

Primary Photoproducts and the Mechanism of Ligand Substitution
in the Photochemistry of Dinuclear Metal Carbonyls

Thomas R. Herrinton

Final Seminar

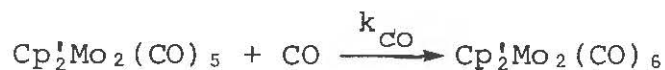
August 3, 1984

The photochemistry of dinuclear metal carbonyl compounds has been studied extensively in the past two decades. Nonetheless, the identities and reaction mechanisms of the primary photoproducts in the photolysis of these complexes have remained elusive. Early work indicated that metal-metal bond homolysis was the sole photo-process [1]. More recently loss of a CO ligand has been shown to occur in some systems [2,3,4]. In order to further the understanding of this problem a study of the photochemistry of bis(pentamethylcyclopentadienylmolybdenumtricarbonyl) ($\text{Cp}_2^{\text{M}}\text{Mo}_2(\text{CO})_6$) was performed to determine its primary photoproducts.

Flash photolysis methods were used to investigate this question. High concentrations of the primary photoproducts are achieved by a brief (FWHM $\cong 35 \mu\text{S}$) pulse of broad band irradiation, and then either the return of the original dimer or the disappearance of the transients can be monitored on the microsecond timescale by optical absorption spectroscopy. Observations of the return of the 495 nm absorbance band of $\text{Cp}_2^{\text{M}}\text{Mo}_2(\text{CO})_6$ following the flash established the existence of two pathways for reforming the parent dimer. The first of these was quite rapid, followed second-order kinetics, and showed no dependence on [CO]. This process is proposed to be a radical recombination reaction (eq. 1).



The value of k_r is $(8.0 \pm 0.6) \times 10^8 \text{M}^{-1}\text{s}^{-1}$. The second, slower pathway followed first-order kinetics under a CO atmosphere, and the observed rate constant did depend on [CO]. Consequently, it is proposed that the second pathway involves CO recapture as shown in equation (2).



The value of k_{CO} is $(4.4 \pm 0.4) \times 10^3 \text{M}^{-1}\text{s}^{-1}$.

Examination of the optical spectrum from 560-800 nm reveals two transients with overlapping absorbance bands. One of these decays rapidly by second-order kinetics, and is believed to be $\text{Cp}^{\text{M}}\text{Mo}(\text{CO})_3 \cdot$. This is the first spectroscopic observation of a molybdenum-based metal carbonyl radical at room temperature. The second transient's absorbance disappears by pseudo-first-order kinetics at the same rate as found in equation (2). This absorbance is assigned to $\text{Cp}_2^{\text{M}}\text{Mo}_2(\text{CO})_5$.

Not all of the original absorbance at 495 nm is restored by these two processes. Some absorbance loss remains for several minutes, although it is all recovered eventually under a CO atmosphere. This slow process is proposed to be the carbonylation reaction shown in eq. (3).



Equation (3) is a known reaction [5]. A combination of flash and continuous photolysis experiments determined that the triply-bonded dimer is formed by loss of CO from $\text{Cp}^{\dagger}\text{Mo}(\text{CO})_3\cdot$ and subsequent radical coupling. Given this fact, the percentage of photolyzed $\text{Cp}_2^{\dagger}\text{Mo}_2(\text{CO})_6$ molecules which undergo CO loss was calculated to be 10%.

The reaction pathways which are utilized by primary photoproducts have also been a subject of controversy. For example, both dissociative [6] and associative [7] mechanisms have been proposed for ligand substitution of $\text{Mn}(\text{CO})_5\cdot$. This question was investigated using a modified version of the competition experiment designed by Fox *et. al.* [8]. For the reaction system $\text{Mn}(\text{CO})_5\cdot + \text{L} + \text{RX}$ the applicable kinetic relationships are given either by equation (4),

$$\frac{[\text{Mn}(\text{CO})_4\text{LX}]}{[\text{Mn}(\text{CO})_5\text{X}]} = \frac{k_d}{ak_t} \frac{1}{[\text{L}]} + \frac{k_a}{ak_t} \quad (4)$$

where $[\text{L}] = a[\text{RX}]$ and all other symbols are as defined by Fox *et. al.*, or by equation (5),

$$\frac{[\text{Mn}(\text{CO})_4\text{LX}]}{[\text{Mn}(\text{CO})_5\text{X}]} = \frac{k_d + k_a[1]}{k_t[\text{RX}]} \quad (5)$$

where the ratio $[\text{L}]:[\text{RX}]$ is not fixed.

The experimental results show that for $\text{L} = \text{PPh}_3$ and $\text{RX} = \text{CCl}_4$, $k_a = (1.8 \pm 0.2) \times 10^7 \text{M}^{-1}\text{s}^{-1}$ while $k_d \leq 2.1 \times 10^3 \text{s}^{-1}$, clearly demonstrating the reaction to be associative in character. The value of k_t was established to be $(1.4 \pm 0.1) \times 10^6 \text{M}^{-1}\text{s}^{-1}$ by independent methods. A second system with $\text{L} = \text{AsPh}_3$ and $\text{RX} = \text{CH}_2\text{Br}_2$ lowered the limiting value of k_d : $k_d \leq 9.0 \times 10^1 \text{s}^{-1}$. Experiments with other phosphorus-based ligands demonstrated that both the steric and electronic properties of the incoming ligand are important in determining the rate constant of the reaction. The observed products for substitution of $\text{Mn}_2(\text{CO})_{10}$ by L , $\text{Mn}_2(\text{CO})_8\text{L}_2$ and $\text{Mn}_2(\text{CO})_9\text{L}$ [6] are therefore proposed to result from substitution of $\text{Mn}(\text{CO})_5\cdot$ and $\text{Mn}_2(\text{CO})_9$, respectively.

References

1. Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; Chapter 2 and references therein.
2. Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. "Laser Photolysis Study of the Photosubstitution of Dimanganese Decacarbonyl"; J. Am. Chem. Soc., 1983, 105, 6249.
3. Caspar, J.V.; Meyer, T. J. "Mechanistic Aspects of the Photochemistry of Metal-Metal Bonds. Evidence for the Intervention of Two Different Primary Photoproducts in the Photochemistry of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ "; J. Am. Chem. Soc., 1980, 102, 7794.
4. Herrick, R. S.; Brown, T. L. "A Flash Photolytic Investigation of Photoinduced Carbon Monoxide Dissociation from Dinuclear Manganese Carbonyl Compounds"; Inorg. Chem., in press, and references therein.
5. Ginley, D. S.; Bock, C. R.; Wrighton, M. S. "Photogeneration of Dinuclear Metal Carbonyls Containing a Metal-Metal Triple Bond"; Inorg. Chim. Acta, 1977, 23, 85.
6. Kidd, D. R.; Brown, T. L. "Photochemical Substitution Reactions of $\text{Mn}_2(\text{CO})_{10}$ "; J. Am. Chem. Soc., 1978, 100, 4095.
7. Poe, A. "Kinetic Studies of Thermal Reactivities of Metal-Metal Bonded Carbonyls"; in "Reactivity of Metal-Metal Bonds"; M. H. Chisholm, ed.; A.C.S. Symposium Series, No. 155, 1981, 7, 135, and references therein.
8. Fox, A.; Malito, J.; Poe, A. "Associative Substitution Reactions of $\cdot\text{Re}(\text{CO})_5$ "; J. Chem. Soc. Chem. Commun., 1981, 1052.