Theor Chim Acta (1994) 87: 441–452

Theoretica
Chimica Acta

The bonding in second row transition metal dihydrides, difluorides and dichlorides

Per E. M. Siegbahn

Institute of Theoretical Physics, University of Stockholm, Vanadisvägen 9, S-11346 Stockholm, Sweden

Received December 7, 1992/Accepted March 11, 1993

Summary. The dihydrides, the difluorides and the dichlorides of the second row transition metal atoms from yttrium to palladium have been studied with methods including electron correlation of all valence electrons. Comparisons are made to the previously studied corresponding diatomic systems. It is found that the general trends of the binding energies of the second hydride and halide remain the same as in the diatomic hydrides and halides. The second ligand binding energies for the dihalides thus vary much more than for the dihydrides. This is due to important attractive effects between the halide lone-pairs and empty 4*d*-orbitals to the left and strong repulsions towards occupied 4*d*-orbitals to the right. For some systems the second ligand binds much more than the first ligand, as for RuF_2 where the difference is 34.3 kcal/mol, whereas for other systems the reverse is true, as for $PdCl_2$ where the first ligand binds more than the second with 20.4 kcal/mol. The results can be explained by strong ligand field effects and differences in the atomic spectra.

Key words: Dihydrides – Difluorides – Dichlorides – Yttrium – Palladium – Bonding

1 Introduction

Hydrides and halides are common ligands in transition metal complexes. Both these types of ligands are of fundamental importance as the simplest possible covalently and ionically bound ligands, respectively. The number of both experimental and theoretical investigations of transition metal hydrides have increased recently, in particular since the recognition of nonclassical hydride complexes, containing dihydrogen ligands. That work has been the subject of a recent monograph devoted to transition metal hydrides [1], in which Bauschlicher and Langhoff has reviewed the current status of accurate theory on this subject [2]. Halides as ligands show similarities but also differences to hydride ligands. The similarities are dominating in the bonding for the complexes of the transition metals to the right in the periodic table where the bonding is more covalent. For the halides of the transition metals to the left the bonding is more ionic and there are also important effects from electron donation to empty *d*-orbitals which are not present for the hydrides. These effects were the focus of interest in a recent study of the diatomic hydrides and halides of the second row transition metal atoms [3]. That study is here followed up by a similar study of the dihydrides and dihalides. In recent systematic model studies of ligand effects in transition metal catalyzed reactions, hydrides have been used to investigate the effects of covalent ligands on the H–H and C–H bond breaking reactions [4]. Similar studies are under way where chlorides and fluorides are used to investigate the effects of a gradually increasing ionic character of the ligands, and the present study represents a first step in this direction.

The main results of the previous study of the second row diatomic transition metal hydrides and halides can be summarized as follows. The halide binding energies vary much more going from left to right in the periodic table than the hydride binding energies. The binding energy for PdH is thus 75% of the one for YH whereas the one for PdF is only 45% of the one for YF. In absolute values the differences are even more pronounced. The binding energy for PdH is 16.9 kcal/mol smaller than the one for YH whereas the binding energy for PdF is as much as 86.9 kcal/mol smaller than the one for YF. There are two major reasons for this trend. First, the bonding in the halides is more ionic due to the larger electron affinity of the halogen atoms. The ionization energy of the metal atom, which increases to the right, will therefore enter more or less directly into the final bond strength of the halides. The second origin of the trend of the binding energies is the direct interaction between the lone-pairs of the halides with the metal 4*d*-orbitals. This interaction is attractive to the left where there are empty 4*d*-orbitals but becomes repulsive to the right due to the repulsion with the increasing number of 4*d*-electrons. Based on these results a few main questions can be raised concerning the bonding in the dihydrides and dihalides. The first question is if the large difference in bond strength of the halides and the hydrides for the atoms to the left will persist also for the second ligand. Since the metal atoms to the left have already received electrons from the first halide lone-pairs, it is possible that the ability of the metal to accept electrons from the second ligand could be somewhat hampered. On the other hand, the cost of ionizing the metal atom and preparing the metal atom for the ligand field is already paid to a large extent by the first halide ligand which should help in stabilizing the second ligand. A second question in the present study concerns the effects of promotion and hybridization. In many cases the first ligand has already caused the proper hybridization on the metal which can then be used also by the second ligand. This could lead to larger binding energies for the second ligand, in particular for the hydrides where covalent effects dominate the bonding. On the other hand, competition for the available metal covalency could reduce the binding energy of the second ligand.

All of the second row transition metal dihydrides have been extensively investigated by Balasubramanian and co-workers [5–11]. With the exception of TcH_2 which was found to have a linear $^6\Sigma_g^+$ ground state, the dihydrides were found to be bent. For all these systems, except for palladium, the ground state metal atoms were found to have large barriers for insertion into the H–H bond of H_2. However, in several cases electronically excited atoms were found to insert without any barrier such as for the excited ^2F-state of the rhodium atom. Also, among other results, a surprisingly large binding energy compared to the free metal atom and H_2 was reported for TcH_2 of 27 kcal/mol. This value is much larger than the value reported in Ref. [4] of 3 kcal/mol. There has, to our knowledge, not been any similar study including electron correlation for any second row transition metal dihalide.

2 Computational details

In the calculations reported in the present paper for the dihydrides and dihalides of the second row transition metal atoms, reasonably large basis sets were used in a generalized contraction scheme. All valence electrons, except the fluorine 2*s*- and chlorine 3*s*-electrons, were correlated using size consistent methods.

For the metals the Huzinaga primitive basis [12] was extended by adding one diffuse *d*-function, two *p*-functions in the 5*p*-region and three *f*-functions, yielding a (17*s*,13*p*,9*d*,3*f*) primitive basis. The core orbitals were totally contracted [13] except for the 4*s*- and 4*p*-orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects [14]. The 5*s*- and 5*p*-orbitals were described by a double zeta contraction and the 4*d* by a triple zeta contraction. The *f*-functions were contracted to one function giving a [7*s*,6*p*,4*d*,1*f*] contracted basis. For fluorine the primitive (9*s*,5*p*) basis of Huzinaga [15] was used, contracted according to the generalized contraction scheme to [3*s*,2*p*]. One even-tempered *p*-function with exponent 0.0795 and one *d*-function with exponent 1.0 was added. For chlorine a similarly contracted basis was used based on the primitive (12*s*,9*p*) basis of Huzinaga [15], and including an even-tempered diffuse *p*-function with exponent 0.044. Two *d*-functions with exponents 0.95 and 0.32 were added [16]. For hydrogen the primitive (5*s*) basis from Ref. [17] was used, augmented with one *p*-function with exponent 0.8 and contracted to [3*s*,1*p*]. These basis sets are used in the energy calculations for all systems.

Since the present study is going to form the basis for future studies of ligand effects in larger transition metal complexes, where the basis sets described above may be too large to be practical, it is interesting to investigate smaller basis sets. Comparative calculations have therefore been done where the *d*-functions on the halides have been removed to find out if this is a sufficient description of the metal halide bonding.

In the geometry optimizations, performed at the SCF level using the GAMESS set of programs [18], somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt [19] was used. The frozen 4*s* and 4*p* orbitals are described by a single zeta contraction and the valence 5*s* and 5*p* orbitals are described by a double zeta basis and the 4*d* orbital by a triple zeta basis, including one diffuse function. The rest of the atoms are described by standard double zeta basis sets, with the chlorine core replaced by an ECP [20].

The correlated calculations were in all cases performed using the Modified Coupled Pair Functional (MCPF) method [21], which is a size-consistent, single reference state method. The zeroth order wave-function is in these cases determined at the SCF level. The metal valence electrons (4*d* and 5*s*) and the five *p*-electrons on the halides were correlated. Since the valence 2*s*-orbitals on fluorine and 3*s*-orbitals on chlorine rotated with the metal 4*p*-orbitals to the left in the row, these electrons were not correlated. Since these orbitals rotate with each other it appears that it is more consistent to consider all these electrons, or none of them, as core electrons. In addition, calculations for yttrium halides [22] have shown that a proper account of correlation of the halide *s*-electrons does not notably improve the description of the bonding in these systems. Because of the rotation between valence and core orbitals a localization of the core orbitals has to be performed and this was done using a localization procedure developed by Pettersson [23], in which $\langle r^2 \rangle$ of the core orbitals is minimized. Relativistic effects were accounted for using first order perturbation theory including the mass-velocity and Darwin terms [24].

3 Results and discussion

The main results of the present study are collected in Tables 1–3 and in Figs. 1–2. The geometries and binding energies for the dihydrides are given in Table 1. The binding energies of both the first hydrogen, ΔE_1 taken from Ref. [3], and of the second hydrogen ΔE_2, are given in the table. To get the binding energy with respect to the metal atom and H_2, the calculated binding energy of H_2 of 105.6 kcal/mol

Table 1. Bond distances (Å), bond angles, populations and binding energies (kcal/mol) for the second row transition metal dihydride systems. ΔE_1 is the binding energy in the diatomic MH systems and ΔE_2 is the binding energy of the second hydrogen in MH_2

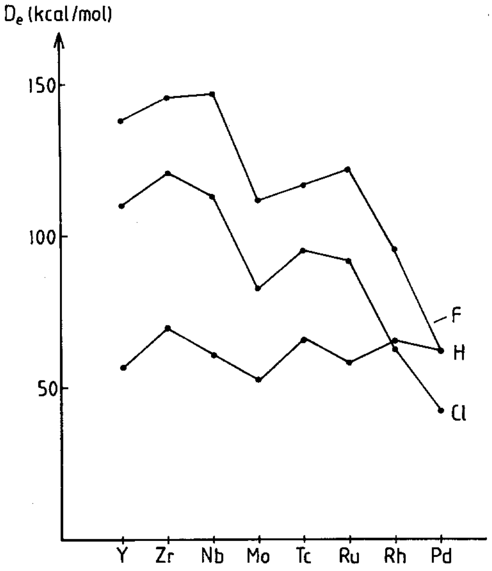
Metal (M)	State	M–H	∠(H–M–H)	M(q)	4d	5s	5p	ΔE_1	ΔE_2
Y	${}^2A_1$	2.01	119.5	+ 0.33	1.05	.99	.58	68.0	56.9
Zr	${}^3B_1$	1.93	127.6	+ 0.37	2.30	.89	.40	56.0	69.3
Nb	${}^4B_1$	1.86	125.5	+ 0.33	3.51	.80	.32	61.1	60.9
Mo	${}^5B_2$	1.76	109.3	+ 0.23	4.79	.74	.20	50.4	52.6
Tc	${}^6\Sigma_g^+$	1.84	180.0	+ 0.36	5.18	.86	.56	42.3	66.0
Ru	${}^3A_2$	1.61	81.8	+ 0.06	7.16	.60	.13	58.9	58.1
Rh	${}^2A_1$	1.56	82.7	− 0.01	8.29	.54	.13	64.1	65.2
Pd	${}^1A_1$	1.53	68.0	0.00	9.25	.55	.14	51.1	61.9

Table 2. Bond distances (Å), bond angles, populations and binding energies (kcal/mol) for the second row transition metal diflouride systems. ΔE_1 is the binding energy in the diatomic MF systems and ΔE_2 is the binding energy of the second flourine in MF_2

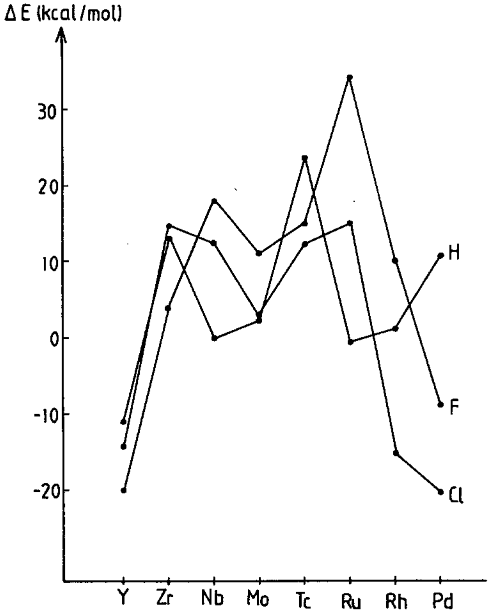
Metal (M)	State	M–F	∠(F–M–F)	M(q)	4d	5s	5p	ΔE_1	ΔE_2
Y	${}^2A_1$	2.02	121.7	+ 1.05	.78	.74	.29	158.1	137.9
Zr	${}^3\Delta_g$	1.99	180.0	+ 1.03	1.93	.73	.18	141.9	145.7
Nb	${}^4\Sigma_g^-$	1.95	180.0	+ 1.00	3.10	.63	.18	129.1	147.2
Mo	${}^5B_2$	1.96	140.1	+ 1.03	4.22	.49	.19	100.2	111.4
Tc	${}^6\Sigma_g^+$	1.99	180.0	+ 1.12	5.17	.45	.20	101.2	116.3
Ru	${}^5\Delta_g$	1.96	180.0	+ 1.06	6.31	.36	.21	87.2	121.5
Rh	${}^4\Sigma_g^-$	1.93	180.0	+ 0.96	7.48	.29	.20	85.0	95.2
Pd	${}^3\Pi_g$	1.94	180.0	+ 0.96	8.48	.28	.22	71.2	62.0

Table 3. Bond distances (Å), bond angles, populations and binding energies (kcal/mol) for the second row transition metal dichloride systems. ΔE_1 is the binding energy in the diatomic MCl systems and ΔE_2 is the binding energy of the second chlorine in MCl_2

Metal (M)	State	M–Cl	∠(Cl–M–Cl)	M(q)	4d	5s	5p	ΔE_1	ΔE_2
Y	${}^2A_1$	2.54	155.3	+ 0.86	.93	.77	.32	124.3	109.9
Zr	${}^3\Delta_g$	2.47	180.0	+ 0.86	2.10	.66	.29	106.1	120.8
Nb	${}^4\Sigma_g^-$	2.43	180.0	+ 0.84	3.28	.55	.27	101.0	113.2
Mo	${}^5B_2$	2.43	142.3	+ 0.84	4.40	.44	.27	79.7	82.5
Tc	${}^6\Sigma_g^+$	2.46	180.0	+ 0.94	5.26	.45	.30	82.8	95.0
Ru	${}^5\Delta_g$	2.42	180.0	+ 0.87	6.40	.38	.30	76.5	91.6
Rh	${}^4\Sigma_g^-$	2.38	180.0	+ 0.73	7.60	.32	.29	77.8	62.3
Pd	${}^1A_1$	2.30	98.4	+ 0.49	8.95	.28	.21	62.4	42.0



1



2

Fig. 1. Calculated bond strengths of the second ligand in the dihydrides, the difluorides and the dichlorides

Fig. 2. The difference between the second and the first bond strength for the dihydrides, the difluorides and the dichlorides

should be subtracted from the sum of these energies. The corresponding results for the difluorides are given in Table 2 and for the dichlorides in Table 3. The calculated binding energy of F_2 is 24.4 kcal/mol and for Cl_2 it is 42.8 kcal/mol. The binding energies of the second hydride, fluoride and chloride are shown in Fig. 1 and the differences between the binding energies of the second and the first ligand in Fig. 2. A figure of the binding energies of the first ligand was given in Ref. [3].

The first conclusion that can be drawn from the results in the tables is that the general trends in the binding energies of the second ligand remain the same as the ones reported earlier for the first ligand. The binding energies for the hydrides are thus still much more constant across the periodic table than those of the halides. The largest difference in binding energies going from yttrium to the left to palladium to the right is also still found for the fluorides. The detailed values of the binding energies do furthermore not show major signs of any hampered ability to accept electrons for the metals to the left. For most of the systems there are not any major signs of competing covalency effects either (although there are notable exceptions to this for some systems to the right, for example for $PdCl_2$, see below). However, these major similarities in the binding of the first and second ligand does not mean that there are not any differences at all in the bond strengths of the first and second ligand. For example, the second fluorine in RuF_2 is bound by as much as 34.3 kcal/mol more than the first fluorine and the second chlorine in $PdCl_2$ is bound by 20.4 kcal/mol less than the first chlorine. Another interesting general observation from the tables is that the differences in bond strengths between the first and second ligand show major differences between the three systems even for the same metal. For example, the second hydrogen in PdH_2 is bound by 10.8 kcal/mol more than the first hydrogen whereas the second chlorine in $PdCl_2$ is bound by 20.4 kcal/mol less than the first chlorine. All these detailed results can be understood or rationalized from a comparison of the results in the tables, from ligand field effects and from the atomic spectra of the metals and underscores the usefulness of a systematic approach where the entire row of metals is being studied.

The curves in Fig. 2 of the differences in bond strengths between the second and first ligand show some notable trends. The curves for the halides are essentially parallel and have marked peaks for ruthenium and in the region of niobium. It is interesting to note that the binding energy *difference* shows a behaviour which is similar to that predicted from ligand field theory for the *total* binding energies. If the metal σ electrons are disregarded, since they are stabilized due to efficient *sd*-hybridization for the atoms to the left, the most repulsive electrons according to ligand field theory should be the metal π-electrons. Therefore, the total binding energies are expected to show marked decreases when the π-orbitals are being occupied. Single occupation of these orbitals starts at molybdenum and double occupation at palladium. The halide curves in Fig. 2 follow these trends rather well but has a large decrease already for rhodium to the right. In order to rationalize these trends of the energy *differences*, it has to be concluded that the first ligand has in large prepared the bonding for the second ligand for ruthenium and niobium, but less so far molybdenum, rhodium and palladium. This bond preparation consists both of partly ionizing the metal and of preparing the atomic state of the metal. For example, an atomic configuration having just two singly occupied π- or two singly occupied δ-orbitals requires a preparation cost (the degenerate components are counted separately here). The spherically symmetrical atomic state consists of a linear combination of these two determinants, one with two singly occupied π- and the other one with two singly occupied δ-orbitals and only one of these determinants is stabilized by the ligand field. For niobium the first ligand has stabilized the configuration consisting of two singly occupied δ-orbitals and this is a low lying state of the niobium halide. This is not so for the rhodium halide where the ground state still has two doubly occupied π-orbitals, and where the state with two singly occupied π-orbitals is relatively highly excited. A large part of the bond-preparation therefore has to be paid by the second ligand. For ruthenium halide the ground state already has one singly occupied π-orbital and the state with two singly occupied π-orbitals is almost degenerate with the ground state. In a similar way the differences in bond strengths between the second and first ligand can be explained for all the dihalides by ligand field effects and bond preparation made by the first ligand.

There is a qualitative difference in the geometries of the dihydrides and dihalides. The dihydrides are all bent except TcH_2 while the dihalides with a few exceptions are linear. The origin of this difference is that the bonding in the dihydrides is dominantly covalent, whereas the bonding in the dihalides is dominantly ionic. The covalent bonds in the dihydrides are formed mainly from *sd*-hybrids where the ideal hybridization angle is 90 degrees. For the atoms to the left there is also a strong $4p$-mixing in the bonds, in particular for the atoms that have low-lying s^2-states. Since the ideal *sp*-hybridized bond angle is 180 degrees, increased $4p$-contribution in the bonding will lead to larger bond angles than 90 degrees for the dihydrides of the atoms to the left in the row. For the atoms to the right there is a tendency for slightly smaller bond angles than 90 degrees which can be explained by increased $4d$-mixing in the bonds. The ideal hybridization angle for two *d*-bonds is 60 degrees. The linearity of TcH_2 is explained by the strong exchange stabilization of the $4d^5$-configuration, which means that the bonds have to be formed from rather pure *sp*-hybrids which have a hybridization angle of 180 degrees, as mentioned above. Ligand field effects at the metal atom are the main reason for the linearity of the dihalides and this is much more important than the fact that direct ligand–ligand repulsion is minimized for a linear structure. As discussed above, the first ligand has in many cases partly paid the price for preparing the metal in a proper atomic state. For example, for RuF the state with two singly occupied π-orbitals is almost degenerate with the ground state. It is then clear that it is preferrable for the second fluorine in RuF_2 to bind along the axis to maximize the ligand field advantage of the interaction with these singly occupied π-orbitals. An additional reason for the linearity is that the contribution from covalency into a dominantly ionic bonding is optimized when the covalent part of the bonding is formed from *sp*-hybrids, since this leads to a mixing of ionic and covalent components with an equal number of *d*-electrons. This leads to a bonding situation close to the one for the dihydride of technetium and therefore to linear structures.

The exceptions to linearity for the dihalides are found for yttrium and molybdenum and for $PdCl_2$. The latter exception is easy to understand. Due to the higher ionization energy for the metals to the right there will be an increased tendency for covalent bonding for these metals. Also, the chlorides show an overall larger tendency for covalent bonding than the fluorides and PdF_2 is therefore found to be linear. This can not be explained by the electron affinity of the halogen atoms since the electron affinity is actually larger for chlorine, but is instead due to the much shorter bond distances for the fluorides which make electron transfer easier. It should be added that the ionic linear structure of $PdCl_2$ is only slightly higher in energy by 1.7 kcal/mol than the covalent bent structure at the present level of accuracy. The origin of the bent structure of the molybdenum halides is that for these systems there will be only one empty $4d$-orbital. Starting from the linear structure it is clear from ligand field arguments that this empty orbital will be a $4d_\pi$-orbital since the $4d_\sigma$-orbital can efficiently hybridize away through *sd*-hybridization. It is also clear from ligand field arguments that the interaction between the empty $4d_\pi$-orbital and the ligands will be maximized for a bent structure. In the case of the yttrium dihalides the only occupied $4d$-orbital will be an *sd*-hybrid pointing away from the ligands. This hybrid can point away from the ligands equally well in a bent structure as in a linear structure and the bent structure is therefore preferred since the covalency is more optimal for this structure. However, the preference for bending is quite small. For YCl_2 the barrier to linearity was computed and found to be 1.0 kcal/mol.

The general trends of the binding energies and some of the detailed differences between the bond strengths of the first and second ligand give clear indications of the major energetic effects involved in the bonding. Starting with the most ionic systems, the difluorides, it was already noted in the previous study that the interaction between the halide lone-pairs and empty $4d$-orbitals is an important attractive effect. This is seen on the very large halide-binding energies for the atoms to the left but perhaps best on the sudden decrease of the binding energy between niobium and molybdenum. The second fluoride bond strengths in YF_2, ZrF_2 and NbF_2 are very large with values in the range 138–147 kcal/mol, while the second fluoride bond strength in MoF_2 is only 111.4 kcal/mol. The repulsion towards an increased number of $4d$-electrons is clearly seen on the bond strengths going from RuF_2 to RhF_2 and to PdF_2 with second bond strengths of 121.5 kcal/mol, 95.2 kcal/mol and 62.0 kcal/mol, respectively. These effects are directly connected with the presence of the halide lone pairs and with the ionicity in the bonding and for the corresponding dihydrides they are not seen at all.

Some of the differences in bond strength between the first and second ligand in the dihydrides and dihalides can also be understood from the respective atomic and diatomic spectra. Starting from the left with yttrium, the second bond is markedly weaker than the first bond for all three systems. The reason for this is that the atom does not have to be promoted to an excited state to form the first bond but the diatomic molecule, which is a singlet in all three cases, has to be promoted to a bonding state. The excitation energy for the lowest bonding state in YF is 24.0 kcal/mol [22] which corresponds reasonably well to the difference in bond strength between the first and second fluorine of 20.2 kcal/mol. For YCl the corresponding excitation energy is somewhat smaller, 19.2 kcal/mol [22], and the difference in bond strengths is therefore also smaller, 14.4 kcal/mol. The differences between YF_2 and YCl_2 are thus well reproduced by the corresponding excitation energies for the diatomic molecules. The same argumentation does not work equally well for YH_2. The computed excitation energy for YH of 21.6 kcal/mol is much larger than the bond strength difference of 11.1 kcal/mol. The reason for this is that already to form the bond in YH, a considerable cost is paid in *sp*-hybridization in order to avoid repulsion with the covalent *d*-bond. Going over to the zirconium systems, the first hydrogen in the dihydride has essentially paid the hybridization cost for the second hydrogen since the excitation energy to a bond-prepared quartet state for ZrH is as low as 2.4 kcal/mol. This leads to a relatively large increase in bond strength for the second hydrogen of 13.3 kcal/mol. A similar increase of 14.7 kcal/mol occurs for the dichloride whereas for the difluoride which is more ionic, the gain in the already prepared hybridization for the diatomic is smaller and there is only a small increase in bond-strength of 3.8 kcal/mol.

Interesting differences between the three systems occur also for the palladium systems. For PdH_2 the second bond strength is 10.8 kcal/mol larger than the first, while for PdF_2 the difference is reversed with the second bond 9.2 kcal/mol stronger than the first. For the palladium systems the effect in the dichloride is not in between that in the dihydride and difluoride as usual but instead, the second bond strength is as much as 20.4 kcal/mol lower than the first. Even though these effects may seem irregular at first sight, they are relatively straightforward to rationalize. For PdH_2, the bonding is dominantly covalent and the bonding state is the $4d^9 5s^1$ state. This state is not the ground state of the Pd atom but there is a promotion energy of 20.3 kcal/mol which is paid by the first hydrogen. The reason the second hydrogen is not stronger bound than the first by the same amount as the promotion energy can be ascribed to some contribution of ionic bonding. The bonding in PdF and PdCl is ionic and can make use of the ground state of Pd^+ to form $^2\Sigma^+$ ground states. This state is not well prepared for ionic bonding of a second halide in a linear geometry and there is therefore a promotion energy to reach a state with a singly occupied π-orbital which is in large paid by the second halide. The bond strength of the second halide is therefore weaker than that of the first. For $PdCl_2$ the gain in this type of ionic bonding is not as large as for PdF_2, since the bond distance is larger, and the dichloride therefore prefers a bent covalent structure. It could in this context be of interest to note that relativistic effects are not decisive for which structure is the most stable one for these palladium dihalide systems. This is in contrast to the case of PdH_2, where the most stable bent minimium is only found when relativistic effects are included in the calculations [11].

The low binding energy of the bent covalent structure of $PdCl_2$ turns out to be one of the most interesting results of the present study. It appears that when there are two covalently bound ligands of which at least one prefers to bind ionically, there will be competition for the valence *s*-electrons for the atoms to the right. Since there is only one *s*-electron in the bonding state of these atoms, the s^1-state, the first ligand will bind much stronger than the second. In a preliminary study of ligand effects on some chemical reactions this effect turns out to be quite general and can explain the lowering of barriers for some olefin insertion reactions and the increase of barriers for some oxidative addition reactions.

The present results for the dihydrides can be compared to previous calculations of Balasubramanian et al. [5–11], who also studied the dihydrides of the entire second row. The assignment of ground state for all these systems is the same as obtained here, with the exception of ZrH_2. In the present study the $^3B_1$ state was found to be the ground state with the $^1A_1$ state 3.9 kcal/mol above. In Ref. [9] the $^1A_1$ state was found to be slightly lower than the other states. The most likely origin of this minor difference between the two studies is that an Effective Core Potential (ECP) retaining only the four valence electrons on zirconium was used in Ref. [9]. The SCF bond distances obtained in the present study are about 0.1 Å longer than those obtained at a correlated level in Refs. [5–11]. This may seem as a large difference but energetically the error of using SCF optimized bond distances have been found to be less than 1 kcal/mol. The present bond angles are within a few degrees of those obtained in Refs. [5–11] except for RuH_2 where the difference is 7 degrees. All these results must be considered to be in reasonable agreement, but this is not so for some of the binding energies which are consistently larger in Refs. [5–11]. For example, the binding energy of TcH_2 was found to be 27 kcal/mol and the one of YH_2 was 31 kcal/mol, with respect to ground state metal atoms and H_2. The present corresponding results are only 3 kcal/mol for TcH_2 and 19 kcal/mol for YH_2. These large differences can not be explained by differences in the level of correlation treatment used. Instead it is likely that the use of an ECP in Refs. [5–11] including only the valence 4*d*- and 5*s*-electrons is not adequate for obtaining reliable binding energies.

There are few experimental results on the systems studied here which can be compared to the present results. One exception is a determination of the ground state spin for RhH_2 in an Electron Spin Resonance (ESR) study by Van Zee et al. [25], who found the spin to be a doublet and also concluded that the molecule is bent. These results are consistent with the present assignment of the $^2A_1$ state as the ground state for this system.

Finally, an investigation has also been made of the importance for the binding energies of 3*d*-functions on the halides. This is of some fundamental interest since, in particular for the chlorides, the 3*d*-orbitals are commonly given properties which should be of chemical importance. The effect of 3*d*-functions is also of technical importance since for larger systems, including many halide ligands, the inclusion of these functions could be costly. For the monohalides a similar investigation was also performed and it was found that the effects of 3*d*-functions was very constant across the row for all these diatomic systems [3]. For the fluorides the effect of removing the 3*d*-functions was a lowering of the binding energies of 11.7 ± 1.1 kcal/mol and for the chlorides the lowering was 14.2 ± 1.1 kcal/mol. It was concluded that the effect was quite localized on the halide and that a large part of the effect was simply due to a less accurate description of the electron affinity of the halogen atom. Furthermore, the similarity of the effect for the fluorides and chlorides did not support a picture where the 3*d*-orbitals of chlorine should play a particularly important chemical role. Most of the present results for the dihalides give a similar picture to the one for the monohalides. The effect of 3*d*-functions on the binding energy of the second chlorine is 12.2 ± 1.3 kcal/mol for all the dichlorides except the ones of rhodium and palladium to the right. In particular for palladium, the effect is much smaller with only 3.5 kcal/mol. For rhodium the effect is 9.1 kcal/mol. The reason for these small effects to the right for the dichlorides is that the bonding is much more covalent than to the left and for the monochlorides. Therefore, the effect from 3*d* basis functions on the electron affinity and other effects localized on the halide are much smaller. Since the effect of 3*d* basis functions can sometimes be very small, as for $PdCl_2$, the *relative* effects of including these functions is not always negligible as it was for the monohalides. It is therefore recommended that at least one 3*d*-function is used for chlorine when studying ligand effects in larger systems. One 3*d* basis function on chlorine reproduces the total binding energy of the second chlorine in the dichlorides to within 0.7 kcal/mol for all systems except for $PdCl_2$ where the error is 2.7 kcal/mol. For the difluorides most of the results are similar to those for the dichlorides, but for the difluorides all systems are strongly ionic and any exception for the palladium and rhodium systems do therefore not appear. For the difluorides the total effect of 3*d*-functions on the second fluorine binding energy is 12.5 ± 1.3 kcal/mol which is quite similar to what was found for the monofluorides. It should be added that the present results for the dihalides do not modify the conclusion drawn for the monohalides, that the chemical effect of the chlorine 3*d*-orbitals is not very important. On the contrary, the result for $PdCl_2$ only shows that there are systems where the importance of the 3*d*-orbitals is even smaller than for the monohalides. For high relative accuracy this still means that 3*d*-functions have to be included.

4 Conclusions

Results for the second row transition metal dihydrides and dihalides have been presented and compared to previous results for the hydrides and halides. The main trends of the binding energies are the same but there are still some relatively large differences in bond strength of the first and second ligand for some systems. The largest differences for the halides are found for RuF_2 and $PdCl_2$. Whenever the second ligand binds better than the first, the first ligand has in some way prepared the bonding for the second. For the dihalides this preparation means that the monohalide has reduced the excitation energy to the most optimal ligand field state of the atom, with the least repulsion towards ligands. For example, the state of RuF where both π-orbitals are singly occupied is almost degenerate with the ground state, and in a linear structure of RuF_2 this is the optimal ligand field state. For the dihydrides, which are much more covalently bound, the preparation is somewhat different. In this case the monohydride sometimes has to be promoted to a state which can form two covalent bonds, one of which can be used by the second hydrogen without any additional cost. For example, the bonding in PdH requires that the palladium atom is promoted to the d^9s^1 state which can then bind also the second hydrogen in PdH_2. The same is true for TcH_2, where the second hydrogen binds much stronger than the first.

The geometries of the presently studied systems show interesting differences and similarities. In general, the dihydrides are bent and the dihalides are linear. This difference can be explained by a dominantly covalent bonding for the dihydride and an ionic bonding for the dihalides. Still there are some notable exceptions to this general trend. Of the dihydrides TcH_2 is linear. The origin of this linearity is a strong exchange stabilization of the d^5 configuration which forces the bonding to be formed by essentially pure *sp*-hybrids. Of the dihalides those of yttrium and molybdenum are bent. For yttrium there is only one non-bonding valence electron and this electron is efficiently polarized away by *sd*-hybridization. This can be done equally well whether the molecule is bent or not and the bent structure is therefore preferred due to more optimal covalency. For the molybdenum systems there is only one *d*-hole and in a linear structure this will be a π-hole. It is then advantageous for both the ligands to point towards the lobes of this empty π orbital and this leads to a bent structure. Finally $PdCl_2$ is bent because it is preferrable to form a bent covalent structure since the repulsive ligand field is so strong for the linear ionic bonding with the large number or repulsive non-bonding *d*-electrons on palladium.

Studies of hydride and halide ligand effects on the oxidative addition reaction and the olefin insertion reaction are under way and will be presented soon. It can already be concluded that studies on simple systems of the present type are highly relevant for interpreting the results for the larger complexes. For example, a dramatic reduction of the barrier height for olefin insertion found in some cases when hydrides are exchanged with halides for complexes of the metals to the right, can be understood from the destabilizing effect of the halide ligand on other covalently bound ligands. This effect has been noted in the present study mainly for $PdCl_2$. The same destabilizing effect of halide ligands can be seen also on both the barriers and reaction energies for the oxidative addition of a hydrogen molecule or of methane for the metals to the right.

References

1. Dediev A (ed) (1992) Transition metal hydrides. VCH Publ, NY
2. Bauschlicher CW Jr, Langhoff SR (1992) in: Dediev A (ed) Transition metal hydrides. VCH Publ, NY
3. Siegbahn PEM, Theoret Chim Acta in press
4. Siegbahn PEM, Blomberg MRA, Svensson M (1993) J Am Chem Soc 115:4191
5. Balasubramanian K, Ravimohan C (1988) Chem Phys Lett 39:145
6. Balasubramanian K, Ravimohan C (1989) J Phys Chem 93:4490
7. Balasubramanian K, Wang JZ (1989) J Chem Phys 91:7761
8. Balasubramanian K, Liao DW, (1988) J Phys Chem 92:6259
9. Wang JZ, Das KK, Balasubramanian K (1990) Mol Phys 69:147
10. Li J, Balasubramanian K (1990) J Phys Chem 94:545
11. Balasubramanian K, Feng PY, Liao MZ (1988) J Chem Phys 88:6955
12. Huzinaga S (1977) J Chem Phys 66:4245
13. (a) Almlöf J, Taylor PR (1987) J Chem Phys 86:4070; (b) Raffenetti RC (1973) J Chem Phys 58:4452
14. Blomberg MRA, Wahlgren U (1988) Chem Phys Lett 145:393
15. Huzinaga S (1971) Approximate atomic functions, II. Department of Chemistry Report, Univ of Alberta, Edmonton, Alberta, Canada
16. Pettersson LGM, Siegbahn PEM (1985) J Chem Phys 83:3538
17. Huzinaga S (1965) J Chem Phys 42:1293
18. GAMESS (General Atomic and Molecular Electronic Structure System): Schmidt MW, Baldridge KK, Boatz JA, Jensen JH, Koseki S, Gordon MS, Nguyen KA, Windus TL, Elbert ST (1990) OCPE Bulletin 10:52
19. Hay PJ, Wadt WR (1985) J Chem Phys 82:299
20. Hay PJ, Wadt WR (1985) J Chem Phys 82:270

21. Chong DP, Langhoff SR, (1986) J Chem Phys 84:5606
22. Langhoff SR, Bauschlicher CW Jr, Partridge H (1988) J Chem Phys 89:396
23. Petersson LGM, Åkeby H (1991) J Chem Phys 94:2968
24. Martin RL (1983) J Phys Chem 87:750. See also Cowan RD, Griffin DC (1976) J Opt Soc Am 66:1010
25. Van Zee RJ, Li S, Hamrick YM, Weltner W Jr (1992) J Chem Phys 97:8123