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Laser Photolysis Study of the Photosubstitution in Dimanganese Decacarbonyl

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Abstract: Two primary photoprocesses in the flash photolysis of $Mn_2(CO)_{10}$ are established with the use of a 10-ns N_2 laser. One is the cleavage of the Mn–Mn bond to form $\cdot Mn(CO)_5$ radicals, and the other is the cleavage of the Mn–CO bond to form $Mn_2(CO)_9$. The reactivity of $Mn_2(CO)_9$ toward ligands is found to decrease in the following order: $P(n\text{-}Bu)_3 >> t\text{-}BuNC \approx EtCN >> CO$. The substitution of CO in the $\cdot Mn(CO)_5$ radical with $P(n\text{-}Bu)_3$ is shown to be associative. The reactivity of $Mn_2(CO)_9$ toward $P(n\text{-}Bu)_3$ is higher than that of $\cdot Mn(CO)_5$.

Photoexcitation of transition-metal carbonyls containing a metal–metal bond has been consistently interpreted to result in preferential homolysis of the metal–metal bond generating radical species in the primary process.[2] Other photoprocesses, however, are not explicitly exempted from the dinuclear systems.[3] Hughey et al.[4] observed nonradical species besides $\cdot Mn(CO)_5$ in the conventional flash photolysis of $Mn_2(CO)_{10}$. The participation of another photointermediate in the reaction of $Mn_2(CO)_{10}$ with CCl_4 was verified kinetically by Fox and Poë.[5] During the progress of our research,[6a] the flash photolysis study of $M_2(CO)_{10}$ (M = Mn and Re) using a flash duration of about 35 μs was reported by Wegman et al.[7] in which under 1 atm of CO pressure the only process is the formation of $\cdot M(CO)_5$ radicals, whereas in the thoroughly degassed solution a second intermediate is observed. They assigned the second intermediate absorptions to $M_2(CO)_n$ (*n* = 8 and 9) formation by facile loss of CO from the sole primary photoproduct $\cdot M(CO)_5$, followed by thermal recombination of the resulting $\cdot M(CO)_4$ radicals with themselves or with $\cdot M(CO)_5$. Their assignment gives rise to controversy in the understanding of the primary photoprocesses of $Mn_2(CO)_{10}$.

We report here the laser flash photolysis study[6b] of $Mn_2(CO)_{10}$ in cyclohexane using a 10-ns laser pulse to elucidate the primary photoprocesses in degassed conditions. A closely related study using picosecond flash photolysis by Rothberg et al.[8] has recently appeared.

Experimental Section

$Mn_2(CO)_{10}$ was synthesized by the method described in the literature[9] and purified by sublimation. $Mn_2(CO)_9(MeCN)$ and $Mn_2(CO)_9(EtCN)$ were synthesized by Koelle's method.[10] The IR spectra of the compounds are in good agreement with those in the literature.[10,11] The UV spectrum of $Mn_2(CO)_9(MeCN)$ in cyclohexane has maximum at 350 nm and a shoulder at 413 nm and that of $Mn_2(CO)_9(EtCN)$ has maximum at 345 nm and a shoulder at 415 nm. EtCN and $P(n\text{-}Bu)_3$ were purified following procedures in the literature.[12,13] *t*-BuNC was prepared by the method of Ugi and Mayr[14] and fractioned by gas chromatography. CCl_4 was treated with Na_2CO_3 solution, washed with water, dried over $CaCl_2$, and distilled under nitrogen atmosphere. Cyclohexane (Merck; Uvasol for fluorometry) and MeCN (Wako Pure Chemical; Spectro grade) were used without further purification.

A N_2 laser (Molectron Model UV 24; 337.1 nm, 10-ns fwhm, 1-MW peak power) is used as an excitation light source. The monitoring light source is a Xe flash lamp or an I_2–W lamp with a current-stabilized DC power supply. The exciting and monitoring lights are in a crossed beam arrangement. The laser photolysis experiments were carried out at room temperature. In order to avoid the effect of generated photoproducts, all the kinetic data are recorded before 20 shots of excitation laser pulse are irradiated to each sample solution.

Oxygen is purged from solvents by bubbling dry nitrogen gas for 15 min under nitrogen atmosphere immediately before the dissolution of $Mn_2(CO)_{10}$. The sample solutions are degassed by six freeze–pump–thaw cycles. The concentrations of $Mn_2(CO)_{10}$ are ranged between 4.0×10^{-4} and 5.5×10^{-4} mol dm^{-3}. The deoxygenation of solvents before dissolution is important to obtain reproducible kinetic data in the laser photolysis experiment.

Results and Discussion

Photolysis of $Mn_2(CO)_{10}$ in Cyclohexane. The transient absorption spectrum observed 50 ns after excitation (Figure 1) is virtually identical with the spectrum of the primary photoproducts in picosecond flash photolysis of $Mn_2(CO)_{10}$ in EtOH.[8] The absorbances of two peaks at 827 (band I) and 500 nm (band II) observed immediately after excitation are proportional to the laser intensity showing that both species are formed in one-photon process. The absorption band I with λ_{max} at 827 nm disappears within 30 μs after excitation, whereas band II with λ_{max} at 500 nm does not decay in the time region. Band I is assigned to the $\cdot Mn(CO)_5$ radical formed by homolysis of the Mn–Mn bond on the basis of the similarity in the absorption spectrum to that of the $\cdot Mn(CO)_5$ radical produced by photolysis of $HMn(CO)_5$ in solid CO matrix by Church et al.[15] and by pulse radiolysis of $Mn_2(CO)_{10}$ in EtOH by Waltz et al.[16] and decay kinetics.

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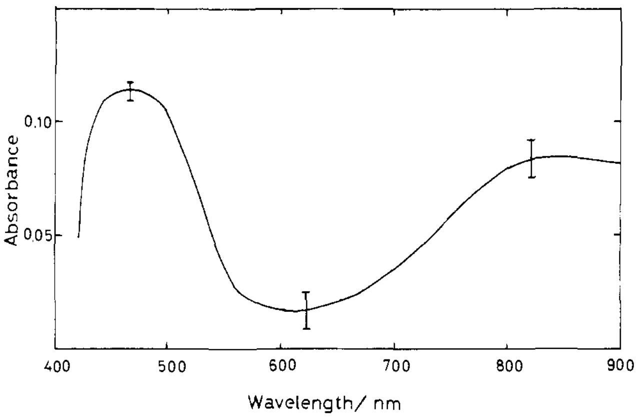


Figure 1. Transient absorption spectrum observed 50 ns after excitation of the cyclohexane solution of $Mn_2(CO)_{10}$.

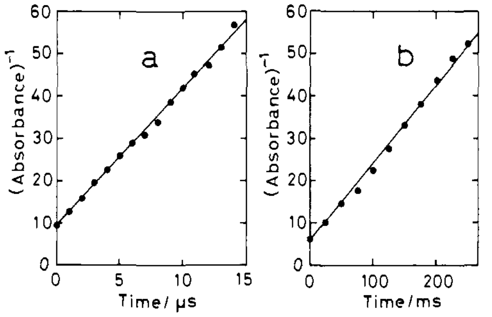
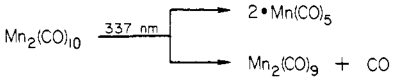


Figure 2. Second-order kinetic plots of transients in the cyclohexane solution of $Mn_2(CO)_{10}$: a, 827 nm; b, 500 nm.

The absorbance at 827 nm in cyclohexane decreases following second-order kinetics (Figure 2, curve a). This can be interpreted in terms of the recombination of the $\cdot Mn(CO)_5$ radicals.



$$2\cdot Mn(CO)_5 \xrightarrow{k_1} Mn_2(CO)_{10} \qquad (1)$$

$$Mn_2(CO)_9 + L \xrightarrow{k_2} Mn_2(CO)_9L \qquad (2)$$

From the analysis of plots (curve a, Figure 2), $2k_1/\epsilon_{827}$ in cyclohexane was determined as $(2.2 \pm 0.1) \times 10^6$ s^{-1} cm, where k_1 is the second-order rate constant of reaction 1 and ϵ_{827} represents the molar absorptivity of $\cdot Mn(CO)_5$ at 827 nm. The value of $2k_1/\epsilon_{827}$ in cyclohexane is a little larger than that obtained in EtOH, 1.5×10^6 s^{-1} cm.[16] The difference is probably ascribed to the lower viscosity of cyclohexane than EtOH. By using the molar absorptivity of $\cdot Mn(CO)_5$ at 830 nm, 800 cm^{-1} mol^{-1} dm^3, in EtOH,[16] the second-order rate constant, k_1, in cyclohexane is estimated to be 8.8×10^8 mol^{-1} dm^3 s^{-1}. This is in relatively good agreement with the reported values in cyclohexane,[7,4] 9.5×10^8 and 1.9×10^9 mol^{-1} dm^3 s^{-1}, and in EtOH,[16] 6.0×10^8 mol^{-1} dm^3 s^{-1}.

The absorption band II with λ_{max} at 500 nm can be assigned to another photoproduct, $Mn_2(CO)_9$, which is formed by loss of CO and possibly with coordination of a solvent molecule,[8] on the basis of the following investigation (vide infra).

The absorbance of band II at 500 nm also decreases following second-order kinetics (Figure 2, curve b). The second-order decay of the second species is due to the reaction of $Mn_2(CO)_9$ and CO in equimolar amount (reaction 2, L = CO). From the analysis of the plots (curve b, Figure 2), k_2/ϵ_{500} was determined to be $(1.2 \pm 0.2) \times 10^2$ s^{-1} cm, where k_2 is the rate constant of disappearance of $Mn_2(CO)_9$ and ϵ_{500} represents the molar absorptivity at 500 nm. The same second-order kinetic behavior in the decaying process was also observed at a different wavelength region of 430–550 nm. It is emphasized that two transient species corresponding to bands I and II are formed directly by the photoexcitation of $Mn_2(CO)_{10}$ and disappear following second-order kinetics independent of each other. A transient with a very long lifetime ($\tau_{1/2}$ = 26 s) formerly observed[4] could be detected when cyclohexane was insufficiently deoxygenated before dissolution.

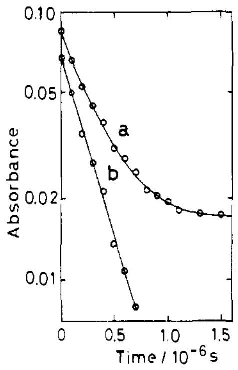


Figure 3. Time dependence of absorbance at 500 nm in the presence of 0.14 mol dm^{-3} of EtCN: curve a, observed time profile; curve b, $A(t) - A(\infty)$ where $A(\infty)$ is the average absorbance at a delay time longer than 1.5 μs.

Photolysis of $Mn_2(CO)_{10}$ in the Presence of RCN in Cyclohexane. Quenching experiments of the absorption band II with RCN were carried out to confirm the assignment to $Mn_2(CO)_9$. The time dependence of the intensity of the absorption at 500 nm induced by the excitation of $Mn_2(CO)_{10}$ solution containing 0.14 mol dm^{-3} of EtCN is shown in Figure 3, curve a. The absorbance decreases to a final value, $A(\infty)$, which is constant for a few seconds. The difference in absorbance between $t = t$ and $t = \infty$, $A(t) - A(\infty)$, decreases exponentially with the increasing time (Figure 3, curve b). This observation indicates that the species reacts with EtCN to form a stable product (reaction 2, L = EtCN). The absorption spectrum of the stable product is very close to that of the authentic $Mn_2(CO)_9(EtCN)$. This supports the assignment of the second species to $Mn_2(CO)_9$. When MeCN is employed as a quencher, the isosbestic point in the absorption spectra of $Mn_2(CO)_9$ and $Mn_2(CO)_9(MeCN)$ is located at 460 nm. With use of the molar absorptivity of $Mn_2(CO)_9(MeCN)$ at 460 nm (1100 mol^{-1} dm^3 cm^{-1}) and the transient absorption spectrum (Figure 1), the upper limit of the molar absorptivity of $Mn_2(CO)_9$ at 500 nm, ϵ_{500}, is determined to be 1000 mol^{-1} dm^3 cm^{-1}. Thus the rate constant of reaction 2 (L = EtCN) is estimated to be smaller than $(4.9 \pm 0.7) \times 10^7$ mol^{-1} dm^3 s^{-1}.

The decay in absorbance at 827 nm in the presence of EtCN also follows second-order kinetics with no apparent difference from that in the absence of EtCN showing that the $\cdot Mn(CO)_5$ radical does not take part in the formation of $Mn_2(CO)_9(EtCN)$ under the present conditions.

The rate constant of the reaction 2 (L = *t*-BuNC) was determined to be $(5.4 \pm 0.5) \times 10^7$ mol^{-1} dm^3 s^{-1} by the similar quenching experiment. The rate constant of the reaction of $Mn_2(CO)_9$ with CO in cyclohexane is calculated as 1.2×10^5 mol^{-1} dm^3 s^{-1}. The reactivity of $Mn_2(CO)_9$ is higher with EtCN than with CO. This fact is consistent with the previous reports that the rate constant[17] of the reaction of $Cr(CO)_5$ with MeCN in cyclohexane, 1.6×10^8 mol^{-1} dm^3 s^{-1}, is much larger than that[18] with CO, 3×10^6 mol^{-1} dm^3 s^{-1}.

With use of these estimated values, the optical path length of our system (0.7 cm), and the transient absorbance, the concentrations of $\cdot Mn(CO)_5$ and $Mn_2(CO)_9$ at the delay time of 50 ns after excitation are estimated to be $\sim 1.5 \times 10^{-4}$ and $\gtrsim 1.4 \times 10^{-4}$ mol dm^{-3}, respectively. The concentrations of both species correspond to one-third of the total concentration of $Mn_2(CO)_{10}$ in

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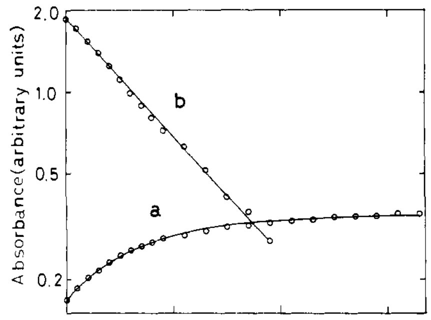

Figure 4. Time dependence of absorbance at 475 nm in the presence of 2.0×10^{-3} mol dm^{-3} of $P(n\text{-}Bu)_3$: curve a, observed time profile; curve b, $A(\infty) - A(t)$.

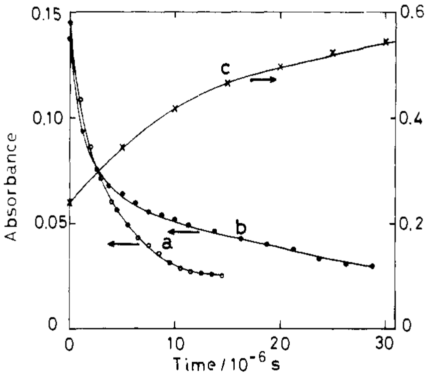

Figure 5. Time dependences of absorbance in the presence of $P(n\text{-}Bu)_3$: curve a, 827 nm, $[P(n\text{-}Bu)_3] = 2.0 \times 10^{-3}$ mol dm^{-3}; curve b, 827 nm, $[P(n\text{-}Bu)_3] = 2.0 \times 10^{-2}$ mol dm^{-3}; curve c, 450 nm, $[P(n\text{-}Bu)_3] = 2.0 \times 10^{-2}$ mol dm^{-3}.

a flashed area showing that the quantum yields for $\cdot Mn(CO)_5$ and $Mn_2(CO)_9$ formation are around 0.3. Therefore in the photolysis of $Mn_2(CO)_{10}$ under the present degassed conditions the cleavage of the Mn–CO bond is roughly as important as the Mn–Mn bond fission.

Photolysis of $Mn_2(CO)_{10}$ in the Presence of $P(n\text{-}Bu)_3$. Although the photolysis in the presence of $P(n\text{-}Bu)_3$ is complicated, there are two distinct features in the time dependence of the transient absorption. One is a rapid increase in absorbance at 475 nm when the concentration of the phosphine is 2.0×10^{-3} mol dm^{-3}. The absorbance increases to a final value within 2 μs after excitation (Figure 4, curve a), whereas the absorbance in the wavelength region of 525–550 nm decreases to a constant final value within 2 μs after excitation. These absorbance changes are ascribed to the formation of $Mn_2(CO)_9[P(n\text{-}Bu)_3]$ (reaction 2, L = $P(n\text{-}Bu)_3$). The absorbance difference, $A(\infty) - A(t)$, at 475 nm follows the first order kinetics (Figure 4, curve b). The rate constant of reaction 2 (L = $P(n\text{-}Bu)_3$) is determined to be $(1.0 \pm 0.1) \times 10^9$ mol^{-1} dm^3 s^{-1}. There is, however, no appreciable difference in the decay curve of the transient absorption at 827 nm under the lower phosphine concentration (Figure 5, curve a) from that observed in the absence of the phosphine.

These experimental results imply no correlation between the formation of $Mn_2(CO)_9[P(n\text{-}Bu)_3]$ and the decay of $\cdot Mn(CO)_5$. Apparently the substitution of CO in $\cdot Mn(CO)_5$ with $P(n\text{-}Bu)_3$ (reaction 3) does not occur appreciably under this lower phosphine concentration.

$$\cdot Mn(CO)_5 + P(n\text{-}Bu)_3 \rightarrow \cdot Mn(CO)_4[P(n\text{-}Bu)_3] + CO \qquad (3)$$

$$2\cdot Mn(CO)_4[P(n\text{-}Bu)_3] \rightarrow Mn_2(CO)_8[P(n\text{-}Bu)_3]_2 \qquad (4)$$

$$\cdot Mn(CO)_4[P(n\text{-}Bu)_3] + \cdot Mn(CO)_5 \rightarrow Mn_2(CO)_9[P(n\text{-}Bu)_3] \qquad (5)$$

The other feature appears in the absorbance changes of the sample containing 2.0×10^{-2} mol dm^{-3} of the phosphine. The absorbance at 450 nm continues to increase even after 2 μs, and the time dependence of the absorbance at 827 nm shows a deviation from that of the lower phosphine concentration (Figure 5, curves b and c). These features are best explained by the occurrence of reaction 3 in this higher phosphine concentration followed by the formation of $Mn_2(CO)_9[P(n\text{-}Bu)_3]$ and $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$ by the recombination reactions 5 and 4 after completion of the formation of $Mn_2(CO)_9[P(n\text{-}Bu)_3]$ by reaction 2. Both phosphine-substituted products have absorptions in the reaction of 450–500 nm although the absorptivity of the monophosphine complex in this region is much weaker than others.[2b,19] This hinders further analysis of the system.

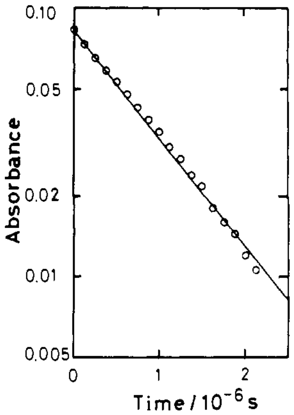

Figure 6. First-order kinetic plot for decay of transient at 827 nm in CCl_4 solution of $Mn_2(CO)_{10}$.

In order to identify the products from the photolysis in the presence of $P(n\text{-}Bu)_3$, they were accumulated by 100 laser shots on one sample of $[Mn_2(CO)_{10}]$ (3×10^{-4} mol dm^{-3}) and $[P(n\text{-}Bu)_3]$ (1×10^{-2} mol dm^{-3}), from which $Mn_2(CO)_9[P(n\text{-}Bu)_3]$ and $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$ in a ratio of 1:3 at about 10% conversion were identified by the IR method. The product ratio of the photolysis system with higher phosphine concentration implies that the formation process of $\cdot Mn(CO)_5$ may be about three times more efficient than the formation process of $Mn_2(CO)_9$ under the same conditions, whereas almost equivalent contribution of both processes is estimated by the quenching experiment with RCN (vide supra). Although the discrepancy in the estimated efficiency of two primary processes requires further study, it can be safely concluded that the apparent effect of the phosphine concentration on the kinetics indicates an associative nature of the substitution on $\cdot Mn(CO)_5$ (reaction 3).

It has been widely accepted[2] that the 17-electron metal-centered carbonyl species undergo facile dissociative loss of CO since Kidd and Brown' work[13] on the photochemical substitution of $Mn_2(CO)_{10}$ with phosphine. However, the controversy[20] of whether the displacement of CO in $\cdot Mn(CO)_5$ is dissociative or associative has not yet been clarified. Recently the closely related reaction of $\cdot Re(CO)_5$ with PPh_3 has been reported to be associative in the photochemical competition reaction with CCl_4 by Fox et al.[21] and also the associative nature of the substitution of $\cdot Mn(CO)_3[P(n\text{-}Bu)_3]_2$ with CO has been shown by McCullen et al.[22]

Photolysis of $Mn_2(CO)_{10}$ in CCl_4 and in $CHCl_3$. The transient absorption intensity at 827 nm decreases following first-order kinetics (Figure 6) showing that the reaction of $\cdot Mn(CO)_5$ with CCl_4 is faster than the recombination reaction (1). The rate constant is determined to be $(9.1 \pm 0.8) \times 10^5$ s^{-1}.[23,24] The decay

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of $Mn_2(CO)_9$ also follows first-order kinetics, and the rate constant is determined to be $(2.1 \pm 0.4) \times 10^2$ s^{-1}. This observed kinetics can be interpreted in terms of the reaction of $Mn_2(CO)_9$ with the CCl_4 and/or CCl_3 radical formed by the reaction of $\cdot Mn(CO)_5$ with CCl_4. The increase in absorbance in the spectral region of 430–500 nm is observed after the disappearance of $Mn_2(CO)_9$. Although the explanation for this observation is not yet clear, the generation of $Mn_2(CO)_9$ even in CCl_4 also supports the nonradical nature of its origin.

The decay of the transient absorption intensity at 825 nm observed for $Mn_2(CO)_{10}$ in $CHCl_3$ follows second-order kinetics. Therefore the reaction rate of $\cdot Mn(CO)_5$ with $CHCl_3$ is much smaller than the recombination rate of the radicals. This is consistent with the report that the reaction rate constant of CCl_4 to the metal radical $(\eta^5\text{-}C_5H_5)W(CO)_3$ is larger than that of $CHCl_3$ by 3 orders of magnitude.[25]

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn(CO)_5$, 15651-51-1; $Mn_2(CO)_9$, 86728-79-2; $Mn_2(CO)_9(t\text{-BuNC})$, 57956-57-7; $Mn_2(CO)_9(MeCN)$, 14837-20-8; $Mn_2(CO)_9[P(n\text{-Bu})_3]$, 24476-71-9; $Mn_2(CO)_8[P(n\text{-Bu})_3]_2$, 15609-33-3; EtCN, 107-12-0; $P(n\text{-Bu})_3$, 998-40-3; CCl_4, 56-23-5; $CHCl_3$, 67-66-3.

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Highly Reduced Organometallics. 15.[1] Coordinatively Unsaturated Tetranuclear Hydrido Carbonyl Clusters of Molybdenum and Tungsten. Structural Characterization of $[(n\text{-}C_3H_7)_4N]_4[HMo(CO)_3]_4$

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Abstract: Treatment of $M(CO)_3(PMTA)$ (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine; M = Mo, W) with $K[sec\text{-}Bu_3BH]$ in refluxing THF, followed by cation exchange, provides 50–60% yields of deep purple $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ and 25–40% yields of deep blue-violet $[R_4N]_4[HW(CO)_3]_4$ (R = Et, *n*-Pr, *n*-Bu). Similar reactions of $Mo(CO)_4(TMED)$ (TMED = *N,N,N′,N′*-tetramethylethylenediamine) with $K[sec\text{-}Bu_3BH]$ give 18–27% yields of $[R_4N]_4[HMo(CO)_3]_4$. While excess $K[sec\text{-}Bu_3BH]$ reacts with $[Et_4N]_2[H_2Mo_2(CO)_8]$ to provide a 12% yield of $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$, substantially lower yields (ca. 4%) of $[Et_4N]_4[HMo(CO)_3]_4$ are obtained from the reactions of $Na_4[Mo(CO)_4]$ with excess CH_3CN or $Mo(CO)_6$ with $NaBH_4$ in refluxing THF, followed by cation exchange. Treatment of $K_2[H_2W(CO)_4]$ with aqueous $[Et_4N]Br$ or $[Me_3O][BF_4]$ in CH_3CN, followed by cation exchange, provides a 19% or 38% yield of $[Et_4N]_4[HW(CO)_3]_4$. These initial examples of hydrido carbonyl clusters of molybdenum and tungsten are coordinatively unsaturated 56-electron tetramers and are characterized on the basis of elemental analyses and IR and ^1H NMR spectra. Analysis of the latter for $[HW(CO)_3]_4^{4-}$ establishes this cluster to be stereochemically nonrigid where there is equivalent coupling of each hydride to all four tungsten atoms from +20 to −40 °C in acetonitrile. Although these clusters are quite resistant to attack by basic reagents, they do readily interact with CO to give initially unsaturated dimers, $H_2M_2(CO)_8^{2-}$, which are then converted in high yields to $M_2(CO)_{10}^{2-}$. A single-crystal X-ray structural determination of $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ shows the presence of an essentially tetrahedral anion in which the carbonyl groups are eclipsed with respect to the M–M edges. The latter structural feature strongly suggests the presence of four face-bridging hydrogen atoms, which were not located directly. The crystals were monoclinic (space group $P2_1$) with cell parameters $a = 15.467$ (6) Å, $b = 15.540$ (14) Å, $c = 15.143$ (4) Å, $\beta = 92.37$ (3)°, $V = 3637$ (6) Å^3, and $z = 2$.

The chemistry and syntheses of polynuclear transition-metal compounds have become an area of great interest due to the possible involvement of such species, especially carbonyl clusters, in the catalyzed hydrogenation of carbon monoxide and related important processes.[2] Although homonuclear carbonyl clusters of metals of groups 7 and 8 are well established and structurally characterized in many cases, corresponding clusters containing the group 6 transition elements are much less common.[3] To our knowledge, $[Cp_3Mo_3(CO)_6S]^+$ is the only previously established homonuclear group 6 carbonyl cluster.[4] Several polynuclear complexes of Cr, Mo, and W are known, but the metals in these species appear to be held together by bridging ligands and at most one metal–metal bond. For example, the unusual $[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]^{3-}$ is best considered to contain only one W–W bond,[5] while $[Mo_3(CO)_6(NO)_3(\mu\text{-}OCH_3)_3(\mu_3\text{-}OCH_3)]^-$,[6] $[Mo_3(CO)_6(NO)_3(\mu\text{-}OCH_3)_3(\mu_3\text{-}O)]^{2-}$,[6] and $[HW(CO)_3(OH)(PPh_3O)]_4$[7] are formulated to contain no significant metal–metal interactions. While trinuclear carbonylmetallates, $M_3(CO)_{14}^{2-}$ (M = Cr, Mo, W), were reported many years ago and formulated on the basis of elemental and gas analyses,[8] no further information has been presented on these mysterious materials.

In this paper we report on the synthesis and characterization of the initial examples of tetranuclear carbonyl clusters of mo-

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