Room-Temperature Reactions of the Intermediate(s) Generated by Flash Photolysis of (η^5-C_5H_5)Fe(CO)$_2$CH$_3$

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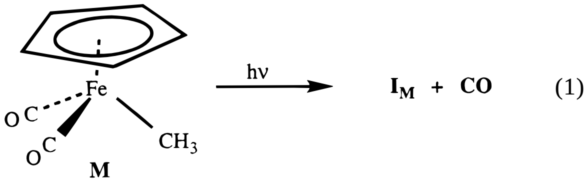
The transient formed by the photolysis of the methyl complex CpFe(CO)$_2$CH$_3$ (**M**, Cp = (η^5-C_5H_5)) has been studied by FTIR spectroscopy in methylcyclohexane solution at 77 K and by time-resolved infrared detection in ambient-temperature solutions in cyclohexane and tetrahydrofuran. The transient IR spectrum of the intermediate **I$_M$** displays a single ν_{co} absorption band and can be characterized as a monocarbonyl. In 295 K solution, the reaction of **I$_M$** with CO occurs with second-order kinetics (rate = k_{co}[**I$_M$**][CO]) with k_{co} values of $(6.3 \pm 0.2) \times 10^8$ and $(3.4 \pm 0.4) \times 10^6$ M^{-1} s^{-1} in cyclohexane and THF, respectively. On the basis of these data, **I$_M$** is concluded to be the solvento complex CpFe(CO)(Sol)CH$_3$.

Introduction

Near-UV photolysis of CpFe(CO)$_2$CH$_3$ (**M**, Cp = (η^5-C_5H_5)) has been argued to effect decarbonylation to give the "unsaturated" intermediate species "CpFe(CO)CH$_3$" (**I$_M$**) (eq 1) based on evidence from trapping studies.[2,3]



The same intermediate has been proposed in thermal reactions of **M** with various ligands.[4] **I$_M$** is also of interest as a model for the reactivity expected for intermediates generated by photolysis of other CpFe(CO)$_2$R compounds in the absence of specific interactions between the coordination site vacated by the photolabilized CO and the ligand R− (e.g., for R = −C(O)CH$_3$).[5] However, direct detection of **I$_M$** in ambient-temperature solutions has not been previously reported. Surprisingly, this species has been proven to be somewhat elusive, even in low-temperature experiments in noble gas matrices,[2,7,8] although a monocarbonyl species has been detected in a poly(vinyl chloride) film at 12 K,[9] the difference in behavior being attributed to rapid cage recombination in the more closely confined gas matrix environment.[9] Described here are time-resolved infrared (TRIR) experiments examining the spectra and reaction dynamics of the intermediate formed by laser flash photolysis of **M** in two common solvents at ambient temperature. Also reported is the FTIR spectrum of **I$_M$** recorded after photolysis of **M** in 77 K methylcyclohexane.

Experimental Section

Reagents. Methylcyclohexane (Aldrich) was treated by standard procedures to remove alkenes and then distilled from sodium metal. Tetrahydrofuran (THF, Aldrich) was distilled from sodium−benzophenone ketyl solution under dinitrogen. Cyclohexane (spectrophotometric grade, B & J Brand, Baxter) was distilled from calcium hydride under dinitrogen. All gases were passed through an Alltech Associates Oxy-trap and a column of 4 Å molecular sieves and Drierite before use. CpFe(CO)$_2$CH$_3$ was prepared by published methods,[10] and then it was chromatographed on a silica gel column in the inert atmosphere box with pentane.

Low-Temperature FTIR Spectra. These were recorded on a Bio-Rad FTS-60 FTIR spectrometer using a R. G. Hansen PFD-FT12.5 fixed temperature pourfill Dewar which was custom fitted with a sample IR cell. The IR cell was first flushed with argon for 10 min and then capped with silicone rubber GC septa. Solutions were prepared by dissolving CpFe(CO)$_2$CH$_3$ (10^{-3} M) in freshly distilled solvent (under Ar), entrained further with argon, and then transferred to the IR cell using a gastight syringe (with an outlet needle in the second port). Initial FTIR spectra were measured at room temperature and again at low temperature after filling the Dewar flask with the cryogen (dry ice/acetone or LN$_2$). The sample was then subjected to 5−10 pulses from a XeCl excimer laser (308 nm), and the spectrum was again measured.

TRIR Spectra. The time-resolved infrared instrumentation with modifications in sample handling, has been described.[1b,11] After flash photolysis by XeCl excimer laser

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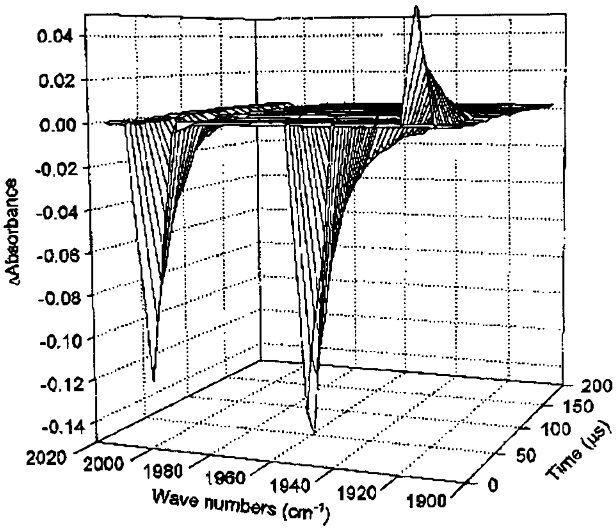


Figure 1. TRIR ΔAbs changes due to laser flash photolysis of **M** in THF (P_{CO} = 1 atm, T = 295 K).

pulses at 308 nm (~20 ns pulse length) to generate transient species, the temporal absorbances were recorded using a continuous IR probe source (lead salt diode laser system), operating at a single, but tunable, frequency, and a fast rise-time Hg/Cd/Te IR detector. Each absorbance vs time (t) trace was signal-averaged at least 30 times or until a good signal-to-noise ratio was obtained. Exponential decay curves were fitted to kinetic traces using the custom program Scopemate by UGI Scientific. Three-dimensional TRIR spectra were generated by compiling absorbance change (ΔAbs) vs t traces for different IR frequencies (spacing about 1 cm^{-1}) using Sigma Plot software.

Results and Discussion

When a solution of **M** (10^{-3} M) in a glassy methylcyclohexane matrix at 195 K was subjected to repetitive 308 nm pulses from a XeCl excimer laser, no net change in the FTIR spectrum was apparent. However, at 77 K, analogous treatment led to a difference spectrum displaying new ν_{co} absorbance(s) at 1949/1942 cm^{-1} and bleaching of the ν_{co} bands at 2014 and 1958 cm^{-1} of **M**. The new absorbance appears to be a single band split by matrix effects,[12] as would be expected for a monocarbonyl complex formed by CO photodissociation (i.e., eq 1), rather than two independent bands, but the latter alternative cannot be excluded given these data alone. Warming the solution to room temperature resulted in regeneration of the initial FTIR spectrum. This is consistent with reversible labilization of CO from **M** as the principal photoreaction pathway, since homolytic fragmentation of the Fe–Me bond to give Fp$^•$ (Fp = CpFe(CO)$_2$) would have been expected to lead to formation of the dimer Fp$_2$.[13]

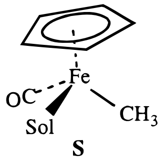
Figure 1 displays the TRIR spectrum following flash photolysis (308 nm) of **M** in ambient-temperature solution. The 3-dimensional time-resolved spectrum of the evolving solution was constructed by laminating together a series of individual experiments, monitoring temporal absorbance at different single IR frequencies. Bleaching of the ν_{co} bands attributed to **M** and formation of the new band were immediate (<100 ns), consistent with photodissociation of one CO to form $\mathbf{I_M}$. Over a few microseconds, the new band decayed to the base line but even under CO (P_{CO} = 1 atm) recovery of **M** was incomplete; net photochemistry corresponding to ~5% of the total bleaching was seen. However, FTIR spectra recorded after photolysis did not detect any new carbonyl complexes, so the fate of the small missing portion of **M** remains unknown.

Table 1. Carbonyl Region IR Bands for CpFe(CO)$_2$CH$_3$ and $\mathbf{I_M}$

solvent	ν_{co}(**M**), cm^{-1}	ν_{co}($\mathbf{I_M}$), cm^{-1}
THF[a]	1999, 1947[b]	1914[c]
cyclohexane[a]	2015, 1959[b]	1938[c]
methylcyclohexane[d]	2014, 1958[b]	1949/1942[b]

[a] At 295 K. [b] FTIR. [c] TRIR. [d] At 77 K.

The TRIR spectrum attributed to $\mathbf{I_M}$ proved to be solvent-sensitive, with ν_{co} values of 1938 cm^{-1} in cyclohexane and 1914 cm^{-1} in THF (Table 1). This suggests that $\mathbf{I_M}$ is the solvento species **S** (Sol = solvent). There are numerous precedents for forming such solvento species within a few picoseconds upon labilization of a coordinated CO from metal carbonyls, both for well-recognized donor solvents such as THF and for alkanes.[14,15] For **S**, the ν_{co} of the single remaining CO should be sensitive to the σ-donor/π-acceptor service of the new ligand, a stronger donor shifting ν_{co} to lower frequency. This, indeed, was seen (Table 1); however, the two ν_{co} bands for **M** are also shifted to lower frequency in THF relative to their respective values in cyclohexane. Although smaller, these shifts are not insubstantial, so one must turn to the kinetics data to address this question.



S

For TRIR experiments under argon, temporal absorbances did not fit well to either first- or second-order kinetics equations; however, for P_{CO} > 0.01 atm, traces of ΔAbs vs t showed exponential behavior. The k_{obs} values obtained from these analyses for the reappearance of **M** and for the decay of $\mathbf{I_M}$ were identical (Figure 1). Furthermore, plots of k_{obs} vs [CO] (0.001–0.01 M)[16] proved to be linear (Figure 2), consistent with second-order kinetics for regeneration of **M** (eqs 2 and 3).

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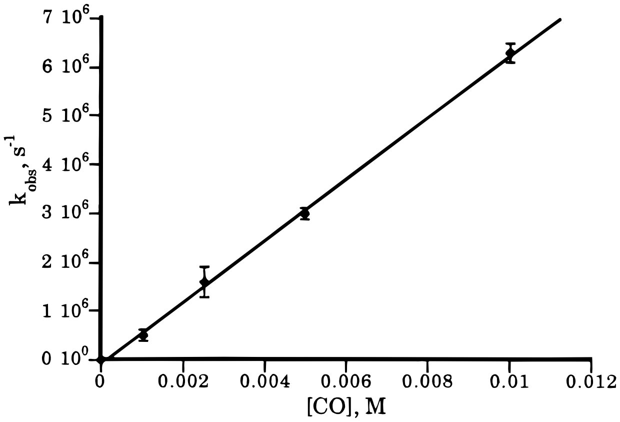

Figure 2. Plot of k_{obs} vs [CO] for the recombination of **I** with CO to form **M**. The slope gives $k_{co} = (6.3 \pm 0.2) \times 10^8$ M^{-1} s^{-1} in cyclohexane ($T = 295$ K).

$$\mathbf{I_M} + \mathrm{CO} \xrightarrow{k_{co}} \mathbf{M} \tag{2}$$

$$\frac{d[\mathbf{M}]}{dt} = -\frac{d[\mathbf{I_M}]}{dt} = k_{obs}[\mathbf{I_M}] = k_{co}[\mathrm{CO}][\mathbf{I_M}] \tag{3}$$

Values of k_{co} determined from these plots are $(6.3 \pm 0.2) \times 10^8$ M^{-1} s^{-1} in cyclohexane and $(3.4 \pm 0.4) \times 10^6$ M^{-1} s^{-1} in THF.

The observations that the TRIR spectrum of $\mathbf{I_M}$ displays a single ν_{co} band and that this band disappears at the same [CO]-dependent rates as those attributed to **M** reappearance argue that $\mathbf{I_M}$ results from photolysis-induced decarbonylation. As noted above, the lower frequency of the single ν_{co} band in THF (relative to cyclohexane solution) is consistent with $\mathbf{I_M}$ being the solvento species **S** but not unequivocal. The 200-fold decrease in reactivity toward CO is more convincing, but the difference is surprisingly attenuated from that seen for the reactivities of analogues such as the $Cr(CO)_5(Sol)$ and $Mn(CO)_4(Sol)CH_3$.[17,18] For example, the values of k_{co} for $Mn(CO)_4(Sol)CH_3$ have been determined to be $(4.5 \pm 0.5) \times 10^8$ and $(1.4 \pm 0.3) \times 10^2$ M^{-1} s^{-1} in cyclohexane and THF, respectively. Nonetheless, we conclude that $\mathbf{I_M}$ is the solvento species **S**. One argument for the higher reactivity of $\mathbf{I_M}$ (relative to the manganese analog) in THF would be different substitution mechanisms in the two cases, given the possibility of $\mathbf{I_M}$ to react via a “ring slip” mechanism leading to an intermediate with an η^3-C_5H_5 ring.[8,19] However, a recent reevaluation of pressure-effect studies probing the reactivity of the analogous intermediate from the photolysis of the acetyl complex $CpFe(CO)_2(CH_3CO)$ argues against this interpretation.[6]

In summary, the present work reports the unprecedented observation of the intermediate $CpFe(CO)CH_3$ generated by laser flash photolysis in ambient-temperature solutions. Both the time-resolved infrared spectra of this species in these media and the dynamics of the reaction of $\mathbf{I_M}$ with CO point to a characterization of this intermediate as the solvated species $CpFe(CO)(Sol)CH_3$.

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