Molecular Hydrogen Complexes

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Transition-metal molecular hydrogen complexes provide new insight into the mechanism of the oxidative addition of hydrogen to transition metals, which is a key step in catalytic hydrogenation [1]. From another perspective, the interaction of a H-H bond with a metal is analogous to that of a C-H bond with a metal, in the other words, an agostic interaction in the sense that an electron pair in a σ bond is donated to the metal orbital [2].

The first molecular dihydrogen complex to be isolated was $[W(CO)_3(P(i-Pr_3))_2(\eta^2-H_2)]$ by Kubas and coworkers in 1984 [3]. Since then numerous other examples of this new class of compounds have been prepared. The matrix isolation technique has proved to be useful in characterizing unstable dihydrogen complexes [4]. MO calculations showed that side-on bonding of dihydrogen to a metal was the energetically most favoured coordination mode [5], which is in agreement with the experimental data [3].

One of the characteristics of dihydrogen coordination for $[W(CO)_3(P(i-Pr_3))_2(n^2-H_2)]$ in solution is that H-D coupling constant for the HD isotopomer is 33.2 Hz [3]. This value is less than 43.2 Hz for gaseous HD [6], but far larger than the expected value for a conventional M(H)(D) complex (≤ 1 Hz) [7]. Short T_1 relaxation times have been found to be another useful criterion for identifying dihydrogen ligands for complexes in solution [8]. Since the dipole-dipole relaxation mechanism is very effective for a dihydrogen ligand, due to the spacial proximity of the two hydrogen nuclei, T_1 can be as short as 4 ms and is generally shorter than those observed for metal hydrides by an order of magnitude. Using this T_1 criterion, FeH₄(PEt₂Ph)₃, which was originally formulated as a tetrahydride complex, was later proposed to contain a dihydrogen ligand, i.e. FeH₂(n^2-H_2)(PEt₂Ph)₃ [9].

Variable temperature ¹H NMR spectroscopy showed that $[W(CO)_3(P(i-Pr_3))_2^{-(\eta^2-H_2)}]$ is in equilibrium with the seven-coordinate dihydride $[W(CO)_3(P(i-Pr_3))_2(H)_2]$ [3]. An analogous equilibrium for $[CpRu(dmpe)(\eta^2-H_2)]^+$ was demonstrated by spin saturation transfer experiments [10]. These observations showed that dihydrogen complexes are intermediates in oxidative addition of hydrogen to metal centers.



 $W(C0)_3(PCy_3)_2(\eta^2-H_2)$

The effect of altering the metal and phosphine was investigated for complexes, $[M(n^2-H_2)(H)(PR_2C_2H_4PR_2)]^+$, (M = Fe, Ru and Os; R = Et and Ph), where the hydride undergoes an intramolecular exchange with the hydrogen of the dihydrogen ligand [11]. It was noted that H-H interactions decrease in the order of Ru > Fe > Os. The effect of altering the phosphine ligand was examined for the complexes $Mo(CO)(PR_2CH_2CH_2PR_2)_2(H_2)$ [12]. For R = Ph, dihydrogen coordination was observed both in solution and in the solid. However, when R = Et, only the dihydride species was found to be present in both states. $[RhH_2(PC_2H_4-PPh_2)_3]^+$ was shown to be a classical dihydride as a solid and in solution below 183 K. In solution above 183 K, however, the dihydrogen form of this complex was claimed to be present [13].

In conclusion, the synthesis, characterization and solution dynamics of molecular dihydrogen complexes have been discussed. Much remains to be learned about the factors which affect the relative stability of the dihydrogen coordination mode and the classical dihydride structure.



Equilibria between dihydrogen and dihydride

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