$\text{Co}_2(\text{CO})_8$ results in the formation of carbide-containing clusters. The ylide moiety is retained in a competing reaction as a bridge to a pendant metal atom. Similar instability toward cluster building is observed for CCO ligands in anionic clusters. Trimetallic ketenylidene-containing compounds are established precursors for higher nuclearity carbide clusters.[23] However, CCO ligands have not yet been reported for clusters with more than three metal atoms. The synthesis of $[\text{PPN}][\text{Fe}_2\text{Co(CO)}_9(\text{CCO})]$ occurs by a metal substitution reaction which is similar to eq 3.[5]

Acknowledgment. This research was supported by the NSF Synthetic Inorganic-Organometallic Chemistry Program.

Registry No. **1**, 119145-85-6; **2**, 119145-86-7; **3**, 119182-71-7; dmpe, 23936-60-9; $[\text{PPN}][\text{Fe}_2\text{CO(CO)}_9(\text{CCO})]$, 88657-64-1; $\text{Co}_2(\text{CO})_8$, 10210-68-1; CO, 7440-48-4; Fe, 7439-89-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles not cited in the text for **3** (3 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Temperature Dependence of the Oxidative Addition of Triethylsilane to Photochemically Generated $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2$

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Received September 19, 1988

Near-UV irradiation of $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_3$ in alkane glasses leads to the loss of CO to form a 16e dicarbonyl species. If the photolysis is effected in alkane solution containing Et_3SiH or in neat Et_3SiH, the dicarbonyl thermally reacts with the silane generating $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2\text{H(SiEt}_3)$. The rate of the reaction is first order in $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2$ and depends on temperature. The $\Delta H^\ddagger$ is 36 ± 4 kJ mol^{-1} and the $\Delta S^\ddagger$ is −140 ± 15 J mol^{-1} K^{-1} from rate measurements in the range 190–240 K. The significant finding is that the value of $\Delta H^\ddagger$ is about the same as that found for the reaction of Et_3SiH with photogenerated $(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_2$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{Mn(CO)}_2$. Thus, for the series $(\eta^5\text{-C}_5\text{R}_5)\text{Mn(CO)}_2$ (R = Cl, H, Me) variation in $\Delta S^\ddagger$, not $\Delta H^\ddagger$, is the source of the variation in the reaction rate with Et_3SiH. For R = Cl the reaction rate constant at a given temperature is extrapolated to be 10^7 times smaller than the reaction rate constant for R = Me.

We wish to report activation parameters for the oxidative addition of Et_3SiH to photogenerated $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2$ (eq 1 and 2). A previous study on the oxidative

$$(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_3 \xrightarrow[-\text{CO}]{h\nu} (\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2 \tag{1}$$

$$(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2 \xrightarrow{\text{Et}_3\text{SiH}} (\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2\text{H(SiEt}_3) \tag{2}$$

addition of Et_3SiH to $(\eta^5\text{-C}_5\text{R}_5)\text{Mn(CO)}_3$ (R = H, Me) shows that $\Delta H^\ddagger$ values for the two complexes are the same and that the difference in the rate of reaction is governed by the difference in $\Delta S^\ddagger$.[1] Our new work concerns the oxidative addition to a Mn center with an electron-withdrawing cyclopentadienyl ring, C_5Cl_5.[2] Even though the rate for oxidative addition is found to be very slow compared to the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{Me}_5$ species, we find $\Delta H^\ddagger$ to be nearly the same for all $\eta^5\text{-C}_5\text{R}_5$ complexes (R = Cl, H, Me).

The photochemistry of $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_3$ has not been detailed, but there is a considerable literature showing that $(\eta^5\text{-C}_5\text{R}_5)\text{Mn(CO)}_3$ complexes are photosensitive with respect to CO loss (eq 1).[1,3–7] Our new findings are in accord with CO loss as the only photoreaction of $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_3$. We have used low-temperature FTIR to quantitatively measure the rate of the thermal process represented by eq 2 under conditions where back reaction according to eq 3 is not competitive.

$$(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_2 \xrightarrow{\text{CO}} (\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_3 \tag{3}$$

Experimental Section

Spectroscopy. IR spectra were recorded on a Nicolet 60SX or 170SX Fourier Transform spectrometer. Solutions of $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn(CO)}_3$ were contained in cells with CaF_2 windows. The low-temperature FTIR spectra were recorded with the cell mounted in a Specac Model P/N 21000 Dewar assembly, using a Neslab cryocool immersion cooler Model CC-100II and a Haake Model FS circulator. The temperature of the cell was monitored by using a Cu–constantan thermocouple in contact with the inner window of the cell. NMR spectra were recorded on a Varian

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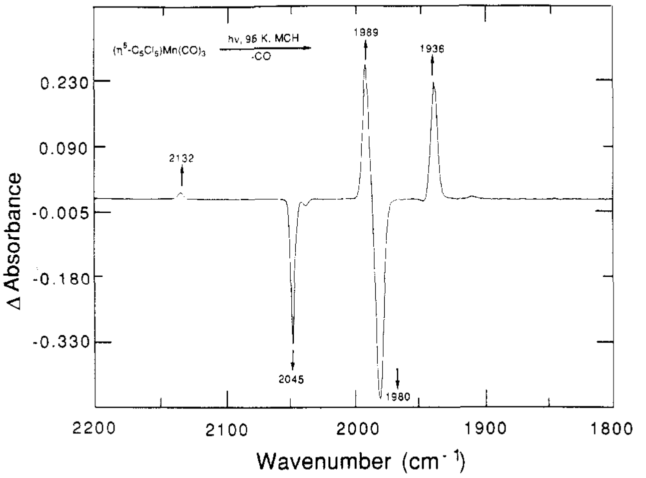

Figure 1. IR spectral changes accompanying near-UV irradiation of (η^5-C_5Cl_5)Mn(CO)$_3$ in a MCH matrix at 95 K. The negative bands at 2045 and 1980 cm^{-1} correspond to consumption of the starting material. The positive band at 2132 cm^{-1} corresponds to free CO, and the bands at 1989 and 1936 cm^{-1} are for (η^5-C_5Cl_5)Mn(CO)$_2$.

XL300 or a Bruker WM270 Fourier transform spectrometer. Mass spectra were recorded on a Finnigan Mat system 8200. UV–vis spectra were recorded on a Cary-17 spectrophotometer or a HP 8451A diode array spectrometer.

Photochemical Procedures. Irradiations were effected with a Bausch and Lomb SP200 high-pressure mercury lamp filtered by a 10-cm water filter with quartz windows. Quantum yields were measured at 298 K by using a Hanovia medium-pressure Hg lamp with the appropriate combination of glass and solution filters to isolate the 366-nm emission. Light intensities were typically 10^{-7} ein/min as measured by ferrioxalate actinometry.[8]

Materials. Et_3SiH (Petrarch) was freshly distilled under Ar. Methylcyclohexane (MCH) was distilled from sodium under Ar and stored over 3-Å molecular sieves. MCH-d_{14} was purchased from Cambridge Isotopes Laboratories and used without further purification. PPh_3 (Fluka) was recrystallized from dry EtOH and dried in vacuo.

(η^5-C_5Cl_5)Mn(CO)$_3$ was prepared by a previously reported procedure[2] and recrystallized twice from pentane before use. ^{13}C NMR ($CDCl_3$): 220.1, 94.69 ppm. Elemental Anal. (Schwarzkopf Microanalytical Laboratories) Calcd (Found): C, 25.54 (25.36); H, 0.00 (<0.06); Cl, 47.11 (47.02). (η^5-C_5Cl_5)Mn(CO)$_2$PPh$_3$ was prepared by irradiation of (η^5-C_5Cl_5)Mn(CO)$_3$ (0.20 g, 5.3 × 10^{-4} mol) and PPh_3 (0.37 g, 1.4 × 10^{-3} mol) in 30.0 mL of MCH. The solution was purged continuously with Ar to remove the photogenerated CO. The irradiation was continued until more than 90% of (η^5-C_5Cl_5)Mn(CO)$_3$ was consumed as monitored by FTIR. The solvent was then evaporated and the product chromatographed (silica gel, hexanes) to give recovered (η^5-C_5Cl_5)Mn(CO)$_3$ and yellow crystals. TLC showed the yellow crystals contained PPh_3 and (η^5-C_5Cl_5)Mn(CO)$_2$PPh$_3$. Sublimation removed the PPh_3 leaving pure (η^5-C_5Cl_5)Mn(CO)$_2$PPh$_3$ in 46% yield. ^{1}H NMR (CD_2Cl_2): 7.37 ppm (m, br). ^{13}C NMR (CD_2Cl_2): 93.89, 128.45, 128.55, 130.43, 133.46, 133.59, 133.73, 134.02 ppm. Exact mass: found, 607.8632 ± 0.0021; calcd, 607.8633.

^{1}H NMR spectra of (η^5-C_5Cl_5)Mn(CO)$_2$H(SiEt$_3$) were recorded for samples prepared by photolysis of a sample of (η^5-C_5Cl_5)Mn(CO)$_3$ in 1.0 mL of Et_3SiH/MCH-d_{14} (1:8). The solution was purged with Ar and photolyzed in a 5-mm NMR tube with a high-pressure Hg lamp for 5 min. The NMR spectrum was then recorded at room temperature on a Varian XL300 spectrometer. A new resonance at −12.2 ppm was observed and is attributed to the Mn–H resonance.[9]

Kinetic Measurements. A typical kinetic measurement was done as follows. A deoxygenated Et_3SiH solution of (η^5-C_5Cl_5)Mn(CO)$_3$ (∼1 × 10^{-4} M) was loaded into a 0.2-mm path length IR cell and cooled to the desired temperature. The sample was then photolyzed for a time much less than $t_{1/2}$ for the reaction. FTIR spectra were then recorded as a function of time in the dark to quantitatively monitor the consumption of (η^5-C_5Cl_5)Mn(CO)$_2$ and the formation of (η^5-C_5Cl_5)Mn(CO)$_2$H(SiEt$_3$). The reaction was monitored for more than 3 half-lives in all cases.

Table I. Spectroscopic Data for Relevant Compounds

compd[a]	IR ν_{CO} (ϵ or rel O.D.)[b]	UV–vis (ϵ)[c]
(η^5-C_5Cl_5)Mn(CO)$_3$	1980 (10100), 2045 (5800)	356 (800), 220 (3000)
(η^5-C_5Cl_5)Mn(CO)$_2$[d]	1936 (*1*), 1989 (*1.1*)	
(η^5-C_5Cl_5)Mn(CO)$_2$(C_2H_4)	1955 (*1*), 2001 (*1*)	
(η^5-C_5Cl_5)Mn(CO)$_2$(N_2)[e]	1967 (*1.1*), 2009 (*1*)	
(η^5-C_5Cl_5)Mn(CO)$_2$H(SiEt$_3$)	1966 (*1.2*), 2014 (*1*)	
(η^5-C_5Cl_5)Mn(CO)$_2$(PPh$_3$)	1923.5 (4600), 1972 (4600)	380, 230
(η^5-C_5H_5)Mn(CO)$_3$[f]	1947, 2028	332, 216
(η^5-C_5H_5)Mn(CO)$_2$[f]	1883, 1952	
(η^5-C_5H_5)Mn(CO)$_2$H(SiEt$_3$)[f]	1914, 1977	
(η^5-C_5Me_5)Mn(CO)$_3$[f]	1927, 2009	332, 242
(η^5-C_5Me_5)Mn(CO)$_2$[f]	1866, 1932	
(η^5-C_5Me_5)Mn(CO)$_2$H(SiEt$_3$)[f]	1888, 1948	

[a] All data recorded in MCH solution at 295 K except where noted. [b] Band positions in cm^{-1}. Extinction coefficients are in L mol^{-1} cm^{-1}. Italicized entries are relative extinction coefficients. [c] Band positions in nm. Extinction coefficients are in L mol^{-1} cm^{-1}. [d] Recorded in MCH glass at 95 K. [e] ν_{N-N} at 2197 cm^{-1}. [f] Reference 1.

Results and Discussion

Photochemistry of (η^5-C_5Cl_5)Mn(CO)$_3$. Figure 1 shows FTIR spectral changes accompanying near-UV photolysis of ∼1 mM (η^5-C_5Cl_5)Mn(CO)$_3$ at 95 K in a MCH glass. The two negative bands correspond to consumption of starting material, while the band at 2132 cm^{-1} is due to uncomplexed CO. From the extinction coefficient for the free CO[10] we calculate that 1.00 ± 0.06 molecules of CO is produced for every (η^5-C_5Cl_5)Mn(CO)$_3$ consumed, consistent with photoreaction according to eq 1. The two new bands at 1936 and 1989 cm^{-1} are assigned to the 16e (η^5-C_5Cl_5)Mn(CO)$_2$. Warming the sample in the dark to 298 K results in quantitative regeneration of the starting material, consistent with back reaction according to eq 3. The IR spectrum of (η^5-C_5Cl_5)Mn(CO)$_2$ shows a pair of bands in position and relative intensity that suggests no unusual interaction with a Cl atom on the C_5Cl_5 ring, as deduced by comparison with the R = H and Me analogues.

If the (η^5-C_5Cl_5)Mn(CO)$_2$ is photogenerated in a MCH matrix that contains a 2e donor ligand, L, such as PPh_3, C_2H_4, or N_2, the corresponding (η^5-C_5Cl_5)Mn(CO)$_2$L complex is formed upon warming the sample (eq 4). Table

$$(\eta^5\text{-}C_5Cl_5)Mn(CO)_2 \xrightarrow{L} (\eta^5\text{-}C_5Cl_5)Mn(CO)_2L \quad (4)$$

I lists spectroscopic data for the relevant compounds. Photolysis of (η^5-C_5Cl_5)Mn(CO)$_3$ at 298 K in alkane solution containing 0.1 M PPh_3 similarly leads only to the formation of (η^5-C_5Cl_5)Mn(CO)$_2$PPh$_3$ in the initial stages of the reaction with a quantum yield of 0.32 for 366-nm irradiation. This is expected chemistry on the basis of photosubstitution studies of the related (η^5-C_5H_5)Mn(CO)$_3$.[3,4]

Et_3SiH Oxidative Addition Kinetics. Near-UV photolysis of (η^5-C_5Cl_5)Mn(CO)$_3$ in neat Et_3SiH or alkane containing Et_3SiH at 298 K results in rapid reaction giving

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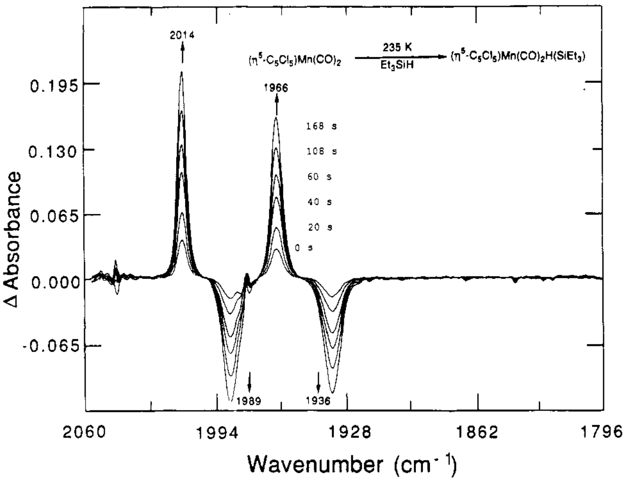

Figure 2. IR spectral changes accompanying the thermal reaction between $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ and Et_3SiH at 235 K. The negative bands at 1989 and 1936 cm^{-1} are due to the consumption of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$, and the positive bands at 2014 and 1966 cm^{-1} correspond to the growth of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$.

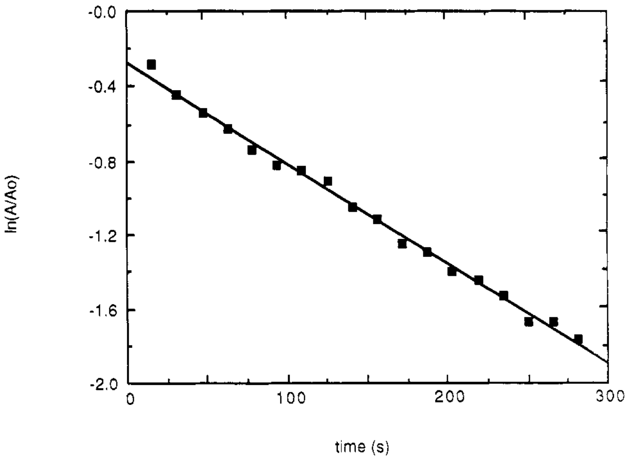

Figure 3. Rate plot for the appearance of the $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$ for reaction at 235 K.

Table II. Rate Constants for Reaction of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ with Et_3SiH

$[Et_3SiH]$, M	T, K	k, $M^{-1}\ s^{-1}$ (±10%)
6.3	193	2.52×10^{-5}
6.3	200	5.46×10^{-5}
6.3	201	3.16×10^{-5}
6.3	202	5.89×10^{-5}
6.3	203	4.30×10^{-5}
6.3	203	1.31×10^{-5}
6.3	210	9.43×10^{-5}
6.3	220	4.71×10^{-4}
6.3	227	6.51×10^{-4}
6.3	229	7.78×10^{-4}
6.3	233	9.63×10^{-4}
6.3	233	1.52×10^{-3}
6.3	235	1.47×10^{-3}

Table III. Activation Parameters for Reaction of 16e $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ with Et_3SiH

complex	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$ J $mol^{-1}\ K^{-1}$
$(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$	36 ± 4	−140 ± 15
$(\eta^5\text{-}C_5H_5)Mn(CO)_2{}^a$	30 ± 4	−28 ± 10
$(\eta^5\text{-}C_5Me_5)Mn(CO)_2{}^a$	31 ± 4	16 ± 30

^{a}Reference 1.

a product having a two-band pattern in the IR at 2014 and 1966 cm^{-1}. Concurrent with the growth of these two new CO stretches is the formation of a Mn–H resonance observed at −12.2 ppm in the ^1H NMR. Prolonged photolysis of the reaction mixture results in eventual loss of all metal carbonyl species. Upon standing in the dark, a sealed sample of photolyzed $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3/Et_3SiH$ back reacts slowly leading to regeneration of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ at the expense of the photoproduct associated with the absorption at 2014 and 1966 cm^{-1}. On the basis of these observations and the similarity of the CO stretching positions to those of the related $(\eta^5\text{-}C_5R_5)Mn(CO)_2H(SiEt_3)$ (R = H, Me) (Table I), the photoproduct having absorptions at 2014 and 1966 cm^{-1} is concluded to be $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$.

Unfortunately, the Mn–H stretch in the IR could not be observed. It is appreciated that there may remain significant Si–H interaction in the oxidative addition adduct.[7] This oxidative addition product is thermally labile at 298 K with respect to reductive elimination, since regeneration of the $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ occurs by reaction with the photogenerated CO. It is worth noting that the CO stretching frequencies for $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$ versus the 16e $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ show larger shifts to higher frequencies than the analogous bands for the $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$ species where the oxidative addition is expected to be more "complete" and where it is found that the oxidative addition product is less labile.

If the photolysis of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ is effected at temperatures between 190 and 240 K, then the thermal reaction rate of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ to form $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$ can be conveniently monitored by IR spectroscopy. Figure 2 shows the time dependence of the consumption of the IR bands at 1989 and 1936 cm^{-1} associated with $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ and the growth of the bands at 2014 and 1966 cm^{-1} for the $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$. At high concentrations of Et_3SiH reaction according to eq 2 is pseudo-first-order. Figure 3 shows a plot of ln (A/A_0) versus time for the 1936 cm^{-1} band of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$.

At high initial concentrations of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ slight curvature of the rate plots is observed; this is believed to be due to competitive back reaction of the $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ with photogenerated CO (eq 3). At lower initial concentrations of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ (and hence less CO) no curvature of the rate plots is observed. Similarly at lower Et_3SiH concentrations back reaction according to eq 3 is more competitive and complicates the kinetic analysis. Note that Figure 2 shows no formation of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ on the time scale shown. All quantitative data are for situations where $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ was generated at initial concentrations of less than 10^{-5} M[11] and Et_3SiH is used as the solvent, that is at 6.3 M concentration.

The second-order rate constant for eq 2 has been obtained at various temperatures (Table II). Figure 4a shows an Arrhenius plot, ln (k) versus $1/T$, giving the temperature dependence of the reaction between 190 and 240 K. Figure 4b shows Arrhenius plots for the reaction of $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ (R = Me, H, Cl) with Et_3SiH. For R = Cl the activation energy, E_a, is +38 ± 4 kJ mol^{-1}, and from the Eyring relation, $\Delta H^\ddagger = +36 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -140 \pm 15$ J $mol^{-1}\ K^{-1}$. Table III lists the activation parameters for these complexes.

Of note is that $\Delta H^\ddagger$ for this reaction is the same, to within experimental error limits, for the oxidative addition of Et_3SiH to all three $(\eta^5\text{-}C_5R_5)Mn(CO)_3$ (R = H, Me, Cl) complexes.[1] Assuming a constant $\Delta H^\ddagger$, extrapolation to

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[11] $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ concentration is controlled by varying the photolysis time.

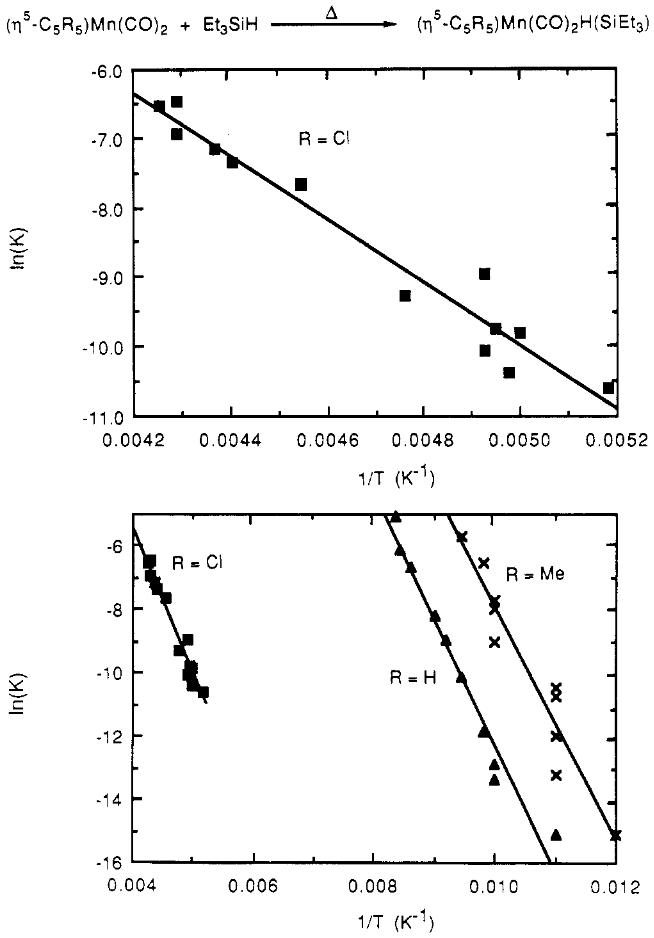

Figure 4. (a) Arrhenius plot for the reaction of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ with Et_3SiH. (b) Comparison of Arrhenius plots for the reaction of $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ with Et_3SiH (■, R = Cl; ▲, R = H; ×, R = Me). Data for R = H, Me are from ref 1.

a given temperature shows that for these three compounds there is a difference of over 7 orders of magnitude in rates. Calculation of the half-life of $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ (R = Me, H, Cl) in 6.3 M silane at 150 K gives a half-life of 0.001 s for R = Me, 0.09 s for R = H, and 1.6×10^6 s for R = Cl. This variation in reaction rate is due mainly to variation in $\Delta S^{\ddagger}$, since $\Delta H^{\ddagger}$ varies by less than 20%. Importantly, neat Et_3SiH is a common medium in which all the kinetics were measured. Comparison of the reactivity over wide temperature ranges (where the property of the silane as solvent changes) is valid as the temperature dependence of the rate of reaction was found to be linear in neat Et_3SiH solution, Et_3SiH glass, and dilute alkane solutions of Et_3SiH.[1]

The constant value of $\Delta H^{\ddagger}$ for the oxidative addition of Et_3SiH to $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ (R = H, Me, Cl) could be interpreted to mean that the "solvent" occupies the open site and that the dissociation of the solvent is the rate-determining process in the oxidative addition reaction. However, while we conclude that solvation of the 16e species is important,[1] the dissociation of the solvent to open the coordination site does not appear to be the rate-determining step. This conclusion stems from the observation that 2e donor ligands (e.g. CO) compete very effectively for $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ even at very low concentrations compared to Et_3SiH. The constant $\Delta H^{\ddagger}$ among the species studied most likely reflects a common level of Si–H bond breaking in the transition state. A study of the kinetic isotope effect is underway to evaluate this conclusion.

The large negative $\Delta S^{\ddagger}$ for the $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ reaction is believed to result from the electron deficiency at the Mn center. We believe the decreasing electron density at the Mn atom in the series C_5Me_5, C_5H_5, C_5Cl_5 causes the transition state to become progressively later, that is, more productlike. The transition state for the reaction of Et_3SiH with $(\eta^5\text{-}C_5Me_5)Mn(CO)_2$ therefore presumably consists of solvated $(\eta^5\text{-}C_5Me_5)Mn(CO)_2$ with little association of the Et_3SiH; this is reflected in the small positive value for $\Delta S^{\ddagger}$. As the transition state becomes later, the transition state consists of a greater degree of association of the Et_3SiH with the Mn center; this is reflected in a decreasing of $\Delta S^{\ddagger}$.[12] Thus, with the $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ reaction the large negative $\Delta S^{\ddagger}$ indicates a large degree of coordination of the silane to the Mn in the transition state. Large negative $\Delta S^{\ddagger}$ values are not unknown for oxidative addition reactions;[13,14] for reaction of $[(dppe)_2Ir][Ph_4B]$ with $(EtO)_3SiH$ $\Delta S^{\ddagger} = -200$ J K^{-1} mol^{-1}.[14]

Conclusion

We find CO loss to be the only detectable photoreaction of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$, as for other $(\eta^5\text{-}C_5R_5)Mn(CO)_3$ complexes.[3,4] The 16e $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ reacts with a variety of 2e donors to give the substituted products $C_5Cl_5Mn(CO)_2L$ and with Et_3SiH to give the oxidative addition product $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$.

Activation parameters for the Et_3SiH oxidative addition to $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ show that the $\Delta H^{\ddagger}$ is the same as for $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ (R = H, Me) in the same reaction. The difference in the rate of the reaction is due mainly to variation in $\Delta S^{\ddagger}$ (Table III). The $\Delta S^{\ddagger}$ for the reaction of Et_3SiH with $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ is -140 J mol^{-1} K^{-1}, which is "as expected" for a bimolecular reaction. For the reaction with $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ (R = H, Me) the contribution to E_a from $\Delta S^{\ddagger}$ is smaller than expected for a bimolecular reaction.

Acknowledgment. We thank the National Science Foundation for support of this research. In addition, K.M.Y. is grateful to the Natural Sciences and Engineering Research Council of Canada for award of a graduate fellowship.

Registry No. $(\eta^5\text{-}C_5Cl_5)MnCO_3$, 56282-21-4; $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2PPh_3$, 119272-37-6; $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$, 119272-38-7; Et_3SiH, 617-86-7; $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$, 119272-39-8.

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(12) Based on arguments similar to those used in: Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334 as applied to entropy instead of enthalpy.

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