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Supporting Information

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

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Preparation of labeled cycloalkanes

General experimental

Before use, tetrahydrofuran and tetraglyme were both dried with and then distilled from sodium and benzophenone under an argon atmosphere. Dichloromethane was dried over and distilled from calcium hydride under argon. Liquid alkanes were purified by washing three times with 98% H_2SO_4 then dried over and distilled from liquid Na/K alloy (ratio *ca.* 1:3) in an argon atmosphere. Cyclopentadienylrhenium tricarbonyl was purchased from Strem Chemicals and used without purification.

[$^{13}C_6$]Cyclohexane

[$^{13}C_6$]Benzene (500 mg, 5.95 mmol) and 0.5% rhodium on alumina (4 pellets, *ca*. 200 mg) were placed in a 300 mL Parr high-pressure reactor which had been pre-flushed with argon. The reactor was sealed, pressurized with excess hydrogen gas (*ca*. 120 psi) and stirred overnight at 60-70 °C with a magnetic stirrer. The product was collected in a liquid nitrogen cooled vacuum trap; all subsequent transfers were performed using the vacuum trap-to-trap method. The product was washed by stirring with concentrated sulfuric acid for several days then dried by stirring over liquid sodium potassium alloy (*ca*. 1:3). Yield: 0.52 g (5.8 mmol, 97 %).

[D_8]1,4-cyclohexanedione[1]

1,4-cyclohexanedione (20.0 g, 178 mmol) was dissolved in a solution prepared by the careful addition of phosphorus pentachloride (1.0 g, 4.8 mmol) to deuterium oxide (20 g, 1.0 mol) and stirred for *ca*. one week under argon at 60-65 °C. The partially deuterated product was extracted into dichloromethane (4 x 50 mL) and the combined washings were dried with anhydrous sodium carbonate, filtered and the solvent evaporated. This procedure was repeated four times, until ^{13}C NMR showed greater than 95% conversion to the product. Yield: 12.0 g (99 mmol, 56 %).

[2,2,3,3,5,5,6,6-D_8]1,4-cyclohexanediol

A solution of [D_8]1,4-cyclohexanedione (14.8 g, 123 mmol) in dry tetrahydrofuran (120 mL) was added drop wise to a vigorously stirred suspension of lithium aluminium hydride powder (13.0 g, 343 mmol) in dry tetrahydrofuran (250 mL), under argon. After further addition of tetrahydrofuran (350 mL) to aid mixing, the reaction mixture was heated to reflux and stirred overnight until all yellow starting material had reacted. The mixture was cooled to 0 °C then water (2.5 mL) and 50 % sodium hydroxide solution (39 g) were added drop wise and the mixture refluxed overnight. The mixture was filtered hot and the supernatant evaporated to give a crude oily product, which was re-dissolved in water and washed with hexane. Evaporation of the water gave the first crop of white crystalline product (11.41 g). The filtration solid was suspended in methanol (350 mL), excess carbon dioxide was bubbled through to convert remaining hydroxide to less soluble hydrogen carbonate and the methanol evaporated. The solid was extracted with hot tetrahydrofuran (4 x 100 mL) and the solvent evaporated, giving the second crop of crystalline product (3.30 g). Yield: 14.71 g (118 mmol, 96 %).

[2,2,3,3,5,5,6,6-D_8]1,4-cyclohexanediol di(*para*-toluenesulfonate)

[2,2,3,3,5,5,6,6-D_8]1,4-cyclohexanediol (14.71 g, 118 mmol) was dissolved in dry distilled dichloromethane (500 mL) over argon. To this was added *para*-toluenesulfonyl chloride (56.5 g, 296 mmol) and 4-dimethylaminopyridine (0.724 g, 5.9 mmol), then triethylamine (33.9 mL, 243 mmol) was added drop wise to the stirred reaction mixture at room temperature. The reaction mixture was stirred overnight until all had dissolved, the solution washed with water (100 mL) then stirred with saturated sodium carbonate solution (ca. 200 mL) for four days. The organic layer was separated, the aqueous layer extracted with dichloromethane (2 x 100 mL) and the dichloromethane fractions combined then washed with water (2 x 100 mL). The dichloromethane solution was dried over anhydrous sodium sulfate, filtered and the solvent evaporated to give a light brown waxy solid product. Yield: 20.9 g (48.4 mmol, 41 %).

[1,1,2,2,4,4,5,5-D_8]Cyclohexane[2]

A solution of lithium triethylborohydride in tetrahydrofuran (1.0 M, 200 mL) was added to dry tetraglyme (200 mL) over argon and the tetrahydrofuran removed by vigorous stirring whilst applying high vacuum. A second solution of [2,2,3,3,5,5,6,6-D_8]1,4-cyclohexanediol di(*para*-toluenesulfonate)

(20.9 g, 48.4 mmol) in dry tetraglyme (150 mL) was added drop wise to the first at 0 °C over argon with vigorous stirring. The reaction mixture was warmed to room temperature and stirred overnight. The crude product was collected via a liquid nitrogen vacuum trap, 4-*tert*-butylpyridine (20 mL) was added at –96 °C to form a nonvolatile adduct with triethylborane side product, then the mixture warmed to room temperature and stirred overnight. The product was collected using the vacuum trap-to-trap method, washed with concentrated sulfuric acid portions (0.5 mL) until the acid remained colorless, washed with water (4 x 0.5 mL) then dried with anhydrous sodium sulfate. Yield: 1.10 g (11.9 mmol, 26 %).

[D_1]Cyclohexane

A solution of cyclohexylmagnesium chloride in ether (2.0 M, 50 mL) was added to dry, vacuum-distilled tetraglyme (50 mL) over argon. The ether and other volatile impurities were removed by applying high vacuum while stirring vigorously. The resulting solution was placed under argon, cooled to 0 °C then to it was added drop wise deuterium oxide (2.5 mL, 0.125 mol) whilst stirring. The reaction mixture was stirred for one half hour then brought to room temperature. The crude product was collected via a liquid nitrogen vacuum trap-to trap transfer, with subsequent transfers also performed using this method. The product was washed by stirring with concentrated sulfuric acid for several days then dried by stirring over liquid sodium potassium alloy (*ca.* 1:3). Yield: 7.49 g (88.0 mmol, 88 %).

References for preparations

[1] G. Wood, E. P. Woo, M. H. Miskow, *Can. J. Chem.* **1969**, *47*, 429

[2] S. Krishnamurthy, *J. Organomet. Chem.* **1978**, *156*, 171

NMR Spectroscopy

Preparation of NMR samples

In a typical procedure, a stock solution of $[CpRe(CO)_3]$ (0.5 ml, ~ 3mM) in pentane was transferred in a nitrogen dry box to a 5mm NMR tube fitted with a Teflon septum screw cap. The solvent was removed *in vacuo* on a Schlenk line then the required NMR solvent, (*e.g.*, 40% cyclohexane/60% $[D_{12}]$pentane or *ca*. 10% cyclohexane/ 82% isobutane/ 8% $[D_{12}]$pentane, *ca*. 0.65 ml) transferred into the NMR tube using a trap-to-trap transfer. The solvent was then degassed further using two freeze pump thaw cycles and finally argon gas admitted to the tube which was then sealed with the screw cap. The septum was punctured to allow threading of the fibreoptic into the tube, the tip of which terminated *ca.* 5mm above the top of the solution.

Acquisition of NMR spectra

Spectra were recorded on either a Bruker DMX 500 equipped with a TBI-Z $^1H/^{31}P$/BB probe or a Bruker DMX 600 equipped with a TBI-Z $^1H/^{13}C$/BB probe.

1D ^1H NMR spectra of samples in alkane solutions were acquired using an excitation sculpting scheme [a) T.-L. Hwang, A. J. Shaka, *J. Magn. Reson., Series A* **1995**, *112*, 275; b) K. Stott, J. Stonehouse, J. Keeler, T.-L. Hwang, A. J. Shaka, *J. Am. Chem. Soc.* **1995**, *117*, 4199;] that does not excite the region containing the resonances of free alkane (δ 0.9-1.7). Typically, the scheme employs a 1000 point, 5 ms, adiabatic, full passage hyperbolic secant 180° pulse (R = 20 Hz, equivalent to μ of 5.929 and β of 5.298), (M.S. Silver,. R.I. Joseph, D.I. Hoult, *J. Magn. Reson.* **1984**, *59*, 347.). This pulse, centered at the mid-point of the non-excited region (δ 1.3) is cosine modulated with a frequency of ± 2750 Hz (500 MHz) to generate two excitation windows covering regions between δ –1.7 to –6.7 and δ 4.3 to 9.3.

Alternatively, for excitation of just the equatorial and axial protons of the bound methylene unit in cyclohexane at δ 0.49 and δ –6.17, a 2000 point, 8ms, 180° Gaussian pulse cascade, centered at the midpoint of these two resonances and cosine modulated with a frequency of half the separation in Hz of these two resonances (e.g., ± 1665 Hz used in Figure 1S below) was employed Pulses were created using the Bruker Shape Tool software. The excitation sculpting scheme was incorporated into 2D experiments as shown in Figure 1S.

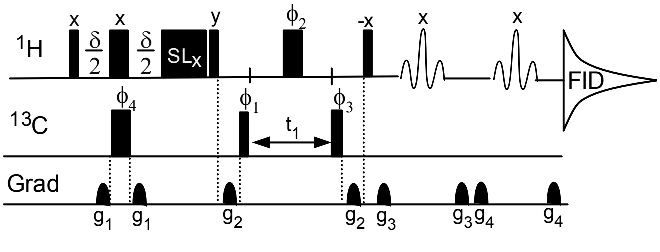


Figure 1S: 2D HSQC type experiment for correlation of protons with attached ^{13}C with selective ^1H excitation.
(Used in Figure 2S)
Phase cycles: ϕ_1 = x, –x; ϕ_2 = x, x, –x, –x; ϕ_3 = x, x, x, x, –x, –x, –x, –x; ϕ_4 = x; receiver = x, –x, x, –x, –x, x, –x, x; ϕ_1 and ϕ_4 incremented using States-TPPI method. δ = 4 ms (1/2J). Gradients: g_1 = 50, g_2 =80, g_3 = 44, g_4 = 68 Gauss cm^{-1}, 750 μs duration.

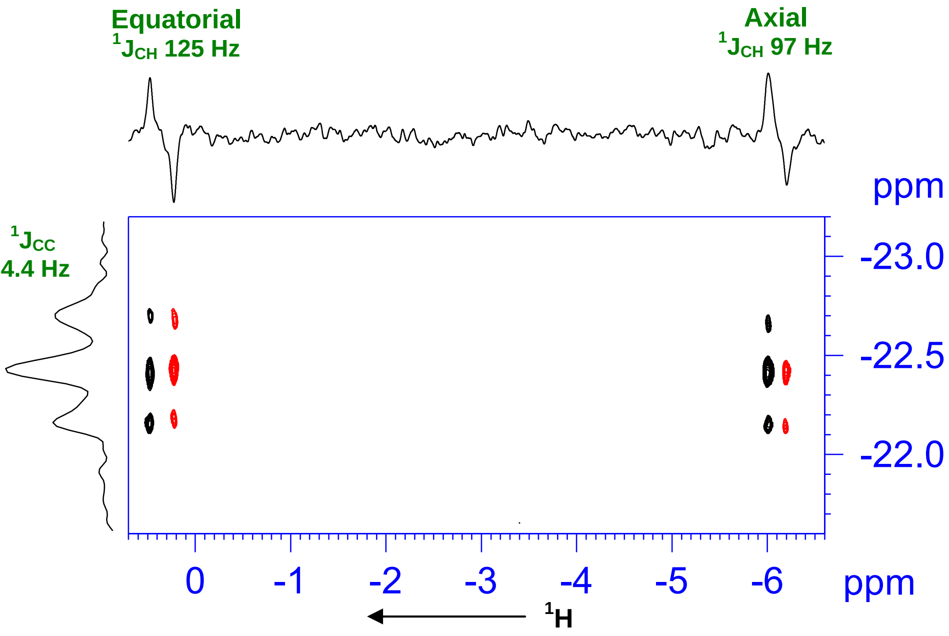


Figure 2S: ^{1}H-^{13}C HSQC spectrum of [CpRe(CO)$_2$([$^{13}C_6$]cyclohexane)] at 179 K. DMX 500, 60:40 [D_{12}]pentane:[$^{13}C_6$]cyclohexane. (^{13}C shift of bound methylene group is δ –22.4 (*cf.* ^{13}C shift of free [$^{13}C_6$]cyclohexane at δ 26.8).

Tables of NMR data

Table 1S. NMR shifts and couplings [in brackets] of free cyclohexane isotopomers at 173-179 K

Free cyclohexanes	40% solution in [D_{12}]pentane.DMX 500 179K		*ca.* 10% solution in 82% isobutane/ 8% [D_{12}]pentane. DMX 600 173 K	
Isotopomer	**equatorial CH**	**axial CH**	**equatorial CH**	**axial CH**
cyclohexane	1.705	1.227	1.728 [^1J(C,H) 127.8±0.5 Hz]	1.243 [^1J(C,H) 128±3 Hz]
[D_8]cyclohexane	1.673	1.189	1.695 [^2J(H,H) 13 Hz]	1.203 [^2J(H,H) 13 Hz]
[D_1]cyclohexane	n/a	n/a	1.72	1.237
[$^{13}C_6$]cyclohexane	n/a	n/a	1.723	1.234

Table 2S. NMR shifts and couplings [in brackets] of bound methylene groups in various cyclohexane isotopomers at 173-179 K

Bound cyclohexanes	40% solution in [D_{12}]pentane. DMX 500 179 K		*ca.* 10% solution in 82% isobutane/ 8% [D_{12}]pentane. DMX 600 173 K	
Isotopomer	**equatorial CH**	**axial CH**	**equatorial CH**	**axial CH**
1	0.348	–6.081	0.485	–6.169
1-d$_8$	0.176	–5.998	0.325	–6.089
1-d$_1$	n/a	n/a	–1.442	–7.793
1-^{13}C$_6$	0.349	–6.092	0.499 [^1J(C,H) 125.0±0.5 Hz]	–6.2047 [^1J(C,H) 96.5±0.5 Hz]

Table 3S. Variable temperature NMR shifts and couplings of protons in the bound methylene unit of **1-^{13}C$_6$** in *ca.* 10% cyclohexane/ 82% isobutane/ 8% [D_{12}]pentane. DMX 600 127 - 173 K

Temperature	**Equatorial H**		**Axial H**	
(K)	δ	^1J(C,H)	δ	^1J(C,H)
173	0.499	124.5±0.5	–6.2047	96.5±0.5
164	0.5605	126±2	–6.233	97.2±1
155	0.623	~125	–6.251	96.5±1.5
145	0.664	~125	–6.253	96±2
127	n/a	n/a	–6.17	94±4

Estimation of 100% complexed and uncomplexed, equatorial and axial chemical shifts in bound CH_2 moiety of [CpRe(CO)$_2$(cyclohexane)].

1e **1a**

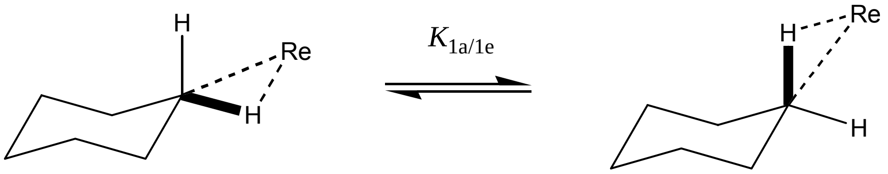


Figure 3S: equatorial/axial equilibrium in [CpRe(CO)$_2$(cyclohexane)] (**1**)

Figure 3S illustrates the exchange occurring in the bound alkane complex **1**, with the equilibrium constant defined as $K_{1a/1e}$. At any instant, there are four chemically distinct protons belonging to the two bound methylene units. These are the complexed axial, the uncomplexed equatorial, the complexed equatorial and the uncomplexed axial; we define their chemical shifts as $\mathbf{b_a}$, $\mathbf{f_e}$, $\mathbf{b_e}$ and $\mathbf{f_a}$, respectively.

The rate of exchange is too fast, relative to the NMR timescale, to permit the observation of these individual chemical shifts. Instead, two shifts are observed, one belonging to the weighted average of the axial protons the other that of the equatorial protons. These observed shifts are labeled $\boldsymbol{\alpha}_\mathbf{H}$ and $\boldsymbol{\varepsilon}_\mathbf{H}$ respectively. It follows that:

$$\boldsymbol{\alpha}_\mathbf{H} = \frac{\mathbf{b_a} \cdot K_{\mathbf{1a/1e}} + \mathbf{f_a}}{K_{\mathbf{1a/1e}} + 1} \quad \text{Eq.[1];} \qquad \boldsymbol{\varepsilon}_\mathbf{H} = \frac{\mathbf{b_e} + \mathbf{f_e} \cdot K_{\mathbf{1a/1e}}}{K_{\mathbf{1a/1e}} + 1} \quad \text{Eq.[2]}$$

Figure 4S illustrates the four possible isomers of **1-d$_1$**, arranged such that the two equatorially-complexed with axially-complexed exchanges actually occurring are shown horizontally. K_a and K_b are the equilibrium constants for these conversions, for the **1-d$_1$**-axial D and **1-d$_1$**-equatorial D isomers respectively.

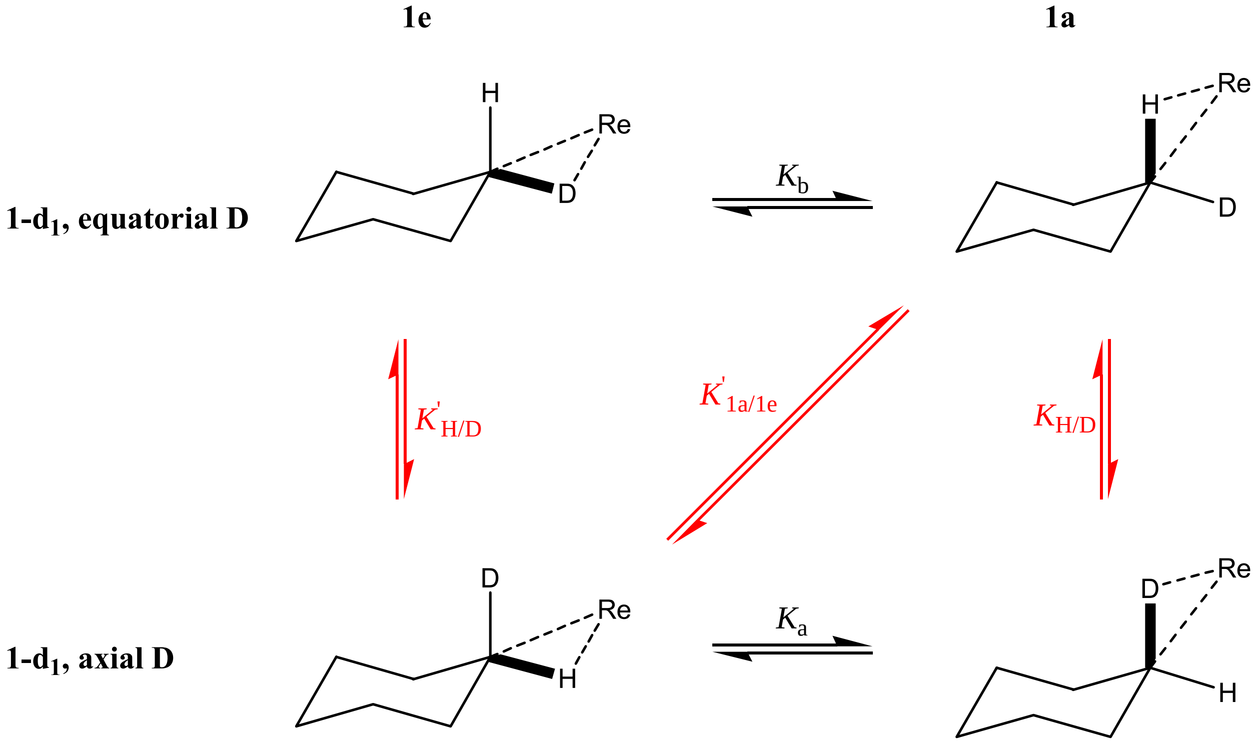


Figure 4S: Four isomers of [CpRe(CO)$_2$(1-[D$_1$]cyclohexane)] (**1-d$_1$**)and associated equilibria.

As with the normal cyclohexane complex, at any instant there are four chemically distinct protons apparent, now in four distinct bound methylene units of this system. Apart from a small standard isotope effect (which was estimated from the free solvent and then its effect subtracted later) these four protons are assumed to have the same chemical shifts as those from **1**. As before, the four proton shifts are not directly observed but instead two weighted averages are observed, this time $\boldsymbol{\alpha}_{\mathbf{D}}$ for the axial protons and $\boldsymbol{\varepsilon}_{\mathbf{D}}$ for the equatorial protons. Hence:

$$\boldsymbol{\alpha}_{\mathbf{D}} = \frac{\mathbf{b_a} \cdot K_{\mathbf{b}} + \mathbf{f_a}}{K_{\mathbf{b}} + \mathbf{1}} \quad \text{Eq.[3];} \qquad \boldsymbol{\varepsilon}_{\mathbf{D}} = \frac{\mathbf{b_e} + \mathbf{f_e} \cdot K_{\mathbf{a}}}{K_{\mathbf{a}} + \mathbf{1}} \quad \text{Eq.[4]}$$

In addition to K_a and K_b there are three equilibria shown in red in Figure 4S. $K'_{1a/1e}$ is the equilibrium constant assigned to the conversion of complex **1e** (**1-d₁** axial D) to complex **1a** (**1-d₁** equatorial D), and describes the preference of equatorial CH binding relative to axial CH binding. This is assumed to be the same as $K_{1a/1e}$ from the normal cyclohexane system. $K_{H/D}$ and $K'_{H/D}$ are the equilibrium constants assigned to the conversion of CD complexed **1-d₁** complexes to CH complexed **1-d₁** complexes, for the axial and equatorial sites respectively. For the calculations following, they are assumed to be equal, and describe the binding ability of CD relative to CH. These equilibria involve essentially hypothetical conversions in that they all require a ring flip of the cyclohexane ring, which does not occur at a significant rate at 173 K. Nevertheless, they allow K_a and K_b to be described in terms of $K_{H/D}$ and $K_{1a/1e}$:

$$K_{\mathbf{a}} = \frac{K_{\mathbf{1a/1e}}}{K_{\mathbf{H/D}}} \quad \text{Eq.[5];} \qquad K_{\mathbf{b}} = K_{\mathbf{1a/1e}} \cdot K_{\mathbf{H/D}} \quad \text{Eq.[6]}$$

Combining equations [3] and [4] with [6] and [5], respectively, gives:

$$\boldsymbol{\alpha}_{\mathbf{D}} = \frac{\mathbf{b_a} \cdot K_{\mathbf{1a/1e}} \cdot K_{\mathbf{H/D}} + \mathbf{f_a}}{K_{\mathbf{1a/1e}} \cdot K_{\mathbf{H/D}} + 1} \quad \text{Eq.[7];} \quad \boldsymbol{\varepsilon}_{\mathbf{D}} = \frac{\mathbf{b_e} \cdot K_{\mathbf{H/D}} + \mathbf{f_e} \cdot K_{\mathbf{1a/1e}}}{K_{\mathbf{1a/1e}} + K_{\mathbf{H/D}}} \quad \text{Eq.[8]}$$

At this point there are four equations ([1], [2], [7] and [8]) and six variables ($\mathbf{b_a}$, $\mathbf{b_e}$, $\mathbf{f_a}$, $\mathbf{f_e}$, $K_{1a/1e}$ and $K_{H/D}$), so it is not possible to a find unique solution. However, by assuming values for $\mathbf{f_a}$ and $\mathbf{f_e}$, estimates for $\mathbf{b_a}$, $\mathbf{b_e}$, $K_{1a/1e}$ and $K_{H/D}$ can be calculated. This is shown in Table 4S.

Table 4S. Calculated values of $\mathbf{b_a}$, $\mathbf{b_e}$, $K_{1a/1e}$ and $K_{H/D}$ assuming various values for $\mathbf{f_a}$ and $\mathbf{f_e}$. [a]

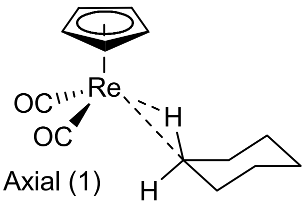
Change in shift of $\mathbf{f_a}$ and $\mathbf{f_e}$ (ppm) compared to shifts in free cyclohexane	δ $\mathbf{f_a}$[b]	δ $\mathbf{f_e}$[c]	δ $\mathbf{b_a}$	δ $\mathbf{b_e}$	$K_{1a/1e}$	$K_{H/D}$
0	1.243	1.728	–8.36	–3.73	3.4	4.7
0.2	1.443	1.928	–8.51	–4.21	3.3	3.9
1	2.243	2.728	–9.11	–5.93	2.9	2.6
1.25	2.493	2.978	–9.30	–6.40	2.8	2.5
2.5	3.743	4.228	–10.27	–8.56	2.4	1.9

[a] Input vales from data in *ca.* 10% cyclohexane/ 82% isobutane/ 8% [D$_{12}$]pentane. DMX 600 173 K. α_H –6.169; α_D –7.787; ε_H 0.485; ε_D –1.434. [b] δ $\mathbf{f_a}$ = 1.227 + change in shift. [c] δ $\mathbf{f_e}$ = 1.705 + change in shift.

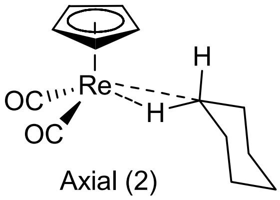
Calculational methods

Geometries were first optimized without symmetry constraints using Dmol^3 [1] using the Becke-Perdew 91 [2] exchange and correlation functionals with the double-numerical + d (DND) [1] basis set and the DSSP norm-conserving pseudopotentials, [1,3] as implemented in Materials Modeling 3.0.1.[4] The PW91/DND geometries were used without calculating their normal vibrations as starting point for further optimization with Gaussian03 [5] using the LANL2dz basis set [6] with an additional set of polarization functions [7] and the Los Alamos pseudopotentials [8] and both the Becke 3-parameter hybrid exchange functional [9] with the Lee-Yang-Parr correlation functional (B3LYP) [10] and the more recent highly parameterized HCTH407 functional. [11] B3LYP/LANL2dz+p and HCTH/LANL2dz+p optimized structures were characterized as minima by calculating their normal vibrations within the harmonic approximation. Further optimizations were carried out using a second-order Møller-Plesset (MP2) correction for electron correlation,[12] but MP2 frequencies were not calculated. Calculations of the NMR chemical shifts and coupling constants used the B3LYP/LANL2dz+p on the HCTH geometries; although the values calculated on test isomers with MP2 geometries are very similar. Chemical-shift calculations used the Gauge-Independent Atomic orbital (GIAO) method[13] and coupling constants were calculated with the default procedure.[14] NMR calculations included a self-consistent reaction field (SCRF) simulation of cyclohexane solvent using the standard polarizable continuum model (PCM).[15]

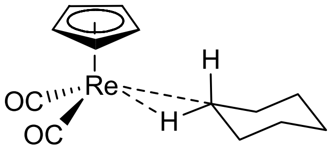
Results and Discussion



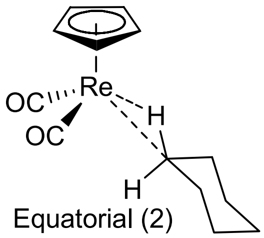
Axial (1)



Axial (2)



Equatorial (1)



Equatorial (2)

Table 5S shows the calculated energies of the four conformations of [CpRe(CO)$_2$(cyclohexane)] (**1**) investigated. Both the PW91 and the HCTH calculations find the axial (2) structure to be marginally (0.1 to 0.7 kcal mol^{-1}, depending on method and conformer) the most stable. B3LYP, however, finds the two equatorial conformers to be more stable than their axial counterparts. PW91 almost certainly overestimates the binding energy of the cyclohexane by about 21 kcal mol^{-1}, whereas B3LYP and HCTH give values of roughly 11 and 8 kcal mol^{-1}, respectively. Table 6S shows the Re-H distances for the two relevant cyclohexane hydrogens at each level of theory. The agostic interaction shows a clear preference for binding to one hydrogen, rather than a bridged structure. The CH bond length for the agostically complexed hydrogen is elongated to about 1.14-1.17 Å in each case. The three different functionals give different Re-H distances, about 1.88 Å for PW91 compared with roughly 1.96 and 2.00 for B3LYP and HCTH, respectively.

Note that the calculated axial/equatorial preferences are electronic (as opposed to vibrational) in nature. The zero-point vibrational energy correction does not change the most stable conformer relative to the Born-Oppernheimer energies. Thus, the fact that the axial CH bond is a better donor than its equatorial equivalent is consistent with the observed preference for axial coordination. Figure 5S (a) shows one of the relevant Re-H bonding orbitals for the axial (2) conformer, which is found to be most stable with PW91 and HCTH. The bonding interaction can be seen but, as often is the case, the lowest unoccupied molecular orbital (Figure 5S(b)), which is the antibonding equivalent, demonstrates the hyperconjugative nature of the interaction most clearly. Note that this orbital (eigenvalue –2.2 eV at PW91/DND) suggests that the axial hydrogen is activated towards nucleophilic substitution.

Structure	PW91/DND (dspp)			B3LYP/LANL2DZ+p				HCTH407/LANL2DZ+p				MP2/LANL2DZ+p		
	E_{Tot} (a.u.)	**E_{Rel}**	**BDE**	**E_{Tot} (a.u.)**	**ZPE**	**E_{Rel}**	**BDE**	**E_{Tot} (a.u.)**	**ZPE**	**E_{Rel}**	**BDE**	**E_{Tot} (a.u.)**	**E_{Rel}**	**BDE**
Axial (1)	–807.74273	0.1	–21.5	–735.28647	169.8	0.5	–10.7	–735.50247 (–735.50646)	168.5	0.2 (0.2)	–8.1	–732.64071	1.4	–28.1
Axial (2)	**–807.74287**	**0.0**	–21.6	– 735.28690	169.9	0.3	–10.9	**–735.50289** **(–735.50689)**	**168.6**	**0.0** **(0.0)**	–8.2	**–732.64306**	**0.0**	–29.5
Equatorial (1)	–807.74239	0.3	–21.3	–735.28679	169.6	0.1	–11.1	–735.50244 (–735.50644)	168.4	0.1 (0.1)	–8.1	–732.63891	2.3	–27.2
Equatorial (2)	–807.74178	0.7	–20.9	**–735.28722**	**169.8**	**0.0**	–11.2	–735.50257 (–735.50673)	168.6	0.2 (0.1)	–8.0	–732.64143	1.0	–28.5
Axial→Equatorial transition state								–735.49912	168.6 [1]	2.4	–5.8	–732.63744	3.5	–26.0
Axial→Equatorial 1-2 shift transition state								–735.49439	168.4 [1]	5.1	–3.1	–732.62368	12.3	–17.2
Axial→Axial 1-3 shift transition state								–735.49624	168.5 [1]	4.1	–4.1	–732.63809	3.0	–26.5
$CpRe(CO)_2$	–571.89880			–499.37815	62.8			–499.59112	62.3			–497.59779		
Cyclohexane	–235.80969			–235.89061	106.6			–235.89834	106.1			–234.99804		
Total	**–807.70849**			**–735.26876**	**169.4**			**–735.48946**	**168.4**			**–732.59583**		

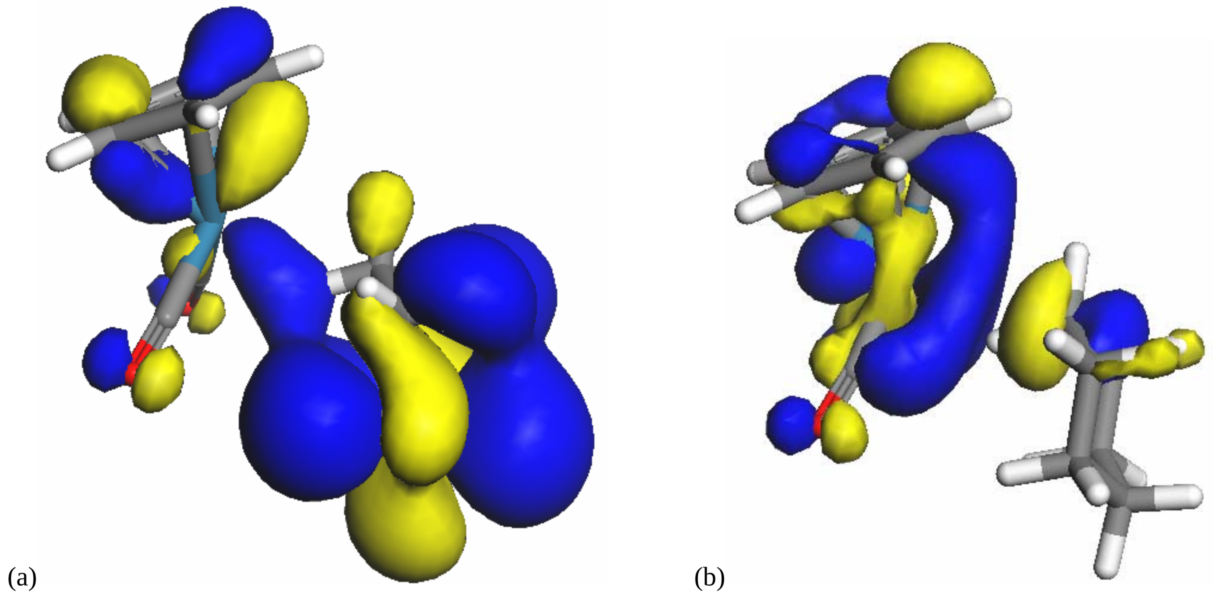
Table 5S: Calculated total (E_{Tot}, a.u.), relative (E_{Rel}, kcal mol^{-1}) zero-point vibrational (ZPE, kcal mol^{-1}) and bond-dissociation (BDE, kcal mol^{-1}) energies for four conformations of $CpRe(CO)_2$(cyclohexane). All species are calculated to be minima. Where zero-point energies are available, relative and bond-dissociation energies have been corrected for the ZPE contribution without scaling. The most stable conformer is marked in bold for each method. Values in parentheses for the $HCTH_{407}$/LANL2DZ+p results include a simulated cyclohexane solvent effect using the PCM method.

Conformer	**PW91/DND (dspp)**				**B3LYP/LANL2DZ+p**				**HCTH$_{407}$/LANL2DZ+p**				**MP2/LANL2DZ+p**			
	Axial		**Equatorial**		**Axial**		**Equatorial**		**Axial**		**Equatorial**		**Axial**		**Equatorial**	
	H-Re	**C-H**	**H-Re**	**C-H**	**H-Re**	**C-H**	**H-Re**	**C-H**	**H-Re**	**C-H**	**H-Re**	**C-H**	**H-Re**	**C-H**	**H-Re**	**C-H**
Axial(1)	1.881	1.141	2.818	1.076	1.971	1.150	2.963	1.092	2.039 (2.035)	1.144 (1.146)	3.076 (3.072)	1.095 (1.095)	1.841	1.158	2.792	1.095
Axial(2)	1.832	1.131	2.772	1.078	1.972	1.145	2.778	1.095	2.020 (2.008)	1.143 (1.145)	2.865 (2.864)	1.096 (1.096)	1.869	1.165	2.569	1.099
Equatorial(1)	2.699	1.080	1.881	1.130	2.930	1.094	1.954	1.147	3.004 (2.993)	1.096 (1.096)	1.997 (1.985)	1.145 (1.149)	2.746	1.096	1.858	1.154
Equatorial(2)	2.957	1.080	1.861	1.140	2.788	1.096	1.956	1.147	2.879 (2.878)	1.097 (1.097)	2.004 (1.997)	1.143 (1.145)	2.534	1.101	1.884	1.162

Table 6S: Calculated Re-H and C-H distances for axial and equatorial hydrogens at the bound position (Å). HCTH values in parentheses are derived from polarized continuum model (PCM) calculations in cyclohexane as solvent.

Conformer	**Axial(1)**	**Axial(2)**	**Equatorial(1)**	**Equatorial(2)**
H-C-H (C1)	115.2	118.5	115.2	118.6
H-C-H (C4)	106.9	107.0	107.1	107.0
C-H-Re (axial)	127.8	114.4	75.8	79.1
C-H-Re (equatorial)	74.4	78.2	125.4	112.6

Table 7S: Calculated (MP2) H-C-H and C-H-Re angles for axial and equatorial hydrogens at the bound position (°). The H-C-H angles for the CH_2 group in the 4-position are also shown for comparison.



(a) (b)

Figure 5S: (a) a bonding orbital showing the Re-H interaction and (b) the LUMO, which is the antibonding equivalent and shows the interaction most clearly.

Species	Gas Phase		Cyclohexane Solution									
	δ^1H(ax.)	δ^1H(eq.)	δ^1H(ax.)	δ^1H(eq.)	$^1J_{CH}$(ax.)	$^1J_{CH}$(eq.)	$^2J_{HH}(CH_2)$	$^3J_{HH}$(ae)	$^3J_{HH}$(aa)	$^3J_{HH}$(ea)	$^3J_{HH}$(ee)	$^1J_{CC}$
Axial(1)	–13.22	3.00	–11.11	2.69	101.7	159.9	–7.53	3.63	8.20	3.77	2.45	49.50
Axial(2)	–12.26	2.68	–9.74	2.33	101.3	156.4	–4.73	3.52	7.95	3.77	2.55	49.45
Equatorial(1)	2.44	–12.30	2.59	–11.46	160.4	100.1	–6.54	3.91	10.70	3.91	2.44	49.30
Equatorial(2)	2.39	–10.45	2.38	–9.78	156.6	103.4	–4.65	3.81	10.55	3.90	2.47	49.29

Table 8S: Calculated (B3LYP//HCTH) ^{1}H chemical shifts and NMR coupling constants for the axial and equatorial hydrogens of the methylene group bound to the rhenium center.

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