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An Investigation into the Reactivity of Organometallic Noble Gas Complexes: A Time-Resolved Infrared Study in Supercritical Noble Gas and Alkane Solution at Room Temperature

David C. Grills, Xue Z. Sun, Gavin I. Childs, and Michael W. George*

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

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A series of Group 7 organometallic noble gas complexes, $(\eta^5\text{-}C_5R_5)M(CO)_2L$ (M = Mn and Re; R = H, Me. and Et (Mn only); L = Kr and Xe) have been characterized in supercritical noble gas solution at room temperature using fast time-resolved infrared spectroscopy. The kinetics and activation parameters for the reaction of these complexes with CO were measured and compared to the analogous alkane complexes, $(\eta^5\text{-}C_5H_5)M(CO)_2$(*n*-heptane) (M = Mn and Re). Evidence obtained from values of the activation enthalpies and experiments, in which the lifetimes of $(\eta^5\text{-}C_5R_5)Mn(CO)_2Xe$ (R = H, Me, and Et) were measured as a function of [CO] at a constant [CO]/[Xe] ratio, suggests that the reaction of the noble gas complexes with CO occurs mainly via a dissociative or dissociative interchange mechanism.

Introduction

Organometallic noble gas and alkane complexes have been known for over 20 years.[1] Perutz and Turner[2] used matrix isolation to show that $M(CO)_5L$ (M = Cr, Mo and W; L = Ar, Kr, Xe and CH_4) could be generated following UV photolysis of $M(CO)_6$ in low temperature (12 K) matrices. Matrix isolation has since become a powerful technique for the characterization of organometallic noble gas complexes including $[Fe(CO)_4Xe]$,[3] $[Mn(CO)_5Kr]$,[4] $[Fe(CO)_5Kr]^+$,[4] $[Cr(CO)_3(dfepe)L]$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; L = Ar and Xe),[5] $[Ru(CO)_2(PMe_3)_2L]$ (L = Ar and Xe)[6] and $[Ru(CO)_2(dmpe)L]$ (dmpe = $Me_2PCH_2CH_2PMe_2$; L = Ar and Xe).[7] Although matrix isolation permits the characterization of unstable species at low temperature, it does not provide any kinetic information quantifying the reactivity of these.

Nanosecond flash photolysis experiments[8] showed that $Cr(CO)_5$(cyclohexane) is formed within 50 ns following photolysis of $Cr(CO)_6$ in cyclohexane solution, and subsequent ultrafast transient spectroscopy[9,10] has shown that the solvation occurs *within the first picosecond* following UV irradiation. 16-Electron intermediates generated by flash photolysis of the metal carbonyls usually form complexes with a solvent molecule. The only exception to this was reported by Bergman and co-workers[11] where $(\eta^5\text{-}C_5R_5)Co(CO)$ (R = H and Me) appeared not to interact with the solvent following flash photolysis of $(\eta^5\text{-}C_5R_5)Co(CO)_2$ in liquefied noble gas solution.

Organometallic noble gas complexes have also been observed in solution. Simpson *et al.*[12] showed that $Cr(CO)_5Xe$ could be detected in solution at low temperature using FTIR spectroscopy; either in liquefied Xe (lXe) at − 98 °C or liquefied Kr (lKr) doped with Xe at −122 °C. Weiller extended this work using rapid scan FTIR[13] to identify $M(CO)_5L$ (M = Cr and W; L= Kr and Xe) in liquefied noble gas solution at low temperature, and Bergman and co-workers used a similar approach to detect $(\eta^5\text{-}C_5Me_5)Rh(CO)L$ (L = Kr and Xe).[14]

Organometallic noble gas complexes have been observed in the gas phase at room temperature. For example, Weitz and co-workers studied the bonding of Xe and Kr atoms to $M(CO)_5$ fragments (M = Cr and Mo (Xe only) and W) in the gas phase using TRIR spectroscopy.[15] Pyykkö performed a theoretical study of the gold(I) cation complexes, AuL^+ and $LAuL^+$ (L = He, Ne, Ar, Kr, and Xe),[16] and found the Au−Xe BDEs to be 87.8 kJ mol^{-1} in $AuXe^+$ and 108.5 kJ mol^{-1} in $XeAuXe^+$, with the Au−Xe bonds having considerable covalent character. More recently Schröder and Pyykkö performed a combined experimental and high level theoretical investigation of cationic gold(I) complexes and the predicted Au−Xe BDE in $AuXe^+$ increased to 126.8 kJ mol^{-1}.[17]

We have recently shown that organometallic noble gas complexes can be observed in fluid solution at room temperature following irradiation of metal carbonyls in supercritical noble gas solution. Using TRIR spectroscopy, we characterized $M(CO)_5L$ (M = Cr, Mo, and W; L = Ar (W only), Kr and Xe)[18] and $(\eta^5\text{-}C_5H_5)Re(CO)_2L$ (L = Kr and Xe).[19] The rate constant for the reaction of these complexes with CO increases as follows: Xe < Kr < Ar; Re ≪ W < Mo ≈ Cr. Surprisingly, we also found that the rate constants for the Xe complexes, $L_mM(CO)_{x-1}(Xe)$ were very similar to those for the corresponding alkane complexes, $L_mM(CO)_{x-1}$(*n*-heptane).

The stability of $(\eta^5\text{-}C_5H_5)Re(CO)_2$(alkane) is significant, and Ball and co-workers have recently been able to characterize $(\eta^5\text{-}C_5H_5)Re(CO)_2$(cyclopentane) at low temperature by ^1H NMR spectroscopy.[20] The factors governing the reactivity of unstable alkane complexes have been investigated. Johnson *et al*. found that the reactivity of $(\eta^5\text{-}C_5R_5)Mn(CO)_2$(*n*-heptane) (R = H, Me and Et) toward small molecules such as CO, N_2, and H_2 in *n*-heptane solution steadily increased in the order H < Me < Et while the reactivity toward PPh_3 did not change.[21] These results indicated that steric rather than electronic factors governed the reactivity of these alkane complexes. Long and co-workers[22] found that the reactivity of $(\eta^6\text{-}C_6R_6)Cr(CO)_2$(cyclohexane) (R = H, Me and Et) toward CO in cyclohexane also increased in the order H < Me < Et. Changing the solvent from cyclohexane to longer and longer linear alkanes resulted in an increased rate of reaction between $(\eta^6\text{-arene})Cr(CO)_2$-

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* E-mail: Mike.George@nottingham.ac.uk

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(alkane) and CO. The enthalpy of activation, $\Delta H^{\ddagger}$, for this reaction did not vary with substituent or alkane (24 ± 2 kJ mol^{-1}) and was only half that of the Cr−cyclohexane bond energy (53 ± 9 kJ mol^{-1}) determined previously by photoacoustic calorimetry (PAC).[23] They concluded that the variation in reactivity of the (η^6-arene)Cr(CO)$_2$(alkane) photoproduct toward CO can be explained by changes in the entropy of activation, $\Delta S^{\ddagger}$, and not by variations in the interaction energy between the coordinatively unsaturated photofragment and the solvent. An interchange mechanism was proposed for the displacement of alkane by CO. More recently, Long and coworkers[24] performed a systematic investigation into the reactivity of M(CO)$_5$(alkane) (M = Cr, Mo and W) and (η^6-arene)Mo(CO)$_2$(alkane) toward CO in alkane solution. For these systems, they also found that $\Delta H^{\ddagger}$ remained constant, and an interchange mechanism was proposed for the Cr systems, with the rate constant, k_2, depending on the $\Delta S^{\ddagger}$ expression. For the Mo and W systems however, the nature of the solvent had much less of an effect on k_2 and a more associative mechanism was proposed.

In this paper, we have investigated the effect of cyclopentadienyl ring substituents on the reactivity of the Group 7 half-sandwich complexes, (η^5-C$_5$R$_5$)M(CO)$_2$L (M = Mn and Re; R = H, Me and Et (Mn only); L = Kr and Xe) toward CO in supercritical fluid solution at room temperature.

Experimental Section

The Nottingham laser TRIR apparatus has been described in detail elsewhere.[25] In these experiments the photochemical reactions were initiated by a pulsed Nd:YAG laser (Quanta-Ray GCR-12), and a cw IR diode laser (Mütek MDS 1100) was used to monitor the transient IR absorptions. The IR spectra are built up on a "point-by-point" basis by repeating this measurement at different infrared frequencies. The stainless steel cell used for supercritical TRIR measurements has been described previously for conventional spectroscopic monitoring.[26] For TRIR experiments, the cells were used with CaF$_2$ windows, and a pressure transducer (RDP Electronics). Heating was achieved with an external aluminum jacket containing cartridge heaters. Kr and Xe (BOC, research grade), CO (Air Products, premier grade), (η^5-C$_5$H$_5$)Mn(CO)$_3$ (Aldrich), (η^5-C$_5$H$_5$)Re(CO)$_3$ (Strem), and (η^5-C$_5$Me$_5$)Re(CO)$_3$ (Strem) were used as supplied. (η^5-C$_5$Me$_5$)Mn(CO)$_3$ and (η^5-C$_5$H$_4$Et)Mn(CO)$_3$ were synthesized according to literature procedures[27,28] and (η^5-C$_5$Et$_5$)Mn(CO)$_3$ was a gift from Dr. A. G. Ginzburg. *n*-heptane was distilled over CaH$_2$ prior to use.

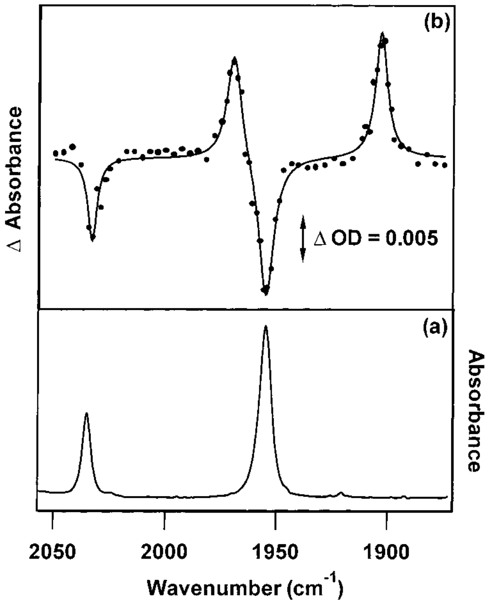


Figure 1. (a) FTIR spectrum of (η^5-C$_5$H$_5$)Mn(CO)$_3$ in scXe (1395 psi, 25 °C) in the presence of CO (30 psi). (b) TRIR spectrum obtained 500 ns after photolysis (355 nm) of this solution.

Results and Discussion

Characterization and Reactivity of (η^5-C$_5$R$_5$)M(CO)$_2$Xe (M = Mn and Re; R = H, Me and Et (Mn only)) in scXe. Figure 1(a) shows the FTIR spectrum of (η^5-C$_5$H$_5$)Mn(CO)$_3$ dissolved in scXe (1395 psi, 25 °C) in the presence of CO (30 psi). Figure 1(b) shows the TRIR spectrum of this solution obtained 500 ns after photolysis (355 nm). The parent absorptions are bleached and two new absorptions are produced which can readily be assigned to (η^5-C$_5$H$_5$)Mn(CO)$_2$Xe by comparison with previous matrix isolation results[29] and TRIR experiments[21] (see Table 1). The formation of (η^5-C$_5$H$_5$)Mn(CO)$_2$Xe is reversible with (η^5-C$_5$H$_5$)Mn(CO)$_2$Xe decaying (observed rate, $k_{\mathrm{obs}} = 2.5\ (\pm\ 0.3) \times 10^5\ \mathrm{s}^{-1}$) to reform ($\eta^5$-C$_5H_5$)Mn(CO)$_3$ ($k_{\mathrm{obs}} = 2.4\ (\pm\ 0.2) \times 10^5\ \mathrm{s}^{-1}$). This pseudo-first-order rate constant depends linearly on CO concentration, affording the second-order rate constant, k_{CO} for the reaction of (η^5-C$_5$H$_5$)Mn(CO)$_2$-

TABLE 1: ν(C−O) Infrared Band Positions (cm^{-1}) of (η^5-C$_5$R$_5$)M(CO)$_2$L Species (M = Mn and Re; R = H, Me and Et (Mn only); L = CO, *n*-heptane, Kr and Xe)[a]

		R		
complex	conditions	H	Me	Et
(η^5-C$_5$R$_5$)Mn(CO)$_3$	matrix/20 K	2033, 1951[b]	2008, 1923[c]	
(η^5-C$_5$R$_5$)Mn(CO)$_3$	*n*-heptane/298 K	2029, 1947[d]	2008, 1925[d]	2008, 1927[d]
(η^5-C$_5$R$_5$)Mn(CO)$_3$	scKr/298 K	2035, 1956	2015, 1936	2014, 1935
(η^5-C$_5$R$_5$)Mn(CO)$_3$	scXe/298 K	2032, 1952	2013, 1932	2011, 1931
(η^5-C$_5$R$_5$)Mn(CO)$_2$	matrix/20 K	1972, 1903[b]	1932, 1863[c]	
(η^5-C$_5$R$_5$)Mn(CO)$_2$(hept)	*n*-heptane/298 K	1962, 1894[d]	1942, 1873[d]	1942, 1873[d]
(η^5-C$_5$R$_5$)Mn(CO)$_2$Kr	scKr/298 K	1973, 1908	1948, 1884	1950, 1885
(η^5-C$_5$R$_5$)Mn(CO)$_2$Xe	scXe/298 K	1970, 1903	1945, 1882	1945, 1880
(η^5-C$_5$R$_5$)Re(CO)$_3$	matrix/20 K	2029, 1934[e]	2015, 1921[f]	
(η^5-C$_5$R$_5$)Re(CO)$_3$	*n*-heptane/298 K	2031, 1940[g]		
(η^5-C$_5$R$_5$)Re(CO)$_3$	scKr/298 K	2038, 1952[g]	2020, 1933	
(η^5-C$_5$R$_5$)Re(CO)$_3$	scXe/298 K	2035, 1946[g]	2016, 1927	
(η^5-C$_5$R$_5$)Re(CO)$_2$	matrix/20 K	1947, 1879[e]	1945, 1879[f]	
(η^5-C$_5$R$_5$)Re(CO)$_2$(hept)	*n*-heptane/298 K	1954, 1890[g]		
(η^5-C$_5$R$_5$)Re(CO)$_2$Kr	scKr/298 K	1966, 1903[g]	1944, 1882	
(η^5-C$_5$R$_5$)Re(CO)$_2$Xe	scXe/298 K	1957, 1894[g]	1936, 1873	

[a] This work unless referenced. [b] Reference 29. [c] Reference 34. [d] Reference 21. [e] Reference 35. [f] Reference 36. [g] Reference 19.

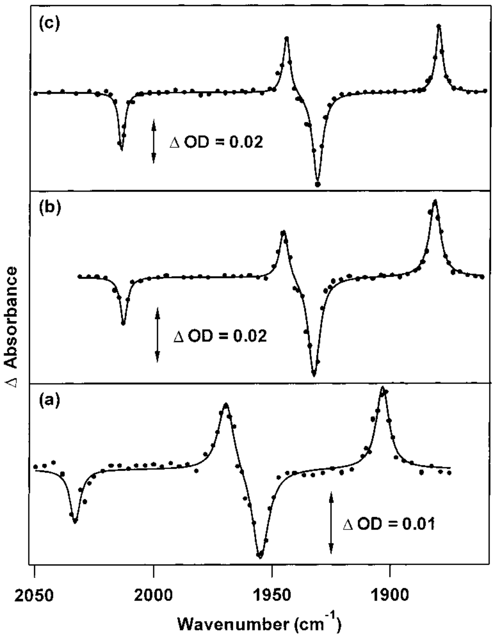


Figure 2. TRIR spectra obtained after photolysis (355 nm) of (a) (η^5-C_5H_5)Mn(CO)$_3$ in scXe (1395 psi, 25 °C) in the presence of CO (30 psi) (b) (η^5-C_5Me_5)Mn(CO)$_3$ in scXe (1420 psi, 25 °C) in the presence of CO (15 psi) and (c) (η^5-C_5Et_5)Mn(CO)$_3$ in scXe (1430 psi, 25 °C) in the presence of CO (30 psi).

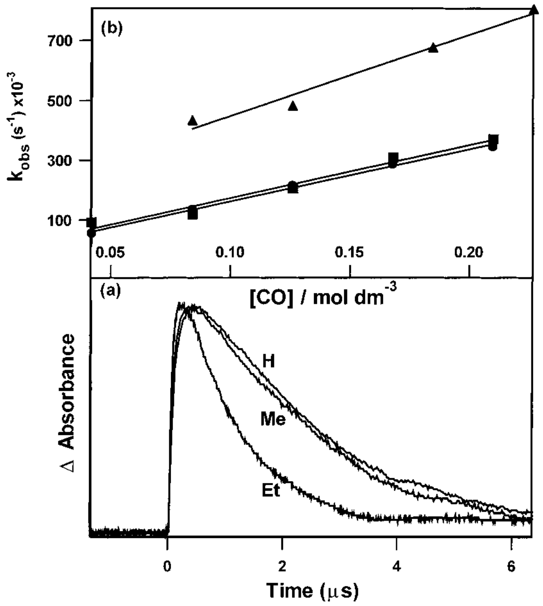


Figure 3. (a) TRIR decay traces recorded at wavenumbers corresponding to (η^5-C_5R_5)Mn(CO)$_2$Xe (R = H, Me and Et), after photolysis (355 nm) of (η^5-C_5R_5)Mn(CO)$_3$ in scXe at 25 °C in the presence of CO (75 psi). The traces were recorded in three separate experiments and have been normalized in intensity. (b) Plots of the observed rate constant, k_{obs} versus [CO] for the reaction of (η^5-C_5R_5)Mn(CO)$_2$Xe (R = H (●), Me (■) and Et (▲)) with excess CO in scXe at 25 °C.

TABLE 2: Values of k_{CO} for Reaction of the Group 7 Noble Gas and *n*-heptane Complexes, (η^5-C_5R_5)M(CO)$_2$L (M = Mn and Re; R = H, Me and Et (Mn only); L = *n*-heptane, Kr and Xe) with CO at 298 K

$$(\eta^5\text{-}C_5R_5)M(CO)_2L + CO \xrightarrow[\text{scL, 25 °C}]{k_{CO}} (\eta^5\text{-}C_5R_5)M(CO)_3 + L$$

M	R	L	conditions	k_{CO} (dm^3 mol^{-1} s^{-1})^a	pressure (psi)^b
Mn	H	*n*-heptane	*n*-heptane	8.1×10^5	
Mn	Me	*n*-heptane	*n*-heptane	1.6×10^6	
Mn	Et	*n*-heptane	*n*-heptane	5.4×10^6	
Re	H	*n*-heptane	*n*-heptane	2.1×10^2	
Mn	H	Xe	scXe	1.6×10^6	2180
Mn	Me	Xe	scXe	1.8×10^6	1720
Mn	Et	Xe	scXe	2.9×10^6	2120
Re	H	Xe	scXe	4.8×10^3	1935
Re	Me	Xe	scXe	6.0×10^3	2570
Mn	H	Kr	scKr	7.2×10^7	3290
Mn	Me	Kr	scKr	7.5×10^7	3360
Mn	Et	Kr	scKr	1.6×10^8	4080
Re	H	Kr	scKr	8.1×10^6	3500
Re	Me	Kr	scKr	7.8×10^6	3080

^{a} ±10%. ^{b} ±10 psi.

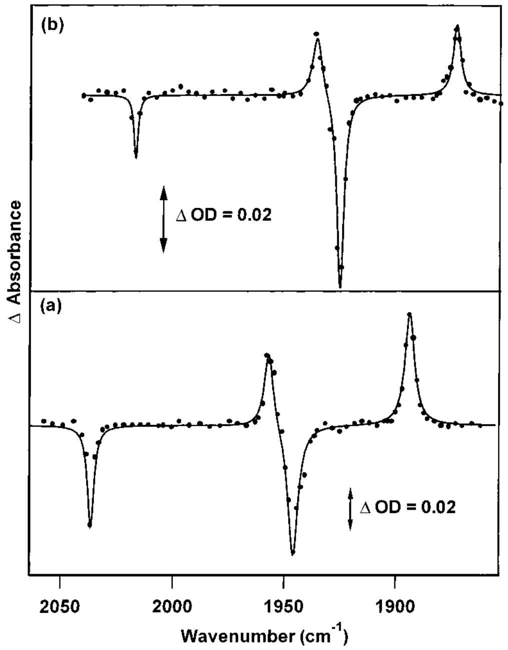


Figure 4. TRIR spectra obtained after photolysis (266 nm) of (a) (η^5-C_5H_5)Re(CO)$_3$ in scXe (1720 psi, 25 °C) in the presence of CO (60 psi) and (b) (η^5-C_5Me_5)Re(CO)$_3$ in scXe (2600 psi, 25 °C) in the presence of CO (80 psi).

Xe with CO in scXe (k_{CO} = 1.6 (± 0.2) × 10^6 dm^3 mol^{-1} s^{-1}). Similarly, TRIR experiments with (η^5-C_5Me_5)Mn(CO)$_3$ and (η^5-C_5Et_5)Mn(CO)$_3$ permit the characterization of (η^5-C_5Me_5)Mn(CO)$_2$Xe and (η^5-C_5Et_5)Mn(CO)$_2$Xe, respectively (see Figure 2 and Table 1). The ν(C−O) band positions of (η^5-C_5Me_5)Mn(CO)$_3$ and (η^5-C_5Et_5)Mn(CO)$_3$ are very similar and are shifted down in wavenumber relative to (η^5-C_5H_5)Mn(CO)$_3$, reflecting the higher electron density on the Mn center in these complexes. The ν(C−O) bands of (η^5-C_5Me_5)Mn(CO)$_2$Xe and (η^5-C_5Et_5)Mn(CO)$_2$Xe are similarly shifted relative to those of (η^5-C_5H_5)Mn(CO)$_2$Xe. The formation of (η^5-C_5Me_5)Mn(CO)$_2$Xe and (η^5-C_5Et_5)Mn(CO)$_2$Xe is reversible.

The reactivity of (η^5-C_5R_5)Mn(CO)$_2$Xe toward CO in scXe follows the order R = Et > Me ≈ H (see Figure 3 and Table 2). This is clearly not the same as the reactivity of the corresponding alkane complexes, (η^5-C_5R_5)Mn(CO)$_2$(*n*-heptane), where the reactivity was found[21] to increase in the order H < Me < Et (Table 2). We have investigated further the similarity in the reactivity of (η^5-C_5H_5)Mn(CO)$_2$Xe and (η^5-C_5Me_5)Mn(CO)$_2$Xe by comparing the reactivity of (η^5-C_5H_5)Re(CO)$_2$Xe and (η^5-C_5Me_5)Re(CO)$_2$Xe in scXe.

We have previously characterized and measured the reactivity of (η^5-C_5H_5)Re(CO)$_2$Xe in scXe.[19] Figure 4(b) shows the TRIR spectrum obtained 15 μs after photolysis (266 nm) of (η^5-C_5-

$Me_5)Re(CO)_3$ in scXe (2600 psi, 25 °C) in the presence of CO (80 psi). As for the analogous Mn system, the parent absorptions of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ are shifted down in frequency by ca. 20 cm^{-1} relative to those of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (Table 2). The two new absorptions that are produced are similarly shifted relative to those of $(\eta^5\text{-}C_5H_5)Re(CO)_2Xe$ and are assigned to $(\eta^5\text{-}C_5Me_5)Re(CO)_2Xe$. We find that $(\eta^5\text{-}C_5H_5)Re(CO)_2Xe$ and $(\eta^5\text{-}C_5Me_5)Re(CO)_2Xe$ have a similar reactivity toward CO (Table 2).

All of the TRIR experiments were carried out in the presence of excess CO under pseudo-first-order conditions. A detailed rate analysis for the decay of noble gas complexes in liquid xenon has been performed by Weiller[13] for $W(CO)_5Xe$ and Bergman *et al.*[14] for $(\eta^5\text{-}C_5Me_5)Rh(CO)Xe$. We have used a similar approach to obtain expressions for the observed rate of decay, k_{obs}, of the xenon complexes $Cp'M(CO)_2Xe$ ($Cp' = (\eta^5\text{-}C_5H_5)$, $(\eta^5\text{-}C_5Me_5)$, and $(\eta^5\text{-}C_5Et_5)$; M = Mn and Re) in their reaction with CO in scXe solution. Plots of k_{obs} versus [CO] for all of the complexes studied were linear with nonzero intercepts. The gradient, k_{CO}, is equal to the second-order rate constant for reaction of $Cp'M(CO)_2Xe$ with CO.

For a *dissociative mechanism* in scXe, the following rate equations would apply for the reaction of $Cp'M(CO)_2Xe$ with CO:

$$Cp'M(CO)_2Xe \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cp'M(CO)_2 + Xe$$

$$Cp'M(CO)_2 + CO \xrightarrow{k_2} Cp'M(CO)_3$$

Application of the steady-state approximation to the intermediate, $Cp'M(CO)_2$, results in the following expression for k_{obs}, where k_1 is the elementary rate constant for dissociation of Xe

$$k_{obs} = \frac{k_1 k_2[CO]}{k_{-1}[Xe] + k_2[CO]} \sim \frac{k_1[CO]}{[Xe]}$$

This expression was reduced using the following approximation: $k_{-1}[Xe] \gg k_2[CO]$. Ligand recombination rates are generally very fast. For example, the rate of reaction of $CpMn(CO)_2$ with CO has been measured[30] in the gas phase to be 6×10^{11} cm^3 mol^{-1} s^{-1}. Therefore, it is likely that in supercritical solution, Xe and CO will compete to react with $Cp'M(CO)_2$ at near diffusion-controlled rates (k_{-1} and k_2, respectively). The diffusion-controlled rate constant, k_d can be estimated in scXe using the Stokes–Einstein relation, giving $k_{-1} \sim k_2 \sim 5 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. Thus, since [Xe] ~ 70 × [CO] under the conditions of this experiment, the above approximation is reasonable.

For an *associative mechanism*, the following rate equation would apply, where k_a is the bimolecular associative rate constant

$$Cp'M(CO)_2Xe + CO \xrightarrow{k_a} Cp'M(CO)_3 + Xe$$

This leads to the expression

$$k_{obs} = k_a[CO]$$

Therefore, under the conditions of this experiment, solely from the room-temperature CO substitution kinetics, it is impossible to distinguish between the two extreme forms of mechanism, since they both predict a linear dependence of k_{obs} on [CO], as was observed.

Measurement of k_{obs} as a Function of [CO] at Constant [CO]/[Xe] Ratio. In the condensed phase, such as lXe and alkane solution, the concentration of solvent cannot be altered. However, supercritical fluids allow the measurement of k_{obs} as a function of Xe concentration. For a dissociative mechanism, k_{obs} will depend on the concentration of the leaving ligand, Xe,

$$k_{obs} \propto 1/[Xe]$$

An associative process would exhibit no such dependence on [Xe]. Therefore, an experiment in which k_{obs} is measured as a function of [Xe] should provide an insight into the nature of the mechanism.

We have previously probed the CO substitution kinetics of $W(CO)_5(CO_2)$ in $scCO_2$.[18] We measured k_{obs} as a function of [CO] while holding the $[CO]/[CO_2]$ ratio constant. The rate equations are analogous to those described here and so it was predicted that under these conditions k_{obs} would only decrease with decreasing density if the reaction with $W(CO)_5(CO_2)$ with CO were partially associative. In fact, k_{obs} was found to increase slightly with decreasing density, implying that associative processes were not significant. The second experiment involved measuring the lifetime of $W(CO)_5(CO_2)$ ($1/k_{obs}$) as a function of $[CO_2]$ at constant [CO]. For a dissociative process, $1/k_{obs} \propto [CO_2]$ and we were able to show that $1/k_{obs}$ exactly follows the change in CO_2 density with pressure, therefore demonstrating that the reaction of $W(CO)_5(CO_2)$ with CO in $scCO_2$ is predominantly a dissociative process.

Figure 5 shows how k_{obs}, for the reaction of $(\eta^5\text{-}C_5R_5)Mn(CO)_2Xe$ (R = H, Me and Et) with CO in scXe, varies with increasing [CO] while maintaining a constant [CO]/[Xe] ratio. The expression for k_{obs}, assuming both dissociative and associative mechanisms, is given below

$$k_{obs} \sim \frac{k_1[CO]}{[Xe]} + k_a[CO]$$

Therefore, if both dissociative and associative pathways are operating simultaneously, a plot of k_{obs} versus [CO] at constant [CO]/[Xe] ratio should produce a straight line with gradient equal to k_a and intercept equal to k_1[CO]/[Xe]. If the slope is zero then associative pathways can be assumed to be insignificant. Figure 5 shows that at a constant [CO]/[Xe] ratio, k_{obs} shows no appreciable dependence on [CO] for the reaction of $(\eta^5\text{-}C_5R_5)Mn(CO)_2Xe$ with CO. From these experiments we conclude that the contribution from an associative mechanism for the reaction of $(\eta^5\text{-}C_5R_5)Mn(CO)_2Xe$ with CO in scXe is not significant and the reaction proceeds via either a purely dissociative or a dissociative interchange mechanism. A more definitive experiment would be to measure $1/k_{obs}$ as a function of [Xe] at constant [CO]. In this case a dissociative mechanism should produce a linear plot of $1/k_{obs}$ versus [Xe], while an associative or interchange mechanism would have no slope. The amount of xenon required for this was prohibitive and these experiments have not been conducted.

Determination of Activation Parameters for the Reaction of $(\eta^5\text{-}C_5R_5)M(CO)_2Xe$ (M = Mn and Re; R = H, Me and Et (Mn only)) with CO in scXe. For a given metal/ligand system the BDE for a metal–Xe bond is expected to be significantly less than that of the corresponding metal–heptane bond. For example, the W–heptane BDE in $W(CO)_5$(*n*-heptane) has been determined[31] using PAC (62.8 kJ mol^{-1}) and is approximately two times the W–Xe BDE in $W(CO)_5(Xe)$, estimated by TRIR experiments in the gas phase at room temperature[15] (34.3 ± 4.2 kJ mol^{-1}) and in lXe at cryogenic

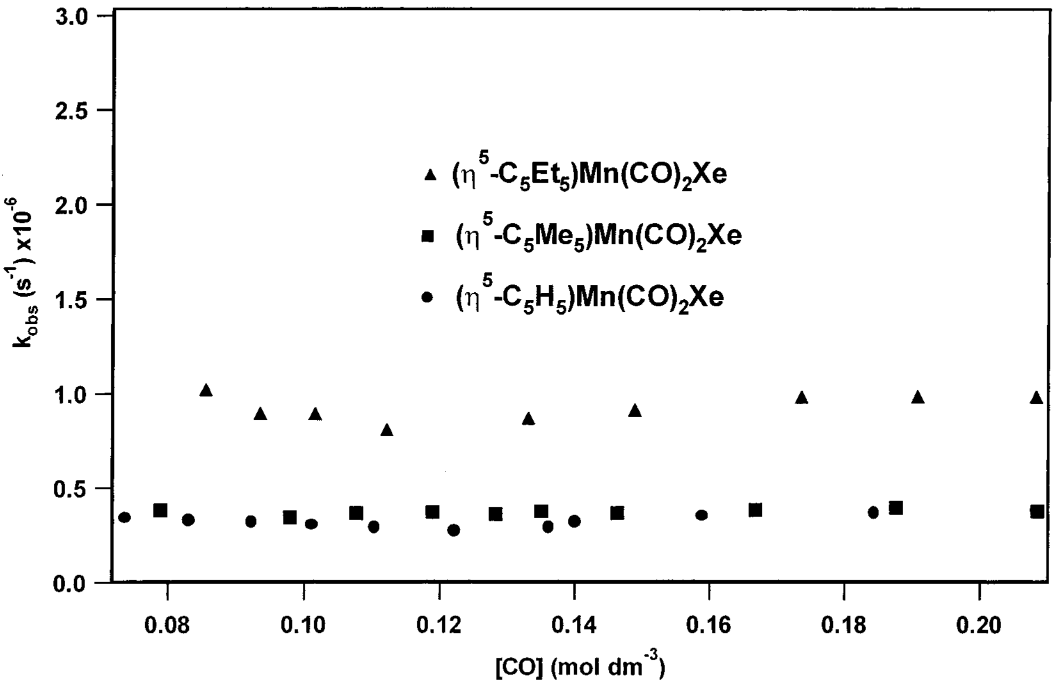


Figure 5. The CO concentration dependence of the observed rate constant, k_{obs} for the reaction of (η^5-C_5R_5)Mn$(CO)_2$Xe (R = H, Me and Et) with excess CO in scXe, while maintaining a constant [CO]/[Xe] ratio.

temperatures[13] (35.1 ± 0.8 kJ mol^{-1}). We have shown[18] that the rate of reaction of W$(CO)_5$Xe with CO in scXe is only ca. 2.5 times the rate for the corresponding reaction of W$(CO)_5$-(*n*-heptane) in *n*-heptane solution. The activation energy, E_a, for the reaction of W$(CO)_5$Xe with CO in scXe is almost identical to the estimated W−Xe BDE. However, Long and co-workers[24] have shown that $\Delta H^\ddagger$ for the reaction of W$(CO)_5$(*n*-heptane) with CO (20 ± 2 kJ mol^{-1}) is less than half the W−heptane BDE (62.8 kJ mol^{-1}). These results are consistent with the alkane complex reacting with CO via an associative mechanism, while the Xe complex is reacting mainly through a dissociative pathway.

We also find that (η^5-C_5R_5)Mn$(CO)_2$Xe and (η^5-C_5R_5)Mn$(CO)_2$(*n*-heptane) (R = H, Me and Et) complexes have very similar reactivity toward CO. We have therefore determined the activation parameters for the reactions of (η^5-C_5H_5)Mn$(CO)_2$(*n*-heptane) and (η^5-C_5R_5)Mn$(CO)_2$Xe (R = H, Me and Et) with CO in *n*-heptane and scXe solution, respectively. In the supercritical fluid environment, CO and Xe are completely miscible over a wide temperature range, which greatly simplifies variable temperature studies. Figure 6 shows Arrhenius and Eyring plots from these experiments (see Table 3 for values of $\Delta H^\ddagger$). It is clear that for (η^5-C_5R_5)Mn$(CO)_2$Xe, all three complexes have a similar $\Delta H^\ddagger$ and that this is similar to the value obtained for the reaction of (η^5-C_5H_5)Mn$(CO)_2$(*n*-heptane) with CO in *n*-heptane solution. The $\Delta H^\ddagger$ value for (η^5-C_5R_5)Mn$(CO)_2$Xe represents a lower limit for the Mn−Xe BDE. Early PAC experiments by Yang and co-workers[32] estimated the Mn−heptane BDE, 8−9 kcalmol^{-1}. The precise determination of the Mn−heptane BDE from PAC data requires the Mn−CO BDE. This value was not known and Yang and co-workers estimated the Mn−alkane binding energy from the enthalpy of activation for the reaction of (η^5-C_5H_5)Mn$(CO)_2$(*n*-heptane) with *cis*-cyclooctene and the enthalpy of activation for the reaction of (η^5-C_5H_5)Mn$(CO)_2$(*cis*-cyclooctene) with PPh_3. They assumed that the reaction was purely dissociative and used these values to calculate the Mn−heptane BDE, 8−9 kcal mol^{-1}. However, Burkey has pointed out that this is a lower limit for the Mn−heptane BDE since the reaction may be an associative process with respect to the alkane.[33] Indeed, Long and co-workers[22,24] have shown that many similar reactions for (η^6-C_6H_6)M$(CO)_2$(alkane) (M = Cr, Mo) do not proceed by a dissociative pathway and the enthalpy of activation for the reaction of (η^6-C_6H_6)M$(CO)_2$(alkane) with CO is only half the M-alkane BDE. The $\Delta H^\ddagger$ determined for reaction of (η^5-C_5H_5)-Mn$(CO)_2$(*n*-heptane) with CO is significantly lower than other first row transition metal alkane BDEs. For example, the Cr−heptane BDE determined[24] by PAC is 50 ± 5 kJ mol^{-1}. We would expect that the Mn−heptane BDE ≫ Mn−Xe BDE, and this suggests that our value of $\Delta H^\ddagger$ is not a good estimate of the Mn−heptane BDE.

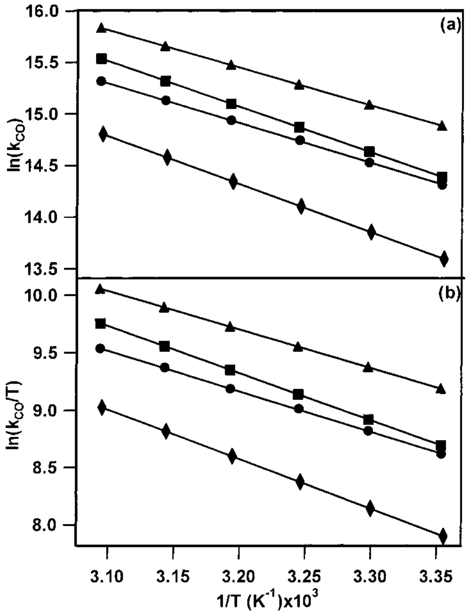


Figure 6. (a) Arrhenius plots and (b) Eyring plots for the reaction of (η^5-C_5R_5)Mn$(CO)_2$Xe with CO in scXe solution, R = H (●), Me (■) and Et (▲) and (η^5-C_5H_5)Mn$(CO)_2$(*n*-heptane) with CO in *n*-heptane solution (◆).

TABLE 3: Activation Enthalpies for the Reaction of (η^5-C_5R_5)M(CO)$_2$L (M = Mn and Re; R = H, Me and Et (Mn only); L = *n*-heptane, Kr and Xe) with CO

M	R	L	conditions	$\Delta H^\ddagger$ (kJ mol^{-1})^a
Mn	H	*n*-heptane	*n*-heptane	36
Mn	H	Xe	scXe	30
Mn	Me	Xe	scXe	34
Mn	Et	Xe	scXe	28
Re	H	*n*-heptane	*n*-heptane	46
Re	H	Xe	scXe	47
Re	Me	Xe	scXe	44
Re	Me	Kr	scKr	31

[a] ±2.

An indication of the nature of the mechanism would come from the values of $\Delta S^\ddagger$ derived from the Eyring plots. Unfortunately, the large errors in these values obtained from the intercept of the Eyring plots prevent such an analysis. However, the fact that the (η^5-C_5R_5)Mn(CO)$_2$Xe complexes are reacting with CO in scXe by a dissociative mechanism is strongly supported by the experiments described earlier in which k_{obs} was measured as a function of [CO] at a constant [CO]/[Xe] ratio. These results are consistent with (η^5-C_5H_5)Mn(CO)$_2$(*n*-heptane) and (η^5-C_5R_5)Mn(CO)$_2$Xe reacting with CO by different mechanisms, and we tentatively suggest that in *n*-heptane (η^5-C_5H_5)Mn(CO)$_2$(*n*-heptane) reacts with CO by an associative or associative interchange mechanism and in scXe (η^5-C_5R_5)Mn(CO)$_2$Xe reacts with CO by a dissociative or dissociative interchange mechanism.

We have also made temperature dependent measurements for the reaction of (η^5-C_5H_5)Re(CO)$_2$(*n*-heptane) with CO in *n*-heptane solution and (η^5-$C_5R'_5$)Re(CO)$_2$Xe (R′ = H and Me) with CO in scXe. We have already shown that (η^5-C_5H_5)Re(CO)$_2$(*n*-heptane) and (η^5-C_5R_5)Re(CO)$_2$Xe have similar reactivity toward CO (see Table 2). We also find that (η^5-C_5H_5)Re(CO)$_2$Xe and (η^5-C_5H_5)Re(CO)$_2$(*n*-heptane) have very similar $\Delta H^\ddagger$ for reaction with CO. The $\Delta H^\ddagger$ values are higher than for the corresponding Mn complexes, reflecting the lower reactivity of the Re complexes toward CO. The Re−heptane BDE has not been estimated by PAC but since Re is a third row transition metal we expect that the Re−heptane BDE will be greater than or equal to the M*n*−heptane BDE. $\Delta H^\ddagger$ for the reaction of (η^5-C_5H_5)Re(CO)$_2$(*n*-heptane) with CO is greater than for the corresponding reaction of the Mn−alkane complex; however, it is still significantly smaller than the W−heptane BDE determined[31] by PAC (62.8 kJ mol^{-1}). We again suggest that $\Delta H^\ddagger$ obtained for the reaction of (η^5-C_5H_5)Re(CO)$_2$(*n*-heptane) with CO is less than the Re−heptane BDE. Although we have not measured the reaction of (η^5-C_5H_5)Re(CO)$_2$(Xe) as a function of [CO] at constant [CO]/[Xe] ratio, we tentatively suggest that the reaction of (η^5-C_5H_5)Re(CO)$_2$(*n*-heptane) with CO in *n*-heptane occurs mainly by an associative or associative interchange mechanism while η^5-$C_5R'_5$)Re(CO)$_2$Xe reacts with CO in scXe predominantly by a dissociative or dissociative interchange mechanism.

We now return to the reactivity of (η^5-C_5Et_5)Mn(CO)$_2$Xe with CO in scXe, which is approximately two times greater than that of (η^5-C_5H_5)Mn(CO)$_2$Xe and (η^5-C_5Me_5)Mn(CO)$_2$Xe. There is not a steady increase in reactivity as was observed[21] for (η^5-C_5R_5)Mn(CO)$_2$(*n*-heptane) (R = H, Me and Et) by Johnson et al.

One possibility is that the greater length of the Et substituents in (η^5-C_5Et_5)Mn(CO)$_2$Xe, compared with the H and Me ring substituents in (η^5-$C_5R'_5$)Mn(CO)$_2$Xe, permits an agostic interaction to occur between the manganese center and the terminal C−H bond of an Et group in scXe. This would require that in *n*-heptane, the stronger Mn−heptane bond displaces the agostic interaction, i.e., the reactive species is (η^5-C_5Et_5)Mn(CO)$_2$ in scXe and (η^5-C_5Et_5)Mn(CO)$_2$(*n*-heptane) in *n*-heptane.

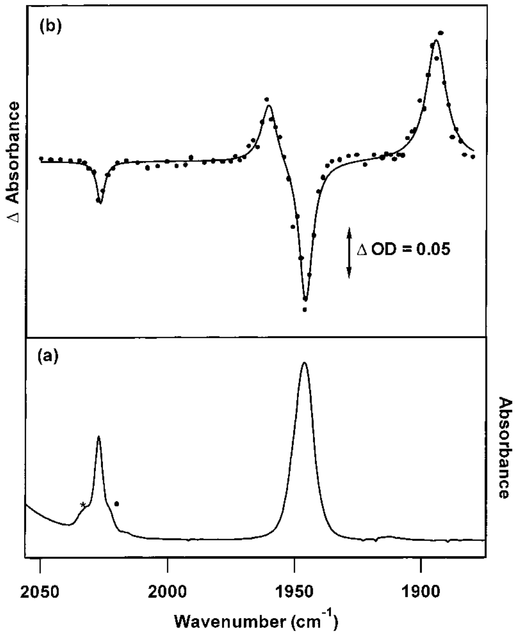
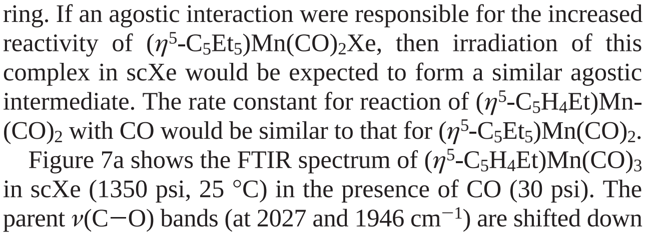


Figure 7. (a) FTIR spectrum of (η^5-C_5H_4Et)Mn(CO)$_3$ in scXe (1350 psi, 25 °C) in the presence of CO (30 psi). Note the small contamination by (η^5-C_5H_5)Mn(CO)$_3$ (*) and (η^5-$C_5H_3Et_2$)Mn(CO)$_3$ (•). (b) TRIR spectrum obtained 500 ns after photolysis (355 nm) of this solution.



We have therefore synthesized[28] (η^5-C_5H_4Et)Mn(CO)$_3$. This molecule has only one Et substituent on the cyclopentadienyl ring. If an agostic interaction were responsible for the increased reactivity of (η^5-C_5Et_5)Mn(CO)$_2$Xe, then irradiation of this complex in scXe would be expected to form a similar agostic intermediate. The rate constant for reaction of (η^5-C_5H_4Et)Mn(CO)$_2$ with CO would be similar to that for (η^5-C_5Et_5)Mn(CO)$_2$.

Figure 7a shows the FTIR spectrum of (η^5-C_5H_4Et)Mn(CO)$_3$ in scXe (1350 psi, 25 °C) in the presence of CO (30 psi). The parent ν(C−O) bands (at 2027 and 1946 cm^{-1}) are shifted down in frequency by ca. 4 cm^{-1} relative to those of (η^5-C_5H_5)Mn(CO)$_3$ in scXe. Figure 7b shows the TRIR spectrum obtained 500 ns after photolysis (355 nm) of this solution. Depletion of the bands due to the starting material is accompanied by the production of two new bands at 1961 and 1895 cm^{-1}, which are assigned to (η^5-C_5H_4Et)Mn(CO)$_2$Xe by comparison with the TRIR spectrum of (η^5-C_5H_5)Mn(CO)$_2$Xe in scXe.

A plot of k_{obs} versus [CO] for the reaction of (η^5-C_5H_4Et)Mn(CO)$_2$Xe with CO in scXe is shown in Figure 8. The linear fit to this graph affords the bimolecular rate constant for reaction with CO, $k_{CO} = 8.0\ (\pm\ 0.8) \times 10^5$ dm^3 mol^{-1} s^{-1}. Interestingly, this value is less than that calculated for each of the (η^5-C_5R_5)Mn(CO)$_2$Xe (R = H, Me and Et) complexes discussed previously (see Table 2) and therefore suggests that the increased reactivity of (η^5-C_5Et_5)Mn(CO)$_2$Xe toward CO in scXe is not due to an agostic interaction.

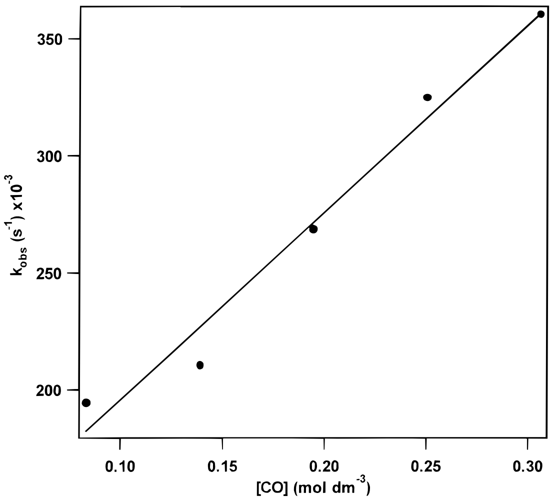


Figure 8. Plot of the observed rate constant, k_{obs} versus [CO] for the reaction of (η^5-C_5H_4Et)Mn(CO)$_2$Xe with excess CO in scXe at 25 °C.

Comparison of the rate constants for the reaction of (η^5-C_5Et_5)Mn(CO)$_2$Xe and (η^5-C_5Et_5)Mn(CO)$_2$Kr with CO in scXe and scKr, respectively, provides further insight into the possible role of an agostic interaction in the reaction of (η^5-C_5Et_5)Mn(CO)$_2$L (L = Xe and Kr) with CO. If an agostic interaction was formed following CO dissociation, then the rates of reaction of (η^5-C_5Et_5)Mn(CO)$_2$Xe in scXe and (η^5-C_5Et_5)Mn(CO)$_2$Kr in scKr should be very similar.

The Reactivity of (η^5-C_5R_5)M(CO)$_2$Kr (M = Mn and Re; R = H, Me and Et (Mn only)) in scKr. The krypton complexes, (η^5-C_5R_5)M(CO)$_2$Kr (M = Mn and Re; R = H, Me and Et (Mn only)) have been characterized in scKr (Table 1) and their room temperature CO substitution kinetics have been determined (Table 2). The rates are significantly higher than those found for the corresponding xenon complexes. More importantly, the trend in reactivity of the krypton complexes is very similar to that observed for the xenon complexes

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2Kr \approx (\eta^5\text{-}C_5Me_5)Mn(CO)_2Kr < (\eta^5\text{-}C_5Et_5)Mn(CO)_2Kr$$

$$(\eta^5\text{-}C_5H_5)Re(CO)_2Kr \approx (\eta^5\text{-}C_5Me_5)Re(CO)_2Kr$$

Activation parameters have been determined for the reaction of (η^5-C_5Me_5)Re(CO)$_2$Kr with CO ($\Delta H^\ddagger = 31.0 \pm 3.0$ kJ mol^{-1}). This $\Delta H^\ddagger$ value represents a lower limit for the Re−Kr BDE. (η^5-C_5Et_5)Mn(CO)$_2$Kr was found to be approximately 50 times more reactive than (η^5-C_5Et_5)Mn(CO)$_2$Xe. This suggests that an agostic interaction is not occurring. It appears that there is no significant effect (electronic or steric) on the reactivity toward CO for the series of group 7 cyclopentadienyl noble gas complexes by changing between (η^5-C_5H_5) and (η^5-C_5Me_5). There is an effect on the reactivity when (η^5-C_5Me_5) is changed to (η^5-C_5Et_5). This suggests that steric factors are responsible for this difference.

Conclusions

In this paper we have described the characterization of the new organometallic noble gas complexes (η^5-C_5R_5)M(CO)$_2$L (M = Mn and Re; R = H, Me and Et (Mn only); L = Kr and Xe) in supercritical noble gas solution at room temperature. The steric bulk of the three types of ring substituent increases steadily in the order H < Me < Et, and the Me and Et substituents have almost identical electron directing effects. This has allowed both the electronic and steric effects of the ring substituents on reactivity to be investigated. Room temperature CO substitution kinetics showed that for both noble gases, the H and Me substituted complexes, (η^5-$C_5R'_5$)Mn(CO)$_2$Xe (R′ = H and Me) and (η^5-$C_5R'_5$)Mn(CO)$_2$Kr have very similar reactivity toward CO, whereas (η^5-C_5Et_5)Mn(CO)$_2$L (L = Xe and Kr) are approximately twice as reactive. Experiments were conducted with the manganese xenon complexes in which the observed rate of decay was measured as a function of [CO] at a constant [CO]/[Xe] ratio. These suggested that the noble gas complexes react with CO in supercritcal solution via a mechanism that is dissociative in nature. Further evidence for the reaction mechanism was obtained from temperature dependence studies in which the enthalpies of activation were calculated for these noble gas complexes and the analogous alkane complexes, (η^5-C_5H_5)M(CO)$_2$(n-heptane) (M = Mn and Re). The value of $\Delta H^\ddagger$ for the reaction of (η^5-C_5H_5)M(CO)$_2$Xe (M = Mn or Re) with CO in scXe was found to be very similar to the analogous reaction of (η^5-C_5H_5)M(CO)$_2$(n-heptane) in n-heptane solution. The value of $\Delta H^\ddagger$ for (η^5-$C_5R'_5$)M(CO)$_2$Xe represents a lower limit for the M−Xe BDE. We suggest that (η^5-C_5H_5)Mn(CO)$_2$(n-heptane) and (η^5-C_5R_5)Mn(CO)$_2$Xe are reacting with CO by different mechanisms. Further studies are currently underway involving different alkanes and ring substituents in order to understand fully the mechanisms involved.

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References and Notes

(1) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.
(2) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.
(3) Poliakoff, M. *Chem. Soc. Rev.* **1978**, *7*, 527.
(4) Fairhurst, S. A.; Morton, J. R.; Perutz, R. N.; Preston, K. F. *Organometallics* **1984**, *3*, 1389.
(5) Brookhart, M.; Chandler, W.; Kessler, R. J.; Liu, Y.; Pienta, N. J.; Santini, C. C.; Hall, C.; Perutz, R. N.; Timney, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 3802.
(6) Mawby, R. J.; Perutz, R. N.; Whittlesey, M. K. *Organometallics* **1995**, *14*, 3268.
(7) Whittlesey, M. K.; Perutz, R. N.; Virrels, I. G.; George, M. W. *Organometallics* **1997**, *16*, 268.
(8) Kelly, J. M.; Hermann, H.; Koerner von Gustorf, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105.
(9) Simon, J. D.; Xie, X. L. *J. Phys. Chem.* **1986**, *90*, 6751.
(10) Xie, X. L.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 1130.
(11) Bengali, A. A.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 3879.
(12) Simpson, M. B.; Poliakoff, M.; Turner, J. J.; Maier, W. B., II.; McLaughlin, J. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1355.
(13) Weiller, B. H. *J. Am. Chem. Soc.* **1992**, *114*, 10910.
(14) Weiller, B. H.; Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 4326.
(15) Wells, J. R.; Weitz, E. *J. Am. Chem. Soc.* **1992**, *114*, 2783.
(16) Pyykkö, P. *J. Am. Chem. Soc.* **1995**, *117*, 2067.
(17) Schröder, D.; Schwarz, H.; Hrusák, J.; Pyykkö, P. *Inorg. Chem.* **1998**, *37*, 624.
(18) Sun, X. Z.; George, M. W.; Kazarian, S. G.; Nikiforov, S. M.; Poliakoff, M. *J. Am. Chem. Soc.* **1996**, *118*, 10525.
(19) Sun, X. Z.; Grills, D. C.; Nikiforov, S. M.; Poliakoff, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521.
(20) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.
(21) Johnson, F. P. A.; George, M. W.; Bagratashvili, V. N.; Vereshchagina, L. N.; Poliakoff, M. *Mendeleev Commun.* **1991**, 26.
(22) Creaven, B. S.; George, M. W.; Ginzburg, A. G.; Hughes, C.; Kelly, J. M.; Long, C.; McGrath, I. M.; Pryce, M. T. *Organometallics* **1993**, *12*, 3127.
(23) Morse, J. M., Jr.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471.

(24) Breheny, C. J.; Kelly, J. M.; Long, C.; O'Keeffe, S.; Pryce, M. T.; Russell, G.; Walsh, M. M. *Organometallics* **1998**, *17*, 3690.

(25) George, M. W.; Poliakoff, M.; Turner, J. J. *Analyst* **1994**, *119*, 551.

(26) Poliakoff, M.; Howdle, S. M.; Kazarian, S. G. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 1275.

(27) Bernal, I.; Korp, J. D.; Herrmann, W. A.; Serrano, R. *Chem. Ber.* **1984**, *117*, 434.

(28) Nesmeyanov, A. N.; Anisimov, K. N.; Valueva, Z. P. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk.* **1961**, 1780.

(29) Rest, A. J.; Sodeau, J. R.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1978**, 651.

(30) Zheng, Y.; Wang, W.; Lin, J.; She, Y.; Fu, K.-J. *J. Phys. Chem.* **1992**, *96*, 7650.

(31) Burney, D. P.; Burkey, T. J. *Abs. Paps. Am. Chem. Soc.* **1994**, *207*, 19.

(32) Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 1267.

(33) Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8329.

(34) Hill, R. H.; Wrighton, M. S. *Organomet.* **1987**, *6*, 632.

(35) Bitterwolf, T. E.; Lott, K. A.; Rest, A. J.; Mascetti, J. *J. Organomet. Chem.* **1991**, *419*, 113.

(36) Ball, R. G.; Campen, A. K.; Graham, W. A. G.; Hamley, P. A.; Kazarian, S. G.; Ollino, M. A.; Poliakoff, M.; Rest, A. J.; Sturgeoff, L.; Whitwell, I. *Inorg. Chim. Acta* **1997**, *259*, 137.