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Second row transition metal mixed hydride–halide triatomic molecules

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Summary. The ground state structures and bond energies have been obtained for the triatomic MHX systems where M is the entire sequence of second row transition metal atoms and X is a halide. The most interesting results of this study appear when these systems are compared to the triatomic MH_2 and MX_2 systems. It turns out that the structure of the MHX systems are quite similar to the corresponding MH_2 systems in general. Most of the MHX systems to the right thus have bent low-spin ground states, indicating large covalent contributions to the bonding. RuHX is a special case and has a high-spin linear ground state. For the systems to the left ionicity dominates the bonding. An important result, with implications for halide ligand effects on carbonyl and olefin insertion into M–H and M–R bonds, is that the M–H bonds for the systems to the right have a different character and are significantly weaker for the MHX than for the MH_2 systems. A similar effect is noted when the M–Cl bond strengths of MCl_2 are compared to the ones in MHCl. Both these effects can be explained by a more cationic metal with more s^0-state character when halide ligands are present.

Key words: Ground state structures – Triatomic MHX systems – Second row transition elements

1 Introduction

A useful approach to systematically understand the reactivity of transition metal complexes is to start out by studying reactions for the naked metal atoms. Ligand effects on the reaction can then be investigated by adding ligands of different types. The technically important reaction of oxidative addition to C–H bonds in alkanes has recently been approached in this way. In the first step, the reaction between methane and the entire sequence of second row transition metal atoms was studied [1]. This step gives a systematic evaluation of the importance of the positions of the various atomic states on the metal atom and also information of the effects of an increased ionization potential and an increased number of d-electrons going from left to right in the periodic table. In the second step, atomic hydrogen ligands were added as the simplest models of covalently bound ligands [2]. In this way information concerning the importance of the oxidation state and the loss of exchange energy in the reaction can be obtained. In the third step, hydride ligands are exchanged with halide ligands [3], allowing for an evaluation of the importance of having more or less electronegative ligands in the complex. In the fourth step, lone-pair ligands are added and mixtures of all of these ligands can finally be studied as the metal complex is gradually made more and more realistic [4]. This type of approach is presently applied also to other fundamental steps in catalytic reactions, such as carbonyl [5] and olefin insertion [6] into M–H and M–C bonds. One type of model complex with particularly interesting properties used in these studies is a triatomic MRX system where R is a hydrogen or methyl group and X is a halide group. The combination of a halide and a hydride ligand leads, for example, to extremely low insertion barriers for both olefins and carbonyls for the metals to the right [5, 6]. It is also interesting to note that many important catalytic reactions involve complexes of this general type such as alkene hydrogenation using the Wilkinson catalyst [7], where also other types of ligands are present. In order to understand the reactivity of these complexes the electronic structure of them has to be fully understood. It is the purpose of the present paper to study the triatomic MHCl and MHF systems in detail for the entire second row transition metals. These systems will be compared with the corresponding triatomic MH_2, MCl_2 and MF_2 systems which have been studied previously [8]. Some comparisons will also be made to the diatomic MH^+ systems [9] and the MH, MCl, MF systems [10].

Before the present results for the triatomic mixed hydride-halide systems are discussed it is useful to recapitulate some of the results for the diatomic hydrides and halides and also the results for the triatomic dihydrides and dihalides. The main result of the previous studies is that 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 $4d$-orbitals. This interaction is attractive to the left where there are empty $4d$-orbitals but becomes repulsive to the right due to the repulsion with the increasing number of $4d$-electrons. These general results remain valid also for the dihydrides and dihalides, but in this case some additional effects of importance appear. In particular, ligand-field effects start to play an important role for the dihalides. For example, for some of the dihalides it is found that the second ligand binds better than the first. This means that the first ligand has in some way prepared the bonding for the second. For the dihalides this preparation means that the mono-halide 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 mono-hydride 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 geometries of the dihydrides and dihalides 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 dihydrides and an ionic bonding for the dihalides. The covalent bonds in the dihydrides are formed mainly from *sd*-hybrids where the ideal hybridization angle is 90°. For the atoms to the left there is also a strong 4*p*-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 4*p*-contribution in the bonding will lead to larger bond angles than 90° for the dihydrides of the atoms to the left in the row. 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 an optimal ligand field state. It is interesting to note in this context that most of the corresponding dioxides are bent [11] in line with a much larger covalent contribution to the bonding than for the dihalides. Since the halide- and the oxide-ligands have about the same charge, about -1, the direct ligand–ligand repulsion is the same, and yet the geometries are qualitatively different.

2 Computational details

In the calculations reported in the present paper on the MHCl, MHF and MCH_3Cl systems 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. 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 carbon and fluorine the primitive (9*s*, 5*p*) basis of Huzinaga [14] was used, contracted according to the generalized contraction scheme to [3*s*, 2*p*]. One even-tempered *p*-function with exponent 0.0795 was added for fluorine. One *d* function with exponent 0.63 was added for carbon and one with exponent 1.0 was added for fluorine. For chlorine a similarly contracted basis was used based on the primitive (12*s*, 9*p*) basis of Huzinaga [14], and including an even-tempered diffuse *p*-function with exponent 0.044. One *d*-function with exponent 0.54 was added [15]. For hydrogen the primitive (5*s*) basis from Ref. [16] 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.

In the geometry optimizations, performed at the SCF level using the GAMESS set of programs [17], somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt [18] 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 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 [19]. For more details of the accuracy of the present type of geometry optimization, see [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-functions are in these cases determined at the SCF level. The metal valence electrons (4*d* and 5*s*) and all valence electrons except the fluorine 2*s* and chlorine 3*s* electrons were correlated. Because of rotation between valence and core orbitals a localization of the core orbitals has to be performed and this was done using a localization procedure 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 [22].

All the present calculations were performed on an FX-80 ALLIANT and on an IBM Risc 6000 computer and the final energy evaluations were performed using the STOCKHOLM set of programs [23].

3 Results and discussion

The entire second row transition metal MHX systems, with X either chlorine or fluorine, have been studied using methods and basis sets described in the previous subsection. The optimal geometries and binding energies for the MHCl systems are given in Table 1 with populations in Table 2. The corresponding fluorine results are

Table 1. Bond distances (Å) and binding energies (kcal/mol) for the second row transition metal MHCl systems. $\Delta E(H)$ is the binding energy of the hydrogen atom to MCl, $\Delta E(\mathrm{Cl})$ is the binding energy of the chlorine atom to MH and $\Delta E(\mathrm{Tot})$ is the total binding energy with respect to three free atoms

Metal(M)	State	M–H	M–Cl	∠(H–M–Cl)	ΔE(H)	ΔE(Cl)	ΔE(Tot)
Y	$^2A'$	1.99	2.55	126.9	56.9	111.0	179.0
Zr	$^3A''$	1.92	2.49	141.2	69.9	118.0	173.7
Nb	$^4A''$	1.86	2.45	139.3	65.7	103.7	164.2
Mo	$^5A'$	1.75	2.45	118.0	53.9	81.5	131.1
Tc	$^6\Sigma^+$	1.80	2.49	180.0	64.9	104.1	144.6
Ru	$^5\Delta$	1.77	2.46	180.0	62.5	78.4	136.1
Rh	$^2A'$	1.52	2.37	93.7	56.8	68.9	131.8
Pd	$^1A'$	1.48	2.35	85.6	52.9	62.8	113.1

Table 2. Populations for the second row transition metal MHCl systems

Metal(M)	State	M(q)	4*d*	5*s*	5*p*	H(q)	Cl(q)
Y	$^2A'$	+0.51	1.01	0.91	0.48	−0.14	−0.37
Zr	$^3A''$	+0.55	2.21	0.80	0.38	−0.17	−0.38
Nb	$^4A''$	+0.53	3.42	0.66	0.33	−0.15	−0.38
Mo	$^5A'$	+0.50	4.66	0.53	0.27	−0.08	−0.42
Tc	$^6\Sigma^+$	+0.60	5.25	0.69	0.41	−0.12	−0.48
Ru	$^5\Delta$	+0.56	6.41	0.59	0.39	−0.11	−0.45
Rh	$^2A'$	+0.29	8.10	0.33	0.21	+0.10	−0.39
Pd	$^1A'$	+0.26	9.14	0.34	0.19	+0.14	−0.40

given in Tables 3 and 4. The binding energies are also plotted in Figs. 1 and 2 with comparisons to results from previous studies on similar systems [8]. Finally, as a comparison the MCH_3Cl systems were studied with results given in Table 5.

As described in the introduction, the MH_2 and MCl_2 systems show a qualitatively different type of bonding. For the MH_2 systems covalency dominates leading to bent low-spin structures with *sd*-hybridized bonds. For most of the MCl_2 systems ionicity and ligand field effects dominate leading to linear high-spin structures. The results in Table 1 show clearly that the covalent description dominates for most of the MHCl systems. The rhodium systems are good examples of this. RhH_2 has a doublet ground state with a bond angle of 82.7°, which is close to the optimal 90° for covalent *sd*-hybridized bonds. $RhCl_2$ is a linear quartet state with two singly occupied d_π-orbitals which minimizes ligand repulsion for the metal. The RhHCl system is very similar to RhH_2 with a doublet ground state with a bond angle of 93.7°. The zirconium and niobium systems behave just like the rhodium systems with bent MH_2 and MHCl systems and linear MCl_2 systems. For yttrium, molybdenum and palladium all the three different types of systems have bent structures with important covalent contributions, while for technetium all systems are linear. Ruthenium constitutes an interesting special example with a bent RuH_2 structure and linear RuHCl and $RuCl_2$ structures. This is in fact the only case where the MH_2 and MHCl systems have a qualitatively different ground state structure.

In order to understand the high spin ground state of RuHCl it is useful to consider the bonding as formed between RuCl and hydrogen. The position of the high- and low-spin states of the MCl systems to the right will to a certain extent depend on the positions of these states for the metal cation. For the palladium and rhodium cations the ground states are low-spin s^0-states with rather high excitation energies to the high-spin s^1-states, with 72 and 46 kcal/mol, respectively. For ruthenium this excitation energy is much smaller, only 20 kcal/mol. Still, for RuCl the low-spin $^4\Phi$-state is the ground state at the present level of treatment but the $^6\Delta$-state is very low lying. For RuF, the $^6\Delta$-state is in fact the ground state at the present level but the $^4\Phi$-state was assigned as the probable ground state in Ref. [10] based on expectations of higher order correlation effects. The $^6\Delta$-state of RuCl has a singly occupied strongly polarized *sp*-orbital which is ideally suited for forming a covalent bond to hydrogen and therefore leads to the formation of a high-spin quintet ground state for RuHCl. For the technetium cation the ground state is a high-spin septet state with an s^1 occupation, which leads to a high-spin septet ground state for TcCl and a high-spin sextet ground state for TcHCl. The high-spin states of all these systems prefer linear structures irrespective of whether the bonding is covalent or ionic. In the ionic case, ligand field repulsion is minimized for a linear structure, while in the covalent case *sp*-polarization dominates the bonding in the high-spin states. The origin of the low-lying high-spin states for the ruthenium and technetium cations is a large *d*–*d* exchange-stabilization for these states, with the spins of all *d*-electrons parallel.

A comparison of the M–H binding energies for the yttrium and zirconium systems gives further examples of the effects of importance for the binding energies in the MHX systems. The Y–H binding energy in YHCl of 56.9 kcal/mol is weaker than the Zr–H bond in ZrHCl of 69.9 kcal/mol. The origin of this difference is not directly obvious if the ground states of the respective neutral metal atoms are considered, since both yttrium and zirconium have s^2 ground states. However, this difference can be understood from differences in the spectra of the cations. The yttrium cation has an s^2 ground state occupation while the zirconium cation has an

s^1 ground state occupation. If the bonding in the MHCl systems is regarded as an ionic bond between MH^+ and Cl^-, this means that for the yttrium system the Y^+ cation has to be promoted to an s^1 state, while no similar promotion has to be made for the zirconium system. The Zr–H bond in ZrHCl will therefore be stronger than the one in YHCl, in agreement with the results in Table 1. The same is true for the corresponding MHF systems, but it is here also interesting to note that the M–H binding energies for the ytrrium and zirconium systems of MHF are 3–5 kcal/mol weaker than those of MHCl. This effect is best understood by also noting that the M–H bonding in the systems to the left have large ionic contributions. In the extreme case of a totally ionic bonding, the bonds will be formed between H^-, M^{2+}, X^-. The M–H bond will then be stronger the further away the halide is from the hydride. Since the M–X bond distance in the fluoride systems is much shorter than in the chloride systems, the ionic contribution to the M–H bonding in the MHCl systems will be larger than in the MHF systems. For the systems where the ionic contribution to the bonding is large, which is mainly for the systems to the far left, the chloride systems will therefore in general form stronger M–H bonds. Another contributing factor to the stronger M–H bonds in the MHCl than in the MHF systems is that the charge on fluoride in general is larger than on chloride, see Tables 3 and 4.

The linear structures of the MHCl and MCl_2 systems show interesting differences, in particular to the right in the periodic table. It should be noted that for MHCl these structures are mostly excited states, while for MCl_2 they are mostly

Table 3. Bond distances (Å) and binding energies (kcal/mol) for the second row transition metal MHF systems. ΔE(H) is the binding energy of the hydrogen atom to MF, ΔE(F) is the binding energy of the fluorine atom to MH and ΔE(Tot) is the total binding energy with respect to three free atoms

Metal(M)	State	M–H	M–F	∠(H–M–F)	ΔE(H)	ΔE(F)	ΔE(Tot)
Y	$^2A'$	2.01	2.02	117.7	53.8	143.4	211.4
Zr	$^3A''$	1.92	1.98	131.3	65.1	151.3	207.0
Nb	$^4A''$	1.87	1.96	138.6	67.3	135.6	196.1
Mo	$^5A'$	1.77	1.96	119.0	56.8	107.1	156.7
Tc	$^6\Sigma^+$	1.81	2.01	180.0	65.1	125.2	165.7
Ru	$^5\Delta$	1.79	1.98	180.0	71.5	100.1	157.7
Rh	$^2A'$	1.54	1.94	96.6	58.6	80.8	143.8
Pd	$^1A'$	1.49	1.95	90.7	48.6	69.6	119.8

Table 4. Populations for the second row transition metal MHF systems

Metal(M)	State	M(q)	4*d*	5*s*	5*p*	H(q)	F(q)
Y	$^2A'$	+0.68	0.90	0.88	0.45	−0.15	−0.52
Zr	$^3A''$	+0.68	2.10	0.81	0.33	−0.17	−0.51
Nb	$^4A''$	+0.67	3.26	0.71	0.29	−0.16	−0.51
Mo	$^5A'$	+0.64	4.48	0.59	0.22	−0.10	−0.54
Tc	$^6\Sigma^+$	+0.76	5.17	0.67	0.34	−0.17	−0.59
Ru	$^5\Delta$	+0.71	6.31	0.58	0.34	−0.15	−0.55
Rh	$^2A'$	+0.45	8.00	0.31	0.17	+0.08	−0.53
Pd	$^1A'$	+0.42	9.02	0.32	0.17	+0.11	−0.53

the ground state structures. The palladium systems are perhaps the best illustrations of these differences between the MHCl and MCl_2 systems. While the linear $PdCl_2$ is a triplet as expected, the linear structure of PdHCl is quite surprisingly a low-spin singlet. This effect can not be understood based on an entirely covalent description since for palladium the d^9s^1 state would form a bent singlet state with a different occupation per symmetry than the linear singlet has. The effect cannot be understood from a purely ionic picture either. The bonding in PdF_2 is strongly ionic and ligand field effects will play an important role. By going to a high spin state and singly occupying the d_σ and one d_π orbital the repulsion towards the halide lone-pairs will be minimized if the dihalide is linear, This leads to an optimal $^3\Pi$-state. It is clear that the optimal *low-spin* state of the linear PdHCl system has to be understood in a different way. The electronic structure of this system is best described starting from an electron donation from the metal to the halide leading to an MH^+ system with an ionic bond to Cl^-. The ground state of MHCl will then be determined by the optimal electronic state of MH^+, which for palladium is $^1\Sigma^+$ [9]. Other convincing examples that this is the best way to describe the bonding in the linear MHCl systems to the right are found for rhodium. There are two low-lying states for linear RhHCl, the optimal $^4\Phi$ state and the $^2\Delta$ state. These are also the lowest lying states of RhH^+, although the order of the states is reserved in that case. If ligand field effects would dominate, as might have been expected, the lowest doublet state should have been a $^2\Pi$-state instead, since the direct repulsion should be larger for a π- than for a δ-orbital. The excitation energy between $^2\Delta$-state and the $^2\Pi$-state is 11 kcal/mol at the SCF level for linear RhHCl. It is somewhat higher for RhH^+ with 18 kcal/mol at the same level. Similarly, if ligand field effects would be dominating for RhHCl the optimal linear state would be, $^4\Sigma^-$-state with two singly occupied π-orbitals just like in $RhCl_2$. The reason the $^4\Phi$-state is lower than the $^4\Sigma^-$-state for RhH^+ is that atomic couplings are important. At long distance the $^4\Sigma^-$-state is a linear combination of the bonding determinant with single occupations of the two π-orbitals and the determinant with single occupations of the two δ-orbitals. The bonding therefore effectively requires a type of promotion to form the bond in the $^4\Sigma^-$-state of RhH^+. In contrast a single occupation of one π and one δ-orbital in Rh^+ can be described by one determinant and the formation of the bond in the $^4\Phi$-state of RhH^+ therefore does not require any similar promotion. In line with these other results, the lowest excited state of linear PdHCl is a $^3\Delta$-state rather than a $^3\Pi$-state as expected solely based on ligand field arguments.

The most interesting results of the present study appears in the comparison of the M–H and M–Cl bond strengths to the corresponding bond strengths in MH_2 and MCl_2. These comparisons have the widest chemical implications, for example, for the catalytically important carbonyl and olefin insertion reactions into M–H and M–R bonds. The discussion will start with the M–H bond strengths. The hydride bond strengths in MH_2, that is the bond between MH and H, and the M–H bond strength in the MHCl systems are compared in Fig. 1. For these systems the exchange effects will essentially be the same and in the comparisons these effects can be ignored for most systems. It can first be noted that for the systems to the left from yttrium to technetium these bond strengths are extremely similar. This is because ionic effects dominate the M–H bonding in both MH_2 and MHCl to the left. This is a quite general finding and implies that significantly different catalytic behaviour should not be expected for complexes to the left when halides are exchanged with hydrides. However, to the right there are clear differences in bond strengths. The Pd–H bond in PdHCl is 9.0 kcal/mol weaker than the

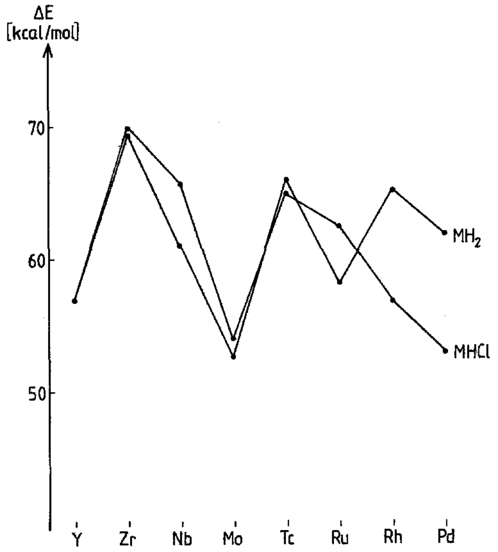

Fig. 1. The M–H bond strengths in MHCl and MH_2. For MH_2 these are the binding energies between MH and H

one in PdH_2, and for rhodium, the corresponding difference is 8.4 kcal/mol. The origin of these differences is a combination of the fact that there are different characters of the electronic structure of the metal in these systems and the fact that the M–H bonding to the right has large covalent contributions. When a covalent bond is formed between the metal and hydrogen an *s*-bond is much stronger than a *d*-bond, and the *s*-bond requires an s^1-state of the metal atom. Since the metal is more neutral in the MH_2 systems the ground state is that of the neutral atom, which normally has an s^1 occupation to the right and therefore does not need any promotion to bind hydrogen. In contrast, the metal in the MHCl systems will be more similar to a cation, due to the presence of the chloride. The ground state of the cations to the right have an s^0 occupation and requires a promotion which weakens the M–H bond. The bonding in the MHCl systems to the right can to some extent be regarded as an ionic bond between MH^+ and Cl^- with a dominantly covalent bond to hydrogen. The M–H bond in MH^+ for rhodium is 22.6 kcal/mol weaker than the one in neutral MH. The weakening of the M–H bonds in RhHCl is thus slightly less than half of the weakening going from M–H and $M–H^+$, again showing that there is a mixture of covalency and ionicity in the bonding of these systems to the right. A second interesting feature in Fig. 1 is the marked minimum of the bond strengths for molybdenum for both systems. Going from the left from zirconium the bond strengths are expected to decrease since there is a larger loss of exchange energy when the bonds are formed the higher the spin is. A similar decrease of binding energies has been noted previously for almost all similar systems. To the right of molybdenum the M–H bond strengths of both technetium and ruthenium are quite strong. The origin of this effect for MHCl has already been discussed above. The large exchange stabilization in MCl leads to low-lying high-spin states of these systems which are perfectly suited for binding hydrogen. For both ruthenium and technetium the bonding states will have a strongly *sp*-polarized orbital which can bind hydrogen without loss of any *d*–*d* exchange. This is where the situation is quite different for the molybdenum system. The exchange stabilization of molybdenum also leads to a high-spin state for MoCl, but in this case there is no singly occupied *sp*-orbital. MoCl therefore has to be promoted, with a large loss of *d–d* exchange, to bind hydrogen. The M–H bond strength difference between MoHCl and TcHCl can also be understood from the corresponding ground states of the cations. Tc^+ has an s^1 ground state which can bind hydrogen without promotion, while molybdenum has an s^0 ground state. The excitation energy to the s^1-state for Mo^+ is 39 kcal/mol.

In Fig. 2 the M–Cl bond strengths are compared for the MHCl and MCl_2 systems. Apart from the stronger decrease of bond strengths going to the right for the M–Cl bonds, the relative behaviour of the curves in Fig. 2 is extremely similar to the one for the M–H bond strengths in Fig. 1. First, the M–Cl bond in MHCl and the second bond in MCl_2 are quite similar for the systems to the left. This is because ionic effects dominate the M–Cl bonding in both these systems. Secondly, for the systems to the right the M–Cl bond strengths in MCl_2 are notably weaker than those in MHCl just as the M–H bond in MHCl is weaker than in MH_2. In both cases this can be explained by contributions of covalency to the right and more cationic metals for the MCl systems. When the cationic metal in MCl forms a bond, either to hydrogen or chlorine, the covalency in the bonding effectively requires a promotion for the metal since the cationic ground state is an s^0-state. In contrast the metal in MH is more neutral and therefore does not require any promotion since the ground state of the neutral atoms to the right in most cases are s^1-states. The significant covalency in the bonding between MCl and Cl to the right is perhaps somewhat surprising but was noted already in the previous study [8]. The effect is best seen for $PdCl_2$, which forms a bent low-spin ground state just like MH_2 rather than a linear high-spin state as expected from ligand field considerations. It is interesting to note that this covalency actually has a larger effect for the M–Cl bonds to the right than it has for the corresponding M–H bonds. For palladium the Pd–Cl bond in MCl_2 is thus as much as 20.8 kcal/mol weaker than

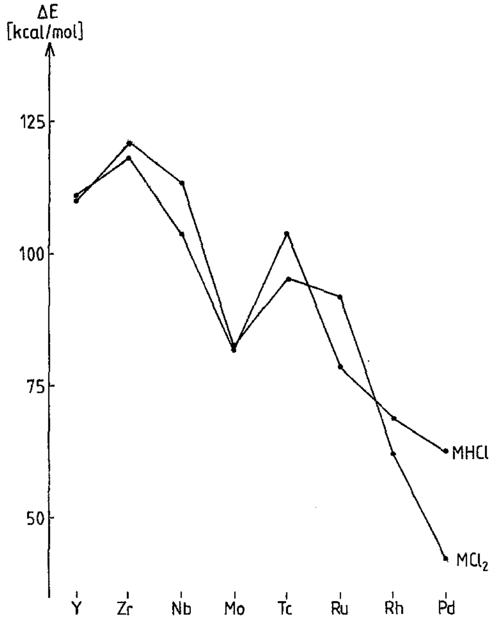

Fig. 2. The M–Cl bond strengths in MHCl and MCl_2. For MCl_2 these are the binding energies between MCl and Cl

the one in MHCl. The corresponding difference between the M–H bond in MHCl and the one in MH_2 is only 9.0 kcal/mol. Other minor effects which can be noted in Table 1 and in Fig. 2 is that for the MHCl systems covalent contributions due to the formations of the M–H bonds are somewhat more important than for MCl_2, while for MCl_2 bond preparation to form optimal ligand field states is more important. There is also a slight general trend towards weaker M–Cl bonds for the MHCl systems to the left, since the ligand field advantage is not as large for MHCl as for MCl_2. Also for the M–Cl bonds there is a large decrease in bond-strength for molybdenum with the same origin as the minimum in Fig. 1 discussed above for the M–H bonds.

Finally as a comparison, the bond strengths in the MCH_3Cl systems were also evaluated. The results are given in Table 5. A major advantage of doing these calculations was that the results for the above triatomic systems were checked. A serious problem, not mentioned above, is that the geometry optimization of the MHX systems had a tendency to converge to the high symmetry linear structures, which only in a few cases is the correct ground state structure. The change of symmetry from C_s to C_{2v} at this point leads to zero gradients even if this is not a minimum. This problem is much less severe for the methyl systems, since there is no symmetry change for linear structures, and in most cases convergence was straightforward to the correct bent minimum. A contributing reason for the convergence to the wrong structure for the MHX systems is that the energy at the SCF level is rather similar between the bent and linear structures. It is only when correlation is added that the bent structures are strongly favoured in most cases.

The main results for the MCH_3Cl systems and the MHCl systems are as expected quite similar. Starting with the M–Cl bond strengths they are within a few kcal/mol of each other for all systems except ruthenium where the difference is 6.2 kcal/mol in favour of MCH_3Cl. As discussed above, the ruthenium system is a special case of the MHCl systems in that it is the only system where the bonding is qualitatively different between the MHCl and MH_2 systems. RuHCl becomes a linear high-spin state with dominating ligand field effects. The fact that the ligand field advantage on methyl is larger than for hydrogen could be the reason the M–Cl bond strength is larger for $RuCH_3Cl$ than for RuHCl. The slightly larger ligand field effects for methyl than for hydrogen can also be seen on the bond angles which are slightly larger for the methyl case, indicating a larger adjustment to the

Table 5. Bond distances (Å) and binding energies (kcal/mol) for the second row transition metal $M(CH_3)Cl$ systems. $\Delta E(CH_3)$ is the binding energy of the methyl radical to MCl, $\Delta E(Cl)$ is the binding energy of the chlorine atom to MCH_3 and $\Delta E(Tot)$ is the total binding energy with respect to three free systems

Metal(M)	State	M–C	M–Cl	∠(C–M–Cl)	$\Delta E(CH_3)$	$\Delta E(Cl)$	$\Delta E(Tot)$
Y	$^2A'$	2.34	2.56	121.9	51.3	109.7	173.4
Zr	$^3A''$	2.27	2.50	138.3	66.3	115.2	170.2
Nb	$^4A''$	2.22	2.46	146.9	62.0	107.8	160.5
Mo	$^5A'$	2.18	2.46	120.5	46.3	83.1	123.5
Tc	$^6A'$	2.22	2.50	180.0	55.9	102.3	135.5
Ru	$^5A'$	2.17	2.47	179.3	55.6	84.8	129.3
Rh	$^2A'$	2.02	2.38	98.7	43.6	70.4	118.7
Pd	$^1A'$	1.99	2.37	94.5	42.1	64.8	102.3

ligand field. The M–CH_3 bond strengths are, also as expected, weaker than the corresponding M–H bond strengths. To the left the bond strength difference is 4–5 kcal/mol while to the right it is larger with differences of 11–13 kcal/mol. This situation is quite similar to the case without chloride ligands. In that case the bond strength differences goes from 4–8 kcal/mol to the left to 13–15 kcal/mol to the right. The reason the bond strength difference is larger to the right is that the repulsion between the carbon center and the *d*-electrons increases to the right with the number of *d*-electrons [2].

4 Conclusions

In order to understand the reactivity of realistic ligated transition metal complexes, it is our experience that the basic principles governing the energetics in these systems has to be fully understood. For this purpose detailed studies of small transition metal complexes are extremely useful. For example, an understanding of why olefins and carbonyls insert much easier into M–H and M–R bonds when halides are present as ligands for complexes to the right follows from an understanding of the bonding in the triatomic MHX systems. From the understanding of the bonding in these small triatomic molecules it can also be understood why the halide effect is not present for the insertion reactions for complexes to the left in the periodic table. This is the background to the the present study of the triatomic MHCl and MHF systems for the second row transition metals.

The most interesting result obtained in this study is that the M–H binding energies of MHX systems undergo a significant decrease compared to the corresponding MH_2 systems for the metals to the right. The origin of this decrease is a loss of covalent bonding. When a halide is bound to the metal, the metal effectively becomes similar to a cation. The cations to the right have s^0 ground states and therefore need to be promoted to form a strong covalent *s*-bond to hydrogen. In contrast, when there are only covalent ligands like in MH_2, the metal is effectively neutral. The ground state of, for example, the neutral ruthenium and rhodium atoms is an s^1-state and can therefore form strong covalent M–H bonds. The neutral palladium atom has an s^0 ground state but has already paid the promotion energy when the first Pd–H bond is formed in PdH_2. For the systems to the left, the bonding is dominantly ionic for both the MH_2 and MHCl systems and the M–H bond energies are therefore much more similar than they are to the right. This difference between a dominance of ionic bonding to the left and covalent bonding to the right is a general effect found in most systems. The origin of this trend is, of course, that the ionization energies increases going to the right. The difference in character of the M–H bonds in MH_2 and MHCl for the systems to the right is the reason olefin and carbonyl insertion becomes much easier when halide ligands are present. The lack of difference in character of the M–H bonds between these systems to the left is the reason halides do not have any significant effects for the insertion barriers to the left.

The differences in M–Cl bond strengths between MCl_2 and MHCl behave very similarly to the corresponding differences in M–H bond strengths between the MHCl and MH_2 systems, and can be explained in the same way. The M–Cl bond strengths are thus very similar to the left where the bonding in both MCl_2 and MHCl are dominantly ionic. To the far right, where covalency comes in, the M–Cl bond is much weaker in MCl_2 than for MHCl, because the metal is more cationic in MCl_2 and therefore needs to be promoted to form an M–Cl bond .

In a forthcoming study the present results will be used to analyze halide ligand effects on the catalytically important olefin and carbonyl insertion reactions into M–H bonds.

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