Influence of a Cis Hydride on a Coordinated H_2 Ligand. Ab Initio Calculations

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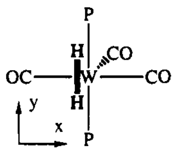
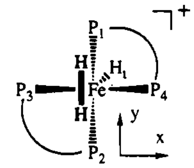
Numerous transition metal complexes of molecular H_2[1] have been characterized by various spectroscopic means, but determination of accurate H atom positions by neutron diffraction has only been possible in three cases.[2–4a] In the crystal, the sideways-bonded H_2 ligand is locked into a preferred orientation, but low-temperature INS measurements show rotation of H_2 around the metal–H_2 axis with a barrier less than 2.5 kcal/mol.[4a,5] The orientations of H_2 are different for the three d^6 $ML_5(H_2)$ complexes (**1**–**3**). H_2 is eclipsed with the P–M–P axis in **1** and **2** and staggered with respect to the four cis ligands in **3**. This unusual staggered orientation for an η^2 ligand bonded to a d^6 ML_5 fragment has been discussed on the basis of EHT calculations.[4a] Theoretical studies[4–7] have suggested that two factors determine the conformation of H_2, i.e., the back-donation from a metal d orbital into σ^*_{HH} (**4**) and the "cis effect". Optimal back-donation is obtained when the highest occupied d level with orbital extention toward H_2 overlaps with σ^*_{HH}. The cis effect is an additional two-electron interaction between σ_{Fe-H} and σ^*_{HH} (**5**), which stabilizes the conformation where H–H eclipses Fe–H. This creates a nascent bond between the closest nonbonded H centers. In the absence of a cis hydride (**1**[6,7] and **2**[4a]), back-donation governs the H_2 conformation and the optimal conformation is one that eclipses H–H with the P–M–P axis. In **3**, the back-donation puts H_2 in the P1–Fe–P2 plane while the cis effect favors eclipsing of H–H and Fe–H bonds, i.e., in the orthogonal direction. The experimental structure is a consequence of balancing the two effects, and H_2 sits in an intermediate position.[4a] While back-donation is a well-known metal–ligand interaction, this is not the case for the cis effect,[4] which may have an important role in the H exchange process.



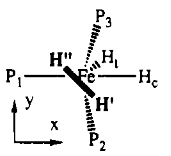
P = P^iPr_3, PPh_3

1



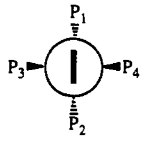
P-P = dppe

2

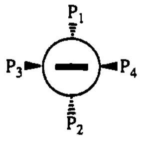


P = $PEtPh_2$

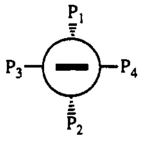
3



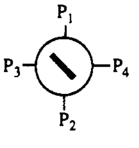
A



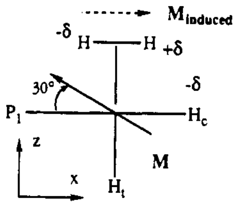
B



C



D



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In order to have a better understanding of the cis effect, we have used ab initio calculations[8] to study the rotation barrier of H_2 in complex **2**, where the cis effect is expected to be absent, and in complex **3**, where it should play a role. The crystal structure geometry is used,[8a] after replacing phosphine ligands with PH_3, unless mentioned otherwise. It is important not to optimize the geometry of the metal fragment in **3**, since the ligands are bonded to the metal in a highly distorted octahedral field due to the large bulk of the $PEtPh_2$ ligand. The rotation of the weakly bonded H_2 ligand is unlikely to modify significantly the geometry of the metallic fragment. We limit ourselves to a section of the potential energy surface in which H_2, at the experimental distance from the Fe center, is allowed to rotate about the Fe–H_2 direction. Our results for **2** and **3** are shown in Figures 1 and 2, respectively.

For $H_t(PH_3)_4Fe(H_2)^+$, conformation A is calculated to be the optimal structure. Rotating the ligand by 90° (B) without relaxing the structure of the metal fragment raises the energy by 3.1 kcal/

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(8) (a) The structure of the $H_t(PH_3)_4Fe$ fragment in **2** has been slightly modified (C_{2v} symmetry) with respect to that in the experimental $H(dppe)_2Fe(H_2)^+$ complex. (b) An effective core potential (ECP) was used for Fe and P. The Durand–Barthelat ECP was used for Fe[11a] with a (3s3p6d) Gaussian basis set contracted into (21/21/411) for the valence shell. Goddard's 6 Gaussian basis set was used for the d shell.[12a] The Stevens–Basch ECP was used for P[11b] with a (4s4p) Gaussian basis set contracted into (31/31) for the valence shell. The H atoms were described with the Huzinaga (4s) Gaussian basis set[12b] contracted into (31) for H bonded to Fe and into (4) elsewhere. For the H atoms bonded to Fe, one p polarization function ($\zeta = 1.0$) was added. (c) The MCSCF calculations (CASSCF level) used a five-orbital active space for complex **2** (σ_{Fe-H}, σ^*_{Fe-H}, σ_{H-H}, σ^*_{H-H} plus one metal d orbital allowing for back-donation) and a nine-orbital active space for the complex **3** (σ_{Fe-H_t}, σ_{Fe-H_c}, $\sigma^*_{Fe-H_t}$, $\sigma^*_{Fe-H_c}$, σ_{H-H}, σ^*_{H-H} plus three metal d orbitals). We also included the correlation in the metal–hydride bonds, which has an important contribution in a second-order perturbational calculation on the SCF ground state. For complex **3**, this small active space is not variationally stable. We had to take into account "intruder states" describing radial correlation by introducing the $3d_{xy}$ and $4d_{xy}$ orbitals into the active space. Test calculations adding other d orbitals on the metal or Fe–P bond orbitals in the active space did not change the results of the calculations. (d) A second-order perturbation was carried out on the CASSCF function developed on the five-orbital active space[8c] following the Møller–Plesset partitioning.[13] (e) This work is based, in part, on results from the MOTTEC package. Calculations were performed using the HONDO8 package (M. Dupuis, IBM Corp., Center for Scientific & Engineering Computations, Department 48B/428, Neighborhood Rd., Kingston, NY 12401) or a modified version of the MELDF system of programs (E. R. Davidson and D. Feller, QCPE Program No. 580, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN 47405).

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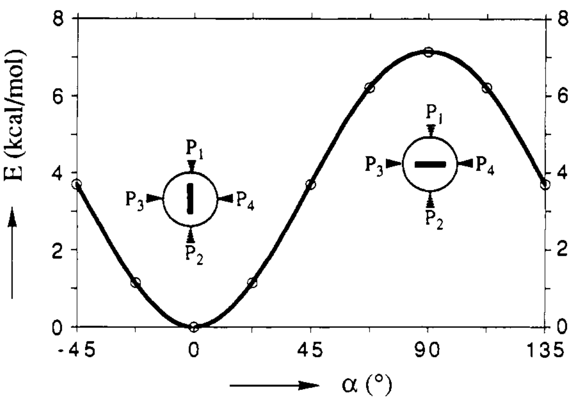

Figure 1. Potential energy (MCSCF) surface (kcal/mol) for rotation of H_2 in **2** as a function of α (α = 0°; H-H and P1-Fe-P2 aligned). P1-Fe-P2 = 166.6° and P3-Fe-P4 = 172.1°.[3]

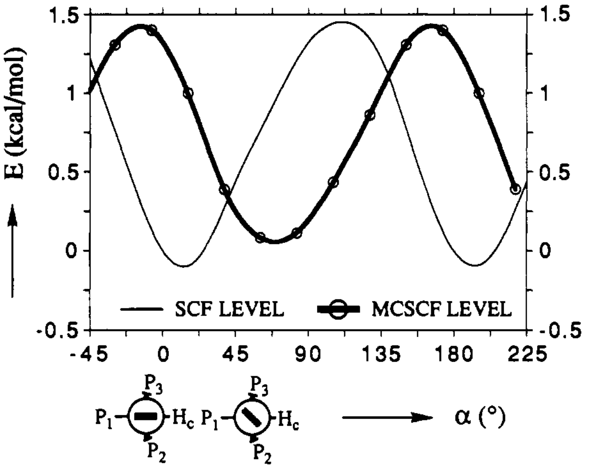

Figure 2. Potential energy surface (kcal/mol) for rotation of H_2 in **3** as a function of α (α = 0°; H-H and Fe-H aligned).

mol (SCF) and 7.3 kcal/mol (MCSCF, Figure 1).[8b] The height of the rotational barrier is 5.9 kcal/mol with CI calculations.[8d] The origin of the rotational barrier is the diminished back-donation in **B** (the d orbital points away from P3 and P4 and thus away from H_2). It was shown by INS measurements that the rotational barrier can be described mainly by a 2-fold potential of the type $V_2(1 - \cos 2\alpha)$ (where α is the rotational angle for the rotation of H_2 about the Fe-H_2 direction; see Figure 1).[5b] The height of the rotational barrier can be diminished significantly while its 2-fold shape is maintained, by slightly moving the two phosphines P3 and P4 away from the H_2 ligand (H_t-Fe-P3(4)) = 90° (**C**) in place of 94°). The rotational barrier is then lowered to 1.9 kcal/mol (MCSCF/CI), a value close to the experimental barrier (2.4 kcal/mol).[5b] Moving the four phosphines as in **D** (H_t-Fe-P = 90°) would also lower the rotational barrier by the same amount, but the barrier would have a dominating $V_4(1 - \cos 4\alpha)$ shape, in contradiction to the INS measurements. These results confirm that the orientation of H_2 is controlled by back-donation. As in **1**,[5a] it appears that the steric bulk of the phosphine ligand plays no role in the height of the H_2 rotational barrier.

At the SCF level, the best conformation (Figure 2) for **3** corresponds to close alignment of H_2 and the Fe-H_c bond (α = 12°). The highest point of the rotational barrier (1.6 kcal/mol) is reached at α = 110°, where H_2 almost aligns with the transoid P2-Fe-P3 direction. The inclusion of the correlation energy modifies drastically the previous results. However, at the MCSCF level,[8c] the preferred conformation is obtained at α = 64°, which is in good agreement with the experimental data, and the top of the barrier (1.4 kcal/mol) is reached for α = 153°. The reason for the good agreement between MCSCF calculated and experimental values assuming the rigid-rotator hypothesis is that no ligand cis to H_2 is tilted toward the dihydrogen ligand so that all d orbitals are properly set for efficient back-donation. These two calculations present the two competing interactions at work in this complex: (i) the expected back-donation which, in **3**, places H_2 perpendicular to the Fe-H bond; (ii) an electrostatic interaction favoring coplanarity of H_2 and Fe-H. The latter interaction may be important for the H-exchange process at work in this complex[4] and in other H_2/H or polyhydride complexes.[1] The electrostatic interaction, well represented at the SCF level, appears via a dipole/induced-dipole interaction. The large dipole moment (4.6 D) of the metallic fragment $H_t(PH_3)_3H_cFe$ lies essentially in the H_c-Fe-H_t plane and makes an angle of 30° with the H_c-Fe-P1 direction (**4**). This induces a dipole moment in the reverse direction on H_2. The Mulliken analysis shows that the hydrogen center H′ closer to H_c is positively charged (0.79) while that on the one H″ is more negatively charged (1.01). The best orientation of H_2 is thus obtained when the two dipoles are coplanar (α = 0°). Within EHT methodology, the cis effect results in a weak bonding between the hydride and the closest hydrogen center of H_2. The Mulliken overlap population of the SCF wave function shows no evidence of a positive bond order.[9] At the MCSCF level where the back-donation is better calculated,[10] a more accurate balance between the two effects is obtained and the calculated preferred orientation of H_2 is closer to the experimental conformation. This shows the need for high-level correlation calculations for a proper description of the competing factors at work in polyhydride complexes.

Note Added in Proof: After acceptance of our manuscript a theoretical study of the exchange between molecular hydrogen and hydride ligands in *cis*-$[Fe(PR_3)_4H(H_2)]^+$ has been published. Masera, F.; Duran, M.; Lledos, A.; Bertran, J. *J. Am. Chem. Soc.* **1992**, *114*, 2922.

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Supplementary Material Available: Tables of structural details and total energies for the optimal conformations at the MCSCF level of complexes **2** and **3** and the ECP and basis set for Fe (3 pages). Ordering information is given on any current masthead page.

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(9) No geometry optimization was performed at the SCF level since the system cannot be properly represented at this level of calculations.

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