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PAPER

Combined experimental and theoretical investigation into C–H activation of cyclic alkanes by Cp'Rh(CO)₂ (Cp' = η^5 -C₅H₅ or η^5 -C₅Me₅)†‡

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Fast time-resolved infrared spectroscopic measurements have allowed precise determination of the rate of C–H activation of alkanes by Cp'Rh(CO) {Cp' = η^5 -C₅H₅ or η^5 -C₅Me₅; alkane = cyclopentane, cyclohexane and neopentane (Cp only)} in solution at room temperature and allowed the determination of how the change in rate of oxidative cleavage varies between complexes and alkanes. Density functional theory calculations on these complexes, transition states, and intermediates provide insight into the mechanism and barriers observed in the experimental results. Unlike our previous study of the linear alkanes, where activation occurred at the primary C–H bonds with a rate governed by a balance between these activations and hopping along the chain, the rate of C–H activation in cyclic alkanes is controlled mainly by the strength of the alkane binding. Although the reaction of CpRh(CO)(neopentane) to form CpRh(CO)(neopentyl)H clearly occurs at a primary C–H bond, the rate is much slower than the corresponding reactions with cyclic alkanes because of steric factors with this bulky alkane.

Introduction

There is considerable interest in the photochemistry of $(\eta^{5}-C_{5}R_{5})MLL'$ (R = H, Me; M = Rh, Ir; L = CO; L' = CO, H₂) since these complexes undergo photolytic oxidative addition *via* alkane carbon–hydrogen (C–H) bond activation.¹⁻¹² The activation of alkanes is the subject of widespread interest, since one of the ultimate goals is the use of methane, the main component of natural gas and a widely available inexpensive source, as a feedstock to produce synthetically useful compounds.¹³ Furthermore, using transition metals to provide a way to activate C–H bonds in hydrocarbons with useful results such as alkane dehydrogenation,¹⁴⁻¹⁷ arene borylation,¹⁸⁻²² and alkane metathesis²³ is being actively pursued.

The mechanism of C-H activation has been widely studied but important factors governing this reaction are still being elucidated. The photochemistry of transition metal complexes has played a pivotal role in many studies of the mechanistic investigation of C-H activation and metal carbonyl complexes lend themselves to such studies since the photoproducts can be easily characterized using IR spectroscopy as the v(CO) bands report on the electron density at the metal centre. $^{24\text{--}34}$ Irradiation of ($\eta^{\text{-}}$ C_5R_5)Rh(CO)₂ in alkane solution results in the formation of (η^5 - C_5R_5)Rh(CO)(alkane), which can be characterised by a downward shift in the position of the v(CO) band of the transient, relative to the parent bands as the loss of a π -accepting CO ligand results in more electron density on the metal centre in the alkane complex. Fast time-resolved infrared (TRIR) spectroscopy, a combination of UV-vis flash photolysis and fast IR detection, has been a particularly powerful technique to probe organometallic reaction mechanisms. This technique has undergone many changes over the last 20 years and IR spectra can now be routinely obtained on femtosecond and picosecond timescales by generating broad IR pulses (150-300 cm⁻¹)¶ using commercially available 1 kHz Ti: sapphire lasers and difference frequency mixing. In such experiments the timing is achieved by delaying the probe (IR) pulse relative to the UV or visible pump pulse using an optical delay line.³⁵ Kinetic measurements were initially limited up to ca. 2 ns because of the requirement to maintain pump-probe overlap and this timescale is significantly shorter than the rise time of

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 $[\]P$ It should be noted that these are typical values and instrumentation continues to evolve and wider tuning ranges have been reported (*e.g.* the ULTRA facility at the Rutherford Appleton Laboratory, Oxfordshire).⁶⁹

ns-IR diode based TRIR systems, which typically allow kinetic measurements on the > 50 ns timescale.³⁶ TRIR kinetics on the 1–50 ns can be achieved using a 1 kHz nanosecond pump laser with ultra-fast IR detection³⁷ and this approach has been used to record kinetics on this timescale and probe ${}^{3}Fe(CO)_{4} \rightarrow {}^{1}Fe(CO)_{4}L$ (L = Xe, CH₄ and *n*-C₇H₁₄) interconversion in solution.^{38,39} We have also used this technique to probe the C–H activation of Re and Rh carbonyl complexes.⁴⁰⁻⁴²

The chemistry of the related $(Tp(^{Tp3,5-Me})Rh(CO)_2)$ $(Tp^{3,5-Me})$ HB(3,5-dimethylpyrazolyl)₃) was up until recently the most comprehensively studied C-H activation system by TRIR, in part, because the final C-H activation step occurs on the 100s of nanoseconds timescale.43 Photolysis results in the formation of a monocarbonyl solvated complex $Rh(\kappa^3-Tp^{3,5-Me)}(CO)(RH)$. This species is not stable and decays to form the more stable $Rh(\kappa^2-Tp^{3,5-Me})(CO)(RH)$ complex, which undergoes C-H activation to form the final oxidative addition product, $Rh(\kappa^3$ -Tp^{3,5-Me})(CO)(R)H. We recently studied the photochemistry of the *tert*-butyl-substituted complex $Rh(\kappa^3-Tp4-tBu-3,5-Me)(CO)_2$ and suggested that the important step in controlling C-H activation in this system is partial rechelation of the Tp ligand to Rh, which forms a less stable intermediate that leads to a product with a fully coordinated Tp.41 We have also recently monitored the kinetics of C–H activation of Cp'Rh(CO) (Cp' = η^5 -C₅H₅ or η^{5} -C₅Me₅) in solution at room temperature and determined how the change in the rate of oxidative cleavage varies from methane to decane. The lifetime of CpRh(CO)(alkane) shows a nearly linear behaviour with respect to the length of the alkane chain, while the related Cp*Rh(CO)(alkane) has clear oscillatory behaviour upon changing the alkane (Fig. 3). The behaviours were investigated using coupled cluster and density functional theory (DFT) calculations on these complexes to probe transition states and the intermediates.42



Fig. 1 TRIR spectra obtained after photolysis (267 nm) of CpRh(CO)₂ in cyclohexane.

There have been extensive theoretical investigations into the C–H activation reaction.⁴⁴ The reaction of CH₄ with CpRh(CO) had been studied by density functional theory (DFT) calculating the initial σ -complex, transition state, and methyl-hydride product.⁴⁵ This work was followed shortly by complementary *ab initio* studies, which showed that the computed thermodynamic values for C–H activation were very sensitive to the computational method and somewhat sensitive to the basis set.⁴⁶⁻⁴⁸ Work was done on the tris(pyrazolyl)borate rhodium complexes, Rh(Tp^{3,5-Me})(CNR)(alkyl)H (R = neopentyl) where the thermodynamic preference for a wide variety of hydrocarbon substrates has been investigated both experimentally and theoretically.⁴⁹⁻⁵³ Our



Fig. 2 TRIR kinetic traces showing (a) the decay of CpRh(CO)(cyclohexane) and (b) the growth of CpRh(CO)(cyclohexyl)H obtained by monitoring the change in IR absorption at 1960 and 2017 cm⁻¹ following irradiation of CpRh(CO)₂ in cyclohexane.



Fig. 3 Shows the measured lifetime of the C–H activation Cp'Rh(CO)(alkane) \rightarrow Cp'Rh(CO)(alkyl)H(Cp—blue and Cp*—red and particularly cyclopentane {(i) and (iv)}; cyclohexane {(ii) and (v)} and neopentane (iii).

calculations on Cp'Rh(CO)(alkane) unexpectedly predicted that the most rapid process in these Cp'Rh(CO)(alkane) systems is the 1,3-migration along the alkane chain. The linear behaviour in the observed lifetime of CpRh(CO)(alkane) results from a mechanism in which the next most rapid process is the activation of primary C–H bonds (–CH₃ groups), while the third key step in this system is 1,2-migration with a slightly slower rate. The oscillatory behaviour in the lifetime of Cp*Rh(CO)(alkane) with respect to the alkane's chain length follows from subtle interplay between more rapid migrations and less rapid primary C–H activation, with respect to CpRh(CO)(alkane), especially when the CH₃ group is near a *gauche* turn. This results in the activation being controlled by the percentage of alkane isomers.⁴²

In this paper we determine the C–H activation rates of Cp'Rh(CO)(c-RH) (*c*-RH = cyclopentane or cyclohexane) and again use theoretical calculations to rationalise the different rates observed for the cyclic compared with the linear alkanes.

Experimental

 $CpRh(CO)_2$ was prepared by an adaptation of a published procedure and separated from solvent residues by trap-to-trap condensation.⁵⁴ Cp*Rh(CO)₂ was purchased from Strem Chemicals, Inc. The liquid alkanes were purchased from Sigma-Aldrich (cyclopentane, >99%; cyclohexane 99.9%), heated to reflux over

CaH₂ for several hours, distilled into storage ampoules and saturated with argon. Neopentane was used as received. A recirculating flow system consisting of Teflon tubing, a peristaltic pump and an IR transmission cell (Harrick Scientific Products, Inc.) equipped with CaF₂ windows (thickness 2 mm) was used for the liquid alkane solutions. The experiments under high-pressure were set up in a manner similar to that described in our previous studies.55 The TRIR experiments were performed at the PIRATE facility at the Rutherford Appleton Laboratory (Oxfordshire, U.K.), which also has been described in detail elsewhere.⁵⁶ Briefly, the IR spectra were obtained using part of the output from a 1 kHz, 800 nm, 150 fs, 2 mJ Ti:Sapphire oscillator and regenerative amplifier, which was pumping a white light continuum seeded BBO OPA. The signal and idler produced by the OPA were difference frequency mixed in a type I AgGaS₂ crystal to generate tunable mid-infrared pulses (ca. 150 cm⁻¹ fwhm, 1 µJ). The fourthharmonic generation of a Nd:YAG laser (1 kHz) was used to excite the samples. Changes in the infrared absorbance were recorded by normalizing the outputs from a pair of 64-element MCT linear infrared array detectors on a shot-by-shot basis. The IR cell is mounted on a rapid 'XY raster' to eliminate laser-induced heating and photochemical decomposition.

All density functional theory (DFT) calculations were performed using the Gaussian 09 suite of ab initio programs.⁵⁷ A Pople-type, all-electron, 6-31++G(d,p) basis set⁵⁸⁻⁶⁰ for H, C and O atoms and Stuttgart quasi-relativistic effect core potential basis set (ECP28MWB) for Rh,^{61,62} four different types of density functionals, TPSS⁶³(non-empirial meta-GGA), B3LYP^{64,65} (hybrid GGA), BMK⁶⁶(hybrid meta-GGA) and wB97XD⁶⁷(long-range corrected with empirical dispersion correction) were used to calculate the C-H activation energy barriers. The geometric structures of all species were optimized as gas-phase. The gas-phase relative enthalpies (ΔH) and free energies (ΔG) were calculated at T = 298.15 K within the harmonic potential approximation at the optimized structures (see Supporting Information). Since all of these reactions happened in pure alkane liquids, the calculated gas-phase relative free energies, where the standard-state units are atm, were changed to standard-state units of mol L⁻¹. The reported free energies from separated reactants to σ -complexes (and remaining reaction steps) are corrected for this change in standard-state units68

There are additional issues with respect to the calculated free energies at the standard state because the high relative concentration of alkane with respect to initially produced Cp'Rh(CO) will shift the equilibrium toward the σ -complexes, Cp'Rh(CO)(alkane). Although the relative free energy of the σ -complexes may be stabilized by several kcal mol⁻¹, explicit corrections for this concentration (activity) difference have not made.

Furthermore, we have not attempted to correct these free-energy values for any effect the condensed phase has on the gas-phase entropy. Thus, the full reduction in the gas-phase entropy as the alkane binds is still included in the calculated values, even though one might expect that there would be less entropic freedom in the liquid.

Results and discussion

Fig. 1 shows a series of time-resolved IR spectra obtained over the first 100 ns after the laser pulse. It is clear that immediately after the flash the parent v(CO) bands are bleached and a new

Table 1 Rate of C–H Activation (s^{-1}) measured by TRIR spectroscopyfor Cp'Rh(CO)(alkane) \rightarrow Cp'Rh(CO)(alkyl)H

Alkane	CpRh(CO)(alkane)	Cp*Rh(CO)(alkane)
Methane ^a	$3.40 (\pm 0.19) \times 10^8$	$2.90(\pm 0.13) \times 10^8$
Ethane ^a	$2.08(\pm 0.06) \times 10^8$	$1.59(\pm 0.05) \times 10^8$
Propanea	$1.60(\pm 0.08) \times 10^8$	$1.58(\pm 0.09) \times 10^8$
Butane"	$1.31(\pm 0.01) \times 10^8$	$1.06(\pm 0.05) \times 10^8$
Pentane ^a	$1.06(\pm 0.06) \times 10^8$	$1.02(\pm 0.01) \times 10^8$
Hexane ^a	$0.94(\pm 0.02) \times 10^8$	$0.89(\pm 0.01) \times 10^8$
Heptane ^a	$0.81(\pm 0.02) \times 10^8$	$0.98(\pm 0.02) \times 10^8$
Octane ^a	$0.72(\pm 0.04) \times 10^8$	$0.83(\pm 0.03) \times 10^8$
Nonane"	$0.63 (\pm 0.01) \times 10^8$	$0.76(\pm 0.01) \times 10^8$
Decane ^a	$0.58(\pm 0.02) \times 10^8$	$0.80(\pm 0.01) \times 10^8$
Cvclopentane ^b	$2.26 (\pm 0.02) \times 10^8$	$0.92 (\pm 0.03) \times 10^8$
Cyclohexane ^b	$1.14 (\pm 0.02) \times 10^8$	$0.45 (\pm 0.01) \times 10^8$
Neopentane ^b	$0.54(\pm 0.06) \times 10^8$	
" Ref. 42. " This wo	rk.	

transient is produced with a band at 1960 cm⁻¹ which can readily be assigned to the complex CpRh(CO)(cyclohexane) by comparison to previous matrix isolation and TRIR experiments.^{24,26-30} CpRh(CO)(cyclohexane) is not stable and decays to form a new species which shows a characteristic v(CO) stretching band at 2017 cm⁻¹, which is shifted to higher energy relative to the band of the alkane complex and is due to the formation of the alkyl hydrido complex CpRh(CO)(cyclohexyl)H.

Fig. 2 shows the TRIR kinetic traces obtained from the v(CO)bands at 1960 and 2017 cm⁻¹ The CpRh(CO)(cyclohexane) decays at the same rate as CpRh(CO)(cyclohexyl)H is formed ($k_{obs} = 1.1$ $(\pm 0.2) \times 10^8$ s⁻¹). This rate is only slightly larger than that observed for the activation of n-hexane by CpRh(CO)₂. As mentioned above, our recent investigation of the factors that govern the rate of C-H activation shows the reaction is complex, occurring at the terminal CH groups with the rate being affected by both rates of the 1,2 and 1,3 sigmatropic rearrangements along the alkane chain, which are dependent on the conformation of the bound alkane. Clearly, the reaction with cyclohexane shown in Fig. 1 and 2 does not involve primary C-H groups and it is unclear whether the similarity in the rate of C-H activation between the linear and cyclic alkane is a coincidence. We extended the TRIR measurement of the C-H activation rate to both CpRh(CO)₂ and $Cp*Rh(CO)_2$ with cyclohexane and cyclopentane and these data are shown in Fig. 3 and Table 1.

The C-H activation reaction of CpRh(CO)(alkane) with cyclopentane occurs at ca. $\times 2$ the rate of the analogous reaction of *n*-pentane. There is less difference between the values compared to n- and c-hexane with the formation of CpRh(CO)(cylohexyl)H occurring at a similar rate to the formation of CpRh(CO)-(hexyl)H. For $Cp*Rh(CO)_2$ the rate of C-H activation occurs at a lower rate than the corresponding linear alkanes and the values for *n*- and cyclopentane are similar, while the C-H activation of cyclohexane is ca. $\times 2$ slower than *n*-hexane. Computational chemistry is very important for the elucidation of reaction mechanisms as it can provide insight that is not available solely from experiment. We have recently demonstrated⁴² that detailed calculations can shed new light into the activation rates of the linear alkanes. We have extended this work in order to understand the new data presented above for the C-H activation of the cyclic alkanes.

Computational

To reproduce such fast reactions with differences of only several nanoseconds in lifetime the error in the calculations must be less than 0.1 kcal mol⁻¹. Unfortunately, this accuracy is unreachable for molecular systems containing heavy metal atoms with current theoretical and computational methods. Therefore, the DFT calculations of important energy changes can only be used as a guide to the origin of the observed trends.

As shown in Fig. 4, Cp'Rh(CO) and alkanes will form σ complexes at the beginning of these reactions. The free-energy difference between the σ -complex and separated Cp'Rh(CO) and alkane is $\Delta G'$. The free-energy barrier for the C–H activation of the σ -complex is ΔG^{\ddagger} . Because the barriers between the reactants and the σ -complexes are low, these species are in rapid equilibrium. Furthermore, since the alkane binding energy is weak ($\Delta G' \sim 0$),



Fig. 4 Energy diagram for the C-H activation of alkanes by Cp'Rh(CO).

the rate of the reaction is controlled by $\Delta G' + \Delta G^{\ddagger}$ as shown in Fig. 4. We refer to this quantity as the free-energy barrier relative to reactants and it is described along with the experimental lifetimes in the analysis below.

Fig. 5 and 6 show the structures of the σ -complexes, transition states (TS) and products. The σ -complexes all display the typical structures with one Rh–H and Rh–C interactions. Unlike the case



Fig. 5 Optimised geometries obtained for CpRh(CO) moiety with alkane {alkane = cyclopentane (CyP); neopentane (NeP) and cyclohexane CyH)} showing the alkane (σ -Cp-alkane) and alkyl hydide (product-Cp-alkane) together with the transition state between these (TS-Cp-alkane).



Fig. 6 Optimised geometries obtained for Cp*Rh(CO) moiety with alkane {alkane = cyclopentane (CyP); neopentane (NeP) and cyclohexane CyH)} showing the alkane (σ -Cp*-alkane) and alkyl hydide (product-Cp*-alkane) together with the transition state between these (TS-Cp*-alkane).

described in the introduction for linear alkanes, where hopping along the chain to reach the activation site at the primary C–H slows the reaction, exchange among C–H, *i.e.* hopping between CH_2 groups, is redundant and does not affect the rate of C–H activation.

The binding enthalpy is stronger for CpRh(CO)(alkane) than for Cp*Rh(CO)(alkane) complexes and is reflected in the shorter Rh–H and Rh–C contacts for CpRh(CO)(alkane). Although substitution of methyls on the cyclopentadienyl ligand makes it a stronger donor and would therefore make Rh more electronrich, the steric crowding prevents stronger alkane binding in Cp*Rh(CO)(alkane). Such steric crowding is also reflected in the transition states which occur geometrically earlier (at longer Rh– H and Rh–C contacts) for the Cp*Rh(CO)(alkane) complexes. Likewise, in the products the CpRh(CO)(alkyl)H complexes have shorter Rh–C and Rh–H bonds than the corresponding Cp*Rh(CO)(alkyl)H complexes. The difference in the alkane binding in both Cp and Cp* σ -complexes is also reflected in these structures where the cyclopentane has closer contacts to Rh than cyclohexane. Furthermore, the C–H bond is longer in the cyclopentane complexes compared with the corresponding cyclohexane complexes and the C–H reactions for cyclohexane have a TS with longer C–H relative to the cyclopentane counterparts, consistent with the higher energy barrier obtained from both the experimental and theoretical investigations.

For the same reaction, the differences in free-energy barriers obtained from these four density functionals vary by up to 10 kcal mol⁻¹, Fig. 7. Although none of the functionals will reproduce the measured lifetimes of cyclic alkanes perfectly, they all give correct trends for the free-energy barriers for each of the two



Fig. 7 Concentration corrected C–H activation free-energy barriers relative to reactants (kcal mol^{-1}) obtained from four density functionals. Experimental lifetimes are shown as ns. CyP = cyclopentane, CyH = cyclohexane, NeP = neopentane.

reactions CpRh(CO) + alkane and Cp*Rh(CO) + alkane. Thus, all functionals show an increase in the free-energy barrier for the Cp system for the series CyP:CyH:NeP and for the Cp* system for the pair CyP:CyH. However, only BMK places the relative free energy of the Cp* system correctly with respect to the Cp system. Both TPSS and B3LYP place the Cp* barriers too high, perhaps because they describe poorly the van der Waals interaction and are too repulsive for the more crowded Cp* case, while the ω B97XD appears to have a van der Waals correction that is too attractive ('D' indicates that this functional has an empirical dispersion correction added).

In transition state theory, the rate constant is expressed as:

$$k = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G^{2}}{RT}}$$

where κ is the transmission coefficient, ΔG^{\ddagger} is the Gibbs free energy of activation, k_B is Boltzmann's constant, h is Planck's constant, and T is the temperature in Kelvin. In this expression, $k_B/h=2.08 \times 10^{10} \text{ s}^{-1} \text{ K}^{-1}$ and R = 1.986 cal mol⁻¹ K⁻¹. Based on these values, the free-energy barrier for a lifetime of 4.4 ns, as observed for the reaction of CpRh(CO) with cyclopentane, is 6.05 kcal mol⁻¹, a value close to the free-energy barrier obtained from the BMK calculation.

Finally, we have measured the C–H activation rate of the neo-pentane complex CpRh(CO)(neopentane). The observed rate is lower than those obtained for *n*- and *cyclo*-pentane but is slightly higher than the rate observed for the reaction of Cp*Rh(CO)(cyclohexane). For all functionals used in the calculations we find that the free-energy barrier is high for neopentane compared to cyclopentane. This is also reflected in the weaker binding of neopentane to the Rh centre (see Fig. 5 and 6).

Conclusions

The C–H activation of Cp- and Cp*Rh(CO)(alkane) is a delicate balance of steric and electronic factors and key factors determining the rate are different from Rh(κ^3 -Tp^{3,5-Me})(CO)(R)H where the important step in controlling C–H activation in this system is

partial re-chelation of the Tp ligand to Rh. For the linear alkanes activation of Cp- and Cp*Rh(CO)(alkane) occurs at the primary C-H bonds and the rate is governed by a balance between these activations and hopping along the chain. For cyclic alkanes there is a reduction in the steric hindrance for C-H activation of secondary C-H bonds particularly compared to the longer linear alkanes. The rate of C-H activation is mainly controlled by strength of the alkane binding and the TS is further along the reaction coordinate. The BMK functional appears to yield results more consistent with the experimental values and trends than the other functionals tested. Although the activation of CpRh(CO)(neopentane) is clearly at a primary C-H bond, the rate is much lower because of the highly sterically constrained environment. Clearly there is still much to be learnt about the fundamental details of C-H activation and the combination of fast TRIR spectroscopy and theory are likely to be useful for this purpose.

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