Relative Importance of Metal-Metal Bond Scission and Loss of Carbon Monoxide from Photoexcited Dimanganese Decacarbonyl: Spectroscopic Detection of a Coordinatively Unsaturated, CO-Bridged Dinuclear Species in Low-Temperature Alkane Matrices

Aloysius F. Hepp and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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We wish to report the spectroscopic detection and characterization of an intermediate from the photoexcitation of $Mn_2(CO)_{10}$ that shows that dissociative loss of CO (eq 1) is the only chemical

$$Mn_2(CO)_{10} \xrightarrow{h\nu} Mn_2(CO)_9 + CO \qquad (1)$$

result of exciting $Mn_2(CO)_{10}$ in rigid media at 77 K. In fluid solution at 298 K scission of the Mn-Mn bond (eq 2)[1] dominates

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5 \qquad (2)$$

the primary chemical results from the photoexcitation of $Mn_2(CO)_{10}$, but other possible intermediates have been suggested.[2,3] New data presented here show that the dissociative loss of CO accounts for ~30% of the excited $Mn_2(CO)_{10}$ that react. The new results accord well with flash photolysis studies[3] of $Mn_2(CO)_{10}$ that show a role for fragments other than $Mn(CO)_5$. Further, the new results add to the understanding of the substitution of 17-e$^-$ radicals[1,4] and the photogeneration of substitution products from $Mn_2(CO)_{10}$.

The irradiation of ~1 mM $Mn_2(CO)_{10}$ in an alkane (methylcyclohexane or 3-methylpentane) matrix at 77 K results in rapid IR spectral changes (Figure 1).[5] The key features are the decline of absorption attributable to $Mn_2(CO)_{10}$, the growth of a band at 2132 cm^{-1} associated with free CO in the matrix, growth of a prominent absorption at ~1760 cm^{-1}, and growth of a number of bands in the region where $Mn_2(CO)_{10}$ absorbs. Within experimental error, the amount of CO detected at low-extent conversion (<20%) is consistent with the appearance of one CO for every $Mn_2(CO)_{10}$ consumed, on the basis of the amount of CO produced in known systems, such as $Cr(CO)_6$ and $Mo(CO)_6$,[6] determined under the same conditions. The absorbances at 1760 and 2132 cm^{-1} grow in with a constant ratio at the initial stages of the reaction. The 1760-cm^{-1} feature signals the generation of a metal carbonyl with a bridging CO and the 2132-cm^{-1} feature suggests dissociative loss of CO from excited $Mn_2(CO)_{10}$. We thus propose that eq 1 represents the low-temperature photochemistry of $Mn_2(CO)_{10}$ in an alkane. The 1760-cm^{-1} feature is accompanied by a 1717-cm^{-1} absorbance when $Mn_2(CO)_{10-x}(^{13}CO)_x$ (30% ^{13}CO) is used instead of $Mn_2(CO)_{10}$.[7] We thus conclude that $Mn_2(CO)_9$, having at least one bridging CO, is the product from irradiation of $Mn_2(CO)_{10}$ at 77 K in an alkane matrix. Warm-up to 298 K of an alkane matrix containing $Mn_2(CO)_9$ + CO leads to regeneration of $Mn_2(CO)_{10}$. Irradiation of 1 mM $Mn_2(CO)_{10}$ in a 77 K alkane matrix containing 10 mM PPh_3 followed by warm-up to 298 K yields $Mn_2(CO)_9PPh_3$.[8] Negligible amounts of $Mn_2(CO)_8(PPh_3)_2$ are obtained, unless the irradiation at 77K is prolonged where the intensity of the 2132 cm^{-1} free CO absorbance indicates secondary photolysis. Irradiation of $Mn_2(CO)_{10}$ at 77 K in an alkane matrix containing 10 mM CCl_4 followed by warm-up to 298 K yields negligible amounts of $Mn(CO)_5Cl$ (the only photoproduct at 298 K in alkane solution[1]). Warm-up of photogenerated $Mn_2(CO)_9$ in the presence of 10 mM CCl_4 and 10 mM PPh_3 yields only the $Mn_2(CO)_9PPh_3$. Finally, consistent with the light-induced dissociative loss of CO from $Mn_2(CO)_{10}$ at 77 K, we find that irradiation of 1-10 mM $Mn_2(CO)_{10}$ in 2-methyltetrahydrofuran (2-MeTHF) does not yield a species with a bridging CO (Figure 1). Rather, the product absorbances are consistent with $Mn_2(CO)_9$(2-MeTHF) as the photoproduct. Free CO, 2132 cm^{-1}, is generated in a 77 K/2-MeTHF matrix in the expected amount, based on $Mn_2(CO)_{10}$ consumed. Warm-up of a 77 K/2-MeTHF matrix containing the photogenerated $Mn_2(CO)_9$(2-MeTHF) and 10 mM PPh_3 again yields $Mn_2(CO)_9PPh_3$, consistent with a loosely bound 2-MeTHF ligand. Generally, photogenerated tetrahydrofuran-substituted metal carbonyl derivatives are thermally substitution labile at 298 K.[9]

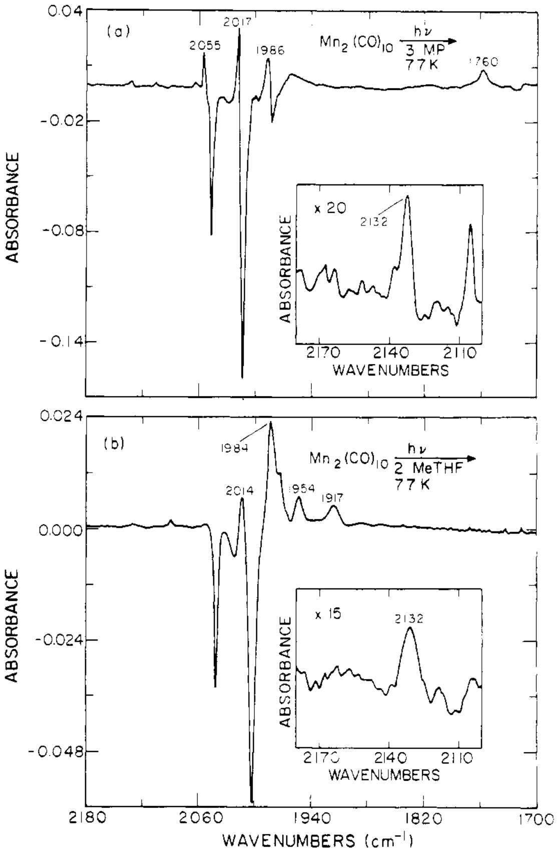

Figure 1. Infrared difference spectra recorded for (a) 1.5 × 10^{-3} M $Mn_2(CO)_{10}$ irradiated at 77 K in 3-methylpentane, 20% conversion, and (b) 8 × 10^{-3} M $Mn_2(CO)_{10}$ irradiated at 77 K in 2-methyltetrahydrofuran, 3% conversion. Negative absorbances due to disappearance of $Mn_2(CO)_{10}$; positive absorbances marked with energies for products.

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[7] The $Mn_2(CO)_{10-x}(^{13}CO)_x$ was generously supplied by Professor D. J. Darensbourg and was synthesized as given in: Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *Inorg. Chem.* **1981**, *20*, 1918-1921.

[8] The identity of all products ($Mn_2(CO)_9PPh_3$, $Mn_2(CO)_8(PPh_3)_2$, $Mn(CO)_5Cl$, $Mn_2(CO)_9(CH_3CN)$) was established by spectral comparison with authentic samples. Details will be given in the full paper.

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A CO-bridged $Mn_2(CO)_9$ formed photochemically in alkane matrices at 77 K is reasonable in view of the fact that the first row $Fe_2(CO)_9$ and $Co_2(CO)_8$ are CO-bridged species.[10] The lack of $Mn(CO)_5$ formation could be due to the fact that geminate recombination is efficient in the rigid medium compared to 298 K fluid solutions. Earlier[1] results are consistent with a "cage" effect on the efficiency of formation of solvent-separated $Mn(CO)_5$.[11]

The finding of clean dissociative loss of CO at 77 K in a rigid medium prompts a consideration of the relative efficiency of Mn–Mn scission vs. Mn–C scission at 298 K in fluid solution. We thus irradiated $Mn_2(CO)_{10}$ in solutions containing a two-electron donor, L, PPh_3, or CH_3CN, and a $Mn(CO)_5$ scavenger, CCl_4. The objective of such experiments is to establish whether the presence of CCl_4 would suppress the formation of $Mn_2(CO)_{10-x}L_x$ to determine whether $Mn_2(CO)_{10-x}L_x$ is formed via substitution of $Mn(CO)_5$ followed by radical coupling (eq 3–5)[1,4] or via direct

$$Mn(CO)_5 \xrightarrow{L} Mn(CO)_4L + CO \quad (3)$$

$$2Mn(CO)_4L \rightarrow Mn_2(CO)_8L_2 \quad (4)$$

$$Mn(CO)_4L + Mn(CO)_5 \rightarrow Mn_2(CO)_9L \quad (5)$$

capture of the photogenerated $Mn_2(CO)_9$ (eq 6). If the prompt

$$Mn_2(CO)_9 + L \rightarrow Mn_2(CO)_9L \quad (6)$$

formation of $Mn_2(CO)_9$ is the exclusive route to the substitution, the expectation is that $Mn_2(CO)_9L$ would be the *only* initial product. However, the $Mn_2(CO)_9L$ could also be very photosensitive in the presence of L and yield $Mn_2(CO)_8L_2$. We thus used a Fourier transform infrared spectrometer to determine the product distributions at very low-extent conversion (<5%) where secondary irradiation is negligible. In an alkalne solvent, near-UV irradiation of $Mn_2(CO)_{10}$ in the presence of 10 mM PPh_3 yields both $Mn_2(CO)_9PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$ as primary products. In the presence of 10 mM PPh_3 and 10 mM CCl_4 the $Mn_2(CO)_9PPh_3$ is formed with the same chemical efficiency based on $Mn_2(CO)_{10}$ consumed, but no $Mn_2(CO)_8(PPh_3)_2$ is observed. Rather, $ClMn(CO)_4PPh_3$ is formed. The CCl_4 thus suppresses formation of $Mn_2(CO)_8(PPh_3)_2$, but not $Mn_2(CO)_9PPh_3$. The amount of $Mn_2(CO)_9PPh_3$ formed is 30 ± 5% of $Mn_2(CO)_{10}$ consumed in the presence of CCl_4. These data are consistent with formation of PPh_3 substitution products via both Mn–Mn bond cleavage and via prompt loss of CO.

Irradiation of $Mn_2(CO)_{10}$ in CH_3CN solvent initially yields only $Mn_2(CO)_9(CH_3CN)$.[12] Irradiation in CH_3CN containing CCl_4 initially yields both $Mn_2(CO)_9(CH_3CN)$ and $Mn(CO)_5Cl$ in a ratio of 1/5 that is the same for CCl_4 concentrations in the range 0.001–3.0 M. The point is that CCl_4 does not suppress the quantum yield for $Mn_2(CO)_9(CH_3CN)$ formation. Irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3\text{–}Mn(CO)_5$ in CH_3CN initially yields only $Mn_2(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$; no $Mn_2(CO)_9(CH_3CN)$ is detected. Under the same conditions but in the presence of 100 mM CCl_4, irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3\text{–}Mn(CO)_5$ yields $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ and $Mn(CO)_5Cl$. The $Mn(CO)_5$ radicals do not undergo substitution by CH_3CN.

To confirm the lack of substitution of $Mn(CO)_5$ by CH_3CN we have oxidized $Mn(CO)_5^-$ by the outer-sphere, one-electron oxidant $Fe(\eta^5\text{-}C_5H_5)_2^+$ in CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ with and without 10 mM PPh_3. In the absence of PPh_3, $Mn_2(CO)_{10}$ is formed as the only product when the $Fe(\eta^5\text{-}C_5H_5)_2^+$ is slowly added to the $Mn(CO)_5^-$.[13] Under the same conditions with 10 mM PPh_3 the products are dominated by $Mn_2(CO)_8(PPh_3)_2$. Thus, PPh_3, but not CH_3CN, will replace a CO of $Mn(CO)_5$ in competition with coupling of the radicals. This result leads to the conclusion that substitution of $Mn(CO)_5$ can occur via an associative mechanism involving a 19-e$^-$ species.[14]

To conclude, dissociative loss of CO from photoexcited $Mn_2(CO)_{10}$ in a rigid matrix yields a CO-bridged $Mn_2(CO)_9$ species that will react with 2-electron donors to yield $Mn_2(CO)_9L$. The rigid matrix apparently precludes the formation of $Mn(CO)_5$ that is invoked in the photochemistry at 298 K in fluid solution.[1] In fluid solution the prompt loss of CO accounts for 30 ± 5% of the excited states that react, and Mn–Mn bond cleavage accounts for the remainder.

Acknowledgment. We thank the National Science Foundation for support of this research. We appreciate the gift of $Mn_2(CO)_{10-x}(^{13}CO)_x$ from Professor Donald J. Darensbourg of Texas A&M University.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(CO)_9$, 86633-01-4; $Mn_2(CO)_9$(2-MeTHF), 86633-02-5; $Mn_2(CO)_9PPh_3$, 14592-26-8; $ClMn(CO)_4PPh_3$, 14841-08-8; CO, 630-08-0; CCl_4, 56-23-5; 2-MeTHF, 96-47-9; PPh_3, 603-35-0; CH_3CN, 75-05-8; methylcyclohexane, 108-87-2; 3-methylpentane, 96-14-0.

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(13) If $Fe(\eta^5\text{-}C_5H_5)_2^+$ is present in excess, the $Mn(CO)_5$ radicals are oxidized: Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258–1261.

(14) It is noteworthy that the $Mn(CO)_5$ radicals are oxidized more rapidly in CH_3CN solvent than in a nondonor solvent[12] consistent with interaction of $Mn(CO)_5$ with CH_3CN. However, in the case of the 19e$^-$ $Mn(CO)_5(CH_3CN)$ the loss of CO does not occur in competition with loss of the CH_3CN. In the oxidation of $Mn(CO)_5$ by TCNE the product is $Mn(CO)_5$(TCNE) and ligation of TCNE to $Mn(CO)_5$ was invoked[12] to account for the fast rate of oxidizing $Mn(CO)_5$.

Enantioselective Carbocyclization: A Facile Route to Chiral Cyclopentanes

Douglass F. Taber*[1] and Krishna Raman

Department of Chemistry, University of Delaware
Newark, Delaware 19711

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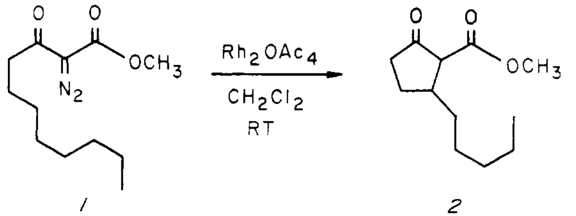
An aspect of enzyme reactivity that synthetic organic chemists have long envied is the ability to regio- and enantioselectively functionalize an unactivated hydrocarbon chain. To duplicate such a process in the laboratory, it would be necessary to first develop a method for efficient bond formation at an unactivated center ("remote functionalization").[2] It would then be necessary to control the folding of the rapidly coiling hydrocarbon chain in such a way that the desired site was particularly available for reaction. We recently reported a method for remote functionalization that showed excellent regioselectivity (**1** → **2**).[3] We now report that substantial chiral induction can in fact be achieved in the course of such cyclizations. This opens a general route to functionalized cyclopentanes of high optical purity, reasonable



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