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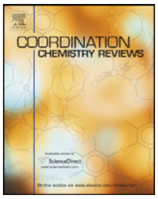

Review

Formation and reactivity of organometallic alkane complexes

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Contents

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ABSTRACT

Organometallic alkane complexes are highly reactive species that have been shown to be key intermediates in the C–H activation of alkanes by transition metal centres. Organometallic alkane complexes were first identified in low temperature matrices over 30 years ago and now sufficiently long-lived examples have been characterised by NMR spectroscopy. We provide a brief overview of the study of these key reactive intermediates and describe recent studies on the characterisation of organometallic alkane complexes and their related C–H activation using fast time-resolved infrared (TRIR) spectroscopy.

1. Introduction

The controlled C–H activation of alkanes by transition metal complexes has been an important reaction within chemistry for over 25 years [1,2]. It is becoming increasingly evident that for transition metal mediated C–H activation to take place, initial coordination of the alkane to the metal centre must occur [3–5]. Although the sigma alkane complexes that are formed tend to be short lived[1] it has become clear that the nature of the organometallic alkane complex can play a major role in determining the reaction outcome.

Herein we aim to provide a brief overview of the early studies of organometallic alkane complexes. This area has been reviewed over the last 10 years [5,9–12] and we will present a more detailed discussion of some recent studies from our laboratory.

2. Group VI metal carbonyl alkane complexes

The characterisation of organometallic alkane complexes was first described over 30 years ago when $Cr(CO)_5(CH_4)$ and $Fe(CO)_4(CH_4)$ were reported to form following the photolysis of $Cr(CO)_6$ [13,14] and $Fe(CO)_5$ [15] in low temperature CH_4 matrices at *ca.* 12 K. The photochemistry of $Cr(CO)_6$ was examined in a range of different matrices (Ne, SF_6, CF_4, Ar, Kr, Xe, CH_4), and it was observed that the UV/visible absorption maxima of the photogenerated $Cr(CO)_5$ fragment depended heavily upon the matrix material employed. This shift in the UV/visible band of $Cr(CO)_5$ could not be accounted for by matrix environment effects and was interpreted to indicate a significant interaction between the matrix material and the $Cr(CO)_5$ fragment. Matrix isolation studies have continued to be useful in characterising very unstable reactive fragments in recent years [16], with the interaction of CH_4 with both organometallic

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[1] Two examples of solid-state alkane complexes are reported in the literature, however there was no evidence for coordination of the alkane to the metal centre in solution [6,7]. Examples of gas phase alkanes adsorbed onto zeolite structures have also been reported [8].

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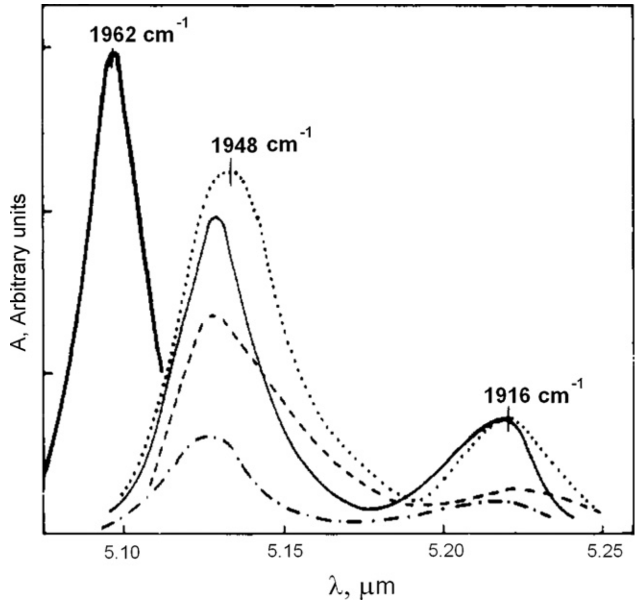


Fig. 1. TRIR difference spectra following the photolysis of $Cr(CO)_6$ in CO saturated cyclohexane. $Cr(CO)_5$(cyclohexane) [Dark solid line], $Cr(CO)_5$(acetone) [light solid line], $Cr(CO)_5$(benzene) [dashed line], $Cr(CO)_5$(methanol) [dotted line], $Cr(CO)_5(H_2O)$ [dot and dash line]. Figure reproduced from ref. [23].

complex fragments [17–19] and with isolated metal atoms being examined [20].

Evidence for the formation of organometallic alkane complexes in solution was first provided by flash photolysis studies of $Cr(CO)_6$ in cyclohexane [21] and perfluoromethylcyclohexane [22]. The $Cr(CO)_5$ intermediate was observed to have an increased lifetime in cyclohexane compared to perfluoromethylcyclohexane. This was also accompanied by a shift in the UV/visible absorption maxima of the $Cr(CO)_5$ transient, which led to the proposal that $Cr(CO)_5$ is significantly stabilised in solution by interactions with the cyclohexane solvent.

These early room temperature spectroscopic experiments reported that the lifetime of $Cr(CO)_5$(cyclohexane) was very sensitive to the presence of impurities. Grevels and co-workers investigated the photolysis of $Cr(CO)_6$ in cyclohexane, in the presence and absence of a range of more coordinating solvents, using time-resolved infrared (TRIR) spectroscopy, Fig. 1 [23]. These experiments reported the first IR spectrum of an organometallic alkane complex in solution at room temperature. IR spectroscopy is a particularly powerful technique for probing the photochemistry of metal carbonyls due to the sensitivity of the ν(CO) band frequencies to the electron density on the metal centre.

The photolysis of $M(CO)_6$ (M = Cr, Mo, W) in alkane solvents has been widely investigated as a model system for organometallic alkane complexes. Complexes of the type $M(CO)_5(L)$ (M = Cr, Mo, W; L = alkane) have been observed following the excitation of $M(CO)_6$ by UV photolysis [24–26] and by pulse radiolysis [27] in both solution and in the gas phase at room temperature. Ultrafast transient absorption experiments have demonstrated that $Cr(CO)_5$(cyclohexane) is formed within 1 ps, following the photolysis of $Cr(CO)_6$ in a room temperature cyclohexane solution [28].

The magnitude of the $M(CO)_5$-alkane bond strength has been estimated by transient absorption experiments on the photolysis of $W(CO)_6$ in methylcyclohexane which examined the rate of reaction of $W(CO)_5$(methylcyclohexane) with added pyridine ligands. From these kinetic experiments an estimate of the W-alkane bond energy of 16 kJ mol^{-1} was reported [29]. A series of TRIR experiments have also examined the activation parameters for the reaction of $M(CO)_5$(alkane) complexes with competing ligands [24–26]. Metal alkane binding energies have previously been determined by photoacoustic calorimetry (PAC) for a range of Group VI metal alkane complexes including: $Cr(CO)_5$(*n*-heptane) (46 (±4) kJ mol^{-1}) [30], Cr(benzene)$(CO)_2$(*n*-heptane) (*ca.* 50 kJ mol^{-1}) [31] and most recently for $Mo(CO)_5$(*n*-heptane) (*ca.* 56 kJ mol^{-1}) [32].

2.1. The role of organometallic alkane complexes in transition metal mediated C–H activation

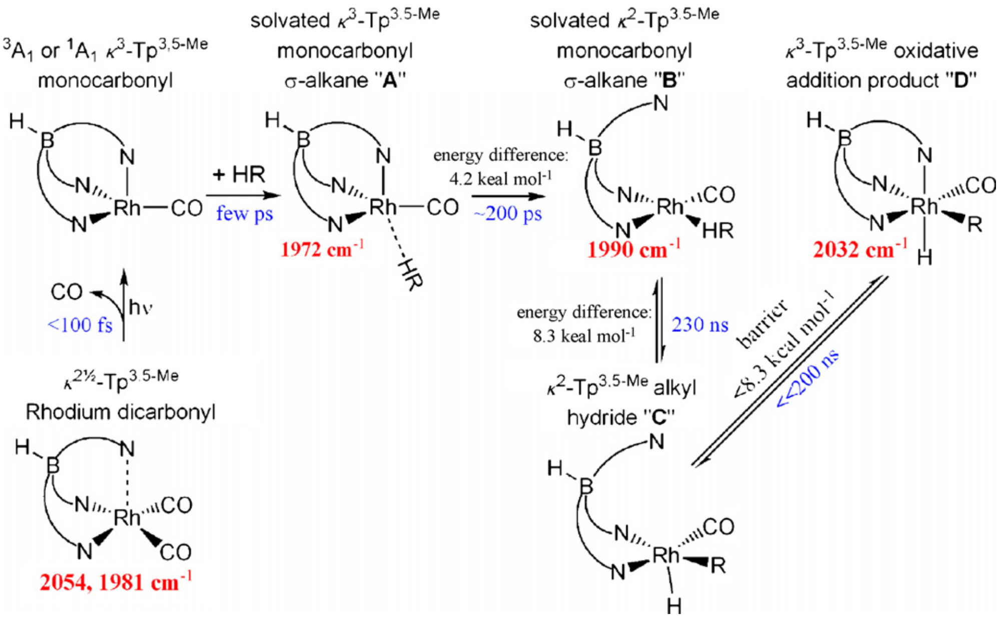
The C–H activation of alkanes by photochemically generated organometallic fragments was reported over 25 years ago [1,2]. Early evidence of the role of organometallic alkane complexes in transition metal mediated C–H activation reactions was obtained by experiments on the interaction between organometallic fragments, including $M(Cp^*)(PMe_3)$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$, M = Rh or Ir), and alkane solvents [33–36]. Whilst organometallic alkane complexes were not directly observed, their presence in the reaction pathway was inferred by examination of isotopic rearrangement patterns and kinetic isotope effects observed when partially deuterated alkane solvents were used. Low temperature matrix isolation experiments on $M(Cp')(CO)_2$ (M = Ir, Rh, Co and Cp' = Cp or Cp*) using CH_4 and Ar matrices doped with either CH_4 or CD_4 demonstrated that photolysis could lead to the formation of both the methyl hydride (or methyl-d_3 deuteride) complex, $M(Cp')(CO)H(CH_3)$ and, albeit in a low concentration the methane (or methane-d_4) complex, $M(Cp')(CO)(CH_4)$ (M = Rh and Ir) [19].

TRIR experiments monitoring the photolysis of $Rh(Cp)(CO)_2$ in solution by Perutz and co-workers has characterised the unstable alkyl hydride complex, $Rh(Cp)(CO)(C_6H_{11})H$, at room temperature [37]. Bergman and co-workers investigated the photolysis of $Rh(Cp^*)(CO)_2$ in low temperature noble gas solutions, doped with alkanes, with TRIR spectroscopy and found evidence for the presence of an organometallic alkane complex as a precursor to C–H activation. However the IR ν(CO) bands of the alkane complex were not resolvable from those of the initially formed noble gas complex [38,39].

Gas phase room temperature TRIR experiments on the photolysis of $Rh(Cp)(CO)_2$ in the presence of a range of alkane solvents demonstrated that the initially formed Rh(Cp)(CO) rapidly decayed to form the alkyl hydride products Rh(Cp)(CO)(R)(H), at or close to, the gas-kinetic rate [40]. Interestingly, it was postulated that the C–H activation occurred *via* an organometallic alkane complex, in which the lighter chain alkanes were suggested to be more weakly bound. Further TRIR experiments on the photolysis of $Rh(Cp^*)(CO)_2$ in low temperature noble gas solutions doped with alkanes also demonstrated that the lighter alkanes were only weakly bound in the organometallic alkane complexes [41]. It was noted that the rate of C–H activation depended heavily on the nature of the alkane involved, with the more weakly bound, light alkanes undergoing the most rapid C–H activation at low temperature [41].

Characterisation of the C–H activation of an organometallic alkane complex in solution by TRIR spectroscopy was achieved shortly afterwards through the monitoring of the photolysis of $Rh(Cp^*)(CO)_2$ in liquid krypton doped with neopentane at low temperature [42]. Additional room temperature TRIR experiments have shown that photolysis of $Rh(Cp)(CO)_2$ in cyclohexane leads to the formation of Rh(Cp)(CO)(alkane) prior to C–H activation occurring [43].

The photochemistry of $Rh(Cp)(CO)_2$ in supercritical (sc) CH_4 has been monitored using TRIR spectroscopy [44]. The organometallic methane complex $Rh(Cp)(CO)(CH_4)$ was observed to be formed immediately following photolysis and this transient was then seen



Scheme 1. Previously reported mechanism [3] for the C–H activation of cyclohexane following the UV photolysis of Rh($Tp^{3,5\text{-}Me}$)$(CO)_2$ at room temperature. Figure adapted from ref. [48].

to decay with a lifetime of *ca.* 2.5 ns at room temperature to form the alkyl hydride species, Rh(Cp)(CO)(CH_3)H.

TRIR studies on the C–H activation of cyclohexane following the photolysis of Rh($Tp^{3,5\text{-}Me}$)$(CO)_2$ ($Tp^{3,5\text{-}Me}$ = tris-3,5-dimethylpyrazolylborate) in cyclohexane at room temperature have provided extensive insights into the C–H activation mechanism at transition metal centres [3,45]. In these experiments it was demonstrated that photolysis led to the ejection of a CO ligand and the formation of a monocarbonyl complex, which was rapidly solvated to form a short lived alkane complex Rh(κ^3-$Tp^{3,5\text{-}Me}$)(CO)(RH). This species then decayed to form the more stable Rh(κ^2-$Tp^{3,5\text{-}Me}$)(CO)(RH) complex, which is able to undergo C–H activation to form a transient κ^2-$Tp^{3,5\text{-}Me}$ alkyl hydride complex which then generates the final oxidative addition product, Rh(κ^3-$Tp^{3,5\text{-}Me}$)(CO)(R)H, Scheme 1. Further experiments on this system have investigated the C–H activation in several alkane solvents [45]. This has allowed for the direct measurement of the rate of C–H activation, and a preference for bond activation to occur at primary C–H sites has been reported that is in good agreement with reductive elimination studies carried out by the group of Jones et al. [46,47].

Recent investigations into the photochemistry of the *tert*-butyl-substituted complex Rh($\kappa^{2.5}$-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)$(CO)_2$ in a range of alkane solvents have reported slightly different behaviour [48]. In these experiments it has been shown that although the ground state structures of Rh($\kappa^{2.5}$-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)$(CO)_2$ and Rh($\kappa^{2.5}$-

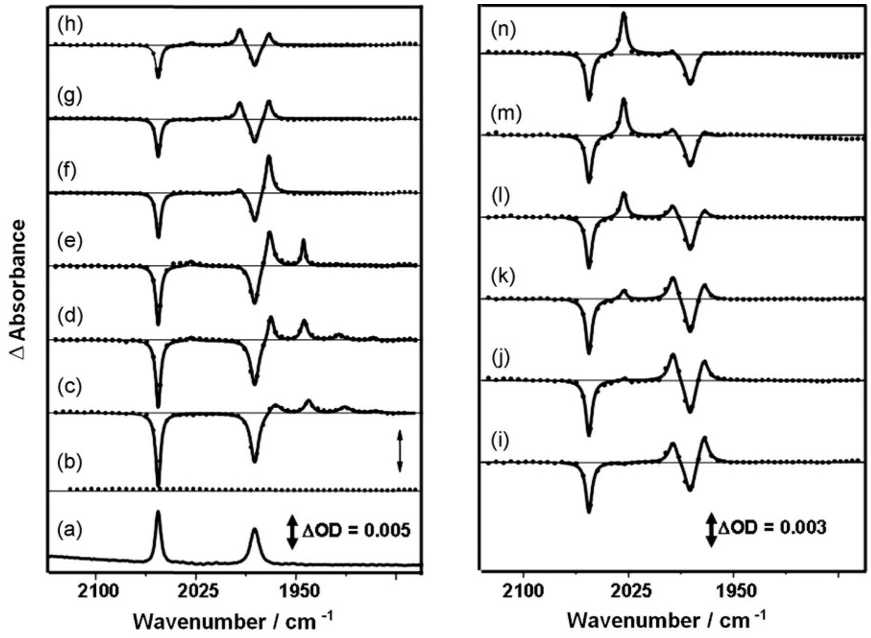


Fig. 2. (a) FTIR spectra of Rh($Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)$(CO)_2$ in *n*-heptane saturated with CO. (b) TRIR difference spectra recorded following the photolysis (267 nm) of the same solution at (b) −20 ps, (c) 2 ps, (d) 10 ps, (e) 30 ps, (f) 100 ps, (g) 500 ps, (h) 2 ns, (i) 1 ns, (j) 4 ns, (k) 10 ns, (l) 30 ns, (m) 70 ns, (n) 600 ns. Figure adapted from ref. [48].

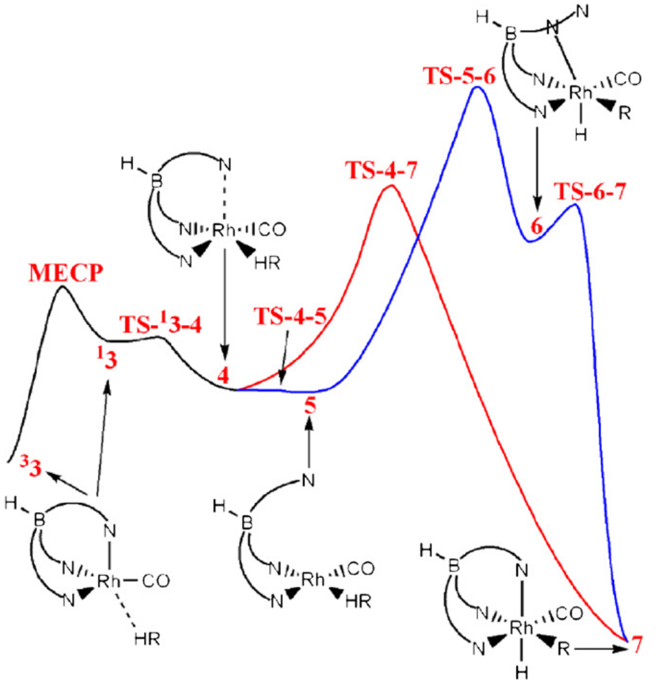
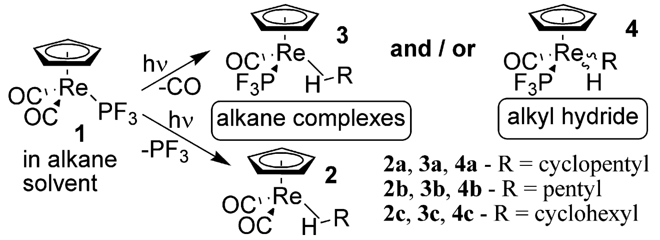


Fig. 3. Energy diagram constructed from DFT calculations, showing the modified mechanism of C–H activation. It should be noted that the barrier between the observed first observed species **3** and the second observed species **5** is reported to be due to a triplet singlet crossing. Figure adapted from ref. [48].



Scheme 3. Transient species detected by NMR and TRIR spectroscopies following the photolysis of Re(Cp)$(CO)_2(PF_3)$ in alkane solvents (pentane, cyclopentane, cyclohexane). Figure reproduced from ref. [59].

$Tp^{3,5\text{-}Me}$)$(CO)_2$ are very similar, a slight modification of the reaction mechanism was required in order to explain the photochemistry of both Rh($Tp^{3,5\text{-}Me}$)$(CO)_2$ and Rh($Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)$(CO)_2$ in alkane solvents [48].

Within 100 ps of the photolysis of Rh($Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)$(CO)_2$ in *n*-heptane the formation of Rh(κ^3-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)(CO)(RH) (1971 cm^{-1}) was observed. This transient was then seen to decay to form Rh(κ^2-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)(CO)(RH) (1993 cm^{-1}), Fig. 2. However, in contrast to the TRIR results on Rh($Tp^{3,5\text{-}Me}$)$(CO)_2$ in cyclohexane, where it was found that the κ^3 alkane complex fully decayed to form the κ^2 alkane complex, Rh(κ^3-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)(CO)(RH) was formed after photolysis and then decayed to an equilibrium mixture of Rh(κ^3-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)(CO)(RH) and Rh($\kappa^2$-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)(CO)(RH). The equilibrium mixture was then found to decay to form the final alkyl hydride product Rh(κ^3-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)(CO)(R)H, Fig. 2.

DFT calculations indicated that that the final alkyl hydride product was not formed from either of the alkane complexes observed, but instead was formed *via* a Rh($\kappa^{2.5}$-$Tp^{4\text{-}tBu\text{-}3,5\text{-}Me}$)(CO)(RH) complex that was not observed due to the overlap of its ν(CO) band with that of the parent material, Fig. 3 [48].

2.2. Factors affecting the reactivity of organometallic alkane complexes

TRIR spectroscopy has been employed for the study of a range of Groups V–VII organometallic alkane complexes, of the type M(η^x-C_xR_x)$(CO)_{y-1}$(alkane) ($x = 5$–6, $y = 3$–4). The ability to vary both the metal centre and the ring substituents (R = H, CH_3, C_2H_5) has allowed for systematic investigations into the electronic and steric factors affecting the stability of transition metal alkane complexes [49–52]. The reactivity of the organometallic alkane complex to ligand substitution is measured and the second order rate constant (k_2) for this reaction, determined by measuring the pseudo-first order rate as a function of CO concentration, can be used as a measure of the relative stability of the alkane complex, Scheme 2 [53,54].

Early studies on the reactivity of Mn(η^5-C_5R_5)$(CO)_2$(*n*-heptane) (R = H, CH_3, C_2H_5) towards small molecules showed two key findings: (i) the reactivity of Mn(η^5-C_5R_5)$(CO)_2$(*n*–heptane) towards incoming ligands is largely determined by the steric bulk of the incoming ligand, and (ii) an increase in organometallic alkane complex reactivity is observed as the cyclopentadienyl ring substituents are changed from $H < CH_3 < C_2H_5$, indicating that steric rather than electronic factors control the reactivity of Mn(η^5-C_5R_5)$(CO)_2$(*n*-heptane) [55]. Studies on the reactivity of a range of Cr(η^6-arene)$(CO)_2$(alkane) complexes also showed that increasing the steric bulk of the arene ring substituents increased the rate of reaction between the organometallic alkane complex and CO [50].

The choice of metal centre has a major effect on the reactivity of the Groups V–VII transition metal alkane complexes. The second order rate constants for the reaction of a series of *n*-heptane complexes with CO (k_{CO}) are shown in Table 1. The reactivity of the organometallic alkane complexes studied has been found to decrease on going both across and down Groups V–VII [49,51,56,57].

The photolysis of Re(Cp)$(CO)_3$ and related complexes in alkanes and noble gases provided significant advances in studying the interaction of weak ligands with transition metals [57–65]. The reaction of Re(Cp)$(CO)_2$(*n*-heptane) with CO is particularly slow when compared with the other previously reported *n*-heptane complexes, Fig. 4. At room temperature in the absence of CO, Re(Cp)$(CO)_2$(*n*-heptane) had a lifetime of *ca.* 25 ms [60].

The long lifetime of Re(Cp)$(CO)_2$(*n*-heptane) at room temperature led to the investigation of the photolysis of Re(Cp)$(CO)_3$ in cyclopentane at 180 K by Geftakis and Ball [61]. In these studies it was found that Re(Cp)$(CO)_2(C_5H_{10})$ persisted for several hours at low temperatures, allowing for the report of an NMR spectrum of an organometallic alkane complex in solution. This important study allowed for the identification of an η^2-C,H σ-interaction between the alkane ligand and the metal centre, in agreement with a previous theoretical study of the possible binding modes of methane to a transition metal centre [66]. M(Cp)$(CO)_2$(cyclopentane) (M = Mn, Re) have been characterised at room temperature and in the absence of CO they have been found to be *ca.* ×3–5 more stable than

$$\mathrm{M}(\eta^x\text{-}\mathrm{C_xR_x})(\mathrm{CO})_y \xrightarrow[\text{- CO, + alkane}]{h\upsilon} \mathrm{M}(\eta^x\text{-}\mathrm{C_xR_x})(\mathrm{CO})_{y\text{-}1}(\text{alkane}) \xrightarrow[k_2]{\text{+ L, - alkane}} \mathrm{M}(\eta^x\text{-}\mathrm{C_xR_x})(\mathrm{CO})_{y\text{-}1}\mathrm{L}$$

Scheme 2. Scheme showing the photochemical formation of the alkane complex and its subsequent decay by reaction with a ligand “L” (e.g. L = CO) with a rate constant of k_2.

Table 1
Second order rate constants for the reaction of the Groups V–VII transition metal *n*-heptane complexes with CO (k_{CO}, $dm^3\ mol^{-1}\ s^{-1}$) in *n*-heptane solution at 298 K

$V(Cp)(CO)_3$(*n*-heptane), 1.3×10^8	$Cr(CO)_5$(*n*-heptane), 9.3×10^6	$Mn(Cp)(CO)_2$(*n*-heptane), 8.1×10^5
$Nb(Cp)(CO)_3$(*n*-heptane), 4.5×10^6	$Mo(CO)_5$(*n*-heptane), 7.8×10^6	
$Ta(Cp)(CO)_3$(*n*-heptane), 2.0×10^6	$W(CO)_5$(*n*-heptane), 1.8×10^6	$Re(Cp)(CO)_2$(*n*-heptane), 2.5×10^3

Figure adapted from reference [56] and references therein.

the analogous *n*-heptane complexes [64]. Subsequent NMR studies on the binding modes of isotopically labelled pentane to the $Re(\eta^5\text{-}C_5H_4\text{-}CH(CH_3)_2)(CO)_2$ moiety were able to characterise binding at the three different C–H sites present, with a slight thermodynamic preference for binding at secondary alkyl (CH_2) sites [67]. A recent NMR study on $Re(Cp)(CO)_2(C_6H_{12})$ reported a preferred binding through axial C–H bonds of cyclohexane to the rhenium metal centre [68].

An investigation into the photolysis of $Re(Cp)(CO)_2(PF_3)$ in both high pressure xenon solutions [62] and in alkane solutions has been reported [59]. This reaction was monitored at room temperature, using TRIR spectroscopy and at low temperatures, using NMR spectroscopy. In high pressure xenon solutions it was shown that photolysis can lead to the loss of either a PF_3 or a CO ligand, to form both $Re(Cp)(CO)_2Xe$ and $Re(Cp)(CO)(PF_3)Xe$. $Re(Cp)(CO)(PF_3)Xe$ was found to be significantly less reactive towards CO than $Re(Cp)(CO)_2Xe$, facilitating its characterisation at low temperature by NMR spectroscopy [62]. Photolysis in alkane solvents led to the formation of both $Re(Cp)(CO)_2$(alkane) and, depending upon the alkane solvent used, either a very long-lived alkane complex, $Re(Cp)(CO)(PF_3)$(alkane) or an equilibrium mixture of $Re(Cp)(CO)(PF_3)$(alkane)/$Re(Cp)(CO)(PF_3)$(alkyl)H Scheme 3. The degree of C–H activation was found to be delicately balanced upon both the alkane solvent and the temperature that the system was studied [59].

Whilst TRIR spectroscopic measurements have clearly shown that the stability of the organometallic alkane complexes increases across the Groups V–VII, a similar trend has not been reported in the experimentally obtained bond dissociation enthalpies of *n*-heptane from the 16 electron organometallic fragments. The metal alkane binding energies determined by PAC of $V(Cp)(CO)_3$(*n*-heptane) (41 (±15) kJ mol^{-1}), $Cr(C_6H_6)(CO)_2$(*n*-heptane) (*ca.* 50 kJ mol^{-1}) [31] and $Mn(Cp)(CO)_2$(*n*-heptane) (*ca.* 42 kJ mol^{-1}) [31] are relatively similar. However recent TRIR experiments have indicated an increased strength for the Re-heptane bond in $Re(Cp)(CO)_2$(*n*-heptane) with a lower limit of 57.3 kJ mol^{-1} being reported [69].

Recent DFT calculations have investigated the M-heptane binding energies in $M(Cp)(CO)_2$(*n*-heptane) (M = Mn, Re) and found them to be *ca.* 10 kJ mol^{-1} greater for $Re(Cp)(CO)_2$(*n*-heptane), for all the binding modes examined. The increased strength of the Re-heptane bond was proposed to be due to a higher overall total amount of charge transfer between the metal centre and the alkane and not to be due to relative differences between the degree of forward (alkane to metal) and of back (metal to alkane) charge donation [70].

It has also been shown that the nature of the alkane ligand can greatly effect the lifetime of an organometallic alkane complex. A range of time-resolved experimental studies has demonstrated that longer lived alkane complexes have been observed after binding of cyclic alkanes to metal centres [50,51,61,64]. The increased lifetimes of these organometallic cyclopentane and cyclohexane complexes at room temperature have been investigated by variable temperature transient absorption and TRIR experiments and a difference in

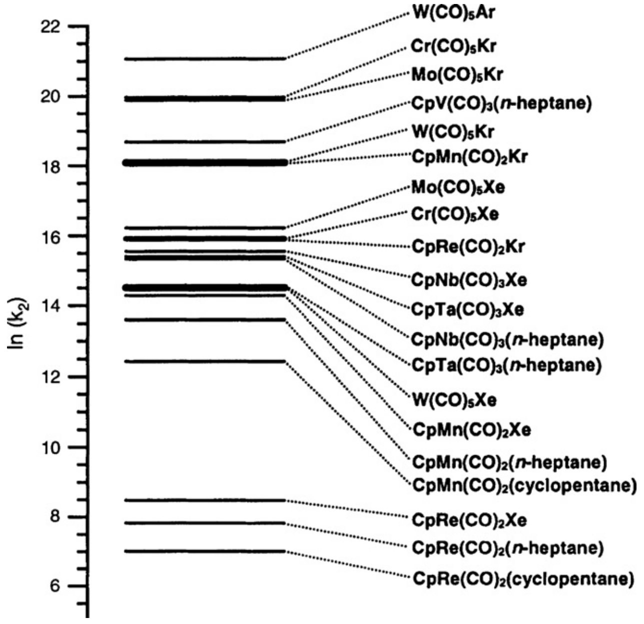


Fig. 4. A plot of the values of ln(k_2) for the reaction of alkane and noble gas complexes with CO at 298 K. Figure reproduced from ref. [56].

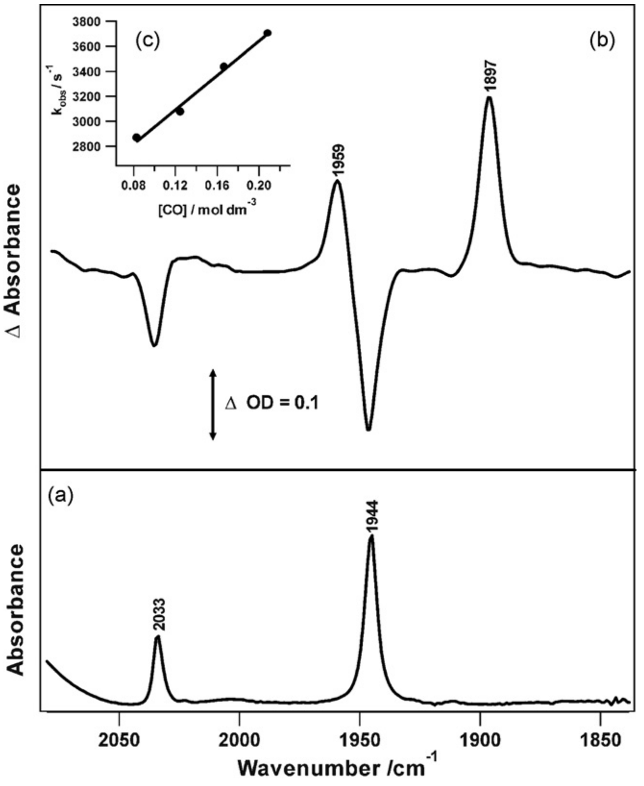


Fig. 5. (a) FTIR spectrum of $Re(Cp)(CO)_3$ in liquid C_2H_6 (298 K, 1550 psi) in the presence of CO (30 psi). (b) Step scan-FTIR spectrum of this solution obtained 4 μs after 266 nm excitation. (c) Plot of observed rate constant, k_{obs}, for the decay of $Re(Cp)(CO)_2(C_2H_6)$ versus CO concentration, yielding the second order rate constant, k_{CO}, for the reaction of $Re(Cp)(CO)_2(C_2H_6)$ with CO in liquid C_2H_6 at room temperature. Figure reproduced from ref. [63].

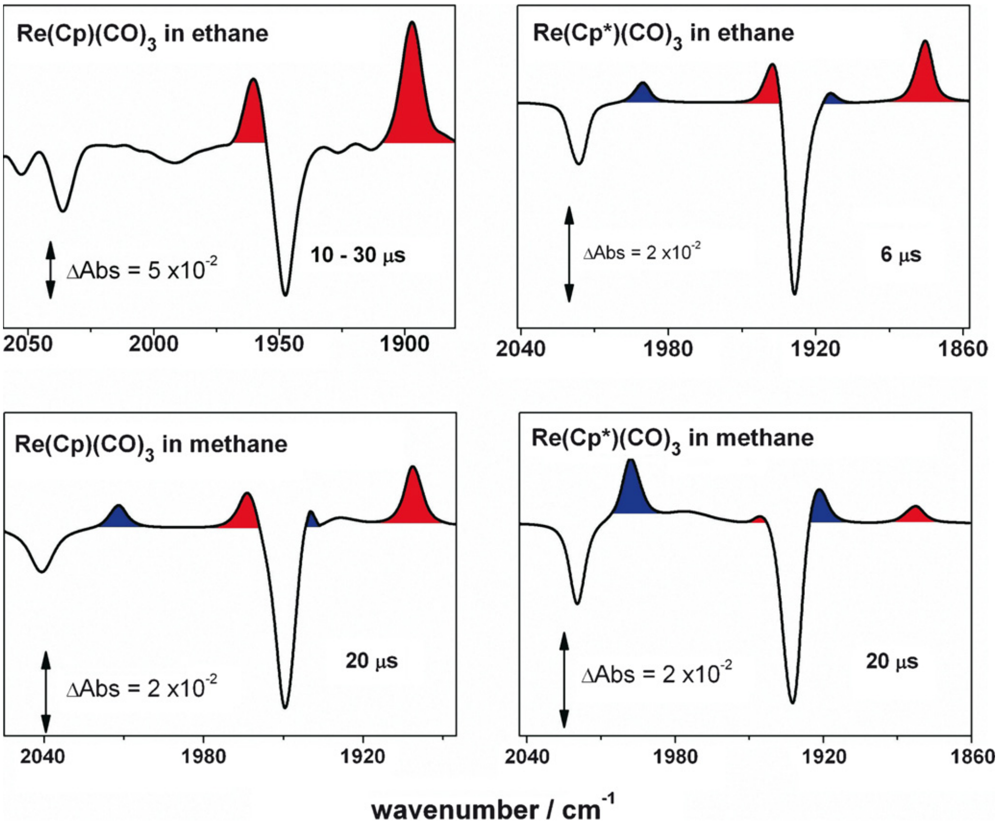


Fig. 6. TRIR difference spectra recorded at the time delays shown after the photolysis of indicated species in ethane (1660 psi) or methane (4000 psi) in the presence of CO at room temperature. Lorentzian fit lines of the experimental data are shown. Red shaded areas indicate ν(CO) bands of the alkane complexes, Re(Cp)(CO)$_2$(C$_n$H$_{2n+2}$), and blue areas indicate the C–H activated complexes, Re(Cp)(CO)$_2$(C$_n$H$_{2n+1}$)H. Figure is reproduced from ref. [58].

the entropy of activation for the reaction of cyclic and linear chain alkane complexes with CO was observed. This has been proposed to be due to differences in the restriction of the motion of the bound alkane ligand. This entropic destabilisation of the organometallic alkane has been suggested to be most pronounced in longer chain linear alkane complexes [50]. A correlation between *n*-alkane chain length and binding energy to organometallic metal centres has also been previously reported, with the lighter alkanes being found to only bind weakly to metal centres [40,71]. Interestingly, a TRIR spectroscopic study on the reaction of Cr(η^6-C$_6$H$_6$)(CO)$_2$(*n*-alkane) (*n*-pentane, *n*-heptane, *n*-decane) with CO, showed an increased rate of reactivity as the alkane chain length was increased attributed to an increase in the entropy of activation with increasing alkane chain length [50].

2.3. Organometallic complexes of the lighter alkanes

The early matrix isolation experiments characterised the interaction of CH$_4$ in complexes such as Cr(CO)$_5$(CH$_4$) and Fe(CO)$_4$(CH$_4$) at cryogenic temperatures [10,14,15]. At room temperature the interaction of the lighter alkanes with metal centres has been studied in the gas phase [71–73]. TRIR experiments in the gas phase have demonstrated that the shortest chain *n*-alkanes, ethane and methane, have lower binding energies to metal centres than the longer chain alkanes such as *n*-heptane [71,73]. W(CO)$_5$(C$_2$H$_6$) could be detected in the gas phase but there was no evidence for the formation of W(CO)$_5$(CH$_4$). This led to the binding energy of methane and ethane to W(CO)$_5$ to be estimated <21 and 31 (±8) kJ mol^{-1}, respectively [71]. Other TRIR experiments monitoring the photolysis of Cr(CO)$_6$ in the gas phase detected a transient species, assigned to be Cr(CO)$_5$(CH$_4$) [72]. Another TRIR study did not directly detect the presence of Cr(CO)$_5$(CH$_4$), following the photolysis of Cr(CO)$_6$ in the presence of a low pressure (11.4 psi) of CH$_4$ and this work reported an estimation of the binding energy of the Cr(CO)$_5$(CH$_4$) bond (33 (±8) kJ mol^{-1}) [74].

In solution, evidence for the presence of organometallic methane complexes has been obtained by isotopic labelling experiments, in which the rate of reductive elimination of methane (or methane-d_4) from methyl hydride and methyl-d_3 deuteride complexes was compared [35,36,75–77]. A TRIR experiment carried out at low temperatures investigating the interaction of the Rh(Cp*)(CO) fragment with alkanes, outlined above (Section 2.2), reported that in liquid krypton doped with an alkane, ethane formed a weakly bound organometallic alkane complex with the Rh(Cp*)(CO) fragment, but methane coordination could not be detected [41].

We have already described above a preliminary report on the photolysis of Rh(Cp)(CO)$_2$ in supercritical methane (scCH$_4$) at room temperature [44]. Performing experiments under high pressures allows reactions to be carried out in either liquid or supercritical fluids (at solvent densities comparable to those of conventional organic solvents), with solvents which would normally be in the gas phase at room temperature and pressure [78–80]. The detection of an organometallic methane complex in solution at room temperature was reported following TRIR investigation into the photochemistry of Fe(CO)$_5$ in scCH$_4$ (3500 psi, 298 K) [81]. Consistent with the previous matrix isolation [15] and TRIR spectroscopic studies in conventional solvents [82], photolysis initially led to the formation of ^{3}Fe(CO)$_4$, which subsequently decayed (k_{obs} = 5 (±1) × 10^6 s^{-1}) as new bands that were assigned to the formation of the singlet solvated complex ^{1}Fe(CO)$_4$(CH$_4$) grew in.

The photolysis of $W(CO)_6$ in $scCH_4$ has also been investigated. The combination of TRIR spectroscopy and supercritical fluids allowed $W(CO)_5(CH_4)$ to be characterised at room temperature in solution [58]. Consistent with the gas phase TRIR studies described above [71] the lifetime of this methane complex was significantly shorter (×3.4) than that of the analogous *n*-heptane complex, recorded under similar conditions. Evidence for the coordination of methane to the $W(CO)_5$ fragment was provided by carrying out TRIR spectroscopic experiments in supercritical Argon (scAr), a much more weakly coordinating solvent, in the absence and presence of a small quantity of methane. In the presence of the low concentration of methane in the scAr solution the $W(CO)_5$ fragment was found to be significantly longer lived than in pure argon alone, indicating a stabilising interaction between methane and the $W(CO)_5$ fragment.

The relatively long lifetime of $M(Cp)(CO)_2(alkane)$ (M = Mn, Re) in conventional alkane solvents has led to our current interest in the photochemistry of $M(Cp')(CO)_3$ (M = Mn or Re; Cp' = Cp* (Re only) or Cp) in $scCH_4$ and liquid ethane ($liqC_2H_6$) [58,63]. Fig. 5 shows the TRIR difference spectrum recorded following the photolysis (266 nm) of $Re(Cp)(CO)_3$ in liquid ethane (1550 psi, 298 K) in the presence of CO (30 psi) [63]. Two new transient ν(CO) bands were observed at a lower energy to the parent ν(CO) bands which were assigned to the transient $Re(Cp)(CO)_2(C_2H_6)$ by comparison with previous TRIR [60,64] and NMR experiments [61]. The ν(CO) bands of $Re(Cp)(CO)_2(C_2H_6)$ decayed as those of $Re(Cp)(CO)_3$ recovered and this decay rate depended linearly on the CO concentration ($k_{CO} = 6.9\ (\pm 0.5) \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$). $Re(Cp)(CO)_2(C_2H_6)$ was found to be significantly more reactive to CO than the analogous cyclopentane (×6.3) and *n*–heptane (×2.8) complexes.

Photolysis of $Mn(Cp)(CO)_3$ in $liqC_2H_6$ and $scCH_4$ led to the formation of $Mn(Cp)(CO)_2(C_2H_6)$ or $Mn(Cp)(CO)_2(CH_4)$. Interestingly the organometallic methane complex was found to be approximately ×6 more reactive to CO than the analogous ethane complex, under similar conditions [58]. Fig. 6 shows the TRIR difference spectrum recorded following photolysis of $Re(Cp)(CO)_3$ in $scCH_4$. There are four main transient bands present 20 μs after photolysis and all of the bands were found to decay at the same rate as the parent bands reformed. Two of the ν(CO) bands were assigned to $Re(Cp)(CO)_2(CH_4)$ by comparison with a range of previously reported $Re(Cp)(CO)_2(alkane)$ complexes. The other two bands were assigned to the alkyl hydride complex, $Re(Cp)(CO)_2(CH_3)H$ [58]. The observation of an equilibrium between the organometallic methane and methyl hydride complexes was in contrast to the previously described experiment carried out in liquid ethane, where only the formation of the organometallic ethane complex was observed [63]. These findings are in agreement with previous experimental studies that have demonstrated an increased relative rate of C–H activation of coordinated methane compared to the relative rate of ethane C–H activation [46,83].

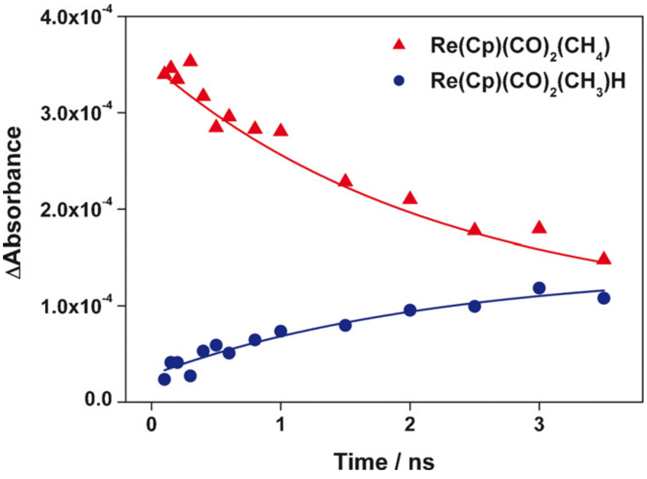


Fig. 7. Kinetic traces of the intensity of the IR bands of $Re(Cp^*)(CO)_2(CH_4)$ and $Re(Cp^*)(CO)_2(CH_3)H$. Figure adapted from ref. [58].

Picosecond TRIR experiments on the photolysis of $Re(Cp^*)(CO)_3$ demonstrated in $scCH_4$ that immediately following photolysis transient bands corresponding to $Re(Cp^*)(CO)_2(CH_4)$ were formed and these bands partially decayed ($\tau \sim 2$ ns) whilst new bands corresponding to an equilibrium mixture of $Re(Cp^*)(CO)_2(CH_4)$ and $Re(Cp^*)(CO)_2(CH_3)H$ were seen to grow in, Fig. 7.

3. Conclusions

There have been major advances over the last 35 years since the initial reports of organometallic alkane complexes. Examples of such complexes have now been characterised using conventional spectroscopic techniques such as NMR spectroscopy and it is hoped that understanding the reactivity of such species will eventually lead to their isolation. Organometallic alkane complexes are key intermediates in the activation of C–H bonds by transition metal complexes and understanding their role in this reaction will also provide further insight into this important process.

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