

# Distance and Scalar HH-Coupling Correlations in Transition Metal Dihydrides and Dihydrogen Complexes<sup>†</sup>

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Received: February 17, 1999

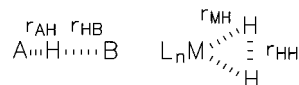
The bond-valence bond-length concept has been applied to derive a correlation between the hydrogen–hydrogen and the metal–hydrogen distances in the nonclassical dihydrogen complexes and classical transition metal dihydrides. The parameters of this correlation are similar to those for strong hydrogen-bonded systems. The predicted correlation is supported by 18 neutron structures of transition metal dihydrides or dihydrogen complexes and 2 neutron structures of transition metal trihydride complexes. It is also shown that the bond-valence bond-length concept can also be used to establish a correlation between the dihydrogen distance  $r_{HH}$  in dihydrogen/dihydride complexes and the scalar coupling constants  $J_{HH}/J_{HD}/J_{HT}$  in the different isotopomers of these complexes.

The concept of the valence-bond bond-length relation developed by Pauling<sup>1</sup> and Brown<sup>2</sup> has been successfully applied to predict geometries of hydrogen-bonded systems  $A-H\cdots B$  (Scheme 1). In particular, a correlation between the distances  $r_{AH}$  and  $r_{HB}$  was obtained, based on a number of neutron crystal structures containing weak and medium strong hydrogen bonds.<sup>3</sup> These correlations provide information about the reaction coordinate of proton transfer in hydrogen bonds, according to the concept of Dunitz and Bürgi<sup>4</sup> of mapping in a sequence of crystal structures pathways of chemical reactions. Recently, some of us have included the so far missing cases of very strong hydrogen bonds in the hydrogen bond correlation, where the information necessary was provided by solid-state NMR and by theoretical calculations.<sup>5</sup> Moreover, a link between the geometric correlation and various hydrogen bond properties was found.

In this paper we apply this concept to the problem of the oxidative addition of dihydrogen to transition metal complexes. It has well been established that the hydrogen–hydrogen distances  $r_{HH}$  increase during this process as the metal–hydrogen distances  $r_{MH}$  decrease, involving a series of transitions between the side-on dihydrogen complexes and the classical transition metal dihydrides.<sup>6</sup> However, the bond-valence concept has not yet been applied to describe this problem. We will show that this concept reproduces not only the structural changes but also the magnetic couplings between the two hydrogen nuclei in a wide range of  $r_{HH}$  values. This problem has been the subject of several experimental<sup>6,7j,n,8</sup> and theoretical<sup>9</sup> studies; however, so far a linear correlation was assumed, which is only valid in the range of short dihydrogen distances.<sup>6c,7n</sup>

The correlation between the distances  $r_{AH}$  and  $r_{HB}$  in  $A-H\cdots B$  arises from the assumption that the total valence bond

## SCHEME 1



order of hydrogen is unity<sup>1–3</sup> and that it is composed of the sum of the individual valence bond orders, which depend exponentially on the bond distances,<sup>1</sup> i.e.,

$$p_{AH} + p_{BH} = 1 \quad (1)$$

$$p_{AH} = \exp\{-(r_{AH} - r_{AH}^0)/b_{AH}\},$$

$$p_{BH} = \exp\{-(r_{BH} - r_{BH}^0)/b_{BH}\} \quad (2)$$

$r_{AH}^0$  represents the equilibrium  $A\cdots H$  distance of the free donor AH where the valence bond order  $p_{AH}$  of the AH bond is unity.  $b_{AH}$  is a decay parameter. By extension of eq 1 to the case of transition metal hydrides it follows for each hydrogen that

$$p_{MH} + p_{HH} = 1 \quad (3)$$

$$p_{MH} = \exp\{-(r_{MH} - r_{MH}^0)/b_{MH}\},$$

$$p_{HH} = \exp\{-(r_{HH} - r_{HH}^0)/b_{HH}\} \quad (4)$$

which immediately leads to the relation

$$r_{HH} = r_{HH}^0 - b_{HH} \ln[1 - \exp\{-(r_{MH} - r_{MH}^0)/b_{MH}\}] \quad (5)$$

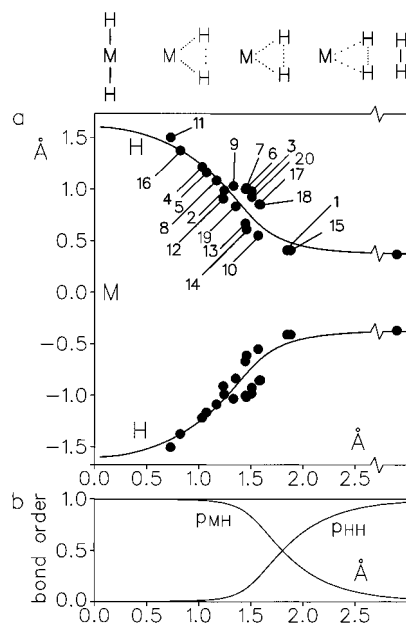
Equation 3 was derived theoretically by Hush<sup>9c</sup> but has not yet been extended to eqs 4 and 5.

To check validity of eq 5, we performed a search for neutron diffraction structures of transition metal dihydrides and dihydrogen complexes. We found 16 neutron structures<sup>7a–p</sup> in the Cambridge Structural Database (CSD)<sup>10</sup> and  $W(PMe_3)_4H_2Cl_2$  (**17**) and  $W(PMe_3)_4H_2F(FHF)$  (**18**) in ref 7q. We included compounds with additional hydrogen ligands only if they were immobile and part of a bridge to another metal. We also added the neutron

<sup>†</sup> Presented at the Symposium on Hydrogen Bonding in Inorganic Chemistry, American Chemical Society National Meeting, Boston, August 24–25, 1998.

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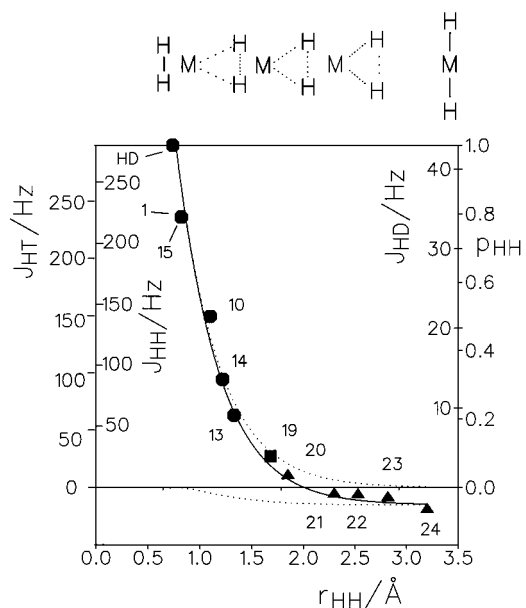


**Figure 1.** (a) Approach of dihydrogen to a transition metal M (origin) according to the valence bond order concept. The solid line was calculated using eq 5 as described in the text. Dihydrides (CSD codes, version 5.15): BOPJUL (1),<sup>7a,b</sup> BORFOD10 (2),<sup>7c</sup> BUXFIJ01 (3),<sup>7d</sup> CIWJAT10 (4),<sup>7e</sup> CONFEQ01 (5),<sup>7f</sup> DECVAI01 (6),<sup>7g</sup> DECVEM01 (7),<sup>7h</sup> GEVNIE05 (8),<sup>7h</sup> HCYPMO02 (9),<sup>7i</sup> JOLWAI01 (10),<sup>7j</sup> OHEP-RH01 (11),<sup>7k</sup> PESFOI (12),<sup>7l</sup> PIYGAF (13),<sup>7m</sup> TEQMIL (14),<sup>7n</sup> WADSAV (15),<sup>7o</sup> ZEGZAM01 (16),<sup>7p</sup> no codes (17, 18).<sup>7q</sup> Trihydrides: GATDOU01 (19),<sup>11a</sup> TACPTH (20).<sup>11b</sup> (b) Valence bond orders  $p_{MH}$  and  $p_{HH}$  as a function of the distance between the metal and the dihydrogen center.

structures of two trihydrides.<sup>11a,b</sup> The data are assembled in Figure 1a, which depicts the metal–dihydrogen plane, i.e., the half-hydrogen distances as a function of the distance between the metal and the dihydrogen center, with the metal at the origin. In Figure 1b we have included the corresponding bond order changes. The data indicate a continuous transition from free dihydrogen to *trans*-dihydrides which makes it difficult to define exact borders between dihydride, stretched dihydrogen complexes,<sup>6b,12</sup> and dihydrogen complexes. It is interesting to note that in *cis*-dihydrides exhibiting values of  $r_{HH} \approx 2.2$  Å  $p_{HH}$  is still around 0.025.

The solid correlation lines represent the hydrogen positions calculated from eqs 3 and 4, using the parameter  $r_{HH}^0 = 0.74$  Å for free dihydrogen.<sup>13</sup> The parameters  $b_{MH} = b_{HH} = b$  were set to 0.404 Å determined previously for a series of N–H...N hydrogen bonded systems,<sup>3b,5</sup> and  $r_{MH}^0$  was set to 1.6 Å, which is typical for the metal–hydrogen distances in dihydrides.<sup>6d</sup> As these parameters may vary from one metal to the other, i.e., be affected by systematic errors, we omit here a detailed analysis of the statistical errors.

To obtain a relation between the scalar couplings  $J_{LL'}$  between hydrogen isotopes L, L' = H, D, T in transition metal hydrides as a function of  $r_{HH}$ , we start from the theoretical result of Hush, who showed for the HD case<sup>9c</sup> that the one-bond coupling constant is proportional to the dihydrogen bond order  $^1J_{HD} = ^1J_{HD}^0 p_{HH}$ , where  $^1J_{HD}^0 = 43$  Hz is the coupling constant in free HD.<sup>14</sup> This expression alone, however, does not take into account magnetic couplings in *trans*-dihydrides where  $p_{HH} \approx$



**Figure 2.** Correlation of the scalar coupling constants  $J_{LL'}$ ,  $LL' = HH$ ,  $HD$ ,  $HT$  of transition metal dihydrides/dihydrogen complexes with the dihydrogen distance  $r_{HH}$ . Solid line: eq 6. Upper dotted line: first term. Lower dotted line: second term of eq 6. Experimental values:  $J_{HD} = 43$  Hz (free HD),<sup>14</sup> 34 Hz (1),<sup>7b</sup> 34 Hz (15),<sup>7o</sup> 21.5 Hz (10),<sup>7j</sup> 13.6 Hz (14),<sup>7n</sup> 9.1 Hz (13),<sup>7m</sup>  $J_{HT} = 27.3$  Hz (19),<sup>11c</sup>  $J_{HH} = 9.5$  Hz (20),<sup>11d</sup>  $-5.6$  Hz (21),<sup>15a</sup>  $-6.1$  Hz (22),<sup>15b</sup>  $-8.5$  Hz [RuH<sub>2</sub>{ $\eta^4$ -HSiMe<sub>2</sub>(CH=CHMe)}(PCy<sub>3</sub>)<sub>2</sub> (23)],<sup>15c</sup>  $-18.2$  Hz (*trans*-FeH<sub>2</sub>-(*meso*-tetraphos-1) (24)).<sup>15d</sup> For complexes with  $r_{HH} > 2.0$  Å, negative signs for the scalar magnetic coupling constants were assumed.

0. Therefore, we add a two-bond term that is proportional to the square of the metal–hydrogen bond order  $p_{MH}$

$$J_{LL'} = J_{HH}\gamma(L)\gamma(L')/\gamma(H)^2 = {}^1J_{LL'}^0 p_{HH} + {}^2J_{LL'}^0 (1 - p_{HH})^2 \quad (6)$$

where  $\gamma(L)$  is the gyromagnetic ratio of L. In eq 6 anharmonic isotope effects are neglected.

To check the validity of eq 6, we have plotted in Figure 2 values of  $J_{LL'}$  as a function of  $r_{HH}$ , where the circles stem from HD pairs, the square from a HT pair, and the triangles from HH pairs. The solid line represents eq 6, where the parameters are assembled in Table 1. The HH distances (except that of free HD) in the upper part of the curve ( $0.74$  Å  $< r_{HH} < 2.0$  Å) are taken from neutron diffraction studies. Due to the lack of suitable neutron diffraction studies in the region  $2.0$  Å  $< r_{HH} < 3.0$  Å, we included here X-ray data<sup>15a–c</sup> obtained at low temperatures, for which the authors claimed to have located the H-atoms precisely. On the other hand, only HH coupling constants were considered of systems that do not exhibit exchange couplings. For all complexes with  $r_{HH} > 2.0$  Å  $J_{LL'}$  was assumed to be negative.  $^1J_{LL'}^0$  in eq 6 was obtained from free HD, and  $^2J_{HH}^0$  was taken from *trans*-FeH<sub>2</sub>-(*meso*-tetraphos-1) (24) which exhibits the largest absolute  $J_{HH}$  value known for a *trans*-dihydride.<sup>15d</sup> On the basis of several studies, we assume that this term is negative.<sup>11d,16</sup>

The agreement between the experimental and the calculated curves is very satisfactory. Besides normalization, the one-bond term  $^1J_{LL'}$  is identical with the HH-bond order and dominates

**TABLE 1: Parameters of Eq 6**

| $^1J_{HH}^0$ | $^1J_{HD}^0$ | $^1J_{HT}^0$ | $^2J_{HH}^0$ | $^2J_{HD}^0$ | $^2J_{HT}^0$ | $\gamma(H)/\gamma(D)$ | $\gamma(H)/\gamma(T)$ |
|--------------|--------------|--------------|--------------|--------------|--------------|-----------------------|-----------------------|
| 280 Hz       | 43 Hz        | 299 Hz       | $-18.2$ Hz   | $-2.8$ Hz    | $-19.4$ Hz   | 6.51436               | 0.93753               |

at HH distances below 1.4 Å (upper dotted line). At larger distances the two-bond order term (lower dotted line) leads to a change of the sign of the coupling constant. Thus, the so far unexplained finding of large coupling constants in *trans*-dihydrides with  $r_{\text{HH}} \approx 3.2$  Å, small values of a few hertz in octahedral *cis*-dihydrides with  $r_{\text{HH}} \approx 2.2$  Å, and again large values of at shorter dihydrogen distances is now rationalized in a simple way.

The determination of  $r_{\text{HH}}$  from eq 6 has the advantage that it is not affected by coherent or incoherent dihydrogen rotations, as in the case of the determination of  $r_{\text{HH}}$  from longitudinal relaxation time measurements.<sup>17</sup>

It is clear that the bond-valence bond-order model, which does not take into account either specific metal or ligand properties, describes both the experimental hydrogen locations and the dependence of the coupling constants  $J_{\text{LL'}}$  of the HH- and MH-distances in a surprisingly good way. Obviously, there are deviations that may have different reasons, e.g., the assumption of a single averaged parameter for all complexes, or dihydrogen librations that may lead to differences between the equilibrium and average HH-distances. It will be tempting in the future to express various properties of dihydrogen complexes in terms of the correlation of eq 5, e.g., hydrogenic vibrational frequencies, barriers of the rotation, etc. We note a great similarity of the correlation lines in Figure 1a with the minimum energy pathway of the rotation of dihydrogen pairs in transition metal dihydrides via dihydrogen configurations.<sup>18</sup> Thus, the correlation in Figure 1 represents snapshots of the pathway describing the approach of dihydrogen to metals, in a way similar to that proposed by Crabtree for the approach of CH groups to metals.<sup>19</sup>

We conclude that we have found evidence that the bond-valence bond-distance concept is valid not only for hydrogen-bonded systems but also for transition metal hydrides. In terms of this concept hydrogen-bonded complexes and transition metal hydrides, and probably also other hydrogen-containing inorganic molecules, are treated in a similar way. Thus, the difference between classical hydrogen bonds and other bonds involving hydrogen disappears. Finally, we note that we are currently extending the concept proposed here for the HH case to the HX case with X = C, Si, etc., which will give interesting insights into the mechanism of the activation of XH bonds by transition metal complexes.

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, the European Community, Brussels, and the Fonds der Chemischen Industrie, Frankfurt, for financial support.

**Supporting Information Available:** A detailed list of all compounds, distances, and coupling constants used in Figures 1 and 2 is available free of charge via the Internet at <http://pubs.acs.org>.

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