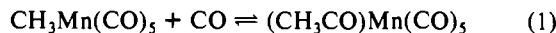


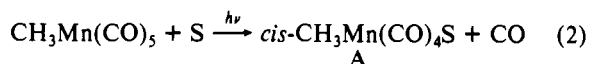
Reactivities of Intermediates Relevant to Metal Alkyl Carbonylation. Flash Photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ Studied by Time-Resolved Infrared and Optical Detection

In this laboratory we have begun an investigation into the photochemistry of some metal alkyl and acyl complexes in order to obtain greater insight into the mechanisms of the reversible carbonylation of metal alkyls such as shown in eq 1. In this



context, we have used a combination of laser flash photolysis with both optical and time resolved infrared (TRIR) detection to probe the transient photochemistry of $\text{CH}_3\text{Mn}(\text{CO})_5$ (I) with the goal of modeling spectroscopic and kinetic data relevant to Mn(I) intermediates. These studies have led to the determination of the kinetics behavior of the solvated intermediates $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{S}$ (S = solvent) in cyclohexane and THF solutions and to the observation that the initial intermediate formed by CO photodissociation must be remarkably selective in reactions with potential donors and hence must be relatively long-lived in comparison to intermediates previously proposed in the photoreactions of d^6 metal carbonyls.

Laser flash photolysis ($\lambda = 308$ nm) of $\text{CH}_3\text{Mn}(\text{CO})_5$ (10^{-4} – 10^{-3} mol dm^{-3}) in cyclohexane or isooctane solutions under Ar or CO results in the 100- μs TRIR spectrum shown in Figure 1. The depletion of I is evident in this spectrum with the negative $\Delta(\text{Abs})$ values noted for ν_{CO} modes at 2014 and 1991 cm^{-1} . Accompanying these changes, a transient species, A, is formed which has three ν_{CO} bands at 1986, 1974, and 1940 cm^{-1} in the TRIR spectrum (Figure 1) and a λ_{max} at 410 nm in the optical spectrum, properties close to those attributed to $\text{cis-CH}_3\text{Mn}(\text{CO})_4(\text{CH}_3)$ formed by CO photodissociation from I in a methane matrix.² These spectroscopic observations are consistent with the labilization of CO following irradiation to give $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{S}$ (eq 2). We have no evidence for trans-CO labilization



or formation of $\text{Mn}(\text{CO})_5$ resulting from homolytic metal–alkyl bond cleavage³ in the present case.

Under an Ar atmosphere, the decay of A follows second-order kinetics with regeneration of $\text{CH}_3\text{Mn}(\text{CO})_5$. Under CO, both the rates of decay of A and the reformation of $\text{CH}_3\text{Mn}(\text{CO})_5$ are accelerated and are pseudo first order (Figure 2). From these observations, the second-order rate constant for the reaction of A with CO in C_6H_{12} is calculated to be $2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ by the TRIR method and $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ by visible detection. These values lie close to those previously found for the reaction of the solvated $\text{Cr}(\text{CO})_5\text{S}$ or $\text{Mo}(\text{CO})_5\text{S}$ intermediates with CO in cyclohexane.⁴ Significantly, when the solvent is changed from an alkane (cyclohexane or isooctane) to THF, the reaction of $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{S}$ with CO (as studied by optical detection), is 4 orders of magnitude slower ($k_{\text{THF,CO}} = 1.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$), consistent with the increased donor strength of THF. Thus, the combined spectroscopic and kinetic data show that photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ in hydrocarbon or THF solutions results in the formation of $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{S}$, which reacts with CO at rates comparable to those found for analogous solvento complexes of d^6 metal carbonyls.

However, we have observed an additional feature regarding the photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ that does not find a place in the group VI metal hexacarbonyl photochemistry. Namely, when the flash photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ in cyclohexane is carried out under

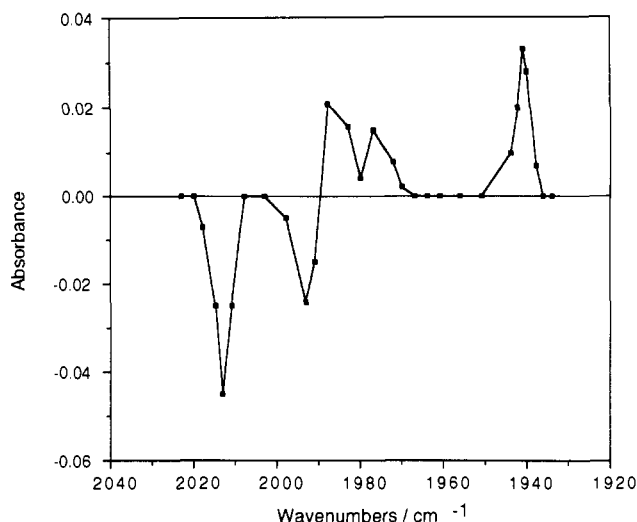


Figure 1. Time-resolved IR spectrum obtained 100 μs after laser flash photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ in isooctane under Ar. The negative bands correspond to the depletion of $\text{CH}_3\text{Mn}(\text{CO})_5$; the positive bands correspond to $\text{cis-CH}_3\text{Mn}(\text{CO})_4(\text{S})$ (S = solvent).

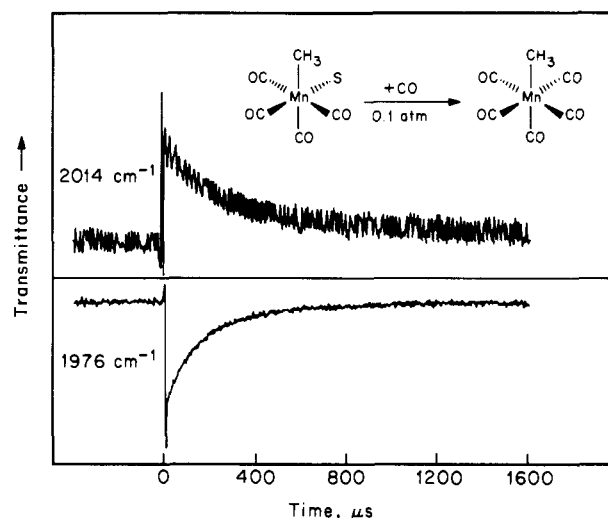


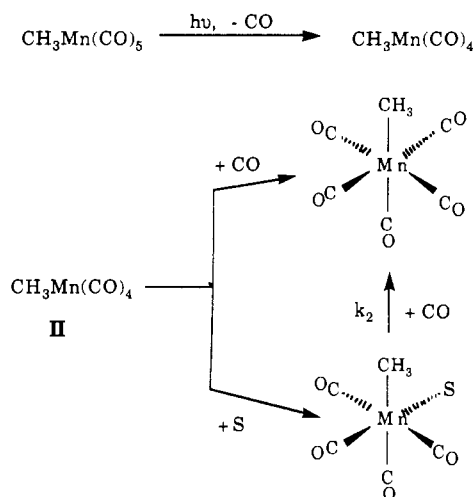
Figure 2. Kinetic traces showing the decay of $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{S}$ (S = cyclohexane) at 1976 cm^{-1} and the reformation of $\text{CH}_3\text{Mn}(\text{CO})_5$ at 2014 cm^{-1} following laser flash photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ in cyclohexane under 0.1 atm of CO. IR changes are shown in transmittance mode.

CO rather than Ar, the yield of A produced is reduced by a factor of 5 as monitored by both IR spectroscopy and optical detection. Similar behavior was noted in isooctane solution. In order to verify this observation, samples were irradiated at constant laser power, cell orientation, and $\text{CH}_3\text{Mn}(\text{CO})_5$ concentration. In addition, this behavior could be verified on a single cyclohexane solution of I by first carrying out the flash photolysis under argon and determining the initial $\Delta(\text{Abs})$ (due to $\text{cis-CH}_3\text{Mn}(\text{CO})_4(\text{C}_6\text{H}_{12})$ formation) and then flushing the solution with CO and noting the much smaller $\Delta(\text{Abs})$ upon flash photolysis. Repeating the cycle on this solution reproduced these observations. In direct contrast, we have not observed similar effects of CO on the initial $\Delta(\text{Abs})$ values following flash photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ in THF or of $\text{Cr}(\text{CO})_6$ in C_6H_{12} .

To account for these observations, we conclude that photolysis of $\text{CH}_3\text{Mn}(\text{CO})_5$ in C_6H_{12} results in CO labilization to give an intermediate, II, that can react competitively either with C_6H_{12} to form $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{S}$ or with CO to regenerate $\text{CH}_3\text{Mn}(\text{CO})_5$ (Scheme 1). From the ratio of $\text{cis-CH}_3\text{Mn}(\text{CO})_4(\text{C}_6\text{H}_{12})$ produced under 1 atm of CO to that formed under Ar, together with the relative concentrations of CO and C_6H_{12} ($[\text{CO}]/[\text{C}_6\text{H}_{12}] = 10^{-3}$), the selectivity of II toward CO over C_6H_{12} is calculated to be $\sim 5 \times 10^3$. While this selectivity is unprecedented for simple metal carbonyls of this type, a similar selectivity toward CO over C_6H_{12} has been observed for the 16-electron fragment (η^5 -

- (1) DiBenedetto, J. A.; Ryba, D. W.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 3503–3507.
- (2) Horton-Mastin, A.; Poliakoff, M.; Turner, J. *Organometallics* **1986**, *5*, 405–408.
- (3) Hudson, A.; Lappert, M. F.; Lednor, P. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1974**, 966–967.
- (4) (a) Kelly, J. M.; Bent, D. V.; Herman, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259–269. (b) Church, S. P.; Herman, H.; Grevels, F.-W.; Schaffner, K. *Inorg. Chem.* **1985**, *24*, 418–422.

Scheme I



$\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)$ following photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$ in cyclohexane under CO .⁵ The different behavior of II in THF would be consistent with the higher nucleophilicity of this solvent, giving it a greater competitive advantage vs CO .¹

A possible explanation of the apparent selectivity of II in C_6H_{12} would be that the $\text{CH}_3\text{Mn}(\text{CO})_4$ intermediate is formed in a triplet electronic state⁶ having either a trigonal-bipyramidal C_{3v} geometry with an axial CH_3 group or a square-pyramidal geometry with a basal CH_3 . Either geometric or electronic constraints might give such species sufficient lifetime to demonstrate selectivity in coordinating a sixth ligand. Formation of $\text{Cr}(\text{CO})_5$ as a singlet state in a naked, open-faced C_{4v} geometry⁷ would explain the contrasting lack of selectivity that this species shows.⁸ Additional studies targeted at probing the reactions of such intermediates among acyl- and alkylmanganese carbonyls are underway.⁹

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- (5) Belt, S. T.; Haddleton, D. M.; Perutz, R. N.; Smith, B. P. H.; Dixon, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1347-1349.
 (6) Daniel, C. *Coord. Chem. Rev.* **1990**, *97*, 141-154.
 (7) Daniel, C.; Veillard, A. *New J. Chem.* **1986**, *10*, 84-90.
 (8) Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* **1989**, *93*, 2876-2878.
 (9) A reviewer has proposed that II might be a species such as a short-lived photogenerated acyl complex. However, in our ongoing flash photolysis studies of $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$, we find no evidence for the formation of any species that could explain the CO effects on the yields of A formed in the flash photolysis of I.

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Oxidatively Enhanced Intramolecular Carbonyl Scrambling in the Mixed-Metal Cluster $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Rh}(\text{CO})_2]^{2-}$

The effect of odd-electron configurations on the reactivity of metal carbonyl clusters has been receiving increased attention recently, as illustrated in several reviews that have been published on the electrochemistry of metal clusters.¹ The most striking result

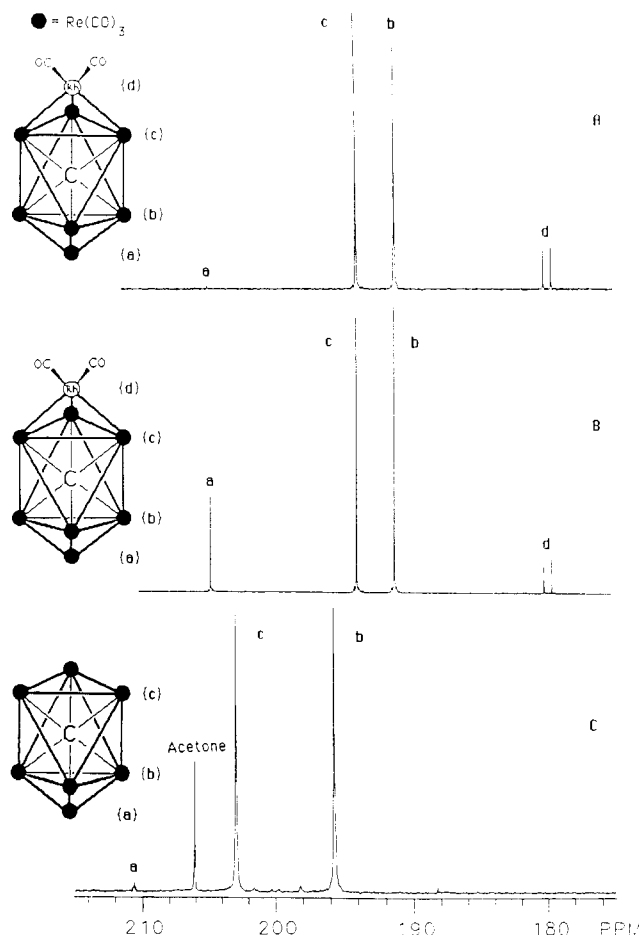


Figure 1. ^{13}C NMR Spectra of (A) $[\text{Re}(\text{CO})_3\text{Re}_6\text{C}(\text{C}^{13}\text{O})_{18}\text{Rh}(\text{C}^{13}\text{O})_2]^{2-}$, (B) $[\text{Re}(\text{C}^{13}\text{O})_2\text{Re}_6\text{C}(\text{C}^{13}\text{O})_{18}\text{Rh}(\text{C}^{13}\text{O})_2]^{2-}$, and (C) $[\text{Re}(\text{CO})_3\text{Re}_6\text{C}(\text{C}^{13}\text{O})_{18}]^{3-}$.

obtained involves intermolecular lability, namely the reductive, electrocatalytic (ETC) substitution of a carbonyl ligand by nucleophiles. These reactions show large rate enhancements with increased selectivity. Increases in intramolecular lability as well as the effect of oxidation have been explored to a much lesser extent.

In mononuclear systems, one-electron oxidation has been shown to promote the rate of migratory insertion reactions,² reductive eliminations,³ and cis-trans isomerization.⁴ Similar studies of metal clusters have been limited to a recent report by Geiger involving the oxidatively electrocatalyzed isomerization of $\text{Cp}_3\text{Rh}_3(\text{CO})_3$ from a C_s isomer to a C_{3v} isomer.⁵ We wish to report a dramatic increase in intramolecular ligand lability upon one-electron oxidation, as evidenced by unusual carbonyl scrambling behavior for the selectively ^{13}CO enriched mixed-metal cluster, $[\text{PPN}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Rh}(\text{CO})_2]$ ($\text{PPN} = \text{N}(\text{PPh}_3)_2$).

The reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ leads to the formation of the mixed-metal cluster $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Rh}(\text{CO})_2]^{2-}$, as reported by Henly et al.⁶ $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Rh}(\text{CO})_2]^{2-}$ is a 1,4-bicapped octahedron in which a $\text{Rh}(\text{CO})_2$ moiety caps the face

- (1) (a) Lemoine, P. *Coord. Chem. Rev.* **1988**, *83*, 169. (b) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87. (c) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.
 (2) (a) Magnuson, R. H.; Meierowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460. (b) Theierin, M. J.; Troglor, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5127.
 (3) (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319. (b) Troupel, M.; Rollin, Y.; Sibelle, S.; Fauarque, J.-F.; Perichon, J. *J. Chem. Res., Synop.* **1980**, 24.
 (4) (a) Vallat, A.; Person, M.; Roullier, L.; Laviron, E. *Inorg. Chem.* **1987**, *26*, 332. (b) Bond, A. M.; Grabaric, B. S.; Jackowski, J. *J. Inorg. Chem.* **1978**, *17*, 2153.
 (5) Mevs, J. M.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 1922.
 (6) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441.