Nature of the Transition-Metal−η^2-H_2 Bond in $TM(CO)_3X_2(\eta^2\text{-}H_2)$ (TM = Cr, Mo, W; X = CO, PH_3, PCl_3, PMe_3) Complexes[†]

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Quantum-chemical calculations at the gradient-corrected DFT level using BP86 of the structures and bond dissociation energies of the title compounds are reported. The nature of the metal−H_2 bonding is quantitatively analyzed with an energy decomposition method. It is found that the metal−H_2 bonds in $TM(CO)_5H_2$ are ~47% covalent and ~53% electrostatic. Two-thirds of the covalent interactions come from $TM \leftarrow \sigma(H_2)$ σ donation, while one-third is due to $TM \rightarrow \sigma^*(H_2)$ π back-donation. Substitution of two CO ligands of the tungsten complex cis to H_2 by PR_3 (R = H, Cl, Me) leads to stronger W−H_2 interactions. The electrostatic and covalent bonding both increase in the PR_3-substituted species. Inspection of the covalent term shows that the $W \rightarrow \sigma^*(H_2)$ π back-donation becomes stronger when CO is substituted by PR_3. The change of the ΔE_π values follows closely the change of the total interaction energy ΔE_{int}. The changes in ΔE_{int} upon rotating the H_2 ligand in $W(CO)_3(PR_3)_2H_2$ also correlate quantitatively with the strength of the $W \rightarrow \sigma^*(H_2)$ π back-donation. Thus, the changes in the metal−H_2 bonding situation which are invoked by different substituents and by rotation of the H_2 ligand can be explained with the π contribution of the covalent bonding.

Introduction

Transition-metal (TM) dihydrogen complexes, also referred to as nonclassical hydrides, are formed between H_2 and the metal center without breaking the hydrogen−hydrogen bond. Since the first isolation of a $TM(\eta^2\text{-}H_2)$ complex by Kubas in 1984, $[W(CO)_3(PR_3)_2H_2]$ (R = cyclohexyl, isopropyl),[1] several representatives have been synthesized,[2,3] and they have become an important class of compounds in inorganic and organometallic chemistry.[4] Such complexes are often involved in catalytic hydrogenation reactions, and even their occurrence in biological reactions has been proposed.[5] The structural and bonding properties of TM−dihydrogen complexes have been the subject of numerous experimental[1,6−15] and theoretical[4,16−30] studies. The chemistry of dihydrogen complexes has been reviewed by Heinekey and Oldham[4] and more recently by Kubas.[31] Reviews about theoretical studies of transition-metal dihydrogen

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complexes have been given by Burdett et al.[32] and by Maseras et al.[33]

The bonding in TM(η^2-H_2) complexes is readily understood in terms of the Dewar–Chatt–Duncanson model[34,35] with donation of charge from the occupied σ-(H_2) HOMO to empty d orbitals of the metal and back-donation from occupied d orbitals to the σ^*(H_2) LUMO. Systematic theoretical studies have shown that the TM–H_2 bonding is strongly influenced by the nature of the metal center as well as by ancillary and trans ligands.[25–27] Recently, we investigated the molecular geometries and the TM–H_2 bond dissociation energies of TML(CO)$_4$H$_2$ (TM = Cr, Mo, W; L = CO, SiO, CS, CN^-, NC^-, NO^+, N_2, H^-, F^-, Cl^-, PH_3)[25,27] complexes. It was found that strong σ-donor ligands in the trans position enhance the TM–H_2 bonding, while strong π-acceptors weaken it. The distance r(H–H) and the TM–H_2 bond dissociation energies correlated well with the donor–acceptor capabilities of L, characterized by the CDA partitioning model.[36] Li and Ziegler investigated the effect of ancillary ligands on the TM-H_2 interaction.[26a] The energy analysis of the $Mo(CO)_n(PH_3)_{5-n}H_2$ (n = 1, 3, 5) series using the extended transition state (ETS) energy decomposition scheme[37] revealed a significant decrease of the Mo(d)$\rightarrow\sigma^*$(H_2) π back-donation[38] with the number of strong π-acceptor (CO) ligands, which was compensated by a simultaneous increase in the Mo(d)$\leftarrow\sigma$(H_2) σ-donation. The net effect was a nearly constant interaction energy of the $Mo(CO)_n(PH_3)_{5-n}$–H_2 bond.[26a] The complexes $TM(PH_3)_n(CO)_{5-n}(H_2)$ have been studied with quantum-chemical methods by Tomàs et al.[26b,c] The authors investigated the factors which govern the interactions betwen the dihydrogen ligand and the metal fragment.

The goal of the present study is a quantitative assessment of the nature of the TM–H_2 bonding in selected $TM(CO)_3X_2H_2$ derivatives, with TM = W, Mo, Cr and ancillary positioned X = CO, PH_3, PCl_3, PMe_3. The above representative set includes both different metal centers and ligands with gradually changing donor–acceptor character. The primary tool of our quantitative analysis is the ETS method,[37] which gives well-defined energy terms for the metal–ligand electrostatic and orbital interactions. Within the latter, the donation and back-donation processes can be separated according to the symmetry of the interacting orbitals. The present work is part of our systematic studies where we analyze the nature of the chemical bond in donor–acceptor complexes of transition metals[39,60] and main-group elements.[40] The previous investigations have recently been summarized in a review article.[41]

Our discussion is divided into two parts. First, we investigate the influence of the metal center on the energetics and donor–acceptor interactions on the basis of the $TM(CO)_5H_2$ (TM = Cr, Mo, W) model compounds. In the second part, the effect of ancillary ligands on the bonding properties is evaluated in $W(CO)_3X_2H_2$ (X = PH_3, PCl_3, PMe_3) complexes with X placed on opposite sites of the metal center. For each complex two structures, with H_2 parallel (||) and perpendicular ($\perp$) to the P–W–P "axis", are investigated.

As mentioned above, some model compounds have already been investigated at various levels of theory.[25–27] The complexes $Mo(CO)_5H_2$ and $W(CO)_3(PH_3)_2H_2$ have even been studied by means of the ETS method.[26a] However, the previous energy analysis used a questionable division of the energy terms, where the electrostatic attraction and the Pauli repulsion are added to a term called steric energy. This is not a meaningful division, because the steric energy which is defined in this way has nothing to do with the steric repulsion of substituents which is generally considered as steric energy. In addition, the information about the strength of the electrostatic attraction is lost. We suggest instead that the latter term should be used together with the orbital interaction term in order to estimate the ratio of electrostatic and covalent bonding.[39–41]

Computational Details

The calculations were performed at the nonlocal DFT level of theory using the exchange functional of Becke[42] and the correlation functional of Perdew[43] (BP86). Scalar relativistic effects have been considered using the zero-order regular approximation (ZORA).[44,45] Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations.[46] The basis sets for the metal atoms have triple-ζ quality augmented with (n)p (Cr) and (n)p and (n + 1)f (Mo, W) polarization functions. Triple-ζ basis sets augmented by two sets of polarization functions were used for the other atoms: i.e., 2p and 3d on hydrogen and 3d and 4f on the remaining main-group elements. This basis set combination is denoted as basis TZP. The $(n-1)s^2$ and $(n-1)p^6$ core electrons of the main-group elements and the $(n-2)s^2$, $(n-2)p^6$, and $(n-1)d^{10}$ core electrons of Mo and W were treated by the frozen-core approximation.[47] An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[48] Unless otherwise stated, all calculated data in this paper have been obtained at the BP86/TZP level of theory. The calculations were carried out with the program package ADF2.3.[49,50]

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The bonding interactions between the TM−carbonyl fragments and H_2 have been analyzed by means of the energy decomposition scheme ETS, developed by Ziegler and Rauk[37] and incorporated in ADF2.3. The bond dissociation energy ΔE ($=-D_e$) between two fragments A and B (in the present case $TM(CO)_5$ or $W(CO)_3X_2$ and H_2) is partitioned into several contributions, which can be identified as physically meaningful entities. First, ΔE is separated into the two major components ΔE_{prep} and ΔE_{int}:

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \tag{1}$$

ΔE_{prep} is the energy necessary to promote the fragments A and B from their equilibrium geometry and electronic ground state to the geometry and electronic state in the compound AB. ΔE_{int} is the instantaneous interaction energy between the two fragments in the molecule. The latter quantity will be in the focus of the present work. The interaction energy can be divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \tag{2}$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments, which is calculated with the frozen electron density distribution of A and B in the geometry of the complex AB. The second term in eq 2, ΔE_{Pauli}, refers to the repulsive interactions between the fragments, which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. The term comprises the four-electron destabilizing interactions between occupied orbitals. ΔE_{Pauli} is calculated by enforcing the Kohn−Sham determinant of AB, which results from superimposing fragments A and B, to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb}, is calculated in the final step of the ETS analysis when the Kohn−Sham orbitals relax to their optimal form. This term can be further partitioned into contributions by the orbitals which belong to different irreducible representations of the interacting system. Note that the polarization of the fragments is included in the latter term, because the ΔE_{elstat} values are calculated using the frozen electron densities of the fragments.[51]

Computations of the vibrational frequencies (in order to check the character of the stationary points) and natural charges[52] were performed with the program package Gaussian 98.[53] These calculations were carried out at BP86 with our standard basis set II[54] using BP86/II optimized geometries.

Results and Discussion

1. $TM(CO)_5H_2$ Complexes. The optimized structures of $TM(CO)_5H_2$ (TM = Cr, Mo, W) complexes are depicted in Figure 1, while the results of the energy decomposition analysis and the natural charges are compiled in Table 1. In agreement with previous studies at the MP2 level, the most favored orientation of the H_2 ligand is the eclipsed conformation with respect to the cis carbonyl groups.[25] That the orientation of H_2 has a very small influence on the strength of the TM−H_2 bonds (characteristic for σ interactions) is shown by the very low energy barrier for rotation around the TM−H_2 axis.[25] The overall symmetry of the complexes is C_{2v}, with the $TM(CO)_5$ moieties having a near-square-pyramidal arrangement. A comprehensive comparison of the computed geometrical parameters with experimental ones of related complexes has been performed in ref 25. Therefore, we focus here on the characteristics of bonding between $TM(CO)_5$ and H_2.

As obtained previously for the computed[25−27,55] as well as experimental[56] dissociation energies of such complexes, the total interaction energies between the TM(CO)$_5$ and H_2 moieties exhibit a typical V-like trend along the metal triad (cf. Table 1).[57] It was pointed out by Li and Ziegler[26] that the reason for this feature is the importance of relativistic effects, especially the relativistic destabilization of 5d orbitals of third-row transition metals. The trend in the interaction energies is well reflected in both the computed H−H bond lengths and the TM−H_2 distances. Donor−acceptor interactions, especially the back-donation to the $\sigma^*(H_2)$ orbital, lead to a lengthening of the H−H bond with respect to the free H_2 molecule. Thus, the longest H−H distance can be observed in $W(CO)_5H_2$ and the shortest in Mo(CO)$_5H_2$. The computed trend in the H−H bond distance is in accordance with the variation of the H−H stretching frequencies of the $TM(CO)_5H_2$ complexes measured by IR spectroscopy in liquid Xe solution.[58]

We note that while the same trend has been reported for the dissociation energy and TM−H_2 distances of TM(CO)$_3(PH_3)_2H_2$ (TM = Cr, Mo, W) complexes, the H−H bond length in the latter compounds gradually increases down the triad.[26] The increasing trend has also been reported for the NMR estimated H−H distances in TM(CO)$_3(PR_3)_2H_2$ (TM = Cr, Mo, W) complexes.[31] This indicates that ancillary ligands can considerably alter the donor−acceptor interactions between H_2 and the metal.

The ETS results in Table 1 show that all three components of ΔE_{int} vary parallel with the total interaction energy. Due to the larger TM−H_2 distance in Mo(CO)$_5H_2$, both the repulsive Pauli interaction and the attractive electrostatic and orbital interactions are considerably weaker in this complex. The larger decrease in the attractive interactions as compared to that in the Pauli forces leads to ca. 3 kcal/mol destabilization with respect to $Cr(CO)_5H_2$ and $W(CO)_5H_2$. On the other

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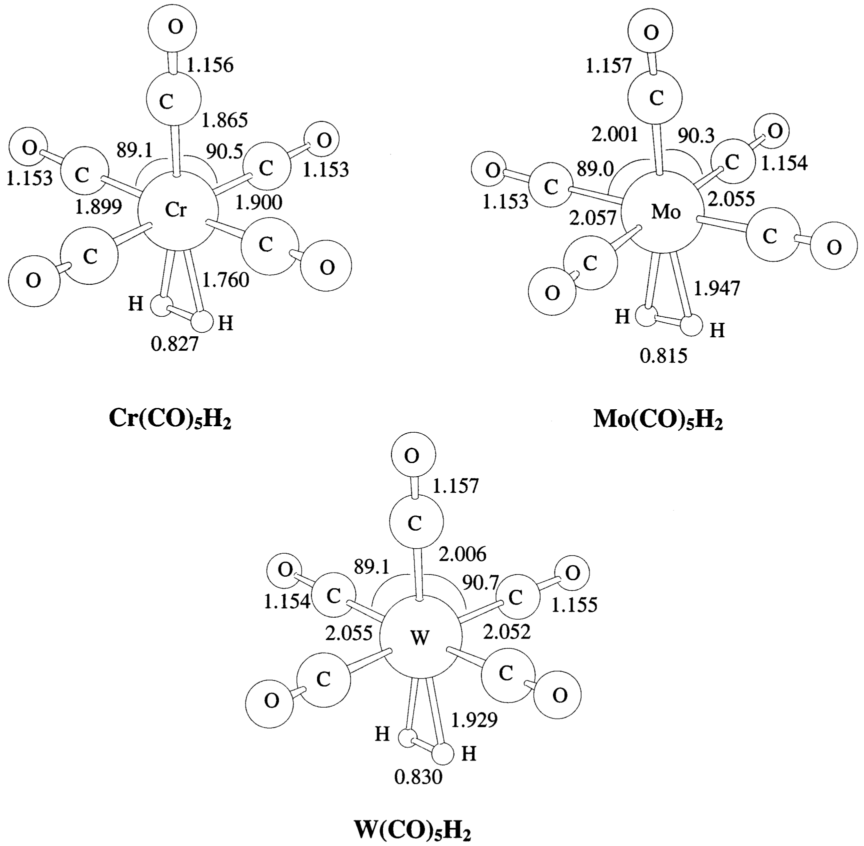

Figure 1. Optimized geometries of $TM(CO)_5H_2$ (TM = Cr, Mo, W) at the BP86/TZP level. Bond distances are given in Å and angles in deg.

Table 1. Results of the Energy Decomposition Analysis (kcal/mol) and Partial Charges q (e) of $TM(CO)_5H_2$ Complexes[a]

	$Cr(CO)_5-H_2$	$Mo(CO)_5-H_2$	$W(CO)_5-H_2$
$\Delta E(=-D_e)$	−18.7	−16.0	−19.4
ΔE_{prep}	2.5	2.3	3.2
ΔE_{int}	−21.2	−18.3	−22.6
ΔE_{Pauli}	51.6	42.8	54.0
ΔE_{elstat}	−38.8 (53.2%)[b]	−32.4 (53.1%)[b]	−41.6 (54.4%)[b]
ΔE_{orb}	−34.0 (46.8%)[b]	−28.6 (46.9%)[b]	−34.9 (45.6%)[b]
ΔA_1	−21.8	−18.0	−22.3
ΔA_2	−0.1	0.0	0.0
ΔB_1	−10.8	−9.3	−11.3
ΔB_2	−1.3	−1.2	−1.3
ΔE_σ	−21.9 (64.3%)	−18.1 (63.1%)	−22.3 (63.9%)
ΔE_π	−12.1 (35.6%)	−10.5 (36.8%)	−12.6 (36.0%)
q_M[d]	−1.37	−1.03	−0.78
q_{H_2}[d]	0.22	0.18	0.18

[a] Calculated at the BP86/TZP level. For the definition of the individual ΔE contributions see text. [b] Percentage of the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [c] Percentage of the total orbital interactions ΔE_{orb}. [d] Natural charges.

hand, the ratios of the electrostatic and orbital interactions, and those of the components of ΔE_{orb}, are rather similar in all three complexes. Thus, the nature of the $TM-H_2$ bonding in $TM(CO)_5H_2$ is slightly more electrostatic (53.1−54.4%) than covalent. We want to point out that the high electrostatic character and the trend of the electrostatic attraction is not obvious from the calculated partial charges. Table 1 shows that the NBO charges of the metal and the H_2 ligand suggest that the electrostatic attraction in $Cr(CO)_5H_2$ should be much higher than in $W(CO)_5H_2$. It has been pointed out by us in previous publications[39a,b,41] that atomic partial charges are not a reliable source for estimating electrostatic interactions, because the electronic charge distribution of the atoms in a molecule is in most cases highly anisotropic. The electrostatic interaction between the H_2 ligand and the $TM(CO)_5$ fragment comes mainly from the attraction between the electronic charge of the dihydrogen ligand, which serves as a Lewis base, and the positively charged nucleaus of the metal. This becomes obvious by the topological analysis of the electron density distribution of the molecules which has earlier been published by us.[25] There is an area of *local charge depletion* of the overall negatively charged metal atom and an area of *local charge concentration* of an overall positively charged ligand which leads to strong electrostatic attraction.[59] The calculated partial charges give the wrong impression that the electrostatic attraction comes from the negatively charged metal atom and the positively charged ligand. A similar situation has been described for other complexes.[39b,41]

On the basis of the energy components we can quantify the relative importance of donation and back-donation for the $TM-H_2$ interaction strength. Since the C_{2v} point group is preserved during the formation of the $TM(CO)_5H_2$ complexes, the energy contribution from the A_1 representation accounts for the donation from $\sigma(H_2)$ to the metal center, whereas the contribution from the B_2 representation can be attributed to the $d_\pi \rightarrow \sigma^*(H_2)$ back-donation. According to the data in Table 1, the σ donation dominates over the π back-donation in the $TM(CO)_5H_2$ complexes. The energy contribution of the former interaction is nearly twice of that of the π back-

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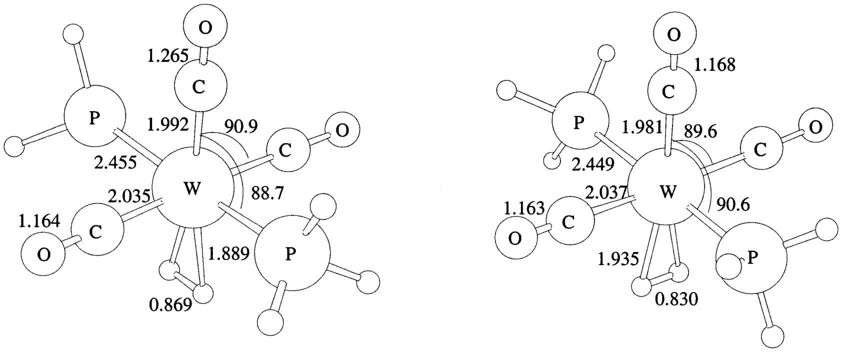
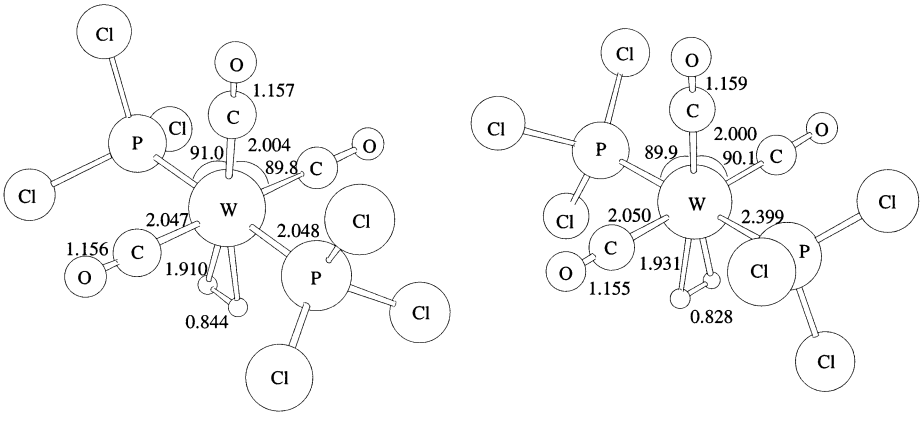
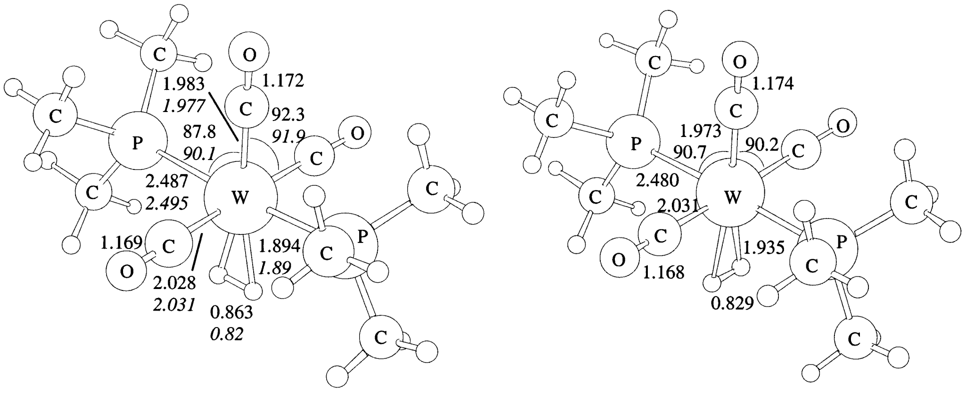
[59] See Figure 2 in ref 25.



$W(CO)_3(PH_3)_2H_2$ (||) **$W(CO)_3(PH_3)_2H_2$ (⊥)**



$W(CO)_3(PCl_3)_2H_2$ (||) **$W(CO)_3(PCl_3)_2H_2$ (⊥)**



$W(CO)_3(PMe_3)_2H_2$ (||) **$W(CO)_3(PMe_3)_2H_2$ (⊥)**

Figure 2. Optimized geometries of $W(CO)_3(PR_3)H_2$. Bond distances are given in Å and angles in deg. Experimental values of $W(CO)_3(PiPr_3)H_2$ are given in italics.

donation. This phenomenon is reasonable in $TM(CO)_5L$ complexes because of the strong π-acceptor character of the CO groups which compete with the poor π-acceptor ligand H_2. Our previous study on various $TML(CO)_4H_2$ complexes showed the importance of the trans ligand for the magnitude of the metal→$\sigma^*(H_2)$ π back-donation.[27] This can also be seen in the consistently longer C−O bond lengths of the trans CO's with respect to those of the cis ones (cf. Figure 1), as an indicator of the stronger π back-donation to the former groups. The stronger donor−acceptor interactions with the trans CO are also manifested in their shorter TM−C bonds. We also want to point out that the previous analysis of the electronic charge distribution in terms of σ donation and π back-donation in $TM(CO)_5H_2$ using the CDA method revealed that the metal→$\sigma^*(H_2)$ π back-donation is significantly smaller by a factor of 2.5−3 than the metal←$\sigma(H_2)$ σ donation.[25]

2. $W(CO)_3X_2H_2$ Complexes. The effect of ancillary ligands on the metal−H_2 donor−acceptor interactions has been investigated in model $W(CO)_3X_2H_2$ derivatives. The substituents on P in the ligand X were selected to cover both electronegative (Cl) and electron-donating (Me) properties. This results in a gradually increasing donor character of the ligands $PMe_3 > PH_3 > PCl_3$.[60] On the other hand, their π-acceptor character varies as

Table 2. Results of the Energy Decomposition Analysis (kcal/mol) and Partial Charges *q* (e) of $W(CO)_3X_2H_2$ Complexes[a]

	X						
	CO	PH_3(‖)	PH_3(⊥)	PCl_3(‖)	PCl_3(⊥)	PMe_3(‖)	PMe_3(⊥)
$\Delta E(=-D_e)$	−19.4	−19.3	−17.7	−16.0	−16.9	−19.7	−17.1
ΔE_{prep}	3.2	8.3	3.5	8.1	3.9	5.9	3.4
ΔE_{int}	−22.6	−27.6	−21.2	−24.1	−20.8	−25.6	−20.5
ΔE_{Pauli}	54.0	66.0	54.4	61.6	57.5	65.3	54.9
ΔE_{elstat}	−41.6 (54.4%)[b]	−50.8 (54.3%)[b]	−41.8 (55.3%)[b]	−45.8 (53.5%)[b]	−42.3 (54.0%)[b]	−49.8 (54.8%)[b]	−42.2 (55.9%)[b]
ΔE_{orb}	−34.9 (45.6%)[b]	−42.7 (45.7%)[b]	−33.8 (44.7%)[b]	−39.9 (46.5%)[b]	−36.0 (46.0%)[b]	−41.0 (45.2%)[b]	−33.3 (44.1%)[b]
ΔA_1	−22.3	−23.1	−20.4	−24.2	−23.4	−22.1	−19.6
ΔA_2	0.0	−0.1	−0.1	−0.1	−0.1	−0.1	−0.1
ΔB_1	−11.3	−18.2	−11.6	−14.3	−11.1	−17.5	−11.9
ΔB_2	−1.3	−1.3	−1.6	−1.3	−1.5	−1.3	−1.8
ΔE_σ	−22.3 (63.9%)[c]	−23.2 (54.2%)[c]	−20.5 (60.6%)[c]	−24.3 (60.8%)[c]	−23.5 (65.1%)[c]	−22.2 (54.0%)[c]	−19.7 (58.9%)[c]
ΔE_π	−12.6 (36.0%)[c]	−19.5 (45.7%)[c]	−13.2 (39.3%)[c]	−15.6 (39.1%)[c]	−12.6 (34.9%)[c]	−18.8 (45.9%)[c]	−13.7 (41.0%)[c]
q_M[d]	−0.78	−1.03	−1.01	−1.08	−1.08	−1.01	−1.01
q_{H_2}[d]	0.18	0.16	0.17	0.20	0.20	0.16	0.16

[a] Calculated at the BP86/TZP level. For the definition of the individual ΔE contributions see text. The two structures of $W(CO)_3X_2-H_2$ are characterized by the orientation of the H−H bond which is parallel (‖) or perpendicular (⊥) to the P−W−P axis (cf. Figure 2). [b] Percentage of the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [c] Percentage of the total orbital interactions ΔE_{orb}. [d] NBO charges.

$PCl_3 > PH_3 \approx PMe_3$, as determined in $W(CO)_5X$ complexes.[60] Among the title complexes, computed data are available for $W(CO)_3(PH_3)_2H_2$, obtained at a somewhat less sophisticated level of theory.[26] In comparison to these previous data, our computed interaction energy is larger by 0.8 kcal/mol, while the bond lengths differ up to 0.02 Å and the bond angles up to 2°.

The optimized geometries of the $W(CO)_3X_2H_2$ complexes are depicted in Figure 2. In the global minimum structures of $W(CO)_3(PH_3)_2H_2$ and $W(CO)_3(PMe_3)_2H_2$ the H_2 bond vector is aligned along the P−W−P axis (‖; cf. Figure 2), whereas the alignment along the C−W−C axis (⊥) corresponds to a first-order saddle point. On the other hand, the global minimum of the PCl_3 complex is the ⊥ conformer, whereas $W(CO)_3(PCl_3)_2H_2$ (‖) is a slightly higher lying local minimum. The interaction energy between the $W(CO)_3(PCl_3)_2$ and H_2 fragments is considerably larger in the latter conformer (cf. Table 2). An additional structural feature of the title complexes are the different relative orientations of the PR_3 groups favored in the various complexes (cf. Figure 2). We note that some small imaginary frequencies were obtained for the C_{2v} constrained $W(CO)_3(PCl_3)_2H_2$ (‖) and $W(CO)_3(PMe_3)_2H_2$ (‖) conformers associated with the rotation of the PR_3 ligands. They, however, should not influence the analysis of the $W-H_2$ bonding.

Experimental geometries are available (X-ray and neutron diffraction)[1] for the complex $W(CO)_3(P\textit{i}Pr_3)_2H_2$. The experimental data may be compared with the calculated data for $W(CO)_3(PMe_3)_2H_2$. Figure 2 shows that there is an excellent agreement between the experimental and computed geometries. The deviations between the theoretical and experimental interatomic distances are <0.01 Å, except for a slightly larger difference in the H−H bond distance. The good agreement indicates the reliability of the computational level.

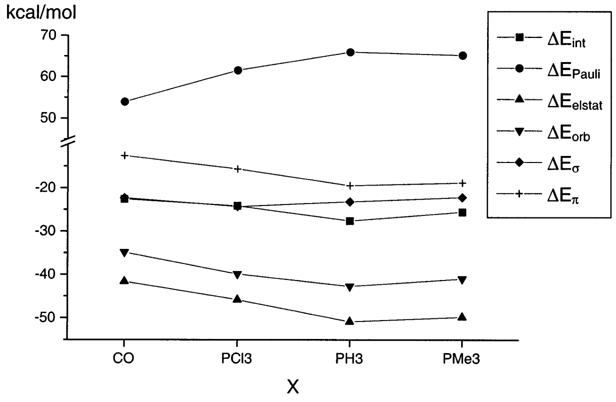


Figure 3. Trend of the energy contributions to the metal−H_2 interaction energy ΔE_{int}.

The most important question of this section is how the nature of the $W-H_2$ bonding varies with different ligands. The results of the energy analysis are given in Table 2. We discuss first the ‖ structures, as they are the well-defined global minima in most complexes.

As expected, substitution of the strong π-acceptor COs by the relatively poor π-acceptor phosphanes increases the $W-H_2$ interaction energy. In agreement with the very weak π-acceptor character of PH_3 (vide supra), the $W-H_2$ interaction becomes the strongest in $W(CO)_3(PH_3)_2H_2$. On the other hand, the comparatively strong[51] π-acceptor character of PCl_3 compared with that of the other phosphanes yields the weakest $W-H_2$ interaction in $W(CO)_3(PCl_3)_2H_2$.

Inspection of the energy contributions to the total interaction energy shows that the relative strengths of ΔE_{elstat} and ΔE_{orb} remain nearly the same in the complexes $W(CO)_3X_2H_2$ for X = CO and X = PR_3 (Table 2). The absolute values of the attractive interations E_{elstat} and ΔE_{orb} are higher for X = PR_3 than for X = CO, but also the values for E_{Pauli} are larger in the former complexes than in the latter. Figure 3 shows nicely that the trend of the E_{elstat} and ΔE_{orb} values follows closely the trend of E_{int}. However, there is a noteworthy difference between the σ and π contributions to the two types of complexes. The increase of the ΔE_{orb} term in the PR_3 complexes is mainly due to the stronger π contributions (Table 2), while the ΔE_σ values change

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very little. In fact, the change of the ΔE_π values follows closely the change of the total interaction energy ΔE_{int}. This is clearly shown in Figure 3, where the trend of ΔE_π is graphically displayed. The calculations show clearly that there is a correlation between the energy contribution of the W→σ*(H_2) π back-donation and the total interaction energy.

Inspection of the energy analysis of $W(CO)_3(PR_3)_2H_2$ (⊥) complexes explains the weaker interaction energy upon rotation of the H_2 ligand by 90°. Together with the W−H_2 distances, all the energy contributions become nearly the same as in $W(CO)_5H_2$. There are slight deviations in the PMe_3 derivative as a result of its strong σ-donation character. Thus, with regard to the electronic effects, it is the strength of the W−σ*(H_2) π back-donation which correlates with the H_2 rotation.

Summary and Conclusion

The results of this work can be summarized as follows.

The bonding analysis of the metal−H_2 bonds in TM(CO)$_5H_2$ shows that the attractive interactions are ∼47% covalent and ∼53% electrostatic. Two-thirds of the covalent interactions come from TM←σ(H_2) σ donation, while one-third is due to TM→σ*(H_2) π back-donation. Substitution of two CO ligands of the tungsten complex cis to H_2 by PR_3 (R = H, Cl, Me) leads to stronger W−H_2 interactions. The electrostatic and covalent bonding both incease in the PR_3-substituted species. Inspection of the covalent term shows that the W→σ*(H_2) π back-donation becomes stronger when CO is substituted by PR_3. The change of the ΔE_π values follows closely the change of the total interaction energy ΔE_{int}. The changes in ΔE_{int} upon rotating the H_2 ligand in $W(CO)_3(PR_3)_2H_2$ also correlate quantitatively with the strength of the W→σ*(H_2) π back-donation.

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