membered-ring closing, even though the ring strain in the product ring must (on the basis of the known instability of silacyclopropanes) to be considerable.

It is also interesting to note the implications of the surprisingly high Arrhenius parameters deduced for reaction 22 (i.e. the silacyclopropane dissociation to olefin and silylene). Past treatments have assumed this to be a concerted process with a "normal" A factor on the order of ekT/h. The present results are consistent only with a consecutive step process, probably involving biradical formation. The addition of silylene to butadiene[19] (forming 3- and 4-silacyclopentene) appears to proceed in a similar fashion so there is some support for this kind of high-entropy, loose transition-state process in silylene additions to (or eliminations from) olefins.

Summary

Intramolecular isomerizations of long-chain alkylsilylenes are very fast processes and at static temperatures proceed exclusively (when possible) via three-membered ring forming cyclizations. The silacyclopropane intermediates so formed decompose (to olefins and silylene) at rates which are several times faster than their isomerizations to alkylsilylenes. This is the case even though the decompositions have activation energies significantly higher (11–12 kcal) than the competing isomerizations. The unusually high activation entropies of decomposition, reflected in the high A factors of reaction (e.g. $A_{22} \approx 10^{17.9}$ s^{-1}), suggest a consecutive step mechanism probably involving biradical intermediates. Thus the reverse reactions and their analogues (i.e. silylene additions to olefin π systems) are high A-factor, biradical, consecutive step processes and not, as formerly believed, concerted single-step processes.

Acknowledgment. We are indebted to AFOSR for financial support of this work under Grant 83-0209.

Registry No. SiH_4, 7803-62-5; $CH_3CH_2CH{=}CH_2$, 106-98-9; SiH_2, 13825-90-6; SiD_4, 13537-07-0; $HSiCH(CH_3)CH_2CH_3$, 110550-55-5; n-$C_4H_9SiH_3$, 1600-29-9; s-$C_4H_9SiH_3$, 18165-84-9; *cis*-$CH_3CH{=}CHCH_3$, 590-18-1; *trans*-$CH_3CH{=}CHCH_3$, 624-64-6; 2,3-dimethylsilacyclopropane, 110550-56-6; disilane, 1590-87-0.

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Structure and Reactivity of (η^5-C_5H_5)$Mn(CO)_2$ in Room-Temperature Solution. Evidence for Formation of a Dinuclear Intermediate Detected by Flash Photolysis and Time-Resolved Infrared Spectroscopy

Bernadette S. Creaven,[1a] Andrew J. Dixon,[1b] John M. Kelly,*[1c] Conor Long,*[1a] and Martyn Poliakoff*[1b]

School of Chemistry, National Institute for Higher Education, Dublin 9, Ireland, Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K., and Department of Chemistry, Trinity College, Dublin 2, Ireland

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UV laser flash photolysis (308 nm, 15 ns) with UV/vis monitoring and with time-resolved IR spectroscopy has been used to characterize two transient species formed by the photolysis of $CpMn(CO)_3$ (Cp = η^5-C_5H_5) in alkane solution. The first species has been identified as $CpMn(CO)_2S$ where S = cyclohexane or n-heptane, from both its kinetic behavior and its IR spectrum. $CpMn(CO)_2S$ reacts with CO, N_2, and PPh_3 with bimolecular rate constants similar to those previously published for the corresponding reactions of the group 6 metal pentacarbonyls. The second transient species $Cp_2Mn_2(CO)_5$ is formed by the reacton of $CpMn(CO)_2S$ with unphotolyzed $CpMn(CO)_3$. ^{13}CO enrichment and IR spectroscopy are used to establish that $Cp_2Mn_2(CO)_5$ has a single bridging CO group. The formation of $Cp_2Mn_2(CO)_5$ can be suppressed by reagents, e.g. PPh_3, added to the solution.

Introduction

A knowledge of the reactivity of coordinatively unsaturated organometallic complexes is of primary importance in understanding the mechanisms of many systems. Transition-metal carbonyl complexes are particularly suitable for mechanistic studies because their chemical and spectroscopic properties permit a wide range of techniques to be applied. The structures of many reaction intermediates have been established by IR spectroscopy of low-temperature matrices[2] or frozen hydrocarbon glasses.[3] Reaction pathways in solution have been followed by using a variety of transient spectroscopic techniques,[4] as well as by more conventional photochemical studies.

(1) (a) NIHE, Dublin. (b) University of Nottingham. (c) Trinity College.

(2) For a general reference to matrix isolation see, e.g.: Perutz, R. N. *Annu. Rep. Prog. Chem., Sect. C* **1985**, 157.

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Laser flash photolysis with UV/vis monitoring[5] and, more recently, with time-resolved IR spectroscopy[6] (TRIR) has been a particularly powerful technique for studying the reactions of coordinatively unsaturated metal carbonyls. Already fascinating chemistry has emerged, some fragments having the ability to coordinate species such as alkanes[5,7] or even xenon,[7,8] which normally would be considered inert.

We are particularly interested in the reactivity of photochemically generated metal carbonyl fragments. Much of our past work has centered on species containing group 6 metals. For example, we have investigated[5,8,9] the reactivity of $M(CO)_5$ (M = Cr, Mo, or W), the 16-electron fragments formed by UV photolysis of $M(CO)_6$. In inert solvents such as perfluoroalkanes, $M(CO)_5$ reacts with hydrocarbons (e.g. cyclohexane) at rates approaching the diffusion-controlled limit.[5] This implies that in most reactions $M(CO)_5$ does not exist as an unsaturated five-coordinate molecule but rather as a $M(CO)_5S$ complex, where the solvent S occupies the sixth coordination site as a weakly bound "token" ligand. Similar experiments have since shown that $M(CO)_5S$ is the only detectable species in hydrocarbon solution even on a picosecond time scale.[10]

In this paper, we report the results of laser flash photolysis of $CpMn(CO)_3$ (Cp = η^5-C_5H_5) in hydrocarbon solution at room temperature. We show how a combination of UV/vis monitoring and time-resolved IR spectroscopy (TRIR) can be used to probe the structure and reactivity of $CpMn(CO)_2$, the primary photoproduct. The $CpMn(CO)_2$ fragment is interesting not only because it is isoelectronic with $M(CO)_5$ but also because it is isostructural with the 17-electron radical $CpFe(CO)_2^{\bullet}$, which we have recently studied under similar conditions.[11]

Strohmeier and co-workers demonstrated[12] that the photolysis of $CpMn(CO)_3$ in fluid solution must proceed via $CpMn(CO)_2$ (eq 1). $CpMn(CO)_2$ has since been generated by UV photolysis of $CpMn(CO)_3$ in CH_4 matrices[13] at 20 K or hydrocarbon glasses[14,15] at 77 K. Prolonged UV irradiation also yields traces of CpMn(CO).[13,14] Recently, in a series of elegant experiments, $CpMn(CO)_2$ has been generated in frozen glasses doped with R_3SiH and activation parameters have been measured for the oxidative addition, which occurs when the glasses are melted.[15]

$$CpMn(CO)_3 \xrightarrow{h\nu} CpMn(CO)_2 + CO \quad (1)$$

Experimental Section

Apparatus: UV/Vis Experiments (TCD, Dublin, Ireland). The system used for this study consisted of a nanosecond kinetic spectrophotometer, with XeCl excimer laser excitation (308 nm) and a Xe-arc lamp for the monitoring source. The apparatus was arranged in the cross beam configuration,[16] and the time resolution of the detection system as used here was 50 ns. UV/vis spectra were recorded on a Pye-Unicam SP-200 or a Hewlett-Packard 8452A spectrophotometer.

Apparatus: Time-Resolved IR Experiments (Nottingham, U.K.). The TRIR spectrometer has recently been described in detail.[17] It is based on an XeCl excimer laser and a continuous-wave (CW) CO IR laser, line-tunable in steps of 4 cm^{-1}. Operation is similar to a conventional flash photolysis apparatus, with a risetime of ~1 μs. For each flash of the UV laser, transient changes in IR absorption are monitored at one IR wavelength. Between UV flashes, the sample cell (CaF_2 windows, 2-mm path length, evacuable flow system) is refilled, and the IR laser is tuned to a different IR wavelength. Once the whole of the required wavelength region has been covered, "point by point" IR spectra, corresponding to particular time delays after the UV flash, are constructed from the accumulated kinetic data. All IR data in this paper were collected as "single shots" without signal averaging. FT-IR spectra of stable compounds were recorded with a Nicolet MX-3600 interferometer.

Materials. The following materials were used without further purification: $CpMn(CO)_3$ (Strem Chemicals Inc.), PPh_3 (BDH), CO (BOC, research grade), Ar (Messer-Griesheim), *n*-heptane (Aldrich, HPLC grade), and ^{13}CO (92%, BOC Prochem). Cyclohexane (BDH, Spectrosol quality) was dried with molecular

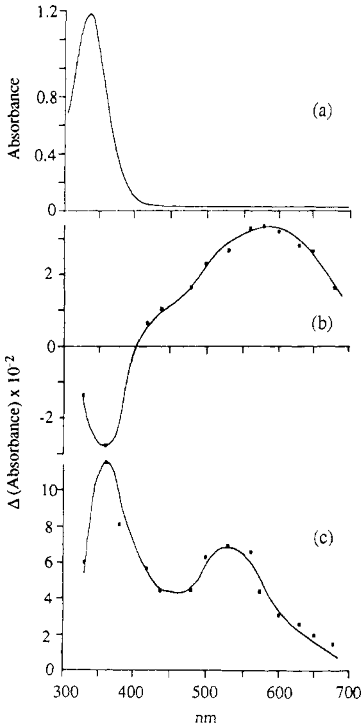

Figure 1. (a) UV/vis spectrum of $CpMn(CO)_3$ in cyclohexane solution (1.5×10^{-2} M, 1-cm path length). (b) UV/vis difference spectrum corresponding to a time delay of 5 μs after UV flash photolysis of $CpMn(CO)_3$; the positive band is assigned to $CpMn(CO)_2S$. (c) Difference spectrum corresponding to a delay of 850 μs after the flash; both bands are assigned to the dinuclear species $Cp_2Mn_2(CO)_5$. Note that uncertainty in the position of the band maxima is greater in the UV region than in the visible of the transient spectra.

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(18) IR data in *n*-heptane solution (assignment: 0, $CpMn(^{12}CO)_3$; 1, $CpMn(^{12}CO)_2(^{13}CO)$; 2, $CpMn(^{12}CO)(^{13}CO)_2$; 3, $CpMn(^{13}CO)_3$): 2029 cm^{-1} (0) 2017.7 cm^{-1} (1), 2004.2 cm^{-1} (2), 1982 cm^{-1} (3), 1947 cm^{-1} (0, 1), 1926 cm^{-1} (2), 1912.7 cm^{-1} (1), 1902 cm^{-1} (2, 3). Force Constants: k = 1575.3, k_i = 43.9 N m^{-1}.

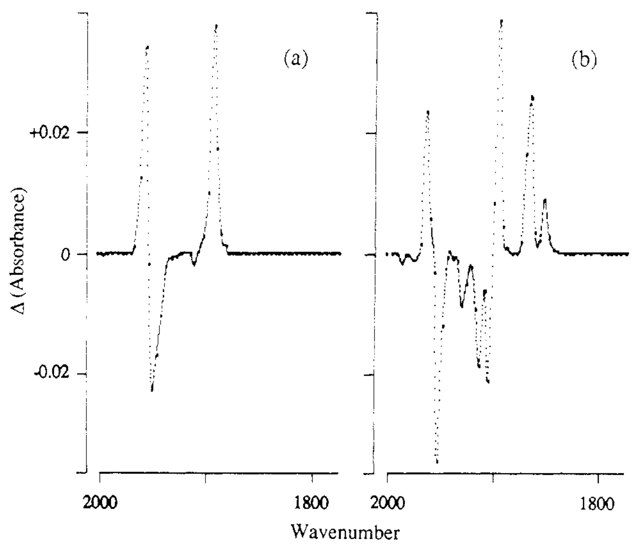

Figure 2. TRIR difference spectra corresponding to a time delay of 5 μs after UV flash photolysis of $CpMn(CO)_3$ in *n*-heptane solution (10^{-3} M): (a) natural abundance ^{13}CO and (b) sample 30% enriched with ^{13}CO. In both spectra the negative bands are those of $CpMn(CO)_3$ and the positive bands are assigned to $CpMn(CO)_2S$. Note that the heavier points are those measured experimentally and the lighter points have been inserted by computer interpolation.[17]

Table I. Observed Wavenumbers (cm^{-1}) of IR Bands of $CpMn(CO)_2S$ in *n*-Heptane Solution at Room Temperature and in Low-Temperature Solids

n-heptane 293 K[a]	CH_4 matrix 15 K[b]	hydrocarbon glasses 77 K[c]	77 K[d]	assignment ν(C=O)
1964	1961.4	1955	1950	$CpMn(^{12}CO)_2S$
1895	1892.8	1886	1880	$CpMn(^{12}CO)_2S$
1866 (1867)[e]				$CpMn(^{12}CO)(^{13}CO)S$
1853 (1852)[e]				$CpMn(^{13}CO)_2S$
				force const, N m^{-1}
1504	1501.6	1490	1481	k_{CO}
54	53.4	53	54	k_{int}

[a] This work. TRIR spectra (frequencies ±2 cm^{-1}). [b] Reference 13. [c] Reference 14. [d] Reference 15. [e] Calculated values in parentheses.

sieves before use. UV/vis experiments were carried out in cyclohexane solution and TRIR experiments in both cyclohexane and *n*-heptane, which is significantly more transparent than cyclohexane in the IR. All solutions were degassed prior to use, and the TRIR experiments were carried out under an atmosphere of Ar. $CpMn(CO)_3$ was enriched with ^{13}CO by UV photolysis (Pyrex filter) in *n*-heptane under 200-Torr pressure of ^{13}CO. The degree of ^{13}CO enrichment was estimated (~30%) from IR spectra.[18] The enriched sample of $CpMn(CO)_3$ was not isolated from the *n*-heptane solvent prior to use.

Results and Discussion

The UV/vis absorption spectrum of $CpMn(CO)_3$ is shown in Figure 1, together with transient spectra corresponding to time delays of 2 and 850 μs after laser flash photolysis in cyclohexane solution. The spectra demonstrate clearly that at least two transient species are formed.

Primary Photoproduct. Formation of $CpMn(CO)_2$. The spectrum of the first intermediate (Figure 1b) consists of a broad band with a maximum near 580 nm. This species is fully formed within the time resolution of the instrument (50 ns), and we have assigned this band to a $CpMn(CO)_2$ species. This assignment is supported by the corresponding TRIR spectrum (Figure 2a) which shows two bands at wavenumbers very close to those reported for $CpMn(CO)_2$ in CH_4 matrices[13] and hydrocarbon glasses;[14,15] see Table I. Furthermore, the TRIR spectrum obtained by photolysis of $CpMn(CO)_3$, partially enriched with ^{13}Co (Figure 2b), confirms that the spectrum arises from a dicarbonyl species with C–O stretching force constants almost identical with those derived from the low temperature spectra[13–15] of $CpMn(CO)_2$ (Table I).

Table II. Bimolecular Rate Constants (dm^3 mol^{-1} s^{-1}) for the Reaction of $CpMn(CO)_2S$ (S = *n*-Heptane and Cyclohexane) with Various Substrates at 295 K

substr	rate const[a]	solv	expt[b]
CO	3.4×10^5	cyclohexane	UV/vis
N_2	3.7×10^5	cyclohexane	UV/vis
$P(OMe)_3$[c]	7.1×10^6	*n*-heptane	TRIR
PPh_3[c]	5.3×10^6	cyclohexane	UV/vis
	1.1×10^7 (296 K)	*n*-heptane	TRIR
	4.2×10^7 (326 K)	*n*-heptane	TRIR
$CpMn(CO)_3$	1.1×10^6	cyclohexane	UV/vis
	1.3×10^6	cyclohexane	TRIR
	3.4×10^6 (295 K)	*n*-heptane	TRIR
	2.2×10^7 (325 K)	*n*-heptane	TRIR

[a] Rate constants are accurate to ±10%. [b] Technique used for the measurement; see Experimental Section. [c] These rate constants have been corrected to allow for the formation of $Cp_2Mn_2(CO)_5$.

Addition of carbon monoxide to the solution reduced the lifetime of the $CpMn(CO)_2$ species but had little effect on its overall yield. The rate constant for the reaction of the $CpMn(CO)_2$ with CO was determined by a comparison of the lifetime of the $CpMn(CO)_2$ in the presence and absence of CO. The value of 3.4×10^5 dm^3 mol^{-1} s^{-1}, obtained by this method, is about 10 times smaller than the rate constant reported for the reaction of $Cr(CO)_5$ with CO in cyclohexane.[5,19]

The rate constant for the reaction of $CpMn(CO)_2$ with N_2 is similar to that for reaction with CO, while those for reaction with $P(OMe)_3$ and PPh_3 are both somewhat larger; see Table II. Measurements at different temperatures show that the reaction of $CpMn(CO)_2$ with PPh_3 has a significant activation barrier leading to formation the known compound $CpMn(CO)_2PPh_3$.[20] Thus, it is unlikely that $CpMn(CO)_2$ exists as a coordinatively unsaturated species in hydrocarbon solvents. As in the case of $Cr(CO)_5$, a molecule of solvent is probably acting as a weakly coordinated token ligand to give a $CpMn(CO)_2S$ species. This conclusion is further supported by the contrast with the reactivity of $CpFe(CO)_2^{\bullet}$; the reaction of $CpFe(CO)_2^{\bullet}$ with $P(OMe)_3$ proceeds with a bimolecular rate constant,[11] ca. 10^9 dm^3 mol^{-1} s^{-1}, over 100 times greater than the corresponding rate constant for $CpMn(CO)_2S$. Presumably $CpFe(CO)_2^{\bullet}$, a 17-electron species, is not solvated under these conditions. Thus, the primary photochemical reactions of $CpMn(CO)_3$ are summarized in eq 2. Previous

$$CpMn(CO)_3 \xrightarrow{h\nu} CpMn(CO)_2 + CO \xrightarrow{+S} CpMn(CO)_2S \quad (2)$$

workers[14] have recognized that an estimate of the OC–Mn–CO bond angle can be obtained from the relative intensities of the two IR bands of $CpMn(CO)_2$ (eq 3, where

$$[\tan(\theta/2)]^2 = I_a/I_s \quad (3)$$

θ is the bond angle, I_s is the intensity of the symmetric (high wavenumber) band, and I_a is the intensity of antisymmetric (low wavenumber) band). From the TRIR

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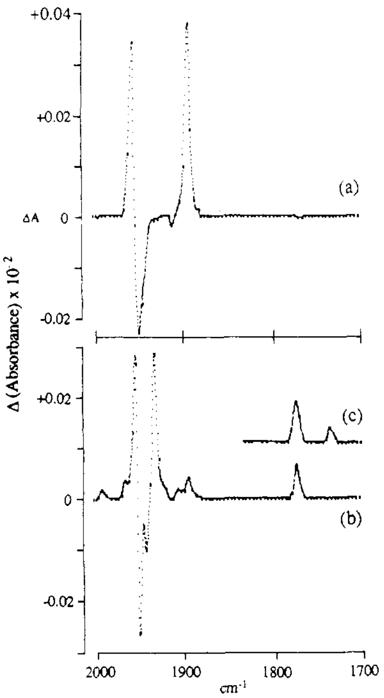


Figure 3. TRIR difference spectra obtained by UV flash photolysis of $CpMn(CO)_3$ in *n*-heptane solution (10^{-3} M) under an Ar atmosphere: (a) 5 μs after the UV flash (negative bands are those of $CpMn(CO)_3$ and positive bands those of $CpMn(CO)_2S$); (b) 1500 μs after the UV flash (the positive bands are now assigned to $Cp_2Mn_2(CO)_5$); (c) part of the spectrum after 1500 μs, obtained with a sample of $CpMn(CO)_3$, 30% enriched with ^{13}CO.

Table III. IR Data for $Cp_2Mn_2(CO)_5$ and Related Species in Hydrocarbon Solution at Room Temperature

compound	$\nu(C{=}O)_{bridge}$	$\nu(C{=}O)_{terminal}$
$Cp_2Mn_2(CO)_5$[a]	1777, 1740[b]	1993, 1955,[c] 1934,[c] 1907
$[CpFe(CO)_2]_2$[d]	1792	2004, 1960
$Cp_2Co_2(CO)_3$[e]	1812	1963
$Cp_2Fe_2(\mu\text{-}CO)_3$[d]	1823	
$Cp^*_2Fe_2(\mu\text{-}CO)_3$[f]	1790	
$Cp^*_2Mn_2(\mu\text{-}CO)_3$[g]	1785	

[a] This work; TRIR spectra, *n*-heptane solution, ±2 cm^{-1}. [b] ^{13}CO satellite, calculated 1737 cm^{-1}. [c] The maxima of these bands may be affected by partial overlap with the band of $CpMn(CO)_3$; see Figure 3b. [d] Reference 17; cyclohexane solution. [e] Reference 31; methylcyclohexane solution. [f] Reference 32; TRIR spectrum, cyclohexane solution. [g] Reference 28; *n*-hexane solution.

spectra (Figure 2), the ratio I_a/I_s is 1.05 ± 0.1, which gives a bond angle of 91.4° (+1.5, −2.9°). This angle is close to those found crystallographically for the parent compound, $CpMn(CO)_3$ (91–94°)[14] and $CpMn(CO)_2PPh_3$ (92.4°)[20] and similar[21] to that which can be calculated for $CpMn(CO)_2$ (92.4°) from published data[15] on the intensity of IR bands in hydrocarbon glasses. Thus loss of CO from $CpMn(CO)_3$ does not appear to have a significant effect on the C–M–C bond angle of the $CpMn(CO)_2$ fragment, possibly as a result of complexation by the solvent.

Formation of Dinuclear Species. Figure 1c illustrates the UV/vis spectrum of a secondary relatively long-lived product ($t_{1/2}$ = ca. 10 ms) which is formed when the photolysis of $CpMn(CO)_3$ is carried out in the absence of any added reagents. The spectrum has two maxima, at 530 nm and in the region of 360 nm, and the ratio of the

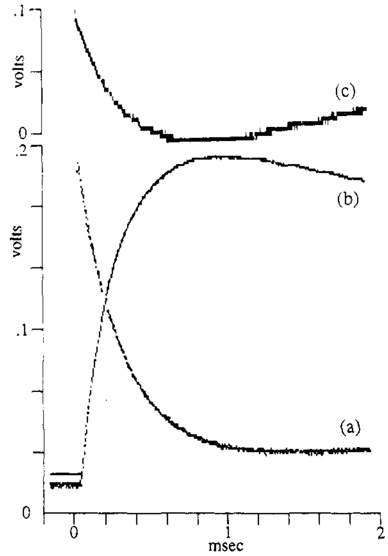


Figure 4. TRIR kinetic traces obtained by UV flash photolysis of $CpMn(CO)_3$ in *n*-heptane solution (10^{-3} M) under an Ar atmosphere, showing (a) the instantaneous formation and slower decay of $CpMn(CO)_2S$ (1894.5 cm^{-1}), (b) the concomitant formation of $Cp_2Mn_2(CO)_5$ (1777 cm^{-1}), and (c) the thermal depletion after the UV flash of $CpMn(CO)_3$ (1947 cm^{-1}). (Note that this depletion is less intense than expected because of partial overlap with the bands of $Cp_2Mn_2(CO)_5$; see Figure 3b.) The traces are shown as voltages on the IR detection system, which are directly related to the percent change in transmittance. The voltage corresponding to a change in transmittance of 100% are (a) 2.69 V, (b) 7.88 V, and (c) 3.14 V.

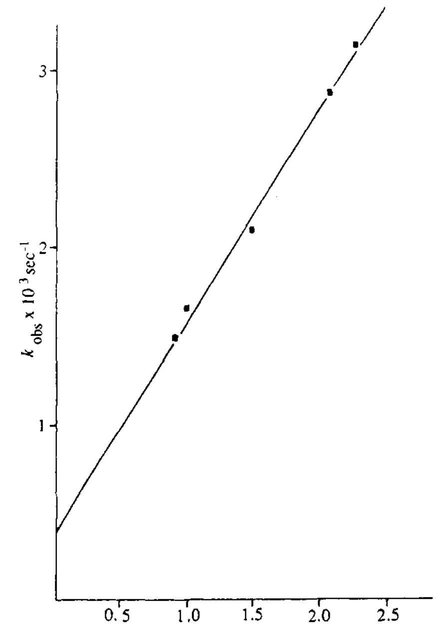


Figure 5. Plot from UV/vis experiments, showing the effect of the initial concentration of $CpMn(CO)_3$ on the value of the pseudo-first-order rate constant for the disappearance of $CpMn(CO)_2S$ in cyclohexane solution.

extinction coefficients[22] at the two maxima was found to be constant [1 (530 nm):1.7 (360 nm)], with varying $CpMn(CO)_3$ concentration. This suggests that the same species is responsible for both bands.

(21) Braterman and co-workers deduced[14] a significantly larger bond angle, 100°, for $CpMn(CO)_2$ in a frozen hydrocarbon glass. The differences between the IR data in ref 14 and 15 may merely reflect the improvement in spectrometer sensitivity for measuring IR band intensities.

(22) The value of the extinction of the band at 360 nm is clearly affected by overlap with the absorption band of $CpMn(CO)_3$ (see Figure 1a). Any assignment of this band in the photoproduct must necessarily be tentative, but this region of the spectrum (~360 nm) is often associated with $\sigma \rightarrow \sigma^*$ transitions of dinuclear species with M–M bonds.[4]

The corresponding TRIR spectrum (Figure 3b) shows that this photoproduct has at least four ν(CO) bands different from those of $CpMn(CO)_2S$. Most significantly, there is a band at 1777 cm^{-1} in a region characteristic of bridging CO groups in polynuclear species. ^{13}CO enrichment shows that this absorption arises from a single bridging CO group[23] (inset spectrum, Figure 3c). The IR data, summarized in Table III, are consistent with a symmetrically bridging CO group, and it is unlikely that the product contains an isocarbonyl linkage, M–CO–M.

Kinetic traces both from TRIR (Figure 4) and from UV/vis experiments (not illustrated) showed that this polynuclear product is formed by the reaction of $CpMn(CO)_2S$ with unphotolyzed $CpMn(CO)_3$. Since each flash of the UV laser converts only a small proportion of $CpMn(CO)_3$ into the photoproduct $CpMn(CO)_2S$, the reaction of $CpMn(CO)_2S$ with $CpMn(CO)_3$ follows pseudo-first-order kinetics. The rate of this reaction was found to increase linearly with increasing $CpMn(CO)_3$ concentration (Figure 5), and the gradient of the plot provides an estimate of the second-order rate constant for the process,[24] 1.1×10^6 dm^3 mol^{-1} s^{-1}, at 295 K.

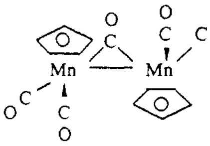
The yield of the product was significantly reduced by the addition of CO and was completely suppressed by PPh_3 (0.05 M), indicating that CO or PPh_3 compete with $CpMn(CO)_3$ for the available $CpMn(CO)_2S$ intermediate. Thus all of the evidence, both spectroscopic and kinetic, points to the formation of a dinuclear compound (eq 4).

$$CpMn(CO)_2S + CpMn(CO)_3 \rightarrow CpMn(CO)_2(\mu\text{-}CO)Mn(CO)_2Cp \quad (4)$$

$$CpMn(CO)_2S + PPh_3 \rightarrow CpMn(CO)_2PPh_3 \quad (5)$$

Kinetic data, over the temperature range 296–331 K, have been obtained from TRIR measurements on $CpMn(CO)_2S$ in n-heptane solution with and without added PPh_3. However, the competitive nature of the reactions in eq 4 and 5 makes it difficult to separate completely the activation parameters for the two processes.[25] Nevertheless, even the limited data given in Table II suggest that the activation energy for formation of $Cp_2Mn_2(CO)_5$ (eq 4) may be significantly higher than that for reaction with PPh_3 (eq 5).

The IR spectra of $Cp_2Mn_2(CO)_5$ are consistent with structure 1, but there are insufficient data to rule out other possibilities. $Cp_2Mn_2(CO)_5$ is thermally unstable with a



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lifetime of ca. 0.1 s at room temperature. The route of its decompositon was not investigated in detail. Although related dinuclear compounds such as $Cp^*Mn(\mu\text{-}CO)_3MnCp^*$ ($Cp^* = \eta^5\text{-}C_5Me_5$) are known,[28] this is the first report[29] of $CpMn(CO)_2(\mu\text{-}CO)Mn(CO)_2Cp$. Its formation, however, is reminiscent of the photochemical synthesis[30] of $CpCo(CO)(\mu\text{-}CO)Co(CO)Cp$ from $CpCo(CO)_2$, which presumably involves a reaction similar to eq 6.

$$CpCo(CO)S + CpCo(CO)_2 \rightarrow CpCo(CO)(\mu\text{-}CO)Co(CO)Cp \quad (6)$$

Conclusions

In this paper, we have shown how the combination of UV/vis detection and time-resolved IR spectroscopy can be a powerful probe in the study of organometallic reaction mechanisms. These flash photolysis techniques can extend the information about reaction intermediates beyond that already available from low-temperature experiments.

UV photolysis of $CpMn(CO)_3$ yields $CpMn(CO)_2$ as the primary photoproduct, and, in alkane solution, $CpMn(CO)_2$ has a significant activation barrier for substitution reactions. This is perhaps surprising for what is, at least formally, an unsaturated reaction intermediate. However, $CpMn(CO)_2$ is almost certainly solvated in alkane solution and the activation barrier probably involves the dissociation of the token solvent ligand S (eq 7).

$$CpMn(CO)_2S \rightarrow CpMn(CO)_2 + S \quad (7)$$

The rate constants for reactions of $CpMn(CO)_2S$ are rather lower than corresponding values[5,18,19] for $Cr(CO)_5S$. This is consistent with the known bonding properties of $Mn(CO)_x$ moieties which, for example, form stable complexes with agostic C–H interactions[33] while $Cr(CO)_5$ does not. However, just as in the case of $Cr(CO)_5S$,[5,19] rate constants for $CpMn(CO)_2S$ are greater in n-heptane than in cyclohexane solution, suggesting that n-heptane may coordinate more weakly to the metal centers.

In the absence of added reagents, $CpMn(CO)_2S$ reacts with $CpMn(CO)_3$ in solution to form a dinuclear compound, $Cp_2Mn_2(CO)_5$. The reaction of a photoproduct with unphotolyzed starting material has already been observed[5] in the photolysis of $M(CO)_6$ in solution. A similar reaction between $Fe(CO)_4$ and $Fe(CO)_5$ has also been reported from gas-phase TRIR studies[6] on $Fe(CO)_5$. It is our belief that such processes may prove to be relatively widespread in the photochemistry of organometallic compounds.

(23) We are, of course, making the assumption that there would be coupling between the bridging CO groups, for a molecule containing more than one CO bridge. Such an assumption seems reasonable in the light of those multiply bridged molecules that have been analyzed in detail, e.g., $Fe_2(CO)_{9\&8}$ (Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 3597) or $Cp_2Fe_2(CO)_3$.[3]

(24) Extrapolation of the plot in Figure 5 to zero concentration of $CpMn(CO)_3$ indicates that there is a further minor route for the decay of the $CpMn(CO)_2S$ species. The reaction of the $CpMn(CO)_2S$ with the photoejected CO may be partly responsible for a this intercept. However, UV/vis experiments show that the presence of water in the system reduced the lifetime of the $CpMn(CO)_2S$. This suggests that $CpMn(CO)_2S$ reacts with water in a manner similar to that observed in group 6 systems[5,19] to form a $CpMn(CO)_2(H_2O)$ complex, as previously observed in matrix-isolation experiments.[14]

(25) Ignoring the competitive reactions (i.e. assuming that $k = k_{obsd}/[X]$, where [X] is the concentration of PPh_3 or $CpMn(CO)_3$, we obtain activation parameters for the reacton of $CpMn(CO)_2S$ with PPh_3 ($\Delta H^* = 35 \pm 3$ kJ mol^{-1}, $\Delta S^* = 5 \pm 8$ J mol^{-1} K^{-1}) and with $CpMn(CO)_3$ ($\Delta H^* = 49 \pm 4$ kJ mol^{-1}, $\Delta S^* = +42 \pm 16$ J mol^{-1} K^{-1}). The value, 35 kJ mol^{-1}, for reaction with PPh_3 is close to the range, 28–33 kJ mol^{-1}, found[15] for the low-temperature oxidative addition of a variety of R_3SiH compounds to $CpMn(CO)_2$. This suggests that the rate-determining step may be similar in the two reactions and that the activation energy for the formation of $Cp_2Mn_2(CO)_5$ may be significantly higher than for oxidative addition. It is tempting to extrapolate these results to other metals. If our observation were generally true, it might explain why some molecules, such as $CpRh(CO)_2$, can activate C–H bonds in low-temperature photochemical reactions[26] but form dinuclear species at ambient temperature.[27]

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Registry No. 1, 110638-28-3; $CpMn(CO)_3$, 12079-65-1; $CpMn(CO)_2$, 38548-46-8; CO, 630-08-0; N_2, 7727-37-9; $P(OMe)_3$, 121-45-9; PPh_3, 603-35-0; *n*-heptane, 142-82-5; cyclohexane, 110-82-7.

Communications

Redox Systems Involving Stable 17-Electron Iron(III)–Methyl Complexes[1]

Janet Morrow, Daniel Catheline,[2] Marie-Hélène Desbois, Juan-Manuel Manriquez,[†] Jaime Ruiz, and Didier Astruc*

Laboratoire de Chimie Organique et Organométallique UA CNRS No. 35, Université de Bordeaux I 351 Cours de la Libération, 33405 Talence, France

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Summary: The electron-rich, thermally stable σ-methyl complexes $[Fe^{II}Cp^*(CO)(P)(CH_3)]$ (P = η^1-dppe, **1**) and $[Fe^{II}Cp^*P_2(CH_3)]$ (P = $P(OMe)_3$, **5**, or P_2 = η^2-dppe, **6**) have been synthesized and oxidized to stable 17-electron iron(III)–methyl isostructural cations by using ferricinium or trityl salts; the latter do not undergo hydrogen atom abstraction, migratory CO insertion, ligand exchange, and Fe–CH_3 cleavage under ambient conditions.

Although compounds with an element–methyl bond were first found 150 years ago,[3] the finding of stable transition-metal–alkyl complexes was considerably delayed, essentially until the relatively recent recognition by Wilkinson of the kinetic basis for instability.[4,5] However, direct homolytic scission of the alkyl–metal bond is an important decomposition pathway in the absence of a closed valence shell.[6] Thus, the isolation of stable 17-electron complexes with a σ-alkyl ligand requires bulkyl alkyls (or aryls)[7] and such exemples with a methyl ligand are scarce.[7d]

We report here the first results of our strategy aimed at the stabilization of the metal–methyl bond in 17-electron complexes by using sterically protecting ancillary ligands.

The complexes $[Fe^{II}Cp^*(CO)(P)(CH_3)]$ (**1**, P = η^1-dppe, and **2**, P = PPh_3) were synthesized by using the classical route shown in eq 1[8] (Cp* = η^5-C_5Me_5 throughout the text).

$$FeCp^*(CO)_2(CH_3) \xrightarrow[P,\ 1\ h]{h\nu\ (UV),\ toluene} FeCp^*(CO)(P)(CH_3) \quad \mathbf{1},\ P = \eta^1\text{-dppe};\ \mathbf{2},\ P = PPh_3 \tag{1}$$

The new complex **1**[9] shows two signals in the ^{31}P NMR spectrum, at +76.4 ppm for the coordinated phosphine and at −13.2 ppm for the free phosphine (vs 85% H_3PO_4). It shows a reversible one-electron wave at E_a = −0.3 V vs SCE in its cyclic voltammogram (DMF, $Bu_4N^+ClO_4^-$, Pt, 20 °C). It is oxidized by a stoichiometric amount of ferricinium hexafluorophosphate in THF; after recrystallization from acetone/ether, a 90% yield of the orange Fe^{III} complex **3** is obtained (eq 2).

$$\underset{\mathbf{1}}{Fe^{II}Cp^*(CO)(P)(CH_3)} \xrightarrow[THF,\ 30\ min,\ 20\ ^\circ C]{Cp_2Fe^+PF_6^-} \underset{\mathbf{3},\ P = \eta^1\text{-dppe}}{[Fe^{III}Cp^*(CO)(P)(CH_3)]^+PF_6^-} \tag{2}$$

Complex **3** shows ν_{CO} at 1950 cm^{-1} (Nujol) in the infrared spectrum, new Mössbauer parameters characteristic of Fe^{III} (IS = 0.55 mms^{-1} vs Fe, QS = 0.62 mm s^{-1}, 77 K), and satisfactory elemental analyses.[10] On the other hand,

† Present address: Universidad Tecnica Federico Santa Maria Casilla 110-V, Valparaiso, Chile.

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(9) Complex 1: a 0.79-g (3-mmol) sample of $[Fe(C_5Me_5)(CO)_2CH_3]$ was irradiated in 150 mL of toluene by using a high-pressure Hanover mercury lamp in the presence of 1.23 g of 1.2-bis(diphenylphosphino)-ethane for 1 h at 30 °C. After the solvent was removed in vacuo, the solid residue was extracted with 3 × 30 mL of pentane; air-stable red crystals of 1 were obtained upon cooling this solution down to −80 °C (1.23 g, 65% yield): ^1H NMR ($CDCl_3$, δ vs TMS) 7.53 (m, 20 H, Ph), 3.60 (m, 4 H, CH_2), 1.40 (s, 15 h, C_5Me_5), −0.60 (d, 3 H, CH_3, $^3J_{PH}$ = 20 Hz); ^{13}C (C_6D_6, δ vs TMS) 188.3 (CO), 134.0, 133.9, 133.7, 133.4, 133.2, 132.7 (coordinated PPh_2), 128.7, 128.6, 127.7, 126.7, 126.30 (noncoordinated PPh_2), 85.5 (C_5Me_5), 29.7 (CH_2), 10.5 (C_5Me_5), −14.9 (CH_3); infrared (Nujol) 1900 cm^{-1} (ν_{CO}, large). Complex 2 is obtained by using the same procedure.

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