Remarkable Stability of (η^5-C$_5$H$_5$)Re(CO)$_2$L (L = *n*-Heptane, Xe, and Kr): A Time-Resolved Infrared Spectroscopic Study of (η^5-C$_5$H$_5$)Re(CO)$_3$ in Conventional and Supercritical Fluid Solution

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Received August 21, 1996[⊗]

Abstract: Employing fast time-resolved infrared (TRIR) spectroscopy we have characterized CpRe(CO)$_2$(*n*-heptane), CpRe(CO)$_2$(Xe), and CpRe(CO)$_2$(Kr) (Cp = η^5-C$_5$H$_5$) at or above room temperature in *n*-heptane, supercritical Xe, and Kr solution. The reactivity of CpRe(CO)$_2$(*n*-heptane) with CO (k_2 = 2.1 ($\pm$0.5) $\times$ 10^3 mol^{-1} dm^3 s^{-1}) shows this complex to be the least reactive of the reported organometallic alkane complexes. We report a trend in reactivity of the early transition metal alkane complexes. CpRe(CO)$_2$(Xe) and CpRe(CO)$_2$(Kr) are also shown to have significant stability. CpRe(CO)$_2$(Xe) is less reactive toward CO than all of the reported alkane complexes except CpRe(CO)$_2$-(*n*-heptane).

Introduction

The first η^2-H$_2$ complex was isolated[1] by Kubas in 1984, and since then a series of isolable dihydrogen complexes have been prepared. Although the photochemical oxidative addition of alkane C−H bonds to group 9 metal centers has been known for over a decade,[2] there is no comparable series of stable isolable organometallic alkane complexes.[3] However, a knowledge of the reactivity of unstable alkane complexes should lead to a better understanding of the metal−alkane interaction and perhaps to the eventual isolation of an organometallic alkane complex.

Perutz and Turner[4] used matrix isolation to show that photolysis of M(CO)$_6$ generates M(CO)$_5$ (M = Cr, Mo, and W), which is sufficiently reactive to form complexes even with methane at 10 K. Although matrix isolation gives an opportunity to characterize unstable species at low temperature, it does not provide the kinetic information needed to quantify the reactivity of these species. In solution, Cr(CO)$_5$(cyclohexane) formed within 50 ns following UV flash photolysis of Cr(CO)$_6$ in room temperature cyclohexane solution,[5] and subsequently ultrafast transient spectroscopy has shown that the solvation process for Cr(CO)$_5$ occurs *within the first picosecond* following UV irradiation.[6] In solution, Cr(CO)$_5$(cyclohexane) is moderately reactive and decays within 50 μs.[7]

The coordination of a solvent molecule to a 16-electron intermediate has now been observed for most of the metal carbonyl compounds studied by flash photolysis, and the solvent has been considered to be a "token ligand".[8,9] Time-resolved IR spectroscopy (TRIR), a combination of UV flash photolysis and nanosecond IR spectroscopy, has played a major role in the study of such species. Solvated 16-electron intermediates have lifetimes in solution which can vary considerably for seemingly similar complexes. Thus, Cr(CO)$_5$(*n*-heptane) and Mo(CO)$_5$(*n*-heptane) both have lifetimes of approximately 15 μs, while the corresponding W(CO)$_5$(*n*-heptane) has a lifetime more than an order of magnitude longer of ca. 200 μs[10] under similar conditions. By contrast the group 5 half-sandwich intermediates CpM(CO)$_3$(*n*-heptane) (M = V, Nb, and Ta) are far more reactive. CpV(CO)$_3$(*n*-heptane) has a lifetime in *n*-heptane solution of ca. 300 ns, while CpNb(CO)$_3$(*n*-heptane) and CpTa(CO)$_3$(*n*-heptane) have similar lifetimes (ca. 15−20 μs).[11] The analogous first row early transition metal alkane complexes increase in stability in the following order, CpV-(CO)$_3$(*n*-heptane) < (η^6-C$_6$H$_6$)Cr(CO)$_2$(*n*-heptane) < CpMn-(CO)$_2$(*n*-heptane).

Simpson *et al.* identified Cr(CO)$_5$(Xe) using FTIR spectroscopy in liquefied Xe solution (*l*Xe) at cryogenic temperature (−98 °C), providing the first evidence for the formation of rare-gas complexes with significant lifetimes in solution.[12] Weiller[13] was able to detect M(CO)$_5$L (M = Cr, W; L = Xe, Kr) in *l*Xe or liquid krypton (*l*Kr) using rapid-scan FTIR. Similarly,

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

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Bergman and co-workers identified Cp*Rh(CO)L (L = Kr, Xe; Cp* = η^5-C$_5$Me$_5$)[14] in liquefied noble gas solution at cryogenic temperatures. We have recently shown[15] that rare-gas complexes can be observed in fluid solution at room temperature following irradiation of metal carbonyls in supercritical noble gas solution at room temperature. A fluid is said to be supercritical when its pressure and temperature both exceed their critical values (P$_c$ and T$_c$).[16] Many gases have a T_c value that is below ambient, including Xe (P$_c$ = 58 atm, T_c = 16 °C) and Kr (P$_c$ = 54 atm, T_c = −64 °C). We have recently reported the TRIR spectra[15] in solution at room temperature of M(CO)$_5$-(Xe), M(CO)$_5$(Kr), and M(CO)$_5$(CO$_2$) (M = Cr, Mo, and W) generated by flash photolysis of M(CO)$_6$ in supercritical Xe, Kr, or CO$_2$ solution. We deduced from the second order rate constants for the reaction of M(CO)$_5$L with CO that the reactivity for each metal was in the order Kr > Xe ≈ CO$_2$ and that for a given ligand the reactivity was in the order Cr ≈ Mo > W.

In this paper we report data for CpRe(CO)$_3$ in *n*-heptane solution at room temperature, and show that CpRe(CO)$_2$(*n*-heptane) is the least reactive of the reported organometallic alkane complexes. We also show that CpRe(CO)$_2$(Xe) and CpRe(CO)$_2$(Kr) are significantly less reactive toward CO than the corresponding W(CO)$_5$(Xe) and W(CO)$_5$(Kr) complexes.

Experimental Section

The Nottingham TRIR apparatus has been described elsewhere.[17] In these experiments a pulsed Nd:YAG laser (Quanta-Ray GCR-11; 266 nm or 355 nm) initiates the photochemical reactions, and a continuous wave IR source, either Mütek IR diode laser or a modified Grubb-Parsons Spectromajor spectrometer, monitors the transient IR absorptions. The change in IR transmission at one particular IR frequency is measured following excitation, and IR spectra are built up on a "point-by-point" basis by repeating this measurement at different infrared frequencies. The high-pressure cells for supercritical TRIR have been described previously.[15] *n*-Heptane (Aldrich HPLC grade) was distilled from CaH$_2$ prior to use. CpRe(CO)$_3$ (Strem), Xe (BOC), and Kr (BOC) were used as supplied.

Results and Discussion

(a) Characterization and Reactivity of CpRe(CO)$_2$(*n*-heptane). Figure 1a shows the FTIR spectrum of CpRe(CO)$_3$ in *n*-heptane solution and Figure 1b shows the corresponding TRIR spectrum obtained 100 μs following UV (266 nm) excitation of CpRe(CO)$_3$ in *n*-heptane solution under a pressure of 2 bar of CO. It is clear that photolysis causes depletion of the bands of CpRe(CO)$_3$ and the production of two new absorptions which can readily be assigned to CpRe(CO)$_2$(*n*-heptane) by comparison with IR data from low temperature matrix isolation experiments (see Table 1)[18] and can be easily distinguished from CpRe(CO)$_2$(H)(*n*-heptyl) where the Re center would be oxidized to Re (+3) and the ν(CO) bands would be shifted to higher frequency relative to the parent CpRe(CO)$_3$. Figure 2 shows the TRIR kinetic traces of CpRe(CO)$_2$(*n*-heptane) under a range of different CO concentrations. The

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Figure 1. (a) FTIR spectrum of CpRe(CO)$_3$ in *n*-heptane solution and (b) TRIR *difference* spectrum at 100 μs after photolysis (266 nm) of CpRe(CO)$_3$ (8 × 10^{-4} mol dm^{-3}) in *n*-heptane solution under a pressure of 2 bar of CO.

Table 1. Wavenumbers (cm^{-1}) of CpRe(CO)$_2$L Species (L = CO, *n*-heptane, Xe, and Kr)

CpRe(CO)$_2$L	wavenumber (cm^{-1})	condition	ref
CpRe(CO)$_3$	2029, 1934	Nujol, 77 K	18
CpRe(CO)$_3$	2031, 1940	*n*-heptane, 298 K	this work
CpRe(CO)$_3$	2035, 1946	scXe, 298 K	this work
CpRe(CO)$_3$	2038, 1952	scKr, 298 K	this work
CpRe(CO)$_3$	2038, 1951	scKr/Xe, 298 K	this work
CpRe(CO)$_2$	1947, 1879	Nujol, 77 K	18
CpRe(CO)$_2$(*n*-heptane)	1954, 1890	*n*-heptane, 298 K	this work
CpRe(CO)$_2$(Xe)	1957, 1894	scXe, 298 K	this work
CpRe(CO)$_2$(Kr)	1965, 1903	scKr, 298 K	this work
CpRe(CO)$_2$(Xe)	1963, 1900	scKr, 298 K	this work
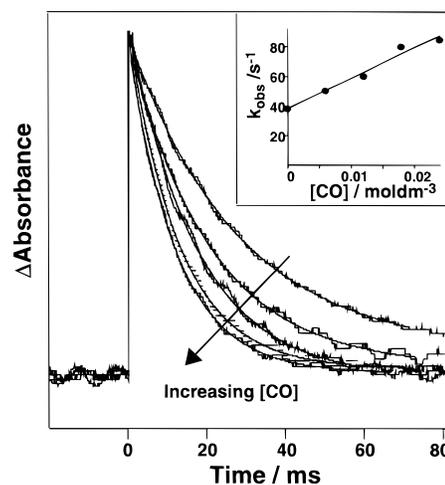
Figure 2. (a) TRIR decay traces recorded following irradiation of CpRe(CO)$_3$ in *n*-heptane solution at 1890 cm^{-1} in the presence of 2, 1.5, 1, 0.5, and 0 bar of CO. In each experiment, the total pressure above the *n*-heptane solution was maintained at 2 bar by using Ar as a buffer gas. (b) The insert shows a plot of k_{obs} versus CO concentration obtained from first order fit to the decay at 1890 cm^{-1}.

rate of decay of CpRe(CO)$_2$(*n*-heptane) is clearly dependent upon CO concentration. Even in the absence of CO, the decay of CpRe(CO)$_2$(*n*-heptane) is pseudo first order because only a small amount of CpRe(CO)$_3$ is destroyed by the UV flash and presumably CpRe(CO)$_2$(*n*-heptane) reacts with CpRe(CO)$_3$ (which is in excess) to form the known[19] dimer Cp$_2$Re$_2$(CO)$_5$. The decay of CpRe(CO)$_2$(*n*-heptane) is also pseudo first order

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Table 2. Second-Order Rate Constants, k_2 (mol^{-1} dm^3 s^{-1}), for the Reaction of Metal−Heptane Complexes with CO in *n*-Heptane Solution at 298 K (s = *n*-heptane)

$(\eta^5$-$C_5H_5)V(CO)_3s^a$	$(\eta^6$-$C_6H_6)Cr(CO)_2s^b$	$(\eta^5$-$C_5H_5)Mn(CO)_2s^c$
1×10^8	2×10^6	8×10^5
$(\eta^5$-$C_5H_5)Nb(CO)_3s^a$		
7×10^6		
$(\eta^5$-$C_5H_5)Ta(CO)_3s^a$		$(\eta^5$-$C_5H_5)Re(CO)_2s^d$
5×10^6		2×10^3

[a] Reference 11. *[b]* Reference 25. *[c]* Reference 26. *[d]* This work.

in the presence of CO since the concentration of CO is significantly greater than the concentration of CpRe(CO)$_2$(*n*-heptane). Figure 2 also shows that the decay of CpRe(CO)$_2$-(*n*-heptane) depends linearly on CO concentration, and from this plot we estimate the rate constant for the reaction of CpRe-(CO)$_2$(*n*-heptane) with CO to be 2.1 ($\pm$0.5) $\times$ 10^3 mol^{-1} dm^3 s^{-1}. The intercept of this plot provides an estimation of the rate constant for the reaction of CpRe(CO)$_2$(*n*-heptane) with CpRe(CO)$_3$, 4.5 ($\pm$0.8) $\times$ 10^4 mol^{-1} dm^3 s^{-1}.

CpRe(CO)$_2$(*n*-heptane) is surprisingly unreactive, and the very low value of the rate constant for the reaction with CO to reform CpRe(CO)$_3$ underlines the stability of this complex. Table 2 summarises the rate constants for a series of early transition metal half-sandwich carbonyl *n*-heptane complexes with CO in *n*-heptane solution at room temperature. Although CpV-(CO)$_3$(*n*-heptane)[11] has a rate constant of 1 $\times$ 10^8 mol^{-1} dm^3 s^{-1}, this highly reactive complex must still have a significant V−heptane interaction since the rate constant is *100 times* smaller than the diffusion controlled rate. Indeed the V−heptane bond strength has been estimated to be 41 kJ mol^{-1} with Photoacoustic Calorimetry (PAC).[20] Table 2 shows that there is a steady progression both *across* and *down* groups 5, 6, and 7 such that CpRe(CO)$_2$(*n*-heptane) reacts with CO *50000 times* slower than does CpV(CO)$_3$(*n*-heptane). This suggests that the Re−heptane bond may be the strongest of the early transition metal−alkane interactions.

To our knowledge, CpRe(CO)$_2$(*n*-heptane) is the longest lived organometallic alkane complex yet reported in room temperature solution. There is clearly a trend in reactivity of the early transition metal alkane complexes, and it may be expected that more stabilized alkane complexes will be produced with the later transition metals. However, CpCo(CO) was found[9] to have no detectable interaction with cyclohexane and Cp*Rh(CO)[14] and Cp*Ir(CO)[2b] react with alkanes to form C−H activated products. Grevels has reported[21] that Fe(CO)$_4$(cyclohexane) has a short lifetime (<10 μs) in CO saturated cyclohexane solution and Perutz and co-workers[22] have shown that C−H activated products are generated following photolysis of either (η^6-C_6H_3-Me$_3$)Os(CO)$_2$ or (η^6-$C_6H_3Me_3$)Os(CO)(H)$_2$ in Ar matrices doped with methane at 20 K. These results for the later transition metals indicate that the lack of reactivity of CpRe(CO)$_2$(*n*-heptane) is significant, and we have investigated the stability of the solvated CpRe(CO)$_2$ moiety further by studying the photochemistry in supercritical fluids.

(b) Characterization and Reactivity of CpRe(CO)$_2$(Xe). Figure 3a shows the FTIR spectrum of CpRe(CO)$_3$ dissolved in supercritical Xe (scXe) in the presence of CO. Figure 3b shows the TRIR spectrum obtained 1 μs following 266-nm

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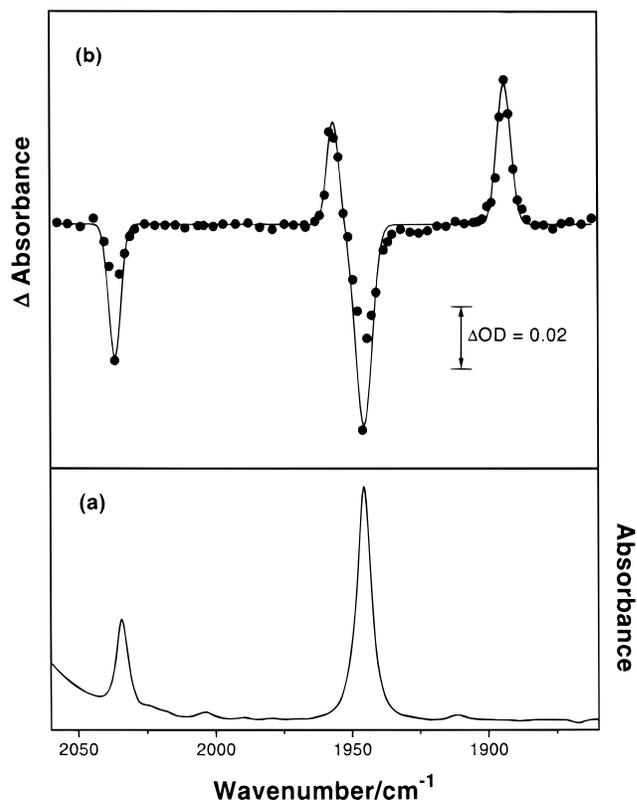
Figure 3. (a) FTIR spectrum of CpRe(CO)$_3$ in scXe (1721 psi, 25 °C) in the presence of CO (60 psi). (b) TRIR *difference* spectrum obtained 1 μs after photolysis (266 nm) of the same solution. The positive peaks are assigned to CpRe(CO)$_2$(Xe), see text.

excitation of this solution. As with *n*-heptane, the parent absorptions are bleached and two new absorptions are produced which can be assigned to CpRe(CO)$_2$(Xe) by comparison with previous matrix isolation results[18] together with the TRIR measurements described above. In the presence of CO, the formation of CpRe(CO)$_2$(Xe) is completely reversible; the two bands decay fully to reform CpRe(CO)$_3$ with no observable secondary photoproducts. This reversibility is demonstrated more clearly in Figure 4, which shows the relevant TRIR kinetic decay traces; CpRe(CO)$_3$ is reformed at a rate (k_{obs} = 2.2 ($\pm$0.5) $\times$ 10^3 s^{-1}) that is identical within experimental error with the rate of decay of CpRe(CO)$_2$(Xe) (k_{obs} = 2.6 ($\pm$0.5) $\times$ 10^3 s^{-1}). Figure 4 also shows that the decay of CpRe(CO)$_2$(Xe) depends linearly on CO concentration, and from this plot we estimate the second order rate constant for the reaction of CpRe(CO)$_2$-(Xe) with CO in scXe, k_2 = 4.8 ($\pm$0.3) $\times$ 10^3 mol^{-1} dm^3 s^{-1}. Thus, CpRe(CO)$_2$(Xe) is ca. 400 times less reactive toward CO than W(CO)$_5$(Xe) (see Table 3). Furthermore, apart from CpRe-(CO)$_2$(*n*-heptane), CpRe(CO)$_2$(Xe) is less reactive toward CO than all of the reported alkane-solvated 16-electron early transition metal intermediates! (See Table 2.) These experiments do not of course prove that Xe is coordinated to the CpRe-(CO)$_2$ moiety, but evidence is provided by repeating the photolysis of CpRe(CO)$_3$ in supercritical Kr (scKr).

(c) Characterization and Reactivity of CpRe(CO)$_2$(Kr). Figure 5a shows the FTIR spectrum of CpRe(CO)$_3$ dissolved in supercritical krypton (scKr) in the presence of CO. It should be noted that IR ν(C−O) absorptions of CpRe(CO)$_3$ dissolved in scKr are shifted relative to the IR bands in scXe (see Table 2). Figure 5b shows the TRIR spectrum obtained 100 ns following 266-nm excitation of this solution. The two transient absorptions are shifted to higher wavenumber relative to the absorptions assigned to CpRe(CO)$_2$(Xe) and are assigned tentatively to CpRe(CO)$_2$(Kr). CpRe(CO)$_2$(Kr) is far more

Figure 4. TRIR decay traces recorded following irradiation (266 nm) of CpRe(CO)$_3$ in scXe (1552 psi, 25 °C) in the presence of CO (60 psi) at (a) 1950 and (b) 1958 cm^{-1}. The two traces have been normalized in intensity. (c) Plot of k_{obs} versus CO concentration obtained from first order fit to the decay at 1894 cm^{-1}.

Table 3. Second-Order Rate Constants, k_2 (mol^{-1} dm^3 s^{-1}), for the Reaction of Metal–L Complexes with CO in scL Solution (L = Xe, Kr)

M(CO)$_5$L	temp/°C	k_2/mol^{-1} dm^3 s^{-1}
Cr(CO)$_5$(Xe)	25	8.4×10^6
Cr(CO)$_5$(Kr)	32	4.7×10^8
Mo(CO)$_5$(Xe)	25	1.1×10^7
Mo(CO)$_5$(Kr)	30	4.3×10^8
W(CO)$_5$(Xe)	25	2.0×10^6
W(CO)$_5$(Kr)	25	7.5×10^7
CpRe(CO)$_2$(Xe)	25	4.8×10^3
CpRe(CO)$_2$(Kr)	25	8.1×10^6

reactive than CpRe(CO)$_2$(Xe), decaying within 5 μs, and the lifetime of CpRe(CO)$_2$(Kr) depends linearly on the concentration of CO in scKr (see Figure 6). We estimate the second order rate constant for the reaction of CpRe(CO)$_2$(Kr) with CO in scKr to be $k_2 = 8.1$ (±0.3) $\times 10^6$ mol^{-1} dm^3 s^{-1}. As remarked above, the ν(C–O) bands assigned to CpRe(CO)$_2$(Kr) in scKr are shifted to higher wavenumber relative to those assigned to CpRe(CO)$_2$(Xe) in scXe. Although this shift in itself does not prove Xe or Kr is coordinating to the metal center, it does allow the coordination of Xe to the metal center to be investigated further. Thus, further confirmation of the coordination of Xe to the metal center can be achieved by repeating the TRIR experiment in scKr doped with a small amount of Xe.

Figure 7 shows kinetic traces recorded in scKr doped with Xe. The two traces were recorded at wavenumbers corresponding to the ν(C–O) bands of CpRe(CO)$_2$(Kr) and CpRe(CO)$_2$-(Xe), respectively, see Figures 3 and 5. It is clear that the lifetime of CpRe(CO$_2$)(Kr) is somewhat shorter than in undoped scKr, Figure 6, even though the concentration of CO was the same in the two experiments. At the same time, the formation of CpRe(CO)$_2$(Xe) is not instantaneous, occurring on a time scale that is much longer than the rise time of the IR detector (ca. 25 ns), which matches exactly the decay of CpRe(CO)$_2$-(Kr), $k_{obs} = 2 \times 10^6$ s^{-1}. Thus the traces are consistent with the kinetic formation of CpRe(CO)$_2$(Kr), followed by the slower
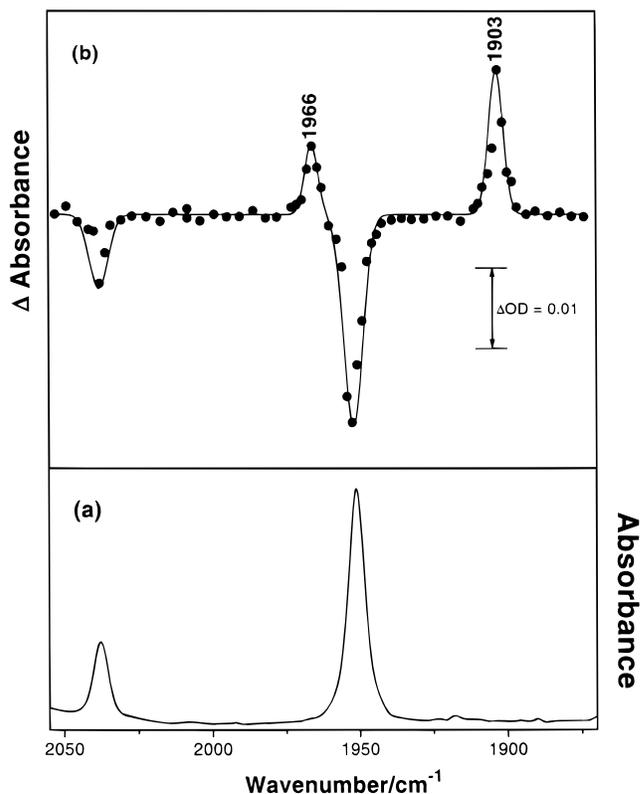
Figure 5. (a) FTIR spectrum of CpRe(CO)$_3$ in scKr (3410 psi, 25 °C) in the presence of CO (30 psi). (b) TRIR *difference* spectrum obtained 100 ns after photolysis (266 nm) of the same solution. The positive peaks are assigned to CpRe(CO)$_2$(Kr), see text.
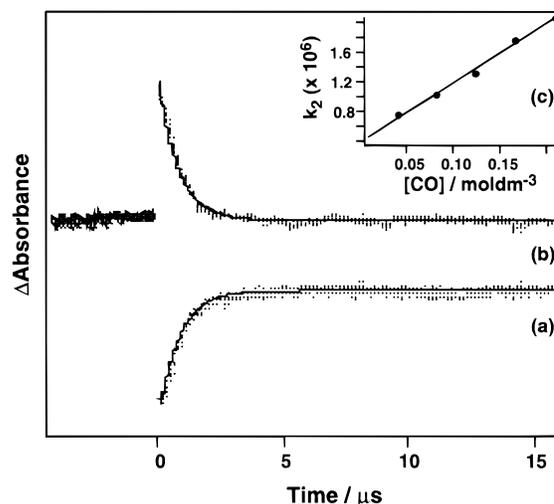
Figure 6. TRIR decay traces recorded following irradiation (266 nm) of CpRe(CO)$_3$ in scKr (3410 psi, 25 °C) in the presence of CO (30 psi) at (a) 2038 and (b) 1903 cm^{-1}. The two traces have been normalized in intensity. (c) Plot of k_{obs} versus CO concentration obtained from first order fit to the decay at 1903 cm^{-1}.

formation of the thermodynamically preferred CpRe(CO)$_2$(Xe), eq 3.

$$CpRe(CO)_3 \xrightarrow{h\nu} CpRe(CO)_2 + CO \qquad (1)$$

$$\text{"CpRe(CO)}_2\text{"} + Kr \rightarrow CpRe(CO)_2(Kr) \qquad (2)$$

$$CpRe(CO)_2(Kr) + Xe \rightarrow CpRe(CO)_2(Xe) + Kr \qquad (3)$$

This interpretation is supported by the full TRIR spectra shown in Figure 8, which shows the TRIR spectrum obtained 100 ns
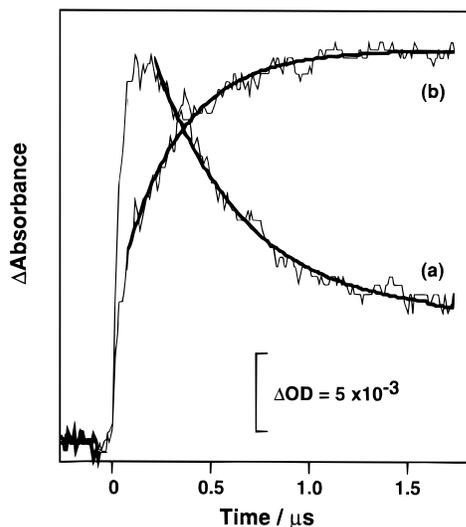
Figure 7. TRIR decay traces recorded following irradiation (266 nm) of CpRe(CO)$_3$ in scKr (3414 psi, 25 °C) in the presence of CO (30 psi) and Xe (50 psi) at (a) 1967 and (b) 1962 cm^{-1}. The two traces have been normalized in intensity.
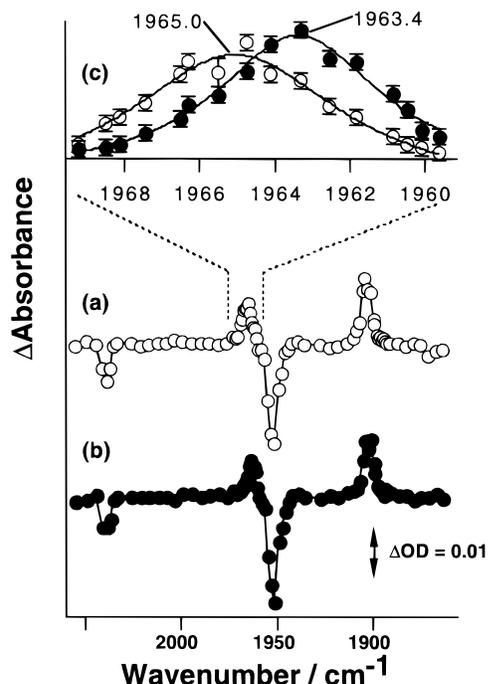
Figure 8. TRIR *difference* spectrum of CpRe(CO)$_3$ in scKr (3414 psi, 25 °C) in the presence of CO (30 psi) and Xe (50 psi) obtained (a) 100 ns (○), and (b) 2 μs (●) after excitation (266 nm). (c) Expanded spectrum around 1965 cm^{-1}, recorded in a separate experiment, where the IR frequency of each data point was determined with a high resolution FTIR spectrometer and the uncertainty in each data point (±0.05 cm^{-1}) is less than the size of the points as printed on the spectrum.

following photolysis of CpRe(CO)$_3$ dissolved in scKr doped with Xe and CO. It is clear that parent absorptions are bleached (note that the ν(C—O) absorptions of CpRe(CO)$_3$ are *not* significantly changed when the scKr is doped with Xe). The new ν(C—O) absorptions at 1966 and 1904 cm^{-1} are identical, within the experimental error of the TRIR spectrometer, with

those observed for CpRe(CO)$_2$(Kr) in undoped scKr and can be assigned to this complex. Within 2 μs, however, the two absorptions have both shifted to lower wavenumber at 1963 and 1900 cm^{-1}. These shifted ν(C—O) absorptions are virtually coincident[23] with those observed for CpRe(CO)$_2$(Xe) in scXe and are assigned to CpRe(CO)$_2$(Xe) in scKr. The bands assigned to CpRe(CO)$_2$(Xe) in scKr have a lifetime that is significantly longer than the lifetime of CpRe(CO)$_2$(Kr) in pure scKr (Figure 6) and similar to the lifetime of CpRe(CO)$_2$(Xe) in scXe (see Figure 4). This behavior should be contrasted with analogous experiments[15] where W(CO)$_6$ was photolyzed in scKr doped with Xe, and preferential coordination of Xe was observed to occur very rapidly (<50 ns). The present data suggest that CpRe(CO)$_2$(Kr) has significant stability, and the rate constants for the reaction of CpRe(CO)$_2$(Xe) and CpRe(CO)$_2$(Kr) with CO shows these complexes to be less reactive than the corresponding M(CO)$_5$(Xe) and M(CO)$_5$(Kr) complexes, Table 3.

Conclusions

The experiments described in this paper show that the CpRe(CO)$_2$ moiety interacts even more strongly with inert ligands than might be predicted from trends in reactivity across the Periodic Table. Indeed, as far as we are aware, this is the first occasion that the formation of a Xe complex has been slow enough to be followed in real time, as a result presumably of a significant Re—Kr interaction in scKr. Noble gas ligands such as Kr and Xe are perhaps the ultimate σ donor with little possibility of acting as electron acceptors. Our observations should therefore be taken as confirmation of the excellent acceptor properties of CpRe(CO)$_2$. Of course CpRe(CO)$_2$ is known to have good electron donor properties, as shown, for example, in the oxidative addition of H$_2$ in scXe, to form *cis*-CpRe(CO)$_2$(H)$_2$.[24] Preliminary TRIR data on CpRe(CO)$_3$ in scCO$_2$ suggest that interaction of CO$_2$ with Re can lead to transient oxidation of the metal center even though there is no overall chemical reaction. This system is now being investigated further.

There is clearly still much to learn about organometallic alkane and noble gas complexes, and it is likely that TRIR spectroscopy will prove increasingly useful for this purpose.

(23) Although the wavenumbers do not appear to be coincident with those of CpRe(CO)$_2$(Xe) in scXe, they are if the solvent shift of the parent bands from scKr to scXe are taken into account, see Table 1.

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