Organometallics **1994,** *13,* 3525−3531

Time-Resolved Infrared Spectral Studies of Intermediates Formed in the Laser Flash Photolysis of $Mn(CO)_5CH_3$

William T. Boese and Peter C. Ford*

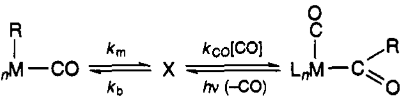
Department of Chemistry, University of California, Santa Barbara, California 93106

Received March 4, 1994®

Laser flash photolysis (308 nm) of $Mn(CO)_5CH_3$ (**I**) in different solvents leads predominantly to CO photodissociation and the formation of reactive intermediates formulated as the solvento complexes *cis*-$Mn(CO)_4(solv)CH_3$. This conclusion is based upon the solvent sensitivity of the time-resolved infrared spectra and the dynamics of reactions with various ligands. For example, the reaction of *cis*-$Mn(CO)_4(solv)CH_3$ with CO displays second-order kinetics with a rate constant k_{CO} nearly 8 orders of magnitude larger for solv = perfluoro(methylcyclohexane) than for solv = tetrahydrofuran. The k_L values for the second-order reaction of *cis*-$Mn(CO)_4(solv)CH_3$ in cyclohexane with various ligands L follow the approximate order 4-phenylpyridine $\approx H_2O \approx$ THF $>$ $P(OMe)_3 \approx PPh_3 > CO \approx N_2$. The quantitative behaviors of intermediates seen in the flash photolysis of **I** are compared with those seen in similar studies of the acetyl complex $Mn(CO)_5(COCH_3)$ (**II**) (*Organometallics*, **1993**, *12*, 4739−4741), and this comparison is used to substantiate the earlier conclusion that CO dissociation from **II** in weakly coordinating solvents leads to an η^2-acyl-coordinated intermediate rather than to a solvento complex.

Introduction

Recent studies in this laboratory have been concerned with applications of time-resolved infrared (TRIR) spectroscopy in generating reactive intermediates relevant to the mechanism of the migratory insertion of CO into metal−alkyl bonds.[1,2] One such intermediate proposed is a coordinatively unsaturated metal−acyl complex (**X**)



$$\overset{R}{\overset{|}{L_nM}}-CO \underset{k_b}{\overset{k_m}{\rightleftharpoons}} X \underset{h\nu\,(-CO)}{\overset{k_{CO}[CO]}{\rightleftharpoons}} \overset{O}{\overset{C}{\overset{|}{L_nM}}}-C\genfrac{}{}{0pt}{}{\diagup R}{\diagdown\!\!\!= O} \qquad (1)$$

formed by migration of the alkyl group to a coordinated CO. Therefore, one strategy for studying this intermediate has been to prepare it via photoejection of CO from the stable acyl complex and to relate its structure and reactivity to those of the acyl intermediates postulated in mechanistic studies of the thermal carbonylation of metal−alkyl complexes.[3] The advantage of the TRIR technique is that it is more structure specific than other fast detection methodologies and thus allows one to identify and to probe the reactivities of a specific metal carbonyl intermediate in the presence of other similar species. During the course of such studies of $Mn(CO)_5(COCH_3)$,[2] it became apparent that in order to evaluate the role of the acyl group in the "unsaturated" intermediate, the reactivity of an appropriate model should be examined. Described here are laser flash photolysis studies of the methylmanganese complex $Mn(CO)_5CH_3$ (**I**) using both TRIR and time-resolved optical (TRO) detection techniques to probe possible structures and reactivities of unsaturated intermediate(s) formed via photolabilization of CO (eq 2). Such species have

$$Mn(CO)_5CH_3 + solv \rightarrow Mn(CO)_4(solv)CH_3 + CO \quad (2)$$

further interest as analogs of the unsaturated complexes formed via flash photolysis of the oft-studied group VI hexacarbonyls such as $Cr(CO)_6$.

Experimental Section

Materials. Solvents were distilled under dinitrogen from an appropriate drying agent immediately before use. Cyclohexane was purchased from Burdick & Jackson and was found to contain less than 25 ppm of cyclohexene by capillary GC analysis. Perfluoro(methylcyclohexane) was purchased from Lancaster and purified by a literature method to remove hydrocarbon impurities.[4] Residual H_2O in the alkane solvents was determined to be ~4 ppm.[5] Argon and carbon monoxide were passed through an Alltech Associates Oxy-trap and through dried molecular sieves. Various CO/Ar gas mixtures were purchased from Liquid Carbonics and treated similarly. The manganese carbonyls $Mn(CO)_5CH_3$ and $Mn(CO)_5CD_3$ were prepared by an adaptation of the method of Gladysz,[6] and $Mn(CO)_5CF_3$ was prepared by thermal decarbonylation of Mn-

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® Abstract published in *Advance ACS Abstracts,* July 15, 1994.

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[3] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 299−311. (b) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87−145. (c) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 30−36. (d) Flood, T. C.; Jensen, J. E.; Slater, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410. (e) Noack, K.; Calderazzo, F. J. *J. Organomet. Chem.* **1967**, *10*, 101−104.

[4] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1980; p 251.

[5] (a) The concentration of H_2O in "wet" cyclohexane was determined by carrying out the TRIR experiment with $Cr(CO)_6$ in cyclohexane under 1 atm of CO in this solvent. Since previous workers[5b] have determined the rate constants for competitive trapping of $Cr(CO)_5(c\text{-}C_6H_{12})$ by CO and by H_2O in cyclohexane, the observation that ~4% of this intermediate was converted to $Cr(CO)_5(H_2O)$ under these conditions was used to estimate $[H_2O]$ as 4×10^{-5} M. (b) Church, S. P.; Grevels, F. W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1985**, *24*, 418−422.

[6] Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553−557.

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$(CO)_5(COCF_3)$.[7] All complexes were sublimed at least once prior to use and were characterized by IR spectroscopy.

Instrumentation. The time-resolved infrared apparatus used was that described previously[8] with the following modification of the sample handling apparatus. Sample solutions were deaerated by entraining with the appropriate gas mixture in a gastight reservoir with needles connected with Ace-Thred electrode adapters. The solution was then transferred to a 50-mL gastight syringe (Hamilton) connected via stainless steel cannula to the IR flow cell (CaF_2 windows, 0.1 mm path length). Control of sample flow through the cell was accomplished by use of a Sage Instruments model 341B syringe pump. A sufficient flow rate was maintained to ensure that each photolysis shot irradiated fresh solution in the cell. Kinetic analyses were done using multiple flash photolysis data acquisitions at each frequency; typically 50–100 traces were averaged in a single acquisition. Three-dimensional (stack) plots of IR spectra vs time were created from a composite of the frequency vs time data using software developed in-house.

Low-temperature spectra were obtained using cooled solutions in sealed CaF_2 cells inside a vacuum-shrouded low-temperature cryostat (R. G. Hanson Associates). Cooled solutions were irradiated with either one pulse from the XeCl excimer or with the 313-nm line of an Hg arc lamp. Difference spectra were recorded with either a Bio-Rad FTS-60 FTIR spectrometer or a Hewlett-Packard Model 8452A diode array UV–vis spectrophotometer.

Time-resolved optical (TRO) experiments were carried out on instrumentation in the UCSB laboratory of Professor R. J. Watts. The excitation source was a nitrogen laser (10 ns, 337 nm) and the probe source a time-delayed xenon lamp nanopulser, and detection was accomplished with a diode array detector. The solutions were contained in a 1-cm quartz cuvette.

Results

TRIR Experiments in Cyclohexane Solution. When the flash photolysis (XeCl excimer laser, 308 nm) of $Mn(CO)_5CH_3$ was carried out in ambient-temperature cyclohexane under argon, the IR detection technique indicated loss of **I** and formation of a new species within the rise time of the TRIR apparatus (100 ns) (Figure 1). A composite of the data accumulated for IR frequencies spaced at 3-cm^{-1} intervals over the range 1920–2050 cm^{-1} allowed observation of the evolving infrared spectra (ν_{CO} bands) over the 250-μs time interval subsequent to the laser flash. The first transient species observed displayed characteristic ν_{CO} absorption bands at 1992 (s), 1986 (m), and 1952 (s) cm^{-1} (Figure 2). The position and pattern of the terminal metal carbonyl stretching bands are consistent with those expected for a *cis*-substituted tetracarbonyl species of the type *cis*-$Mn(CO)_4(L)CH_3$. A similar spectrum has been reported for the initial product of irradiating **I** in frozen methane (14 K)[9] (although with ν_{CO} values slightly higher than those in Figure 2), and this was also interpreted in terms of *cis* labilization. Furthermore, flash photolysis in the presence of excess CO leads to the nearly complete recovery of **I** by rates dependent on the nature of the solvent (see below). Thus, the primary photoreaction appears to be largely

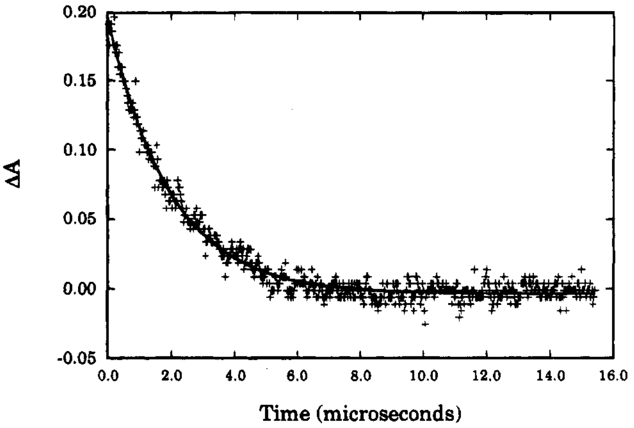


Figure 1. Temporal absorbance change at 1993 cm^{-1} observed after 308-nm photolysis of $Mn(CO)_5CH_3$ in 295 K cyclohexane ([CO] = 0.001 M). Shown are the accumulated data of ~50 laser pulses from a single experiment with a flowing solution. The curve is the fit of these data, which gives $k_{obs} = 5.2 \times 10^5$ s^{-1}.

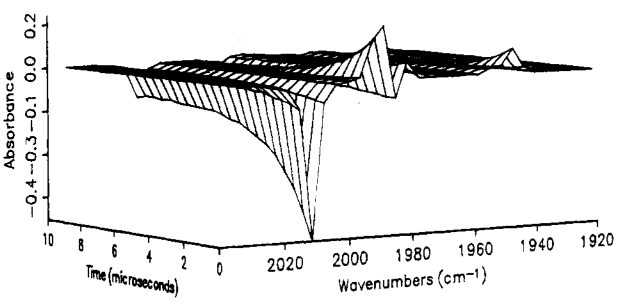
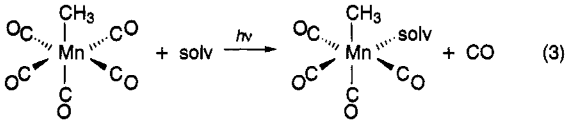


Figure 2. Transient IR spectral changes following 308-nm laser flash photolysis of $Mn(CO)_5CH_3$ in 295 K cyclohexane under 10% CO (0.001 M). TRIR spectra are shown at 500-ns intervals.



(3)

However, there was a small fraction of net reaction which suggested that another, minor pathway, perhaps homolytic cleavage of the methyl–manganese bond, was also occurring.[10]

The eventual fate of the initially observed *cis*-$Mn(CO)_4(c\text{-}C_6H_{12})CH_3$ (**A**) photoproduct in cyclohexane depends on the nature of other species present in the reaction solution. In the presence of added CO, the reaction observed is the rapid, nearly quantitative re-formation of $Mn(CO)_5CH_3$ at rates

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(7) (a) $Mn(CO)_5CF_3$ was prepared from $Mn(CO)_5C(O)CF_3$ by the following method:[7b] A 100-mg sample of $Mn(CO)_5C(O)CF_3$ was placed in a 100-mL Schlenk tube, and the tube was evacuated. The flask was heated in a 110 °C oven for 1 h; then the tube was cooled to room temperature, during which time $Mn(CO)_5CF_3$ crystallized on the walls of the tube. The product was isolated in near-quantitative yield. (b) Ryba, D. W. Ph.D. Dissertation, University of California, Santa Barbara, CA, 1991.

(8) (a) DiBenedetto, J. A.; Ryba, D. W.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 3503–3507. (b) Ford, P. C.; DiBenedetto, J. A.; Ryba, D. W.; Belt, S. T. *Proc. SPIE-Int. Soc. Opt. Eng.* **1992**, *1636*, 9–16.

(9) Horton-Mastin, A.; Poliakoff, M.; Turner, J. *Organometallics* **1986**, *5*, 405–408.

(10) (a) Close inspection of the photolysis of $Mn(CO)_5CH_3$ in cyclohexane by TRIR revealed that even under 1 atm of CO there is small (~10%) but reproducible net photochemistry at the end of the 1-ms maximum observation time, along with small but reproducible absorbance increases. Earlier workers[10b] reported qualitative studies indicating that Mn–CH_3 bond homolysis is (at least) a minor photoreaction pathway of **I**. Thus, a possible long-lived transient under these conditions is the $Mn(CO)_5$ radical. To explore this possibility, the TRIR technique was used to probe transients formed in the flash photolysis of $Mn_2(CO)_{10}$ in cyclohexane. Two species were seen; the major one (ν_{CO} 2056, 2020, 2002, 1990, 1966 cm^{-1}) has been assigned[10c] as $Mn_2(CO)_9$ and is relatively stable, while the other (ν_{CO} 1987, 1956 cm^{-1}), assigned[10d] as $Mn(CO)_5$, decays nonexponentially in a few microseconds, concomitant with the recovery of some $Mn_2(CO)_{10}$. The bands observed for $Mn(CO)_5$ agree with those of the minor product in the photolysis of $Mn(CO)_5CH_3$ (1986 and 1956 cm^{-1}). (b) Grismond, T. E.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *284*, 59–71. (c) Zhang, S.; Zhang, H.; Brown, T. L. *Organometallics* **1992**, *11*, 3929–3931. (d) Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7517–7520.

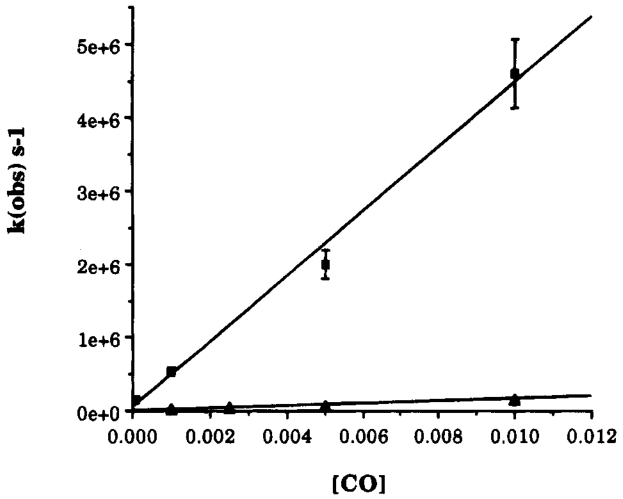


Figure 3. Plots of k_{obs} vs [CO]: (squares) disappearance of $Mn(CO)_4(solv)CH_3$ in 295 K cyclohexane; (triangles) disappearance of $Mn(CO)_4(solv)CF_3$ in 295 K cyclohexane.

linearly dependent on [CO] over the range 10^{-4}–10^{-2} M.[11] Under such (pseudo-first-order) conditions, simple exponential decays of **A** were observed, i.e., $d[\mathbf{I}]/dt = k_{obs}[\mathbf{A}]$, and a plot of k_{obs} vs [CO] proved to be linear (Figure 3), indicating second-order kinetics for

$$cis\text{-}Mn(CO)_4(solv)CH_3 + CO \xrightarrow{k_{CO}} Mn(CO)_5CH_3 + solv \quad (4)$$

The value of k_{CO}(295 K) was determined to be $(4.5 \pm 0.7) \times 10^8\ M^{-1}\ s^{-1}$ from the slope of this plot. Notably, the products formed and the rate of reaction of **A** with CO were shown to be independent of the initial concentration of **I** over the range $0.33–1.4 \times 10^{-3}$ M. Thus, reaction of $Mn(CO)_4(c\text{-}C_6H_{12})CH_3$ with $Mn(CO)_5CH_3$ does not appear to be significant under the conditions used.

When the photolysis was carried out using the perdeuterio analog of **I**, $Mn(CO)_5CD_3$, the spectrum of the initially formed transient was identical with that of **A** under similar conditions. Furthermore, the kinetics of the back-reaction with CO gave a second-order rate constant k_{CO} ($5.0 \times 10^8\ M^{-1}\ s^{-1}$) the same, within experimental uncertainty, as that seen for perprotio species.

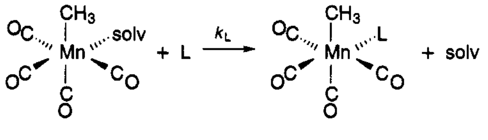
When 308-nm photolysis of **I** was carried out under N_2 at 1.0 atm, the initially formed intermediate **A** was observed to decay exponentially (k_{obs} $(2.8 \pm 0.5) \times 10^6\ s^{-1}$) to give a new species with ν_{CO} bands at 2004 and 1975 cm^{-1}. Since this new species, which was stable for the longest observation time available to the TRIR apparatus (~1 ms), was formed only under N_2 and not under argon (see below), a likely identity is the dinitrogen complex $Mn(CO)_4(N_2)CH_3$. Attempts to observe an IR band corresponding to ν_{N_2} in the TRIR spectrum proved unsuccessful, a not surprising result given the 2200-cm^{-1} upper limit to the frequency range available to the TRIR experiment. (The $Cr(CO)_5N_2$ analog has been reported to have a ν_{n_2} value of 2240 cm^{-1}.)[12] If it is assumed that reaction of N_2 with **A** follows second-order kinetics in analogy to reaction with CO, a k_{N_2} value of $(3.9 \pm 0.6) \times 10^8\ M^{-1}\ s^{-1}$ can be estimated from the k_{obs} value noted above and the solubility of N_2 in cyclohexane.[13]

Table 1. ν_{CO} **Frequencies for** $Mn(CO)_4(L)CH_3$ **Complexes**[a]

ligand	solvent	T (K)	method	ν_{CO} (cm^{-1})
dinitrogen	cyclohexane	295	TRIR	–, 2004, –, 1975
cyclohexane	cyclohexane	295	TRIR	–, 1992, 1986, 1952
MCH	MCH	77	FTIR	2082, 1992, 1986, 1948
H_2O	cyclohexane	295	TRIR	–, 1984, 1973, 1935
PPh_3	cyclohexane	295	TRIR	–, 1982, 1969, 1939
PPh_3	heptane	295	ref 14b	2055, 1983, 1969, 1939
4-Ph-py	cyclohexane	295	TRIR	–, 1980, 1970, 1932
THF	THF	295	TRIR	–, 1974, 1964, 1921
THF	THF	195	FTIR	–, 1974, 1960, 1920
2-Me-THF	2-Me-THF	195	FTIR	–, 1974, 1960, 1920
2-Me-THF	2-Me-THF	77	FTIR	–, 1974, 1955, 1920
PFMC	PFMC	295	TRIR	–, 2008, –, 1964
H_2O	PFMC	295	TRIR	–, 1988, 1979, 1944

[a] PFMC = perfluoro(methylcyclohexane). IR stretching frequencies for $Mn(CO)_5CH_3$ in cyclohexane: 2113 (w), 2011 (s), 1984 (m) cm^{-1} (2119 (w), 2022 (s), 1996 (m) cm^{-1} in PFMC).

Similar behavior was noted when laser flash photolysis of $Mn(CO)_5CH_3$ was carried out in the argon-flushed cyclohexane in the presence of other ligands such as Ph_3P. In each case, transient **A** is the initial species formed, and this reacts with the added ligand to give product IR spectra (Table 1) consistent with *cis* substitution, i.e., eq 5. For example, the product of



(5)

the reaction of **A** with PPh_3 has ν_{CO} values nearly identical with those of the known *cis*-$Mn(CO)_4(PPh_3)CH_3$ complex.[14] However, the sensitivity of the experiment and the locations of ν_{CO} bands for the *cis* and *trans* isomers do not allow for the exclusion of a statistical amount of the *trans* product. Stereochemical aspects are further addressed in TRO experiments below.

The k_{obs} values for the (pseudo-first-order) reactions of **A** with various L were shown to be linear in [L] over the following ranges: PPh_3 ($(1.2–4.3) \times 10^{-3}$ M), $P(OMe)_3$ ($(2.0–6.0) \times 10^{-3}$ M), 4-phenylpyridine ($(1.0–2.0) \times 10^{-3}$ M), tetrahydrofuran ($(0.5–4.0) \times 10^{-3}$ M), and H_2O (only 3×10^{-3} M). From these data were calculated the second-order rate constants k_L, which in each case is $>10^8\ M^{-1}\ s^{-1}$. These are summarized in Table 2.

When the laser flash photolysis of **I** was carried out under argon with no added ligands, **A** was found to undergo first-order decay ($k_{obs} = 1.7 \times 10^5\ s^{-1}$) to form another transient manganese carbonyl species **B** with ν_{CO} bands at 1984, 1974, and 1937 cm^{-1}. This second species reacts with the photoliberated CO to re-form $Mn(CO)_5CH_3$ over the course of a few milliseconds. A second-order rate constant of $1.5 \times 10^6\ M^{-1}\ s^{-1}$ can be estimated for this process, much slower than that determined for the solvento complex **A**. Formation of **B** was not seen in the presence of CO or other donor ligands at concentrations >0.001 M. Various experiments to identify **B** proved unsuccessful, and it was concluded that it may result from reaction of **A** with some low-level impurity in the high-quality cyclohexane used in most experiments. Repeated attempts to purify this cyclohexane or to use purified cyclo-

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(11) (a) The solubility of CO in 298 K cyclohexane is reported[11b] to be 9.2×10^{-3} M atm^{-1}. In 298 K THF, the solubility of CO is reported[11c] to be 1.1×10^{-2} M atm^{-1}. The temperature dependence of the solubility of CO in THF was calculated on the basis of solution theory[11d] and published parameters.[11e] (b) Wilhelm, E.; Battino, R. *J. Chem. Thermodyn.* **1973**, *5*, 117–120. (c) Payne, M. W.; Leussing, D. L.; Shore, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 617–618. (d) Prausnitz, J. M. *Molecular Dynamics of Fluid Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969. (e) *Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1978; Vol. 21, p 377.

(12) (a) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B.; Graham, M. A. *Inorg. Chem.* **1983**, *22*, 911–920. (b) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1984**, *23*, 3830–3833.

(13) The solubility of N_2 in cyclohexane is taken as 7.1×10^{-3} M atm^{-1}: Dymond, J. *J. Phys.* Chem. **1967**, *71*, 1829–1831.

(14) (a) FTIR analysis of photolyzed cyclohexane solutions of $Mn(CO)_5CH_3$ in the presence of PPh_3 indicate formation of a species with ν_{CO} frequencies at 2057 (w), 1982 (s), 1969 (m), and 1939 (s) cm^{-1}, identical with those observed in the TRIR experiment and in good agreement with the literature[14b] values determined for *cis*-$Mn(CO)_4(PPh_3)CH_3$ in heptane (2055, 1983, 1969, and 1939 cm^{-1}). (b) Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *9*, 1806–1815.

Table 2. Rate Constants for Substitution Reactions of $Mn(CO)_4(solv)CH_3$ (solv = solvent)

$$Mn(CO)_4(solv)CH_3 + L \xrightarrow{k_L} Mn(CO)_4(L)CH_3 + solv$$

solvent	ligand	T (K)	k_L ($M^{-1}\ s^{-1}$)
cyclohexane	CO	295	$(4.5 \pm 0.5) \times 10^8$
cyclohexane	N_2	295	$(3.9 \pm 0.6) \times 10^8$
cyclohexane	$P(OMe)_3$	295	$(1.1 \pm 0.2) \times 10^9$
cyclohexane	PPh_3	295	$(1.0 \pm 0.2) \times 10^9$
cyclohexane	4-Ph-py	295	$(2.5 \pm 0.3) \times 10^9$
cyclohexane	H_2O	295	$(3.0 \pm 0.6) \times 10^9$
cyclohexane	THF	295	$(2.5 \pm 0.4) \times 10^9$
THF	CO	295	$(1.4 \pm 0.3) \times 10^2$
THF	CO	273	7.3 ± 1.5
THF	CO	255	$(2.1 \pm 0.4) \times 10^{-1}$
THF	CO	233	$(4.0 \pm 1.0) \times 10^{-2}$
PFMC	CO	295	$(1.0 \pm 0.5) \times 10^{10}$

hexane from other sources led to greater interference of such reactions. Notably, this impurity is not water, since deliberate addition of H_2O to the system led to formation of a *cis*-coordinated species, presumably *cis*-$Mn(CO)_4(H_2O)CH_3$, with an IR spectrum (Table 1) different from that of **B**. The ν_{CO} frequencies and reactivity of **B** agree with those for a transient described in a preliminary report from this laboratory on the photoreactivity of **I**.[15] *In that report, this transient was incorrectly attributed to the solvento complex cis*-$Mn(CO)_4$-(c-C_6H_{12})CH_3, i.e., **A**. The failure to detect **A** in that study was likely due to the use of a different excimer laser with greater RF noise, which may have obscured the presence of this very reactive species. The IR spectrum of **B** as well as its lesser reactivity toward CO suggests that **B** is a *cis*-substituted species and that the unknown ligand in that site is a stronger donor than is cyclohexane.[16] As noted before,[15] this phenomenon was not observed in THF, which is reasonable given the much greater donor ability of the ether oxygen.

TRIR Experiments in Perfluoro(methylcyclohexane) and Tetrahydrofuran. When the 308-nm laser flash photolysis of $Mn(CO)_5CH_3$ was carried out in 295 K perfluoro(methylcyclohexane) (PFMC) under an argon atmosphere, the TRIR detection technique indicated loss of **I** and formation of a new species within the rise time of the TRIR apparatus (100 ns). This transient displayed terminal CO stretches (2008 and 1964 cm^{-1}) at higher frequencies than the ν_{CO} value seen for the cyclohexane complex **A**. However, it is notable that the positions of the $Mn(CO)_5CH_3$ ν_{CO} bands were comparably shifted to higher energy in PFMC. The TRIR spectral changes for the reaction of the initial transient with CO are shown in Figure 4. Under these conditions the intermediate, presumed to be $Mn(CO)_4(PFMC)CH_3$, decays to re-form **I** via a second-order reaction with photoliberated CO. The rate constant k_{CO} determined under these conditions ($(1.0 \pm 0.5) \times 10^{10}$ $M^{-1}\ s^{-1}$) is more than 1 order of magnitude larger than for the comparable reactions of **A** and approaches the diffusion-controlled limit for this solvent.[17] Kinetics experiments were attempted with added CO sufficient to ensure pseudo-first-order conditions, but the transient decayed too rapidly (<100 ns) to follow with our system.

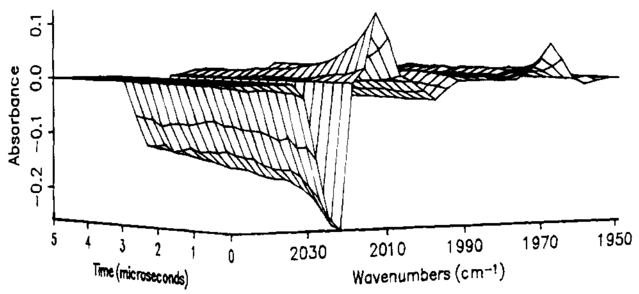

Figure 4. Transient IR spectral changes following 308-nm laser flash photolysis of $Mn(CO)_5CH_3$ in 295 K perfluoro(methylcyclohexane) under argon. Spectra correspond to 250-ns intervals.

As one might expect, significantly different behavior was noted when the laser flash photolysis of $Mn(CO)_5CH_3$ was carried out in the much stronger donor solvent tetrahydrofuran. The transient **C** formed promptly upon flash excitation. However, as reported earlier from this laboratory,[15] in THF this species reacted with CO to re-form **I** at a rate too slow to follow using the TRIR technique; therefore, TRO detection was used to study the reaction kinetics (see below). The TRIR spectrum of **C**, assigned to be the solvento species $Mn(CO)_4$-$(THF)CH_3$ in analogy to **A**, displayed ν_{CO} bands at 1974 (s), 1964 (m), and 1921 (s) cm^{-1}. These ν_{CO} values are an average of ~24 cm^{-1} less than those seen for **A**, an observation consistent with the higher donor ability of THF.

TRIR Studies of the Trifluoro Analog $Mn(CO)_5CF_3$ in Cyclohexane. When laser flash photolysis was carried out using the perfluoro analog $Mn(CO)_5CF_3$ in cyclohexane, the behavior proved to be similar to that of the methyl complex. The TRIR spectrum of the initially formed transient displayed four bands in the CO stretching region with ν_{CO} 2063 (w), 2028 (s), 1995 (m), and 1985 (s) cm^{-1}, and this behavior suggests again that cis CO labilization is the principal photoreaction. Second-order kinetics were observed for the back-reaction with CO to regenerate the starting complex (0.001–0.01 M), and the value of k_{CO} was determined from the linear plot of k_{obs} vs [CO] to be $(1.6 \pm 0.3) \times 10^7$ $M^{-1}\ s^{-1}$, about a factor of 30 less than that determined for the reaction of **A** with CO (Figure 3).

Low-Temperature Experiments using FTIR Detection. Several photolysis experiments were carried out using glassy solvents at low temperature as the reaction medium and using FTIR detection in order to obtain more highly resolved infrared spectra of the transients observed in the TRIR experiments. When the photolysis of $Mn(CO)_5CH_3$ was carried out in aa 77 K methylcyclohexane (MCH) glass, the FTIR spectrum (ν_{CO} 2082 (w), 1992 (s), 1986 (m), and 1948 (s) cm^{-1}) of the resulting photoproduct was found to be quite close to the TRIR spectrum of $Mn(CO)_4(c\text{-}C_6H_{12})CH_3$ recorded at room temperature. Thus, a reasonable conclusion is that the two species are closely analogous and that the photoproduct in the low-temperature glass is *cis*-$Mn(CO)_4(MCH)CH_3$. A similar result was obtained when the low-T experiment was repeated with $Mn(CO)_5CD_3$. Similarly, when **I** was photolyzed in a 77 K 2-methyltetrahydrofuran glass, the FTIR spectrum of the resulting photoproduct displayed bands at 1974 (s), 1955 (m), and 1920 (s) cm^{-1}, very similar to those obtained by TRIR for the flash photolysis of **I** in ambient-temperature THF.

Experiments using TRO Detection. The time-resolved optical spectrum of **A** was probed briefly by carrying out flash

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(15) Belt, S. T.; Ryba, D. W.; Ford, P. C. *Inorg. Chem.* **1990**, *29*, 3633–3634.

(16) Although the second intermediate **B** was incorrectly assigned as the solvento species $Mn(CO)_4(solv)CH_3$ in the previous report,[15] the probable presence of a more reactive species was inferred in that report by the observation that the yield of **B** decreased 5-fold on going from an argon to a CO atmosphere. This observation was consistent with the presence of a more reactive species (such as **A**) undergoing competitive trapping by CO and by the impurity(ies) leading to **B** on time scales shorter than those found useful in the earlier experiments. In cyclohexane under argon, we observe **B** to undergo second-order decay to re-form $Mn(CO)_5CH_3$ with a rate constant of ~1×10^6 M^{-1} s^{-1}, in approximate agreement with the kinetics described for similar conditions in the previous report[15] and incorrectly attributed to the reaction of $Mn(CO)_4(solv)CH_3$ with CO.

(17) (a) The diffusion-controlled limit in cyclohexane was calculated to be 7.3×10^9 $M^{-1}\ s^{-1}$ from $k_d = 8RT/3000\ \eta$[17b] and a viscosity (η) of 9.0×10^{-3} P;[17c] in perfluoro(methylcyclohexane) k_d was calculated to be 4.0×10^9 $M^{-1}\ s^{-1}$, based on $\eta = 1.5 \times 10^{-2}$ P.[17d] (b) Connors, K. A. *Chemical Kinetics*; VCH: New York, 1990; p 135. (c) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1965; Vol. 2, p 158. (d) *Beilstein Handbuch der Organischen Chemie*; Springer-Verlag: Berlin, 1976; Vol. 5, Suppl. 4, p 97.

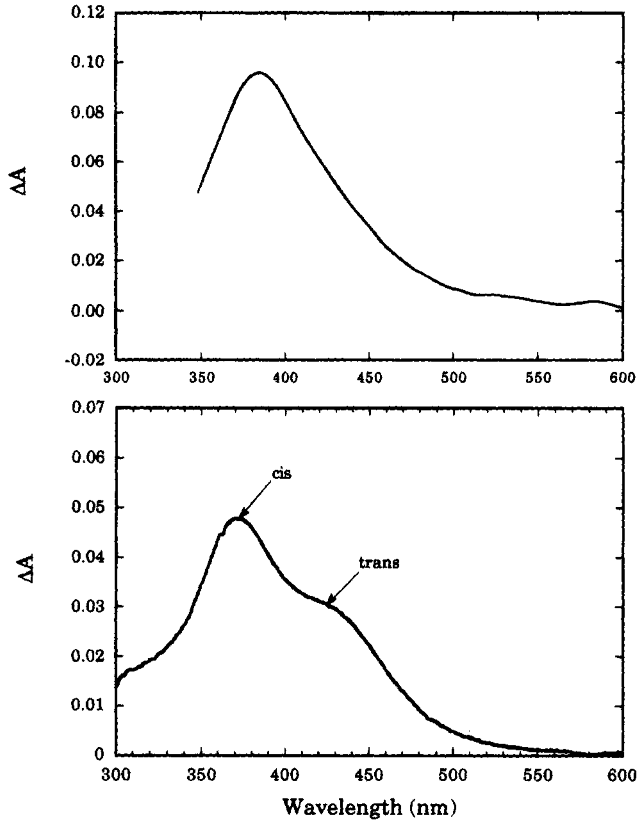

Figure 5. (top) UV–vis spectral changes observed 50 ns after 337-nm photolysis of Mn(CO)$_5$CH$_3$ in 295 K cyclohexane (smoothed numerically). (bottom) UV–vis spectral changes approximately 30 s after 308–nm photolysis of Mn(CO)$_5$CH$_3$ in 295 K THF.

photolysis of Mn(CO)$_5$CH$_3$ in room-temperature cyclohexane using a nitrogen laser (337 nm) excitation source and a fast diode array detection system in the UCSB laboratory of R. J. Watts. The transient species seen 50 ns after the flash (Figure 5) displayed a single absorption band at λ_{max} 383 nm. The position of this band lies at somewhat higher energy than that reported for the *cis*-Mn(CO)$_4$(solv)CH$_3$ species formed by irradiation of **I** in a methane matrix[9] but lower than the band assigned for the THF analog below. Comparison of these data supports the assignment of this species as being principally *cis*-Mn(CO)$_4$(c-C$_6$H$_{12}$)CH$_3$, in accord with the TRIR experiments.

The sluggish reactivity of the photolysis intermediate Mn(CO)$_4$(THF)CH$_3$ (**C**) in THF precluded characterization of the reaction kinetics by TRIR owing to the short time window (~1 ms) available for convenient observation. Therefore, experiments were initiated in which a variable-temperature cryostat was used as the reaction vessel and a conventional diode array UV–vis spectrophotometer was used to record the TRO spectra. For example, 308-nm photolysis of **I** in 295 K THF solution in the absence of added ligands resulted in the formation of transient species with an increased absorption (λ_{max} 370 and 430 nm (shoulder)) in the visible region relative to those for **I** (Figure 5). Earlier workers[9] reported observing two visible range absorption bands in the photolysis of Mn(CO)$_5$CH$_3$ in inert-gas matrices and attributed these to the *cis* and *trans* isomers of Mn(CO)$_4$CH$_3$. Although the bands seen in THF are at ~70 nm higher energy, a similar assignment seems reasonable; the two band maxima can be attributed to the *cis* and *trans* isomers of Mn(CO)$_4$(THF)CH$_3$, respectively, with the *cis* isomer being the major component.[18] Previous flash photolysis studies with optical detection demonstrated[15] that photolytic formation of **I** in THF solutions in the presence of CO led to transients which react with CO to re-form Mn(CO)$_5$CH$_3$. For this reaction the second-order rate constant $k_{CO} = 1.4 \times 10^2$ M^{-1} s^{-1} was determined at ambient temperature.[15] When the reaction was probed at lower temperature, it was possible to follow reactions of the intermediates using a diode array spectrometer (Figure 6). Under these conditions, the temperature dependence on k_{CO} was investigated over the range 232–293 K, and an Eyring plot gave $\Delta H^{\ddagger} = 18 \pm 3$ kcal mol^{-1} and $\Delta S^{\ddagger} = +14 \pm 5$ cal mol^{-1} K^{-1}. The observed rates were independent of the wavelength of observation.

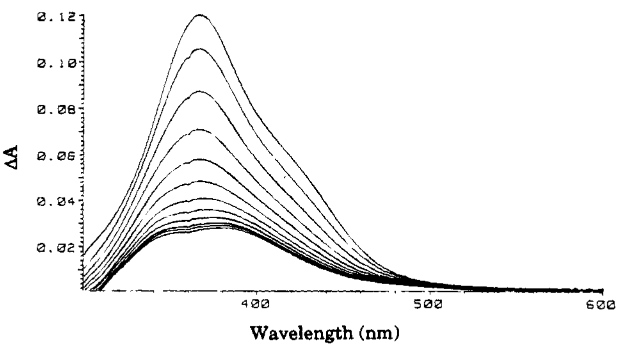

Figure 6. TRO spectra of Mn(CO)$_4$(solv)CH$_3$ in 255 K THF under 1 atm of CO (0.008 M). The k_{obs} value for the disappearance of this species is $(1.9 \pm 0.2) \times 10^{-3}$ s^{-1}. Spectra were taken at 90-s intervals.

Discussion

The above results demonstrate that 308-nm excitation of Mn(CO)$_5$CH$_3$ in various solvents leads to labilization of one CO and the formation of the solvento species Mn(CO)$_4$(solv)CH$_3$, as depicted in eq 2. In cyclohexane solution, both TRIR and low-temperature FTIR experiments (Table 1) and UV–vis spectra (Figure 5) as well as products of phosphine substitution strongly suggest the stereochemistry of this intermediate to be predominantly *cis* (eq 3). However, the TRO spectra in THF solution display a long-wavelength shoulder suggestive of the formation of the *trans* isomer as a minor product.[18] If this indeed is the case, it is notable that the kinetics studies reported for the reactions of the photogenerated intermediates proved to be single-exponential decays under conditions where first-order kinetics were appropriate. Thus, the observed kinetics were dominated by spectral changes due to reactions of the predominant *cis* isomer of the solvento intermediate, *and/or* the two isomers have similar reactivities, *and/or* the *trans* isomer is formed in very small concentration. The third potential reaction, homolysis of the

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[18] The optical spectrum obtained by Horton-Mastin et al.[9] upon photolysis of Mn(CO)$_5$CH$_3$ in a methane matrix at 14 K shows bands at 403 and 489 nm, which were assigned to square-pyramidal species of C_s and C_{4v} symmetry, respectively. The absorption bands of these species appear to have similar extinction coefficients; therefore, an estimate of the *cis/trans* ratio among the Mn(CO)$_4$(solv)CH$_3$ intermediates may be drawn by comparing intensities of the two bands. The spectral data (optical density vs frequency) obtained in the present study by the TRO technique in 295 K THF were analyzed using LabCalc software (Galactic Industries) and shown to resolve into two Gaussian bands at λ_{max} 372 and 444 nm with an intensity ratio of 3.2/1. Similar analysis of the difference spectral data obtained in 255 K THF gave bands at 368 and 433 nm with an intensity ratio of 4.3/1. Although the TRO spectrum in 295 K cyclohexane showed no shoulder at longer wavelength, there is some tailing to longer wavelength; therefore, these data were also analyzed accordingly in terms of summed Gaussian bands. This analysis suggested the presence of two bands, one at 383 nm and the other at ~442 nm with an intensity ratio of 4.0/1. These analyses suggest that a *trans* isomer may be formed in an approximately statistical (20%) yield in each of these media, although neither the TRIR spectra nor kinetic behavior provides evidence supporting this contention.

methyl–manganese bond, is also a minor contributor to the overall photochemistry but apparently does not play a role in the reaction dynamics of the solvento intermediates. Thus, the kinetics described here, largely from use of the TRIR technique, will be interpreted in terms of reactions by the principal solvento species *cis*-$Mn(CO)_4(solv)CH_3$.

The presence of a solvent molecule in the coordination sphere of *cis*-$Mn(CO)_4(solv)CH_3$ is indicated by the sensitivity of the ν_{CO} spectra to the nature of solv; e.g., lower frequencies for all bands were observed in THF than in either cyclohexane or PFMC (Table 1). Similar behavior is seen for the pentacarbonyl intermediate formed in the flash photolysis of $Cr(CO)_6$, and this has been concluded to be the solvento species $Cr(CO)_5(solv)$ with significant Cr---solv interactions, even in hydrocarbon solutions.[19] The analogy is strengthened by the observation that the solvento species *cis*-$Mn(CO)_4(solv)CH_3$ and $Cr(CO)_5(solv)$ each react with N_2 to form the respective dinitrogen complexes in alkane solution.[12] The terminal CO stretching bands of $Mn(CO)_4(N_2)CH_3$ in cyclohexane occur at slightly higher energy (2004, 1975 cm^{-1}) than do those of *cis*-$Mn(CO)_4(solv)CH_3$ yet lower than those of **I**, consistent with the weak σ-donating/π-accepting characteristics of N_2. Analogous $Cr(CO)_5(L)$ complexes show a similar trend; the ν_{CO} bands for $Cr(CO)_5(N_2)$ occur at higher energy than those of $Cr(CO)_5(c\text{-}C_6H_{12})$.[12] In PFMC, the solvento intermediate has terminal CO stretches at 2008 and 1964 cm^{-1}, higher than those of the cyclohexane complex; however, bands of $Mn(CO)_5CH_3$ are also comparably shifted to higher energy.

A more dramatic indication of solvent coordination in *cis*-$Mn(CO)_4(solv)CH_3$ comes from comparing the reactivities of this species with CO to regenerate **I** (Table 2). At ambient temperature, the rate constants k_{CO} for eq 4 differ by 8 orders of magnitude, depending upon the solvent, with the respective values 1.4×10^2, 4.5×10^8, and $\sim 1 \times 10^{10}$ M^{-1} s^{-1} in THF, cyclohexane, and PFMC. The k_{CO} value in PFMC approaches the calculated value of the diffusion limit.[17a] A similar demonstration that the reactivity of $Cr(CO)_5$ with CO is much faster in perfluoroalkanes than in alkanes led Kelly and co-workers to propose the presence of a kinetically significant solvento species in $Cr(CO)_5(solv)$ in alkane media,[20] and this proposal has been confirmed by a number of subsequent studies.[21] The approximately diffusion limited rate in PFMC indicates that the direct interactions between metal and perfluoroalkane solvent are quite weak.

Second-order kinetics were the rule for reaction of the solvento intermediate **A** with various ligands in cyclohexane solutions (eq 5), and respective k_L values proved to be dependent on the nature of L (Table 2). Such behavior would be consistent with a simple associative or concerted mechanism for displacement of solv by L, which would give the rate law

$$\frac{d[\mathbf{A}]}{dt} = -k_L[L][\mathbf{A}] \qquad (6)$$

Alternatively, a limiting dissociative pathway such as

$$Mn(CO)_4(solv)CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{U} + solv \qquad (7)$$

$$\mathbf{U} + L \xrightarrow{k_2} Mn(CO)_4(L)CH_3 \qquad (8)$$

would give the rate law

$$\frac{d[\mathbf{A}]}{dt} = \frac{-k_1k_2}{(k_{-1} + k_2[L])}[L][\mathbf{A}] \qquad (9)$$

which, under the likely condition $k_{-1} \gg k_2[L]$, would give

$$k_L = \frac{k_1k_2}{k_{-1}} \qquad (10)$$

where the response of k_2 to the nature of L would be reflected by a similar sensitivity of k_L. In such a scheme, the new intermediate **U** would have the composition of the unsaturated species $Mn(CO)_4CH_3$, although stabilization by an α-agostic interaction of the methyl group with the vacant coordination site is possible. This would also explain the sensitivity of k_{CO} to solvent, given that both k_1 and k_{-1} will be dependent on the nature of solv.

Although the present data do not clearly differentiate between associative and dissociative pathways or multiple mechanisms as argued for reactions of $Cr(CO)_5(solv)$,[22] observation of $\Delta H^‡$ (+18 kcal mol^{-1}) near the energy expected for a Mn---THF bond[19] as well as the positive $\Delta S^‡$ value (+14 eu) suggests that considerable Mn–solv bond breaking is occurring in the rate-limiting step of this substitution reaction in THF. The slower rate for reaction of the trifluoromethyl analog $Mn(CO)_4(solv)CF_3$ with CO in cyclohexane also suggests that the more electron-withdrawing CF_3 group might be slowing solvent dissociation. Nonetheless, it seems likely that ligand substitution on the solvento species occurs via an interchange mechanism with the relative importance of Mn–solv bond breaking and Mn–L bond formation being functions of the solvent.

As noted above, one goal of investigating the spectra and reactivities of transients generated by flash photolysis of $Mn(CO)_5CH_3$ was to provide a frame of reference when considering intermediates from flash photolysis of the acyl analog $Mn(CO)_5(COCH_3)$ (**II**). The latter complex and related species have been investigated by TRIR techniques with the goal of providing better insight into the mechanism of the migratory insertion of carbon monoxide into metal–alkyl bonds. In a recent communication from this laboratory,[2] it was noted that the "unsaturated" species *cis*-$Mn(CO)_4(COCH_3)$ (**X**), formed by flash photolysis of **II**, has a surprisingly long lifetime in each solvent investigated. From the apparent lack of reactivity even under CO,

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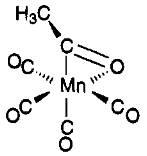
(19) Yang, G. K.; Vaida, V.; Peters, K. S. *Polyhedron* **1988**, *7*, 1619.

(20) (a) For example, $Cr(CO)_5(solv)$ reacts with CO with the following respective k_{CO}'s: 3.6×10^6 M^{-1} s^{-1} in cyclohexane and 3×10^9 M^{-1} s^{-1} in PFMC.[20b] (b) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220–1221. Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344. (c) A similar difference in the rate constants for reaction of $Cr(CO)_5(solv)$ with N_2 has been reported.[12b]

(21) Ford, P. C.; Boese, W.; Lee, B.; MacFarlane, K. Photocatalysis Involving Metal Carbonyls. In *Photosensitization and Photocatalysis by Inorganic and Organometallic Compounds*; Graetzel, M., Kalyanasundaram, K., Eds.; Kluwer: Dordrecht, The Netherlands, 1993; pp 359–390, and references therein.

(22) (a) Zhang, S.; Dobson, G. R. *Organometallics* **1992**, *11*, 2447. (b) Zhang, S.; Zang, V.; Bajaj, H.; Dobson, G. R.; van Eldik, R. *J. Organomet. Chem.* **1990**, *397*, 279.

upper limits of $<2 \times 10^4$ M^{-1} s^{-1} were estimated for k_{CO} in PFMC, THF, and cyclohexane using the TRIR technique, while preliminary TRO studies in cyclohexane gave a k_{CO} value of 3.8×10^3 M^{-1} s^{-1} for the reaction of **X** with CO and a k_m value of 10 s^{-1} for the migration of the methyl group to the metal to form **I**. Thus, **X** is about 5 orders of magnitude less reactive than is **A** in cyclohexane. It is unlikely that this difference results from an inductive effect due to replacing the methyl with a more electron-withdrawing acetyl, since replacing CH_3 with the even more electron-withdrawing CF_3 decreases k_{CO} only by a factor of 30. Thus, one is led to the conclusion that another factor must be giving unusual stabilization to **X**, at least in the weakly coordinating solvents cyclohexane and PFMC. Thus, the sluggish kinetics of this unsaturated acyl complex have been attributed[2] to the ability of the acetyl group to chelate the metal center and, hence, stabilize the coordination site vacated by photolabilized CO. Although such chelation could be in the form of an agostic interaction between manganese and a methyl C—H bond,[23] we favor the η^2 interaction of the acyl C=O group,[2] given theoretical calculations which indicate the latter to be the lower in energy.[2,24]



In summary, flash photolysis of $Mn(CO)_5CH_3$ (**I**) in various solvents leads primarily to the formation of the solvento species *cis*-$Mn(CO)_4(solv)CH_3$. These react with CO to regenerate **I** and with other nucleophiles L to form *cis*-$Mn(CO)_4(L)CH_3$ at rates strongly dependent on the nature of the solvent and somewhat dependent on the nature of L. For example, reaction with CO is nearly 8 orders of magnitude faster in perfluoro(methylcyclohexane) than in THF solution. Notably in cyclohexane, **A** is a factor of 10^2 more reactive with CO than is the $Cr(CO)_5(solv)$ analog. These data confirm an earlier claim from this laboratory,[15] that a highly reactive, but still selective, intermediate is formed in the flash photolysis of **I**, but we conclude that this species is a highly reactive cyclohexane complex (i.e. **A**) rather than the unsaturated species $Mn(CO)_4CH_3$ originally suggested. Nonetheless, the solvento species **A** is sufficiently reactive to coordinate N_2 at rates comparable to those for stronger nucleophiles. Lastly, comparison of the reactivity of **A** to the sluggish behavior of the intermediate **X** formed upon flash photolysis of the acetyl complex $Mn(CO)_5(COCH_3)$ under analogous conditions clearly suggests the acetyl group must provide unusual stabilization of the $Mn(CO)_4(COCH_3)$ configuration, perhaps via η^2 coordination of the acetyl oxygen to the vacated *cis* coordination site.

Acknowledgment. This research was sponsored by a grant (No. DE-FG03-85ER13317) to P.C.F. from the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. Some instrumentation development was facilitated by a grant (No. DE-PS05-91ER75608) from the University Research Instrumentation Program of the U.S. Department of Energy. The able assistance of Brian Lee of this department in the care of the TRIR apparatus contributed significantly to the success of these studies. We thank Professor Richard J. Watts of this department for allowing us access to flash photolysis equipment in his laboratory and for his patient help in utilizing software for the presentation of data. Preliminary experiments on this system were initiated by David Ryba and Simon Belt and are described in refs 7b and 15.

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[23] Carmona, E.; Contreras, L.; Poveda, M. L.; Sanchez, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4322–4324.

[24] (a) Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572; *J. Am. Chem. Soc.* **1988**, *110*, 3728. (b) Marynick, D. S. Private Communication.