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Time-Resolved Infrared Observation of a Long-Lived Transient in the Photo-Decarbonylation of $Mn(CO)_5C(O)CH_3$: Potential Relevance to the CO Migratory Insertion Mechanism

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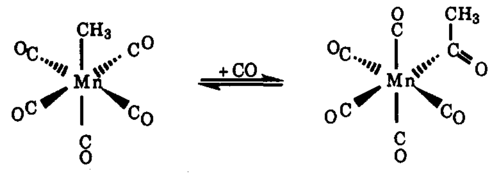
*Summary: Flash photolysis experiments have been carried out at ambient temperature to probe potential reaction intermediates in the carbonylation of the methylmanganese complex $CH_3Mn(CO)_5$ (**M**) to give the acyl product $CH_3C(O)Mn(CO)_5$ (**A**). Photo-decarbonylation of **A** gives a long-lived transient C, whose time-resolved infrared spectrum shows but modest sensitivity to the coordinating ability of the solvent such as cyclohexane, perfluoromethylcyclohexane, tetrahydrofuran, and 2,5-dimethyl-THF. Notably, C has an unexpectedly long lifetime (exceeding milliseconds) in each of the solvents investigated. Kinetics studies in cyclohexane show the competing trapping by CO to re-form **A** and isomerization to **M** occurs with the respective rate constants $k_{CO} = 3.8 \times 10^3\ M^{-1}\ s^{-1}$ and $10\ s^{-1}$. The former value is 3 orders of magnitude less than expected for a solvento complex under these conditions. Thus, it is concluded that TRIR spectra and reactivity patterns of C reflect stabilization of this intermediate by η^2-coordination of the acyl group.*

Migratory insertion of carbon monoxide into metal alkyl bonds is a key step in mechanisms proposed for catalytic carbonylations of organic substrates[1] and is of fundamental interest in organometallic chemistry.[2] A prototype for migratory insertion is the carbonylation of methylmanganese carbonyl $CH_3Mn(CO)_5$ (**M**) to form the acyl analog $CH_3C(O)Mn(CO)_5$ (**A**) (eq 1).[3] Various thermochemical



(1)

studies have concluded that this reaction proceeds via the migration of CH_3 from the Mn to an adjacent CO followed by trapping of the resulting intermediate **I** with CO or another ligand.[4] The nature of **I** has been the subject of various experimental and theoretical studies;[3–6] however, direct observation of intermediates in fluid solution has proved elusive, except in very strongly coordinating media such as dimethyl sulfoxide.[7] Described here are laser flash photolysis experiments with time-resolved infrared (TRIR) detection[8–10] designed to prepare **I** and to interrogate its spectrum and kinetics. These experiments demonstrate that the putative intermediate is surprisingly stable and suggest that it may have an η^2-acyl structure in weakly coordinating solvents such as alkanes and perfluoroalkanes.

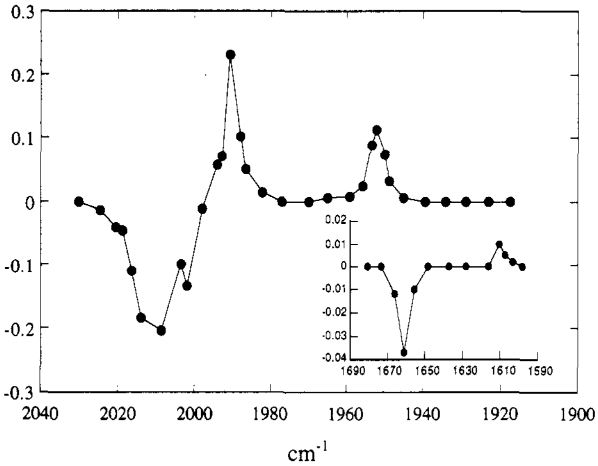


Figure 1. TRIR spectrum of C in cyclohexane formed by 308-nm flash excitation of $CH_3C(O)Mn(CO)_5$. Data points represent the absorbance change measured 100 μs after the laser flash at individual monitoring frequencies. Conditions: $[A] = 1 \times 10^{-3}$ M; $P_{CO} = 1.0$ atm; $T = 22$ °C. Inset: spectral changes in acyl stretching region from analogous experiment with $[A] = 3 \times 10^{-3}$ M.

Pulse laser excitation (308 nm) of **A** in 295 K cyclohexane or methylcyclohexane gave a TRIR difference spectrum (Figure 1) showing disappearance of the ν_{CO} bands for **A** and the formation of a long-lived transient **C** with ν_{CO} bands at 1990, 1952, and 1607 (w, br) cm^{-1}.[11] Disappear-

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(7) (a) Cotton, J. D.; Bent, T. L. *Organometallics* **1991**, *10*, 3156. (b) The solvento species $CH_3C(O)MnS(CO)_4$ has been observed as a stable "intermediate" in strongly coordinating solvents such as DMSO.

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(11) In alkane and PFMC solutions (but not in THF), a low yield of **A** was observed to form promptly (τ < 100 ns) along with **C**. The same result was seen when the reaction is investigated in a methylcyclohexane glass at 77 K. This is believed to be the result of reaction from an electronic or vibrational excited state of **A** manifesting itself as a CO-independent component in the formation of **M**. A similar result was obtained when the photolysis was carried out in a solid inert-gas matrix; see ref 6.

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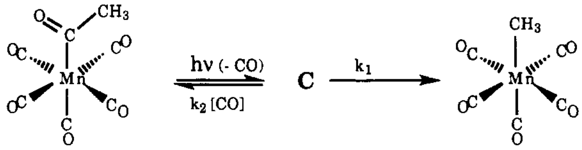
Table I. Carbonyl Bands (ν_{CO} Values in cm^{-1}) for Intermediate C Formed by 308-nm Excitation of A[a] in Various Solvents at Ambient Temperature and at −78 °C As Measured by TRIR and FTIR, Respectively

solvent[b]	ν_{CO} data at room temp[c]	ν_{CO} data at −78 °C[d]
perfluoromethylcyclohexane	1997, 1959	2082 (w), 1998, 1958
cyclohexane[d]	1990, 1952, 1607 (w)	
methylcyclohexane	1990, 1952	2080 (w), 1988, 1941, 1607 (w)
dichloromethane	1987 (br), 1940 (br)	
tetrahydrofuran	1981 (br), 1931 (br)	2077 (w), 1977, 1928, 1602 (w)
2-methyltetrahydrofuran	1979 (br), 1932 (br)	2077 (w), 1977, 1928, 1600 (w)
2,5-dimethyl-THF	1982 (br), 1932 (br)	2077 (w), 1979, 1931, 1603 (w)

[a] The CO stretching frequencies for A are 2110, 2051, 2012, and 1661 cm^{-1} and are independent of solvent. [b] All solvents were dried and redistilled before use. [c] Room-temperature data taken from TRIR spectra 100 μs after 308-nm flash excitation. [d] Low-T data recorded on a Bio-Rad FTS-60 FTIR spectrometer immediately after 308-nm excitation with one pulse from an XeCl excimer laser.

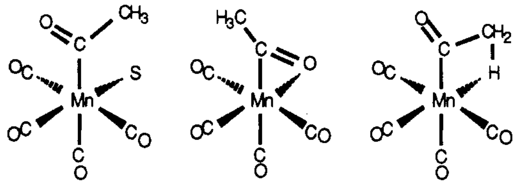
ance of A and formation of C occurred within the rise time of the detection apparatus (~100 ns). Subsequently, C reacted to give M, but under CO, trapping of C by CO to re-form A proved competitive with the methyl migration step (i.e., eq 2).[12] Even under CO (1 atm), C displayed remarkably long lifetimes (several seconds), significantly longer than the ~1 ms upper limit for direct observation by the TRIR apparatus. Comparably long lifetimes extended to every solvent for which TRIR spectra were recorded (Table I).



(2)

The relatively unreactive nature of C made it convenient to carry out photolyses at a lower temperature (200 K), where the transient spectra were recorded with an FTIR spectrometer. At this T, 308-nm irradiation (XeCl laser pulses) of A gave transient C with a lifetime of hours in each solvent. In methylcyclohexane, the FTIR spectrum recorded within a few minutes displayed ν_{CO} bands (2080 (w), 1988 (s), 1941 (s), 1607 (w, br) cm^{-1}), similar to the TRIR spectra in cyclohexane and methylcyclohexane.[13] Furthermore, the spectra of C under these conditions are similar to that reported[6] for the species generated by photolysis of A in frozen methane (12 K) (ν_{CO}: 2084 (w), 1992 (s), 1948 (s), 1610 (vw) cm^{-1}).[14] Thus, it is likely that the species formed in the varied alkane media are structurally analogous.

TRIR (295 K) and FTIR (200 K) spectra in various solvents ranging from perfluoromethylcyclohexane (PFMC) to the differently methylated tetrahydrofurans are summarized in Table I. These are qualitatively similar to those described above for the alkanes and are consistent with labilization of a CO adjacent to the acetyl ligand to give a tetracarbonyl intermediate such as proposed in thermal carbonylation. The bands shift modestly to lower frequency on going from poorly coordinating perfluoroalkane to the stronger donor THF, an effect which one might attribute to solvent molecule coordination at the site previously occupied by the photodissociated CO. However, the relative languor of C in reacting with CO, even in alkane and perfluoroalkane media, clearly points to a different explanation (see below). Furthermore, transient spectra recorded in tetrahydrofuran, 2-methyl-THF, and 2,5-dimethyl-THF each gave identical ν_{CO} band frequencies for C despite differences in the coordinating abilities of these solvents. If C were the solvento complex $CH_3C(O)Mn(CO)_4S$ (S = solvent), ν_{CO} would be expected to shift to higher energy on going from THF to the bulkier 2,5-dimethyl-THF.[15]



(1) (2) (3)

Figure 2. Prospective structures for C.

Prospective structures for C are illustrated in Figure 2. The solvento species 1 and the coordinatively unsaturated pentacoordinate species $CH_3C(O)Mn(CO)_4$ proposed in the matrix studies[6] can also be excluded given the sluggishness of the reactions of C. As noted above, C did not undergo measurable reaction with CO in cyclohexane at P_{CO} = 1 atm within the 1-ms time window of the TRIR detection device. If one conservatively assumes a 10% loss of signal would have been detected, upper limits of $k_2 < 2 \times 10^4$ M^{-1} s^{-1} for trapping C by CO and of $k_1 < 2 \times 10^2$ s^{-1} for unimolecular methyl migration to M can be calculated for eq 2. Notably, C proved to be surprisingly unreactive in each of the solvents investigated, *including PFMC.* More accurate rate constant values were determined in cyclohexane by carrying out kinetic flash photolysis studies of A using optical detection (which allowed for observing longer lived species). These gave the respective rate constants k_1 = 10 s^{-1} and $k_2 = 3.8 \times 10^3$ M^{-1} s^{-1} under the same conditions.

The relatively low reactivity of C in alkane and perfluoroalkane solutions is remarkable when compared to reactivities of other unsaturated metal carbonyls. For example, earlier studies here[16] demonstrated that the intermediate *cis*-$Mn(CO)_4(CH_3)S$ (generated by flash photolysis of M) reacts with CO with a k_2 of 2.0×10^6 M^{-1}

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(12) Continuous photolysis of A (313 nm) in ambient-temperature cyclohexane results in CO photodissociation and clean formation of M according to FTIR and UV–vis spectral changes. Under argon the quantum yield was determined to be 0.63; under CO (1 atm) it had the much lower value of 0.16.

(13) ν_{CO} values are largely temperature independent with the exception of the lower frequency band in alkanes which shifts from 1952 to 1941 cm^{-1} on lowering of T to −78 °C. As a reviewer has pointed out, this may represent some subtle variation in the conformation of C.

(14) The 1992-cm^{-1} ν_{CO} band of C in the methane matrix (12 K) is split into several components due to local environmental (matrix) effects (see ref 6), so the average value is described here.

(15) (a) The UV–vis spectrum of C at low temperature was obtained, in a manner analogous to that for the FTIR spectra. In methylcyclohexane and in tetrahydrofuran the spectra feature a broad band centered at ~384 nm, invariant of solvent. This may be taken as further evidence for an similar intermediate in both solvent. In contrast, the electronic spectrum of $Cr(CO)_5$ depends strongly on the medium in which it is formed. (b) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

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s^{-1} in alkane solution but is 4 orders of magnitude slower (1.4×10^2 M^{-1} s^{-1}) in THF. Similarly, flash photolysis of $Cr(CO)_6$ leads to formation of the solvento complex $Cr(CO)_5S$, which reacts with CO at k_2 values of 3×10^6 M^{-1} s^{-1} and $\sim 3 \times 10^9$ M^{-1} s^{-1} in cyclohexane and perfluoroalkanes, respectively.[17] The acyl intermediate **C** is orders of magnitude less reactive than are the above solvento complexes in the latter solvents, thus, **C**'s extraordinary stability must be due to some type of intramolecular stabilization such as chelation by the acyl ligand as shown in structures **2** and **3**. Of these, agostic coordination of the methyl group as in **3** has the appeal of appearing to be closer to the transition state expected for the methyl migration pathway. However, *ab initio* calculations[5b] have concluded that isomer **2** should be the much more stable of these two. Thus, the unusual longevity of **C** appears to be the result of its stabilization by η^2-coordination of the acyl.[18]

The acyl ν_{CO} band (1607 cm^{-1}) recorded for **C** in cyclohexane is significantly shifted to lower frequency from **A** and falls within the range (1470–1625 cm^{-1}) observed for stable η^2-(C=O) coordinated acyl complexes.[18] However, this is not as convincing evidence for such coordination as is the kinetic properties, since parameters such as ligand substitution can have comparable effects on the acyl ν_{CO} band. The relatively high frequency would be consistent with the "lightly stabilized" nature of this reactive intermediate.

In summary, the surprisingly slow reactivity of **C** even in weakly donor solvents suggests η^2-coordination of the acyl ligand under such conditions in accord with theoretical analyses which indicate the probable stability of such a species. One might ask whether **C**, which is generated as the result of photolabilization of CO from **A**, and **I**, which is the purported intermediate in the thermal transformation of **M**, are indeed the same, since the principles of microscopic reversibility do not apply given the independent pathways involved. Nonetheless, the two species have the same stoichiometry, and the reported thermal reaction kinetics[3] are consistent with the intermediacy of a species **I** which undergoes back-reaction to re-form **M** competitive with trapping by CO to give **A** when P_{CO} is 1 atm. The kinetic flash photolysis experiments reported here indicate that this is also the case for **C**. Further studies are in progress to determine quantitative solvent and temperature effects on the kinetics of **C** and of other transients formed in reactions of related manganese complexes.

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(18) For other examples of η^2-acyl complexes, see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.