J|A|C|S
COMMUNICATIONS

Insight into Binding of Alkanes to Transition Metals from NMR Spectroscopy of Isomeric Pentane and Isotopically Labeled Alkane Complexes

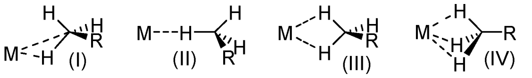
Douglas J. Lawes, Spili Geftakis, and Graham E. Ball*

NMR Facility and School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia

Received September 23, 2004; E-mail: g.ball@unsw.edu.au

It is now well established that, in alkane solvent, photodissociation of a ligand from many transition metal complexes leads to the generation of a complex containing a weakly bound alkane ligand.[1,2] In this work, we have directly observed and clearly differentiated three complexes of pentane binding via the three different types of hydrogen present in the pentane molecule using NMR spectroscopy. Binding site preferences have been determined. This work builds on extensive IR studies by George and coworkers[3,4] and our previous observations.[5,6]

Potential modes of interaction of CH_3 groups with a metal include η^2-C,H (I − *asymmetric* interaction mostly with just one C−H bond), η^1-H (II), η^2-H,H (III − *symmetric* equal interaction with two hydrogens), and η^3-H,H,H (IV) as shown below:



There are two X-ray studies of simple alkanes interacting significantly with transition or lanthanide metals in the solid state. In a recent study, several alkanes were found to interact with a uranium(III)−hexadentate macrocyclic ligand complex and an η^2-C,H binding mode was proposed, although the hydrogens were not directly located.[7] In the second example, *n*-heptane interacts with an iron(II)−double A-frame porphyrin complex. Positional disorder complicated direct crystallographic analysis, and an asymmetric mode of binding between modes I and III was calculated.[8] Notably, neither of these types of complexes retain their alkane ligands long enough in solution for them to have been characterized using routine NMR experiments, and the interaction of the alkane with co-ligands may be responsible for significantly stabilizing these complexes in the solid state.

Since the observation of $Cr(CO)_5(C_6H_{12})$ following laser flash photolysis of $Cr(CO)_6$ in cyclohexane,[9] numerous other alkane complexes have been observed in solution, primarily using "fast" techniques, such as time-resolved infrared (TRIR) spectroscopy. Often, they have been detected as intermediates in the extremely important C−H activation process prior to formation of the alkyl hydride product.[10,11] Classic examples in this category include $CpRh(CO)(C_6H_{12})$[12] and Tp*Rh(CO)(alkane)-type species (Tp* = tris(3,5-dimethylpyrazolyl)borate).[13]

Indirect evidence has been found that alkyl hydride complexes, such as $\{(1,4,7\text{-triazacyclononane})Rh(hexyl)H[P(OMe)_3]\}^+$ and [Tp*Rh(CNR)(*i*-Pr)H] (R = neopentyl), may convert to transient alkane complexes in which the Rh center may bind to each of the methylene and methyl sites of the corresponding propane or longer alkane and switch between these sites.[14−16] Significantly, these complexes are typical in their preference for C−H activation occurring at primary carbons; most complexes that activate linear alkanes selectively activate the C−H bonds of CH_3 groups in preference to CH_2 groups.[10] Oxidative cleavage to form alkyl hydrides does not occur readily in $CpRe(CO)_2$(alkane) complexes.

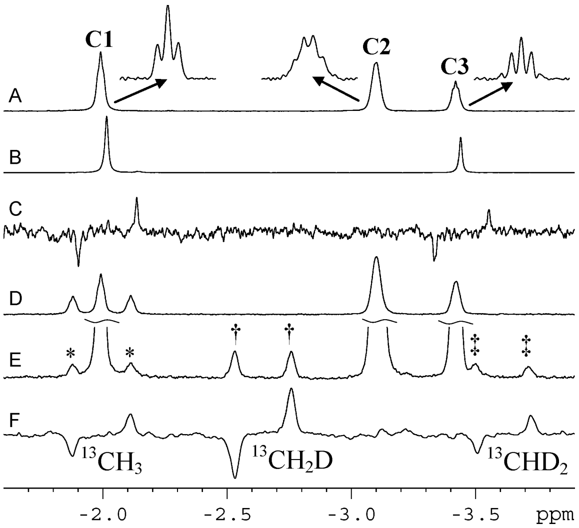
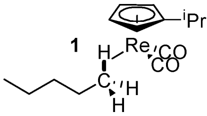


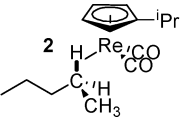
Figure 1. The 500 MHz ^1H NMR spectra of products obtained from the photolysis of (*i*-PrCp)$Re(CO)_3$ (ca. 3 mM) at 163 K in various pentane isotopomers. With 5% pentane-d_{12} present in A and D. See text for details.

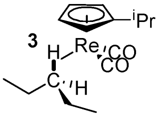
Figure 1 shows the region of the ^1H NMR spectrum that includes the resonances of protons in alkane complexes, formed after photolysis of (*i*-PrCp)$Re(CO)_3$ (*i*-PrCp = η^5-(isopropyl)cyclopentadienyl), that are directly bound to the metal center. The photolysis was conducted on precooled samples in the probe of a 500 MHz NMR spectrometer, as described previously.[5] The spectra were obtained using an excitation sculpting scheme to suppress the resonances of the free alkane.[17] The scheme effectively excites the region containing the resonances shown in Figure 1 and those of the Cp rings (not shown) relatively uniformly and avoids excitation of the window between δ 0.6 and 1.6 containing the free solvent. Spectrum A and resolution-enhanced expansions (arrowed) show the result of photolysis in natural abundance *n*-pentane. The visible resonances are assigned to the three possible pentane complexes, wherein the metal is bound to C1, C2, or C3, namely, (*i*-PrCp)$Re(CO)_2$(1-pentane) (**1**) at δ −1.99 (t, $^3J_{H1H2} = 6.4$ Hz), (*i*-PrCp)$Re(CO)_2$(2-pentane) (**2**) at δ −3.10 (m, $J \approx 6$ Hz), and (*i*-PrCp)$Re(CO)_2$(3-pentane) (**3**) at δ −3.42 (quintet, $^3J_{H3H2} = 6.0$ Hz), respectively. Integration of the resonances due to **1**, **2**, and **3** showed relative intensities of 6:6.07(±0.21):2.90(±0.11), compared with a statistical ratio of 6:4:2.[18] This slight favoring for binding of CH_2 sites over CH_3 in this mixture corresponds to a thermodynamic preference of 0.13 ± 0.02 kcal mol^{-1}. That this is an equilibrium mixture is confirmed by performing ROESY NMR experiments[17] that show the isomers **1**, **2**, and **3** are slowly interconverting intramolecularly ($\sim$1−10 s^{-1}) at 173 K.[19] The favoring of binding to CH_2 sites is in marked contrast to the observation that C−H activation occurs preferentially at the terminal carbon of linear alkanes in most systems that activate C−H bonds[10] and supports the idea that activation at the methyl carbon occurs

10.1021/ja044208m CCC: $30.25

due to other factors rather than a preference for the intermediate alkane complex. It may also confirm why activation of ethane has been found to be more rapid than for higher alkanes[15,20] since ethane contains only CH_3 groups. Binding to methylenes of higher alkanes requires a rearrangement process to occur to give the methyl-bound isomer prior to C−H activation, reducing the rate.


1


2


3

The resonances in spectrum A show the same multiplicity and similar $^3J_{HH}$ values to those in free pentane, indicative of alkane complexes. That the bound CH_2 resonances of **2** and **3** are shifted to significantly lower frequency than the bound CH_3 of **1** suggests that just one hydrogen in each of these groups interacts with the metal at one instant, and that these are time-averaged shifts. Hence, each of the CH_2 hydrogens interacts directly for 50% of the time and each of the CH_3 hydrogens for 33% of the time. Spectra of complexes containing the Cp ligand[17] are almost identical to those containing the more soluble, hence, preferable, *i*-PrCp ligand. No evidence of an agostic interaction involving the *i*-Pr group is seen.

Spectrum B shows the same experiment conducted using pentane-2,2,4,4-d_4. The resonance at δ −3.10 due to **2** is now absent due to deuteration, confirming its assignment. The remaining resonances due to *i*-PrCpRe$(CO)_2$(1-pentane-2,2,4,4-d_4) and *i*-PrCpRe$(CO)_2$(3-pentane-2,2,4,4-d_4) are now broad singlets, confirming that the protons on C2 were the source of the couplings for these resonances in spectrum A. Spectrum C is acquired on the same sample as B, and only ^{13}C satellites were selected in this experiment.[17] Large $^1J_{CH}$ values, diagnostic for alkane complexes ($^1J_{CH} = 109 \pm 3$ Hz for **3**), are seen. Spectrum D shows the result of employing pentane-1-^{13}C as solvent. Fifty percent of the bound methyl groups are ^{13}C labeled and show the $^1J_{CH}$ splitting. The observed $^1J_{CH} = 116.5 \pm 0.5$ Hz is only slightly reduced from that in free pentane (124.7 Hz). Again, this coupling is an averaged value, consistent with one of the three C−H bonds having a reduced $^1J_{CH}$, averaged with two typical $^1J_{CH}$ values. The ^{13}C NMR shift of the bound carbon of **1** (δ −42.4) is highly shielded, suggesting a significant metal−carbon interaction. Spectra E and F (same sample; only ^{13}C isotopomers are selected in F[17]) show the result of using a mixture of ^{13}C and ^2H doubly labeled isotopomers, namely, pentane-1-^{13}C, pentane-1-^{13}C,1-d_1, and pentane-1-^{13}C,1,1-d_2. This sample contains three types of ^{13}C-labeled bound methyl groups, $^{13}CH_3$, $^{13}CH_2D$, and $^{13}CHD_2$, allowing evaluation of deuterium isotope effects on ^1H and ^{13}C chemical shifts and *J*-couplings. A large isotopic perturbation of resonance (IPR)[21−23] is observed for the ^1H shifts in these three isotopomers of **1**, with δ −1.99, −2.64, and −3.62 being observed for zero (**1-^{13}C**), one (**1-^{13}C,d_1**), or two (**1-^{13}C,d_2**) deuteriums incorporated, respectively. A correspondingly large IPR is observed in CpRe$(CO)_2$(cyclopentane-*cis*-1,2-d_2) with δ −4.09 for bound CHD groups versus δ −2.32 for bound CH_2 groups.[17] These effects are consistent with a rapid exchange of the hydrogen within a methyl or methylene unit that is interacting with the metal center and a shifting of equilibria when deuterium is incorporated in favor of isotopomers in which a C−H is bound to the metal center rather than C−D. We calculate[17,23] δ(bound) −8.22, δ(unbound) 1.12, and an equilibrium constant, $K_{(C-H_{bound}/C-D_{bound})} = 2.02 \pm 0.06$, for one of each type of bond in **2** and **3** and estimate $K = 2.6$ for a CHD group in cyclopentane complexes. This leads to a preference of C−H over C−D bonds by 0.23 ± 0.03 kcal mol^{-1} in 1-pentane complexes. Preferential binding of the C−H bonds leads to a parallel reduction in $^1J_{CH}$ in the deuterated bound methyl groups, with $^1J_{CH}$ values being 116.5 ± 0.5, 113.2 ± 1.0, and 108.5 ± 2.5 Hz for **1-^{13}C**, **1-^{13}C,d_1**, and **1-^{13}C,d_2**, respectively. Using the value of $K = 2.02$, a model in which the bound C−H has $^1J_{CH} = 85$ Hz and the unbound C−H bonds have $^1J_{CH} = 132$ Hz fits the data.

The IPR data indicate an *asymmetric* interaction. Combined with the shielded ^{13}C shift data, this suggests an η^2-C,H interaction (type I). This binding model is also supported by theoretical calculation. Ab initio calculations on the ethane derivative, CpRe$(CO)_2(CH_3CH_3)$, show that one C−H bond is coordinated and elongated to 1.17 Å.[24,25] Calculations have also predicted 2-propane complexes to be more stable than 1-propane complexes in the case of W$(CO)_5$(propane).[26]

In conclusion, the CpRe$(CO)_2$ fragment binds to all three types of C−H bonds in pentane with a slight preference for those in CH_2 units. Binding to rhenium occurs primarily through one C−H bond at any one instant, and this bond exchanges rapidly with the other bonds in the CH_2 or CH_3 unit that is attached to the Re center.

Acknowledgment. We thank Dr. G. Edwards, Professor B. Hibbert, A/Professor R. Read, and Dr. N. Roberts for helpful discussions, and the Australian Research Council for funding.

Supporting Information Available: General Experimental. Preparation of labeled alkanes. NMR experimental. NMR spectra: ^1H NMR of CpRe$(CO)_2$(pentane) and CpRe$(CO)_2$(pentane-2,2,4,4-d_4) at 163−193 K; ^1H NMR of CpRe$(CO)_2$(cyclopentane-*cis*-1,2-d_2); HSQC of **1-^{13}C-d_{0-2}**; exchange (ROESY) spectrum of a mixture of **1**, **2**, and **3** at 173 K. Calculation of $K_{(C-H_{bound}/C-D_{bound})}$ for isotopomers of **1**. Method for accurate extraction of integrals in ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.
(2) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.
(3) Sun, X.-Z.; Grills, D. C.; Nikiforov, S. M.; Poliakoff, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521.
(4) Childs, G. I.; Grills, D. C.; Sun, X. Z.; George, M. W. *Pure Appl. Chem.* **2001**, *73*, 443.
(5) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.
(6) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1999**, *121*, 6336.
(7) Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 15734.
(8) Evans, D. R.; Drovetskaya, T.; Bau, R.; Reed, C. A.; Boyd, P. D. W. *J. Am. Chem. Soc.* **1997**, *119*, 3633.
(9) Kelly, J. M.; Hermann, H.; Koerner Von Gustore, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105.
(10) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.
(11) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437.
(12) Bengali, A. A.; Arndtsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995**, *67*, 281.
(13) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260.
(14) Flood, T. C.; Janak, K. E.; Iimura, M.; Zhen, H. *J. Am. Chem. Soc.* **2000**, *122*, 6783.
(15) Northcutt, T. O.; Wick, D. D.; Vetter, A. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 7257.
(16) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140.
(17) Details are given in the Supporting Information.
(18) Integration values were corrected for minor site-dependent excitation effects; see Supporting Information. Errors are 95% confidence limits.
(19) Accurate quantitative, mechanistic studies are currently underway.
(20) McNamara, B. K.; Yeston, J. S.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1999**, *121*, 6437.
(21) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558.
(22) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.
(23) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.
(24) Yang, H.; Asplund, M. C.; Kotz, K. T.; Wilkens, M. J.; Frei, H.; Harris, C. B. *J. Am. Chem. Soc.* **1998**, *120*, 10154.
(25) DFT calculations on the cyclopentane and pentane analogues also support this view, and calculations on the methane analogue show that the barrier to exchange of coordinated hydrogen on the same carbon is predicted to be less than 2 kcal mol^{-1}. Dance, I. G.; Harris, H.; Ball, G. E. Manuscript in preparation. See also: Bergman, R. G.; Cundari, T. R.; Gillespie, A. M.; Gunnoe, T. B.; Harman, W. D.; Klinckman, T. R.; Temple, M. D.; White, D. P. *Organometallics* **2003**, *22*, 2331.
(26) Zaric, S.; Hall, M. B. *J. Phys. Chem. A* **1997**, *101*, 4646.

JA044208M