Contribution from the Kenan Research Laboratories,
Department of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27514

Photochromism in the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ + Br^- System

Joseph L. Hughey IV and Thomas J. Meyer*

Received August 9, 1974 AIC40564Q

In an earlier paper[1] we reported on the light-induced reactions between $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and X^- (X = Cl, Br, I, or NCS). In these reactions the metal–metal bond is cleaved in a net disproportionation reaction $[Mo^I_2 \rightarrow Mo^{II} + Mo^0]$

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + X^- \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Mo(CO)_3X + (\pi\text{-}C_5H_5)Mo(CO)_3^- \quad (1)$$

The initial reaction is followed by a second light-catalyzed step in which CO is displaced from $(\pi\text{-}C_5H_5)Mo(CO)_3X$[2]

$$(\pi\text{-}C_5H_5)Mo(CO)_3X + X^- \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Mo(CO)_2X_2^- + CO \quad (2)$$

The thermal reverse of eq 1, in which a halide ion is displaced by an organometallic anion, *e.g.*

$$MX + M{:}^- \rightarrow M\text{-}M + X^- \quad (3)$$

has proven to be a useful general reaction for the preparation of metal–metal bonds. In some cases, although the metal–metal bond appears to be favored thermodynamically, the reactions are slow. However, the metal–metal bonds can be prepared by using long reaction times or, in some cases, elevated temperatures.

The known examples provided by reactions 1 and 3 suggested to us that it might be possible to design a photochromic system in which the photochromism was based upon the net formation and cleavage, by disproportionation, of a metal–metal bond. We report here the results of our studies on the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ + Br^- system.

Experimental Section

Solvents. Reagent grade solvents were predried with Drierite ($CaSO_4$) and fractionally distilled. Tetrahydrofuran was freshly distilled from lithium aluminum hydride and kept under a nitrogen atmosphere.

Chemicals. Both $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (Alfa Inorganics) and $(\pi\text{-}C_5H_5)Mo(CO)_3Br$[5] were recrystallized by slowly adding hexane to a prefiltered, saturated methylene chloride solution. The solutions were manipulated under nitrogen and without excess light. $[(n\text{-}C_4H_9)_4NBr]$ (Eastman Organics) was predried in a vacuum oven (80° (2 mm)) for 2 hr. The dried salt was dissolved in benzene (5 ml/g) and heptane was added (1 ml/g). The solution was warmed until clear and then frozen to effect crystallization. The crystals were washed with heptane and dried in a vacuum oven (80° (2 mm)) for 20 hr. The crystalline solid was stored in a vacuum desiccator in pretared 10-ml volumetric flasks.

Spectral Measurements. Uv–visible spectra were recorded on a Cary Model 14 spectrophotometer. The progress of the photochemical and thermal reactions was monitored on Cary 14 or Gilford Model 240 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer Model 421 spectrophotometer and were calibrated against polystyrene.

General Procedures. All solutions were manipulated in subdued lighting and were transferred with syringes which had been previously deaerated with nitrogen. Infrared solution cells were fitted with serum caps and were preflushed with nitrogen. The solutions were also shielded from ambient light prior to measurements. The serum caps were preextracted with warm tetrahydrofuran.

For the photochromism experiments, a tetrahydrofuran solution of $[(n\text{-}C_4H_9)_4NBr]$ of the appropriate concentration was transferred *via* syringe to a light-shielded volumetric flask containing a preweighed amount of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$. Aliquots of 4.0 ml were subjected to three freeze–pump–thaw cycles on a high vacuum line and sealed at 2×10^{-6} mm.

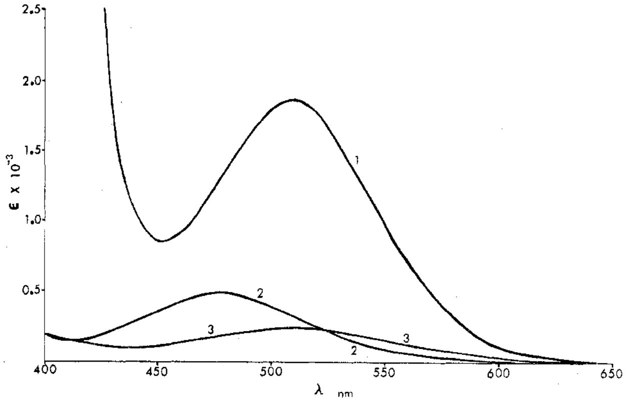


Figure 1. Visible spectra of (1) $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (λ_{max} 507 nm, ε 1870), (2) $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ (λ_{max} 476 nm, ε 490), and (3) $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$ (λ_{max} 512 nm, ε 250 ± 10%) in tetrahydrofuran.

Samples were irradiated on a merry-go-round apparatus equipped with a Hanovia 450-W medium-pressure mercury lamp (Model 679A36) in a water-jacketed Pyrex immersion well. A Corning 3-70 (No. 3384) filter was used to transmit radiation of wavelengths longer than 490 nm. Irradiation was continued until the absorbances (Gilford) reached a minimum value (~10–25 min). The samples were then heated (60 ± 2°) in the dark, and the absorbance changes at 526, 507, 476, and 387 nm (whenever possible) were monitored.

For each run two sealed sample tubes were prepared. One sample tube had a 1 mm cylindrical fused quartz cell attached for uv–visible monitoring. The extra sample tube was included in order to correlate infrared spectra with the observed absorbance changes due to irradiation. Blank runs were made for tetrahydrofuran with and without $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

Results and Discussion

The visible spectra of the complexes $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, and $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$ in tetrahydrofuran (THF) are shown in Figure 1. The molybdenum dimer, $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, also has an intense absorption band at 387 nm (ε 21,000). The band at 387 nm, which is apparently the $\sigma \rightarrow \sigma^*$ transition of the metal–metal bond, is useful for monitoring $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ since the other compounds are essentially transparent in this region. The anion $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ does not absorb appreciably above 335 nm.

Each of the complexes has characteristic ν(CO) bands in the infrared, making infrared spectra a useful means for following net reactions. In THF the ν(CO) bands appear at 2011 (w), 1961 (s) and 1917 (s) cm^{-1} for $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$; 2049 (m) and 1964 (s) cm^{-1} for $(\pi\text{-}C_5H_5)Mo(CO)_3Br$; 1900 (s), 1781 (s) and 1765 (s) cm^{-1} for $(\pi\text{-}C_5H_5)Mo(CO)_3^-$; and at 1943 (s) and 1842 (s) cm^{-1} for $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$.

Visible photolysis of solutions of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and Br^- in THF results in two stepwise photochemical reactions (eq 1 and 2). The first reaction, in which $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ are the products, is photochemically more efficient than the second reaction under the conditions used for the photolyses. As a consequence, by using limited photolysis times or a less than stoichiometric amount of Br^-, the dominant net reaction is eq 1. With a stoichiometric excess of Br^-, the first step is followed by the light-catalyzed displacement of CO from $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ by Br^- and the net reaction becomes

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + 2Br^- \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_2Br_2^- + CO + (\pi\text{-}C_5H_5)Mo(CO)_3^- \quad (4)$$

By controlling photolysis times and conditions it is, therefore, possible to prepare solutions containing $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ rather cleanly.

Thermal Reactions with Excess $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$. Solutions of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and Br^- in THF which have been photolyzed to give $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ (eq 1) are stable at room temperature for several hours as shown by the invariance in their infrared and visible spectra. The stability of the solutions indicates that the thermal back-reaction

$$(\pi\text{-}C_5H_5)Mo(CO)_3Br + (\pi\text{-}C_5H_5)Mo(CO)_3^- \rightarrow [(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^- \qquad (5)$$

is very slow at room temperature. The same conclusion was reached by Dessy and Weissman for solutions containing $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ in 1,2-dimethyoxyethane.[6] On the other hand, Abel, Singh, and Wilkinson have reported that the reaction

$$(\pi\text{-}C_5H_5)W(CO)_3Cl + (\pi\text{-}C_5H_5)Mo(CO)_3^- \rightarrow (\pi\text{-}C_5H_5)(CO)_3W\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + Cl^-$$

occurs in 65% yield by heating a THF solution to reflux for 2 hr.[7] The latter experiment indicated that if the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^-$ system were to be photochromic

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^- \overset{h\nu}{\rightleftharpoons} (\pi\text{-}C_5H_5)Mo(CO)_3Br + (\pi\text{-}C_5H_5)Mo(CO)_3^-$$

the reverse, thermal reaction (eq 5) would have to be carried out at an elevated temperature.

In Figure 2 is shown the results of a typical experiment at elevated temperatures. A solution containing $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (4.0×10^{-3} *M*) and Br^- (3.0×10^{-3} *M*) was photolyzed to completion. At this point the solution contained $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ (3.0×10^{-3} *M* ± 10%) and unreacted $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (1.0×10^{-3} *M* ± 10%).[8] The solution was then heated in the dark at 60 ± 2° until the absorbance at 507 nm (a λ_{max} for $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$) had reached a maximum (32 hr). Infrared analysis of the solution at this point showed that only ~30% of the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, which had been photolyzed, was recovered. The infrared spectrum showed the presence of all four complexes: $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, $(\pi\text{-}C_5H_5)Mo(CO)_3^-$, and $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$.

The origin of the low photochromic efficiency (~30%) of the system was investigated by carrying out thermal blank experiments. When a solution of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (5.0×10^{-3} *M*) and Br^- (16×10^{-3} *M*) in THF is heated (60 ± 2°) for 60 hr, all four of the molybdenum complexes appear to be in thermal equilibrium

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^- \rightleftharpoons (\pi\text{-}C_5H_5)Mo(CO)_3Br + (\pi\text{-}C_5H_5)Mo(CO)_3^- \qquad (6)$$

$$(\pi\text{-}C_5H_5)Mo(CO)_3Br + Br^- \rightleftharpoons (\pi\text{-}C_5H_5)Mo(CO)_2Br_2^- + CO \qquad (7)$$

as indicated by infrared spectra.[9]

The low photochromic efficiency of the system then arises because of competing side reactions involving not only $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ but also $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$. Since the side reactions have Br^- as a reactant, they increase in importance as reaction 3 proceeds.

Thermal Reactions with Excess Br^-. A solution containing $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (4.0×10^{-3} *M*) and excess Br^- (16×10^{-3} *M*) was photolyzed until reaction 1 was complete. The solution, which then contained $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, $(\pi\text{-}C_5H_5)Mo(CO)_3^-$, and excess Br^-, was heated at 60° until the ultraviolet–visible spectrum became constant (57 hr). The visible spectral changes associated with the various processes are shown in Figure 3. An infrared spectrum of the solution (Figure 4, dotted line) showed, once again, the presence of all four molybdenum complexes—$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, $(\pi\text{-}C_5H_5)Mo(CO)_3^-$, $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, and $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$—indicating that the system had reached equilibrium (reactions 5 and 6).

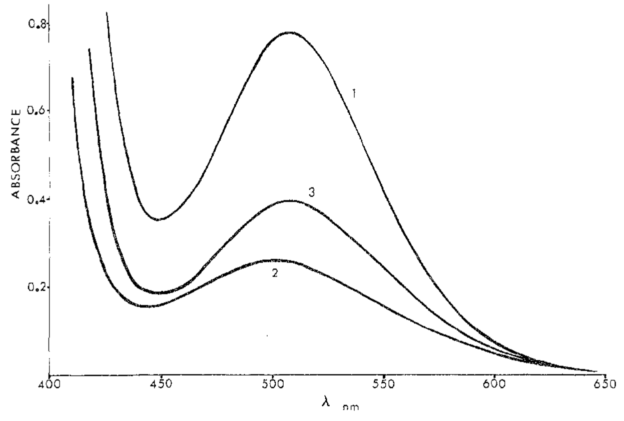


Figure 2. Spectral changes of a solution containing excess $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ with Br^-: (1) before photolysis, (2) after 25 min of photolysis (λ >490 nm), (3) after subsequently heating (60 ± 2°) for 32 hr.

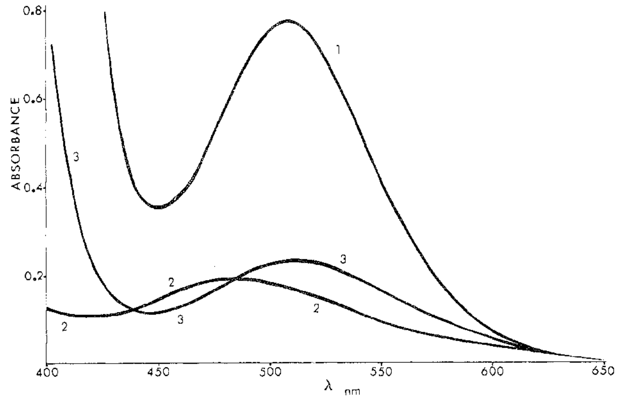


Figure 3. Spectral changes of a solution containing $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ with a stochiometric excess of Br^-: (1) before photolysis, (2) after 13 min of photolysis (λ >490 nm), (3) after heating (60 ± 2°) for 57 hr.

From the absorbance of the solution at 387 nm, the concentration of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ was found to be 0.46×10^{-3} *M*. From the infrared spectrum it was estimated that the concentration ratio $[(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-]:[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ was *ca.* 8:1.

The low photochromic efficiency of the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^-$ system in the presence of excess Br^- is not unexpected in light of the known thermal chemistry of the complexes $(\pi\text{-}C_5H_5)Mo(CO)_3X$ (X is halide). White and Mawby[5] have studied the kinetics of the net reactions (L is PPh_3 or $P(OPh)_3$)

$$(\pi\text{-}C_5H_5)Mo(CO)_3X + L \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_2LX + CO$$

under similar conditions and have concluded that the rate-determining step involves prior dissociation of CO

$$(\pi\text{-}C_5H_5)Mo(CO)_3X \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_2X + CO \quad \text{(slow)}$$

$$(\pi\text{-}C_5H_5)Mo(CO)_2X + L \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_2LX \quad \text{(fast)}$$

The appearance of $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$ as a major product when solutions of $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, $(\pi\text{-}C_5H_5)Mo(CO)_3^-$, and Br^- are heated can be accounted for by the existence of a related series of reactions in which the lower coordinate (or solvent-coordinated) intermediate, $(\pi\text{-}C_5H_5)Mo(CO)_2Br$, is captured by Br^-. We have been

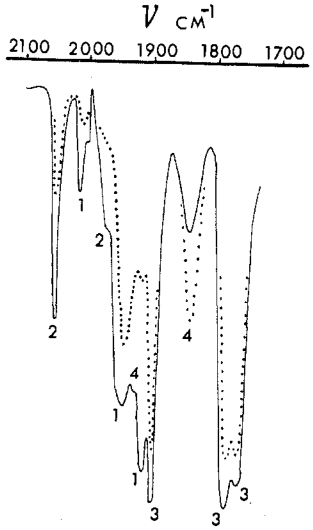
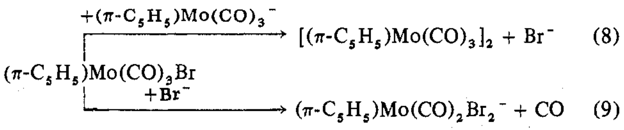


Figure 4. Carbonyl infrared spectrum of a solution containing $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and excess Br^- which had been first photolyzed to give $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ and then allowed to stand at room temperature (——). For comparison purposes the spectrum of a similar solution which had been first photolyzed to give $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ and then allowed to equilibrate at 60° is also given (· · · · ·). The dotted-line spectrum is from the solution used to obtain curve 3 of Figure 3. Characteristic bands are shown for (1) $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, (2) $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, (3) $(\pi\text{-}C_5H_5)Mo(CO)_3^-$, and (4) $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$.

unable to obtain accurate kinetic data because of the competing reaction in which $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ is formed and because of the fact that the reactions reach a measurable equilibrium. However, by assuming that the rate law for the formation of $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$ is first order in $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ and zero order in Br^-, one can obtain initial rate constants consistent with the kinetic data of White and Mawby (within ±10%).

The formation of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ as a product may occur by the initial competitive capture of $(\pi\text{-}C_5H_5)Mo(CO)_2Br$ by $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ or perhaps by an unrelated bimolecular path involving $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$. In either case the origin of the low photochromic efficiency is that a competing reaction involving the loss of CO from $(\pi\text{-}C_5H_5)Mo(CO)_3Br$ becomes important at temperatures sufficient to re-form the Mo–Mo bond



$$(\pi\text{-}C_5H_5)Mo(CO)_3Br \begin{cases} \xrightarrow{+(\pi\text{-}C_5H_5)Mo(CO)_3^-} [(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^- & (8) \\ \xrightarrow{+Br^-} (\pi\text{-}C_5H_5)Mo(CO)_2Br_2^- + CO & (9) \end{cases}$$

In this context it is interesting to note that the photochromic efficiency of the system may be considerably higher at room temperature, although the thermal recombination reaction (eq 5) is much slower. A solution containing $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (0.77×10^{-3} *M*) and Br^- (3.5×10^{-3} *M*) was photolyzed to completion giving $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ (eq 4). The solution was allowed to stand at room temperature, and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ slowly appeared, as shown by the infrared spectrum of the solution in Figure 4 (solid line). After 10 days, approximately 55% of the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ had reappeared. The room-temperature experiment suggests that, under the conditions used in the experiments, $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ is thermodynamically more favored at lower temperatures than at 60°.

Conclusions

Although the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^-$ system is somewhat photochromic when the $Br^-:[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ ratio is less than 1.0, the reverse thermal reaction (eq 5) occurs at an appreciable rate only at elevated temperatures. However, under these conditions competing thermal reactions involving Br^- lower the photochromic efficiency, and, in fact, the four molybdenum complexes $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$, and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ appear to be interrelated chemically by measurable equilibria.

The attempt to obtain a highly efficient photochromic system based upon the net formation and cleavage by disproportionation of a metal–metal bond may be more feasible in a different system. In order to avoid complications from competing side reactions it is essential that the thermal recombination reaction (eq 3) be rapid compared to other thermal reactions and specifically that it be rapid compared to net ligand exchange for CO in CO-containing systems.

The thermal chemistry of the $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + Br^-$ system is also revealing in terms of the preparation of metal–metal bonds by reaction 3. In cases where reactions do not appear to proceed at room temperature, the limitation may be kinetic and not thermodynamic. However, at higher temperatures competing side reactions and/or the existence of significant equilibrium processes may result in low yields. In such cases it may be possible to maximize yield by carrying out the reactions at intermediate temperatures for long periods of time.

Acknowledgment. Acknowledgments are made to the National Science Foundation (Grant No. GP17083) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, 12091-64-4; $(\pi\text{-}C_5H_5)Mo(CO)_3Br$, 12079-79-7; $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$, 52418-54-9; $(\pi\text{-}C_5H_5)Mo(CO)_3^-$, 12126-18-0; Br^-, 24959-67-9.

References and Notes

(1) A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organometal. Chem.*, **67**, 67 (1974).

(2) We have recently obtained evidence for the appearance of an intermediate in this reaction, presumably $[(\pi\text{-}C_5H_5)Mo(CO)_2Br]_2$.[3] The closely related dimer $[(\pi\text{-}C_5H_5)Mo(CO)_2Cl]_2$ has been reported.[4] With excess Br^- the intermediate has a transient existence and the ultimate product is $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$.

(3) J. L. Hughey IV, work in progress.

(4) L. H. Ali, A. Cox, and T. J. Kemp, *J. Chem. Soc., Dalton Trans.*, 1475 (1973).

(5) C. White and R. J. Mawby, *Inorg. Chim. Acta*, **4**, 261 (1970).

(6) R. E. Dessy and P. M. Weissman, *J. Amer. Chem. Soc.*, **88**, 5124 (1966).

(7) E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960).

(8) Infrared and visible spectral results indicated that a small amount (<10%) of $(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$ was also present in the solution.

(9) For longer time periods, an additional, unidentified component (ν(CO) at 1930 and 1860 cm^{-1}) is also present. Prolonged heating at 60° for 650 hr results in the ultimate formation of this unidentified component and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ as the major products.