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Ligand Effects in Transition Metal Dihydrogen Complexes: A Theoretical Study[1]

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Ab initio calculations at the MP2 and CCSD(T) level of theory using effective core potentials for the heavy atoms have been carried out in order to investigate systematically the trans influence of different ligands L upon H_2 coordination in the dihydrogen complexes $ML(CO)_4(H_2)$ (M = Cr, Mo, W; L = CO, SiO, CS, CN^-, NC^-, NO^+, N_2, H^-, F^-, Cl^-, PH_3). The optimized geometries and the theoretically predicted $M-H_2$ bond dissociation energies are reported. The ligands L are characterized in terms of their donor and acceptor capability using the CDA partitioning scheme. Strong σ-donor ligands in the trans position enhance the $M-H_2$ bonding, while strong π-acceptors weaken the $M-H_2$ bond. There is a good correlation between the calculated acceptor strength of L and the distance $r(H-H)$ and the $M-(H_2)$ bond dissociation energy D_e, respectively. Finally, the dihydrogen complexes are compared with the related classical hydrides $ML(CO)_4(H)_2$.

Introduction

Transition metal (TM) dihydrogen complexes have become an important class of compounds in inorganic and organometallic chemistry.[2] They are often involved in catalytic hydrogenation reactions, and even their occurrence in biological reactions has been proposed.[3] Though the first isolation of a TM dihydrogen complex was in 1984, when Kubas and co-workers[4] reported the synthesis of $[W(CO)_3(PR_3)_2(H_2)]$ (R = cyclohexyl, isopropyl), systematic studies focusing on the influence of different ligands upon the stability of TM dihydrogen complexes are rather limited.[2]

Theoretical calculations on dihydrogen and dihydride compounds[2,5−18] are not restricted to experimentally known complexes. They provide a unique possibility for systematic studies in cases where structural and energetic data are difficult to determine experimentally. Up to now only six neutron diffraction studies of dihydrogen complexes have been published.[4,19−23] Even more difficult than the geometry is the experimental determination of the $M-(H_2)$ bond dissociation energy.

In a prior theoretical study, we investigated the equilibrium geometries, vibrational frequencies, and $M-(H_2)$ bond energies of $M(CO)_5(H_2)$ (M = Cr, Mo, W).[24] The theoretically predicted geometries and bond energies were in excellent agreement with experiment. We decided to investigate the influence of different ligands upon the geometries and dissociation energies of the dihydrogen compounds. Starting from the parent compounds $M(CO)_5(H_2)$ (M = Cr, Mo, W), the CO ligand in trans position to dihydrogen has been replaced by isoelectronic (CN^-, NC^-, NO^+, N_2) and valence isoelectronic (SiO, CS) species. Furthermore, complexes with the anionic ligands H^-, F^-, and Cl^- and with PH_3 are considered (Figure 1).

This paper also aims for an understanding of the factors influencing the geometry and bond dissociation energy of the dihydrogen ligand. Recently, we developed a practical tool for analyzing donor−acceptor interactions in TM compounds.[25] The charge decomposition analysis (CDA) is a simple scheme which focuses on overlap populations within a fragment MO basis. In previous investigations,[24−27] the CDA has been proven

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[1] Theoretical Studies of Organometallic Compounds. 23. Part 22: Pidun, U.; Frenking, G. *J. Organomet. Chem*., in press.

[2] Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

[3] Crabtree, R. H. *Inorg. Chim. Acta* **1986**, *125*, L7.

[4] Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

[5] Dedieu, A. *Transition Metal Hydrides*; VCH: New York, 1992.

[6] Sabo-Etienne, S.; Chaudret, B.; Abou el Makarim, H.; Barthelat, J.-C.; Daudey, J.-P.; Moise, C.; Leblanc, J.-C. *J. Am. Chem. Soc.* **1994**, *116*, 9335.

[7] Gusev, D. G.; Notheis, J. U.; Rambo, J. R.; Hauger, B. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 7409.

[8] Musaev, D. G.; Koga, N.; Morokuma, K. *J. Phys. Chem.* **1993**, *97*, 4064.

[9] Li, J.; Dickson, R. M.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *117*, 11482.

[10] Ma, B.; Collins, C. L.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1996**, *117*, 870.

[11] Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 2569.

[12] Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 2928.

[13] Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6574.

[14] Lin, Z.; Hall, M. B. *Inorg. Chem.* **1992**, *31*, 4262.

[15] Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482.

[16] Koga, N.; Jin, S. Q.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3417.

[17] Daniel, C.; Koga, N.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773.

[18] Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1991**, *113*, 2879.

[19] Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823.

[20] van der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831.

[21] Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569.

[22] Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677.

[23] Hasegawa, T.; Li, Z.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352.

[24] Dapprich, S.; Frenking, G. *Angew. Chem.* **1995**, *107*, 383; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 354.

[25] Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352.

[26] Ehlers, A.; Dapprich, S.; Vyboishchikov, S. F.; Frenking, G. *Organometallics* **1996**, *15*, 105.

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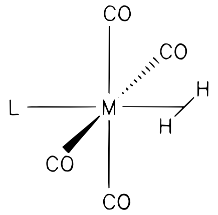

M = Cr, Mo, W
L = CO, SiO, CS, CN^-, NC^-,
NO^+, N_2, H^-, F^-, Cl^-, PH_3

Figure 1. Schematic structure of $ML(CO)_4(H_2)$.

to be a valuable tool for the interpretation of metal−ligand interactions. The results for the model complexes $M(CO)_5L$ (M = Cr, Mo, W; L = CO, SiO, CS, CN^-, NC^-, NO^+, N_2, PH_3, H_2) are in agreement with the standard textbook classification of the ligands L.[26] The CDA method can be used as a quantitative extension of the Dewar−Chatt−Duncanson model.

Methods

All geometry optimizations have been carried out at the MP2[28] level of theory using an effective core potential (ECP) for the metals developed by Hay and Wadt.[29] The ECPs are derived from nonrelativistic atom calculations of Cr and from relativistic calculations of Mo and W. A (441/2111/N1) split-valence basis set is used for the metals, which is derived from a (55/5/N+1) minimal basis set ($N = 4, 3, 2$ for Cr, Mo, W, respectively). The $(n-1)s^2$ and $(n-1)p^6$ electrons are treated explicitely as part of the valence space. A 6-31G(d,p) all-electron basis set is used for the light atoms, with the d polarization functions having five spherical components.[30,31] This basis set combination is our standard basis set II. The dissociation energies are calculated using coupled-cluster theory with singles and doubles and a noniterative estimation of triple substitutions (CCSD(T)).[32−35] The calculations have been carried out using the program packages TURBOMOLE,[36] ACES II,[37] and GAUSSIAN92.[38]

In the CDA method[25,39] the electron density distribution $\rho_{AB}(\vec{r})$ of a complex AB is expressed in terms of natural orbitals $\{\phi_i\}$ (NOs)

$$\rho_{AB}(\vec{r}) = \sum_i n_i \phi_i(\vec{r})\phi(\vec{r}) \tag{1}$$

where the eigenvalues of the density matrix are the occupation numbers n_i. The NOs are transformed in a basis set constructed from the NOs $\{u_\mu\}$ of appropriately chosen fragments A and B.

$$\rho_{AB}(\vec{r}) = \sum_\mu Q_{\mu\nu} u_\mu(\vec{r}) u_\nu(\vec{r}) \tag{2}$$

with

$$Q_{\mu\nu} = \sum_i n_i g_{\mu i} g_{\nu i} \tag{3}$$

Based on the occupation numbers of the fragment orbitals, four weighting factors w are introduced. They provide a partitioning scheme for the overlap density $Q_{\mu\nu}$ between fragments A and B. For example, the electron density $\rho^{d}_{AB,O}(\vec{r})$, which indicates the electron shift from fragment A to B, is given by

$$\rho^{d}_{AB,O}(\vec{r}) = \sum_\mu \sum_\nu Q_{\mu\nu,O} O w^{d}_{\mu\nu} u_\mu(\vec{r}) u_\nu(\vec{r}) \tag{4}$$

with

$$w^{d}_{\mu\nu} = \left(\frac{n_\mu}{2}\right)\left(1 - \frac{n_\nu}{2}\right) \tag{5}$$

if $u_\mu(\vec{r})$ is located on fragment A and $u_\nu(\vec{r})$ is located on B. For the summations running over $u_\mu(\vec{r})$ on B and $u_\nu(\vec{r})$ on A the weighting factor is

$$w^{d}_{\mu\nu} = \left(1 - \frac{n_\mu}{2}\right)\left(\frac{n_\nu}{2}\right) \tag{6}$$

The total charge donation is then given by integrating over the entire space v:

$$d = \int \rho^{d}_{AB,O}(\vec{r})\, dv \tag{7}$$

In a similar way, expressions for back donation b and repulsive polarization r can be derived. The entity b represents the interaction between occupied orbitals on fragment B and unoccupied orbitals on fragment A. r represents the interaction between occupied orbitals on both fragments A and B. The CDA studies were carried out using natural orbitals which were obtained from the MP2 density matrix. The analysis has been performed using the program CDA.[39]

Results and Discussion

The MP2/II optimized geometries and the calculated $M-H_2$ bond energies for the title compounds $ML(CO)_4(H_2)$ are listed in Table 1. The calculations were carried out under the assumptions that the H_2 ligands have an eclipsed conformation with respect to the cis carbonyl groups. Previous calculations of the vibrational frequencies of $M(CO)_5(H_2)$ (M = Cr, Mo, W) at the MP2 level using numerical second derivatives have shown that the energy minima have an eclipsed conformation.[24] The energy barrier for rotation about the the $M-(H_2)$ axis is very low, however (<0.2 kcal/mol at CCSD(T)/II//MP2/II). We did not calculate the vibrational frequencies of the $ML(CO)_4(H_2)$ complexes at the MP2/II level. The calculations are very expensive, and it can be assumed that the conformation of the H_2 ligand is not important for the topic of this study. Experimental D_0 values are only available for $Cr(CO)_5(H_2)$ ($D_0 = 15.0 \pm 1.3$ kcal/mol) and $W(CO)_5(H_2)$ ($D_0 > 16$ kcal/

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(27) Pidun, U.; Frenking, G. *Organometallics* **1995**, *14*, 5325.
(28) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(29) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(30) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
(31) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
(32) Cizek, J. *J. Chem. Phys.* **1066**, *45*, 4256.
(33) Cizek, J. *Adv. Chem. Phys.* **1966**, *14*, 35.
(34) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quant. Chem.* **1978**, *14*, 545.
(35) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.
(36) TURBOMOLE. Ahlrichs, R.; Universität Karlsruhe, Deutschland, 1991.
(37) ACES II. Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J., University of Florida, Gainsville, FL, 1991.
(38) GAUSSIAN92, Revision C. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Pittsburgh, PA, 1992.
(39) CDA2.1. Dapprich, S.; Frenking, G.; Universität Marburg, Deutschland, accessible under ftp://ftp.chemie.uni-marburg.de, 1995.

Table 1. Calculated Bond Lengths (MP2/II) (Å) of $ML(CO)_4(H_2)$ Complexes and Theoretically Predicted Bond Dissociation Energies D_e (CCSD(T)/II//MP2/II) (kcal/mol) for the $ML(CO)_4{-}H_2$ Bond

M	L	sym	M−H	H−H	M−L	D_e
Cr	CO	O_h	1.745	0.814	1.787	19.8
Mo			1.959	0.791	1.989	16.1
W			1.918	0.810	2.006	19.8
Cr	SiO	C_{2v}	1.675	0.841	2.120	19.0
Mo			1.929	0.798	2.333	16.2
W			1.893	0.817	2.359	20.2
Cr	CS	C_{2v}	1.811	0.790	1.742	17.8
Mo			2.055	0.775	1.923	12.5
W			1.981	0.794	1.958	16.0
Cr	CN^-	C_{2v}	1.655	0.910	1.939	26.3
Mo			1.876	0.838	2.154	21.6
W			1.844	0.870	2.163	26.5
Cr	NC^-	C_{2v}	1.625	0.956	1.988	24.4
Mo			1.838	0.861	2.158	24.7
W			1.817	0.893	2.147	30.6
Cr	NO^+	C_{2v}	2.137[a]	0.742[a]	1.770[a]	13.1[a]
Mo			2.161	0.757	1.844	11.7
W			2.105	0.763	1.854	14.4
Cr	N_2	C_{2v}	1.687	0.895	1.845	21.8
Mo			1.868	0.821	2.081	21.8
W			1.847	0.840	2.067	26.8
Cr	H^-	C_{2v}	1.668	0.884	1.513	30.1
Mo			1.909	0.827	1.733	19.0
W			1.868	0.861	1.759	27.7
Cr	F^-	C_{2v}	1.618	0.958	1.956	26.0
Mo			1.832	0.879	2.062	25.5
W			1.741	1.756	2.065	[c]35.6
Cr	Cl^-	C_{2v}	1.593	0.980	2.424	24.2
Mo			1.804	0.886	2.573	26.3
W			1.727	1.693	2.576	39.1[c]
Cr	PH_3	C_s	1.638	0.886	2.216	34.2[b]
Mo			1.881	0.818	2.439	22.7[b]
W			1.856	0.840	2.450	27.6[b]

[a] HF/II values. [b] MP2/II values. [c] The value refers to the dissociation of two hydrogen atoms forming H_2.

mol).[40,41] While the HF method tends to underestimate and MP2 tends to overestimate the bond energies, the agreement with the energies calculated at the CCSD(T) level of theory is excellent.[24,26,42] Very recently, Poliakoff and co-workers used a high-pressure photoacoustic calorimetry technique to study the bond energies of dihydrogen compounds.[43] They found the $(CO)_5Mo{-}(H_2)$ bond to be more stable than the $(CO)_5Cr{-}(H_2)$ bond, in contradiction to previous results and to our calculations. However, this technique may not be reliable.

The ligands L can be divided into several groups, depending on their influence on the structure and the bond strength of the $M{-}H_2$ moiety. For L = CS and L = NO^+, the $M{-}H_2$ dissociation energy D_e is lowered relative to L = CO. For the other ligands, D_e is increased. For $[WF(CO)_4H_2]^-$ and $[WCl(CO)_4H_2]^-$, no energy minimum structure with a dihydrogen coordination could be found. The optimization yields classical cis dihydrido compounds with comparatively high dissociation energies with respect to loss of H_2 of 35.6 and 39.1 kcal/mol. There is a nearly linear correlation between the calculated bond energies D_e and the r(H−H) values (Figure 2). It follows that the stronger the $M{-}H_2$ bond, the longer is the calculated distance between the hydrogen atoms. For $[Cr(NO)(CO)_4(H_2)]^+$, the geometry optimization at the MP2 level of theory did not converge. Therefore, we have omitted the HF data from Figures 2−4.

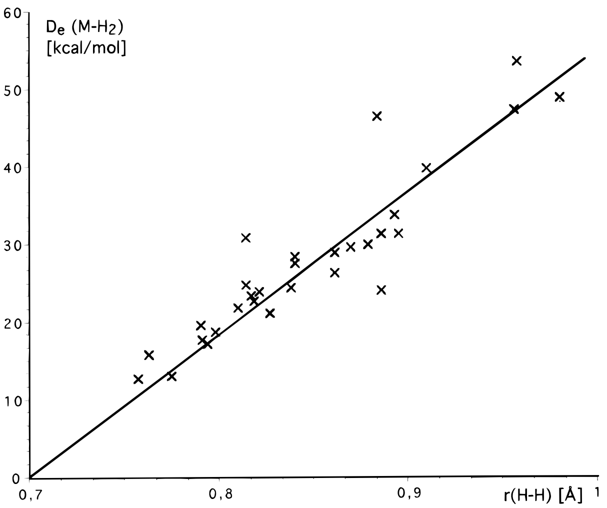

Figure 2. Calculated dissociation energies D_e (kcal/mol) and the bond lengths r(H−H) (Å) in the complexes $ML(CO)_4(H_2)$ at the MP2/II level of theory.

How can these results be rationalized? The $M{-}(H_2)$ bond is often explained in the framework of the DCD model.[44,45] Electron donation arises from the interaction of the occupied σ-orbital of the dihydrogen moiety with vacant orbitals of the metal fragment. Back-donation populates the formerly unoccupied σ^*-orbital of H_2. Both contributions should weaken the H−H bond. It is generally assumed that $M \rightarrow (H_2)$ back-donation has a stronger influence upon the coordination geometry of H_2 than $M \leftarrow (H_2)$ donation.[5] In a recent investigation of $M(CO)_5L$ compounds, we classified the ligands L = CO, SiO, CS, CN^-, NC^-, NO^+, and N_2 as to their donation and back-donation ability using the CDA method.[26] The results are shown in Table 2 together with the data for L = PH_3. The data shall be used for comparison with the $ML(CO)_4H_2$ complexes. It becomes obvious that the trans influence on CO caused by the ligand L depends strongly on the acceptor strength b of L (Table 2). Pure donor ligands such as CN^- increase the $M{-}CO_{trans}$ bond strength, while acceptor ligands like NO^+ lower the $M{-}CO_{trans}$ bond energy significantly.[26]

If the classification of the ligands L given by the CDA results for $M(CO)_5L$ could be correlated with the properties of the $L(CO)_4M{-}(H_2)$ complexes, it would be possible to predict the trend of the geometries and the bond energies of the dihydrogen complexes without calculating them explicitely. In a previous study of $MO(CO)_5L$ complexes, we could show that the amount of the calculated $(CO)_5M \rightarrow L$ back-donation correlates with the change of the $M{-}CO_{trans}$ bond length; i.e., the the $M{-}CO_{trans}$ bond length becomes longer when the $(CO)_5M \rightarrow L$ back-donation increases.[26] No such correlation was

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(40) Wells, J. R.; House, P. G.; Weitz, E. *J. Phys. Chem.* **1994**, *98*, 8343.

(41) Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Phys. Chem.* **1989**, *93*, 652.

(42) Frenking, G.; Antes, I.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboishchikov, S. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds. VCH: New York, 1996; Vol. VIII, pp 63−144.

(43) Walsh, E. F.; Popov, V. K.; George, M. W.; Poliakoff, M. *J. Phys. Chem.* **1995**, *99*, 12016.

(44) Dewar, J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, c79.

(45) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, *2939*.

(46) Dapprich, S.; Pidun, U.; Ehlers, A. W.; Frenking, G. *Chem. Phys. Lett.* **1995**, *242*, 521.

Table 2. Results of the Charge Decomposition Analysis of $M(CO)_5L$ Complexes: Calculated Donation *d*, Back-Donation *b*, and Repulsive Polarization *r* of the M−L bond at MP2/II, Calculated M−L Bond Energies D_0 at CCSD(T)/II//MP2/II

M	L	*d*	*b*	*r*	D_e
Cr	CO	+0.460	+0.314	−0.266	45.8
Mo		+0.342	+0.244	−0.255	40.4
W		+0.315	+0.233	−0.278	48.0
Cr	SiO	+0.299	+0.208	−0.374	39.9
Mo		+0.138	+0.231	−0.254	39.4
W		+0.214	+0.213	−0.239	45.8
Cr	CS	+0.310	+0.345	−0.426	65.8
Mo		+0.292	+0.337	−0.373	60.8
W		+0.259	+0.308	−0.387	70.7
Cr	CN^-	+0.604	+0.089	−0.206	92.1
Mo		+0.499	+0.043	−0.211	89.2
W		+0.488	+0.024	−0.241	99.6
Cr	NC^-	+0.482	+0.038	−0.188	75.6
Mo		+0.358	+0.005	−0.219	76.3
W		+0.361	+0.002	−0.252	85.8
Cr	NO^+	+0.152	+0.326	−0.274	106.7
Mo		+0.108	+0.386	−0.313	104.4
W		+0.119	+0.378	−0.318	110.0
Cr	N_2	+0.166	+0.173	−0.214	24.8
Mo		+0.028	+0.094	−0.206	22.0
W		+0.027	+0.107	−0.252	26.4
Cr	PH_3	+0.323	+0.139	−0.342	[a]*42.2*[a]
Mo		+0.215	+0.106	−0.287	[a]*37.9*[a]
W		+0.278	+0.091	−0.297	[a]*43.8*[a]

[a] Estimated using isostructural reactions.[46]

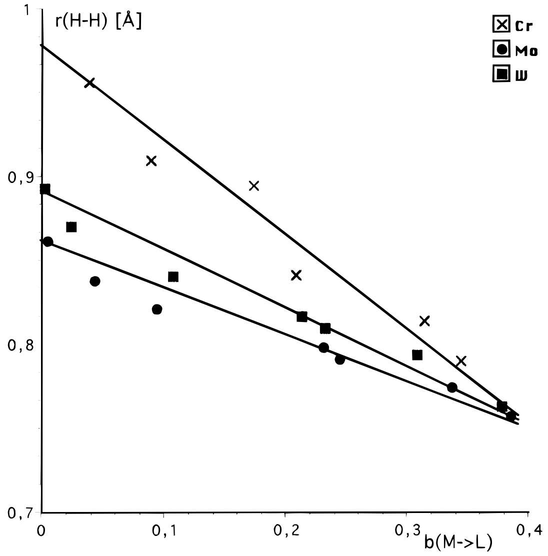

Figure 3. Calculated bond lengths *r*(H−H) (Å) in the complexes $ML(CO)_4(H_2)$ and the $(CO)_5M \rightarrow L$ back-donation at the MP2/II level of theory.

observed for the $(CO)_5M \leftarrow L$ donation, however. Figure 3 shows a plot of the calculated H−H distances of $ML(CO)_4(H_2)$ and the M → L back-donation as given by the CDA results. There is clearly a correlation between the back-donation and the H−H distance; i.e., ligands L that are strong acceptors yield a short H−H bond length. Since the H−H distances are an indicator of the $M-(H_2)$ bond strength (see Figure 2), it follows that ligands in a position trans to the (H_2) substituent that are strong acceptors tend to weaken the $M-(H_2)$ bond, while ligands that are poor acceptors tend to strengthen the $M-(H_2)$ bond.

The results support the classical picture of ligands that are competing for electron density of the transition metal. As we have shown before,[26] back-donation in $M(CO)_5L$ complexes involves mainly π-orbitals. The competition for π-electron density becomes obvious from the results shown in Table 3, where the CDA partitioning scheme has been applied to the $ML(CO)_4-H_2$ bonds. In all cases, $(H_2) \rightarrow M$ donation *d* is larger than $M \rightarrow H(_2)$ back-donation *b*. However, there are large differences in the absolute numbers. The values for *b* cover a range from 0.015 electron in $[MoNO(CO)_4(H_2)]^+$ up to 0.586 electron in the classical dihydride compound $[WF(CO)_4(H)_2]^-$. In the latter case, back-donation is very large causing the cleavage of the H−H bond. Figure 4 shows the correlation between the $(CO)_5M \rightarrow L$ back-donation and the $L(CO)_4M \rightarrow (H_2)$ back-donation. The diagram given by the CDA results clearly demonstrates that the $M \rightarrow (H_2)$ back-donation competes with the M → L back-donation.

Table 3. Results of the Charge Decomposition Analysis of $ML(CO)_4-H_2$ Complexes: Calculated $H_2 \rightarrow M$ Donation *d*, $M \rightarrow H_2$ Back-Donation *b*, and $M \leftrightarrow H_2$ Repulsive Polarization *r* at MP2/II

M	L	*d*	*b*	*r*
Cr	CO	+0.393	+0.143	−0.147
Mo		+0.315	+0.105	−0.117
W		+0.349	+0.129	−0.132
Cr	SiO	+0.236	+0.312	−0.225
Mo		+0.351	+0.083	−0.126
W		+0.431	+0.108	−0.139
Cr	CS	+0.308	+0.080	−0.122
Mo		+0.314	+0.053	−0.083
W		+0.399	+0.088	−0.098
Cr	CN^-	+0.475	+0.240	−0.229
Mo		+0.330	+0.179	−0.152
W		+0.427	+0.237	−0.155
Cr	NC^-	+0.488	+0.276	−0.303
Mo		+0.362	+0.222	−0.175
W		+0.475	+0.281	−0.170
Cr	NO^+			
Mo		+0.373	+0.015	−0.053
W		+0.436	+0.028	−0.062
Cr	N_2	+0.488	+0.146	−0.199
Mo		+0.408	+0.130	−0.141
W		+0.470	+0.169	−0.144
Cr	H^-	+0.312	+0.267	−0.239
Mo		+0.243	+0.173	−0.149
W		+0.376	+0.235	−0.151
Cr	F^-			
Mo		+0.372	+0.258	−0.205
W		+0.835	+0.586	−0.179
Cr	Cl^-			
Mo		+0.310	+0.246	−0.207
W		+0.828	+0.580	−0.184
Cr	PH_3	+0.225	+0.171	−0.282
Mo		+0.333	+0.123	−0.151
W		+0.432	+0.157	−0.152

Our study focused so far on the influence of the ligands L upon the structures and bond energies of the $ML(CO)_4(H_2)$ dihydrogen complexes. An important question concerns the existence of and possible equilibrium with isomeric dihydride complexes $ML(CO)_4(H)_2$. Four qualitatively different situations can be envisaged for the equilibrium between the two types of structures. The four possibilities are schematically shown in Figure 5. There is the possibility of an equilibrium between the dihydrogen complex and the dihydride where either the former (class a) or the latter (class c) is more stable. The other possibilities are that only the dihydrogen complex (class b) or the dihydride (class d) is a minimum on the ground-state potential energy surface.

As shown above, the geometry optimizations of the dihydrogen complexes $[WF(CO)_4(H_2)]^-$ and $[WCl(CO)_4(H_2)]^-$ gave the repsective dihydride structures as the

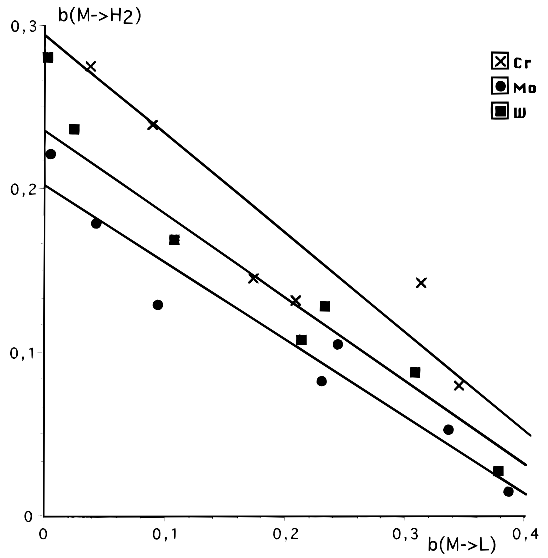

Figure 4. Calculated $(CO)_5M \rightarrow L$ back-donation and $L(CO)_4M \rightarrow H_2$ back-donation at MP2/II.

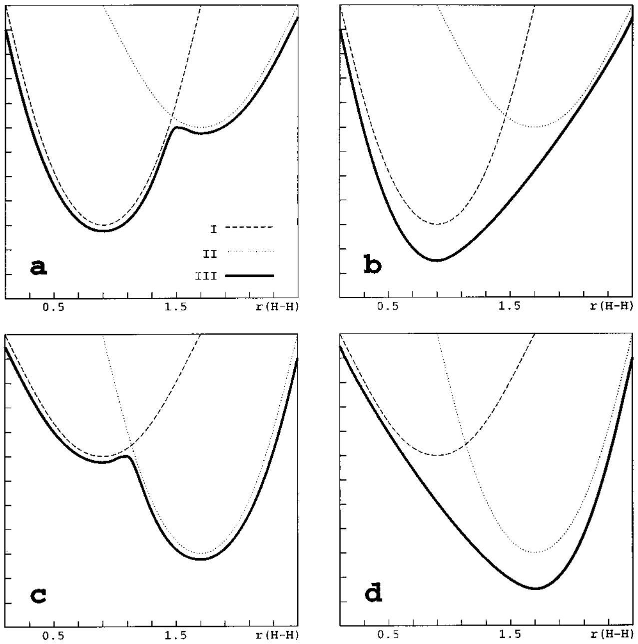

Figure 5. Schematic diagram of the possible forms for the potential energy surface (III) along the r(H−H) coordinate constructed from two idealized hypothetical potentials I and II.

only energy minimum structures. It follows that these two molecules are examples for class d compounds. We searched the potential energy surface of the other compounds for the possible existence of dihydride structures as isomeric forms. The results are shown in Table 4. At the MP2/II level of theory, most of the compounds calculated here belong to class b; i.e., the dihydrogen forms are the only energy minimum structures. Five molecules were found that have a dihydride form as a second energy minimum structure. The hydride complexes $[W(CN)(CO)_4(H)_2]^-$, $[W(NC)(CO)_4(H)_2]^-$, $[CrH(CO)_4(H)_2]^-$, and $[MoH(CO)_4(H)_2]^-$ are slightly (2−5 kcal/mol) higher in energy than the respective dihydrogen complex, while $[WH(CO)_4(H)_2]^-$ is 2.1 kcal/mol more stable the $[WH(CO)_4(H_2)]^-$ (Table 4).

Table 4. Calculated Bond Lengths (Å) of the Dihydride Complexes $ML(CO)_4(H)_2$ at MP2/II, Relative Energies ΔE (kcal/mol) with Respect to $ML(CO)_4(H_2)$, and Classification of the Potential Surfaces As Given by Figure 4

M	X	r(M−H)	r(H−H)	ΔE	class[a]
Cr	CO				b
Mo					b
W					b
Cr	SiO				b
Mo					b
W					b
Cr	CS				b
Mo					b
W					b
Cr	CN^-				b
Mo					b
W		1.747	1.846	3.0	a
Cr	NC^-				b
Mo					b
W		1.735	1.697	2.4	a
Cr	NO^+				b
Mo					b
W					b
Cr	N_2				b
Mo					b
W					b
Cr	H^-	1.542	1.797	3.9	a
Mo		1.753	2.055	4.9	a
W		1.769	2.117	−2.1	c
Cr	F^-				b
Mo					b
W		1.741	1.756		d
Cr	Cl^-				b
Mo					b
W		1.727	1.693		d
Cr	PH_3				b
Mo					b
W					b

[a] See Figure 4.

Summary

This study has shown that variation of the trans ligand L in the complexes $ML(CO)_4H_2$ critically determines the coordination of the dihydrogen moiety. Strong acceptor ligands such as NO^+ weaken the M−(H_2) bond and destabilize the oxidative addition of dihydrogen. Weak acceptor ligands like CN^- increase the M−(H_2) bond energy and favor classical dihydride coordination. The analysis of the ab initio wave functions using the CDA method shows that there is a correlation between the calculated M → L acceptor strength b and the M−(H_2) geometries, bond energies, and nonclassical stabilizations.

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