

Do early and late transition metal noble gas complexes react by different mechanisms? A room temperature time-resolved infrared study of $(\eta^5\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})_2$ ($\text{R} = \text{H}$ or Me) in supercritical noble gas solution at room temperature

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Using fast time-resolved infrared spectroscopy, the late transition metal noble gas complexes $\text{CpRh}(\text{CO})(\text{L})$ and $\text{Cp}^*\text{Rh}(\text{CO})(\text{L})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{L} = \text{Xe}$ and Kr) have been characterized at room temperature in supercritical noble gas solution. The krypton complexes are more reactive than the corresponding xenon compounds. There is a significant difference in reactivity with CO between $\text{CpRh}(\text{CO})(\text{L})$ and $\text{Cp}^*\text{Rh}(\text{CO})(\text{L})$ with $\text{CpRh}(\text{CO})(\text{Xe})$ ($k_{\text{CO}} = 6.7 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) being *ca.* 20 times less reactive than $\text{Cp}^*\text{Rh}(\text{CO})(\text{Xe})$ ($k_{\text{CO}} = 1.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Similarly $\text{CpRh}(\text{CO})(\text{Kr})$ ($k_{\text{CO}} = 1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is also less reactive than $\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})$ ($k_{\text{CO}} = 4.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). This should be contrasted to the early transition metal noble gas complexes, where for a given metal–noble gas complex, $\text{CpM}(\text{CO})_2(\text{L})$ and $\text{Cp}^*\text{M}(\text{CO})_2(\text{L})$ ($\text{M} = \text{Mn}$ or Re) have similar reactivity towards CO. The activation parameters for the reaction of $\text{CpRh}(\text{CO})(\text{L})$ and $\text{Cp}^*\text{Rh}(\text{CO})(\text{L})$ with CO have been determined above room temperature, and suggest that the reaction proceeds by an associative mechanism.

Introduction

There is considerable interest in transition metal noble gas complexes, particularly since the isolation of $[\text{AuXe}_4^{2+}][\text{SbF}_{11}^-]_2$, the *first* stable metal–noble gas complex.¹ Organometallic noble gas complexes have been known for more than 25 years. Poliakoff and Turner used matrix isolation to demonstrate that $\text{Fe}(\text{CO})_5$, when photolysed in frozen Xe at 12 K, forms the complex $\text{Fe}(\text{CO})_4(\text{Xe})$.² Using a similar method, Perutz and Turner³ generated $\text{M}(\text{CO})_5(\text{L})$ ($\text{M} = \text{Cr}$, Mo , or W ; $\text{L} = \text{Xe}$, Kr or Ar) from the photolysis of $\text{M}(\text{CO})_6$ in matrices at 20 K. Matrix isolation has since become a powerful technique for the characterization of organometallic noble gas complexes⁴ including *fac*-(η^2 -dfepe) $\text{Cr}(\text{CO})_3(\text{L})$ (dfepe = $(\text{C}_2\text{F}_5)_2\text{PCH}_2\text{-CH}_2\text{P}(\text{C}_2\text{F}_5)_2$; $\text{L} = \text{Ar}$ or Xe),⁵ $\text{CH}_3\text{Mn}(\text{CO})_4(\text{Ar})$,⁶ $\text{KrMn}(\text{CO})_5$,⁷ $\text{Fe}(\text{CO})_4\text{Xe}$,² $[\text{KrFe}(\text{CO})_5]^+$,⁷ $\text{Ru}(\text{CO})_2(\text{PMe}_3)_2(\text{L})$ ($\text{L} = \text{Ar}$ or Xe)⁸ and $\text{Ru}(\text{CO})_2(\text{dmpe})(\text{L})$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{-CH}_2\text{PMe}_2$; $\text{L} = \text{Ar}$ or Xe).⁹ Recently laser ablation and matrix isolation have been combined to characterize the first noble gas–actinide complexes, CUOL ($\text{L} = \text{Ar}$, Kr or Xe).¹⁰ However matrix isolation does not provide the kinetic information needed to quantify the reactivity of these unstable species.

Organometallic noble gas complexes have been observed in solution. Simpson *et al.* characterized $\text{Cr}(\text{CO})_5(\text{Xe})$ at cryogenic temperatures in liquefied Xe (lXe) at -98°C and liquefied Kr (lKr) doped with Xe at -122°C using conventional FTIR spectroscopy following UV photolysis of $\text{Cr}(\text{CO})_6$.¹¹ Subsequently, Weiller detected $\text{M}(\text{CO})_5(\text{L})$ ($\text{M} = \text{Cr}$ or W ; $\text{L} = \text{Xe}$ or Kr) in liquefied noble gas solution at low temperature using rapid-scan FTIR spectroscopy.¹²

Time-resolved infrared spectroscopy (TRIR), a combination of UV flash photolysis and fast infrared detection, is a powerful spectroscopic tool for characterizing highly reactive intermediates.¹³ Bergman and co-workers used TRIR to investigate the C–H activation of alkanes with $\text{Cp}^*\text{Rh}(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in lKr and lXe in the presence of cyclohexane¹⁴ and neopentane.¹⁵ This permitted the detection of the noble gas intermediates, $\text{Cp}^*\text{Rh}(\text{CO})(\text{L})$ ($\text{L} = \text{Kr}$ and Xe). $\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})$ decayed much more rapidly than $\text{Cp}^*\text{Rh}(\text{CO})(\text{Xe})$, due to the latter complex having a stronger metal–noble gas bond. The Rh–Xe bond energy was estimated from the activation parameters ($\Delta H_{\text{Rh-Xe}} \geq 11.7 \pm 1.3 \text{ kJ mol}^{-1}$). Recent TRIR experiments on $\text{Tp}^*\text{Rh}(\text{CO})_2$ and $\text{Bp}^*\text{Rh}(\text{CO})_2$ ($\text{Tp}^* = \text{hydrido-tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$; $\text{Bp}^* = \text{dihydrido-bis}(3,5\text{-di-$

methylpyrazolyl)borate) in lXe at 223 K¹⁶ characterized the xenon complexes; $(\eta^3\text{-Tp}^*)\text{Rh}(\text{CO})(\text{Xe})$ and $(\eta^2\text{-Tp}^*)\text{Rh}(\text{CO})(\text{Xe})$. This assignment was supported by comparison to $\text{Bp}^*\text{Rh}(\text{CO})(\text{Xe})$ which is formed from irradiation of $\text{Bp}^*\text{Rh}(\text{CO})_2$ in lXe. Noble gas complexes have also been observed in the gas phase at room temperature.¹⁷

Using TRIR spectroscopy, we have shown that organometallic noble gas complexes can be observed in solution at room temperature. The complexes $\text{M}(\text{CO})_5(\text{L})$ ($\text{M} = \text{Cr}$, Mo or W ; $\text{L} = \text{Ar}$ (W only), Kr or Xe),¹⁸ $\text{CpM}(\text{CO})_3(\text{L})$ ($\text{M} = \text{Nb}$ and Ta ; $\text{L} = \text{Xe}$)¹⁹ and $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2(\text{L})$ ($\text{M} = \text{Mn}$ and Re ; $\text{R} = \text{H}$, Me and Et (Mn only); $\text{L} = \text{Ar}$ ($\text{CpRe}(\text{CO})_2(\text{Ar})$ only), Kr and Xe)^{20,21} were generated following irradiation of metal carbonyls in supercritical noble gas solution. The reactivity of these complexes increases in the order $\text{Xe} < \text{Kr} < \text{Ar}$ and $\text{Re} \leq \text{W} < \text{Mn} < \text{Mo} \approx \text{Cr} \approx \text{Nb} \approx \text{Ta}$. For all these complexes we found that a given Xe complex had similar reactivity to the corresponding alkane complex. The comparison of reactivities between organometallic noble gas and alkane complexes is important. We reported $\text{CpRe}(\text{CO})_2(n\text{-heptane})$ as being the longest lived alkane complex at room temperature²⁰ and this proved significant as Ball and Geftakis were subsequently able to characterize $\text{CpRe}(\text{CO})_2(\text{cyclopentane})$ at low temperature using NMR spectroscopy.²² $\text{CpRe}(\text{CO})_2(\text{Xe})$ was found to be only twice as reactive toward CO in scXe compared to $\text{CpRe}(\text{CO})_2(n\text{-heptane})$ in *n*-heptane solution.²⁰ The comparison between the reactivities of the alkane and xenon complexes cannot be extended for the later transition metal complexes such as $\text{CpRh}(\text{CO})(\text{alkane})$ since these complexes are known to undergo C–H activation. In this paper we have characterized $\text{Cp}'\text{Rh}(\text{CO})(\text{Xe})$ and $\text{Cp}'\text{Rh}(\text{CO})(\text{Kr})$ ($\text{Cp}' = \text{Cp}$ ($\eta^5\text{-C}_5\text{H}_5$) or Cp^* ($\eta^5\text{-C}_5\text{Me}_5$)) in supercritical fluid solution at room temperature and determined the reactivity and activation parameters for the reaction between $\text{Cp}'\text{Rh}(\text{CO})(\text{L})$ ($\text{L} = \text{Xe}$ or Kr ; $\text{Cp}' = \text{Cp}$ or Cp^*) and CO. These results show clear differences between the Cp and Cp^* complexes and also the early and late transition metal noble gas complexes.

Experimental

Materials

$\text{CpRh}(\text{CO})_2$ was prepared according to an earlier literature procedure.²³ Pentamethylcyclopentadienyl rhodium dicarbonyl

[Cp*Rh(CO)₂] (Strem), Xe (BOC, research grade), Kr (BOC, research grade), and CO (Air products, premier grade) were used as received.

Time-resolved infrared apparatus

Two different types of TRIR instrumentation were used to monitor the transient IR absorptions, both employing a pulsed Nd:YAG laser (Spectra Physics Quanta-Ray GCR-12; 266 nm) to initiate the photochemical reactions. For the Cp*Rh(CO)(L) (L = Xe or Kr) spectra and kinetic experiments, a continuous wave IR diode laser (Mütek MDS 1100) was used. Details of the Nottingham diode laser based TRIR apparatus have been described elsewhere.¹³ In these experiments, the change in IR transmission at one IR frequency was measured following UV excitation and a spectrum was built up on a 'point-by-point' basis by repeating this measurement at different infrared frequencies. The time-resolved spectra of CpRh(CO)(L) (L = Xe or Kr) were obtained using a *step-scan* FTIR interferometer, details of which have also been reported elsewhere.²⁴ Briefly, the apparatus comprises of a commercially available step-scan FTIR spectrometer (Nicolet Magna 860) equipped with a 100 MHz 12-bit digitizer and a 50 MHz MCT detector interfaced to a Nd:YAG laser with data collection achieved using a pulse generator (Stanford DG535).

Supercritical noble gas solutions were formed in a high-pressure cell described previously for conventional spectroscopic monitoring.²⁵ The cell was used with CaF₂ windows and a pressure transducer (RDP Electronics).

Results and discussion

Characterisation and reactivity of Cp'Rh(CO)L (Cp' = Cp, Cp*; L = Xe, Kr)

Fig. 1(a) shows the FTIR spectrum of CpRh(CO)₂ dissolved in scXe (2500 psi, 25 °C) in the presence of CO (15 psi). Fig. 1(b) shows the TRIR spectrum of CpRh(CO)(Xe) obtained 1.0 μs after photolysis (266 nm) of this solution. The parent ν(C–O) absorptions are clearly bleached and a new photoproduct with a band at 1967 cm⁻¹ is produced. This is consistent with the loss of CO from the parent to form a monocarbonyl species. This new species can be readily assigned to CpRh(CO)(Xe) by comparison with the previously obtained TRIR spectrum of Cp*Rh(CO)Xe in IXe.²⁶

CpRh(CO)(Xe) decays ($k_{\text{obs}} = 9.5 (\pm 1.0) \times 10^4 \text{ s}^{-1}$) at the same rate as the parent dicarbonyl CpRh(CO)₂ is reformed (k_{obs}

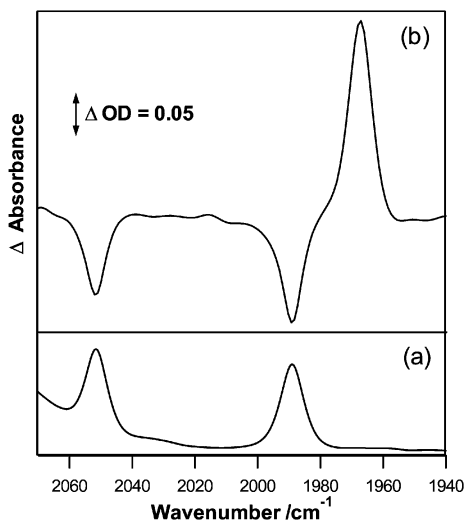


Fig. 1 (a) FTIR spectrum of CpRh(CO)₂ in scXe (2500 psi) and (b) step-scan FTIR spectrum obtained 1.0 μs after UV laser excitation (266 nm).

$= 9.3 (\pm 0.9) \times 10^4 \text{ s}^{-1}$, Fig. 2. The rate of decay of CpRh(CO)(Xe) in scXe depends linearly on the concentration of CO, affording the second order rate constant ($k_{\text{CO}} = 6.7 (\pm 0.7) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for the reaction of CpRh(CO)(Xe) with CO in scXe, Fig. 3. Using a similar methodology in either scXe or scKr, we were able to characterize Cp*Rh(CO)(Xe), CpRh(CO)(Kr), and Cp*Rh(CO)(Kr) at room temperature (Tables 1 and 2).

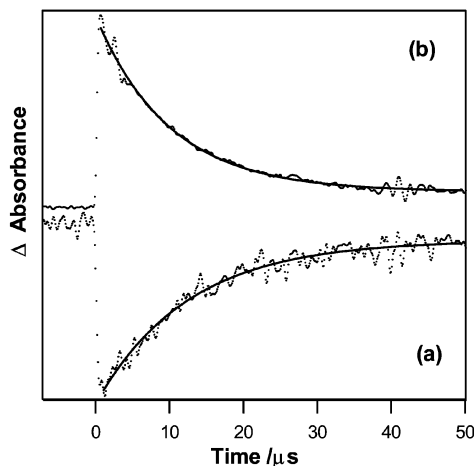


Fig. 2 Kinetic traces taken of CpRh(CO)₂ in scXe. (a) Parent bleach (1988 cm⁻¹) and subsequent regeneration and (b) formation and decay of the xenon complex (1967 cm⁻¹).

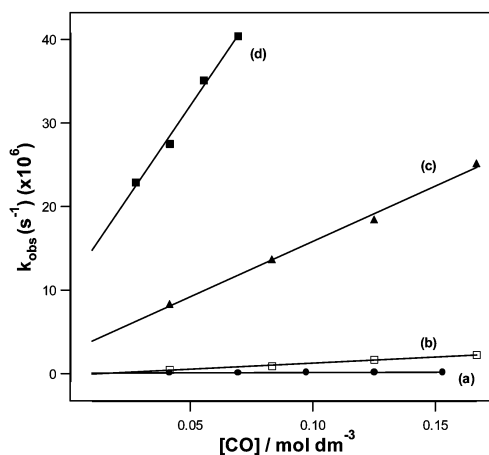


Fig. 3 CO concentration dependence of k_{obs} at room temperature yielding the slope of the line as the second-order rate constant for the reactions with CO for (a) CpRh(CO)(Xe) ($k_{\text{CO}} = 6.7 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), (b) Cp*Rh(CO)(Xe) ($k_{\text{CO}} = 1.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), (c) CpRh(CO)(Kr) ($k_{\text{CO}} = 1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and (d) Cp*Rh(CO)(Kr) ($k_{\text{CO}} = 4.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

The second-order rate constants for the reaction of Cp'Rh(CO)(L) with CO (Fig. 4) in scL (Cp' = Cp or Cp*; L = Xe or Kr) reflect the difference in reactivity of these complexes in solution at room temperature. In both cases, the expected increase in reactivity of the krypton complex over the corresponding xenon complex is observed. This agrees with previous results in liquefied noble gases,¹² the gas phase¹⁷ and supercritical fluids.^{18–21}

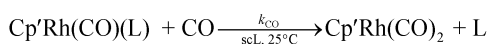
A comparison of the second-order rate constants for the reaction of the xenon and krypton complexes with CO at room temperature shows that Cp*Rh(CO)(Kr) is *ca.* ×30 more reactive than Cp*Rh(CO)(Xe). This should be contrasted to their reactivity in liquefied noble gas solution at low temperatures when the krypton complex is more than ×200 more reactive than the xenon complex.²⁶ However, the reactivity of Cp*Rh(CO)(Kr) towards CO in liquefied Kr was shown to exhibit no significant temperature dependence over the range

Table 1 Table showing $\nu(\text{C-O})$ IR band positions of $\text{Cp}'\text{Rh}(\text{CO})(\text{L})$ complexes ($\text{L} = \text{CO}, \text{Xe}$ or Kr)

Complex	Conditions	Wavenumber/ cm^{-1}
$\text{Cp}^*\text{Rh}(\text{CO})_2^a$	IXe (242 K)	2031, 1969
$\text{Cp}^*\text{Rh}(\text{CO})_2^a$	IKr (242 K)	2027, 1963
$\text{Cp}^*\text{Rh}(\text{CO})(\text{Xe})^a$	IXe (242 K)	1940
$\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})^a$	IKr (242 K)	1947
$\text{CpRh}(\text{CO})_2^b$	scXe (298 K)	2051, 1988
$\text{CpRh}(\text{CO})_2^b$	scKr (298 K)	2056, 1994
$\text{Cp}^*\text{Rh}(\text{CO})_2^b$	scXe (298 K)	2034, 1966
$\text{Cp}^*\text{Rh}(\text{CO})_2^b$	scKr (298 K)	2033, 1972
$\text{CpRh}(\text{CO})(\text{Xe})^b$	scXe (298 K)	1967
$\text{CpRh}(\text{CO})(\text{Kr})^b$	scKr (298 K)	1975
$\text{Cp}^*\text{Rh}(\text{CO})(\text{Xe})^b$	scXe (298 K)	1944
$\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})^b$	scKr (298 K)	1951
$\text{Cp}^*\text{Rh}(\text{CO})_2^b$	scAr (298 K)	2035, 1976

^a See ref. 26. ^b This study.

Table 2 Rates of reactivity with CO at room temperature (298 K) for the reaction ($\text{L} = \text{Xe}$ or Kr)



Complex	Conditions	$k_{\text{CO}}^a/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
$\text{W}(\text{CO})_5\text{Ar}^b$	scAr	1.4×10^9
$\text{Cr}(\text{CO})_5\text{Kr}^b$	scKr	4.7×10^8
$\text{Cp}^*\text{Rh}(\text{CO})\text{Kr}^c$	scKr	4.3×10^8
$\text{Mo}(\text{CO})_5\text{Kr}^b$	scKr	4.3×10^8
$\text{CpRh}(\text{CO})\text{Kr}^c$	scKr	1.3×10^8
$\text{W}(\text{CO})_5\text{Kr}^b$	scKr	7.5×10^7
$\text{Cp}^*\text{Mn}(\text{CO})_2\text{Kr}^d$	scKr	7.5×10^7
$\text{CpMn}(\text{CO})_2\text{Kr}^d$	scKr	7.2×10^7
$\text{Cp}^*\text{Rh}(\text{CO})\text{Xe}^c$	scXe	1.4×10^7
$\text{Mo}(\text{CO})_5\text{Xe}^b$	scXe	1.1×10^7
$\text{Cr}(\text{CO})_5\text{Xe}^b$	scXe	8.4×10^6
$\text{CpRe}(\text{CO})_2\text{Kr}^d$	scKr	8.1×10^6
$\text{Cp}^*\text{Re}(\text{CO})_2\text{Kr}^d$	scKr	7.8×10^6
$\text{CpNb}(\text{CO})_3\text{Xe}^e$	scXe	5.7×10^6
$\text{CpTa}(\text{CO})_3\text{Xe}^e$	scXe	4.9×10^6
$\text{W}(\text{CO})_5\text{Xe}^b$	scXe	2.0×10^6
$\text{Cp}^*\text{Mn}(\text{CO})_2\text{Xe}^d$	scXe	1.8×10^6
$\text{CpMn}(\text{CO})_2\text{Xe}^d$	scXe	1.6×10^6
$\text{CpRh}(\text{CO})\text{Xe}^c$	scXe	6.7×10^5
$\text{Cp}^*\text{Re}(\text{CO})_2\text{Xe}^d$	scXe	6.0×10^3
$\text{CpRe}(\text{CO})_2\text{Xe}^d$	scXe	4.8×10^3

^a $\pm 10\%$. ^b See ref. 18. ^c This study. ^d See ref. 21. ^e See ref. 19.

163–193 K. The k_{CO} obtained at room temperature ($k_{\text{CO}} = 4.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is only 4 times greater than that at 163–193 K ($k_{\text{CO}} = 1.1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). This suggests that the reactivity of $\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})$ has little temperature dependence over this temperature range. The difference in these rate constants is probably due to the activation parameters for the reaction of the noble gas complexes with CO.

The comparison between organometallic xenon and alkane complexes is important. However, the similarity of the reactivity of early transition metal xenon complexes to that of their corresponding alkane complex is not so relevant in the case of these rhodium complexes because of the C–H activation process. The xenon complexes have a lifetime of microseconds, the σ -alkane complex lives only on the nanosecond timescale due to the activation of the C–H bond.²⁷

$\text{Cp}^*\text{Rh}(\text{CO})(\text{Xe})$ ($k_{\text{CO}} = 1.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is shown here to be *ca.* 2 orders of magnitude more reactive than the non-methyl substituted complex $\text{CpRh}(\text{CO})(\text{Xe})$ ($k_{\text{CO}} = 6.7 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). This difference in reactivity is very different to that of the early transition metal half-sandwich complexes. It was found that for a given metal, $\text{CpM}(\text{CO})_2(\text{Xe})$ and $\text{Cp}^*\text{M}(\text{CO})_2(\text{Xe})$ ($\text{M} = \text{Mn}$ or Re) complexes have a similar reac-

tivity towards CO.²¹ In this study, the difference of reactivities between the cyclopentadienyl and methyl-substituted cyclopentadienyl complexes shows the same trend as observed with half-sandwich organometallic alkane complexes, where sterics were implicated as being the major contributor to the difference in reactivity.²⁸ The reactivity of the rhodium noble gas complexes relative to the other organometallic noble gas complexes is easily visualised by examining the ordering of the $\ln(k_2)$, Fig. 4. As can be clearly seen, the analogous krypton complexes are by far more reactive than the corresponding xenon complexes for all known complexes, $\text{CpM}(\text{CO})_x(\text{L})$ and $\text{M}(\text{CO})_5(\text{L})$ (where $\text{M} = \text{Re}, \text{Rh}, \text{Mn}, \text{Ta}, \text{Nb}, \text{W}, \text{Mo}$, and Cr ; $\text{L} = \text{Xe}$ and Kr). $\text{CpRh}(\text{CO})(\text{Xe})$ is much less reactive than all the organometallic xenon complexes apart from the rhenium complexes. A trend in reactivity can be seen across the periodic table where the stability of the metal–noble gas complexes increase. This is also true when moving down each group with the heavier metal complexes (*e.g.* rhenium) shown to be less reactive. We have investigated this further by determining the activation parameters for the reaction of $\text{CpM}(\text{CO})_x(\text{Xe})$ and $\text{Cp}^*\text{M}(\text{CO})_x(\text{Xe})$ with CO.

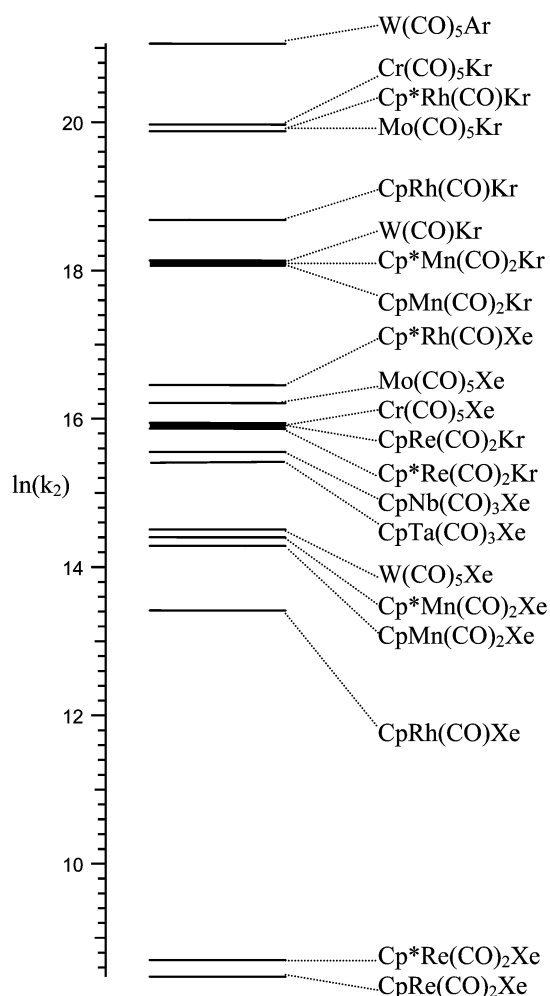


Fig. 4 Graph showing contrast of reactivity obtained for all the noble gas complexes $\text{Cp}'\text{M}(\text{CO})_x(\text{L})$ and $\text{M}(\text{CO})_5(\text{L})$ with CO.

Determination of activation parameters for the reaction of $\text{Cp}'\text{Rh}(\text{CO})(\text{Xe})$ with CO in scXe

Fig. 5 shows the Arrhenius and Eyring plots for the reaction of $\text{CpRh}(\text{CO})(\text{Xe})$ and $\text{Cp}^*\text{Rh}(\text{CO})(\text{Xe})$ with CO. Interpretation of the differences between the activation parameters for the reaction of the alkane complexes with CO requires careful consideration, since the reaction may proceed *via* an associative, associative interchange, dissociative interchange or dissociative

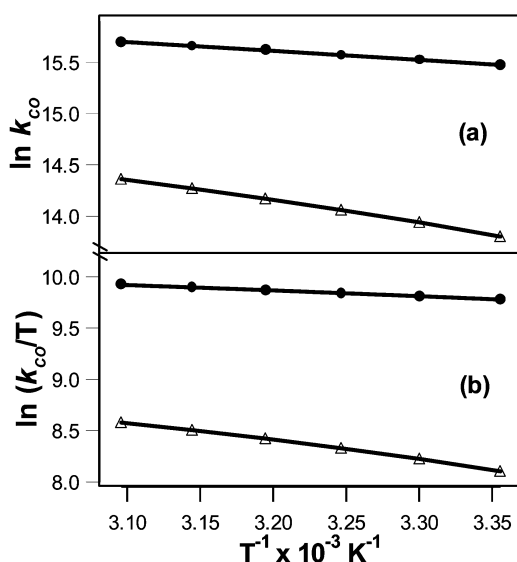
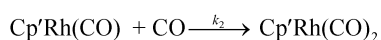
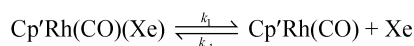


Fig. 5 Results from variable temperature experiments following the reaction of Cp'Rh(CO)(Xe) and CO assuming an associative mechanism. (a) Arhenius plot of CpRh(CO)(Xe) (top) and Cp*Rh(CO)(Xe) (bottom) and (b) Eyring plot of CpRh(CO)(Xe) (top) and Cp*Rh(CO)(Xe) (bottom).

mechanism, or by a combination of these pathways. Ligand substitution kinetics of CpRh(CO)₂ and related compounds has been reported to proceed by an associative mechanism.^{29,30} CO and Xe are completely miscible over a wide temperature range in the supercritical environment, which greatly simplifies these variable temperature experiments. Pseudo-first-order conditions were maintained for all experiments and at each temperature the second-order rate constant (k_{CO}) was obtained by a plot of k_{obs} versus [CO].

Calculation of the activation parameters depends on the reaction pathway assumed. † A strong indication of the nature of

† For a dissociative mechanism in scXe, the following rate equations would apply for the reaction of Cp'Rh(CO)(Xe) (Cp' = Cp or Cp*) with CO:

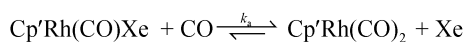


Applying the steady-state approximation to the intermediate, Cp'Rh(CO), results in the following expression for k_{obs} :

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

where k_1 is the elementary rate constant for dissociation of Xe. This means that for a purely dissociative mechanism the rate constant for the reaction of Cp'Rh(CO)(Xe) with CO is dependent on xenon concentration. Assuming that Cp'Rh(CO) reacts with both Xe and CO at near-diffusion-controlled rates, the diffusion-controlled rate constant, k_d can be estimated in scXe using the Stokes–Einstein relation, giving $k_{-1} \approx k_2 \approx 5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Since $[\text{Xe}] \approx 70 \times [\text{CO}]$ in our 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. This leads to the expression

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

For an associative mechanism the rate constant is independent of Xe concentration. Both mechanisms therefore predict a linear relationship of k_{obs} with CO as we have already shown.

the mechanism can be obtained from the values of ΔS^\ddagger derived from the Eyring plots. Extreme caution must be taken when obtaining ΔS^\ddagger values from Eyring plots since small deviations in gradient of such plots can have a dramatic effect on the result. A large negative entropy of activation was calculated and although the precise value of ΔS^\ddagger may change slightly we are confident in a large negative value of ΔS^\ddagger obtained from the data shown in Fig. 5. This is characteristic of an associative mechanism. Only the values obtained using an associative mechanism for the reaction of Cp'Rh(CO)(Xe) with CO in scXe are given in Table 3. The activation parameters for the reactivity of the early transition metal noble gas complexes Cp'M(CO)₂(Xe) (M = Mn or Re) indicate that these reactions may occur *via* a dissociative interchange mechanism.

Bergman and co-workers have previously measured the activation parameters of Cp*Rh(CO)(Xe) in liquefied Xe solution at cryogenic temperatures (202–242 K).²⁶ We have found the values obtained at low temperatures are in good agreement with our results in supercritical solution (Table 3). The activation parameters strongly indicate that the reaction of Cp'Rh(CO)(Xe) with CO is occurring *via* an associative pathway in scXe at room temperature. Supercritical fluids offer a unique opportunity to probe the mechanism of such reactions further. In the condensed phase, such as alkane solution, the concentration of solvent cannot be altered. However, supercritical fluids allow the measurement of k_{obs} as a function of Xe concentration. Such a measurement was pioneered by Turner *et al.* for monitoring the reactivity of Ni(CO)₃(N₂) in lKr.³¹ For a dissociative mechanism, k_{obs} will depend on the concentration of the leaving ligand, Xe,

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

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(CO₂) in scCO₂.¹⁸ We measured k_{obs} as a function of [CO] whilst holding the [CO]/[CO₂] 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 of W(CO)₅(CO₂) 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(CO₂) ($1/k_{\text{obs}}$) as a function of [CO₂] at constant [CO]. For a dissociative process, $1/k_{\text{obs}} \propto [\text{CO}_2]$ and we were able to show that $1/k_{\text{obs}}$ exactly follows the change in CO₂ density with pressure, therefore demonstrating that the reaction of W(CO)₅(CO₂) with CO in scCO₂ is predominantly a dissociative process. We used a similar approach to probe the reaction of ($\eta^5\text{-C}_5\text{R}_2$)Mn(CO)₂(Xe) (R = H, Me or Et) with CO in scXe.²¹

Fig. 6 shows how k_{obs} , for the reaction of CpRh(CO)(Xe) and Cp*Rh(CO)(Xe) with CO in scXe, varies with increasing [CO] whilst maintaining a constant [CO]/[Xe] ratio.

The expression for k_{obs} , assuming both dissociative and associative mechanisms, is given below,

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

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 $k_1 [\text{CO}]/[\text{Xe}]$. If the slope is zero then associative pathways can be assumed to be insignificant. Fig. 6 shows that at a constant [CO]/[Xe] ratio, k_{obs} shows

Table 3 Activation parameters for the reaction of Cp'Rh(CO)(Xe) and Cp'M(CO)₂(Xe) with CO (M = Re or Mn; Cp' = Cp or Cp*) assuming a purely associative mechanism by using k_{CO} as the rate constant^a

Compound	E_a^b /kJ mol ⁻¹	ΔH^\ddagger^c /kJ mol ⁻¹	ΔS^\ddagger^d /J K ⁻¹ mol ⁻¹	Conditions
CpMn(CO) ₂ (Xe) ^e	32.0	29.5	-5	scXe
Cp*Mn(CO) ₂ (Xe) ^e	36.7	34.1	+11	scXe
CpRe(CO) ₂ (Xe) ^e	49.9	47.2	+5	scXe
Cp*Re(CO) ₂ (Xe) ^e	46.5	43.9	+2	scXe
CpRh(CO)(Xe) ^f	17.9	15.2	-79	scXe
Cp*Rh(CO)(Xe) ^g	11.8	10.1	-84	liqXe
Cp*Rh(CO)(Xe) ^f	7.2	4.6	-100	scXe

^a See ref. 32. ^b ± 2 kJ mol⁻¹. ^c ± 2 kJ mol⁻¹. ^d ± 10 J K⁻¹ mol⁻¹. ^e See ref. 21. ^f This study. ^g See ref. 26.

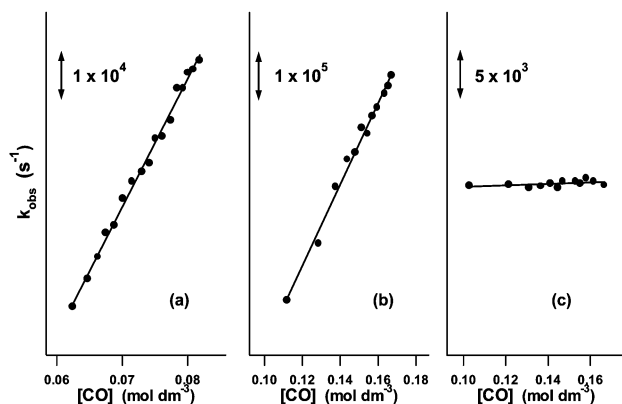


Fig. 6 Plot of k_{obs} vs. $[\text{CO}]$ maintaining a constant $[\text{CO}]/[\text{Xe}]$ ratio for the reaction of Cp'M(CO)₂(Xe) with CO: (a) CpRh(CO)(Xe), (b) Cp*Rh(CO)(Xe) and (c) CpRe(CO)₂(Xe).

an appreciable dependence on $[\text{CO}]$ for the reaction of both CpRh(CO)(Xe) and Cp*Rh(CO)(Xe) with CO. This should be contrasted to the results obtained previously for the reaction of CpMn(CO)₂(Xe) with CO at constant $[\text{CO}]/[\text{Xe}]$ ratio,²¹ which shows no significant dependence upon $[\text{CO}]$. We have also performed such measurements on the reaction of CpRe(CO)₂(Xe) with CO and again found no significant dependence on $[\text{CO}]$ at a constant $[\text{CO}]/[\text{Xe}]$ ratio, Fig. 6(c). From these experiments we conclude that there is not a large contribution from a purely associative mechanism for the reaction of Cp'Rh(CO)(Xe) with CO in scXe. The slope obtained from the plot of k_{obs} versus $[\text{CO}]$ at constant $[\text{CO}]/[\text{Xe}]$ ratio for the reactions of CpRh(CO)(Xe) ($k_a = 2.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and Cp*Rh(CO)(Xe) ($k_a = 9.7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) with CO are slightly different to the k_{CO} values obtained at constant Xe density however. These values do show however, that the associative processes are significant in the reaction of the rhodium noble gas complexes and CO. Another experiment that could be performed to elucidate the reactivity further would be to measure $1/k_{\text{obs}}$ as a function of $[\text{Xe}]$ at constant $[\text{CO}]$. In this case a dissociative mechanism should produce a linear plot of $1/k_{\text{obs}}$ versus $[\text{Xe}]$ whilst 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.

Recent work in our group on Group 7 noble gas complexes²¹ in supercritical solution has shown a significant difference in the activation parameters obtained (Table 3). The ΔH^\ddagger values for the reaction of the metal-xenon complexes with CO give an indication of the metal-xenon bond strengths. The Cp'Rh(CO)(Xe) (Cp' = Cp and Cp*) complexes have much lower ΔH^\ddagger values than the Cp'Re(CO)(Xe) complexes. If the reaction pathway for the decay of the xenon complexes were totally dissociative, then the ΔH^\ddagger values calculated would equate to the metal-xenon bond dissociation energy (BDE). Since the reaction of Cp'Rh(CO)(Xe) with CO proceeds with associative behaviour a low value of ΔH^\ddagger is expected ($\Delta H^\ddagger = 15.2$ and 4.6

kJ mol⁻¹ for CpRh(CO)(Xe) and Cp*Rh(CO)(Xe) respectively) and we expect that the Rh-Xe BDE is significantly greater than the ΔH^\ddagger values obtained from the Eyring plots.

Conclusion

In this paper we have described the characterisation of the organometallic noble gas complexes, Cp'Rh(CO)(L) (Cp' = Cp or Cp*; L = Xe or Kr) in supercritical noble gas solution at room temperature. CO substitution kinetics have shown that for both noble gases, the H and Me substituted complexes, CpRh(CO)(L) and Cp*Rh(CO)(L) have a very different reactivity towards CO, with the methyl substituted complexes being approximately 20 times more reactive. This behaviour has been shown to be very different to that of the early transition metal half-sandwich noble gas complexes, where the reactivities of the Cp and Cp* complexes have very similar reactivities.

We have also presented the activation parameters calculated for the reaction of Cp'Rh(CO)(Xe) with CO. A comparison can be made between these activation parameters and those obtained from the analogous reaction of Group 7 half-sandwich noble gas complexes with CO. The vast differences in the calculated values have suggested that these reactions proceed by two different mechanisms. From the values obtained and by comparison with results gained in lXe at low temperatures, we can conclude that the reaction of Cp'Rh(CO)(Xe) with CO proceeds by an associative mechanism. Experiments were also performed where the $[\text{CO}]/[\text{Xe}]$ ratio was kept constant which enabled us to confirm the mechanistic behaviour of the system. Similar experiments for the reaction of CpM(CO)₂(Xe) and CO indicated that the Group 7 complexes contained negligible associative behaviour, in stark contrast to the Group 9 complexes. Evidently there is still much to learn about organometallic noble gas complexes and it has been shown that TRIR spectroscopy is a very useful method for probing these complexes.

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