the second hydride reduces the barrier to rotation by the very same effect that increased it in the first place.

There is another interesting feature of this complex, namely the interactions between the three bridging hydrides. A thorough theoretical analysis of dinuclear complexes with bridging hydrides has been previously carried out.[15] The possibility of three bridging hydrides having real chemical bonds between them, and hence being a "trihydrogen" fragment, has also been discussed.[16] Such an interaction was concluded to be highly improbable by later workers.[17] The three bridging hydrides in **5** form an equilateral triangle in our calculation with side length of 1.42 Å. We find a MOP between these hydrides at 0.047 between HB3 and HB1 (HB2) and 0.039 between HB1 and HB2. These MOP values indicate that there is some sort of positive interaction between these bridging hydrides but by no means on the scale of a trihydrogen complex.

Conclusions

We conclude that the conformation of nonclassical H_2 on a metal center in dinuclear transition-metal complexes is influenced by the same factors as in mononuclear complexes. Here these factors are the attractive effect of a hydride cis to the site of H_2 and the optimization of metal-σ^*_{HH} back-bonding. Bridging hydrides are found to be equally as capable of having an attractive cis effect as terminal hydrides. The distortion of the ligand field can also hybridize the metal d orbitals to give optimum conditions for metal to H_2 back-bonding. It is important to take into account the exact positions of all the ligands around the metal, since some of the d orbitals are thus distorted to become stronger or weaker candidates for back-bonding into σ^*_{HH}. Apparently the orientation of H_2 is very sensitive to all these factors. The low barriers to rotation of the ligand H_2 in its complexes are derived from the high energy of σ^*_{HH}, leading to a weak interaction with the occupied metal orbitals.

The cis interaction induces a nascent bond between an H of H_2 and the closest (terminal or bridged) hydride. We have already suggested that this nascent bond is likely to be a factor that might lower the activation energy of intramolecular H exchange. In mononuclear complexes this exchange could be viewed as site exchange between molecular H_2 and terminal H, accompanied by H center scrambling. If a similar process is operating in dinuclear complexes, then it is possible that molecular H_2 could bridge two metals. We certainly have no evidence for such a species, but the fact that diatomics such as CO or N_2 are known to bridge two metals gives some support to this hypothesis. Related structures have just been proposed to explain the exchange process in $Re_2H_8(PPh_3)_4$.[18]

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Additions and Corrections

1990, Volume 29

D. Min, R. D. Larsen, K. Emerson, and E. H. Abbott*: Synthesis and Crystal and Molecular Structures of Potassium Bis(μ-hydroxo)bis[dinitritoplatinate(II)] Sesquihydrate and Potassium *cyclo*-Tris(μ_3-oxo-1:2:4;1:3:4;2:3:4)tris[dinitritoplatinate(II)]trinitritoplatinate(IV) Trihydrate.

Pages 73–76. We wish to call the attention of the readers to the fact that potassium *cyclo*-tris(μ_3-oxo-1:2:4;1:3:4;2:3:4)tris[dinitritoplatinate(II)]trinitritoplatinate(IV) trihydrate, one of the compounds whose crystal and molecular structure we discussed, was first reported by Koz'min and co-workers (Koz'min, P. A.; Lapkin, V. V.; Shubochkin, L. K.; Surazhakaya, M. D.; Subochkina, E. F.; Larina, T. B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1988**, *33*, 532; *Dokl. Chem.* (*Engl. Transl.*) **1986**, *286*, 125). Also, Professor Koz'min has reported infrared and partial structural data on bis(μ-hydroxo)bis[dinitritoplatinate(II)] (Koz'min, P. A.; Lapkin, V. V.; Surazhakaya, M. D.; Shubochkin, L. K.; Larina, T. B.; Shubochkina, E. F. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1986**, *31*, 1177). Our work confirms structural suggestions contained in his paper.—E. H. Abbott