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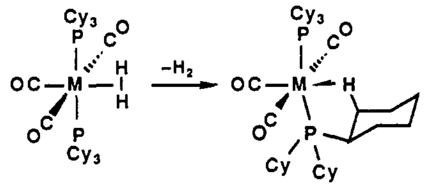
The Barrier to Rotation of Dihydrogen in $Cr(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$, a Complex with an Unusually High Difference in Solid- and Solution-State Stabilities

The details of the unique chemical bond[1,2] that is formed between the dihydrogen ligand and a metal are of major interest in the effort to elucidate the factors that govern stable η^2-H_2 binding as opposed to oxidative addition to hydrides. We have shown[3] in previous work that the barrier to rotation of η^2-H_2 is largely determined by the electronic interaction with the metal, or more specifically, that it is the $d\pi$ (metal) $\rightarrow$ σ^* (H_2) backbonding that gives the metal–H_2 bond its directional property. The beauty of the H_2 ligand is its diminutive size (~20° "bite-angle") and lack of extraneous electrons, which eliminate "steric" factors such as repulsions between ligand π and metal a_2 orbitals in the case of ethylene rotation[4] on a ML_5 fragment. We have now synthesized the first-row member of our group 6 series, $Cr(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ (Cy = cyclohexyl), as a stable solid and measured its rotational barrier by an inelastic neutron scattering technique, which also is invaluable as an *unambiguous proof of dihydrogen binding*. Classical hydride ligands cannot give rotational spectra[5] and do not interfere in the measurements.

$Cr(CO)_3(PCy_3)_2(H_2)$ has previously been prepared by Hoff only in solution under >300 psi of H_2 and had been thought to be unstable under normal pressure.[6] However, we recently found that under proper conditions the solid complex could be isolated under 1 atm of H_2. H_2 addition to toluene or THF solutions of the 16-e precursor, $Cr(CO)_3(PCy_3)_2$,[6a] does not give the H_2 complex, *unless* the solution is highly concentrated or supersaturated. In this case the H_2 complex precipitates as bright yellow microcrystals, presumably because of its lower solubility. It immediately turns green in air, but is indefinately stable under H_2. The best method to synthesize $Cr(CO)_3(PCy_3)_2(H_2)$ is similar to that for $Cr(CO)_3(PCy_3)_2$[6a] (reaction of $Cr(CO)_3$(naphthalene) with 2 equiv of PCy_3 in THF), except for the use of an *H_2 atmosphere instead of argon.* $Cr(CO)_3(PCy_3)_2(H_2)$ precipitates in 81% yield upon stirring for 18 h. This synthesis is then analogous to that of the Mo and W congeners from $M(CO)_3$(cycloheptatriene).[7]

There is a large difference between solid- and solution-state stabilities here, at least in a practical if not thermodynamic sense. When the Cr–H_2 complex is dissolved in toluene, instantaneous complete dissociation of H_2 occurs (H_2 gas is evolved), *even under an H_2 atmosphere*, to give a deep blue-purple solution of $Cr(CO)_3(PCy_3)_2$. Only partial dissociation occurs for the Mo analogue while the more strongly bound W complex completely retains H_2 in solution. Crystal lattice stabilization energy could favor H_2 binding in the solid, but why does the small H_2 molecule not eventually dissociate and escape out of the lattice as it does in solution? The answer lies in the fact that the H_2 is not just leaving the coordination site in these complexes but is actually being "displaced" by a cyclohexyl ring C–H to give an agostic interaction, identified by X-ray crystallography (M = Cr,[8a] W[8b]):



In solution the molecule is much more flexible in its ability to move a cyclohexyl ring into position to displace the H_2, and weak solvent interactions[9] can also possibly aid in ousting the H_2. However, since the above reaction is reversible to some degree, driving forces such as solubility could "trap out" the H_2 complex in solid form. Once this occurs, the structural rigidity (e.g. crystal packing forces) could favor H_2 binding over intramolecular C–H binding, for which significant rearrangements and bond angle changes would have to occur.[8] The energies[10] of the metal σ-bond interactions in these complexes are so low (~10–15 kcal/mol) that entropic factors[10a] can even become important. A general analogy can be made to biological metal coordination sites wherein competition between external small molecule substrates and intramolecular protein residues occurs.

The rotational barrier can directly be determined essentially only from inelastic neutron scattering measurements of the low-lying rotational energy levels of the hindered dihydrogen rotor. In fact, it is the rotational tunnel splitting of the librational ground state[5] which is most sensitive to the barrier: for relatively weak hindering potentials the value of the tunnel splitting varies approximately exponentially with barrier height. This has been demonstrated[3] by the dramatic change observed when replacing W with Mo in $M(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$. Here the tunnel splitting was found to change by about a factor of three, from 0.89 to 2.82 cm^{-1}, with an attendant change in the barrier from 2.2 to 1.7 kcal/mol, where the latter value is somewhat uncertain because the H–H distance (and therefore the rotational constant **B**) is not known for the Mo analogue.

The barrier in these two complexes thus scales qualitatively as one might expect, i.e., that the ligand bond strength of W be

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(7) Kubas, G. J. *Inorg. Synth.* **1990**, *27*, 1. This synthesis does not work either for $Cr(CO)_3$(cycloheptatriene) or for $Cr(CO)_3$(naphthalene) in *toluene* (*THF* must be used) because PCy_3 will not displace toluene from the $Cr(CO)_3$(toluene) formed in situ. For steric reasons, THF is actually a weaker ligand in these systems than H_2 and does not bind to $Cr(CO)_3(PCy_3)_2$.

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(9) For steric reasons, toluene or any other aromatic solvent *cannot coordinate through π interactions* to the $M(CO)_3(PCy_3)_2$ fragment. Thus any metal–solvent interaction would have to involve a C–H bond of the solvent. We tried to test for possible C–H interactions by placing $Cr(CO)_3(PCy_3)_2(H_2)$ in bulky aromatic solvents such as 1,3,5-triisopropylbenzene and 3,5-di-*tert*-butyltoluene, hoping that the H_2 would *not* dissociate because the solvent would be too sterically encumbered to assist H_2 loss even by metal···H–C interactions. Unfortunately the complex was virtually insoluble in these solvents at room temperature. Raising the temperature to ~45 °C did give some solubilization, but also H_2 loss, to form the blue-purple $Cr(CO)_3(PCy_3)_2$ (color is a clear indicator here). In this case thermally-induced loss of H_2 could be occurring, which would be indistinguishable from solvent effects. As for the toluene case, placing the H_2 complex in mesitylene (1,3,5-trimethylbenzene) at 23 °C also gave a blue color indicative of the agostic species, but much paler (lower solubility).

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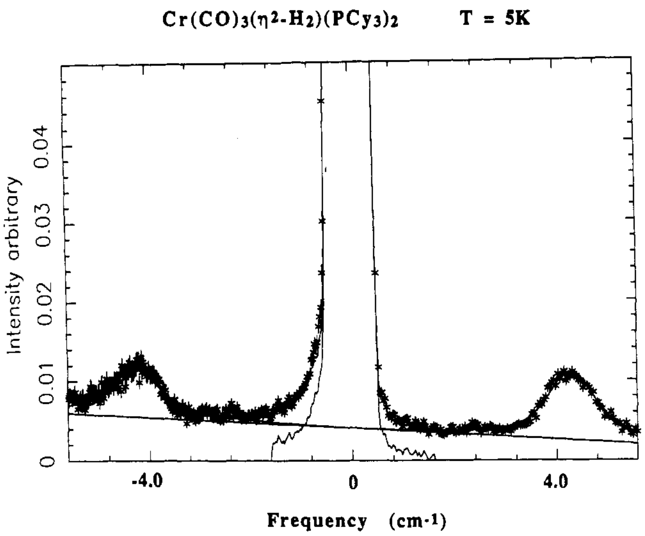

Figure 1. Rotational tunneling spectrum of $Cr(CO)_3(PCy_3)_2(H_2)$ at 5 K. Contributions to the fitted curve through the data points shown include a linear sloping background and the measured resolution function in the elastic region (see text).

greater than that for Mo. Calculations using ab initio and Fenske–Hall methods[3] demonstrate this tendency as well, as both the dihydrogen binding strength and the barrier to rotation were found to increase from W to Mo. In fact, the amount of change in the barrier obtained in the Fenske–Hall calculation agrees perfectly with experiment.

Inelastic neutron scattering measurements on $Cr(CO)_3(PCy_3)_2(H_2)$ were carried out on both the IN5 and IN6 cold neutron time-of-flight spectrometers of the Institut Laue-Langevin. Results from IN6 showed two weak peaks riding on either side on the tail of the elastic peak. They correspond to the energy-gain and energy-loss rotational tunneling transitions within the librational ground state. Additional measurements were carried out with better resolution on the IN5 spectrometer in an effort to determine if the tunneling peak had structure as it does for the W and Mo complexes. However, the peaks were only found to be somewhat broadened. The IN5 data are shown in Figure 1. The data were fit with a δ function at zero energy and two Lorentzians for the tunneling peaks all convoluted with the instrumental resolution, which was measured separately using a vanadium sample. The rotational tunneling peaks were found at a frequency of 4.33 (3) cm^{-1}, which in turn is larger than that for the Mo analogue. This value of the rotational tunneling corresponds closely to the temperature (5 K) at which this measurement was performed. One would therefore expect both levels of the librational ground state to be occupied. However, we have found in all our previous measurements on these complexes[3,11] that the relative population of both levels does not change appreciably with temperature. The reason for this is that in all likelihood the spin conversion that has to accompany depopulation of the upper level is slow on the timescale of our experiment.

The barrier height that can be derived from this measurement by use of the same model for rotation of the dihydrogen ligand as in our previous work;[3,11] i.e., planar rotation about the metal–dihydrogen axis in a double-minimum potential well, is 1.3 kcal/mol, if we assume that B is the same as for dihydrogen in the W complex. If, on the other hand we use d(HH) calculated for the Mo complex (0.79 Å),[3] we obtain a barrier height of 1.5 kcal/mol, as compared with 1.7 kcal/mol for the Mo complex.

We have also collected IR spectra on the title compound, but were only able to associate two bands with the dihydrogen ligand, namely $\nu_s(M-H_2)$ at about 950 cm^{-1} and $\nu_{as}(M-H_2)$ at 1540 cm^{-1}. These values are similar to those obtained for the W analogue,[1] namely 951 and 1568 cm^{-1}, respectively, whereas for the Mo complex we have found $\nu_s(M-H_2)$ of 885 cm^{-1}.

These results in conjunction with those for the barrier heights and solution stabilities suggest a somewhat complicated picture of dihydrogen binding. The trend in barrier heights W > Mo > Cr would imply less back-donation into the dihydrogen σ^* orbital from Cr than Mo or W. Solution stabilities agree with the above order for overall $M-H_2$ bond strength. The values of $\nu_s(M-H_2)$, on the other hand, might lead to the conclusion that the $M-H_2$ bond strength is less for the Mo compound than either the Cr or W compounds.

Further comparisons may be made with IR studies[12] of the $M(CO)_5(H_2)$ complexes of the same series of metals, which were carried out in liquid xenon at −70 °C. The values of ν(H–H) for this series were found to be in the order Mo > Cr > W, i.e., 3080, 3030, and 2711 cm^{-1}, respectively. However, the Mo complex was reported to have much lower thermal stability than either the W or Cr form. Since the H–H bond is weakened both by σ-donation from H_2 and $d\pi \rightarrow \sigma^*$ back-donation, the values of ν(H–H) would reflect both these effects, while the barrier to rotation is only sensitive to the latter. If one were to combine the information on these two series of dihydrogen complexes under the assumption that they are comparable, one can conclude that the Mo center is a better back-donor with a much weaker σ-interaction than Cr.

No experimental data is available on the rotational barriers in the low-temperature stable pentacarbonyl complexes. A calculation[13] finds that the apparent equilibrium orientation at 45° between two CO ligands is more stable than the eclipsed orientation by about 0.65 kcal/mol, whereas the stable configuration for the present compounds has the H–H axis eclipsing the P–M–P axis. One might therefore question the validity of direct comparisons between these complexes and the $M(CO)_3(PCy_3)_2(H_2)$ series. Since, however, the H–H stretching frequency in $W(CO)_3(PCy_3)_2(H_2)$ is only 21 cm^{-1} lower than that in $W(CO)_5(H_2)$ we may safely conclude that this information from these low-temperature stable species is useful in the semiquantitative comparison used above. The small difference in frequencies is actually surprising because one would have expected the more electron-rich phosphine complex to be more effective at weakening the H–H bond by back-donation.

We have thus shown that while the values of the barrier to rotation of the dihydrogen ligand for the group W, Mo, and Cr in the PCy_3–dihydrogen complexes roughly follow the expected trend in metal–ligand bond strength, the detailed picture of metal–dihydrogen binding requires additional input from experiments. The reason for this is that this barrier is mainly sensitive to the $d\pi \rightarrow \sigma^*$ back-donation while other observables such as ν(H–H) depend on the σ-interaction as well. A combination of such information can then provide substantial detail on the metal–dihydrogen bond as indicated above.

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