

Recent advances in organometallic alkane and noble gas complexes*

James A. Calladine, Khuong Q. Vuong, Xue Z. Sun, and Michael W. George[‡]

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Abstract: Fast time-resolved infrared (TRIR) spectroscopy has been useful for studying the reactions of a wide range of organometallic alkane and noble gas complexes at ambient temperature following irradiation of metal carbonyl precursor complexes. The reactivity of organometallic alkane and xenon complexes decreases both across and down groups V, VI, and VII, and for a given metal/ligand combination the alkane and xenon complexes have similar reactivities. Systematic studies of reactivity have produced long-lived Re complexes which have allowed such complexes to be characterized using NMR spectroscopy. A new approach using liquid propane at low temperature as a solvent to monitor the interaction of such weakly coordinating ligands with transition-metal centers is outlined. TRIR studies monitoring the coordination and activation of methane and ethane in supercritical methane and liquid ethane solvents at room temperature are also reviewed.

Keywords: alkane complexes; infrared; noble gas complexes; organometallic; photochemistry.

INTRODUCTION

Organometallic alkane and noble gas complexes were first observed over 30 years ago when complexes such as $\text{Cr}(\text{CO})_5(\text{CH}_4)$ and $\text{Cr}(\text{CO})_5\text{Xe}$ were characterized following the photolysis of $\text{Cr}(\text{CO})_6$ in a range of cryogenic matrices at 12 K [1]. Evidence for the coordination of alkanes or noble gases to the $\text{Cr}(\text{CO})_5$ fragment came from shifts in the UV/visible absorption maxima, λ_{max} , as well as in the IR $\nu(\text{CO})$ band positions of the photoproduct. The position of λ_{max} for $\text{Cr}(\text{CO})_5$ was found to depend strongly on the nature of the host matrix, and a marked blue shift was observed when the matrix was changed from Ne (624 nm) to Xe (492 nm) and CH_4 (489 nm). This was interpreted to indicate a significant interaction between the matrix material and the vacant coordination site of the photofragment. Organometallic alkane complexes were first observed in solution at room temperature following photolysis of $\text{Cr}(\text{CO})_6$ in cyclohexane solution, which showed that $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ is formed within 50 ns after photolysis [2,3]. Further ultrafast studies have demonstrated that solvation actually occurs within the *first picosecond* following photolysis [4,5]. Organometallic alkane complexes are proposed as intermediates in many C–H activation reactions and have been observed in mechanistic investigations of this important class of reaction [6–8].

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[‡]Corresponding author

Since these early studies, there have been many reports characterizing organometallic alkane complexes in solution at room temperature. Systematic studies have shown that their reactivity decreases going both across and down groups V, VI, and VII (see Fig. 1) [9]. This led to the discovery of the long-lived $\text{CpRe}(\text{CO})_2(n\text{-heptane})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) complex [10], which is ca. 50 000 times *less* reactive than the analogous $\text{CpV}(\text{CO})_3(n\text{-heptane})$ complex [11].

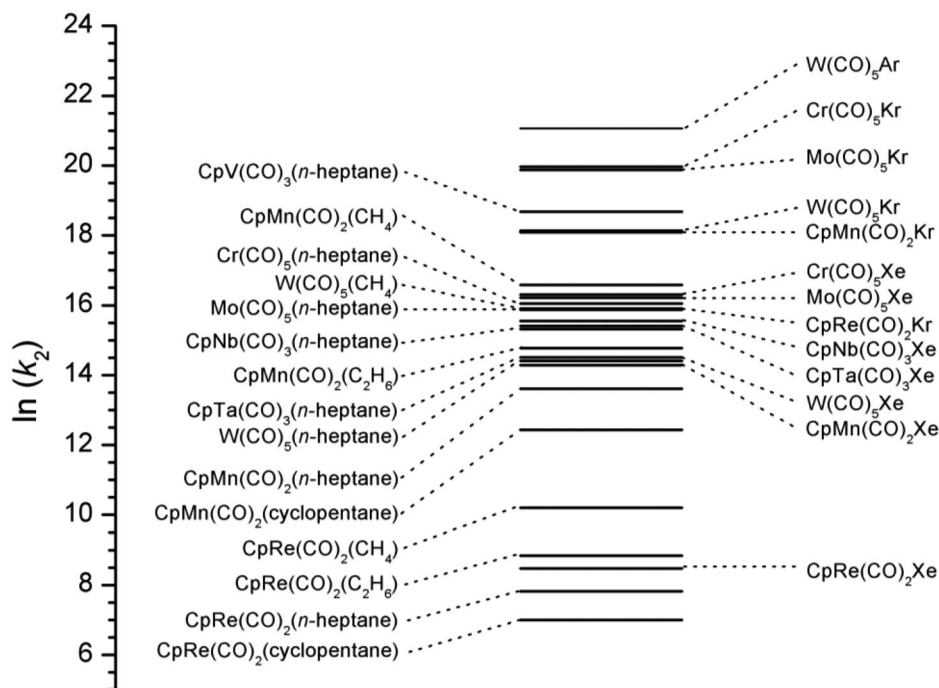


Fig. 1 Values of $\ln(k_2)$ for the reaction of alkane and noble gas complexes with CO in either alkane or supercritical noble gas solution at room temperature.

The stability of $\text{CpRe}(\text{CO})_2(\text{alkane})$ complexes is significant and has enabled Ball and coworkers to record the first NMR spectrum of an organometallic alkane complex, $\text{CpRe}(\text{CO})_2(\text{cyclopentane})$, which persisted for several hours at low temperature (~ 180 K) [12]. Time-resolved infrared (TRIR) spectroscopy studies of $\text{CpRe}(\text{CO})_3$ in *n*-heptane and cyclopentane at room temperature have shown that the cyclopentane complex is ca. $2 \times$ longer lived than the *n*-heptane complex [13]. A number of room-temperature TRIR and transient absorption studies on organometallic compounds in a range of different alkane solvents (linear or cyclic) have shown that cyclic alkanes give rise to longer-lived organometallic alkane complexes than linear alkanes [13–15]. Measurements of the enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of activation for reaction of the alkane complex with CO have shown that, although ΔH^\ddagger for both linear and cyclic alkane complexes tend to be similar, large differences in ΔS^\ddagger are observed [13].

Liquefied noble gases (Kr and Xe) have been used for characterizing organometallic noble gas complexes, at both low and ambient temperatures [16]. Low-temperature Fourier transform infrared (FTIR) studies have been used to characterize $\text{M}(\text{CO})_5\text{Xe}$ ($\text{M} = \text{Cr}$ and W) in liquefied Xe solution [17,18]. The formation of $\text{M}(\text{CO})_5\text{Xe}$ complexes were confirmed by using liquid Kr doped with 5 % Xe where preferential coordination of Xe was observed. The $\text{W}(\text{CO})_5\text{Kr}$ complexes are much shorter lived with a lifetime of ca. 0.1 s at 150 K in liquid Kr, whilst $\text{W}(\text{CO})_5\text{Xe}$ has a lifetime of ca. 1.5 min at 170 K in liquid Xe solution.

Organometallic noble gas complexes have also been observed in solution at room temperature following irradiation of metal carbonyls dissolved in supercritical fluids [19]. Xe, by comparison with the other noble gases, forms the most stable organometallic complexes and, for the range of complexes studied, the reactivity of the early transition-metal carbonyl Xe complexes followed the same trend in reactivity as the corresponding alkane complex [16]. Furthermore, the reactivity of a given Xe complex is only ca. 2× greater than the corresponding *n*-heptane complex. The use of TRIR to elucidate organometallic alkane and noble gas complexes was summarized in 2001 [9], and this paper covers some recent developments in both of these areas.

ORGANOMETALLIC ALKANE COMPLEXES

Further characterization of organometallic alkane complexes by TRIR and NMR

Following the initial characterization of $\text{CpRe}(\text{CO})_2(\text{cyclopentane})$ by NMR [12], further experiments on $\text{CpRe}(\text{CO})_3$ in cyclopentane and cyclohexane have shown that the alkane binds via an $\eta^2\text{-C,H}$ mode with a rapid equilibrium between the two ^1H of the CH_2 unit. Indeed, further experiments using *n*-pentane have shown that although all three C–H units can coordinate to the Re center, there is a small preference ($\sim 0.1 \text{ kcal mol}^{-1}$) for the coordination of secondary C–H bonds vs. primary C–H bonds [20].

Recent experiments on a related compound $\text{CpRe}(\text{CO})_2(\text{PF}_3)$, using a combination of TRIR and low-temperature NMR spectroscopies, have shown that this compound not only forms the alkane complex, $\text{CpRe}(\text{CO})(\text{PF}_3)(\text{alkane})$ (alkane = *n*-pentane, cyclopentane, and cyclohexane), but also the alkyl hydride, $\text{CpRe}(\text{CO})(\text{PF}_3)(\text{alkyl})\text{H}$, as well [21]. This is in marked contrast to the $[\text{CpRe}(\text{CO})_2]$ fragment which only forms alkane complexes with these solvents. It was also noted that the proportion of the alkyl hydride species followed the trend: *n*-pentane > cyclopentane > cyclohexane, with very little, if any of the cyclohexyl hydride being present.

Characterization of organometallic methane and ethane complexes at room temperature

The C–H activation of methane and ethane is of particular interest because of the potential for utilizing these abundant molecules as an energy source or a chemical feedstock [22]. Photolysis of $\text{W}(\text{CO})_6$ in supercritical CH_4 (sc CH_4) at room temperature generated $\text{W}(\text{CO})_5(\text{CH}_4)$ [23]. The methane complex was found to be short lived and significantly more reactive than the analogous *n*-heptane complex [15]. However, photolysis of $\text{Cp}^*\text{Re}(\text{CO})_3$ ($\text{Cp}^* = \text{Cp}$ or Cp^* , with $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in (sc CH_4) or liquid C_2H_6 at room temperature, leads to a mixture of the alkane complex and the alkyl hydride (see Fig. 2) [23]. We have used picosecond time-resolved infrared spectroscopy to directly monitor the photolysis of $\text{Cp}^*\text{Re}(\text{CO})_3$ in sc CH_4 and demonstrated that the initially generated $\text{Cp}^*\text{Re}(\text{CO})_2(\text{CH}_4)$ forms an equilibrium mixture of $\text{Cp}^*\text{Re}(\text{CO})_2(\text{CH}_4)/\text{Cp}^*\text{Re}(\text{CO})_2(\text{CH}_3)\text{H}$ within the first few nanoseconds. The ratio of alkane to alkyl hydride complexes varies in the order $\text{CpRe}(\text{CO})_2(\text{C}_2\text{H}_6) : \text{CpRe}(\text{CO})_2(\text{C}_2\text{H}_5)\text{H} > \text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_2\text{H}_6) : \text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_2\text{H}_5)\text{H} \approx \text{CpRe}(\text{CO})_2(\text{CH}_4) : \text{CpRe}(\text{CO})_2(\text{CH}_3)\text{H} > \text{Cp}^*\text{Re}(\text{CO})_2(\text{CH}_4) : \text{Cp}^*\text{Re}(\text{CO})_2(\text{CH}_3)\text{H}$. The activation parameters for the reactions of the organometallic methane and ethane complexes with CO have been measured, and the ΔH^\ddagger values represent lower limits for the CH_4 binding enthalpies to the metal center of W-CH_4 [$7.2 (\pm 0.5) \text{ kcal mol}^{-1}$], Mn-CH_4 [$9.3 (\pm 0.5) \text{ kcal mol}^{-1}$], and Re-CH_4 [$12.2 (\pm 0.5) \text{ kcal mol}^{-1}$] bonds in $\text{W}(\text{CO})_5(\text{CH}_4)$, $\text{CpMn}(\text{CO})_2(\text{CH}_4)$, and $\text{CpRe}(\text{CO})_2(\text{CH}_4)$, respectively.

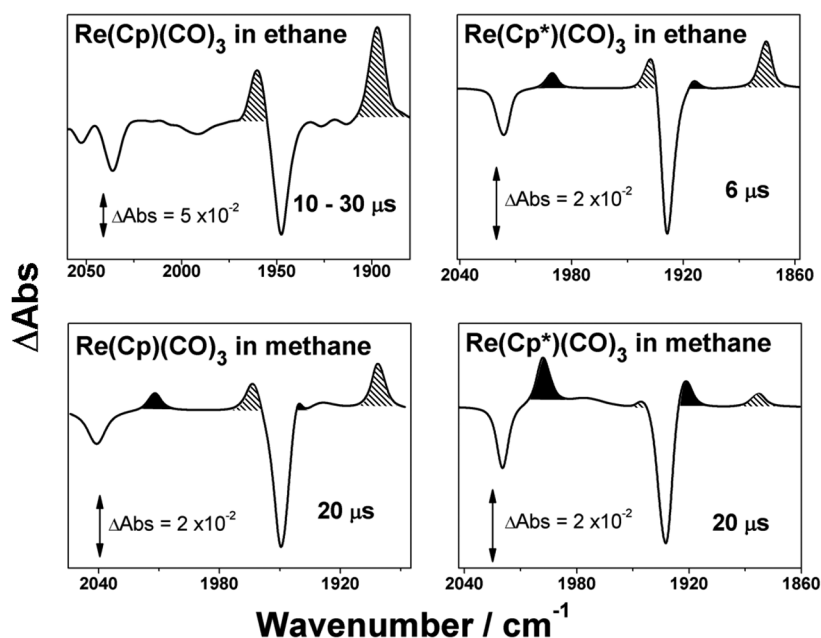


Fig. 2 TRIR difference spectra obtained after photolysis (266 nm) of $\text{Cp}'\text{Re}(\text{CO})_3$ ($\text{Cp}' = \text{Cp}$ or Cp^*) in scCH_4 or liquid C_2H_6 solution at room temperature. Striped bands indicate the alkane complex $[\text{Cp}'\text{Re}(\text{CO})_2(\text{C}_n\text{H}_{2n+2})]$ whilst shaded bands show the C–H activated product, $[\text{Cp}'\text{Re}(\text{CO})_2(\text{C}_n\text{H}_{2n+1})\text{H}]$. Figure adapted from ref. [23].

ORGANOMETALLIC XENON COMPLEXES

The interaction of noble gases with organometallic fragments has been well studied over the past few decades. However, it was only recently that complexes have become sufficiently stable to be studied by NMR spectroscopy [24]. The IR spectrum obtained 20 μs after photolysis of $(i\text{PrCp})\text{Re}(\text{CO})_2(\text{PF}_3)$ $\{i\text{PrCp} = \eta^5\text{-C}_3\text{H}_4(\text{CH}(\text{CH}_3)_2)\}$ in supercritical Xe (scXe) showed the presence of three new $\nu(\text{CO})$ bands indicating the production of at least two transient species. These transients were assigned to $(i\text{PrCp})\text{Re}(\text{CO})_2\text{Xe}$ and $(i\text{PrCp})\text{Re}(\text{CO})(\text{PF}_3)\text{Xe}$ with the latter being slightly longer lived. The rate of decay of the intermediates was determined as a function of temperature, and this dependence was used to estimate the activation energy for the reaction of the Xe complexes with CO in scXe . The activation energies obtained for $(i\text{PrCp})\text{Re}(\text{CO})_2\text{Xe}$ [$11.7 (\pm 0.4) \text{ kcal mol}^{-1}$] and $(i\text{PrCp})\text{Re}(\text{CO})(\text{PF}_3)\text{Xe}$ [$12.4 (\pm 0.4) \text{ kcal mol}^{-1}$] were found to be very close to the value for the previously investigated Re complex $\text{CpRe}(\text{CO})_2\text{Xe}$ [$11.9 (\pm 0.5) \text{ kcal mol}^{-1}$] [25]. FTIR was used to monitor the photochemistry of $(i\text{PrCp})\text{Re}(\text{CO})_2(\text{PF}_3)$ in liquefied Xe at low temperature, and these experiments demonstrated that both $(i\text{PrCp})\text{Re}(\text{CO})_2\text{Xe}$ and $(i\text{PrCp})\text{Re}(\text{CO})(\text{PF}_3)\text{Xe}$ were generated following UV photolysis and that the latter compound has a significantly longer lifetime. The lifetime of $(i\text{PrCp})\text{Re}(\text{CO})(\text{PF}_3)\text{Xe}$ is longer than for all other related complexes, such as $\text{CpRe}(\text{CO})_2\text{Xe}$ and $\text{CpMn}(\text{CO})_2\text{Xe}$. This long lifetime is significant since it was sufficient to allow this complex to be characterized using NMR spectroscopy in liquid Xe solution at low temperature. ^{19}F , ^{31}P , and ^{129}Xe chemical shifts of $(i\text{PrCp})\text{Re}(\text{CO})(\text{PF}_3)\text{Xe}$ were determined. The ^{129}Xe chemical shift of $(i\text{PrCp})\text{Re}(\text{CO})(\text{PF}_3)\text{Xe}$, $\delta = -6179 \text{ ppm}$, is significantly shielded, on the order of 1000 ppm with respect to free Xe. The coupling constants between coordinated ^{129}Xe and both the ^{19}F and ^{31}P nuclei provided definitive characterization of this compound (Fig. 3).

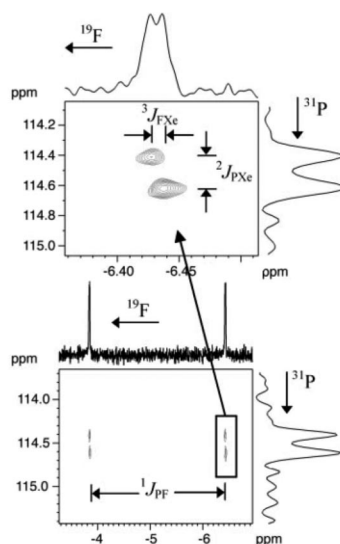


Fig. 3 2D NMR ^{19}F - ^{31}P spectrum of ^{129}Xe -labeled $(i\text{PrCp})\text{Re}(\text{CO})(\text{PF}_3)(^{129}\text{Xe})$ recorded at 163 K showing the coupling between the ^{19}F , ^{31}P , and ^{129}Xe nuclei. Figure from ref. [21].

NEW APPROACH USING LIQUID PROPANE AS A SOLVENT TO STUDY HIGHLY REACTIVE ORGANOMETALLIC COMPLEXES IN SOLUTION

The majority of the work in the area of organometallic alkane and noble gas complexes has been to monitor their formation and reactivity using indirect spectroscopic techniques, which infer the formation of the alkane and noble gas complexes, either by the position of IR or UV/visible bands or by monitoring the kinetics of transient species under a variety of conditions. The major advance in both fields is the pioneering work of Ball and coworkers to use NMR spectroscopy to directly monitor the metal–alkane [12,20,21,26] or metal–Xe interaction [24]. Up until now this has been limited to two related groups of Re complexes based on the $[\text{CpRe}(\text{CO})_2]$ (alkane only) and $[\text{CpRe}(\text{CO})(\text{PF}_3)]$ moieties; this is because these complexes are the only complexes with sufficient lifetime at low temperature to allow for characterization by NMR. Advances in this area require more extensive use of NMR to study a wider range of complexes, both in terms of different metals and ligand sets. To achieve this, we believe the solvent requires certain properties in order to facilitate widespread studies of these systems. The solvent must: (i) be photochemically inert in isolation; (ii) be relatively noncoordinating, as a major objective will be doping the solvent with a ligand in order to monitor its coordination; (iii) have a low freezing point since lower temperatures will extend the lifetime of species in solution; and (iv) be produced relatively easily without the need for very high pressures.

Noble gases may seem like ideal solvents, particularly since they are transparent in the IR and UV regions, which allow the use of long pathlengths. However, they have certain disadvantages in that they have comparable solvating properties to the heavier hydrocarbons, and doping experiments in such solvents may be difficult. For example, photolysis of $\text{W}(\text{CO})_6$ dissolved in liquid Xe doped with CH_4 is unlikely to generate $\text{W}(\text{CO})_5(\text{CH}_4)$ in detectable quantities, since $\text{W}(\text{CO})_5\text{Xe}$ would be the major photoproduct. Furthermore, the use of high pressure is required to expand the otherwise small liquid range of the gas (e.g., for Xe, 161–165 K at 15 psi and 161–245 K at 320 psi [27]) and therefore restricts somewhat the simplicity of the experiments. Finally, the prohibitive cost of noble gas solvents limits their widespread usage. Liquid propane, on the other hand, is an underused but very attractive solvent for studying the coordination of weak ligands to transition metals in solution at low temperature. A very low melting point (85 K), which is considerably lower than would otherwise be achievable using

conventional alkane solvents such as *n*-pentane (143 K), makes propane appealing for use as a low-temperature solvent. Figure 4a shows the phase diagram of propane. At quite modest pressure (125 psi), propane has a significant liquid range, and the low melting temperature (85 K) means that the apparatus required to handle this solvent is less demanding in terms of the pressure requirements than liquid Xe and Kr. It must be mentioned for safety that high-pressure experiments require specialized equipment with an appropriate pressure rating and it is the responsibility of individual researchers to verify that their particular apparatus meets the necessary safety requirements. We have used a miniature high-pressure cell which was originally developed for the spectroscopic study of reactions between organometallic compounds impregnated into polymer films and gases such as N₂ or H₂ at any temperature between ambient and 20 K, Fig. 4b [28].

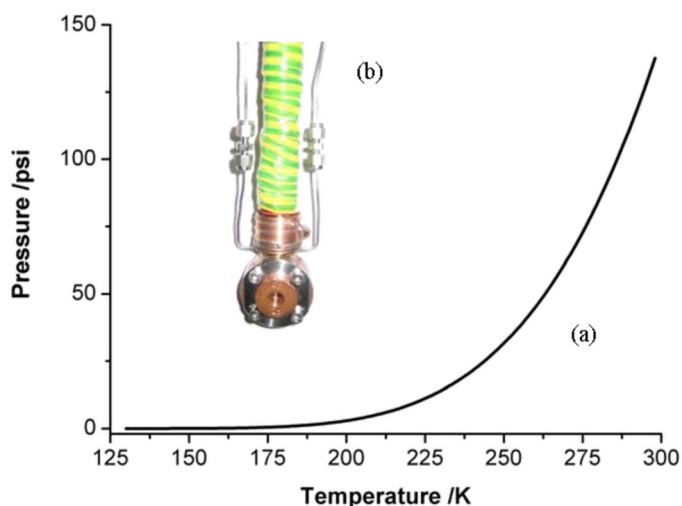


Fig. 4 (a) Phase diagram for propane [27] and (b) a picture of the Cu high-pressure, low-temperature cell used in these experiments.

We have investigated the photochemistry of CpRe(CO)₃ in order to explore the use of propane as a solvent for studying the interaction of weak ligands to metal centers. We have initially monitored the photochemistry at room temperature using fast TRIR. The IR spectrum obtained 20 μs following 266 nm irradiation of CpRe(CO)₃ in liquid propane (150 psi) in the presence of CO (15 psi) clearly shows that the parent ν(CO) bands are bleached and two new transient bands are produced at 1956 and 1892 cm⁻¹ (Fig. 5a), which can readily be assigned to CpRe(CO)₂(propane) by comparison with the previous TRIR studies [10]. Under these conditions, CpRe(CO)₂(propane) is not stable and decays ($k_{\text{obs}} = 318 (\pm 2) \text{ s}^{-1}$) to reform CpRe(CO)₃. This is close to that observed for the decay of the analogous C₂H₆ complex under similar conditions [29], but it is ca. 6× faster than for the *n*-heptane complex [13]. The activation energy [12.4 (± 0.5) kcal mol⁻¹] for this reaction indicates that CpRe(CO)₂(propane) should have a significant lifetime at low temperature (Fig. 5b).

The IR spectrum obtained following photolysis of CpRe(CO)₃ in liquid propane (160 K, 150 psi) shows that irradiation causes the parent ν(CO) bands to be bleached and two new photoproduct bands are produced at 1951 and 1886 cm⁻¹, Fig. 5c. These new bands can be assigned to CpRe(CO)₂(propane) by comparison to previous TRIR studies [29]. The bands of CpRe(CO)₂(propane) are not stable and decay over 60 min. This lifetime is comparable to that of CpRe(CO)₂(cyclopentane) in cyclopentane at a much higher temperature (180 K) and represents the first characterization of a long-lived organometallic alkane complex of a lighter alkane.

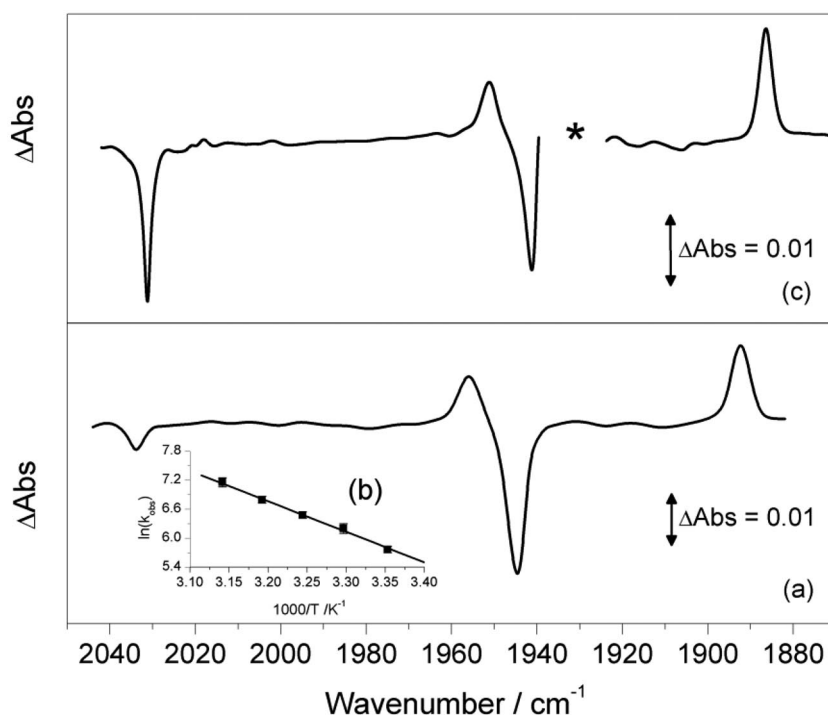


Fig. 5 (a) Point-by-point TRIR difference spectrum 20 μ s after 266 nm photolysis of $\text{CpRe}(\text{CO})_3$ in liquid propane (150 psi) and CO (15 psi) at room temperature, (b) Arrhenius plot for the decay of $\text{CpRe}(\text{CO})_2(\text{propene})$, 293–318 K, and (c) FTIR difference spectrum obtained after photolysis of $\text{CpRe}(\text{CO})_3$ in liquid propane at 160 K. * denotes the presence of a strong solvent absorption.

CONCLUSIONS AND OUTLOOK

There is a general decrease in the reactivity of both alkane and noble gas complexes upon moving from group V to VII, and this has allowed for the characterization of $\text{Re}-(\text{alkane})$ and $\text{Re}-\text{Xe}$ complexes by NMR. New experiments demonstrate that liquid propane is a very versatile solvent for studying the interaction of weakly coordinating ligands to transition-metal centers, particularly since it offers a low-temperature weakly coordinating solvent which can be used to study the coordination of higher alkanes and other ligands such as Xe. This development is likely to increase the number of organometallic alkane and noble gas complexes that can be characterized in the future, and we believe that this solvent will be important in furthering such studies, particularly extending the range of complexes characterized by NMR spectroscopy. There is clearly still much to learn about organometallic alkane and noble gas complexes, and TRIR spectroscopy will continue to prove useful for this purpose.

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