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Halide Ligand Effects on the Oxidative Addition Reaction of Methane and Hydrogen to Second Row Transition Metal Complexes

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The oxidative addition reactions of methane and hydrogen to second row transition metal halide complexes have been studied and compared to previous results for hydride complexes. Both halide and hydride ligands are found to have pronounced effects on the oxidative addition, and these effects are very similar for most systems. This means that the gross features of the effects of both halide and hydride ligands can be explained by promotion and exchange loss energies. The two main conditions for a low barrier for the oxidative addition are also the same for halide and hydride complexes. There must be a low-lying state with a different spin than the ground state, and the low-spin state of these must have a low population of 5s, 5p electrons. In addition to these effects there is a tendency for the halides to destabilize the complexes to the right. This effect can be understood from the higher promotion energies required for cations to reach the bonding s^1-state than for the neutral atoms. Another important effect in this context is that the halides tend to have higher spin than the hydrides for the systems to the right, which in some cases increases the exchange loss energies for the halides.

I. Introduction

Ligand effects on the reactivity of transition metal complexes can be divided into essentially two different classes. Ligand effects that are of electronic origin belong to one class, and those which have a steric origin belong to the other class. The optimal theoretical treatment of these two types of effects are quite different. The electronic structure effects from ligands require highly accurate theoretical methods, including a treatment of correlation effects of all valence electrons using large basis sets. This type of method is not required to treat ligand effects of basically steric origin. In fact, if the steric effect is just a blocking of a coordination site, no calculations at all are needed, but a simple reasoning about the effects is often sufficient. In more complicated situations, steric effects are best handled by classical methods like molecular mechanics. At the end, the results of these different treatments have to be combined into a unified picture of ligand effects. The present study will focus on the electronic structure effects of ligands. The reaction chosen for this study is the oxidative addition reaction, which is a simple reaction and a common step in many important catalytic processes. The addition of both a methane and a hydrogen molecule will be considered in reactions with complexes of the entire sequence of second row transition metal atoms from yttrium to palladium. The main reason for studying an entire row of the periodic table is not in the first place to locate the most optimal metal for this reaction. Rather, by studying an entire row of metals, a suitable group of systems is chosen with different spectra, different number of d-electrons, and different ionization potentials, which makes it possible to identify the effects of main importance for the reactions. The present study is part of a systematic project with this common general strategy.[1-12]

Only a few transition metals are represented among those metal complexes which have been observed to insert into C–H bonds in saturated hydrocarbons via an oxidative addition mechanism. The first observations of alkane C–H insertion in solution were made in 1982 for iridium complexes, where the active intermediates were believed to be coordinatively unsaturated fragments of the general formula Cp*IrL (L = CO, PR_3).[13,14] Shortly afterward, the analogous rhodium fragment (Cp*RhL) was found to be active[15] and later on also the $ClRhL_2$ (L = PPh_3) fragment.[16] It is interesting to note in the present context that the small number of metals observed to be active implies very special electronic structure requirements for oxidative addition. Also, a strongly electronegative ligand like Cl or Cp is present for all these complexes.

The present study of halide ligand effects is a natural continuation of two previous studies of the oxidative addition reaction for second row transition metal complexes. In the first of these studies, the reactivity between the naked transition metal atoms and methane was

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(1) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Am. Chem. Soc.* **1992,** *114,* 6095.

(2) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Phys. Chem.* **1992,** *96,* 9794.

(3) Siegbahn, P. E. M.; Blomberg, M. R. A. *J. Am. Chem. Soc.* **1992,** *114,* 10548.

(4) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Am. Chem. Soc.* **1993,** *115,* 1952.

(5) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Am. Chem. Soc.* **1993,** *115,* 4191.

(6) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Phys. Chem.* **1993,** *97,* 2564.

(7) Siegbahn, P. E. M. *Theor. Chim. Acta,* in press.

(8) Siegbahn, P. E. M. *Chem. Phys. Lett.* **1993,** *201,* 15.

(9) Siegbahn, P. E. M. *Theor. Chim. Acta,* in press.

(10) Siegbahn, P. E. M. *J. Am. Chem. Soc.,* in press.

(11) Siegbahn, P. E. M. *Theor. Chim. Acta,* in press.

(12) Siegbahn, P. E. M. *Chem. Phys. Lett.* **1993,** *205,* 290.

(13) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982,** *104,* 352, (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983,** *105,* 3929.

(14) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982,** *104,* 3723, (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983,** *105,* 7190.

(15) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982,** *104,* 4240.

(16) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990,** *112,* 7221.

0276-7333/94/2313-0354$04.50/0

studied.[1] By removing the ligands, it was possible to isolate the factors of main importance for the metal itself in these reactions. Three main conclusions concerning the electronic structure aspects emerge from that study and also from other similar previous theoretical studies of the oxidative addition reaction.[17-19] First, the main state involved in the binding in the insertion products for the methane reaction is the s^1 state (or the $d^{n+1}s^1$ state). For the second row atoms to the left, there are also imported contributions from s^1p^1 states (or $d^ns^1p^1$ states). The second main conclusion is that at the transition state the s^0 state (or longer, the d^{n+2} state) plays a key role. It is the presence of this low-lying state that leads to the lowest barriers for the atoms to the right, ruthenium, rhodium, and palladium. In particular, the lowest barrier of the second row atoms is found for rhodium since this atom has both low-lying s^0 and s^1 states. It is interesting to note in this context that rhodium complexes (see above) are the only second row complexes which have been found to activate alkanes.[15,16,20] The third main conclusion concerns the loss of exchange energy[1,21,22] in the reaction. This energy loss is particularly large for the atoms in the middle of the row since there is a large number of unpaired 4d electrons for these atoms. Therefore, the binding energies between naked metal atoms and practically any ligand will display a marked minimum in the middle of the row.

Table 1. Reaction Energies ΔE (kcal/mol) for $MF_n + H_2 + \Delta E \rightarrow MF_nH_2$ and Difference in Reaction Energies ΔD (kcal/mol) between the MF_n and the Corresponding MH_n Reactions, Where a Positive Sign for ΔD Means That the Fluoride System Is More Stable Than the Hydride System

	ΔE			ΔD		
metal (M)	$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$
Y	−19.3			−4.7		
Zr	−34.9	−44.9		−2.6	+3.6	
Nb	−28.4	−20.7	−9.7	+8.6	−2.1	−5.2
Mo	−10.2	−12.8	17.7	+7.7	+6.2	−16.7
Tc	−10.9	11.1		+5.7[a]	−1.7[a]	
Ru	−14.9	0.8		0.0	−15.6[a]	
Rh	−20.1			−8.4		

[a] Different spin for the hydride and fluoride systems.

The second previous study of the oxidative addition reaction, relevant for interpreting the results of the present study, is an investigation of covalent ligand effects.[5] Hydrogen atoms were chosen as covalent ligands, both because they are simple and since the addition of hydrogens lowers the spin of the complexes in a systematic way. The main results of that study are the following. First, promotion and exchange effects continue to play a dominant role also for the effects of adding covalent ligands. If the promotion and exchange effects are subtracted from the results, two new trends can be identified. First, there is a systematic decrease of the reaction energies as one goes from left to right in the periodic table. This trend is explained by the important role played by electron repulsion between the metal electrons and the ligand electrons, which increases with the increasing number of metal electrons to the right in the row. The second trend is a systematic decrease of the reaction energies as the number of hydrogen ligands is increased. Since this effect is practically identical for the H_2 and the CH_4 reaction, the effect has to be dominated by local rehybridization on the metal, which should be the same for hydrogen and methyl ligands, and not by steric effects. Two additional trends could be noted in the previous study. First, the difference between the reaction energies for the H_2 and CH_4 reactions increases to the right in the periodic table. The second trend in the difference between the reaction energies of H_2 and CH_4 is more surprising. Even though methyl is bulkier than the hydrogen atom, the difference in reaction energy between H_2 and CH_4 decreases as the number of ligands increases. Both these trends are explained by the fact that the repulsive effect between the metal and the ligands is the dominating origin also for the difference in the reaction energies between H_2 and CH_4. When more ligands are added, this repulsion is decreased both by local metal rehybridization and by electron transfer from the metal to the ligands.

The main advantage of having already studied the main effects of adding covalent ligands in detail is that the present study can focus on the difference between hydrogen and halogen ligand effects. In this way, the effects of promotion and exchange will to a large extent be canceled for most systems, and the new aspects will stand out. It should thus be possible to see what the isolated effect is of having a more electronegative ligand, which also has electron-donating capability, like the halogen ligands compared to the hydrogen ligands. A few of the systems presently studied obtain a different electronic ground state when a hydrogen ligand is replaced by a halogen ligand. In these cases promotion and exchange effects will not be canceled. Instead, the modification of these effects that is introduced by this ligand exchange turns out to give some of the most interesting results of the present study.

II. Results and Discussion

The effects of exchanging hydride with halide ligands have first been studied for the equilibrium of the oxidative addition of H_2. The results for the reaction of MX_n ($X = F, Cl$; $n = 1$–3) with H_2 are presented in Tables 1–3 and Figures 1 and 2, and they are discussed in the first subsection below. In the second subsection the results for the oxidative addition of methane are discussed and the results for the reaction of MX_n ($X = F, Cl$; $n = 1$–2) with CH_4 are given in Tables 4–9 and Figures 3 and 4. For methane both equilibrium and transition state energies have been obtained. Two typical transition state geometries are shown in Figure 5 for RhCl and $RuCl_2$. The discussion below will be focused on the differences in the results compared to the results obtained when all ligands are hydrides.[5] Therefore the MX_n systems studied in the

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(17) (a) Blomberg, M.; Brandemark, U.; Pettersson, L.; Siegbahn, P. *Int. J. Quantum Chem.* **1983**, *23*, 855, (b) Blomberg, M. R. A.; Brandemark, U.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1983**, *105*, 5557, (c) Blomberg, M. R. A.; Schüle, J.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1989**, *111*, 6156, (d) Blomberg, M. R. A.; Siegbahn, P. E. M.; Nagashima, U.; Wennerberg, J. *J. Am. Chem. Soc.* **1991**, *113*, 476, (e) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Phys. Chem.* **1991**, *95*, 4313, (f) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *New J. Chem.* **1991**, *15*, 727.

(18) (a) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 8321, (b) Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609, (c) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 6928, (d) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

(19) Svensson, M.; Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1991**, *113*, 7077.

(20) *Perspectives in the Selective Activation of C-H and C-C Bonds in Saturated Hydrocarbons*; Meunier, B., Chaudret, B. Eds.; Scientific Affairs Division—NATO: Brussels, 1988.

(21) (a) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H.; Barnes, L. A. *J. Chem. Phys.* **1989**, *91*, 2399, (b) Rosi, M.; Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Phys. Chem.* **1990**, *94*, 8656.

(22) (a) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1988**, *92*, 5679, (b) Carter, E. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 2180.

Table 2. Reaction Energies ΔE (kcal/mol) for $MCl_n + H_2 + \Delta E \rightarrow MCl_nH_2$ and Difference in Reaction Energies ΔD (kcal/mol) between the MCl_n and the corresponding MH_n Reactions, Where a Positive Sign for ΔD Means That the Chloride System Is More Stable Than the Hydride System

	ΔE			ΔD		
metal (M)	*n* = 1	*n* = 2	*n* = 3	*n* = 1	*n* = 2	*n* = 3
Y	−23.7			−0.3		
Zr	−38.0	−36.4		+0.5	−4.9	
Nb	−23.7	−14.9	−2.0	+3.9	−7.9	−12.9
Mo	−3.1	−5.1	18.4	+0.6	−1.5	−17.4
Tc	−8.6	14.5		+3.4[a]	−5.1[a]	
Ru	−6.8	1.7		−8.1	−16.5[a]	
Rh	−14.4			−14.1		

[a] Different spin for the hydride and chloride systems.

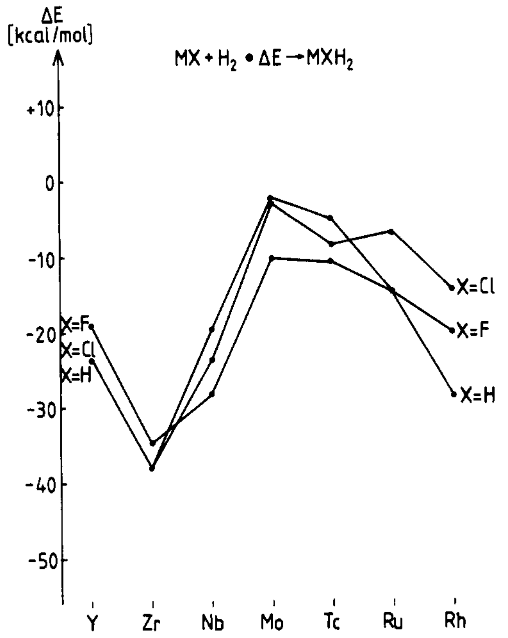

Figure 1. Energies for the MXH_2 insertion products, calculated relative to MX and free H_2 using the ground state of each system. Negative values for ΔE correspond to exothermic insertion reactions.

Table 3. Difference in Reaction Energies (kcal/mol) between X = F and X = Cl for $MX_n + H_2 + \Delta E \rightarrow MX_nH_2$, Where a Positive Sign Means That the Chloride System is More Stable Than the Corresponding Fluoride System

metal (M)	*n* = 1	*n* = 2	*n* = 3
Y	+4.4		
Zr	+3.1	−8.5	
Nb	−4.7	−5.8	−7.7
Mo	−7.1	−7.7	−0.7
Tc	−2.3	−3.4	
Ru	−8.1	−0.9	
Rh	−5.7		

present paper are determined by the MH_n systems studied in ref 5, where the maximum number of H ligands included for each metal was chosen to give a covalently saturated final product. The details of the reactions with hydride ligands can be found in ref 5. The ground-state spin varies in a regular way for most of the hydrides. For example, for the dihydrides the ground state of PdH_2 is a singlet and the spin $(2S + 1)$ increases by one unit for every metal going towards the middle where the spin starts to be reduced by one unit for every metal. The maximum spin for the dihydrides is reached for technetium. Most of the halides studied here have the same spin as the corresponding hydrides. There are three notable exceptions occurring only to the right in the periodic table, and in these cases the spin is always higher for the halides. The three exceptions occur for TcX of the diatomic halides and for TcX_2 and RuX_2 of the dihalides. After the oxidative addition reaction the spin is reduced by two units in all cases except for TcH, where the spin is unchanged. The origin of the tendency for higher spin for

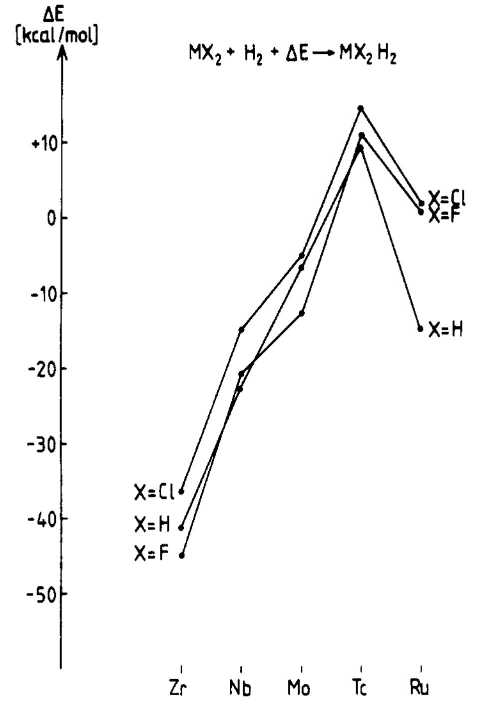

Figure 2. Energies for the MX_2H_2 insertion products, calculated relative to MX_2 and free H_2 using the ground state of each system. Negative values for ΔE correspond to exothermic insertion reactions.

Table 4. Reaction Energies ΔE (kcal/mol) for $MF_n + CH_4 + \Delta E \rightarrow MF_nHCH_3$ and Difference in Reaction Energies ΔD (kcal/mol) between the MF_n and the Corresponding MH_n Reactions Where a Positive Sign for ΔD Means That the Fluoride System Is More Stable Than the Hydride System

	ΔE		ΔD	
metal (M)	*n* = 1	*n* = 2	*n* = 1	*n* = 2
Y	−9.7		−4.8	
Zr	−28.7	−39.8	−3.3	1.9
Nb	−23.1	−12.5	+10.5	−5.9
Mo	−3.5	−5.9	+8.4	+10.8
Tc	2.7	19.8	+2.3[a]	−3.0[a]
Ru	−1.4	13.0	+1.3	−17.7[a]
Rh	−2.1		−10.0	

[a] Different spin for the hydride and fluoride systems.

Table 5. Reaction Energies ΔE (kcal/mol) for $MCl_n + CH_4 + \Delta E \rightarrow MCl_nHCH_3$, and Difference in Reaction Energies ΔD (kcal/mol) between the MCl_n and the Corresponding MH_n Reactions, Where a Positive Sign for ΔD Means That the Chloride System is More Stable Than the Hydride System

	ΔE		ΔD	
metal (M)	*n* = 1	*n* = 2	*n* = 1	*n* = 2
Y	−14.5		0.0	
Zr	−32.7	−32.5	+0.7	−5.4
Nb	−19.8	−8.0	+7.2	−10.4
Mo	3.8	0.2	+1.1	−0.5
Tc	2.6	23.4	+2.4[a]	−6.6[a]
Ru	4.2	15.4	−4.3	−20.1[a]
Rh	0.8		−12.9	

[a] Different spin for the hydride and chloride systems.

Table 6. Difference in Reaction Energies (kcal/mol) between X = F and X = Cl for $MX_n + CH_4 + \Delta E \rightarrow MX_nHCH_3$, Where a Positive Sign Means That the Chloride System Is More Stable Than the Corresponding Fluoride System

metal (M)	$n = 1$	$n = 2$
Y	+4.8	
Zr	+4.0	-7.3
Nb	-3.3	-4.5
Mo	-7.3	-6.1
Tc	-0.1	-3.6
Ru	-5.6	-2.4
Rh	-2.9	

Table 7. Barrier Heights ΔE (kcal/mol) for $MF_n + CH_4 + \Delta E \rightarrow MF_nHCH_3$ and Difference in Barrier Heights ΔD (kcal/mol) between the MF_n and the Corresponding MH_n Reactions, Where a Positive Sign for ΔD Means That the Fluoride System Has a Lower Barrier than the Hydride System

	ΔE		ΔD	
metal (M)	$n = 1$	$n = 2$	$n = 1$	$n = 2$
Y	42.1		-7.7	
Zr	19.3	9.2	-7.2	-1.5
Nb	18.5	22.6	+2.0	-9.8
Mo	34.7	24.6	+2.4	+9.1
Tc	15.5	31.7	+13.4[a]	+0.1[a]
Ru	18.6	28.6	-5.6	-26.6[a]
Rh	13.3		-6.6	

[a] Different spin for the hydride and fluoride systems.

Table 8. Barrier Heights ΔE (kcal/mol) for $MCl_n + CH_4 + \Delta E \rightarrow MCl_nHCH_3$ and Difference in Barrier Heights ΔD (kcal/mol) between the MCl_n and the Corresponding MH_n Reactions, Where a Positive Sign for ΔD Means That the Chloride System Has a Lower Barrier Than the Hydride System

	ΔE		ΔD	
metal (M)	$n = 1$	$n = 2$	$n = 1$	$n = 2$
Y	34.0		+0.4	
Zr	11.2	11.7	+0.9	-4.0
Nb	16.4	23.9	+4.1	-6.2
Mo	34.7	28.0	+2.4	+5.7
Tc	14.9	35.0	+14.0[a]	-3.2[a]
Ru	19.0	31.5	-6.0	-29.5[a]
Rh	16.5		-9.8	

[a] Different spin for the hydride and chloride systems.

Table 9. Difference in Barrier Height (kcal/mol) between X = F and X = Cl for $MX_n + CH_4 + \Delta E \rightarrow MX_nHCH_3$ Where a Positive Sign Means That the Chloride System has a Lower Barrier Than the Corresponding Fluoride System

metal (M)	$n = 1$	$n = 2$
Y	+8.1	
Zr	+8.1	-2.5
Nb	+2.1	-1.3
Mo	+0.0	-3.4
Tc	+0.6	-3.3
Ru	-0.4	-2.9
Rh	-3.2	

the halides to the right is a more ionic bonding than for the hydrides.

a. Results for the Oxidative Addition of H_2. From the results displayed in Figures 1 and 2 for the reaction energies between the metal complexes, MX_n (X = H, F, Cl; n = 1–2), and hydrogen, two main observations can be made. First, the absolute binding energies for the addition of H_2 to the metal complexes vary considerably from system to system. The largest reaction energy of the systems studied here was found for ZrF_2 with -44.9 kcal/mol and the smallest one for $MoCl_3$ where the reaction is endothermic with +18.4 kcal/mol (Table 3). The second main observation which can be made in Figures 1 and 2 is that the curves for the halide complexes are very similar to the ones for the hydrides. The large variations of the reaction energies in Tables 1 and 2 are therefore not explained by special properties of halide ligands, such as a large electron affinity or an ability to back-donate electrons. Instead, the variations are explained by promotion and exchange effects as discussed in ref 5. The exchange effects depend on the number of unpaired 4d electrons, and the promotion effects can often be traced back to the electronic spectra of the metal atoms. One of the main conclusions from the present results is therefore that to a first approximation hydride and halide ligands are quite similar. As will be seen below, there are some notable exceptions to this general rule.

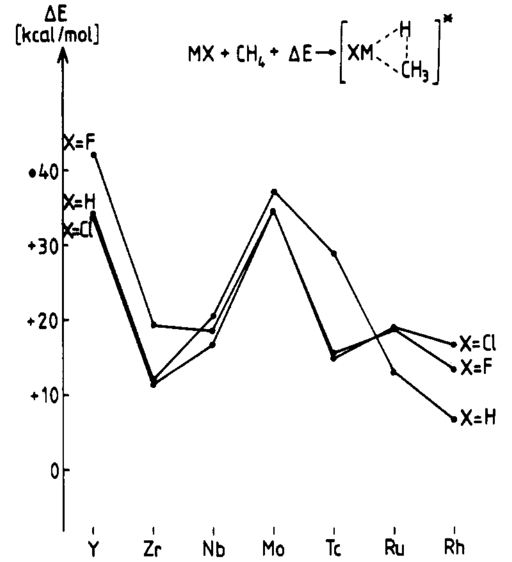

Figure 3. Barrier heights for the reaction between MX and methane, calculated relative to MX and free methane using the ground state of each system.

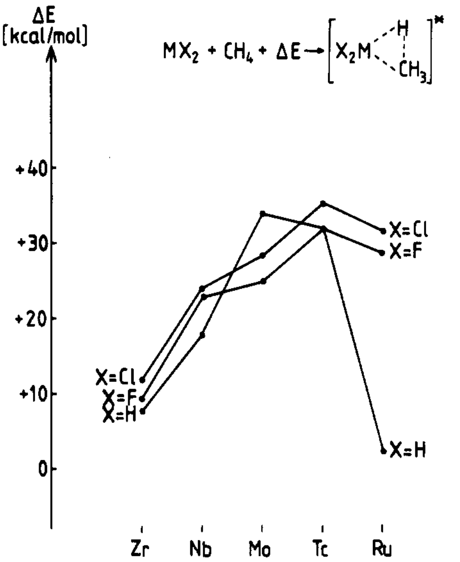

Figure 4. Barrier heights for the reaction between MX_2 and methane, calculated relative to MX_2 and free methane using the ground state of each system.

The main appearance of the curves in Figures 1 and 2 is easy to rationalize. For the systems with one ligand, the curves go through a maximum for molybdenum, whereas for the case with two ligands the maximum appears for

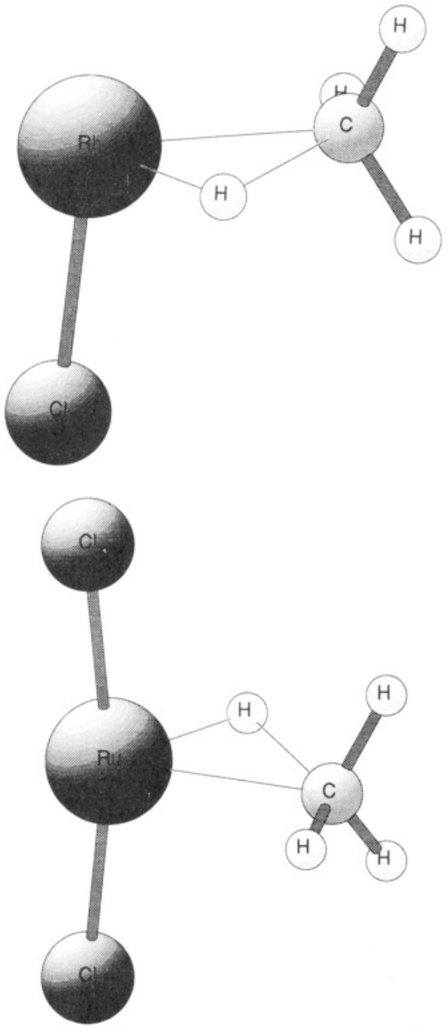

Figure 5. Structures of the transition states for the reactions of RhCl and $RuCl_2$ with methane.

technetium. The variations of these curves coincide with the variations of spin state of the hydride complexes. For the diatomic hydrides the maximum spin is reached for molybdenum, which is a sextet state, while for the dihydrides the maximum spin is reached for technetium, which is also a sextet. It is therefore clear that the main effect involved in the shapes of the curves in Figures 1 and 2 is loss of exchange energy. The direct correspondence between spin and reaction energy is somewhat oversimplified. This can, for example, be seen from the fact that for the diatomic halides the maximum in the curve in Figure 1 occurs for molybdenum while the maximum in spin occurs for technetium. The importance of electronic promotion is best seen on the results for yttrium for the case with one ligand, in Figure 1. Going to the left from molybdenum to zirconium all three curves decrease monotonically in energy, but for yttrium there is a sudden increase in energy. This increase is due to a promotion effect. The diatomic YX systems are singlets and therefore has to be promoted to a triplet to be able to bind two hydrogens. The promotion energy is 20–24 kcal/mol for the three different systems and corresponds well to the increase in energy going from zirconium to yttrium.

In order to identify particular electronic properties of halide ligands on the oxidative addition reaction, it is absolutely essential to study the reaction energy differences given in Tables 1–3. Already a quick glance at the figures indicates that the differences between the halides and the hydrides vary much less than the absolute energies. This is true, in particular, for the systems with few ligands. For most of the chloride complexes with one and two ligands the differences in the reaction energies to the corresponding hydride systems are thus in the range 0–5 kcal/mol. The differences are somewhat larger for the fluoride complexes but they are still rather small.

If the difference entries in Tables 1–3 are studied in detail, two new trends can be identified. First, there is a general trend toward lower (less exothermic) reaction energies when hydride ligands are exchanged with halide ligands to the right in the periodic table. For the chloride systems with one ligand the difference in Table 2 goes from −0.3 kcal/mol for YCl to the left to −14.1 kcal/mol for RhCl to the right, where the minus sign indicates that the chloride system is less stable than the hydride. With two ligands the difference goes from −4.9 kcal/mol for zirconium to −16.5 kcal/mol for $RuCl_2$. The second trend seen in the energy differences is toward smaller reaction energies as the number of halide ligands increases. The reaction energy difference thus goes from +3.9 kcal/mol for NbCl to −12.9 kcal/mol for $NbCl_3$. Both these trends can be rationalized in terms of a weak destabilizing electronic structure effect from halide ligands as compared to hydride ligands for the metals to the right, that originates from a competition between the halide and hydride ligands for the 5s, 5p electrons. This effect can be understood from a purely ionic picture and differences in the spectra of cations and neutral atoms. In the oxidative addition of H_2, the resulting hydrides have to be bound by the metal. For the atoms to the right this is optimally done using two sd-hybrids. In the ligand free case this bonding uses the s^1 state for both the neutral atom and the cation. When a halide ligand is added to the metal, the metal will effectively resemble a cation. This means that the spectrum of the metal has changed from that of the neutral atom to that of the cation. For the metals to the right there is a general difference between these spectra in that for the cations the s^1 state is raised in energy in comparison to the s^0 state. Most of the cations to the right have in fact s^0 ground states whereas most of the neutral atoms have s^1 ground states. This means that in order to form the bonds in the products a promotion is needed for the cation, and the cation will therefore in general form weaker bonds than the neutral atoms. Translated to the halide ligand case, this means that when hydride ligands are exchanged with halide ligands, the metal will form weaker bonds in the product of the oxidative addition, for the atoms to the right.

For most of the systems studied here, the comparison between the results for the halide and corresponding hydride complexes is straightforward. For the entries that are marked with a note in the tables, the situation is somewhat different but still relatively easy to understand. For these systems, the ground-state spin is different for the halide and the hydride systems. For the case with one ligand (n = 1) this only occurs for technetium, and for n = 2 it occurs for technetium and ruthenium. For these systems the halide complexes have a higher spin state. The origin of the higher spin for the halides is a more ionic bonding than for the hydrides.[7,9] One effect of a higher spin for the halides is that the exchange loss energies in the bond formation will be larger. It should be noted that this exchange effect is not present for the differences between the TcX systems even though TcF and TcCl have a higher spin than TcH. The reason for this is that the *products* of the oxidative addition have the same spin for the halides and the hydride of TcX. From Tables 1 and 2, it can be seen that the effects of exchanging hydride with halide ligands have opposite effects on the oxidative addition for TcX and RuX_2. For TcX, the product of the oxidative addition of H_2 is more stable for the halide system than for the hydride system, whereas the opposite is true for RuX_2. The simplest way to understand this difference between the technetium and the ruthenium complexes is to study the spectra of these atoms and of their respective cations and to note that the optimal bonding state is the s^1 state. It is then found that the ground states of the Ru atom and the Tc^+ cation are s^1 states. The ground state of the Ru^+ cation is s^0, and there is a rather high promotion energy to the s^1 state of 25.1 kcal/mol. Therefore, since ruthenium in $RuCl_2$ is more like a cation than it is in RuH_2, the reaction energy for the dihalide will be smaller than for the dihydride. This is thus a good example of the competition for the bonding s, p electrons, discussed above, which is introduced by exchanging hydrides with halides for complexes of the atoms to the right. For technetium the situation is reversed compared to ruthenium and in this case the neutral atom needs to be promoted to reach the s^1 state. The reaction energy for TcCl is therefore larger than for TcH. For these technetium complexes the difference in reaction energies with H_2 can also be understood directly from the promotion energies of the respective diatomic systems. The products of the reactions between TcX and H_2 are quintet states for boht the hydride and the halides. TcF and TcCl are septet ground states and therefore do not need to be promoted to form the bonds to the hydrogens. In contrast, the ground state for TcH is a quintet and a small promotion energy of 4.1 kcal/mol is needed to form the bonds to the hydrogens. This promotion energy corresponds very well to the ΔD value of +3.4 kcal/mol for chlorine in Table 2. For the ruthenium complexes a larger loss of exchange energy for the halides also plays a role, as mentioned above.

One situation where the reaction energy will obviously be increased by exchanging hydride with halide ligands is for systems with zero or doublet spin. In these cases the complex has to be promoted to a higher spin state in order to be able to bind the two products of the oxidative addition reaction. This promotion energy will always be smaller for the halide complexes, where high spin is favored due to a more ionic bonding. For example, RuH_3 is a doublet state and can not bind two more hydrogens without a costly electronic promotion. $RuCl_3$, on the other hand is a quartet state and should therefore bind two hydrogens covalently without any promotion.

b. Results for the Oxidative Addition of CH_4. The trends of the reaction energies for the oxidative addition of methane are very similar to the trends for the hydrogen reaction discussed in the previous section; see Tables 4–6. No further discussion of these reaction energies is therefore required, and the present subsection will instead focus on the results for the barrier of the oxidative addition of methane. These barrier heights, as shown in Figures 3 and 4, have a rather similar behaviour to the corresponding reaction energies. For the case with one ligand ($n = 1$) there is in both cases a maximum at molybdenum, and the curves also go down markedly between yttrium and zirconium. For $n = 2$, both sets of curves have a maximum at technetium. The general similarity of the reaction energy and the activation energy curves means that exchange effects play a significant role also for the barrier of the methane reaction. However, if the energies for the case of $n = 1$ for the systems to the left are compared to those to the right there is a notable difference between the methane barriers and the reaction energies. The methane reaction barriers tend to be lower to the right whereas the largest reaction energies are found to the left. There is a similar shift of energies for $n = 2$, but in this case it only leads to a smaller increase of the barrier heights than for the reaction energies going to the right. This general energy shift between the reaction energies and the barrier heights for methane is due to the importance of the s^0 state in the barrier height region.[1] This is the state with the least repulsion toward ligands and allows the metal to approach methane close enough to effectively interact with the C–H bond. The s^0-state can only mix into the wave function for the atoms to the right, since it has the wrong spin for the atoms to the left, and this will therefore lead to a general lowering of the barriers to the right for the methane reaction. This effect can be seen in Figures 3 and 4 in comparison to the hydrogen reaction energies in Figures 1 and 2. For the atoms to the left, the s^2 and sp states will instead mix into the wave function. This is a contributing factor for the large reaction energies to the left, but this mixing is not very effective in the transition state region. For example, for the complexes of yttrium, which has an s^2 atomic ground state, there will be large contributions from this state. This leads to relatively large exothermicities for the yttrium complexes but also to some of the highest barriers of the systems studied here, due to the large repulsion from almost two sp-electrons.

To study the particular effects of the halide ligands on the methane barrier it is, just as in the case of the hydrogen molecule reaction discussed in the previous subsection, more informative to study the differences to the corresponding reaction with hydride ligands. When this is done a few major conclusions can be drawn. For the atoms to the left from yttrium to molybdenum, there is a rather small effect of exchanging hydride with halide ligands. For chlorine the effect is 0–4 kcal/mol on the barrier heights for $n = 1$ and 4–6 kcal/mol for $n = 2$. For fluorine the effects are also small in most of these cases, but there are some exceptions which will be discussed below.

For the atoms to the right the exchange of hydrides with halides has a much more marked effect on the methane barrier than it has to the left. For the group of systems to the right, where the spin state is the same for the hydride and the halide reactions, there is a marked destabilizing effect from the halide ligands. For RuCl the barrier for the methane reaction is 6.0 kcal/mol higher than for RuH and for RhCl the increase in barrier height is 9.8 kcal/mol. This is the same destabilizing effect as described above for the hydrogen reaction and is due to a competition for the bonding 4s electrons. These electrons are to a large extent removed from the metal when halide ligands are present, but they are needed to form the bonds to the hydride and methyl group formed in the oxidative addition.

For the systems to the right where there is a change of spin state, the differences between the halide and hydride reactions are even larger. In order to understand these results, the optimal situation for a low barrier for the oxidative addition reaction should first be summarized. The first condition for a low barrier is that there is a low-lying excited state with a different spin than the ground state. One of these two close-lying states, the ground state and one excited state, should have two steps higher spin ($2S+1$) than the insertion product, and this state is needed to form strong covalent bonds. The other state should have a lower spin, which is needed to decrease the repulsion toward the approaching methane molecule. The second condition is that the state with the lowest spin should have a small population of the repulsive 4s, 4p electrons. These two conditions are well exemplified by the rhodium atom which has a quartet ground state and where there is a low-lying doublet s^0 state. This leads to a low barrier for the oxidative addition for the rhodium atom. For the complexes of the metals to the right the main effect of replacing hydride with halide ligands is that the metal has fewer 4s, 4p electrons, both in the high-spin and in the low-spin state. For the binding high-spin state this is a drawback and a destabilization of the product of the oxidative addition can therefore be noted in the halide case for the atoms to the right, as discussed above. In contrast, for the low-spin state the reduction of the number of 4s, 4p electrons in the halide case will be an advantage for an effective approach of the bond of the reactant. Going to the results in Tables 7–9, the barrier height for $RuCl_2$ is as much as 29.5 kcal/mol higher than for RuH_2, while for TcCl the barrier height is 14.0 kcal/mol lower than for TcH. The change for RuH_2 is particularly interesting, since this complex has the lowest barrier of all systems studied so far with only 2.0 kcal/mol. The main origin of this low barrier is that the excited low-spin state of RuH_2 has a low 4s, 4p population of only 0.48 electron. The 4d population is 7.40, and taking the limitations of the Mulliken population analysis into account, this is indicative of a rather pure s^0 state. The excitation energy to the singlet state is also relatively low with 19.7 kcal/mol. For $RuCl_2$ no promotion to bind the products is needed either, but the competition for the bonding 4s electrons, which was discussed above, is a strongly destabilizing effect. However, of even larger importance for the high barrier for $RuCl_2$ is the fact that the low-spin triplet state of $RuCl_2$ is as high as 37.8 kcal/mol above the ground state.

For the TcX systems the situation is opposite to the one for the RuX_2 systems. In the TcX case the barrier is actually substantially lower for the halides than for the hydride. The barrier for TcCl to break the bond in methane is only 14.9 kcal/mol, which is 14.0 kcal/mol lower than it is for TcH. The key difference between TcCl and TcH is the nature of the low-spin state. As mentioned above, a low spin-state with few 4s, 4p electrons is perfectly suited for approaching the C–H bond in methane since it is not so repulsive towards the ligand electrons. For TcCl the lowest low-spin state is a $^5\Sigma^+$ state which is indeed such a state. The 4s, 4p population in this state is only 0.46 electrons. In contrast, the lowest low-spin state of TcH, which is also a $^5\Sigma^+$ state, has 1.38 4s, 4p electrons. This rather high 4s, 4p population makes this state less useful for breaking the bond in methane. The complicating factor for the TcX-systems, which requires the above more detailed analysis, is that the excitation energy between the high-spin and the low-spin state is lower for TcH than for TcCl, with absolute values of 4.1 kcal/mol for TcH and 23.3 kcal/mol for TcCl. Normally, this would lead to a lower barrier for TcH, but not in this case. This must be considered a special case and is connected with the fact that technetium is precisely in the middle of the row where both the spin and character of the states change in a rather irregular way.

From the results for the barrier heights of the TcX and RuX_2 systems, discussed above, it is clear that the effects on the barrier heights for the oxidative addition reaction by exchanging hydride with halide ligands depend on the spectra of the individual complexes of the atoms to the right. If there is no change of spin for the ground state, exchanging hydrides with halides should increase the excitation energy to the low-spin state since the bonding is more ionic for the halides and there will therefore normally be a larger barrier height for the oxidative addition reaction for the halides. In addition to this effect there is the competition for bonding 4s electrons which will also tend to make the barrier higher in the halide case. However, when there is a change of spin state between the hydride and the halide case, the halide reaction may well have a lower barrier than the hydride reaction. This is, for example, the case for the $RhCl(PH_3)_2$ system which has recently been studied by us[1] and by Koga and Morokuma.[23] For this system, the barrier for breaking the C–H bond in methane is higher when the chlorine is exchanged by hydrogen. One reason for this effect is the following. The ground state of the hydride system $RhH(PH_3)_2$ is a singlet, which thus needs to be promoted to bind the products. The excitation energy to the lowest triplet state is 34.5 kcal/mol. By exchange of the hydride with a chloride, the high-spin triplet is brought down in energy, as is always the case. In this case this leads to a much smaller energy difference between the high-spin and the low-spin states which is in general a major advantage (TcX discussed above is a special case where this is not true). The ground state of $RhCl(PH_3)_2$ is a triplet which does not need to be promoted to form the bonds in the product. In this context it is worth noting that the lowering of the high-spin state, which will always occur for the halides, does not always lead to a decreased splitting between the high-spin and the low-spin states, but this will obviously also depend on which of these states is the lowest state. For example, for the case of RuX_2 discussed above, the splitting between the states is much larger for the halides than for the hydride, which in turn leads to higher barriers for the halides. It should finally be added that another contributing factor for the higher stability of $RhCl(PH_3)_2$ compared to $RhH(PH_3)_2$ is that the ability to bind lone-pair ligands for complexes of metals to the right is larger when the system is ionic, and this effect will favor the oxidative addition for the halide complexes.

In the normal chemical notation, a diatomic metal–halide compound is considered to have an M(I) metal valence state. This state of the metal is usually considered to be similar to an M^+ cationic state. Since the oxidative addition reaction between the second row cations M^+ and methane has been studied recently,[24] it is of interest to make a few comments on those results in comparison to the present results. There are two main differences between the cationic reactions and the neutral reactions. The presence of the charge in the cationic systems leads to rather strongly electrostatically bound molecular complexes between methane and the cation. This electrostatic effect stays to some extent also in the transition state region and will have a lowering effect on the barrier heights.

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[23] Koga, N.; Morokuma, K. *J. Phys. Chem.* **1990**, *94*, 5454.

[24] Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. Submitted for publication in *J. Phys. Chem.*

However, the presence of the charge for the cations will also tend to increase the promotion energy to the bonding s^1 state, in particular for the metal atoms to the right. This effects leads to weaker bonds in the product for the cations than for the neutral atoms. Overall, these two effects lead to rather similar barrier heights for the neutral systems and the cations in most cases. Even in a purely ionic picture of MCl, there is a fundamental difference between this system and M^+, and this concerns the presence of the negative charge on chlorine. The presence of this negative charge will tend to lower the excitation energy to the bonding s^1 state and the bond strengths in the products will therefore increase compared to the purely cationic case. Another way to express this effect is to note that the presence of the negative charge will lower the ionization energy of the metal compared to the cationic systems and thus make the metal in MCl a better electron donor than M^+. Another effect of the negative charge is a reduction of the long-range charge-induced dipole attraction. The differences between the modeling of the reactivity between MCl systems by an M^+ cation or by an M^+ cation together with a negative point charge at the position of Cl, has interesting general implications and these will be discussed in detail in a separate paper.[25]

There are some results of the present study which are interesting to comment on in connection with the simple point charge models mentioned above. These are the results for the barrier heights of YF and ZrF in comparison to the results for YCl and ZrCl. For most systems there are only small differences between the fluorides and the chlorides, but for these particular systems there are markedly lower barriers for the chloride systems by 8.1 kcal/mol in both cases. The populations of these systems are very similar and give no indication of the origin of this difference. However, this difference could be due to the differences in bond lengths between the fluorides and the chlorides of approximately 0.5 Å with the longer distances for the chlorides. Indeed, modeling the methane reaction of the YF and YCl systems by Y^+ cations and negative point charges placed at positions corresponding to the fluoride and the chloride distances reproduces the difference in barrier height reasonably well. The barrier heights obtained with the point charge model is 44.3 kcal/mol for YF and 32.3 kcal/mol for YCl, showing that in this case also the absolute values of the barrier heights are quite well reproduced. The simplest interpretation of these model results is that the most important electrostatic effect in this case appears to be the stabilization due to the positive charge on the metal. This stabilization is decreased by the presence of the negative point charge, and it is decreased more in the case of fluorine since the point charge is closer to methane in that case.

III. Conclusions

The main conclusions drawn in a previous study concerning the effects involved in the oxidative addition reaction remain true also in the present study of halide ligand effects. Loss of exchange energy is thus still a dominating effect for the general behavior of the reaction energies and barrier heights across the periodic table. The loss of exchange energy is largest for the systems with the largest number of unpaired 4d electrons in the middle of the row and leads to a minimum in the reaction energies and a maximum in barrier heights in this region. Furthermore, there are two optimal conditions for a low barrier in the oxidative addition reaction. First, there must be two low-lying states (including the ground state) with opposite spin. The high-spin state of these is needed to bind the products and the low-spin state is needed in the transition state region. The second condition is that the low-spin state has a small population of the repulsive 5s, 5p electrons so that the metal complex can approach the reactant with a minimum of direct repulsion. In connection with the last condition the s^0 state of the metal plays a key role, and the barriers for the oxidative addition are therefore in general lower for the complexes to the right where this is a low-lying state. For the complexes to the left, the s^0 state has the wrong spin to mix into the wave function.

In order to best see the particular effects halide ligands have on the oxidative addition reaction, the halide results should be compared to the results for the corresponding complexes with hydride ligands. When this is done, a few main conclusions can be drawn. First, with a few exceptions the results for the halide complexes are very similar to those for the hydride complexes. This is true, in particular, for the complexes of the atoms to the left where the bonding is more ionic. Second, there is a notable trend toward a destabilizing effect of halide ligands to the right in the periodic table. The origin of this effect is a more covalent bonding to the right with the 5s electrons playing a key role. The simplest way to understand this effect is to consider the metal as a cation when halide ligands are present. Since the bonding s^1 state is higher in energy for the cations than for the neutral atoms to the right, the cations will form weaker bonds than the neutral atoms. The consequence of this competition for the metal 5s electrons can be noticed already for the simplest possible hydrides and halides. For example, for RhH_2 the first and the second hydrogen bind about equally strongly with energies of 64.1 and 65.2 kcal/mol. In contrast, for RhHCl the hydrogen is bound by only 39.7 kcal/mol.

Halides bind with more ionic bonds than the hydrides, and this has two immediate simple consequences of importance for the oxidative addition reaction. First, when a 4d electron is donated to a ligand, this will lead to an increase of the spin for the atoms to the right where the 4d shell is more than half-filled. For the atoms to the left there will instead be a decrease of the spin. In contrast, when a covalent bond is formed there will be a decrease of the spin both to the left and to the right. Transition metal halides will therefore in general have the same spin as the hydrides for the atoms to the left, but there is a tendency toward higher spin for the halides compared to the hydrides for the atoms to the right since the hydrides are more covalently bound. In other words, exchanging hydrides with halides for complexes of the atoms to the right will bring down high-spin states in comparison to low-spin states. Since one of the conditions for a low barrier for the oxidative addition reaction is that there are two low-lying states of different spin, this will be an advantage for the halide complexes in cases where the high-spin state of the hydrides is high in energy. This is, for example, the case for the $RhCl(PH_3)_2$ complex, which has recently been studied.[1,23] In the opposite situation, where the low-spin state is high in energy for the hydride, it will be a disadvantage for the oxidative addition to

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(25) Siegbahn, P. E. M.; Svensson, M.; Wahlgren, U. To be submitted for publication.

replace the hydrides with halides. The second important effect of the more ionic bonds for the halides is that the metal 5s,5p-population will tend to be smaller than for the hydrides. This is a disadvantage, as already mentioned above, for the high-spin state since this state should bind the products, and there will be a competition for these bonding electrons between the halides and the R groups of the dissociated reactant. For the low-spin state the low metal 5s, 5p population for the halides is an advantage, since this allows the metal to approach the reactant more closely and thus interact more effectively with the bond to be broken.

In summary, the main effects of exchanging hydride with halide ligands for the oxidative addition reaction are relatively easy to rationalize in terms of a more ionic bonding for the halides. For the complexes of the metals to the left this exchange will not have any major effects, but for the atoms to the right the effects can be significant, and they will in general depend on the positions of the low-spin and high-spin states in these complexes. The present paper is the second in a systematic study of ligand effects in the oxidative addition reaction. One important class of systems not yet studied is the one where also lone-pair ligands are present. The combined effects of halide, hydride, and lone-pair ligands will therefore be the subject of a forthcoming study of the same type.

Appendix A. Computational Details

In the calculations reported in the present paper of halide ligand effects on the oxidative addition reaction of hydrogen and methane to complexes of second row transition metal atoms, reasonably large basis sets were used in a generalized contraction scheme. All valence electrons, except the fluorine 2s and chlorine 3s electrons, were correlated using size consistent methods.

For the metals the Huzinaga primitive basis[26] was extended by adding one diffuse d function, two p functions in the 5p region and three f functions, yielding a (17s, 13p, 9d, 3f) primitive basis. The core orbitals were totally contracted[27] except for the 4s and 4p orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects. The 5s and 5p orbitals were described by a double-ζ contraction, and the 4d orbital was described by a triple-ζ contraction. The f functions were contracted to one function giving a [7s, 6p, 4d, 1f] contracted basis. For carbon and fluorine the primitive (9s, 5p) basis of Huzinaga[28] was used, contracted according to the generalized contraction scheme to [3s, 2p]. 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 (12s, 9p) basis of Huzinaga,[28] including an even-tempered diffuse p function with exponent 0.044. One d function with exponent 0.54 was added.[29] For hydrogen the primitive (5s) basis from ref 30 was used, augmented with one p function with exponent 0.8 and contracted to [3s, 1p]. 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,[31] somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt[32] was used. The frozen 4s and 4p orbitals are described by a single-ζ contraction, the valence 5s and 5p orbitals are described by a double-ζ basis, and the 4d orbital is described by a triple-ζ basis, including one diffuse function. The rest of the atoms are described by standard double-ζ basis sets, with the chlorine core replaced by an ECP.[33]

The correlated calculations were in all cases performed using the modified coupled pair functional (MCPF) method,[34] 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 (4d and 5s) and all valence electrons except the fluorine 2s and chlorine 3s 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 developed by Pettersson,[35] 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.[36]

All the present calculations were performed on an FX-80 ALLIANT computer and on an IBM Risc 6000 computer, and the final energy evaluations were performed using the STOCKHOLM set of programs.[37]

A few words should be said about the level of calculation chosen in the present study. As described above the geometries are optimized at the SCF level and the relative energies are calculated at the MCPF level; i.e., electron correlation effects are included. First, it should be emphasized that the correlation effects on both the reaction energies and the barrier heights are large. The size of the correlation effects also varies strongly across the periodic table so that the diagrams shown in the figures would have appeared very differently if SCF results had been used instead of correlated results.[2,12] The conclusion is that correlation effects have to be included in the calculations to give reliable trends for activation energies and binding energies. In this context it should be noted that the correlation effects for this type of systems are well described by the single reference MCPF method.[1,17d,38] Second, it can be questioned if the use of SCF-optimized geometries give reliable results, in particular since the correlation effects are so large. There are several results on systems similar to those studied in the present paper showing that SCF-optimized and MCPF-optimized ge-

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(26) Huzinaga, S. *J. Chem. Phys.* **1977**, *66*, 4245.

(27) (a) Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070. (b) Raffenetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452.

(28) Huzinaga, S. *Approximate Atomic Functions, II*; Department of Chemistry Report; University of Alberta: Edmonton, Alberta, Canada, 1971.

(29) Pettersson, L. G. M.; Siegbahn, P. E. M. *J. Chem. Phys.* **1985**, *83*, 3538.

(30) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(31) GAMESS (General Atomic and Molecular Electronic Structure System). Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *OCPE Bull.* **1990**, *10*, 52.

(32) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(33) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(34) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606.

(35) Pettersson, L. G. M.; Åkeby, H. *J. Chem. Phys.* **1991**, *94*, 2968.

(36) Martin, R. L. *J. Phys. Chem.* **1983**, *87*, 750. See also Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. Am.* **1976**, *66*, 1010.

(37) STOCKHOLM is a general purpose quantum chemical set of programs written by P. E. M. Siegbahn, M. R. A. Blomberg, L. G. M. Pettersson, B. O. Roos, and J. Almlöf.

(38) Bauschlicher, C. W., Jr.; Partridge, H.; Sheehy, J. A.; Langhoff, S. R.; Rosi, M. *J. Phys. Chem.* **1992**, *96*, 6969.

ometries give very similar relative energies.[1,39] The origin of this surprising behavior is that in the most interesting region of the potential energy surfaces (including both the transition state and the insertion products) the SCF and the MCPF surfaces are quite parallel.[4] Another reason SCF geometries can be used is that the potential energy surfaces are often rather flat in both the transition state region and the insertion product region, so that discrepancies in SCF- and MCPF-optimized structures have very small effects on the relative energies. A more systematic investigation of the accuracy of the geometry optimization scheme have recently been performed.[40] For seven different metal hydride methyls, containing different second row metals and a varying number of ligands, equilibrium geometries were determined both at the SCF level and at the QCISD (quadratic configuration interaction singles and doubles) level. The energy of each structure was obtained at the MCPF level. For each system the total energies calculated in the SCF and in the QCISD geometries are very similar, within 1.5 kcal/mol, with the energies at the SCF geometries actually lowest in all cases. This study also contains a test of the barrier height for the oxidative addition of water to the palladium atom, comparing the MCPF energies for the SCF- and the QCISD-optimized geometries, which gives agreement within less than 1 kcal/mol. The conclusion is that the use of SCF-optimized structures gives reliable results for the trends in activation energies and binding energies if correlation effects are included in the energy calculations.

The present level of calculation, where all valence electrons are correlated using basis sets including f functions on the metal, is a major improvement compared to calculations done at the Hartree–Fock level. However, even in the present treatment the errors compared to exact results can not be neglected. Exact errors are difficult to give but reasonable estimates can be given. The present treatment has errors of 3 kcal/mol for the H–H bond and about 5 kcal/mol for the C–H bond. It is reasonable to expect that the error should be 7–8 kcal/mol for a bond involving a second row transition metal. These error estimates are essentially confirmed in recent comparisons with measured bond strengths in cationic systems.[24,41] Three points are important to note in this context. First, the errors in the bond strengths are not random but highly systematic. The bond strengths are thus always underestimated. This means that corrections for these errors are expected to leave the trends shown in the figures and the tables essentially unchanged. Second, even though an error in a bond strength of 7 kcal/mol is not negligible it should be remembered that the errors at the Hartree–Fock level is almost one order of magnitude larger and that useful results still have been generated at this level. The same argumentation can of course be applied to an even greater extent to results obtained at the extended Hückel level. Thirdly, to increase the accuracy notably from the present level is extremely costly. For example, a large correlated calculation of the C–H bond strength in methane including d functions on hydrogen and f functions on carbon, still gives an error of 2 kcal/mol,[42] to be compared to the present error of 5 kcal/mol.

Finally, all the results reported are for the ground state of each system. In most cases the ground state of the reactants has a different total spin than the ground state of the products. Two comments can be made in this context. First, the question whether the binding energies should be given relative to reactants with the same spin as the products or relative to the spin of the ground-state reactants is mainly a pedagogical problem. One set of energies can be easily transferred to the other set using available excitation energies. The common practice has been to relate to the energies for the ground spin states of the reactants, and this procedure will be followed here. The main advantage with this procedure is that it is well-defined. A more serious question concerning the spin states is what actually happens dynamically during the reaction. If the reaction starts with ground-state reactants and ends up with ground-state products with a different spin, the spin has to change through spin–orbit effects. These effects are known to be strong for transition metals so this surface-hopping is intuitively expected to occur with a high probability. This problem has been studied in detail by Mitchell,[43] who showed that in the case of the association reaction between the nickel atom and carbon monoxide, the crossing probability is near unity. Also, in order to rationalize the experimental results for the oxidative addition reaction between the nickel atom and water, a high crossing probability has to be assumed.[44] Since the potential surface for the high spin reactants is normally strongly repulsive, the crossing between the two spin surfaces will in most cases occur far out in the reactant channel, long before the saddle point of the reaction is reached. This is at least true in the most interesting cases where the low spin surface of the reactants is not too highly excited. This means that the probability for surface-hopping through spin–orbit coupling will affect the preexponential factor of the rate constant, but not the size of the barrier. The computed barrier heights discussed here should therefore in most cases be directly comparable to experimental measurements of activation energies.

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(39) (a) Sodupe, M.; Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Phys. Chem.* **1992**, *96*, 2118, (b) Rosi, M.; Bauschlicher, C. W., Jr. *Chem. Phys. Lett.* **1990**, *166*, 189, (c) Bauschlicher, C. W., Jr.; Langhoff, S. R. *J. Phys. Chem.* **1991**, *95*, 2278.

(40) Siegbahn, P. E. M.; Svensson, M. *Chem. Phys. Lett.*, in press.

(41) Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845.

(42) Bauschlicher, C. W., Jr.; Langhoff, S. R. *Chem. Phys. Lett.* **1992**, *177*, 133.

(43) Mitchell, S. A. In *Gas-Phase Metal Reactions*; Fontijn, A., Ed.; Elsevier: Amsterdam; 1992; Chapter 12.

(44) Mitchell, S. A.; Blitz, M. A.; Siegbahn, P. E. M.; Svensson, M. *J. Chem. Phys.*, in press.