Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Low-Temperature Photochemistry of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$: Identification of an Unexpectedly Stable Coordinatively Unsaturated Heterodinuclear Carbonyl Complex

Keith R. Pope and Mark S. Wrighton*

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The low-temperature photochemistry of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ has been investigated in rigid methylcyclohexane at 93 K. Irradiation at either 313 or 366 nm results in loss of CO as the only photoreaction, and the relative efficiency of CO loss in the glass was established as $\Phi_{313}/\Phi_{366} \approx 15$, with $\Phi_{diss} = 10^{-3}$ at 313 nm. The origin of photoejected CO (Mo or Mn) cannot be established by a selective ^{13}CO labeling of the starting complex because ^{13}C NMR shows rapid scrambling of CO at 298 K. IR and UV–vis measurements made after the glass was warmed and cooled establish that two isomers of the CO loss product exist, and the more unstable isomer undergoes rapid thermal conversion to the more stable isomer upon melting the glass. No significant wavelength dependence on the product distribution is observed, indicating that both isomers are formed from the decay of the same excited state. The structure of the more stable isomer of (η^5-C_5H_5)MoMn(CO)$_7$ features six terminal CO ligands and one bridging CO as deduced from the IR spectrum and is assigned a structure featuring a bridging CO, (η^5-C_5H_5)Mo(CO)$_2$(μ-CO)Mn(CO)$_4$. The less stable isomer of (η^5-C_5H_5)MoMn(CO)$_7$ is formulated as having a μ-η^1, η^2-CO. Both isomers react with CO in fluid methylcyclohexane to yield (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$. At 298 K (η^5-C_5H_5)MoMn(CO)$_7$ reacts with CO to quantitatively yield (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ with a rate constant of 1.4×10^2 M^{-1} s^{-1}. Kinetic measurements were made to determine the activation parameters ($\Delta H^\ddagger = 24.0 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = -140 \pm 20$ J mol^{-1} K^{-1}) for the reaction of the more stable isomer of (η^5-C_5H_5)MoMn(CO)$_7$ with CO, and the results indicate that the rate is controlled by a large entropic contribution.

In this article we report our findings on the photochemistry of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ at low temperature in a rigid alkane glass. Recent investigations have established that metal–metal bond cleavage (eq 1) is an important primary photoprocess for

$$L_xM\text{–}M'L_y \xrightarrow{h\nu} L_xM^\bullet + {}^\bullet M'L_y \qquad (1)$$

$$L_xM\text{–}M'L_y \xrightarrow{h\nu} L_xM\text{–}M'L_{y-1} + L \qquad (2)$$

homo- and heterodinuclear complexes such as [M(CO)$_5$]$_2$ (M = Mn, Re), [(η^5-C_5H_5)M(CO)$_3$]$_2$ (M = Mo, W), [η^5-(C_5R_5)Fe(CO)$_2$]$_2$ (R = H, Me), (η^5-C_5H_5)M(CO)$_3$M′(CO)$_5$ (M = Mo, W; M′ = Mn, Re), and (η^5-C_5H_5)Fe(CO)$_2$Mo(CO)$_3$(η^5-C_5H_5).[1,2] Although it is also known that photoinduced CO loss is an important primary photoprocess for mononuclear[3] and homodinuclear[1,4] carbonyl complexes, little is known concerning the importance of CO loss (eq 2, L = CO) in the photochemistry of heterodinuclear complexes.[5,6] Our interest in the low-temperature photochemistry of heterodinuclear carbonyl complexes stems from the observation that simple ligand substitution reactions can be directed to occur thermally at one metal center or another, as was recently reported for (CO)$_4$Ru(μ-PPh$_2$)Co(CO)$_3$[7] and H$_2$FeRu$_3$(CO)$_{13}$,[8] and that CO loss can be effected photochemically at low temperature, as was shown for (η^5-C_5H_5)Fe(CO)$_2$Co(CO)$_4$.[6] We have recently shown that CO loss occurs from photoexcited (η^5-C_5R_5)Fe(CO)$_2$Mn(CO)$_5$ (R = H, Me) at low temperature in a rigid glass without detectable Fe–Mn bond cleavage, whereas Fe–Mn bond homolysis dominates the fluid-solution photochemistry.[5b] In this situation the loss of CO gives rise to net substitution on Mn when the low-temperature photoproduct (η^5-C_5R_5)FeMn(CO)$_6$ is warmed in the presence of a P-donor ligand.[5b] However, in general, little is known about the structure or reactivity of coordinatively unsaturated heterodinuclear complexes. The present work describes the application of low-temperature techniques to the study of a new species, (η^5-C_5H_5)MoMn(CO)$_7$, photogenerated from (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$.

Experimental Section

Instrumentation. Infrared spectra were obtained with a Nicolet Model 60SX or 7199 Fourier transform IR spectrometer. UV–vis spectra were recorded by using a Cary 17 spectrophotometer or a Hewlett-Packard 8451A diode array spectrometer.

Low-temperature measurements were performed with a Precision Cell, Inc., Model P/N 21000 variable-temperature cell with CaF$_2$ inner and outer windows, using liquid N$_2$ as the coolant. The temperature of the alkane glass was monitored by using a copper–constantan thermocouple in contact with the inner window of the cell.

Kinetic measurements were performed with a CTI Cryogenics Model 21 helium refrigerator and a custom-built brass cell fitted with CaF$_2$ inner windows and sapphire outer windows. The concentrations of (η^5-C_5H_5)MoMn(CO)$_7$ and uncomplexed CO were measured by using the IR absorptivities (vide infra) in the alkane glass at 93 K before warming to the temperature at which the kinetic measurement was performed. Following each kinetic run, the cell was recooled to 93 K, and the concentration of CO was again measured to ensure that no depletion of CO resulted from cell leakage. Temperatures for the kinetic measurements were monitored by a gold–chromel thermocouple in contact with the base plate of the cell and are accurate to ±1 °C.

^{13}C NMR spectra were recorded on a Bruker WM270 FTNMR spectrometer equipped with a B-VT 1000 variable-temperature unit. The ^{13}C chemical shifts were referenced to the ipso carbon of toluene-d_8 at 137.5 ppm.

Irradiations. Irradiations were carried out at 313 nm with a Bausch and Lomb SP250 high-pressure Hg lamp filtered by a 10-cm H$_2$O filter with Pyrex windows followed by a 1-cm cell containing a K$_2$CrO$_4$/K$_2$CO$_3$ solution to give 313 ± 20 nm. Quantum yield determinations at low temperature were made by first measuring the light flux through the low-temperature cell by using the photochemical reaction of Mn$_2$(CO)$_{10}$

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* To whom correspondence should be addressed.

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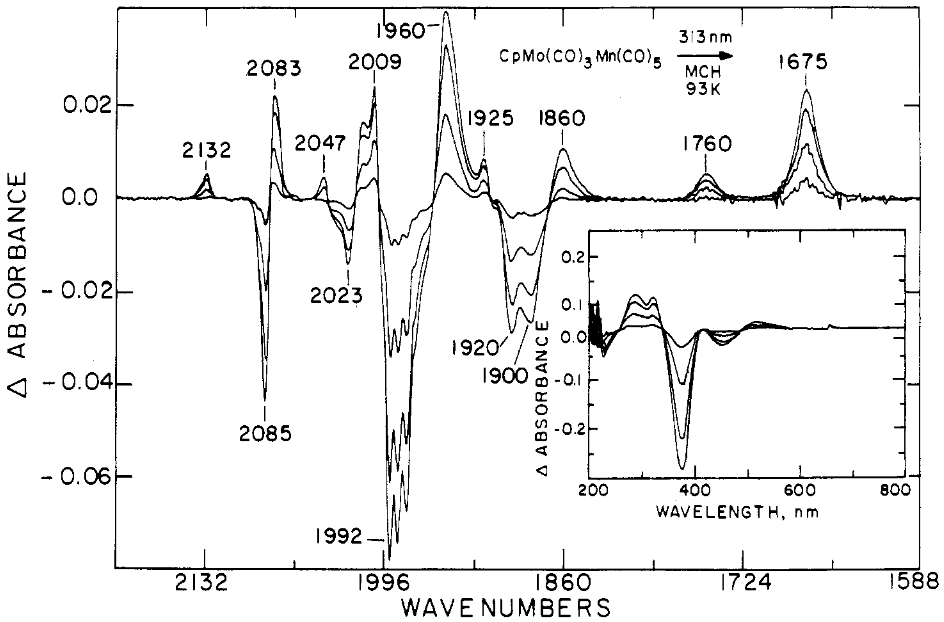

Figure 1. Irradiation of 5 × 10^{-4} M (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ at 313 nm in rigid MCH at 93 K. The inset shows UV-vis absorbance changes accompanying irradiation. Irradiation times are 10, 30, 40, and 48 min.

with CCl_4 in pure CCl_4 solution as an actinometer.[9]

Materials. Methylcyclohexane (MCH) was distilled from sodium under argon and stored in an argon-filled glovebox prior to use. CCl_4 was distilled from P_2O_5 and stored in the dark under argon prior to use. [(η^5-C_5H_5)Mo(CO)$_3$]$_2$ and [Mn(CO)$_5$]$_2$ were purchased from Strem Chemicals, Inc., and were used without further purification for the synthesis of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$. A previously reported procedure[2a] for the synthesis of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ was used with the modification that the product was recrystallized twice from concentrated hexane solutions before use. Samples of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ for ^{13}C NMR study were enriched with ^{13}CO by preparing the heterodinuclear complex under 1 atm of ^{13}CO (Cambridge Isotope Laboratories). In a typical procedure 0.39 g of $Mn_2(CO)_{10}$ and 0.49 g of [(η^5-C_5H_5)Mo(CO)$_3$]$_2$ were dissolved in 250 mL of toluene in a 500-mL flask under 1 atm of ^{13}CO. This solution was stirred and irradiated with a 550-W Hanovia medium-pressure Hg lamp for 6 h. Irradiation was discontinued, and the solvent was removed in vacuo. The reaction residue was taken up in the minimum amount of hexane (~20 mL) and chromatographed on grade 1 alumina with hexane. The product eluted as an orange band, second after residual $Mn_2(CO)_{10}$. The yield was 0.28 g (32%). The ^{13}CO enrichment level was such that the absorptivity of the IR band at 2084 cm^{-1} was decreased by 90%.

Results and Discussion

Low-Temperature Photoreaction of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$. Spectroscopic properties of relevant compounds are presented in Table I. The spectroscopic properties of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ have been previously reported, but it is important to note that the relatively intense UV-vis absorption at 370 nm and the less intense absorption at 450 nm have been assigned as the $\sigma\sigma^*$ and $\pi d\sigma^*$ transitions, respectively.[2c] When an MCH solution of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ is cooled to 93 K, these two absorptions increase in intensity somewhat but do not shift appreciably in energy. The IR spectrum remains qualitatively the same upon cooling, except for a slight increase in line width of the carbonyl stretching modes.

Figure 1 shows FTIR spectral changes accompanying the 313-nm irradiation of 5 × 10^{-4} M (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ in a MCH glass at 93 K. The appearance of the feature at 2132 cm^{-1} is associated with the production of uncomplexed CO in the glass. Consumption of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ is evidenced by the disappearance of the bands at 2085, 2023, 1992, 1920, and 1900 cm^{-1}. The disappearance of the band at 1982 cm^{-1} is obscured by the appearance of two bands due to the photoproducts in the region 2000–1970 cm^{-1} and contributes to the unusual appearance of the negative peak at 1992 cm^{-1} in Figure 1. Previous work[10] in our laboratory has enabled us to establish the molar absorptivity of uncomplexed CO as 400 cm^{-1} M^{-1} under these conditions. Thus, a comparison of the absorbance at 2132 cm^{-1} with those at 2085, 2023, and 1920 cm^{-1} establishes that there is a 1:1 molar ratio of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ consumed to uncomplexed CO produced in the glass. The important point to be made is that CO loss accounts for all of the starting material consumed and the ejection of CO from (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ results in the formation of one or more compounds formulated as (η^5-C_5H_5)MoMn(CO)$_7$. The bands appearing at 2083, 2047, 2009, 1960, 1925, 1860, 1760, and 1675 cm^{-1} are assigned to the CO-loss product(s). The features that appear at 1760 and 1675 cm^{-1} suggest that bridging carbonyls are structural features of the photoproduct(s). The seven isosbestic points that appear in the IR spectrum suggest a constant ratio of (η^5-

Table I. Spectroscopic Data for Relevant Compounds

compd[a]	IR ν_{CO} (ϵ)[b]	UV-vis λ_{max} (ϵ)[c]
(η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$	2085 (4700), 2026 (2900), 1995 (15 500), 1982 (8000), 1923 (1900), 1907 (4500)	376 (19 500), 450 (1700)
(η^5-C_5H_5)MoMn(CO)$_7$[d]	2084 (3100), 2009 (5900), 1993 (6500), 1981 (5700), 1960 (5300), 1925 (2600), 1680 (2500)	330 (7000), 520 (600)
(η^5-C_5H_5)MoMn(CO)$_7$P(n-Bu)$_3$[e]	2068 (1.1), 2024 (1.0), 1963 (2.5), 1955 (3.2), 1941 (2.0), 1930 (1.9), 1886 (0.5), 1867 (1.2), 1834 (0.7)	

[a] Spectra were recorded in MCH solution at 298 K. [b] Band positions in cm^{-1} (ϵ in M^{-1} cm^{-1}). [c] Band positions in nm (ϵ in M^{-1} cm^{-1}). [d] Spectra were recorded in MCH solution at 273 K. [e] Spectra were recorded in MCH solution at 273 K (relative absorptivities in parentheses).

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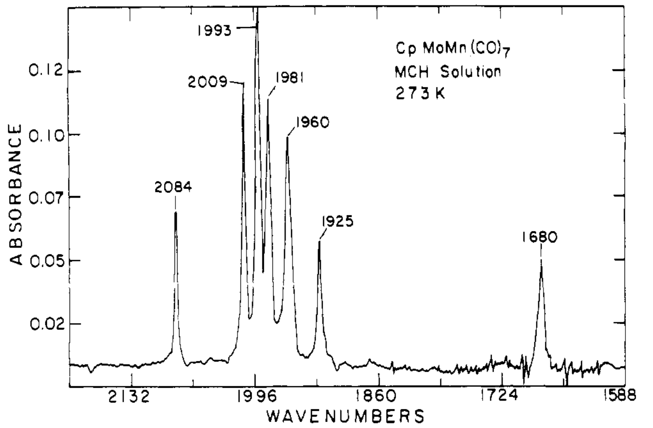


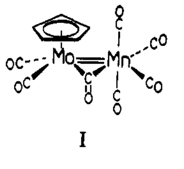
Figure 2. IR spectrum of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ obtained after warming an irradiated MCH glass initially containing 4×10^{-4} M $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ to 273 K. Bands due to unreacted (~70%) $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ have been removed by computer subtraction.

$C_5H_5)Mo(CO)_3Mn(CO)_5$ consumed to product(s) produced.

The inset of Figure 1 shows the UV–vis spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$. Upon irradiation at 313 nm, the appearance of a weak visible band at 520 nm, lower in energy than the $d\pi\sigma^*$ transition for $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$, and a more intense band at 320 nm is concomitant with the disappearance of the absorptions at 376 and 450 nm due to $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$. The energies and relative intensities of the UV–vis absorptions that appear upon irradiation are consistent with the photoproduct(s) being formulated as coordinatively unsaturated and dinuclear, as indicated in eq 2.

When a glass containing $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ is warmed, CO is consumed and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ is partially regenerated. However, there is also a notable change in the IR spectrum of the photoproduct(s). An IR spectrum recorded at 150 K, immediately after the glass melts completely, reveals complete disappearance of the bands at 2047, 2018, 1860, and 1760 cm^{-1}. The absorptions at 2084, 2008, 1960, 1925, and 1675 cm^{-1} are still present and maintain the same relative intensities. If, after the sample is warmed to 150 K, the solution is recooled to 93 K, the bands at 2047, 2018, 1860, and 1760 cm^{-1} do not reappear; this proves that these absorptions are not due to a temperature dependence of the IR spectrum of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$. The UV–vis spectrum remains qualitatively unchanged after the thermal excursion to 150 K. The results obtained from the warming and recooling of a glass containing $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ clearly show that two isomers of the photoproduct are generated at 93 K. Furthermore, an analysis of the IR spectrum obtained after recooling indicates that the disappearance of the photoproduct that has an IR band at 1760 cm^{-1} can be accounted for in terms of additional generation of the photoproduct that has a band at 1675 cm^{-1} as well as reaction with CO to regenerate $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$. This suggests that there is some thermal conversion from the less stable to the more stable isomer of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$.

Figure 2 shows an IR spectrum of the photoproduct $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ measured at 273 K in MCH with the absorptions due to unreacted (~70%) $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ removed by computer subtraction. We note that there are six well-resolved bands at 2084, 2009, 1993, 1981, 1960, and 1925 cm^{-1} associated with terminal CO's and one bridging mode at 1680 cm^{-1} associated with a fully bridging CO. The stable isomer of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ is proposed to have the structure represented by I, having a fully bridging CO associated with the 1680-cm^{-1} absorption. The six other absorptions in the CO stretching region are consistent with the low symmetry of I which has six terminal CO's. Low-temperature irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ yields I along with a small amount of a less stable isomer (II) of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ having a feature at 1760 cm^{-1}, which we attribute to $\mu\text{-}\eta^1,\eta^2$-CO. Such a species is analogous to $Mn_2(CO)_9$,[4b,c] which is formed by photoexcitation of $[Mn(CO)_5]_2$ in a low-temperature matrix and shows a semibridging CO with an associated absorption at 1760 cm^{-1}. The fact that $Mn_2(CO)_9$ and II both have a feature at 1760 cm^{-1} is, of course, coincidental, but the point here is that I has a significantly lower frequency bridging CO feature at 1680 cm^{-1}. It is tempting to conclude that I and II are derived from loss of CO from one metal or another. The Mn–Mo double bonds in I and II are included to indicate that the complexes are coordinatively unsaturated. It should be pointed out that there are other formulations for I and II, including one with a formal 18e count at both Mn and Mo where a C-bound CO on one metal is also a 2e donor to the other metal, from which a CO has been ejected. Further resolution of this structural issue requires additional spectroscopic data.



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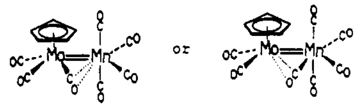

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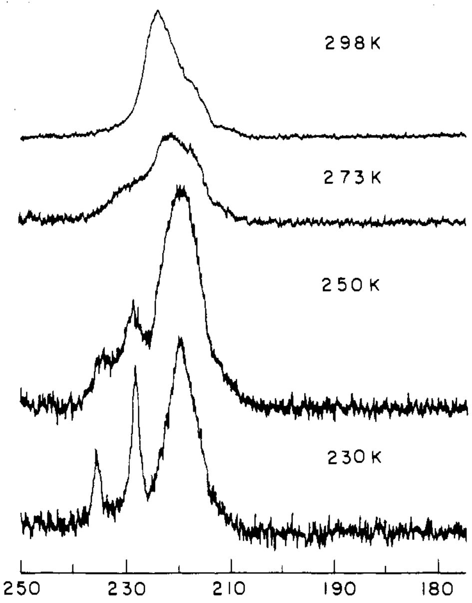

Figure 3. Temperature-dependent ^{13}C NMR spectra (67.3 MHz) of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ in toluene-d_8 solution. The resonance due to the cyclopentadienyl ring carbons (not shown) was observed at 91.7 ppm.

The question of whether the photoejected CO was originally bonded to Mn or to Mo can be answered for a stereorigid molecule where the CO's on only one of the metal centers are enriched with ^{13}C, as has recently been accomplished for $(CO)_5ReMn(CO)_5$.[11] The temperature-dependent ^{13}C NMR spectrum of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ in toluene-d_8 is presented in Figure 3. At 293 K a broad resonance centered at 223.6 ppm is observed. This signal separates into three broad singlets at 235.4, 227.9, and 219.2 ppm when the sample is cooled to 230 K. Throughout this temperature excursion there is no noticeable change in the sharp signal due to the cyclopentadienyl ring carbons at 91.7 ppm (not shown). This behavior is attributed to metal site exchange of the CO ligands, and this evaluation suggests the impossibility of a se-

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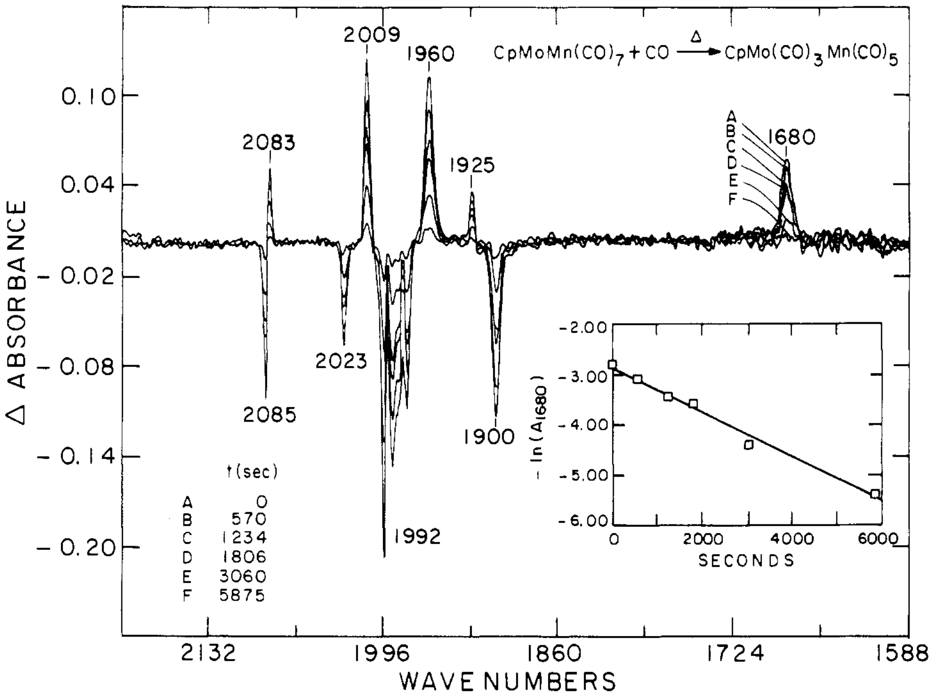

Figure 4. Kinetics of the back-reaction of 3.0×10^{-5} M (η^5-C_5H_5)MoMn(CO)$_7$ with 7.1×10^{-4} M CO in MCH solution at 200 K. Positive peaks decay with time and correspond to disappearance of (η^5-C_5H_5)MoMn(CO)$_7$. The growth of negative peaks corresponds to regeneration of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$. The inset shows a plot of ln (A_0/A) for the disappearance of the band at 1680 cm^{-1}.

lective-labeling experiment for (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$. We cannot, therefore, establish the metal from which CO is extruded for (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$.

The low-temperature irradiation of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ has been carried out by using 313- or 366-nm exitation wavelengths, and it was determined that the relative efficiencies for CO loss in the glass are $\Phi_{313}/\Phi_{366} \approx 15$. The absolute value of Φ_{diss} for (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ at 313 nm is low, 2×10^{-3}. The fact that there is no significant wavelength dependence on the relative ratios of the photoproducts suggests that the distribution of isomers produced in the glass involves decay of the same excited state.

Thermal Reactions of (η^5-C_5H_5)MoMn(CO)$_7$. The more stable CO-loss product, I, reacts with CO slowly in solution, and the spectral changes can be monitored at temperatures as high as room temperature, at which the compound persists for a few seconds. Eventually, there is nearly complete regeneration (>85%) of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$. It is noteworthy that there is no detectable formation of [Mn(CO)$_5$]$_2$ or [(η^5-C_5H_5)Mo(CO)$_3$]$_2$, which would form if metal-centered radicals were present following photolysis. Further, if the photoproduct is warmed to 298 K in the presence of 1×10^{-3} M CCl_4 (~10-fold excess), no formation of the corresponding metal carbonyl chlorides, (η^5-C_5H_5)Mo(CO)$_3$Cl and ClMn(CO)$_5$, is observed, as would be expected if metal carbonyl radicals were present.[2a] The flash photolysis (~20-μs Xe lamp pulse) of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ in room-temperature MCH solution, with IR detection less than 10 s after the flash, results in conversion only to the corresponding homodinuclear dimers, [(η^5-C_5H_5)Mo(CO)$_3$]$_2$ and [Mn(CO)$_5$]$_2$, and no detectable formation of (η^5-C_5H_5)MoMn(CO)$_7$. The flash photolysis of 1.2×10^{-3} M (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ in pure CCl_4 results in the quantitative formation of (η^5-C_5H_5)Mo(CO)$_3$Cl and ClMn(CO)$_5$. The main point is that low-temperature irradiation of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ yields CO loss to give I and II. Warmup results in CO uptake, not radical abstraction or coupling chemistry.

Although the ligand (other than CO) uptake reactions of (η^5-C_5H_5)MoMn(CO)$_7$ have not been extensively investigated in this study, preliminary experiments indicate that the coordinatively unsaturated species (4×10^{-4} M) reacts rapidly with PPh$_3$ or P(n-Bu)$_3$ (1×10^{-4} M) at or above the melting point of the MCH glass. The IR bands of the P(n-Bu)$_3$ addition product(s) are presented in Table I. If the product mixture containing starting material and the P-donor adduct(s) is then irradiated in CCl_4 solution to convert the compounds to the metal carbonyl chlorides, only (η^5-C_5H_5)Mo(CO)$_3$Cl, ClMn(CO)$_5$, and ClMn(CO)$_4$PR$_3$ are observed as primary photoproducts. This indicates that addition of PR$_3$ to (η^5-C_5H_5)MoMn(CO)$_7$ is occurring only on the Mn atom. In contrast, if a CCl_4 solution of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$ (5×10^{-3} M) containing PR$_3$ (2×10^{-3} M) is irradiated at room temperature, the primary products observed are (η^5-C_5H_5)Mo(CO)$_3$Cl, ClMn(CO)$_5$, and ClMn(CO)$_4$PR$_3$. Formation of (η^5-C_5H_5)Mo(CO)$_2$(PR$_3$)Cl occurs, but this results only from the photolysis of (η^5-C_5H_5)Mo(CO)$_3$Cl in the presence of PR$_3$. Importantly, (η^5-C_5H_5)Mo(CO)$_2$(PR$_3$)Cl is not observed as a primary product from irradiation of (η^5-C_5H_5)MoMn(CO)$_7$PR$_3$ in CCl_4, consistent with the conclusion that the P-donor is bonded to the Mn as found in the photosubstitution reaction of (η^5-C_5H_5)Fe(CO)$_2$Mn(CO)$_5$.[5b]

We have quantitatively monitored the thermal reaction of (η^5-C_5H_5)MoMn(CO)$_7$ with CO as a function of temperature and CO concentration. Our results show that the rate law given in eq 3 applies. It is possible to generate (η^5-C_5H_5)MoMn(CO)$_7$

$$\text{rate} = k_2[\text{CO}][(\eta^5\text{-}C_5H_5)\text{MoMn(CO)}_7] \qquad (3)$$

in a rigid alkane glass that already contains a known amount of uncomplexed CO. By control of the extent of photochemical depletion of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$, a glass can be prepared that contains (η^5-C_5H_5)MoMn(CO)$_7$ and a known excess (>10-fold) of CO. The glass can then be melted and warmed to a temperature that is appropriate for monitoring the rate of CO back-reaction. Data presented in Figure 4 are typical of the kind of information that has been obtained. Under the conditions used, the reaction is pseudo first order in the disappearance of (η^5-C_5H_5)MoMn(CO)$_7$ and in the appearance of (η^5-C_5H_5)Mo(CO)$_3$Mn(CO)$_5$. The value of the bimolecular rate constant k_2 was calculated at various temperatures by using the functional dependence of the disappearance of the band at 1680 cm^{-1}, shown in the inset, and the known concentration of CO as determined by IR spectra taken in the glass before and after irradiation. All experiments are in accord with the rate law expressed in eq 3, and the results are summarized in an Eyring plot spanning the temperature range 170–210 K as shown in Figure 5. $\Delta H^{\ddagger}$ was determined to be 24.0 ± 2 kJ mol^{-1}, and the associated $\Delta S^{\ddagger}$ was

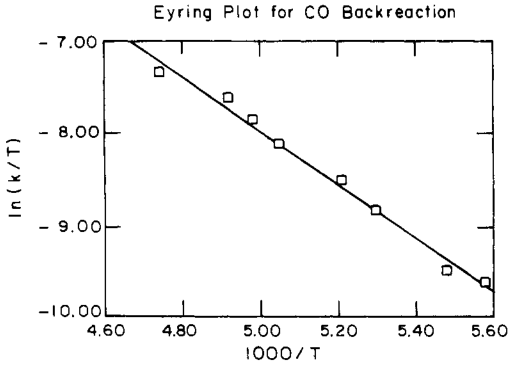

Figure 5. Plot of ln (k_2/T) vs. $1000/T$ for the back-reaction of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ with CO in MCH solution between 170 and 210 K. Data were calculated on the basis of the disappearance of the band at 1680 cm^{-1}.

found to be -140.0 ± 20 J mol^{-1} K^{-1}.

The ΔH^* value is comparable to the enthalpy of activation measured for the reaction of photogenerated $Cr(CO)_5$(alkane) with CO, which has a bimolecular rate constant of 3.6×10^6 M^{-1} s^{-1} at 298 K.[12] By way of comparison, the photogenerated carbonyl-bridged intermediates $Mn_2(CO)_9$ and $(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_3Fe(\eta^5\text{-}C_5H_5)$ react with CO in 298 K alkane solution with bimolecular rate constants of 1.2×10^6 and 4.5×10^4 M^{-1} s^{-1}, respectively.[13,14] The sluggish reaction of the triply CO bridged iron dimer was attributed to the fact that this intermediate has a triplet ground state, and the addition of CO is thus spin-fobidden.[4a,15] The persistence of the intermediate $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ is evidently due to the overwhelming entropic contribution to the rate constant, measured to be 1.4×10^2 M^{-1} s^{-1} at 298 K. The large, negative value of ΔS^* is consistent with an associative reaction, and this may be further interpreted to mean that an initial dissociation of the bridging carbonyl from one of the metal centers is not rate-limiting.

Summary

The low-temperature photochemistry of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ has been investigated in rigid MCH at 93 K. Irradiation at either 313 or 366 nm results in loss of CO as the only photoreaction, and the relative efficiency of CO loss in the glass was established as $\Phi_{313}/\Phi_{366} \approx 15$, with $\Phi_{diss} = 10^{-3}$ at 313 nm. The low absolute quantum yield of the CO loss at low temperature is consistent with the conclusion that the process is quantum-inefficient. The fluid-solution quantum yield for Mo–Mn homolysis in CCl_4 is about 0.5,[2a] meaning that the CO loss in solution will never be a dominant excited-state process in a fluid medium either. Interestingly, a rigid matrix completely suppresses net Mo–Mn bond cleavage upon photoexcitation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ to produce $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$. Presumably, the matrix exerts a large "cage effect" such that the large radicals that would be expected from Mo–Mn bond homolysis are unable to move apart. The unsaturated species from CO loss cannot be generated in high yield in fluid solution (where the cage effect is smaller), owing to efficient ($\Phi_{366nm} = 0.5$)[2a] Mo–Mn bond cleavage upon photoexcitation of the starting material, illustrating the importance of low temperature/rigid media in understanding photoprocesses of metal complexes.

The origin of photoejected CO from $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ (Mo or Mn) cannot be established by a selective ^{13}CO labeling of the starting complex because ^{13}C NMR shows rapid scrambling of CO at 298 K. IR and UV–vis measurements establish that two isomers of the CO-loss product exist, and the more unstable isomer undergoes rapid thermal conversion to the more stable isomer above the melting point of the glass in competition with back-reaction with CO. No significant wavelength dependence on the product distribution was observed, indicating that both isomers of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ are formed from the decay of the same excited state. Both isomers react with CO in fluid MCH to yield $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$. The structure of the more stable isomer of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ features six terminal CO ligands and one bridging CO as deduced from the IR spectrum, and the isomer is assigned a structure featuring a fully bridging CO, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\mu\text{-}CO)Mn(CO)_4$. The less stable isomer of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ has a semibridging CO. Kinetic measurements were made to determine the activation parameters ($\Delta H^* = 24.0 \pm 2$ kJ mol^{-1} and $\Delta S^* = -140 \pm 20$ J mol^{-1} K^{-1}) for the reaction of the more stable isomer of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ with CO, and the results indicate that the rate is controlled by a large entropic contribution. At 298 K $(\eta^5\text{-}C_5H_5)MoMn(CO)_7$ reacts with CO with a rate constant of 1.4×10^2 M^{-1} s^{-1}.

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