Flash Photolysis of [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$: Mechanism of the Formation and Decay of the Linear Semibridged Species (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_4$(μ-η^1,η^2-CO)

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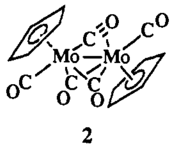
Abstract: The photochemistry of [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ (**1**) has been studied, employing flash photolysis techniques in combination with variable-temperature IR and UV–visible spectroscopy. Solutions of **1** in 3-methylpentane were flash photolyzed at temperatures between 93 and 298 K. The linear semibridging species (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_4$(μ-η^1,η^2-CO) (**2**) was found to be relatively stable in fluid solution at 200 K, but at 240 K it decays, forming **1** and [(η^5-C$_5$H$_5$)Mo(CO)$_2$]$_2$ (**3**). The linear semibridging species is thus established as the key intermediate in the reversible reaction between **1** and **3**. At 200 K another photoproduct was observed and found to decay to **1**. This species was identified as the cis-gauche rotamer (**4**) of the starting dimer (**1**). Two additional unknown species, **5** and **6**, were also observed in minor amounts after flash photolysis at room temperature. Comparison of the low-temperature IR and UV–visible spectra with conventional xenon flash and laser pulse transient spectra allows the assignment of absorption bands and decay rates to **2** and **4**, which have been confused in earlier studies. Additional transient flash photolysis studies of **1** with added CO provide the rate constants for interconversions of **1**, **2**, and **3**. From the information gained in both the low-temperature and transient studies it is also argued that dissociation of CO from **1** is a primary photoprocess. Low-temperature IR spectroscopy following flash photolysis of **1** in the presence of acetonitrile revealed the existence of the unstable monosubstituted dimer at temperatures between 200 and 256 K. At the higher temperatures the substituted dimer was found to decay primarily to **3**. Room temperature rate constants for the addition of acetonitrile to **2** and dissociation of acetonitrile from the monosubstituted dimer (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_5$(CH$_3$CN) (**7**) were obtained with conventional flash photolysis methods.

The photochemistry of [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ (**1**) has been studied extensively.[1-6] A few reports have suggested that there are two primary photoproducts. Homolytic cleavage of the metal–metal bond leads to the (η^5-C$_5$H$_5$)Mo(CO)$_3$ radical; the second primary photoproduct results from CO loss.[1a,b] Rest and coworkers[2] were first to characterize the CO loss product, by photolyzing **1** in PVC and frozen gas matrixes. On the basis of the IR stretching frequencies, the structure was proposed to contain two terminal CO ligands, one 4-electron bridging ligand, and two 2-electron bridging ligands. The CO loss product was found to recombine with CO upon warming to room temperature, reforming **1** quantitatively.

Our interest in semibridging structures and their reactivities has led us to study [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ using a combination of flash photolysis and low-temperature IR spectroscopy. Flash photolysis is preferable to the more commonly used continuous photolysis methods because it permits observation of initial photoproducts, which are frequently destroyed under continuous irradiation. Flash photolysis with UV–visible time-resolved detection has been employed in the past to study [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$, but the results from two groups are inconsistent.[3,4] We have chosen to use a combination of flash photolysis with low-temperature IR detection, so that we might more readily characterize intermediates which are short-lived at room temperature. Using these techniques, we have recently been able to identify new examples of 4-electron semibridge (or linear semibridge) structures.[7] We report here on the identification and study of the semibridging species (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_4$(μ-η^1,η^2-CO) (**2**) in low-temperature solution.



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Prior to the characterization of **2**, photolysis of **1** to form [(η^5-C$_5$H$_5$)Mo(CO)$_2$]$_2$ (**3**) was proposed to proceed through a radical pathway. Wrighton and co-workers showed that [(η^5-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ reacts rapidly with CO to form [(η^5-C$_5$Me$_5$)Mo(CO)$_3$]$_2$ at room temperature; [(η^5-C$_5$Me$_5$)Mo(CO)$_3$]$_2$ was found to lose CO in refluxing toluene with an N$_2$ purge to reform [(η^5-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ quantitatively.[5] Curtis et al.[6] also reported the thermal conversion of **1** to **3**.

In these reports the reversible reactions were proposed to proceed through the mechanism depicted in Scheme I. The 17-electron intermediate produced loses a CO, forming a 15-electron species that would dimerize at a rate comparable to the rate of recombination of the 17-electron species. By removing CO, the N$_2$ purge pushes the equilibrium toward the 15-electron complex and thus to the tetracarbonyl species.

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[1] (a) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187. (b) Stiegman, A. E.; Tyler, D. R. *Acc. Chem. Res.* **1984**, *17*, 61. (c) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1978. (d) Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 338 and references therein.

[2] (a) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Organomet. Chem.* **1983**, *254*, C25. (b) Barker, M. L.; Bloyce, P. E.; Campen, A. K.; Rest, A. J.; Bitterwolf, T. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2825.

[3] Hughey, J. L.; Carl, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.

[4] Van Vlierberge, B. A.; Abrahamson, H. B. *J. Photochem. Photobiol., A: Chem.* **1990**, *52*, 69.

[5] (a) Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 3533. (b) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chem. Acta* **1977**, *23*, 85.

[6] (a) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535. (b) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.

[7] (a) Zhang, S.; Brown, T. L. *J. Am. Chem. Soc.* **1992**, *114*, 2723. (b) Zhang, H. T.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 107.

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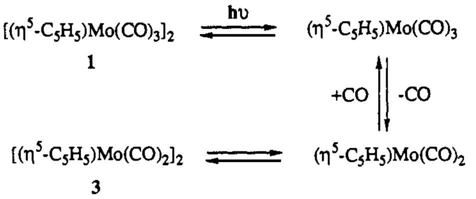
Scheme I



Evidence for this mechanism included the reaction of CCl_4 with **1** upon photolysis. **3** was not generated, which suggested that all of the radicals had reacted with CCl_4 before CO loss and dimerization could occur. Curtis also showed that the methyl-substituted species $[(\eta^5\text{-}C_5H_4Me)Mo(CO)_3]_2$ and **1**, when heated together, produce a mixture of the two unmixed complexes, **3** and $[(\eta^5\text{-}C_5H_4Me)Mo(CO)_2]_2$, and the third mixed complex, $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)Mo_2(CO)_4$. The results were interpreted to demonstrate that the dimers, $[(\eta^5\text{-}C_5H_4Me)Mo(CO)_3]_2$ and **1**, must undergo homolysis to form radicals that lose CO and recombine to form the mixed pair, $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)Mo_2(CO)_4$.

In light of Rest's work showing the existence of a CO loss product, Turaki and Huggins[8] attempted crossover experiments similar to those performed by Curtis and concluded that radicals could not be involved in the interconversion of **1** and **3**. After showing that metal–metal bond homolysis in **1** occurs faster than CO loss to form **3**, it was proposed that the mixing observed by Curtis for the tetracarbonyl products could occur on a reaction path that did not involve CO loss. Thus, the faster radical formation would produce hexacarbonyl crossover products, followed by loss of CO from the already-mixed species to form the mixed tetracarbonyl products. By adding CO to a tetracarbonyl species, Turaki and Huggins could observe whether the same mechanism applied to the reverse reaction. Adding 1 atm of CO to a solution of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)Mo_2(CO)_4$ at room temperature yields only $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)Mo_2(CO)_6$ and none of the unmixed crossover products. The same reaction performed at 383 K, where CO loss from **1** is reversible, also did not yield the statistical distribution of mixed products. Thus, 2 equiv of CO add directly to the tetracarbonyl species without metal–metal bond rupture. On the basis of the principle of microscopic reversibility, it was concluded that the thermal loss of CO from **1** also does not involve radical intermediates.

Rate constants for the decay of a transient absorption ascribed to a CO loss product from **1** have been reported in two flash photolysis studies. A second-order rate constant of 1×10^8 M^{-1} s^{-1} in cyclohexane was reported by Hughey et al.;[3] a first-order rate constant of 4 to 8×10^2 s^{-1} in toluene was reported by Van Vlierberge and Abrahamson.[4] In this paper we report flash photolysis formation of **2** and studies of its reactions, using variable-temperature IR and UV–vis spectroscopy. We observe two decay pathways for **2**, neither of which has been previously identified. We also describe the role of **2** in the interconversion between **1** and **3**.

Experimental Section

$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, obtained from Pressure Chemical Co., was used as received.

$[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ was prepared according to the literature procedure.[9]

Solvents. Hexane, obtained from Burdich and Jackson Laboratories Inc., was purified by stirring over concentrated H_2SO_4 for at least 1 week, followed by washing with aqueous $NaHCO_3$ and then water and predried with $CaCl_2$. It was then passed over freshly activated silica gel and refluxed over CaH_2 under Ar for a minimum of 12 h prior to distillation. The distilled hexane was collected under an Ar atmosphere and freeze–pump–thawed with Ar three times before use.

Toluene, obtained from EM Science, was purified by refluxing over Na under Ar. The distilled toluene was collected under an Ar atmosphere, freeze–pump–thawed with Ar three times, and stored in an oven-dried bottle in a glovebox (Ar) and 4Å molecular seive.

3-Methylpentane, obtained from Aldrich Chemical Co., was dried with freshly activated 4Å molecular seive and freeze–pump–thawed with Ar three times. The 3-methylpentane was stored in a Schlenk flask equipped with a high-vacuum stopcock.

Acetonitrile, obtained from Mallinckrodt, was purified by distilling first over P_2O_5, followed by distillation over CaH_2. The distilled acetonitrile was degassed by freeze–pump–thawing with Ar three times.

Argon, obtained from Linde Specialty Gas Co., was passed through columns of Drierite and MnO prior to use.

Carbon monoxide, CO (Matheson purity grade, minimum purity 99.99%), was obtained from Matheson Gas Products, Inc. Trace $Fe(CO)_5$ was removed by passing the CO through an activated charcoal trap in a sand bath at 200+ °C, followed by passage through another activated charcoal trap cooled in a dry ice–ethanol bath. Oxygen was also removed by passing the CO through an O_2 trap obtained from American Scientific.

Low-Temperature IR Apparatus. A Specac Model 21500 jacketed vacuum dewar assembly, equipped with CaF_2 or NaCl windows, was employed.

Instrumentation. A Perkin-Elmer 1710 FTIR spectrometer was used to collect the data. Transfer and storage to a PC was accomplished with the program 17DX provided by Perkin-Elmer. An HP 8452 spectrophotometer was used to obtain UV–visible spectra. Mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois on a 70-VSE mass spectrometer.

Conventional Flash Photolysis. The Xenon lamp flash photolysis apparatus has been described previously.[10] Solutions of **1** (0.10 mM) in toluene were prepared in a glovebox under argon and placed in cells used for flash photolysis. The cells consist of a jacketed Pyrex cylindrical sample chamber about 10 cm in length and 1 cm in diameter, an attached 25-mL round-bottom flask in which the solutions can be frozen and degassed, and a high-vacuum Teflon stopcock. The cells could be attached to a manifold for degassing and adding the appropriate CO/Ar mixture. Partial pressures of CO smaller than 1 atm were obtained using a 2-L mixing flask attached to CO and an Ar/vac manifold. The degassed mixing flask was filled with CO, followed by application of a partial vacuum to the desired pressure and back-filling with Ar to a total pressure of 2.5 psig. The mixture was stirred for at least 15 min with a large magnetic stirring bar before being added to a degassed (freeze–pump–thawed) solution. Each solution was stirred for at least 10 min prior to use and vented to 1 atm total pressure. The resulting CO partial pressure was used to calculate the CO concentration in solution by the method of Field et al.;[11] 1 atm of CO over toluene provides a CO concentration of 7.55×10^{-3} M. Experiments were performed at 298 K by circulating water between a thermostated bath (Precision Scientific Co.) and the jacketed cell. The reactions were monitored at 450 nm to observe the decay of **2** and at 505 nm to observe the growth of **3**. Solutions of **1** (0.10 mM) and acetonitrile (1.0–90 mM) in toluene were prepared as described above and were monitored at 450 nm.

Laser Flash Photolysis. Pulsed laser light at 308 nm was obtained with an XeCl excimer laser; 581-nm light was obtained from a flash-pumped dye laser using Rhodamine 6 G (tuned to 581 nm). In both cases pulse widths were 30 ns. The detailed operation of the instrument is similar to that described elsewhere.[12] Solutions of **1** (1.0 mM) in toluene were prepared as described above, except that the cells were equipped with a 1-cm quartz sample chamber instead of the 10-cm Pyrex sample chamber. The samples contained either 1 atm of CO or no added CO. The decays of the cis-gauche rotamer of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (**4**) and **2** were monitored at 450 nm. The solutions were mixed by shaking between each flash when 308-nm irradiation was used.

Infrared Spectra following Flash Photolysis at Low Temperatures. Solutions of **1** (0.20–0.35 mM), and where appropriate, acetonitrile (3.0–30 mM) in 3-methylpentane were prepared under argon and degassed by freeze–pump–thawing with argon three times. When CO was used the solution was degassed in the same way and CO added. A portion of the solution was then loaded by gas-tight syringe into an IR cell under

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(8) Turaki, N. N.; Huggins, J. M. *Organometallics* **1985**, *4*, 1766.

(9) Birdwhistle, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239.

(10) (a) Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 9162. (b) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 3748.

(11) *Carbon Monoxide*; Cargill, R. W.; Solubility Data Series; Pergamon Press: New York, 1990; p 126.

(12) Herrick, R. J.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42.

argon in a bell jar attached to a vacuum/argon manifold. For low-temperature experiments the cell was loaded into a Specac variable-temperature vacuum jacket and cooled to the appropriate temperature. The sample was then irradiated with the conventional flash system and moved to the IR spectrometer. Spectra were obtained before and at various times following the flash.

UV–Visible Spectra following Flash Photolysis at Low Temperature. A solution of **1** in 3-methylpentane was prepared and loaded into the Specac variable-temperature apparatus as in the variable-temperature IR flash photolysis experiments. The sample was irradiated with the conventional flash system and then moved to the UV–vis spectrophotometer: spectra were obtained at various time intervals. IR spectra were also obtained before and after the flash to verify sample integrity.

Continuous Photolysis. A saturated solution of **1** in hexane (40 mL) was irradiated with a 275 W GE sun lamp for a total of 30 min with an Ar purge and vigorous magnetic stirring. The reaction was monitored by IR spectroscopy. The concentration of an unknown species we label **5** (vide infra) reached a maximum value at about 15 min and declined with further irradiation. A brown precipitate which formed was allowed to settle and the solution above transferred to another flask. The solvent was removed from the transferred solution under vacuum, leaving a brown powder. A similar experiment was performed by irradiating [(η^5-C_5H_5)W(CO)$_3$]$_2$. The crude sample of the tungsten analog of **5** was submitted for electron impact mass spectral analysis, yielding mass numbers up to 1120.

Results

Variable-Temperature IR Experiments. When a sample of **1** in a 3-methylpentane glass is flash-photolyzed at 93 K under argon, the difference spectra from before and after the flash reveal four of the five bands due to **2** (ν_{CO} = 1982, 1942, 1913, 1868, 1667 cm^{-1}). The band at 1913 cm^{-1} is observed after correcting for the negative bands due to bleaching caused by consumption of **1**. When the experiment is repeated in fluid solution at 200 K, two species are observed; **2** is formed as in the lower temperature glass, and decays less than 10% in 50 min. Thus, **2** is relatively stable at 200 K. The second species, **4** (ν_{CO} = 2021, 1966, 1930, 1905, 1895 cm^{-1}), decays back to **1** with a half-life of about 2 min; it is attributed to the cis-gauche rotamer of **1**, described by Adams and Cotton.[13] Because the concentration of **2** does not change appreciably in the short time interval, bands due to **2** are subtracted out in successive post-flash difference spectra, permitting observation of five of the six predicted bands of **4**.[13a] Added CO does not change the half-life of **4**, whereas it dramatically shortens the half-life of **2** to less than 2 min at 200 K.

Flash photolysis of **1** in hexane at 298 K yields three species 1 min after the flash. The difference spectrum from before and after the flash reveals four bands. The two predominant bands, at 1898 and 1870 cm^{-1}, are assignable to **3**.[14] Two other weak bands (having intensities $\leq$5% of those due to **3**), at 2030 and 1947 cm^{-1}, belong to an as yet unknown compound, **5**. Another unknown species, **6**, is apparent after **3** and **5** have decayed (both having half-lives of about 10 min), leaving a single peak at 1871 cm^{-1}, which is initially hidden under a band due to **3**. By using post-flash spectral subtraction it was determined that the concentration of **6** does not change during an interval of 90 min following the flash. When **1** in hexane is saturated with 1 atm of CO, only **5** is seen about 1 min after flash irradiation at 298 K. Therefore **3** and **6** react more rapidly with CO than **5**. Because the concentration of **5** is small after only one flash, a similar solution of **1** in hexane was irradiated by continuous photolysis with an Ar purge. IR spectroscopy revealed that the concentration of **5** increases to a maximum and then decreases, indicating that it is photosensitive. Thus, only dilute solutions of **5** could be prepared. When the tungsten complex [(η^5-C_5H_5)W(CO)$_3$]$_2$ is irradiated in the same manner, bands analogous to those seen for the molybdenum compound are observed (ν_{CO} = 2027, 1939 cm^{-1}). A mass spectrum of an impure sample of the tungsten analog of **5** provided mass numbers from 700 to 1120, indicating fragments with three and four metal centers.

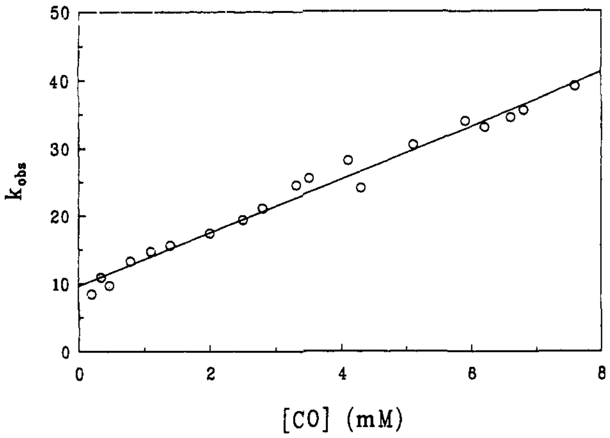

Figure 1. Plot of the variation in k_{obs} for the decay of **2** at 450 nm as a function of [CO].

When **1** in 3-methylpentane is flash photolyzed at 240 K, bands due to **2** are present in the spectrum taken within the first minute after the flash. As **2** decays, bands due to **3** appear and grow. Absorbances due to **1** also grow at the same time. These observations indicate that **2** engages in two competitive processes: loss of CO to form **3**, and addition of CO to form **1**.

Flash photolysis of **1** in 3-methylpentane at 200 K using an optical filter (λ_{cutoff} = 450 nm) to remove the short-wavelength light produced **4** and no detectable amount of **2**. The absolute intensity of each would be expected to decrease due to a reduction in the quantity of photons passing through the sample. Comparing the bands at 2021 cm^{-1} for **4** and 1942 cm^{-1} for **2**, the **4**:**2** ratio is 1:5 without the filter and at least 6:1 with the filter (the ratio is limited by the noise level of the spectrum). The difference in ratios indicates that high-energy light is required for production of **2**.

Flash photolysis of **1** and acetonitrile in 3-methylpentane at 200, 248, and 256 K yields five bands in the IR difference spectrum from before and after the flash: ν_{CO} = 1970, 1926, 1886, 1861, and 1851 cm^{-1}. These bands are assigned to the monosubstituted dimer, (η^5-C_5H_5)$_2$Mo$_2$(CO)$_5$(NCCH$_3$) (**7**). A similar complex, (η^5-C_5H_5)$_2$Mo$_2$(CO)$_5$(CNCH$_3$), has been shown to have five terminal CO bands in alkane solvent and to be a mixture of monosubstituted isomers.[15] When a sample of **1** and acetonitrile irradiated at 248 K is warmed to room temperature over a period of 27 min, **7** decays, leaving **1**. At 256 K the five bands assigned to **7** decay at the same rate, while bands due to **1** and **3** grow in a ratio similar to that observed for the decay of **2** without additional ligand present. At 298 K, **3** is the only observed product 1 min after the flash. These observations indicate that the substituted dimer is not stable near room temperature and that it decays to form the linear semibridge, **2**.

UV–Visible Detection of Flash Photolysis Products. Flash photolysis of **1** in toluene produced a transient absorption at 450 nm, attributed to **2**. In solution under Ar at 298 K, the transient disappears over a period of about 1 s and follows a first-order decay. Upon adding CO to the solution at concentrations of 10^{-4} to 10^{-2} M the decay rate, which follows a pseudo-first-order rate law, increases. A plot of k_{obs} vs [CO] is linear with a non-zero intercept, as shown in Figure 1. This result indicates that **2** decays via two pathways, one first order and the other second order. In Scheme II, **2** is shown to recombine with CO to form **1** or lose CO to form **3**, as indicated by IR spectroscopy at 240 K. The slope in Figure 1 yields a second-order rate constant of 3.9×10^3 M^{-1} s^{-1}, which, from the IR spectra, clearly relates to the

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[13] (a) Adams, R. D.; Cotton, F. A. *Inorg. Chim. Acta* **1973**, *7*, 153. (b) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

[14] The bands at 1898 and 1870 cm^{-1} differ from the reported values for **3**.[5a,6b] We therefore confirmed these assignments with a sample prepared according to literature methods.[6b]

[15] (a) Adams, R. D.; Brice, M.; Cotton, F. A. *J. Am. Chem. Soc.* **1972**, *94*, 6193. (b) Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6594.

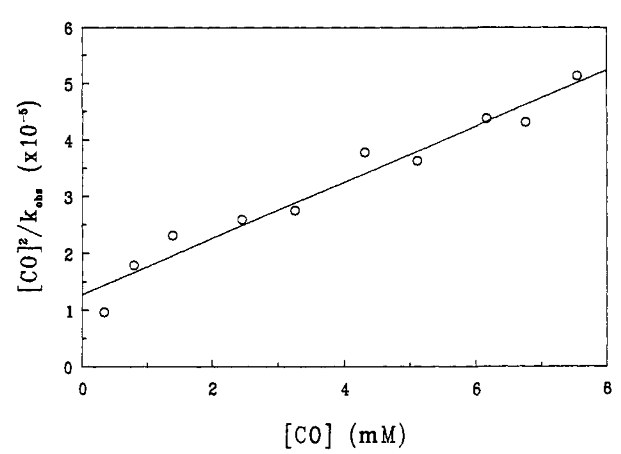
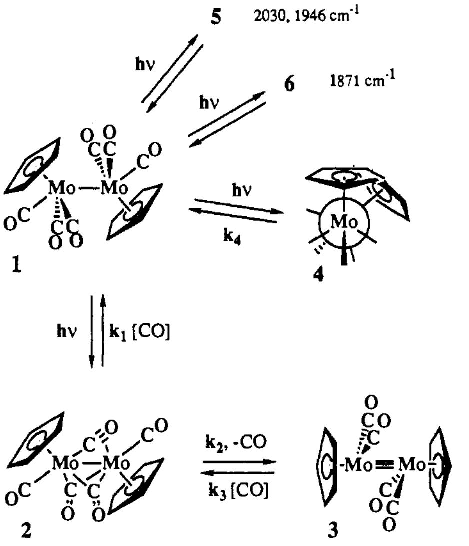


Figure 2. Plot of the variation in $[\mathrm{CO}]^2/k_{\mathrm{obs}}$ for the growth of **1** at 505 nm as a function of [CO].

Scheme II



recombination of **2** with CO. The intercept corresponds to a first-order decay of **2** at a rate of 9.7 s^{-1}, which we ascribe to the loss of CO from **2** to form **3**.

Because we could not find a suitable means of monitoring the decay of **3** for kinetics purposes over a significant range of CO concentration, we obtained the required information indirectly, by observing the recovery of **1** after the flash. Solutions of **1** in toluene with added CO were flash photolyzed and monitored at 505 nm. On the basis of IR spectroscopic evidence, the system is described by the substances and processes shown in Scheme II. When the steady state approximation is applied to **2**, k_{obs} for the recovery of **1** is described by eq 1; rearrangement yields eq 2.

$$k_{\mathrm{obs}} = \frac{k_1 k_3[\mathrm{CO}]^2}{k_1[\mathrm{CO}] + k_2} \qquad (1)$$

$$\frac{[\mathrm{CO}]^2}{k_{\mathrm{obs}}} = \frac{[\mathrm{CO}]}{k_3} + \frac{k_2}{k_1 k_3} \qquad (2)$$

Figure 2 shows a graph of $[\mathrm{CO}]^2/k_{\mathrm{obs}}$ vs [CO]. The second-order rate constant $k_3 = 2.0 \times 10^2\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ was obtained from the inverse of the slope in Figure 2.

Following flash irradiation of a solution of **1** in 3-methylpentane at 200 K, the UV–visible spectrum changes during the first 10 min due to conversion of **4** to **1**. As shown in Figure 3, the band due to **4** ($\lambda_{\max} = 362$ nm) declines, while the band due to **1** ($\lambda_{\max} = 390$ nm) recovers.

The results of flash photolysis of **1** in toluene depend on whether visible or UV irradiation is employed. As seen in Figure 4, 581-nm irradiation at room temperature produces a small absorbance at 450 nm which undergoes first-order decay with a rate constant of $3.0 \times 10^2\ \mathrm{s}^{-1}$. On the basis of the IR results, this transient is attributed to the decay of **4**. The rate is independent of [CO] to 7.6×10^{-3} M. When 308-nm irradiation is used, two first-order processes are observed (curve a; Figure 4). The slower process matches the rate of decay for **2**. The faster process is the same first-order decay observed using 581-nm irradiation, attributed to **4**, curve b. It is noteworthy that curve b exhibits a simple decay to the base line, whereas decay curve a falls below the base line. The process in curve b involves conversion of **4** to **1**, requiring only a simple rotation. In curve a the slower decay involves conversion of a significant portion of **2** to **3**, which does not absorb as strongly as **1** at 450 nm. These observations correlate well with the low-temperature UV–vis and IR experiments.

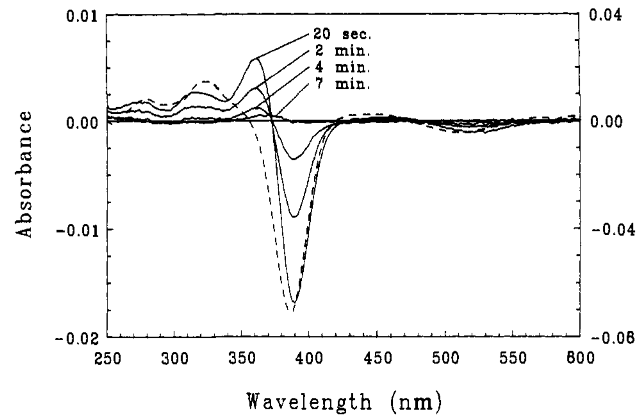


Figure 3. UV–vis difference spectra for the decay of **4** ($\lambda_{\max} = 362$ nm) and growth of **1** ($\lambda_{\max} = 390$ nm) over 10 min at 200 K. Absorbances due to **2** are removed by subtracting the spectrum obtained at 10 min after the flash from those at 20 s and 2, 4, and 7 min after the flash. The difference spectrum of **2** (dashed line) is shown for comparison ($\lambda_{\max} = 326$ nm) (absorbance axis on right).

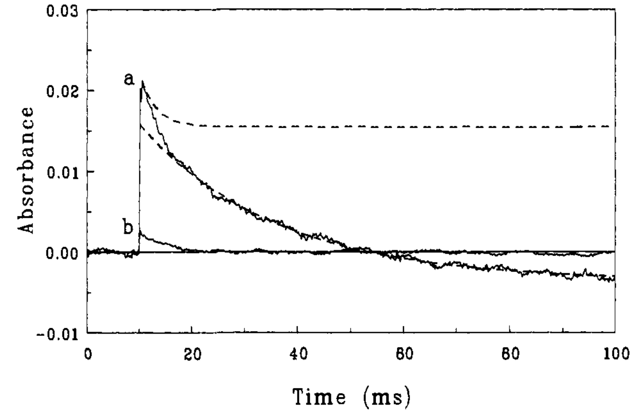


Figure 4. Transient absorption spectra at 450 nm following flash photolysis of a toluene solution containing **1** (1.0×10^{-3} M) and CO (7.6×10^{-3} M): (a) using 308-nm irradiation (dotted lines represent the exponential fitting used for the fast and slow processes); (b) using 581-nm irradiation.

Flash photolysis of **1** and acetonitrile in toluene with no added CO yields a transient absorption at 450 nm which decays at a rate inversely proportional to acetonitrile concentration. A plot of $1/k_{\mathrm{obs}}$ vs acetonitrile concentration is linear with a non-zero intercept, as shown in Figure 5. While no **2** is observed, the inverse relationship of decay rate to acetonitrile concentration combined with the IR data described above indicates that dissociation of acetonitrile from the monosubstituted dimer, **7**, is being observed. The rate law derived for the decay of the monosubstituted dimer is described according to Scheme III. After the steady state approximation is applied to **2**, the rate law in eq 3 is obtained. The terms involving [CO] are considered small relative to the other terms in the expression due to the small amount of CO present in solution ([CO] ~ $1\text{–}2 \times 10^{-5}$ M based

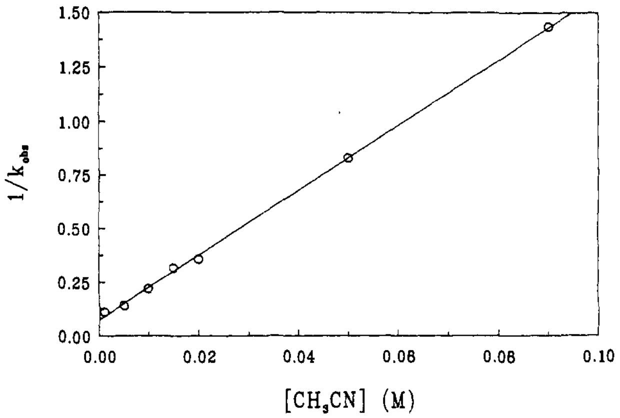
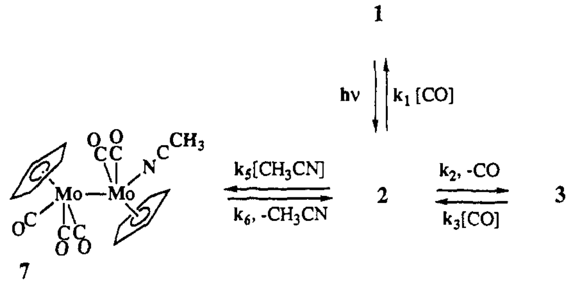


Figure 5. Plot of the variation in $1/k_{obs}$ for the decay of **7** at 450 nm as a function of $[CH_3CN]$.

Scheme III



$$\frac{-d[7]}{dt} = k_6[7] - \frac{k_5[CH_3CN](k_3[CO][3] + k_6[7])}{k_1[CO] + k_2 + k_5[CH_3CN]} \tag{3}$$

upon the amount of **2** and **3** produced). Evidence showing that $k_3[CO][3]$ is much less than $k_6[7]$ comes from the IR flash photolysis experiment at 256 K. The substituted dimer decays with a half-life of about 10 min, while **1** and **3** grow in concentration, with **3** being relatively stable at this temperature. As shown above, $k_1[CO]$ was demonstrated to be much less than k_2 at low concentrations of CO by the experiments performed with CO as the added ligand. Thus, for $k_6[7] \gg k_3[CO][3]$ and $k_2 \gg k_1[CO]$:

$$\frac{-d[7]}{dt} = \frac{k_2 k_6[7]}{k_2 + k_5[CH_3CN]} \tag{4}$$

and

$$k_{obs} = \frac{k_2 k_6}{k_2 + k_5[CH_3CN]} \tag{5}$$

By rearranging we obtain eq 6. The inverse of the intercept in Figure 5 provides the first-order rate constant k_6, which is 13 s^{-1}.

$$\frac{1}{k_{obs}} = \frac{1}{k_6} + \frac{k_5}{k_2 k_6}[CH_3CN] \tag{6}$$

This rate constant is attributed to the dissociation of acetonitrile from **7**. The slope in Figure 5 provides the second-order rate constant k_5, 1.9×10^3 M^{-1} s^{-1}, ascribed to the addition of acetonitrile to **2**.

Discussion

The experimental results obtained in this work, by combining the analytical power of IR spectra obtained at low temperature following flash photolysis, with kinetics results based on UV–visible transient spectra at room temperature, provide a new picture of the important processes that ensue from the primary photochemical processes in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (**1**). The IR spectra at temperatures from 200 to 298 K reveal that several distinct species are formed, either as primary photoproducts or as successor products formed in fast reactions. Two of these, which we label **5** and **6**, are minor products which have not been fully characterized. We speculate that **5** is a tetranuclear product; it is under further investigation. The other minor product, **6**, possessing only a single CO stretching band in the IR, reacts rapidly with CO to reform the starting material.

The new results presented here are significant in illuminating the relationships (illustrated in Scheme II) between four major species: **1**; the semibridge species $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ (**2**); the tetracarbonyl compound $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ (**3**); and the cis-gauche rotamer of the starting dimer, **4**.

The semibridge form, **2**, reacts by two parallel pathways: addition of CO to form **1** and CO loss to form **3**. Our results call for a reinterpretation of earlier observations made by other workers. Van Vlierberge and Abrahamson observed a flash photolysis product that decayed via a first-order process, with a rate constant of 4 to 8 × 10^2 s^{-1}, independently of CO concentration. It is probable they observed conversion of **4** to **1**. In our experiments, the half-life of **4** in 3-methylpentane at 200 K is 2 min. By using the activation energy obtained by Adams and Cotton ($E_a = 15.3 \pm 0.5$ kcal mol^{-1}) and our observed half-life, a room temperature rate of 1.5×10^3 s^{-1} is estimated. Given that different solvents are involved, this is fairly close to the value reported by Van Vlierberge and Abrahamson.

We have noted that when only long wavelength irradiation is used, **2** is not observed in either the IR at low temperature or the UV–visible transient spectroscopy (Figure 4). The irradiation employed by Van Vlierberge and Abrahamson, 589 nm, thus could not have produced significant amounts of **2**, leaving **4** as the only species to be observed in this time regime. Our UV–vis spectra (Figure 3) for the decay of **4** (λ_{max} = 362 nm, 3-methylpentane) match the time-resolved spectra reported for what the authors ascribed to a CO loss intermediate ($\lambda_{max} \sim 365$ nm, toluene). Further, the spectrum we have obtained for **2** (λ_{max} = 326 nm, 3-methylpentane) agrees with that reported by Rest (λ_{max} = 332 nm, Ar matrix) and is significantly different from that reported by Van Vlierberge and Abrahamson.

Hughey et al. detected a species to which they assigned an upper-limit second-order decay rate constant of 1 × 10^8 M^{-1} s^{-1} in cyclohexane. The assumed second-order behavior was not based upon a study using added CO, and therefore it leaves room for doubt. The time scale of the decay reported by Hughey, 2–50 ms, is roughly that which we observe for the decay of **4**. The species observed by Hughey also showed a strong absorption in the UV, indicating the presence of a metal–metal bond. This absorption ($\lambda_{max} \sim 365$ nm, cyclohexane) is consistent with the spectrum of **4**. It therefore appears that Hughey et al. also observed **4** and not a CO loss product.

Another study of the flash photolysis of **1** in cyclohexane has been reported by Moore using time-resolved IR spectroscopy.[18] The radical $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ and three unknown species were reported to have been observed. One of the unknown species exhibited a half-life of 1.4 ms and was identified by three bands at 1933, 1907, and 1895 cm^{-1}. These bands match three of the bands ascribed to **4**. Another transient, with a half-life similar to the first, was said to have a single detectable band at 1966 cm^{-1}. This matches precisely with another band of **4**. (The fifth band we ascribe to **4** lies outside the range of the IR apparatus.) The band at 1966 cm^{-1} is described by Moore as growing in at a rate consistent with radical recombination. This suggests that **4** is formed via radical recombination and then undergoes rotation about the metal–metal bond to form **1**.

The third species described by Moore has a single band at 1942 cm^{-1} and is long-lived on the time scale studied, in agreement

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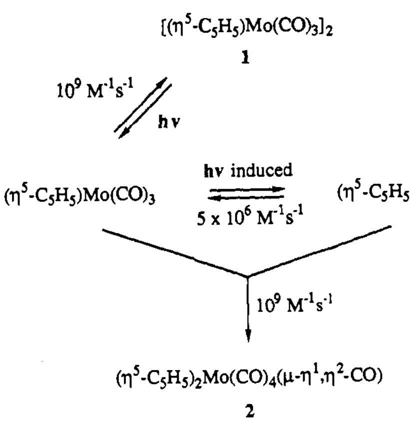
(16) Coville, N. J. *J. Organomet. Chem.* **1981**, *218*, 337.

(17) (a) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43. (b) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725.

(18) Moore, B. D., Ph.D. Thesis, University of Nottingham, October 1985.

Scheme IV



with our observations of **2**. The bands at 1913 and 1667 cm^{-1} would not have been observed by Moore; the first overlaps with a strong band of **1**, and the second is out of the range of the IR apparatus. It is not clear why they did not observe bands at 1982 and 1968 cm^{-1}. These bands might have been easily overlooked, since the resolution attained in time-resolved IR is not high.

Turaki and Huggins argued that the radical mechanism described by Meyer and Curtis for the formation of **3** or **2** could not take place, thermally or photolytically. It is probable that CO loss from **1** is a primary photochemical reaction and is also kinetically important in the thermal pathway. However, because Turaki and Huggins studied only thermal reactions, the radical path to form **2** cannot be ruled out a priori in the case of photolysis. It is possible that homolysis leads to a high-energy form of the 17-electron radical, in which some CO loss could occur before thermal equilibration with solvent. However, we observe that added CO does not affect the amount of **2** produced in the photochemical reaction. If $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ radicals were being formed by CO loss, the added CO should compete with $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radicals for reaction, thus reducing the amount of **2** formed following the flash.

Assuming a photoinduced loss of CO from $(\eta^5\text{-}C_5H_5)Mo(CO)_3$, the recombination of $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ with CO would have to be slow with respect to radical recombination to form **2**. We illustrate this requirement for a radical pathway to **2** in Scheme IV. Metal–metal bond homolysis in **1** is reported to have a quantum efficiency of 0.45 with 366-nm irradiation.[1b] Judging from the observation that production of **2** is about 10% of **1** in a single flash, the initial concentration of $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ is probably on the order of 3 to 5×10^{-5} M. The maximum CO concentration used was 7.6×10^{-3} M. Assuming that the bimolecular rate constant for reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ with $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ to form **2** is $\sim 10^9\ M^{-1}\ s^{-1}$, and if the rate constant for recombination of CO with $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ to form $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ were $5 \times 10^6\ M^{-1}\ s^{-1}$, the added CO would result in about a 50% reduction in concentration of **2**. No data on ligand addition to 15-electron radicals exists, but it is probable that the rate constant for CO addition to such a highly electrophilic center would be greater than $5 \times 10^6\ M^{-1}\ s^{-1}$. Thus, the absence of an effect from added CO on the resulting concentration of **2** argues against a radical pathway to **2**.

The wavelength dependence of the formation of **2** also argues against a radical pathway. Cleavage of the metal–metal bond to form radicals is evident using irradiation wavelengths from 308 to 580 nm. In contrast, **2** is observed only following UV irradiation. The fact that the wavelength affects the production of **2** and the radicals in a different manner is consistent with distinct excited state origins for the two products. In view of the observed wavelength dependence, and the lack of effect on the formation of **2** by added CO, we propose that CO loss from **1** is the only major photochemical pathway to **2**.

To further investigate the reactivity of **2**, flash photolysis studies were carried out using a ligand other than CO. Low-temperature IR spectra obtained following flash photolysis of **1** in the presence of acetonitrile indicate the presence of the substituted product at 200, 248, and 256 K. At 298 K only **1** and **3** are observed 1 min after the flash. Because each of the five IR bands observed at 256 K decay at the same rate, these bands must belong to the same complex or to more than one complex in fast equilibrium. We originally considered that two compounds might be responsible for these bands: the monosubstituted dimer, **7**, and a disubstituted dimer $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(NCCH_3)]_2$ (**8**). Isonitrile, phosphine, and phosphite analogs of **7** and **8** have been observed, each being a mixture of isomers and having four or five bands.[13,15–17]

Considering the appearance of a new substituted species, it is possible that **8** would arise via acetonitrile substitution into the $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radicals, followed by recombination. This path would generate the new dimer, but it does not account for the presence of the linear semibridge. Either **2** should be observed or, as in the case with CO as added ligand, acetonitrile should also add to **2** to form **7**. This would require the observation of two products, the disubstituted dimer and the linear semibridge or the monosubstituted dimer. Since **2** is not observed and it is not expected that the mono- and disubstituted dimers would be in rapid equilibrium, the hypothesis that **7** and **8** are concurrently formed products is not viable.

The appearance of a single substituted species could arise by addition of acetonitrile to **2**, forming **7** as suggested above. This path would require that little substitution of the $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radicals occurs. No data on the rate of acetonitrile substitution of these radicals are available, but substitution of the $(\eta^5\text{-}C_5H_5)W(CO)_3$ radicals with $P(OMe)_3$ occurs with a rate constant of $1.3 \times 10^4\ M^{-1}\ s^{-1}$, which suggests that substitution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radicals may be slow relative to recombination.[19]

Observations of the decay for the substituted dimer are also consistent with the decay of a monosubstituted dimer. Decay of the IR bands attributed to **7** at 256 K is concurrent with the growth of bands due to **1** and **3**. This suggests that loss of acetonitrile leads to a product which can add CO to form **1** or lose CO to form **3**, consistent with the reactivity of **2** shown previously. A pre-equilibrium between **7** and **2** involving acetonitrile dissociation and addition is also consistent with the inverse dependence of the decay rate of **7** on acetonitrile concentration. On the basis of the above observations, we propose that **7** is the only kinetically competent species to which the low-temperature IR bands and transient decay can be attributed.

In summary, the use of flash photolysis in combination with variable-temperature IR and UV–visible spectroscopy has permitted a more precise description of the photochemistry of **1**. The linear semibridging species, **2**, has been shown to be the key intermediate in the reversible reaction between the hexacarbonyl and the tetracarbonyl cyclopentadienyl molybdenum dimers, **1** and **3**. Further, the role of the cis-gauche rotamer, **4**, has been described and distinguished from that of **2**. Adding a second ligand, acetonitrile, to the flash photolysis studies of **1** has revealed the new transient species, the monosubstituted dimer, **7**. Additional studies of the reactivity of **2** with other ligands, such as phosphines, were hindered by the prevalence of disproportionation reactions.[1d]

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Supplementary Material Available: Tables listing concentration vs observed rate constants for Figures 1, 2, and 5 (1 page). Ordering information is given on any current masthead page.

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(19) Turaki, N. N.; Huggins, J. M. *Organometallics* **1986**, *5*, 1703.