Cp$_2$Ti(CO)(η^2-PhC≡CPh) and a four-electron-donor acetylene ($\nu_{C≡C}$ = 1701 cm^{-1}) in (OEP)Ti(η^2-PhC≡CPh). Finally, the ^{13}C NMR spectrum for (OEP)Ti(η^2-PhC≡CPh) provides further support for this bonding interaction. The ^{13}C chemical shift for the C≡C carbon occurs at 219.4 ppm. Despite a significant upfield shift due to the porphyrin ring current,[15] this signal falls well within the region expected for a four-electron-donor ligand.[16] In this regard, the alkyne complexes 1 and 2 represent the first metallo-

porphyrins that contain Ti(II). Reactivity studies of these novel complexes are also consistent with a Ti(II) formalism.[17]

(15) ^{13}C resonances for ligands held above a porphyrin are typically shifted 20 ppm upfield relative to those for the non-porphyrin analogues. See for example: (a) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (b) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887.
(16) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

(17) Woo, L. K.; Hays, J. A., to be submitted for publication.

Articles

Mechanism of the Photoreaction between (η^5-C$_5$H$_5$)M(CO)$_3$X (M = Mo, W) and Allylic Halides
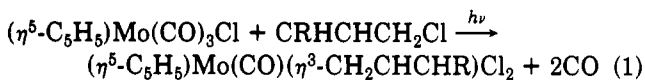
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Photolysis of (η^5-C$_5$H$_5$)Mo(CO)$_3$Cl in the region of 100 K in allyl halide leads to CO loss and the generation of (η^5-C$_5$H$_5$)Mo(CO)$_2$(η^2-C$_3$H$_5$X)Cl (X = Cl, Br, I). This molecule reacts thermally to produce (η^5-C$_5$H$_5$)Mo(CO)(η^3-C$_3$H$_5$)ClX. The activation barrier to this reaction is 34 kJ/mol (X = Cl). This is contrasted with the results obtained upon photolysis of (η^5-C$_5$H$_5$)M(CO)$_3$X with allyl halides (M = Mo, X = Br; M = W, X = Cl, Br, I). Although initial formation of (η^5-C$_5$H$_5$)M(CO)$_2$(η^2-C$_3$H$_5$CX)X is observed upon photolysis, the subsequent thermal chemistry differs. Warming results in halogen loss to produce [(η^5-C$_5$H$_5$)M(CO)$_2$(η^3-C$_3$H$_5$)X][X]. For M = W, X = Cl the activation barrier for the reaction is 69 kJ/mol. When it is warmed further, [(η^5-C$_5$H$_5$)W(CO)$_2$(η^3-C$_3$H$_5$)X][X] decomposes to produce (η^5-C$_5$H$_5$)W(CO)$_2$X$_3$. These results are discussed in terms of an electron transfer from the metal to the coordinated allyl halide.

Herein we report a study of the mechanism of the photoreaction between (η^5-C$_5$H$_5$)M(CO)$_3$X (M = Mo, W) and allylic halides. This reaction was recently reported by Davidson and Vasapollo[1] to generate, in the case of (η^5-C$_5$H$_5$)Mo(CO)$_3$Cl, good yields of the allylic product according to eq 1. The products obtained for the other

$$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{Cl} + \text{CRHCHCH}_2\text{Cl} \xrightarrow{h\nu}$$
$$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}(\eta^3\text{-CH}_2\text{CHCHR})\text{Cl}_2 + 2\text{CO} \quad (1)$$

$$\text{R = H, Me}$$

metals were not the allylic complexes but rather the complexes (η^5-C$_5$H$_5$)W(CO)$_2$Cl$_3$ and [CrCl$_2$(η^5-C$_5$H$_5$)]. It was postulated that the difference in reactivity arises from an initial CO loss product that undergoes oxidative addition with allyl halide to generate (η^5-C$_5$H$_5$)M(CO)$_2$Cl$_2$(η^1-CH$_2$CHCHR) for each of the metals. The differing reactions of these species were suggested to account for the variation in reactivity.

We have recently studied the reaction of allyl halides with a variety of transition-metal centers. Complexes of

the type (η^5-C$_5$H$_5$)M(CO)$_n$ (M = Mn, n = 3; M = Co, Rh, n = 2) were found to lose CO upon photolysis to generate complexes in which the allyl was bound as an olefin, (η^5-C$_5$H$_5$)M(CO)$_{n-1}$(η^2-C$_3$H$_5$X). In each case we were able to show that, at an appropriate temperature, the η^2-allylic olefin underwent an intramolecular electron-transfer reaction to yield the allylic products, (η^5-C$_5$H$_5$)M(CO)$_{n-1}$(η^3-C$_3$H$_5$)$^+$.[2]

Since no reason for a difference in reactivity between the complexes we studied and the (η^5-C$_5$H$_5$)M(CO)$_3$X series was obvious to us, we decided to investigate this reaction. It should be noted that several reports have established that the initial reaction of (η^5-C$_5$H$_5$)M(CO)$_3$Cl (M = Mo, W) upon photolysis is CO loss.[3–5] Here we describe our efforts to determine the result of photolysis in the presence of allyl halides. Related studies include the investigation of the mechanism of the photoreaction of (η^5-C$_5$H$_5$)W(CO)$_3$Cl with other halocarbons.[5] The main points we will address in this study are the overall mech-

(1) Davidson, J. L.; Vasapollo, G. *J. Organomet. Chem.* **1985**, *291*, 43.

(2) Hill, R. H. *J. Chem. Soc., Chem. Commun.* **1989**, 293.
(3) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1231.
(4) Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1980**, *19*, 1533.
(5) Goldman, A. S.; Tyler, D. R. *Organometallics* **1984**, *3*, 449.

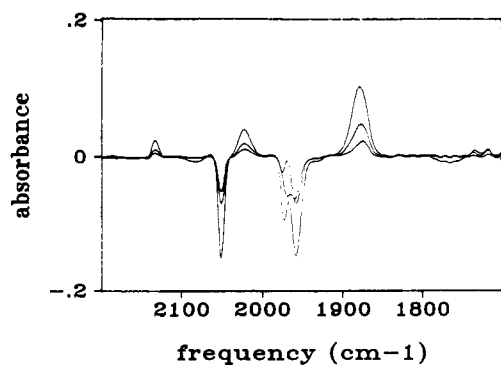**Figure 1.** Spectral changes associated with the photolysis of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ in allyl chloride at 85 K for 10, 20, and 30 s. Negative peaks correspond to loss of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, whereas positive peaks are associated with free CO, $(\eta^5\text{-}C_5H_5)$-$Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$, and $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$.

anism for the photoreactivity in each case and the reason for the differing reactivity of the Mo and W complexes.

Results

Photolysis of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ in allyl chloride at 85 K results in the changes in the FTIR spectra depicted in Figure 1. Loss of absorbance due to $(\eta^5\text{-}C_5H_5)Mo(CO)_2Cl$ at 2052, 1971, and 1963 cm⁻¹ is observed with concomitant growth of peaks due to free CO in the matrix at 2132 cm⁻¹ and a low-energy band at 1872 cm⁻¹ and a high-energy band at 2025 cm⁻¹. The high-energy band observed at 2025 cm⁻¹ is associated with the monocarbonyl allyl complex $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$ reported earlier.[1] Upon close inspection it is apparent that the peaks due to starting material do not decrease in a ratio consistent with their extinction coefficients. This indicates the existence of an absorption band obscured by absorptions due to $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$. By computer subtraction of the spectra due to starting material the high-energy band is found to be at 1965 cm⁻¹ and of intensity equal to that of the absorbance at 1872 cm⁻¹. These last two bands we assign as due to $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$.

The alternative assignment, either $(\eta^5\text{-}C_5H_5)Mo(CO)_2Cl$ with no solvent interaction or $(\eta^5\text{-}C_5H_5)Mo(CO)_2Cl_2(\eta^1\text{-}C_3H_5)$ as suggested earlier[1] as a possible intermediate, we dismiss on the following grounds. We previously showed that $(\eta^5\text{-}C_5H_5)Mo(CO)LCl$, in (epoxyethyl)benzene, undergoes rapid reaction with free CO at temperatures as low as 20 K.[6] That we observe no thermal reaction with CO is most consistent with the formation of a coordinatively saturated intermediate. This leaves us with distinguishing between an oxidatively added adduct, of the type suggested earlier, and an η^2-olefin complex. It is notable that we find similar IR band positions in allyl chloride with those observed following photolysis in only weakly interaction (epoxyethyl)benzene. The observed band positions for this unsaturated fragment in the epoxide solvent are 1973 and 1875 cm⁻¹, which are slightly higher energy than those observed here. In order to further investigate the absorption positions, we consider the FTIR data in methylcyclohexane and 4-methyl-1-cyclohexene presented in Table I. In methylcyclohexane, where an η^2-olefin complex is not possible, the band positions are different and are farther from those observed in 4-methyl-1-cyclohexene, where an η^2-olefin is possible. We conclude that our results are consistent with η^2-olefin complexes being formed in both allyl chloride and 4-methyl-1-cyclohexene. It is well-known that oxidative addition causes a large increase

(6) Debad, J. D.; Hill, R. H. *Can. J. Chem.* **1990**, *68*, 2216.

Table I. FTIR Spectroscopic Data for the Complexes at 77 K

complex	solvent[a]	$\nu(CO)$, cm⁻¹ (rel intens)
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$	A	2052 (0.61), 1971 (1), 1963 (0.72)
$(\eta^5\text{-}C_5H_5)Mo(CO)_2Cl$	B	1970 (1), 1853 (0.7)
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_7H_{12})Cl$	C	1974 (1), 1868 (0.7)
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$	A	1965 (1), 1872 (1)
$(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$	A	2027
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Br)Cl$	D	1970 (1), 1876 (1)
$(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)ClBr$	D	2024
$(\eta^5hC_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5I)Cl$	E	1965 (1), 1880 (0.8)
$(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)ClI$	E	2020
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Br$	D	2046 (1), 1965 (1,1)
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Br)Br$	D	1962 (1), 1886 (1.3)
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)Br^+Br^-$	D	2070 (1), 2023 (1.5)
$(\eta^5\text{-}C_5H_5)W(CO)_3Cl$	A	2044 (0.84), 1951 (1), 1945 (1)
$(\eta^5\text{-}C_5H_5)W(CO)_2Cl$	B	1947 (1), 1849 (0.7)
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_7H_{12})Cl$	C	1954 (1), 1849 (0.9)
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$	A	1954 (1), 1852 (1)
$(\eta^5\text{-}C_5H_5)W(CO)(\eta^3\text{-}C_3H_5)Cl_2$	A	2019
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_5)Cl^+Cl^-$	A	2070 (0.7), 2013 (1)
$(\eta^5\text{-}C_5H_5)W(CO)_2Cl_3$	A	2112 (2), 2022 (3)
$(\eta^5\text{-}C_5H_5)W(CO)_3Br$	D	2039 (0.84), 1949 (1), 1943 (0.94)
$(\eta^5\text{-}C_5H_5)W(CO)_2Br$	B	1952 (0.8), 1845 (1)
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_7H_{12})Br$	C	1954 (1), 1852 (1)
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Br)Br$	D	1953 (1.1), 1853 (1)
$(\eta^5\text{-}C_5H_5)W(CO)(\eta^3\text{-}C_3H_5)Br_2$	D	
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_5)Br^+Br^-$	D	2067 (1), 2011.6 (3)
$(\eta^5\text{-}C_5H_5)W(CO)_2Br_3$	D	2085 (1), 2034 (3)
$(\eta^5\text{-}C_5H_5)W(CO)_3I$	E	2030 (0.88), 1944 (0.94), 1936 (1)
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5I)I$	E	1949 (1.2), 1858 (1)
$(\eta^5\text{-}C_5H_5)W(CO)(\eta^3\text{-}C_3H_5)I_2$	E	2005
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_5)I^+I^-$	E	2068 (1), 2010 (3)
$(\eta^5\text{-}C_5H_5)W(CO)_2I_3$	E	2061 (1), 2017 (3)

[a] Solvents for each case were as follows: A, allyl chloride; B, methylcyclohexane; C, 4-methyl-1-cyclohexene; D, allyl bromide; E, allyl iodide.

in the CO absorption energy.[7] For example the complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2X_3$ (X = Cl, Br, I) have absorptions[8] in the region of 2105–2071 and 2063–2034 cm⁻¹. The previously suggested intermediate $(\eta^5\text{-}C_5H_5)Mo(CO)_2Cl_2(\eta^1\text{-}C_3H_5)$, the result of a simple addition of the Mo center to the C–Cl bond, would be expected to have similar absorptions. We conclude that the species studied is $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$. From the relative intensity of the two CO absorption bands ($\sim$1:1) we assign a cis geometry to the CO ligands.

Since previous results indicate that CO loss is the primary photoprocess in a variety of low-temperature media, we conclude that this is operative here.[3] The unsaturated CO loss product is, upon its production, rapidly solvated by the allyl chloride solvent. The stoichiometry of the primary photoreaction has been measured by using the reported[9] extinction coefficient of uncomplexed CO and is as shown in eq 2. Now we will establish that this

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl + C_3H_5Cl \xrightarrow{h\nu}$$
$$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl + CO \quad (2)$$
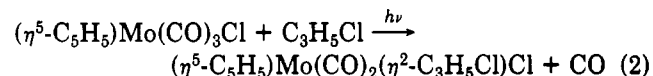
dicarbonyl adduct is indeed an intermediate in the production of $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$.

If a sample is photolyzed to generate the mixture, as described above, at a sufficiently high temperature a thermal process is found to occur on a measurable time

(7) Miller, T. J.; Ahmed, K. J.; Wrighton, M. S. W. *Inorg. Chem.* **1989**, *28*, 2347. Brisdon, B. J.; Enger, S. K.; Weaver, M. J.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3340.

(8) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1966**, 1606.

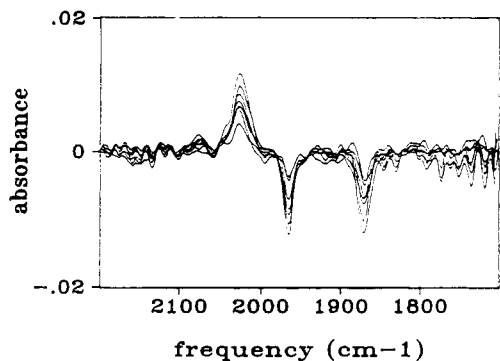(9) Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 2792.

Figure 2. Spectral changes associated with a thermal reaction at 104.4 K. The positive peak at 2027 cm^{-1} is due to the production of $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$, and the negative peaks are associated with the loss of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$. Spectra were obtained at 30, 50, 70, 100, 125, 165, and 305 min.
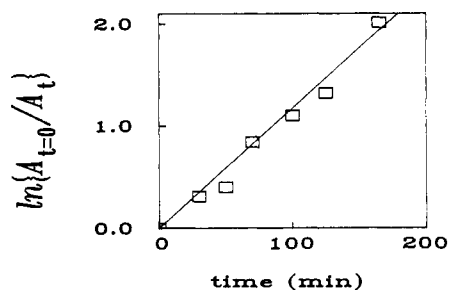

Figure 3. Kinetic plot of ln $(A_{t=0}/A_t)$ vs time for the reaction of eq 3. The data are from Figure 2.

scale. The changes in the FTIR spectra at 104.4 K, as a function of time, are shown in Figure 2. Note that under these conditions the concentration of $(\eta^5\text{-}C_5H_5)Mo(CO)_2$-$(\eta^2\text{-}C_3H_5Cl)Cl$ produced is lower than that observed at 85 K (Figure 1). This is apparently due to reaction of this complex prior to obtaining thermal equilibrium with the glass. Loss of absorption bands associated with $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ is observed along with a proportional production of a new absorption band at 2027 cm^{-1}. This product is identified as $(\eta^5\text{-}C_5H_5)Mo\text{-}(CO)(\eta^3\text{-}C_3H_5)Cl_2$ by comparison of its FTIR spectrum with that of an authentic sample prepared by published procedures.[1] The reaction is hence given by eq 3. We also observed that $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ is photolabile, undergoing loss of CO upon photolysis.

$$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl \rightarrow$$
$$(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2 + CO \quad (3)$$
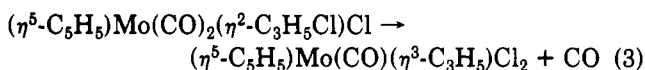
The decay of photogenerated $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ was monitored and fits a single-exponential decay. The rate of loss of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ was also found to coincide with the rate of appearance of $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$. From these results we can conclude that the thermal reaction is indeed as shown by eq 3.

The reaction is first order, as demonstrated by a linear plot of ln $(A_{t=0}/A_t)$ vs time shown in Figure 3. The slope of this line yields a rate constant for this process of 1.9 × 10^{-4} s^{-1} at 104.4 K. By varying the temperature of photolysis, it is possible to obtain rate constants at a variety of temperatures, and we have done this. The results are summarized in Table II. A plot of ln k vs $1/T$ was then made and is shown in Figure 4. The slope of this plot multiplied by R yields an activation barrier to the reaction of eq 3 of 34 kJ/mol.

The reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ were also studied in allyl bromide and iodide. The results are summarized

Table II. Kinetic Data for the Reaction of $(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ (M = Mo, W)

complex	temp, K	ln k
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$	100.4	-10.89
	104.4	-8.56
	108.6	-7.55
	112.6	-6.55
	116.5	-4.87
$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$	93.5	-10.96
	96.8	-7.33
	99.8	-5.20
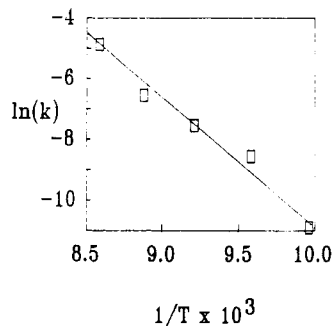
Figure 4. Plot of ln k vs $1/T$ for the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ to produce CO and $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$.

in Table I. The overall chemistry is similar to that which was observed in allyl chloride. It is notable that the FTIR frequency, as expected, shifts to lower energy throughout the Cl, Br, I series of complexes for $(\eta^5\text{-}C_5H_5)Mo\text{-}(CO)(\eta^3\text{-}C_3H_5)X_2$.

We also studied $(\eta^5\text{-}C_5H_5)Mo(CO)_3Br$ in an allyl bromide glass. Once again photolysis resulted in formation of an η^2-olefin complex. When the thermal reaction was allowed to proceed at 100 K, loss of signals due to the olefin adduct and the appearance of two new absorptions in the metal carbonyl region at 2070 and 2023 cm^{-1} were observed. These are assigned as due to the formation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)Br][Br]$. As in the monocarbonyl adducts the CO frequency is shifted to higher energy, indicative of an oxidative-addition product. The presence of two absorptions in the CO region indicates that the product is a dicarbonyl oxidative-addition product. The only other alternatives consistent with two CO ligands are either $(\eta^5\text{-}C_5H_5)Mo(CO)_2Br_3$ or the simple oxidative-addition adduct $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^1\text{-}C_3H_5)Br_2$. The first is ruled out, as its known IR absorptions are observed at 2101 and 2058 cm^{-1},[10] significantly higher energy than those observed here. The simple oxidative-addition adduct is also ruled out, as its IR absorptions are expected to be similar to those of the trihalide.[11] Lastly, it should be noted that there is precedent for this reaction. This reaction has been reported for the complexes $(\eta^5\text{-}C_5R_5)M\text{-}(CO)_n(\eta^2\text{-}C_3H_5Cl)$ (M = Rh, Co, n = 1; M = Mn, n = 2; R = H, Me).[2] The relevant spectral data are given in Table I.

The chemistry of the tungsten complexes is quite similar to that observed for the molybdenum described above, although there are minor differences. Photolysis of $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ at 83.5 K in allyl chloride leads to a result

(10) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1967**, 686.
(11) We are unaware of any complex of the formula $(\eta^5\text{-}C_5H_5)Mo(CO)_2RBr_2$; however, from the comparison between the known species $(\eta^5\text{-}C_5H_5)W(CO)_2BrCl_2$ and $(\eta^5\text{-}C_5H_5)W(CO)_2(CH_2Ph)Cl_2$ a shift of 1 and 3 cm^{-1} to higher energy for the two CO bands may be expected as a result of substitution of CH$_2$Ph for Br.[5] Although the magnitude of any shift would differ in comparison of the Mo and W systems, we expect that the direction of the shift would be the same, leading to the expectation that the IR bands due to $(\eta^5\text{-}C_5H_5)Mo(CO)_2RBr_2$ would appear at higher energy than those due to $(\eta^5\text{-}C_5H_5)Mo(CO)_2Br_3$.

similar to that found for $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$. FTIR-monitored photolysis indicates loss of absorptions attributable to $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ and the formation of free CO in the matrix. In addition to these changes production of a monocarbonyl band at 2019 cm^{-1} and two bands associated with a dicarbonyl at 1954 and 1852 cm^{-1} in a 1:1 ratio were observed. We assign the high-energy monocarbonyl absorption as indicative of $(\eta^5\text{-}C_5H_5)W(CO)Cl_2$-$(\eta^3\text{-}C_3H_5)$ in analogy to the Mo system above (see also below). This result is confirmed by comprison of the FTIR absorptions with those obtained in both methylcyclohexane and 4-methyl-1-cyclohexene. The data are presented in Table I. Clearly, the FTIR positions are similar with those found in 4-methyl-1-cyclohexene, confirming an η^2-bound olefin in each case. The dicarbonyl is assigned as due to $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$. In this case an oxidative-addition adduct with benzyl chloride, $(\eta^5\text{-}C_5H_5)W(CO_2)Cl_2(CH_2Ph)$, is known.[5] The benzyl chloride complex exhibits CO stretching frequencies at 2090 and 2030 cm^{-1}, much higher than observed here. The initial photoproduct in this case is clearly not an oxidative-addition product but $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$. Although the initial photolytic changes are similar to those of the Mo analogue, the thermal chemistry is substantially different.

If a glass containing $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ is kept at constant temperature in the dark, a thermal reaction occurs at 83.5 K. This reaction results in loss of $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ and the formation of a new dicarbonyl, as evidenced by an increase in intensity of bands at 2070 and 2013 cm^{-1}. The half-life for the reaction is approximately 10 h. This product is an oxidized species, as evidenced by the shift of the CO stretching modes to higher energy.[7] Comparison of the FTIR spectrum with that due to authentic samples of $(\eta^5\text{-}C_5H_5)W(CO)_2Cl_3$ demonstrates that this is not the oxidized product.[10] In addition the substitution of a single halide by an alkyl group results in only a small perturbation of the spectra,[5] allowing us to exclude $(\eta^5\text{-}C_5H_5)W(CO)_2Cl_2(CH_2CHCH_2)$ as a possible product. It is notable that no $(\eta^5\text{-}C_5H_5)W\text{-}(CO)Cl_2(\eta^3\text{-}C_3H_5)$ is formed during this thermal reaction. We assign these new absorptions as due to the ionic species $[(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_5)Cl][Cl]$. The relative intensity of the two CO absorption bands has been used to calculate[12] the angle between the CO ligands as 100°. This indicates that the structure of this product is similar to that of the known molybdenum(IV) allyls[1,13] except that one halide is replaced by a CO ligand. The overall thermal reaction observed is hence given by eq 4.

$$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl \rightarrow$$
$$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_4R)Cl^+ + Cl^- \quad (4)$$
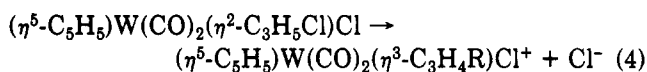
This type of reaction has been observed in a large number of systems.[2] It is notable that at temperatures near 100 K photolysis does not lead to the production of appreciable amounts of $(\eta^5\text{-}C_5H_5)W(CO)Cl_2(\eta^3\text{-}C_3H_5)$, as was observed at lower temperatures, but rather $[(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_5)Cl][Cl]$ is observed. Clearly at these temperatures the reaction to produce $[(\eta^5\text{-}C_5H_5)W(CO)_2\text{-}(\eta^3\text{-}C_3H_5)Cl][Cl]$ occurs at a high rate. This reaction prevents the buildup of observable concentrations of $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ at temperatures in excess of 100 K. Since the photostationary-state concentration of $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ is low at these temperatures, the product of its photoreaction, $(\eta^5\text{-}C_5H_5)W\text{-}$

$(CO)Cl_2(\eta^3\text{-}C_3H_5)$, is not observed.

When glasses containing $(\eta^5\text{-}C_5H_5)W(CO)(\eta^3\text{-}C_3H_5)Cl_2$ and $[(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_5)Cl][Cl]$ were warmed, both complexes decomposed. The only product found at room temperature to result from this decomposition is $(\eta^5\text{-}C_5H_5)W(CO)_2Cl_3$. This was demonstrated by comparison with an authentic sample.[5] It is notable that this is the observed product following photolysis at room temperature.[1]

The reactions of $(\eta^5\text{-}C_5H_5)W(CO)_3X$ in C_3H_5X (X = Br, I) have also been studied. The observations are similar to those found for the chloride derivative. The FTIR absorptions of the various species are given in Table I. The two departures from what was observed in the chloride derivative are outlined below. The first difference is that no monocarbonyl was observed upon photolysis (X = Br). The second major difference is that the relative CO intensities indicate that the product of the thermal reaction has a much larger angle between the CO ligands.

As was found in the study of the chloride derivative, these allyltungsten complexes decomposed upon warming to room temperature. Consistent with the earlier room-temperature study, the products of these decompositions were the W(IV) complexes $(\eta^5\text{-}C_5H_5)W(CO)_2X_3$. These assignments were confirmed by comparison with authentic samples.[5,10]

The rate of the thermal transformation according to eq 4 has also been measured. The rate of $(\eta^5\text{-}C_5H_5)W\text{-}(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ loss and the rate of $(\eta^5\text{-}C_5H_5)W\text{-}(CO)_2(\eta^3\text{-}C_3H_5)Cl^+$ appearance were found to coincide. A first-order dependence on the concentration of $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ was found, as evidenced by linear plots of ln $(A_{t=0}/A_t)$ vs time. The temperature-dependent rate constants determined for reaction 4 are given in Table II. An analysis of these data provides the activation energy as 69 kJ/mol.

Discussion

In all the systems discussed, our results are in accord with the room-temperature observations reported previously.[1] The low-temperature studies do, however, expose the complexity of the mechanism required to explain the different final products observed for the photochemitry of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ in allyl halides.

The results are summarized in Scheme I. All the complexes discussed here undergo initial CO loss as their primary photoprocess. Following this reaction, coordination of the allylic halide occurs rapidly to produce the family of complexes cis-$(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^2\text{-}C_3H_5X')X$. Related complexes of the formula $(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^2\text{-}C_2H_4)H$ (M = Mo, W) have been described previously.[14] It should be noted that in these hydride complexes the cis isomer is more difficult to observe, undergoing facile rearrangement to the trans species. We observe only cis-$(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^2\text{-}C_3H_5X')X$, which undergoes other reactions more radily than isomerism.

This is consistent with the known chemistry of other derivatives, where the rearrangement of halide-substituted species is slower than for the corresponding hydrides. For the tungsten derivatives further photolysis results in CO loss and the formation of $(\eta^5\text{-}C_5H_5)W(CO)(\eta^3\text{-}C_3H_5)X_2$ (X = Cl, Br, I) according to eq 5. This proces, although important at temperatures below 100 K, is not expected to

(12) King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 183.
(13) Faller, J. W.; Ma, Y. *Organometallics* **1986**, *5*, 1949.

(14) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005. Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1727. Mahmoud, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Janson, B. M. *J. Chem. Soc., Dalton Trans.* **1984**, 175. Mahmoud, K. A.; Rest, A. J.; Alt, H. *J. Chem. Soc., Dalton Trans.* **1984**, 187.

Scheme I
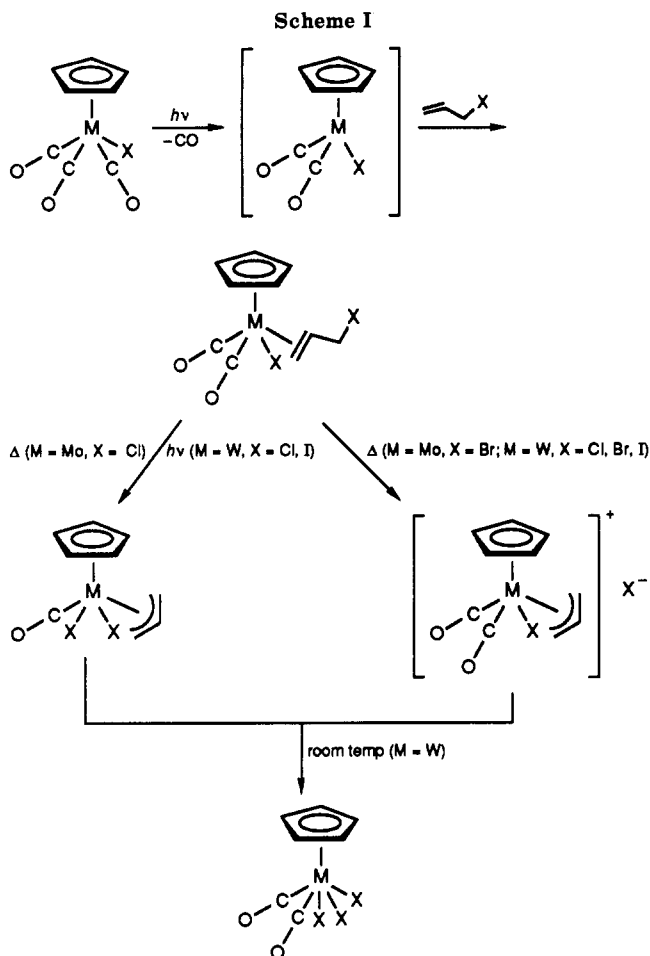
be significant at higher temperatures because of the limited lifetime of the dicarbonyl fragment.

$$(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_3H_5X)X \xrightarrow{h\nu}$$
$$(\eta^5\text{-}C_5H_5)W(CO)(\eta^3\text{-}C_3H_5)X_2 + CO \quad (5)$$
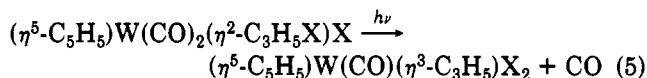
It is notable that none of these tungsten allyl complexes are thermally stable in allyl halide. When the matrix containing $(\eta^5\text{-}C_5H_5)W(CO)(\eta^3\text{-}C_3H_4R)X_2$ is discussed, deomposition occurs, resulting in the final production of $(\eta^5\text{-}C_5H_5)W(CO)_2X_3$.

Each of the dicarbonyl fragments $(\eta^5\text{-}C_5H_5)M(CO)_2$-$(\eta^2\text{-}C_3H_5Cl)Cl$ then react thermally. In the case of Mo the product is the same as that observed upon room-temperature photolysis, $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$. For the tungsten derivative an ionic product, $[(\eta^5\text{-}C_5H_5)W(CO)_2\text{-}(\eta^3\text{-}C_34H_5)Cl][Cl]$, is formed. This reaction has been observed previously in the chemistry of Mn, Co, and Ir. The difference in this reactivity is possibly a result of the greater ease with which CO is lost from the Mo derivative. It is known that the rate of thermal CO loss from the hexacarbonyl compound is much greater for molybdenum than for tungsten.[15] The change upon moving to the bromide derivative, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Br)Br$, resulted in a change in thermal chemistry and the production of the dicarbonyl adduct $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)\text{-}Br][Br]$.

The demonstrably different reactivities of the η^2-allyl halide complexes of molybdenum and tungsten are not sufficient to explain the different products observed following room-temperature photolysis. At low temperature

We can make the complexes $(\eta^5\text{-}C_5H_5)M(CO)(\eta^2\text{-}C_3H_5)Cl_2$ (M = Mo, W), but only the molybdenum complex is stable. In addition, the other tungsten allyl complex produced thermally following low-temperature photolysis, $[(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_3H_5)Cl][Cl]$, is unstable at room temperature. The result of warming both of these complexes to room temperature is $(\eta^5\text{-}C_5H_5)W(CO)_2Cl_3$.

It appears that the difference in the room-temperature photochemistry of the complexes is not the simple result of differing chemistry of one common intermediate. The results of room-temperature photolysis are a result of varying stability of the allylic complexes of Mo and W. We will now consider the different reactions of the common intermediate, $(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ (M = Mo, W).

The reaction of the common intermediates, although different for the two species, we believe to be initiated in each case by an electron-transfer process. Previously we demonstrated that electron transfer to coordinated allyl chloride resulted in the reaction of a variety of organometallic complexes. This was shown on the basis of the kinetic results, which fit the form predicted by Marcus theory for electron transfer.[2] In the study at hand qualitative reasoning suggests the same initial step.

Both intermediate species $(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ (M = Mo, W) are coordinatively saturated 18e⁻ complexes. As such, they are not expected to undergo low-energy associative reactions. For example, the known associative reaction of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ with triphenylphosphine occurs only at much higher temperatures.[16] Other substitution reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_3X$ (X = Cl, Br, I) with PR₃ are in fact dissociative in nature, the associative process being too high in energy to observe.[17,18] On the basis of the precedent of such slow associative reactions with other ligands we rule out the possibility of a simple associative reaction occurring at the low temperatures studied here.

The second possibility, dissociative los of a ligand to initiate the reaction, will now be considered. Once again, thermal loss of a ligand is without precedent at such low temperatures. Dissociative substitution of CO is known to occur, but only at much higher temperature, for $(\eta^5\text{-}C_5H_5)Mo(CO)_3X$ (X = Cl, Br, I).[17] The related complex $(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)Me$ undergoes rotation of the ethylene fragment through a process, presumably not ligand loss, that in any case occurs only at temperatures much higher than those used in this study.[19] Given these precedents, it is difficult to imagine any simple dissociative process occurring in the region of 100 K.

We propose that electron tranfer from a metal-centered d orbital to the σ*(C–Cl) orbital precedes any bond making or breaking. It should be noted that following electron transfer from the metal to the allyl moiety the metal is a 17e⁻ center. It has been demontrated by others that the associative chemistry of 17e⁻ centers is both thermodynamically downhill and kinetically much more facile than for an 18e⁻ metal.[20,21] For example, one of the few measurements for 17e⁻ associative reactions is for the association of $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ with Cl⁻, which occurs with a

(15) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082.

(16) Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2715.

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

(18) It should be noted that these studies also found an associative component with the smaller phosphines. The nature of this was suggested to be direct attack at the ring.

(19) Alt, H. G.; Schwarzle, J. A.; Kreiter, C. G. *J. Organomet. Chem.* **1978**, *153*, C7. Kreiter, C. G.; Nist, K.; Alt, H. G.; *Chem. Ber.* **1981**, *114*, 1845.

(20) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

(21) Philbin, C. E.; Granatir, C. A.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4806.

driving force ΔG of 8.6 kJ/mol. The reactions considered here are most amenable to interpretation if they are electron-transfer reactions. The electron-tranfer reaction is consistent with high reactivity of a coordinatively saturated species at low temperatures. It is worth noting that the systems reported earlier were not amenable to this type of qualitative evidence of electron transfer, since they did not involve coordinatively saturated metal centers. It is the consequent reactivity that must now be considered.

The postulate of rate-limiting electron transfer is consistent with the observed reactivity. Following electron transfer the complex may be represented as $[(\eta^5\text{-}C_5H_5)M\text{-}(CO)_2(\eta^2\text{-}C_3H_5)Cl][Cl]$. In the case of tungsten, radical collapse leads to the initial kinetic product, $[(\eta^5\text{-}C_5H_5)W\text{-}(CO)_2(\eta^3\text{-}C_3H_5)Cl][Cl]$. For molybdenum, the observed product is consistent with CO substitution by Cl^- at the 17e^- metal center. This substitution reaction, occurring rapidly at 100 K, is consistent with the expected high reactivity of a diradical intermediate.

It is notable that the thermal reactions of $(\eta^5\text{-}C_5H_5)M\text{-}(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ require quite different energetics. The activation energy for Mo is only 34 kJ/mol, whereas the W derivative has an activation energy of 69 kJ/mol. This difference, we believe, is consistent with electron-transfer initiation. As observed previously in our investigation of the η^2-allyl halide to η^3-allyl conversion, the relative rate is temperature-dependent. In addition, the large difference in activation entropy is consistent with electron transfer, where solvent reorganization may dominate this term.

Currently, we are extending the kinetic analysis both to allylic halides and to other metal halides. With subsequent study we hope to shed more light on the nature of the electron-transfer step by quantitative assessment of the activation parameters.

Experimental Section

The complexes $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$,[1] $(\eta^5\text{-}C_5H_5)W\text{-}(CO)_2X_3$,[1,8] and $(\eta^5\text{-}C_5H_5)M(CO)_3X$ (M = Mo,[22] W[23]) were prepared and purified by published methods. All spectra at 77 K were obtained in a liquid-N_2-cooled sample holder with CaF$_2$ optics. The temperature was monitored with a silicon diode sensor. The FTIR spectra were obtained with a Bomem MB-120 FTIR spectrometer. Variable-temperature FTIR spectra were obtained with a Bruker IFS 85 spectrophotometer. In each case spectra were calculated as difference spectra with use of the formula log (R/S), where R is the transmitted intensity of the appropriate reference state (i.e. prior to photolysis or time zero of the thermal reaction) and S is the intensity of the sample spectrum. Samples were cooled with a CTI-Cryogenics Model 22 cryocooler attached to a Model 350R compressor system. The cold head was equipped with CaF$_2$ windows. Temperatures were controlled and monitored

with use of a Lake Shore Cryotronics silicon diode sensor (Model DT500 DRC) in conjunction with a Model DRC 80C temperature controller.

The solvents used in the spectroscopic studies were obtained from Aldrich and used without further purification, except allyl iodide, which was purified by chromatography.

Photolysis of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$. Several experiments were conducted in the same manner; here we describe a typical experiment. The complex $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ was dissolved in allyl chloride to produce a solution of optical density 0.3 for its most intense IR absorption band in the carbonyl region. The sample was then transferred to a CaF$_2$-faced FTIR cell and loaded into the cold head of the cryostat. The sample chamber was evacuated and then cooled to 77 K. During the cooldown, FTIR spectra were obtained at different temperatures. At 77 K the sample was photolyzed for 10 s with a 75-W Xe lamp. The FTIR spectrum was then recorded again and the procedure of photolysis-record spectra was repeated several times.

The approximate stoichiometry was determined as follows. The extinction coefficient of the high-energy band of $(\eta^5\text{-}C_5H_5)Mo\text{-}(CO)_3Cl$ was measured (3700) and used in further calculations. For photolysis in methylcyclohexene the extinction coefficient for free CO in MCH[9] of 400 was used. The production of 1 mol of free CO per photoreaction of 1 mol of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ establishes the reaction stoichiometry. For the reaction in allyl chloride the situation becomes more complex. Since initial production of both $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl$ and $(\eta^5\text{-}C_5H_5)Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$ is observed, we must establish the extinction coefficients of both these species. If we assume the thermal reaction noted in Figure 2 is without byproducts, then from the relative intensity we find that the extinction coefficients of these two species are equal. From the relative intensity of these in the photolysis shown in Figure 1, we determined that the loss of 1 mol of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ is accompanied by the production of a 2.33:1 ratio of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}C_3H_5Cl)Cl:(\eta^5\text{-}C_5H_5)\text{-}Mo(CO)(\eta^3\text{-}C_3H_5)Cl_2$. The loss of 1 mol of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ should hence be accompanied by the production of 1.3 mol of CO. Using the published extinction coefficient of CO and the spectra of Figure 3, we find values of 0.87, 1.34, and 1.47 or an average value of 1.23. The error in the reported extinction coefficient of uncomplexed CO is 15%, and our fit to the theoretical stoichiometry is accurate within 6%.

Kinetic Measurements. Several experiments were done by the following procedure. An allyl chloride solution of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ was prepared, loaded into a CaF$_2$-faced FTIR cell, and cooled to 104.4 K as above. After the system reached a constant temperature, the FTIR spectrum was recorded. The sample was then removed from the FTIR spectrometer and photolyzed for 30 s with the water-filtered output of a 75-W high-pressure Hg lamp. The sample was then returned to the FTIR spectrometer and FTIR spectra obtained as a function of time. In different experiments the irradiation of the FTIR cell (both Nernst glower and HeNe laser) was blocked between obtaining the FTIR spectrum. This was found to have no impact on the rate of the reaction.

(22) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
(23) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246.