workers have observed a CO-bridged complex of this stoichiometry upon low-temperature photolysis of 1 in a matrix.[13] But direct loss of CO from 1 also gives III; thus both the direct CO dissociation and the metal–metal bond homolysis pathways can lead to this intermediate.

The principal observation supporting the metal–metal bond homolysis mechanism under thermal conditions is the formation of a nearly statistical distribution of the dimers **2a–c** upon heating a mixture of **1a** and **1c** under an argon purge.[8b] However, the kinetic studies of the reaction of 1 with O_2 and alkynes by Poë and co-workers clearly establish that metal–metal bond cleavage is much faster than CO loss.[14] Indeed their data for the reaction of 1 with alkynes is most consistent with direct dissociation of CO from 1.[14b] Our data in Table I confirm this and show that equilibration of the dimers **1a–c** is nearly complete in about 15 min at 110 °C at which point only about 12% of 2 has formed. In principle this question could resolved by examining the **2a–c** dimer ratios at early reaction times; however, in practice our HPLC method fails to give adequate data at such low **2a–c** concentrations due to the large excesses of **1a–c** present. Together these observations show that metal–metal bond homolysis is a facile and reversible process, but they do not require that homolysis be on the pathway for CO dissociation.

To solve this problem we have studied the reverse reaction, addition of CO to the triply bonded dimer **2**, under conditions where metal–metal bond cleavage in 1 does not occur. Under a variety of conditions reaction of the mixed dimer **2b** with CO at ambient temperature gave exclusively **1b**, eq. 2. Similarly, mixtures of the dimers **2a** and **2c** gave only **1a** and **1c**. In no case were the corresponding crossover products expected for a mechanism involving the combination of the intermediates $CpMo(CO)_3$ and $MeCpMo(CO)_3$ observed. This is true even under equilibrium conditions. At 110 °C the loss of CO from 1 is completely reversible, with the equilibrium position entirely on the side of the singly bonded dimer 1 under an atmosphere of CO. Significant yields of 2 can only be achieved by removing CO from the reaction vessel. Even under these conditions treatment of **2b** with CO did not give the statistical distribution of **1a–c** expected for a metal–metal bond homolysis pathway, Figure 1. Note that in using **2b** the intermediates $CpMo(CO)_3$ and $MeCpMo(CO)_3$ would necessarily be formed in equal concentrations upon metal–metal bond cleavage, thus avoiding the possible problem of different rates of carbonylation for the dimers **2a** and **2c**.

These observations are only consistent with a mechanism for the reaction of 2 with CO which does not involve metal–metal bond breaking. The most plausible alternative is the sequential addition of two molecules of CO as shown in Scheme II. *Then, according to the principle of microscopic reversibility, the conversion of 1 into 2 must also occur by direct loss of carbon monoxide and dissociation of CO from the 17-electron intermediate CpMo(CO)$_3$ cannot be involved.*[15] Our results do not place an absolute value on the rate of CO dissociation from $CpMo(CO)_3$ but rather argue that CO dissociation from 1 must be faster. Thus metal–metal bond homolysis in 1 must be a highly reversible process that simply is not on the reaction pathway for CO loss.

Scheme II



Under photochemical conditions reaction 1 has been proposed to involve photoinduced metal–metal bond homolysis followed by dissociation of CO from CpMo(CO)$_3$(I) in a subsequent thermal process.[9] Our results argue that CO dissociation from I is not competitive with the near diffusion–controlled combination in solution.[17] Indeed, the flash photolysis studies of Meyer and co-workers indicate competitive photoinduced metal–metal bond homolysis and CO dissociation.[17] Futhermore, Rest and co-workers have observed a CO-dissociated intermediate upon low-temperature photolysis of 1 in a matrix.[13] We propose that the photochemical pathway for reaction 1 like the thermal process involves direct photoinduced loss of CO from 1 and not thermal CO dissociation from the intermediate $CpMo(CO)_3$.

Conclusion

The crossover experiments reported here establish that the reaction of the triply bonded dimer 2 with CO occurs by the sequential addition of two molecules of CO and not by a mechanism involving metal–metal bond breaking. Invoking the principle of microscopic reversibility we conclude that the formation of 2 from 1 must also occur by this mechanism. Furthermore, the same must be true under photochemical conditions. Nevertheless, the evidence supporting facile ligand substitution in 17-electron complexes remains overwhelming.[5-7] Our results simply argue that thermal CO dissociation from $CpMo(CO)_3$ is slow, allowing CO dissociation from $Cp_2Mo_2(CO)_6$ to compete. Results to be communicated shortly will establish that the ligand substitution reactions of the related CpW-

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[15] Application of the principle of microscopic reversibility[16] says that for the scheme

$$\begin{tikzcd}
1 \arrow[r, shift left, "k_1"] \arrow[d, shift right, "k_2"'] & \mathrm{III} \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_5"] \arrow[d, shift left, "k_{-4}"] & 2 \arrow[l, shift left, "k_{-5}"] \\
\mathrm{I} \arrow[u, shift right, "k_{-2}"'] \arrow[r, shift left, "k_3"] & \mathrm{II} \arrow[l, shift left, "k_{-3}"] \arrow[u, shift left, "k_4"]
\end{tikzcd}$$

the relationship $k_1/k_{-1}[CO] = k_2k_3k_4/k_{-2}k_{-3}k_{-4}[CO]$ will hold. From our results we know that $k_{-4}/k_{-1}[CO] = 0$, therefore $k_2k_3k_4/k_1k_{-2}k_{-3}[CO] = 0$. Reasonable values are $k_2 = 10^3\ s^{-1}$,[10] $k_{-2} = k_4 = 10^9\ M^{-1}\ s^{-1}$,[17] $k_{-3} = 10^6\ M^{-1}\ s^{-1}$,[2b,19] and $[CO] = 10^{-3}$ M. Thus $k_2k_4 \approx k^{-2}k_{-3}[CO]$, this requires that k_3/k_1 must go to zero or that CO dissociation from I is much slower than from 1.

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$(CO)_3$ radical with phosphines occur by a predominantly associative reaction pathway.[18]

Experimental Section

All manipulations were carried out under an atmosphere of purified nitrogen either in a Vacuum Atmospheres Model HE-553 glovebox or using standard Schlenk techniques. Toluene, xylenes, and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl, and pentane was stirred over H_2SO_4, washed with H_2O, predried with Na_2SO_4, and then distilled from a ketyl preformed in tetraglyme. Infrared spectra were obtained on a Perkin-Elmer Model 781 spectrophotometer. ^1H NMR spectra were obtained on a Varian EM-390 spectrometer. Ultraviolet–visible spectra were recorded on a Cary 210 UV–visible spectrophotometer. High performance liquid chromatography (HPLC) was performed as described before[10] using an Eldex Model B-100 pump and Milton Roy UV-monitor absorbing at 254 nm. The C-18 reversed-phase column (10 μm, 0.5 × 25 cm) employed was purchased from Altex Corp. and elution was with an argon purged CH_3CN/H_2O mixture (5:1). Compounds 1a and 1c were prepared by literature methods.[20] The C_5H_6 impurity in commercial $(CH_3C_5H_5)_2$ (Aldrich) could be reduced, but not eliminated, by low pressure distillation of the dimer, taking a late cut. 2a and 2c were prepared from 1a and 1c by the literature method[8] and purified by chromatography on Florisil eluting with toluene, followed by recrystallization from toluene pentane mixtures. All solutions of 1 and 2 were protected from light by using foil wrapped flasks and indirect lighting.

Preparation of $(\eta^5\text{-}CH_3C_5H_4)Mo(CO)_2{\equiv}Mo(CO)_2(\eta^5\text{-}C_5H_5)$ (2b) and $(\eta^5\text{-}CH_3C_5H_4)Mo(CO)\_Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (1b).[12] A solution of 1.30 g (5.0 mmol) $(\eta^5\text{-}CH_3C_5H_4)Mo(CO)_3H$ and 1.45 g (5.3 mmol) of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_2CH_3$ in 50 mL of THF was allowed to stir for 48 h at ambient temperature in the dark. The solvent was removed and the red residue chromatographed in the dark in several portions on Florisil eluting with toluene/pentane (1:1) first **1b** and then **2b** as two clearly separable bands. The combined **2b** fractions were crystallized from toluene/pentane to give 150 mg of pure **2b** as red plates. **2b** was identified as the correct isomer by HPLC, was devoid of **1b**, and contained only traces of **2a** and **2c**. Similarly, the combined **1b** fractions yielded 270 mg of pure **1b** as red prisms from toluene/pentane.

2b: IR (CH_3CN): 1955 (m), 1885 (s), 1850 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (s, 3 H), 5.08 (m, 4 H), 5.22 (s, 5 H); UV (CH_3CN) 324 nm (ϵ 8400 L/mol·cm); mass spectrum, *m/e* 454 (0.22), 453 (0.12), 452 (0.47), 451 (0.42), 450 (0.68), 449 (0.66), 448 (1.02), 447 (0.55), 446 (0.97), 445 (0.53), 444 (0.46), 443 (0.28), 442 (0.15), 440 (0.09). Anal. Calcd for $C_{15}H_{12}Mo_2O_4$: C, 40.20; H, 2.70. Found: C, 40.41; H, 2.77.

1b: IR (CH_3CN) 2005 (m), 1953 (s), 1908 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16 (s, 3 H), 5.16 (m, 4 H), 5.32 (s, 5 H); UV (CH_3CN) 500 nm (ϵ 1980 L/mol·cm), 385 (14 900). Anal. Calcd for $C_{17}H_{12}Mo_2O_6$: C, 40.50; H, 2.40. Found: C, 40.78; H, 2.42.

Decarbonylation of 1a and 1c Mixture. A solution of 24 mg (0.05 mmol) of **1a** and 27 mg (0.05 mmol) of **1c** in 50 mL of toluene was added to 50 mL of refluxing toluene under a vigorous nitrogen purge with exclusion of light. At intervals, 8-mL aliquots were taken by syringe and the solvent was removed. The resulting residues were dissolved in CH_3CN for analysis by HPLC. The data in Table I were obtained from the relative peak areas of the UV-detector output (254 nm) of the HPLC system correcting for differences in molar absorptivity. Molar absorptivities at 254 nm for **1a** (ϵ 11 900 L/mol·cm), **1b** (ϵ 12 900 L/mol·cm), **1c** (ϵ 13 100 L/mol·cm), **2a** (ϵ 12 500 L/mol·cm), **2b** (ϵ 11 900 L/mol·cm), and **2c** (ϵ 14 600 L/mol·cm) were determined in CH_3CN by using authentic samples.

Crossover Experiments. In a typical experiment 10 mg of **2b** was dissolved in 10 mL of toluene in the glovebox and placed along with a stir bar in a reaction flask sealed to a Teflon stopcock. The flask was wrapped in foil. The solution was thoroughly degassed by three freeze–pump–thaw cycles and then treated with 1 atm of CO on a vacuum line. After 1 h the solvent was removed and the residue dissolved in CH_3CN for HPLC analysis.

Carbonylation at 110 °C was performed as follows. A solution of **2b** in xylenes was thoroughly degassed then preheated to 110 ± 2 °C for 10 min, the stopcock was opened to expose the reaction to an atmosphere of CO for 5 min, and then the flask was evacuated to remove CO and cooled to room temperature in that order. Removal of the remaining solvent and analysis of the residue followed as above. All experiments were repeated with mixtures of **2a** and **2c**.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. **1a**, 12091-64-4; **1b**, 74482-83-0; **1c**, 33056-03-0; **2a**, 56200-27-2; **2b**, 69140-96-1; **2c**, 69140-73-4; I, 12079-69-5; $(\eta^5\text{-}CH_3C_5H_4)Mo(CO)_3H$, 78353-19-2; $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_2CH_3$, 12083-68-0; CO, 630-08-0; Mo, 7439-98-7.

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