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FULL PAPER

Investigation into the reactivity of M(η^5-C$_5$R$_5$)(CO)$_2$(alkane) (M = Mn or Re; R = H, Me or Ph; alkane = *n*-heptane or cyclopentane) and Re(η^5-C$_5$H$_5$)(CO)$_2$(Xe) in solution at cryogenic and room temperature

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A series of M(η^5-C$_5$R$_5$)(CO)$_2$(C$_5$H$_{10}$) complexes (R = H, Me or Ph; M = Mn or Re) have been characterised at low (Re only) and room temperature (R = H only) using infrared spectroscopy. The decay rates of these complexes have been measured and compared to those of the corresponding *n*-heptane analogues. These comparisons show that the organometallic cyclopentane complexes are significantly longer-lived than the related *n*-heptane complexes. The activation parameters for the reaction of the alkane complexes with CO, determined above room temperature, suggest that the reactivity of these complexes is governed by entropic rather than enthalpic factors. The decay rates measured for the permethylated and perphenylated cyclopentadienyl rhenium cyclopentane complexes show that these are more reactive towards CO than Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_5$H$_{10}$). The complex Re(η^5-C$_5$H$_5$)(CO)$_2$(Xe) has been characterised in liquid xenon at low temperature, with decay rate studies showing this to have a similar lifetime to Re(η^5-C$_5$H$_5$)(CO)$_2$(*n*-C$_7$H$_{16}$) in heptane at a similar temperature.

Introduction

Organometallic alkane complexes are of fundamental interest and there are several recent reviews in this area.[1–4] One of the interests in this field is the key role of these complexes as intermediates in the C–H activation process.[1,5–12] Information regarding both the structure and reactivity of alkane complexes is important for a better understanding of this process. Hence the isolation of a stable transition metal alkane complex remains an unfulfilled but realistic goal.[3,13]

Organometallic alkane and noble gas complexes have been known for over 20 years. Poliakoff and Turner used matrix isolation to show[14,15] that photolysis of Fe(CO)$_5$ generates Fe(CO)$_4$, which is sufficiently reactive to form complexes with CH$_4$ and Xe at 12 K. Similarly, Perutz and Turner found that[16,17] photolysis of M(CO)$_6$ generates M(CO)$_5$ (M = Cr, Mo or W), which can react to form complexes with CH$_4$, Xe and Kr at 12 K. Although matrix isolation permits the characterisation of unstable species at low temperature, it does not provide the kinetic information needed to quantify the reactivity of these species. In solution, Cr(CO)$_5$(C$_6$H$_{12}$) is formed at room temperature within 50 ns following UV flash photolysis of Cr(CO)$_6$ in cyclohexane.[18] Subsequently, ultrafast transient spectroscopy has shown[19,20] that the solvation process for Cr(CO)$_5$ occurs *within the first picosecond* following UV irradiation. In solution, Cr(CO)$_5$(C$_6$H$_{12}$) is reactive and decays within 50 μs. Grevels and co-workers[21,22] demonstrated that fast time-resolved infrared spectroscopy (TRIR), a combination of UV flash photolysis and fast infrared detection, was a particularly useful technique for characterising these solvated intermediates.

The photochemistry of the Group VI hexacarbonyls has been widely exploited to generate unstable organometallic alkane complexes, both at cryogenic temperatures in matrices and at room temperature. For example, photolysis of W(CO)$_6$ has been used to generate W(CO)$_5$L (L = CH$_4$, C$_2$H$_6$, C$_3$H$_8$, *n*-C$_4$H$_{10}$, *i*-C$_4$H$_{10}$, *n*-C$_5$H$_{12}$, *n*-C$_6$H$_{14}$, *c*-C$_3$H$_6$, *c*-C$_5$H$_{10}$, *c*-C$_6$H$_{12}$ or *n*-C$_7$H$_{16}$).[17,23–25] Other Group VI carbonyl complexes have been used to generate alkane complexes including *fac*-Cr(CO)$_3$(dfepe)(L) (dfepe = 1,2-bis[bis(pentafluoroethyl)phosphino]ethane; L = CH$_4$, *n*-C$_6$H$_{14}$ or *c*-C$_6$H$_{12}$),[26] M(CO)$_2$(η^6-C$_6$R$_6$)(*c*-C$_6$H$_{12}$) (R = H, Me or Et; M = Cr or Mo)[27,28] and M(CO)$_2$(η^6-C$_6$H$_6$)(L) (L = *n*-C$_5$H$_{12}$, *n*-C$_7$H$_{16}$, *n*-C$_{10}$H$_{22}$ or *n*-C$_{12}$H$_{26}$; M = Cr or Mo).[27,28]

The generation of unstable organometallic alkane complexes in solution has also been observed for M(η^5-C$_5$H$_5$)(CO)$_3$(*n*-C$_7$H$_{16}$)[29] (M = V, Nb or Ta) and M(η^5-C$_5$H$_5$)(CO)$_2$(L)[30–32] (M = Mn or Re; L = *n*-C$_7$H$_{16}$ or *c*-C$_6$H$_{12}$ (Mn only)) in solution at room temperature. Organometallic alkane complexes have also been generated from non-carbonyl precursors. Hall and Perutz,[4] for example, characterised a methane complex following the photolysis of M(dmpe)$_2$H(H$_2$) (M = Mn or Re; dmpe = 1,2-bis(dimethylphosphino)ethane) in methane matrices at low temperature.

Previous work in our group[29,32] has shown that the stability of organometallic alkane complexes increases both *across* and *down* Groups V, VI and VII, with the Re(η^5-C$_5$H$_5$)(CO)$_2$(*n*-C$_7$H$_{16}$) complex reacting 50000 times slower than V(η^5-C$_5$H$_5$)(CO)$_3$(*n*-C$_7$H$_{16}$). Group VIII and IX metals form less stabilised alkane complexes, with Co(η^5-C$_5$H$_5$)(CO) having no detectable interaction with cyclohexane[33] and M(η^5-C$_5$Me$_5$)(CO) (M = Rh or Ir) reacting with alkanes to form C–H activated products.[10,11,34] The least reactive of the reported organometallic alkane complexes is Re(η^5-C$_5$H$_5$)(CO)$_2$(*n*-C$_7$H$_{16}$),[32] with a lifetime of *ca.* 30 ms in solution at room temperature. We have also found[32] that Re(η^5-C$_5$H$_5$)(CO)$_2$(Xe) is relatively long-lived in supercritical xenon at room temperature. The stability of Re(η^5-C$_5$H$_5$)(CO)$_2$(alkane) is significant and Ball and Geftakis[35] have been able to characterise Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_5$H$_{10}$) at low temperature (≈ 180 K) using ^{1}H NMR spectroscopy, with Re(η^5-C$_5$H$_5$)(CO)$_2$(C$_5$H$_{10}$) typically taking *ca.* 1 h to decay.

The factors controlling the reactivity of unstable organo-

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metallic alkane complexes have been the subject of several investigations. The reactivity of $Cr(CO)_2(\eta^6\text{-}C_6R_6)(C_6H_{12})$ (R = H, Me or Et) towards CO in cyclohexane[27] and of $Mn(\eta^5\text{-}C_5R_5)(CO)_2(n\text{-}C_7H_{16})$ (R = H, Me or Et) towards small molecules (CO, N_2, H_2) in *n*-heptane[31] steadily increases in the order H < Me < Et. These results indicated that steric rather than electronic factors govern the reactivity of these alkane complexes. Long and co-workers[27] found that changing the solvent from cyclohexane to increasingly longer linear alkanes resulted in an increased rate of reaction between $Cr(CO)_2(\eta^6\text{-arene})$(alkane) and CO. The value of $\Delta H^‡$ for this reaction did not vary with substituent or alkane (24 ± 2 kJ mol^{-1}), and was only half that of the Cr–alkane bond dissociation energy (50 ± 5 kJ mol^{-1}) previously determined by photoacoustic calorimetry (PAC).[36] They concluded that the variation in reactivity of $Cr(CO)_2(\eta^6\text{-arene})$(alkane) towards CO can be explained by changes in the entropy of activation, $\Delta S^‡$, and not by variations in the interaction energy between the co-ordinatively unsaturated photofragment and the solvent. Similar findings have also been obtained by the same workers[28] for the reactivity of $M(CO)_5$(alkane) (M = Cr, Mo or W) and $Mo(CO)_2(\eta^6\text{-arene})$(alkane) towards CO in alkane solution. For these systems they also found that the enthalpy of activation ($\Delta H^‡$) remained constant, with the rate constant for the reaction of the alkane complex with CO being dependent on the entropy of activation. They suggested that when an alkane solvent occupies the final co-ordination site on a metal the freedom of motion of the alkane is restricted. This restriction is removed upon displacement of the alkane by CO, increasing the $\Delta S^‡$ term. This effect is more pronounced for the longer chain alkanes, hence the rate of decay is greater than for shorter chain and cyclic alkanes.

Following the identification of $Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$ by ^1H NMR at low temperature,[35] we have investigated the effect of changing both the cyclopentadienyl ring substituents and the alkane solvent on the reactivity of the Group VII half-sandwich complexes $M(\eta^5\text{-}C_5H_5)(CO)_2(L)$ (M = Mn or Re; L = *n*-heptane or cyclopentane) and $Re(\eta^5\text{-}C_5R_5)(CO)_2(C_5H_{10})$ (R = H, Me or Ph) towards CO in alkane solution, at both low temperature (M = Re only) and room temperature (R = H only). We have also compared the reactivity of $Re(\eta^5\text{-}C_5H_5)(CO)_2(Xe)$ in liquid xenon at low temperature with those of the corresponding *n*-heptane and cyclopentane complexes.

Experimental

Materials

All operations were performed under inert gas atmospheres. The complexes $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ (Aldrich), $Re(\eta^5\text{-}C_5H_5)(CO)_3$ and $Re(\eta^5\text{-}C_5Me_5)(CO)_3$ (Strem Chemicals Inc.) were used as supplied; $Re(\eta^5\text{-}C_5Ph_5)(CO)_3$ was synthesised by modifying a literature procedure[37] for $Rh(\eta^5\text{-}C_5Ph_5)(CO)_2$ (see below). *n*-Heptane and cyclopentane (Aldrich HPLC grade) were distilled from CaH_2 prior to use; CO (Air Products) was used as supplied. The solubilities[38,39] of CO in *n*-heptane and cyclopentane† were taken to be 1.2×10^{-2} and 0.9×10^{-2} M respectively, under 1 atm of CO at 298 K. For the TRIR experiments the concentrations of solutions used were 3×10^{-4} (for Re) and 5×10^{-4} M (for Mn).

Synthesis of $Re(\eta^5\text{-}C_5Ph_5)(CO)_3$

n-Butyllithium in hexane (1.6 M, 1.56 cm^3) was added dropwise to a stirred solution of 1,2,3,4,5-pentaphenylcyclopentadiene (0.892 g, 2 mmol) in THF (20 cm^3) at 0 °C. Stirring was continued for five hours. The compound $Re(CO)_5Br$ (0.813 g, 2 mmol) was then added and the mixture refluxed overnight. The solution afforded an off white precipitate upon cooling. This was filtered off and the solvent removed under reduced pressure. The residue was extracted into dichloromethane and filtered. The filtrate was reduced in volume, layered with *n*-hexane and left at −18 °C overnight resulting in the precipitation of a white solid. The product was filtered off and dried under reduced pressure to yield $Re(\eta^5\text{-}C_5Ph_5)(CO)_3$. IR (*n*-heptane): ν(CO) 2023 and 1936 cm^{-1}. MS: *m*/*z* 716 (M^+).

Matrix apparatus

The high pressure–low temperature (HP-LT) cell used in the low temperature experiments has been described in detail elsewhere.[40,41] Briefly, the HP-LT cell was filled with a solution of organometallic compound dissolved in degassed alkane solvent. The cell was attached to a cold finger of a cryogenic cooling system and cooled to the required temperature (either 180 or 190 K). The photolysis source used in these experiments was a Philips HPK 125W medium-pressure mercury arc lamp, which provided broadband UV and visible light. IR spectra were recorded using a Nicolet 730 interferometer linked to a computer running Omnic software.

Time-resolved infrared (TRIR) apparatus

The Nottingham laser TRIR apparatus has been described in detail elsewhere.[42] In these experiments two different types of TRIR instrumentation were used, both using a pulsed Nd:YAG laser (either Spectra Physics Quanta-Ray GCR-12 or Spectrum SL805G) to initiate the photochemical reactions. We used either a *step-scan* FTIR interferometer (Nicolet Magna 860) or a continuous wave (cw) IR diode laser (Mütek MDS 1100) to monitor the transient IR absorptions. The use of step-scan FTIR for TRIR spectroscopy in our laboratory has not previously been described, and a full account of the experimental apparatus will be given elsewhere.[43] 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 (Spectron SL80SG). Synchronisation of the Nd:YAG laser with data collection was achieved using a pulse generator (Stanford DG535). A commercially available IR cell (Harrick, 0.5 mm) was used with a home built flow system.

In the experiments using cw IR lasers the change in IR transmission at one particular IR frequency was measured following excitation by a Nd:YAG laser (Spectra Physics Quanta-Ray GCR-12), and IR spectra were built up on a "point-by-point" basis by repeating this measurement at different infrared frequencies. Heating of the IR cells was achieved with an external aluminium jacket containing cartridge heaters.

Results and discussion

(a) Characterisation and reactivity at low temperature

Fig. 1 shows the conventional FTIR difference spectra obtained following UV irradiation at low temperature of $Re(\eta^5\text{-}C_5R_5)(CO)_3$ in *n*-heptane (R = H only), cyclopentane (R = H, Me or Ph) and xenon (R = H only). It is clear that in all cases photolysis causes depletion of the parent tricarbonyl bands, and the production of two new absorptions that can readily be assigned to $Re(\eta^5\text{-}C_5R_5)(CO)_2(L)$ (L = alkane or xenon) by comparison with previous results from matrix isolation and TRIR experiments[32,44] (see Table 1). These new bands are easily distinguished from those expected for the C–H activated products where the Re would be oxidised to Re (+3) and the ν(CO) bands would be shifted to a higher frequency relative to the parent bands. Fig. 2 shows decay plots for the four alkane

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† To our knowledge, the solubility of CO in cyclopentane has not been determined. We have therefore used the value for the solubility of CO in cyclohexane. In all of our experiments we have assumed that the solubility of CO in both *n*-heptane and cyclopentane is unaffected over the small temperature ranges of our studies.

Table 1 IR band positions of $MCp(CO)_2(L)$ (M = Mn or Re) species (L = CO, *n*-heptane or cyclopentane)

$MCp(CO)_2L$	Wavenumber/cm^{-1}	Conditions	Ref.
$Re(\eta^5\text{-}C_5H_5)(CO)_3$	2029, 1934	Nujol, 77 K	39
	2030, 1938	*n*-Heptane, 190 K	This work
	2031, 1940	*n*-Heptane 298 K	28
	2029, 1936.5	Cyclopentane, 180 K	This work
	2031, 1939.5	Cyclopentane, 298 K	This work
	2032, 1940.5	Xe, 170 K	This work
$Re(\eta^5\text{-}C_5Me_5)(CO)_3$	2013, 1930	Cyclopentane, 180 K	This work
$Re(\eta^5\text{-}C_5Ph_5)(CO)_3$	2022, 1934	Cyclopentane, 180 K	This work
$Mn(\eta^5\text{-}C_5H_5)(CO)_3$	2028, 1947	*n*-Heptane, 298 K	27
	2028, 1946	Cyclopentane, 298 K	This work
$Re(\eta^5\text{-}C_5H_5)(CO)_2$	1947, 1879	Nujol, 77 K	39
$Re(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$	1948, 1883	*n*-Heptane, 190 K	This work
	1945, 1890	*n*-Heptane, 298 K	28
$Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$	1947.5, 1881.5	Cyclopentane, 180 K	This work
	1951, 1886	Cyclopentane, 298 K	This work
$Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_5H_{10})$	1928.5, 1864	Cyclopentane, 180 K	This work
$Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$	1943, 1881	Cyclopentane, 180 K	This work
$Mn(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$	1962, 1894	*n*-Heptane, 298 K	27
$Mn(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$	1953, 1893	Cyclopentane, 298 K	This work
$Re(\eta^5\text{-}C_5H_5)(CO)_2(Xe)$	1953.5, 1888.5	Xe, 170 K	This work

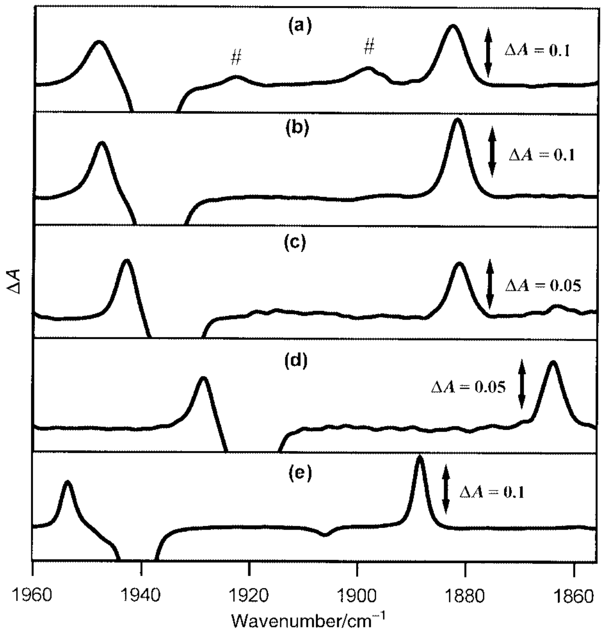

Fig. 1 FTIR difference spectra following UV irradiation of (a) $Re(\eta^5\text{-}C_5H_5)(CO)_3$ in *n*-heptane (190 K), (b) $Re(\eta^5\text{-}C_5H_5)(CO)_3$ in cyclopentane (190 K), (c) $Re(\eta^5\text{-}C_5Ph_4)(CO)_3$ in cyclopentane (190 K), (d) $Re(\eta^5\text{-}C_5Me_5)(CO)_3$ in cyclopentane (190 K) and (e) $Re(\eta^5\text{-}C_5H_4)(CO)_3$ in liquid xenon (170 K). Only positive peaks due to new species are shown, with the decay of the parent species not shown. Additional peaks (marked #) in (a) can be attributed to dimer formation.

complexes and the xenon complex at low temperature. As the alkane complexes decay the parent bands are partially regenerated. This is presumably due to the recombination of $Re(\eta^5\text{-}C_5R_5)(CO)_2$(alkane) with the photo-ejected CO. No regeneration was observed as the xenon complex decayed. The incomplete recovery of $Re(\eta^5\text{-}C_5R_5)(CO)_3$ suggests that the xenon and alkane complexes are decaying to form a new species. Evidence for formation of the $Re_2(\eta^5\text{-}C_5R_5)_2(CO)_5$ dimer[45] is seen upon the decay of the $Re(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ complex. However no new bands are seen following the decay of the three cyclopentane complexes or the xenon complex. One possibility is that these other complexes decay to form dimeric or polymeric species which were not identified using FTIR spectroscopy.

In order to compare the reactivity of the different alkane complexes we have fitted the decay plots using first order kinetics (see Appendix). From Fig. 2 it can clearly be seen that the $Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$ complex is significantly longer lived (*ca.* × 9) than the corresponding *n*-heptane complex. It is also apparent (Fig. 2b) that both $Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_5H_{10})$ and $Re(\eta^5\text{-}C_5Ph_5)(CO)_2(C_5H_{10})$ are more reactive (*ca.* × 6 and × 4 respectively) than the unsubstituted $Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$ complex. The lifetimes of $Re(\eta^5\text{-}C_5H_5)(CO)_2(Xe)$ at 170 K ($\tau = 3.5$ min) and $Re(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ ($\tau = 2.5$ min) at 190 K are similar.

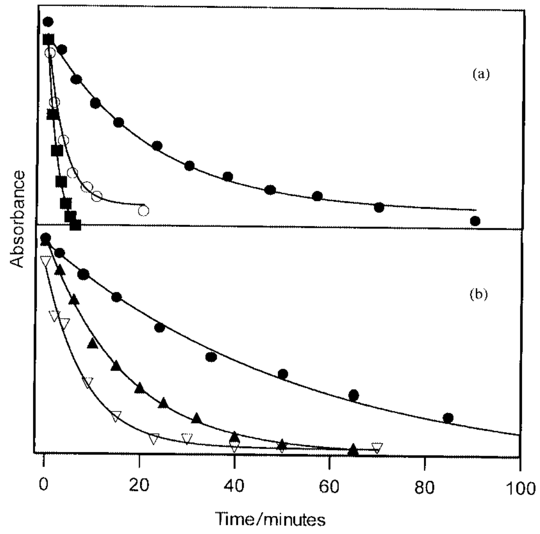

Fig. 2 Decay plots of (a) $Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$ (●) and $Re(\eta^5\text{-}C_5H_5)(CO)_3(n\text{-}C_7H_{16})$ (■) at 190 K and $Re(\eta^5\text{-}C_5H_5)(CO)_2(Xe)$ (○) at 170 K, and of (b) $Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$ (●), $Re(\eta^5\text{-}C_5Ph_5)(CO)_2(C_5H_{10})$ (▲) and $Re(\eta^5\text{-}C_5Me_5)(CO)_2(C_5H_{10})$ (▽) at 180 K. Decay of the lowest wavenumber carbonyl stretch was monitored in each case. These plots have been autoscaled.

These results show that the reactivity of the alkane complexes is affected by both changing the alkane and the substituents on the cyclopentadienyl ring. The cyclopentane complex is longer-lived than the corresponding heptane complex and this will be discussed in more detail later. The alkane complexes with substituted cyclopentadienyl rings (pentamethyl and pentaphenyl) are more reactive than $Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$. The increased reactivity may be due to the bulky methyl and phenyl side groups interacting with the co-ordinated alkane, resulting in a destabilisation of the complex.

(b) Characterisation and reactivity at room temperature

Fig. 3 shows the step-scan TRIR spectra of $M(\eta^5\text{-}C_5H_5)$-

Table 2 Second-order rate constants for the reaction of metal–alkane complexes with CO in alkane solution at 298 K

Complex	k_{CO}/dm^3 mol^{-1} s^{-1}
$Re(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$	2.5 (± 0.2) × 10^3
$Re(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$	1.1 (± 0.2) × 10^3
$Mn(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$	8.0 (± 0.6) × 10^5
$Mn(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$	2.5 (± 0.4) × 10^5

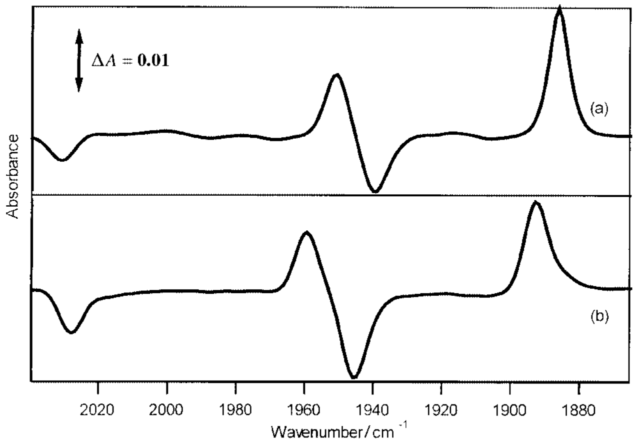

Fig. 3 Step-scan FTIR spectra obtained 1 μs after UV irradiation of (a) $Re(\eta^5-C_5H_5)(CO)_3$ (266 nm) and (b) $Mn(\eta^5-C_5H_5)(CO)_3$ (355 nm) in cyclopentane.

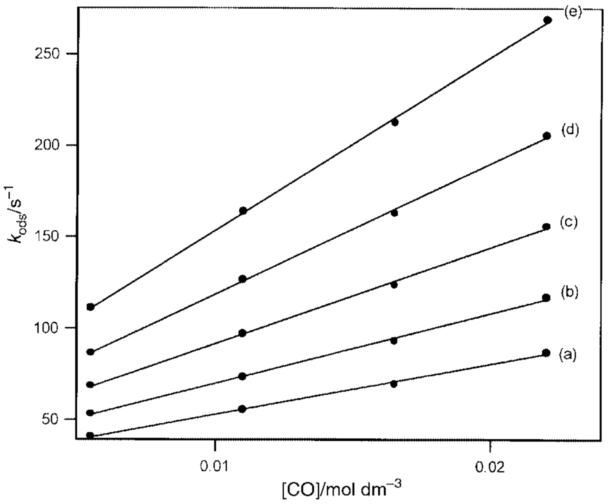

Fig. 4 A plot of k_{obs} for $Re(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$ (obtained from a first-order fit to the decay at 1890 cm^{-1}) *versus* CO concentration at (a) 298, (b) 303, (c) 308, (d) 313 and (e) 318 K. The gradients of these plots give the second-order rate constant (k_{CO}) at each temperature. Similar results were obtained for each of the other TRIR experiments described.

Table 3 Activation parameters for $M(\eta^5-C_5H_5)(CO)_2$(alkane) (M = Mn or Re) measured over the range 298–323 K

Compound	E_a[a]/ kJ mol^{-1}	$\Delta H^{\ddagger}$[b]/ kJ mol^{-1}	$\Delta S^{\ddagger}$[c]/ J K^{-1} mol^{-1}	$\Delta S^{\ddagger}$[d]/ J K^{-1} mol^{-1}
$Re(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$	48.7	46.2	−24.9	−8.9
$Re(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$	34.8	32.2	−78.3	−58.6
$Mn(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$	38.7	36.1	−10.7	5.2
$Mn(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$	26.2	23.6	−62.4	−42.7

[a] ±2 kJ mol^{-1}. [b] ±2 kJ mol^{-1}. [c] Assuming an associative mechanism (±10 J K^{-1} mol^{-1}). [d] Assuming a dissociative mechanism (±10 J K^{-1} mol^{-1}).

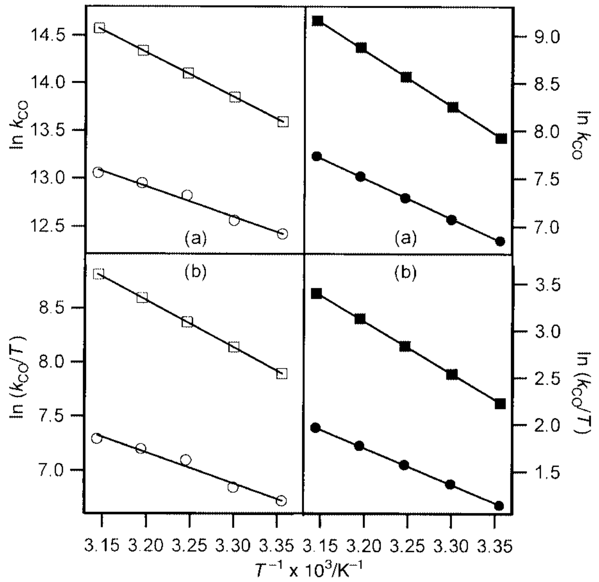

Fig. 5 (a) Arrhenius and (b) Eyring plots obtained for the reaction of $Mn(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$ (□), $Mn(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$ (○), $Re(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$ (●) and $Re(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$ (■) with CO.

$(CO)_2(C_5H_{10})$ obtained following UV laser excitation of $M(\eta^5-C_5H_5)(CO)_3$ (M = Mn or Re) in cyclopentane at room temperature, Table 1. The corresponding IR spectra of the analogous *n*-heptane complexes, $M(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$ (M = Mn or Re), have been obtained previously[30,32] (see Table 1). The observed rates of decay, derived from TRIR decay traces of $M(\eta^5-C_5H_5)(CO)_2$(alkane) under a range of different CO concentrations, show a linear dependence upon CO concentration (see Fig. 4). In the presence of CO the organometallic alkane complexes decay *via* pseudo first order kinetics (k_{obs}), and plots of k_{obs} *versus* CO concentration afford the second-order rate constants (k_{CO}) for the reaction of $M(\eta^5-C_5H_5)(CO)_2$(alkane) (M = Mn or Re) with CO (see Table 2). These plots have non-zero intercepts, which are attributed to the formation of the dimeric species $M_2(\eta^5-C_5H_5)_2(CO)_5$, by reaction of $M(\eta^5-C_5H_5)(CO)_2$(alkane) with the parent complex in the absence of any CO. In the presence of an excess of CO this dimerisation is a minor pathway.

It is clear from Table 2 that both of the heptane complexes are *ca.* 2.5–3 times more reactive towards CO than the corresponding cyclopentane complexes. In the absence of CO, $Re(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$ (τ = 125 ms) is again longer-lived than $Re(\eta^5-C_5H_5)(CO)_2(n-C_7H_{16})$ (τ = 25 ms).

Cyclopentane was the alkane chosen for the NMR studies by Ball and Geftakis, because only one carbon environment is present,[46] thus simplifying interpretation of the NMR spectra. However the NMR studies did not report[46] any information concerning the relative stability of the cyclopentane complex compared to other alkane complexes. The results from our study show that $Re(\eta^5-C_5H_5)(CO)_2(C_5H_{10})$ is significantly longer-lived than the corresponding heptane complex, and that it is the longest-lived organometallic alkane complex yet reported in room temperature solution.

(c) Determination of activation parameters

TRIR experiments were carried out at a range of CO concentrations as a function of temperature. 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]. The Arrhenius and Eyring plots for the reaction of $M(\eta^5-C_5H_5)(CO)_2$(alkane) (M = Mn or Re) with CO are shown in Fig. 5 and the activation parameters are summarised in Table 3.

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 mechanism, or by a combination of these pathways (see Appendix). In principle, $\Delta S^{\ddagger}$ values can give an indication of the nature of a reaction. In practice, it is notoriously difficult to obtain accurate $\Delta S^{\ddagger}$ values from TRIR experiments due to the errors incurred when extrapolating the data. Furthermore, the calculated value of $\Delta S^{\ddagger}$ differs according to the mechanism of the reaction considered.‡ However, the calculated $\Delta S^{\ddagger}$ values show a clear trend, with the metal–cyclopentane complexes having a more negative value of $\Delta S^{\ddagger}$ than the corresponding metal–heptane complexes.

The $\Delta H^{\ddagger}$ values for the metal–alkane complexes give an indication of the metal–alkane bond strengths. These complexes have higher $\Delta H^{\ddagger}$ values for the reaction of $M(\eta^5\text{-}C_5H_5)(CO)_2(alkane)$ with CO than the corresponding metal–cyclopentane complexes. Early photoacoustic calorimetry (PAC) experiments by Yang and co-workers[47] estimated the Mn–heptane bond dissociation energy (BDE) to be 33–37 kJ mol^{-1} for $Mn(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$. However, its precise determination from PAC data requires the Mn–CO BDE and this was not available. Yang and co-workers therefore estimated the Mn–alkane binding energy from the enthalpy of activation for the reaction of $Mn(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ with *cis*-cyclooctene and the enthalpy of activation for the reaction of $Mn(\eta^5\text{-}C_5H_5)(CO)_2(cis\text{-}C_8H_{14})$ with PPh_3, assuming that these reactions occurred by a purely dissociative reaction mechanism. Burkey[48] has pointed out that 33–37 kJ mol^{-1} is the lower limit to the Mn–heptane BDE since the reaction may proceed *via* an associative pathway. We have recently[49] compared the activation enthalpy for the reaction of $Mn(\eta^5\text{-}C_5H_5)(CO)_2(Xe)$ with CO in supercritical xenon ($\Delta H^{\ddagger} = 34$ kJ mol^{-1}) and of $Mn(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ with CO in *n*-heptane ($\Delta H^{\ddagger} = 36$ kJ mol^{-1}). We suggested that these data supported the idea that the reaction of the alkane complex with CO occurs mainly *via* an associative pathway (either associative or associative interchange) since the activation enthalpy is significantly lower than those for other first row transition metal alkane complexes (*e.g.* for $Cr(CO)_5(n\text{-}C_7H_{16})$ the Cr–heptane BDE = 50 kJ mol^{-1}),[28] and we expected that the Mn–Xe BDE would be lower than the Mn–heptane BDE. This assumption leads to the $\Delta H^{\ddagger}$ value for the reaction of $Mn(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ with CO being the lower limit for the Mn–heptane BDE, and similarly we suggest that the $\Delta H^{\ddagger}$ values calculated in this study are the lower limits for the M–alkane BDE (M = Mn or Re; alkane = *n*-heptane or cyclopentane).

Therefore it seems that the variation in $\Delta S^{\ddagger}$ values for these experiments is significant in understanding the relative stabilities of $M(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ and $M(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$, with the cyclopentane complexes having a much lower (more negative) $\Delta S^{\ddagger}$ term (by *ca.* 50 J K^{-1} mol^{-1}) for both Mn and Re. The more negative value of the $\Delta S^{\ddagger}$ term is reflected in the relative stabilities of the cyclopentane and heptane complexes, with the cyclopentane complexes being longer-lived. These findings are consistent with those of Long and co-workers,[27,28] who also found that metal–alkane (metal = Cr, Mo or W) complexes incorporating cyclic alkanes were less reactive than those with linear alkanes. Furthermore, a negative $\Delta S^{\ddagger}$ value would preclude a dissociative mechanism for the decay of the alkane complexes. A negative value of $\Delta S^{\ddagger}$ for the decay of $M(\eta^5\text{-}C_5H_5)(CO)_2(alkane)$ is obtained from the Eyring plots when assuming an associative mechanism. The values of $\Delta S^{\ddagger}$ are increased when assuming a dissociative mechanism (see Table 3). However, even with this increase, only the $\Delta S^{\ddagger}$ value calculated for $Mn(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ is slightly positive. Considering the large errors associated with these values, we have no significant evidence to support a dissociative mechanism. Long and co-workers[27,28] have previously stated that an associative mechanism is unlikely for the decay of the related $Cr(\eta^6\text{-}C_6R_6)(CO)_2(alkane)$ complexes, since such a mechanism would not discriminate between different alkane solvents as the co-ordination of CO to the metal centre is the dominant factor in the rate of decay. We tentatively suggest that the reaction of $M(\eta^5\text{-}C_5R_5)(CO)_2(alkane)$ with CO occurs mainly *via* an associative interchange mechanism.

Conclusions

The studies at low temperature and room temperature described here have shown that both $M(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$ (M = Mn or Re) complexes are longer-lived than the corresponding heptane complexes. In addition, the activation parameters for the reaction of $M(\eta^5\text{-}C_5H_5)(CO)_2(alkane)$ with CO suggest that the major factor controlling the relative reactivity of these alkane complexes is the difference in activation entropy. These studies have also shown that $Re(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_{10})$ is the longest-lived alkane complex seen in room temperature solution to date. It is hoped that the similar reactivity of $Re(\eta^5\text{-}C_5H_5)(CO)_2(n\text{-}C_7H_{16})$ and $Re(\eta^5\text{-}C_5H_5)(CO)_2(Xe)$ at low temperature will make the characterisation of an organometallic xenon complex by low temperature NMR a realistic goal.

Appendix

A dissociative mechanism for the reaction of $M(\eta^5\text{-}C_5R_5)(CO)_2(alkane)$ with CO in alkane solution would have the rate equations (A1) and (A2). Application of the steady state approximation to the intermediate $M(\eta^5\text{-}C_5R_5)(CO)_2$ results in the expression (A3) for k_{obs}, where k_1 is the elementary rate constant for dissociation of the alkane. Assuming that $M(\eta^5\text{-}C_5R_5)(CO)_2$ reacts with both CO and alkane at near the diffusion-controlled rate, k_d, then $k_d \approx k_{-1} \approx k_2$ and [alkane] $\gg$ [CO], then eqn. (A4) applies where $k_1' = k_1/[\text{alkane}]$.

$$M(\eta^5\text{-}C_5R_5)(CO)_2(\text{alkane}) \xrightleftharpoons[k_{-1}]{k_1} M(\eta^5\text{-}C_5R_5)(CO)_2 + \text{alkane} \quad (A1)$$

$$M(\eta^5\text{-}C_5R_5)(CO)_2 + CO \xrightarrow{k_2} M(\eta^5\text{-}C_5R_5)(CO)_3 \quad (A2)$$

$$k_{obs} = \frac{k_1 k_2[CO]}{k_{-1}[\text{alkane}] + k_2[CO]} \quad (A3)$$

$$k_{obs} = k_1[CO]/[\text{alkane}] \approx k_1'[CO] \quad (A4)$$

For an associative mechanism in alkane solution the following rate equation (A5) would apply, where k_a is the bimolecular associative rate constant.

$$M(\eta^5\text{-}C_5R_5)(CO)_2(\text{alkane}) + CO \xrightarrow{k_a} M(\eta^5\text{-}C_5R_5)(CO)_3 + \text{alkane} \quad (A5)$$

Under the conditions of our experiments [CO] $\gg$ $[M(\eta^5\text{-}C_5R_5)(CO)_2(\text{alkane})]$ and $k_{obs} = k_a[CO]$. Therefore, solely from the room temperature CO substitution kinetics, it is impossible to distinguish between the two extreme forms of mechanism,

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‡ For a purely associative mechanism the rate constant is independent of alkane concentration, whereas for a dissociative mechanism it is dependent on alkane concentration (see Appendix). Multiplying the rate constant by the alkane concentration (6.826 M for *n*-heptane and 10.707 M for cyclopentane) will alter the intercepts of our activation plots. This means when considering a dissociative mechanism the Eyring plots will give greater $\Delta S^{\ddagger}$ values than for when an associative mechanism is considered (see Table 3).

since they both predict a linear dependence of k_{obs} on [CO]. If a dissociative and associative mechanism were operating simultaneously then eqn. (A6) would be valid where $k_{CO} = k_a + k_1'$. Therefore a plot of k_{obs} *versus* [CO] would yield a linear plot with slope equal to k_{CO}.

$$k_{obs} = [k_a + k_1'][CO] = k_{CO}[CO] \qquad (A6)$$

To separate k_a and k_1 requires experiments to be performed at different alkane concentrations. In alkane solution it is impossible to vary the solvent concentration in this way. However, such experiments have previously been performed in liquid krypton at low temperature to elucidate the reaction mechanism for the decay of $Ni(CO)_3(N_2)$,[50] and in supercritical CO_2 to probe the reactivity of $W(CO)_5(CO_2)$.[51]

To analyse our data for the decay of $M(\eta^5\text{-}C_5R_5)(CO)_2$-(alkane) we have considered two extreme cases, where either $k_a \gg k_1'$ or $k_1' \gg k_a$. If $k_1' \gg k_a$, then we expect the $\Delta H^\ddagger$ value to approximate to the M–alkane BDE since the rate determining step is the breaking of the M–alkane bond. We would also expect $\Delta S^\ddagger$ to be positive. If $k_a \gg k_1'$, then we expect the $\Delta H^\ddagger$ value to be less than the M–alkane BDE and $\Delta S^\ddagger$ to be negative.

In the absence of an excess of CO, $M(\eta^5\text{-}C_5R_5)(CO)_2$(alkane) could react either with photoejected CO to reform $M(\eta^5\text{-}C_5R_5)(CO)_3$ or with parent to form the known[45] dimer $M(\eta^5\text{-}C_5R_5)_2(CO)_5$. The reaction of $M(\eta^5\text{-}C_5R_5)(CO)_2$(alkane) with photoejected CO will display second-order kinetics irrespective of whether the reaction is dissociative or associative since the concentrations of CO and $M(\eta^5\text{-}C_5R_5)(CO)_2$(alkane) are the same. The reaction of $M(\eta^5\text{-}C_5R_5)(CO)_2$(alkane) with parent to form $M_2(\eta^5\text{-}C_5R_5)_2(CO)_5$ will occur *via* pseudo first-order kinetics since the concentration of $M(\eta^5\text{-}C_5R_5)(CO)_3$ is much greater than that of $M(\eta^5\text{-}C_5R_5)_2(CO)_2$(alkane). Our low temperature data are fit more accurately by first order kinetics, therefore we have used an exponential fit to allow comparison of the stabilities of the different alkane complexes.

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