Alkane Ligands

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A Rhenium–Cyclohexane Complex with Preferential Binding of Axial C–H Bonds: A Probe into the Relative Ability of C–H, C–D, and C–C Bonds as Hyperconjugative Electron Donors?**

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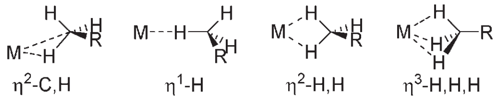
Dedicated to Professor Gernot Frenking
on the occasion of his 60th birthday

Formation of alkane σ complexes with agostic-like interactions is widely accepted as being a prerequisite for C–H activation by transition-metal centers and has therefore received considerable attention by experimental and theoretical chemists.[1–3] One important aspect of σ-complex or agostic interactions is their specificity. Do, for instance, such interactions prefer η^2-C,H, η^1-H, η^2-H,H, or η^3-H,H,H binding (Scheme 1)[1b] and can this preference be influenced by electronic differences between the hydrogen atoms?

We now describe experimental (NMR) and theoretical investigations of an alkane complex, [CpRe(CO)$_2$-(cyclohexane)] (**1**), in which competition exists between axial and equatorial C–H bonds for binding to the metal



Scheme 1. Possible binding modes for σ-complex or agostic interactions.

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center. Given the role of alkane complexes as intermediates in the C–H activation reaction, knowledge of the selectivity of alkane coordination sites may prove relevant to directing the site selectivity of C–H activation products. Complex **1** allows the order of relative hyperconjugative donor strengths of bonds, C–H > C–D > C–C, to be probed experimentally. Our experiments and calculations suggest that the interaction of the alkane with the metal is primarily with one hydrogen atom of the methylene unit and that the axially complexed isomer is preferred.

Some of us have previously reported the direct NMR observation of an alkane complex in solution, $[\mathrm{CpRe(CO)_2(cyclopentane)}]$.[3a,b] This complex was generated through exposure of a photolabile rhenium precursor, $[\mathrm{CpRe(CO)_3}]$, dissolved in cyclopentane to UV/visible light at 180 K [Eq. (1)]. A resonance is observed at $\delta = -2.32$ ppm and

$$[\mathrm{CpRe(CO)_3}] \xrightarrow[\text{cyclopentane, }-\mathrm{CO}]{h\nu,\ 180\ \mathrm{K}} [\mathrm{CpRe(CO)_2(cyclopentane)}] \qquad (1)$$

assigned to the protons of the bound methylene unit. The fact that a single resonance is observed, coupled with a highly shielded ^{13}C resonance and a large equilibrium isotope shift accompanying deuterium incorporation,[3c] suggests a fast exchange between two equivalent complexes in which one of the C–H bonds in this methylene unit is complexed with the metal center. A rapid, mutual exchange between two alternative η^2-C,H structures renders the two protons equivalent, and the net result is that each proton is directly complexed with the metal center half of the time.

More recently, we have demonstrated that three isomeric pentane complexes, $[\mathrm{CpRe(CO)_2(pentane\text{-}\eta^2\text{-}}C^x,H^x)]$, ($x = 1$–3) are observable in which the pentane ligand may bind using either of the methylene or the methyl moieties.[3c] Using partially deuterated, bound methyl groups in $[\mathrm{CpRe(CO)_2(pentane\text{-}\eta^2\text{-}}C^1,H^1)]$, it was demonstrated that: 1) one hydrogen (deuterium) atom is directly complexed with the metal center at any given instant and there is a rapid exchange of which hydrogen (deuterium) atom is engaged in this direct interaction; 2) binding of hydrogen is preferred over that of deuterium ($K_{\mathrm{H/D}} = 2.02$); 3) the observed shielding in the ^{1}H NMR spectrum is directly related to the fraction of time a hydrogen atom spends directly complexed with the metal center. Similarly, the ^1J(C,H) value decreases as the fraction of time that a hydrogen atom spends directly complexed with the metal center increases.

We have now extended our studies to the binding of cyclohexane, since, at the temperatures used, it exists in a chair form and the exchange between the chair forms is slow.[4] Hence, axial and equatorial protons with discrete NMR shifts are present and it is possible to observe an alkane complex that exhibits preferential complexation of one hydrogen atom within a $\mathrm{CH_2}$ unit. The discrete shifts for axial and equatorial hydrogen atoms will be retained in a complex-bound cyclohexane even if, as expected, there is rapid exchange between the two isomeric structures.

When photolysis experiments similar to those described previously[2,3] [see Eq. (1)] are carried out at 173 K in the presence of cyclohexane, two new signals of similar intensity are observed in the ^{1}H NMR spectrum at $\delta = -6.17$ and 0.49 ppm (Figure 1a). These resonances are due to the formation of $[\mathrm{CpRe(CO)_2(cyclohexane)}]$ (**1**). The experiment was performed using either 60:40 $[\mathrm{D_{12}}]$pentane/cyclohexane or 8:82:10 $[\mathrm{D_{12}}]$pentane/isobutene/cyclohexane to allow very low temperatures to be used with the otherwise high-melting cyclohexane. Any bound $[\mathrm{D_{12}}]$pentane (formation of $[\mathrm{CpRe(CO)_2([D_{12}]pentane)}]$) is not observed in the ^{1}H NMR spectra as it is fully deuterated. When isobutane is also present as solvent, a resonance due to formation of the isobutane complex $[\mathrm{CpRe(CO)_2(isobutane\text{-}\eta^2\text{-}}C^1,H^1)]$ ($\delta = -2.13$ ppm (d, ^3J(H,H) = 6 Hz)) is also seen.

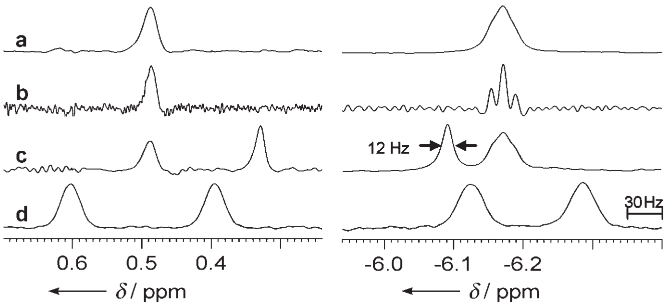


Figure 1. Signals due to the protons of a bound methylene unit in a, b) $[\mathrm{CpRe(CO)_2(cyclohexane)}]$ (**1**), c) a mixture of **1** and $[\mathrm{CpRe(CO)_2([2,2,3,3,5,5,6,6\text{-}D_8]cyclohexane\text{-}\eta^2\text{-}}C^1,H^1)]$ ($[\mathrm{D_8}]$-**1**), and d) $[\mathrm{CpRe(CO)_2([^{13}C_6]cyclohexane)}]$ ($[^{13}\mathrm{C_6}]$-**1**) in their ^{1}H NMR spectra at 173 K.[5] The spectra in (a), (c), and (d) have line broadening of 5 Hz and the spectrum in (b) is resolution-enhanced with Gaussian multiplication. All spectra shown were obtained for 8:82:10 $[\mathrm{D_{12}}]$pentane/isobutene/cyclohexane solvent mixtures.

Repeating the experiment using uniformly ^{13}C-labeled cyclohexane (Figure 1d) confirms this molecule to be an alkane complex, with large ^1J(C,H) coupling constants of (96.5 ± 0.5) and (125.0 ± 0.5) Hz for the resonances at $\delta = -6.17$ and 0.49 ppm, respectively. The latter is close to the ^1J(C,H) coupling constants found in free cyclohexane at this temperature (≈ 128 Hz). A ^{1}H-^{13}C HSQC experiment confirms that both protons are attached to the same carbon atom with a shielded shift ($\delta = -22.4$ ppm) characteristic of a bound alkane. We attribute the two ^{1}H NMR resonances to the axial and equatorial protons, respectively, of a bound methylene unit. The axial hydrogen atom would be anticipated to show a large coupling ($J > 8$ Hz) to three other hydrogen nuclei (geminal, 2 × *trans*), whereas the equatorial hydrogen atom is expected to have only one large coupling (geminal). After resolution enhancement (Figure 1b), a triplet structure is evident for the signal at $\delta = -6.17$ ppm, indicating *two* large coupling constants of (9.8 ± 0.5) Hz. No large coupling constants were resolved for the signal at $\delta = 0.49$ ppm. This suggests that the geminal ^2J(H,H) splitting is unexpectedly small.

In order to confirm assignment of these resonances, $[1,1,2,2,4,4,5,5\text{-}\mathrm{D_8}]$cyclohexane was prepared.[6] When this $[\mathrm{D_8}]$cyclohexane was used as alkane ligand under the same conditions, signals were observed at $\delta = -6.09$ and 0.33 ppm, the former having a line width of about 7 Hz (Figure 1c) due to $[\mathrm{CpRe(CO)_2([2,2,3,3,5,5,6,6\text{-}D_8]cyclohexane\text{-}\eta^2\text{-}}C^1,H^1)]$

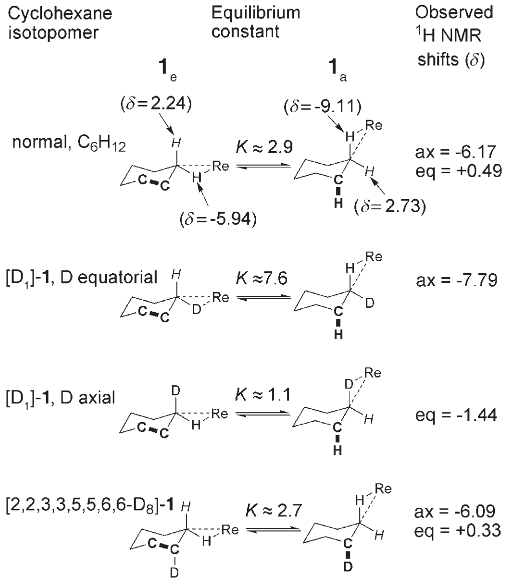
([D$_8$]-**1**). As all vicinal H,H couplings have been removed through deuteration, this confirms that the geminal H,H coupling constant is small (<6 Hz) and that the signal at $\delta = -6.09$ ppm corresponds to a bound axial hydrogen atom. This geminal coupling is weak, possibly because this formally two-bond (H–C–H) coupling now contains a three-bond component (H···Re···C–H) of opposite sign to the two-bond component, and our calculations indicate an increase of the H-C-H angle to 118.5° (MP2, most stable conformation), both of which would reduce the coupling strength.[7] The calculated value for this geminal ^2J(H,H) coupling in the most stable conformation is <5 Hz (Table 1), and the value for the *trans* diaxial ^3J(H,H) coupling between the bound axial proton and vicinal axial protons is calculated to be in the range 7.9–10.6 Hz, consistent with our experimental observation.[8]

Table 1: NMR parameters of **1** obtained from calculations[a] and from experiments.

Isomer	δ(H$_a$) [ppm]/ ^1J(C,H) [Hz]	δ(H$_e$) [ppm]/ ^1J(C,H) [Hz]	^2J(H,H) [Hz]	$K_{\mathbf{1}_a/\mathbf{1}_e}$[b]
$\mathbf{1}_a$	−9.74/101.3	+2.33/156.4	−4.73	2.4
$\mathbf{1}_e$	+2.38/156.6	−9.78/103.4	−4.65	5.6
experimental values	−6.17/96.5	+0.49/125	<6	2.4–3.4

[a] In each case, the values shown are calculated using the lowest-energy conformation as predicted by the MP2 calculations. Calculations were performed using B3LYP-GIAO on the HCTH-optimized geometries and the default SCRF-PCM treatment in cyclohexane solvent.[8] [b] The equilibrium constant calculated is the value required to give the observed δ at 173 K assuming that the calculated δ values are correct.

The observed chemical shift of both the axial and equatorial protons is the result of an equilibrium between two isomeric complexes, $\mathbf{1}_a$ and $\mathbf{1}_e$ which have the axial and the equatorial hydrogen atom, respectively, directly complexed with the metal center (Scheme 2). Interconversion of $\mathbf{1}_a$ and $\mathbf{1}_e$ is fast on the NMR timescale at the temperatures employed. This is confirmed by variable-temperature NMR experiments on **1**. Decreasing the temperature results in a significant increase in the separation of the axial and equatorial shifts, indicative of an increasing equilibrium constant at lower temperatures. The separation of the two shifts increases from 6.65 ppm at 173 K to 6.91 ppm at 145 K. The amount of shielding can be used to estimate the proportion of time that each type of C–H bond is complexed with the rhenium center. Likewise, the reduction of the C–H coupling gives an independent measure of the same parameters. Given that the axial proton is highly shielded, by about 7.4 ppm compared to free cyclohexane, and ^1J(C,H) is greatly reduced (96.5 Hz compared to 128 Hz in free cyclohexane), while the shielding (by ≈ 1.2 ppm) and reduction in coupling (^1J(C,H) = 125 Hz) is much smaller for the equatorial proton, it is clear that binding of the axial proton is significantly preferred in this system.



Scheme 2. Equilibria between axially and equatorially complexed species for various isotopomers with midrange-fitted empirical equilibrium constants. All equilibria are in fast exchange on the NMR timescale at the temperatures employed resulting in only weighted-averaged shifts being observed. In each case one of the two (equivalent) bonds antiperiplanar to the complexed bond is shown in bold. Chemical shifts in brackets are estimated values based on empirical data for each proton that would be observed if no exchange were occurring.

It is not possible to extract a precise equilibrium constant, $K_{\mathbf{1}_a/\mathbf{1}_e}$, for this case of axially vs. equatorially complexed as only the weighted-averaged chemical shifts and ^1J(C,H) values are observed and the values of these parameters for the axial and equatorial protons in the two isomers are not known. However, further measurements such as equilibrium isotope effect (isotopic perturbation of resonance) experiments on [CpRe(CO)$_2$([1-D$_1$]cyclohexane-η^2-C^1,H^1)] ([D$_1$]-**1**) aid the prediction of the chemical shifts and coupling constants of both the complexed and uncomplexed hydrogen atoms in the two isomers of the complex. Combined with knowledge of the pentane system, sensible estimates for the equilibrium constants and NMR parameters can be extracted. In the case of the bound methyl group of [CpRe(CO)$_2$(pentane-η^2-C^1,H^1)], an analytical solution was possible: the directly complexed hydrogen atom has a shielded shift of $\delta = -8.22$ ppm and the uncomplexed hydrogen atoms within the same methyl group a shift of $\delta = 1.12$ ppm, slightly deshielded (by ≈ 0.20 ppm) compared to a free methyl group. By making assumptions about the chemical-shift change upon binding of the more remote proton in a bound methylene group (i.e., the hydrogen atoms shown in italics in Scheme 2) it is possible to extract values for the equilibrium constants $K_{\mathbf{1}_a/\mathbf{1}_e}$ and $K_{H/D}$.

We have chosen to make assumptions about the chemical shift of this type of proton as it is likely to be less affected by different binding situations than the strongly complexed proton. Using a range of values for the change in chemical shift for this uncomplexed proton that vary from 0 to +2.5 ppm, a range that brackets the observed value for pentane (deshielded by 0.20 ppm) and the larger deshielding predicted by calculations (up to 1.24 ppm), a range of values for $K_{\mathbf{1}_a/\mathbf{1}_e} = 3.4$–$2.4$ and $K_{H/D} = 4.7$–1.9, respectively, is obtained.[9] Using a value for this deshielding of 1 ppm relative to free cyclohexane leads to the midrange values shown in Scheme 2, $K_{\mathbf{1}_a/\mathbf{1}_e} = 2.9$ and $K_{H/D} = 2.6$. Note that in general, there is no reason to assume that the $K_{H/D}$ value will be the same for cyclohexane as for pentane, or indeed that the same value applies to axial and equatorial sites.

Ab initio and DFT calculations[8] on **1** give structures in which the alkane is complexed through one hydrogen atom at any time. The PW91 and HCTH DFT calculations prefer the more stable axially complexed isomer $\mathbf{1}_a$ by 1.3 and 0.4 $kJ\,mol^{-1}$, respectively, and ab initio MP2 calculations prefer it by 4.2 $kJ\,mol^{-1}$ relative to the equatorially complexed isomer $\mathbf{1}_e$; in comparison a value of 1.5 $kJ\,mol^{-1}$ is estimated from the empirical data. In contrast, the B3LYP hybrid density functional prefers $\mathbf{1}_e$ by 1.2 $kJ\,mol^{-1}$. As seen in calculated structures of smaller alkanes,[10] the Re-H-C angle for the complexed C–H moiety is large: the lowest-energy conformations of $\mathbf{1}_a$ and $\mathbf{1}_e$ have values of 114.4° and 112.6°, respectively (MP2), although these values can be as large as 128° in the other conformations.

The barrier to exchange between the two isomers is calculated to be 10.0 and 14.6 $kJ\,mol^{-1}$ at the HCTH and MP2 levels, respectively. This energy barrier is sufficiently low for the two isomers to remain in fast exchange on the NMR timescale even at the lowest temperatures employed in this study, consistent with our observations. The calculated barriers for 1,2-(axial-equatorial) and 1,3-(axial-axial) hydrogen shifts are 21 and 29 $kJ\,mol^{-1}$, respectively, at HCTH and 52 and 13 $kJ\,mol^{-1}$, respectively, at MP2. Experimental data indicate that these 1,2 and 1,3 shifts are not occurring rapidly on the NMR timescale and that these barriers are underestimated. The calculated binding energies at the different levels vary widely but in the expected fashion. PW91 and MP2 apparently overestimate the binding, whereas B3LYP and HCTH agree moderately well. Given the disagreement between B3LYP and the other methods as to the relative stabilities of the isomers, the HCTH binding energies are probably most reliable.

In agreement with experiment, calculations predict very different NMR parameters (δ and J) for the complexed and uncomplexed hydrogen atoms within the bound methylene group (Table 1).

Our empirical data suggest that the calculated shifts of the complexed hydrogen atoms are slightly more extreme than the experimental ones, but the basic principle is well demonstrated. The ^1J(C,H) values are clearly overestimated as they cannot give a weighted average of 96.5 Hz as was observed in the case of the axial C–H coupling. However, they do predict the reduction of ^1J(C,H) upon complexation and an increase of it for the uncomplexed hydrogen atom compared to the free alkane. This behavior was observed empirically in the case of $[CpRe(CO)_2(\text{pentane-}\eta^2\text{-}C^1,H^1)]$ (^1J(C,H) of the complexed H: 85 Hz; of the uncomplexed: 132 Hz).

The expected mode of complexation of cyclohexane to the rhenium center, confirmed by our calculations, is shown in Scheme 2, with the metal center positioned between the axial and equatorial C–H bonds.[1] Steric interactions with the cyclohexane ligand would be expected to disfavor any other options. From this, it is not apparent that a steric argument could account for the selective formation of the complex of an axial C–H bond of cyclohexane. At best, complexation of the axial and equatorial C–H bonds would be the same, although long-range steric interactions with the ring would favor the equatorially complexed isomer. This is supported by the crystal structure of a complex of uranium with a very bulky hexadentate ligand with the equatorial C–H bond of methylcyclohexane being complexed,[11] though it is noted that this is in the solid state rather than in solution as observed here and stabilizing interactions between the cyclohexane ring and the co-ligand may be significant. Below, we propose an electronic argument to explain the observed preference for binding.

In 1981, Cieplak proposed a radical argument to account for the selectivity observed in nucleophilic additions to cyclohexanones.[12a] The Cieplak model relies on the assumption that a C–H bond is a better electron donor than a C–C bond when both are available for hyperconjugation, for example, when they have an antiperiplanar relationship to an electron-depleted bond. This assumption sparked some controversy and has stimulated many groups to examine its validity.[12–17] The earliest experimental evidence supporting Cieplak's hypothesis used the ^{19}F NMR chemical shifts of bicycloalkyl fluorides as probes to the extent of delocalization of electrons from C–X bonds into the σ* orbital of the C–F bond.[13a,b] This indicated that alkyl groups are electron-withdrawing when compared to hydrogen. Subsequent experimental studies, including those examining the hydrochlorination and fluorination of 5-substituted adamant-2-ols,[13e] the reduction of 5-substituted adamantan-2-ones,[14a,b] and the conformations of α,β-unsaturated esters and aldehydes,[15a] further support this model.

While these experimental results indicate that C–H bonds are better hyperconjugative donors than C–C bonds, the magnitude of this difference has not been derived experimentally. Computational studies of 2-substituted 1-fluoroethanes[18a] and 2,5-dimethyl-2-adamantyl cations[18b] report the difference as about 4 and 1.6 $kJ\,mol^{-1}$, respectively.

The preference for axial coordination in **1** is an electronic, not a vibrational effect. The slightly weaker axial C–H bonds are better donors than their equatorial counterparts. There is a stereoelectronic preference for conformations in which the best donor lone pair or bond is antiperiplanar to the best acceptor bond.[19] A C–H bond complexed with a rhenium center is more electron-deficient than a regular C–H bond (as there is insignificant electron back donation from the metal center[20]) and thus is a better electron acceptor. Since axial C–H bonds in chair conformations of cyclohexanes are antiperiplanar to some of the other C–H bonds, while the equatorial C–H bonds are antiperiplanar to certain C–C bonds (Scheme 2), the selectivity described in this paper suggests that a C–H bond is a better hyperconjugative donor than a C–C bond. Taking into account that two such effects are operating in each case, this corresponds to an energy difference of about 0.75 $kJ\,mol^{-1}$, which is in reasonable agreement with the computed differences, given the small magnitude of the effect.[8]

It is worth noting that preferential reaction of equatorial C–H bonds has been found in the monooxygenation of methylene C–H bonds in substituted cyclohexanes.[21] This was explained qualitatively using long-range hyperconjugative stabilization, though this difference could not be quantified.

The equilibrium constant $K_{\mathbf{1}_a/\mathbf{1}_e}$ is reduced somewhat by the introduction of deuterium into vicinal sites (using [D$_8$]cyclohexane). Assuming that the "normal" deuterium isotope shifts are similar for axial and equatorial protons, which is the case in free cyclohexane, it is apparent (Figure 1c) that the shifts of the two protons are closer together in this isotopomer and that the equilibrium constant is therefore reduced (from ≈ 2.9 to ≈ 2.7). Ascribing this effect entirely to the replacement of two *trans*-diaxial C–H bonds by two C–D bonds leads to a reduction in energy of about 46 J mol^{-1} per bond. This is consistent with the fact that the stronger C–D bond is less likely to donate its electrons. This observation adds further weight to the hypothesis that the observed phenomenon is indeed caused by an electronic effect since the steric effect of replacing hydrogen with deuterium in vicinal sites is expected to be negligible.

Qualitative MO arguments also suggest that the axial hydrogen atoms are better electron donors than the equatorial ones. The degenerate HOMOs of cyclohexane are delocalized over the C–C and equatorial C–H bonds. However, the contribution on each equatorial hydrogen atom is only 5.6 % (sum of the squared coefficients of the two H basis functions in the Eigenvector). Three occupied combinations of essentially pure axial $\sigma_{\text{C–H}}$ orbitals are only roughly 0.5 eV lower in energy than the HOMO and provide more effective electron donation than the HOMOs.[22] These orbitals reflect exactly the hyperconjugation arguments given above.

In conclusion, we have identified an alkane complex, [CpRe(CO)$_2$(cyclohexane)], in which binding occurs preferentially through the axial C–H bond of a methylene group. The ratio of the complexation of each type of C–H bond in cyclohexane ($K_{\mathbf{1}_a/\mathbf{1}_e} \approx 2.9$) suggests the difference in the electron-donating abilities of C–H, C–C, and even C–D bonds may be determined, assuming that there is no steric preference for either mode of complexation.

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