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Halide ligand effects on olefin insertion into metal–hydrogen bonds for second row transition metal complexes

Per E.M. Siegbahn

Department of Physics, University of Stockholm, Box 6730, S-113 85 Stockholm (Sweden)

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Abstract

Halide ligand effects have been studied for the olefin insertion reaction into second row transition metal–hydrogen bonds. The specific effect of the halide is identified by comparing the insertion reaction for MH_2 and MHX, where X is a chlorine or a fluorine atom. In this comparison the exchange and promotion effects are effectively cancelled. There is a dramatic lowering effect of 20 kcal/mol on the olefin insertion barrier for the metals to the right in the Periodic Table when halide ligands are present. In contrast, exchanging hydride and halide ligands for the metals to the left has almost no effect on the reaction. The large effect to the right is explained by a larger contribution of the s^0-state of the metal when there are halide ligands. The barrier-determining effect is the repulsion between the olefin and the non-bonding electrons of the metal, and the s^0 state is less repulsive than the s^1-state. When a halide is bound to the metal the metal becomes more cationic to the right, and the ground states of the naked metal cations to the right are s^0-states. When hydrides are the only ligands the metal becomes more neutral, and the ground states of the naked neutral atoms to the right are in most cases s^1-states.

Key words: Transition metals general; Olefin insertion; Hydride; Molecular orbital calculations

1. Introduction

Olefin insertion into metal–hydrogen and metal–alkyl bonds are essential steps in many important catalytic reactions. Probably the most important of these is the Ziegler-Natta process for polymerization of olefins [1,2], where olefin is inserted into a metal–alkyl bond. An example of where olefin insertion into a metal–hydrogen bond may occur is the hydrogenation of alkenes by the Wilkinson catalyst, where this is the rate-limiting step [3]. Theoretical, mainly *ab initio*, studies of these types of reaction have recently been reviewed by Koga and Morokuma [4]. These studies have focussed on the complexes found to be of main experimental interest. During the past year a different, more systematic, approach to study basic catalytic reactions has been initiated. In the first step of this approach the reactions, as simplified as possible, without additional ligands, are studied for an entire row of the Periodic Table. This has been done for the second transition metal row for both olefin insertion into a metal–hydrogen [5] and that into a metal–alkyl [6] bond; the goal is to identify the main properties of the metal itself on the reactions. The next natural step in this systematic approach is to investigate the effects on the reactions by adding hydrogen ligands as the simplest possible covalent ligands. The results of these studies, which were also presented in refs. 5 and 6, allow identification of the importance of, for example, exchange and rehybridization effects.

The present paper presents the results from the third step of this approach, which is concerned with the effects of exchanging hydride ligands with more electronegative ligands like chloride and fluoride ligands. One reason for the interest in this type of ligands is that most catalysts used in practice for these reactions contain strongly electronegative ligands. By comparing the results for hydride and halide ligands the specific effects of ligands that are more electronegative and also have electron donating capability can be isolated and identified. Other effects, such as exchange and promotion effects, should effectively be cancelled in this type of comparison.

A few main conclusions have been drawn in the

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previous study of the ligand-free olefin insertion reactions [5,6]. The most important of these conclusions is that electron repulsion effects between non-bonding metal electrons, in particular the 5s-electrons, and the olefin is a dominating factor in the reaction and is responsible for the main differences between the metals. This effect is most clearly seen for the case of the ligand-free insertion for rhodium, for which a very low barrier is found. The reason for this is that the low-lying $4d^9$-state (the s^0-state) of rhodium has no repulsive 5s-electrons and can still form the d-bond required at the transition state. The preference for binding with an s^0 state at the transition state also explains why the barriers for ligand-free palladium and ruthenium are very much higher than those for rhodium. A further notable finding in this context is that for the metals to the left empty 4d-orbitals can hybridize with the 5s-orbitals to reduce markedly the repulsion towards the olefin leading to low barriers for these metals. This also has the effect that the barrier height between niobium and molybdenum increases significantly both with and without additional hydride ligands. The reason for this is that for molybdenum the 4d- and the 5s-orbitals have the same occupation and any mixing between these orbitals will therefore not change the total energy and can consequently not reduce the repulsion towards the olefin. The addition of the hydride ligands leads to a general lowering of the barrier heights. The origin of this decrease is that the electronegative hydrides remove some of the repulsive electrons from the metal. This effect is of particular interest for the present study where more strongly electronegative ligands are added. From the previous results one might expect a general decrease in the barrier heights when halide ligands are present. Another way of reducing the repulsion between the metal and the olefin, and thereby reducing the barrier, is simply to ionize the metal. Recent calculations for cationic zirconium and titanium complexes without additional ligands did, indeed, give very low barriers [7–10]. It is in this context noteworthy that some of the most efficient homogeneous catalysts recently found experimentally are cationic species [11,12].

It is of interest to compare the results of the previous study of the olefin insertion into a metal–hydrogen bond [5] with the results for the insertion into the metal–alkyl bond [6]. When hydride ligands are added the barriers for insertion into the metal–alkyl bonds are between 10 and 20 kcal/mol for most neutral metal complexes, which is in the expected range for heterogeneous catalysts [13]. The barriers for the corresponding olefin insertion into a metal–hydride bond are generally about 20 kcal/mol lower. The origin of this difference is the directional character of the metal–alkyl bond, which means that a tilting of the methyl group is required in the transition state. This effect causes an increase in the barrier compared to that in the metal-hydrogen case. It is reasonable to expect that the more ionic the bonding, the less costly the tilting of the methyl group. In line with this expectation Brookhart *et al.* [14] recently observed experimentally a difference in barrier heights of only 10.3 kcal/mol between insertion into M–H and M–R bonds for a cationic rhodium complex in which the bonding should be quite ionic.

A few further results of the previous studies are also worth mentioning. For example, as hydride ligands are added to the metal, there is a reduction in the variation of the barrier heights going across the Periodic Table. The explanation of this effect is that since the main origin of the differences between the metals is the varying degree of repulsion between non-bonding metal electrons and olefin electrons, the removal of some of these metal electrons by the electronegative ligands will also remove part of the difference between the metals. It is furthermore relevant to note the absence of some expected relations. For example, there is no correlation between the metal–hydrogen bond strength and the ease of olefin insertion into this bond. Neither is there any relationship between the exothermicity of the insertion reaction and the barrier height, nor between the olefin π-bond strength and the barrier height.

Since most of the present paper is concerned with a comparison of olefin insertion into the M–H bonds of MH_2 and MHCl, the electronic structure aspects of these triatomic systems are of great importance in the present context. The binding in these two systems for second row transition metals have been discussed and compared recently [15,16]. The main conclusion is that the M–H bonding in these two systems is very similar for the metals to the left but show significant difference for those to the right, where the bonding is more covalent. Covalent bonds are preferentially formed by use of the s^1-state of the metal. When a halide is present, as in MHCl, the metal tends to be more cationic than it is in MH_2. The ground states of the metal cations to the right are s^0-states, and must therefore be promoted to form the covalent M–H bonds. The metal in MH_2 is more neutral and the ground state of most metals to the right is the s^1-state. The consequence of this difference between the neutral atoms and the cations to the right is that the M–H bonds will be weaker for MHCl than they are for MH_2. The bonding in MHCl will also to a large extent involve the non-repulsive s^0-state of the metal, which has direct consequences for the olefin insertion reaction, as will be seen below.

2. Results and discussion

Our calculations on effects of halide ligands on the olefin insertion reaction were, for simplicity, performed for insertion into metal–hydrogen bonds only. The results are expected to have some bearing also on insertion into metal–alkyl bonds, since in previous studies [5,6] it was found that the results are to a large extent parallel for insertions into these two types of bonds. The simplest possible systems containing both metal–hydrogen bonds and halide ligands are the MHX systems, where X is either fluorine or chlorine. Most of the results presented here are therefore for olefin insertion into the M–H bonds of these triatomic complexes. The results are directly compared with those for the corresponding insertion into the M–H bonds of the MH_2 systems [5] in order to isolate the effects specific to the halide ligands. It should be emphasized that the barrier heights discussed below are given with respect to the isolated metal complexes and free ethylene. Experimentally, the reaction is normally viewed as a migratory insertion reaction starting from the olefin addition complexes. However, it was shown previously [5,6] that the analysis of the trends in the barrier heights is much simpler starting from the free metal complexes.

TABLE 1. Geometries and energies for the olefin addition reaction: $MHCl + C_2H_4 + \Delta E \rightarrow MHClC_2H_4$. The energies are calculated relative to ground state MHCl systems and ethylene. H_1 is the hydrogen atom directly bonded to the metal atom. ΔE(H) is the corresponding result for MH_2

M	State	M–C	M–Cl	M–H_1	C–C	∠(Cl–M–H_1)	ΔE	ΔE(H)
Y	^{2}A"	2.54	2.58	2.03	1.42	123.1	−25.8	−25.1
Zr	^{1}A'	2.19	2.48	1.90	1.50	125.2	−52.6	−53.3
Nb	^{2}A'	2.18	2.42	1.82	1.45	127.1	−38.0	−43.3
Mo	^{3}A"	2.17	2.40	1.73	1.43	124.3	−21.6	−18.3
Tc	^{4}A"	2.30	2.46	1.66	1.39	112.2	−11.7	−13.4
Ru	^{3}A"	2.41	2.41	1.59	1.36	100.4	−21.1	−18.4
Rh	^{2}A'	2.45	2.39	1.52	1.36	94.8	−30.1	– [a]
Pd	^{1}A'	2.42	2.36	1.48	1.36	89.0	−29.4	– [a]

[a] H_2 becomes molecularly bound.

TABLE 2. Transition state geometries and barrier heights for the olefin insertion reaction: $MHCl + C_2H_4 + \Delta E \rightarrow MClC_2H_5$. The energies are calculated relative to ground state MHCl systems and ethylene. C_1 is the carbon atom closest to the metal atom and H_1 is the hydrogen atom in the M–H bond which is inserted by the olefin. ΔE(H) is the corresponding result for MH_2

M	State	M–C_2	M–C_2	M–H_1	C_2–H_1	C_1–C_2	ΔE	ΔE(H)
Y	^{2}A	2.55	2.85	2.05	1.80	1.39	−7.7	−6.9
Zr	^{1}A	2.29	2.42	1.88	1.60	1.47	−3.5	−3.1
Nb	^{2}A	2.25	2.39	1.81	1.57	1.45	−5.8	−10.7
Mo	^{3}A	2.22	2.36	1.75	1.60	1.44	+4.7	+4.3
Tc	^{4}A"	2.20	2.39	1.72	1.65	1.42	+10.4	+2.4
Ru	^{3}A"	2.21	2.42	1.64	1.64	1.41	−22.9	−2.4
Rh	^{2}A'	2.19	2.40	1.59	1.57	1.41	−23.5	−0.9
Pd	^{1}A'	2.17	2.40	1.57	1.62	1.40	−24.1	−1.4

TABLE 3. Populations at the transition state of the olefin insertion reaction: $MHCl + C_2H_4 + \Delta E \rightarrow MClC_2H_5$. C_1 is the carbon atom closest to the metal atom, H_1 is the hydrogen atom in the M–H bond which is inserted by the olefin

Metal(M)	M(q)	4d	5s	5p	C_1(q)	C_2(q)	H_1(q)	Cl(q)
Y(^{2}A)	+0.40	1.16	0.78	0.54	−0.22	−0.42	−0.09	−0.40
Zr(^{1}A)	+0.54	2.65	0.35	0.37	−0.30	−0.45	+0.01	−0.42
Nb(^{2}A)	+0.41	3.57	0.59	0.36	−0.33	−0.41	+0.03	−0.38
Mo(^{3}A)	+0.36	4.79	0.47	0.33	−0.31	−0.37	+0.05	−0.39
Tc(^{4}A")	+0.35	5.86	0.45	0.29	−0.29	−0.34	+0.04	−0.48
Ru(^{3}A")	+0.31	6.93	0.42	0.28	−0.30	−0.29	+0.08	−0.50
Rh(^{2}A')	+0.20	8.05	0.36	0.34	−0.31	−0.26	+0.13	−0.51
Pd(^{1}A')	+0.22	9.05	0.40	0.26	−0.32	−0.23	+0.12	−0.54

The discussion starts with the results for chloride ligands. The optimized geometries and energies of the π-complexes between MHCl and C_2H_4 are shown in Table 1. The corresponding results for the transition states of the olefin insertion are presented in Table 2, with populations in Table 3. The corresponding results for the MHF systems are given in Table 4–6. The results for the π-complexes between MCl and C_2H_4 are given in Table 7. A typical π-complex is shown for $RhHCl(C_2H_4)$ in Fig. 1 and for a typical transition

TABLE 4. Geometries and energies for the olefin addition reaction: $MHF + C_2H_4 + \Delta E \rightarrow MHFC_2H_4$. The energies are calculated relative to ground state MHF systems and ethylene. H_1 is the hydrogen atom directly bonded to the metal atom

M	State	M–C	M–F	M–H_1	C–C	∠(F–M–H_1)	ΔE
Ru [a]	^{3}A”	–	–	–	–	–	–12.3
Rh	^{2}A’	2.45	1.96	1.54	1.36	96.2	–31.2
Pd	^{1}A’	2.40	1.96	1.50	1.36	92.4	–32.4

[a] Rhodium geometry used.

TABLE 5. Transition state geometries and barrier heights for the olefin insertion reaction: $MHF + C_2H_4 + \Delta E \rightarrow MFC_2H_5$. The energies are calculated relative to ground state MHF systems and ethylene. C_1 is the carbon atom closest to the metal atom and H_1 is the hydrogen atom in the M–H bond which is inserted by the olefin

M	State	M–C_1	M–C_2	M–H_1	C_2–H_1	C_1–C_2	ΔE
Y	^{2}A	2.57	2.86	2.07	1.79	1.40	–6.7
Zr	^{1}A	2.30	2.40	1.89	1.56	1.48	–2.1
Nb	^{2}A	2.25	2.38	1.81	1.57	1.45	–6.5
Mo	^{3}A	2.22	2.36	1.76	1.59	1.45	+1.1
Tc	^{4}A”	2.21	2.41	1.72	1.67	1.42	+10.7
Ru	^{3}A”	2.22	2.42	1.65	1.63	1.41	–17.1
Rh	^{2}A’	2.18	2.37	1.62	1.56	1.42	–27.1
Pd	^{1}A’	2.16	2.40	1.58	1.64	1.40	–27.3

TABLE 6. Populations at the transition state of the olefin insertion reaction: $MHF + C_2H_4 + \Delta E \rightarrow MFC_2H_5$. C_1 is the carbon atom closest to the metal atom, H_1 is the hydrogen atom in the M–H bond which is inserted by the olefin

Metal(M)	M(q)	4d	5s	5p	C_1(q)	C_2(q)	H_1(q)	F(q)
Y(^{2}A)	+0.56	1.02	0.76	0.52	–0.22	–0.42	–0.10	–0.53
Zr(^{1}A)	+0.70	2.53	0.34	0.32	–0.30	–0.47	+0.01	–0.54
Nb(^{2}A)	+0.56	3.41	0.61	0.34	–0.32	–0.42	+0.03	–0.51
Mo(^{3}A)	+0.53	4.61	0.49	0.30	–0.32	–0.38	+0.03	–0.51
Tc(^{4}A”)	+0.50	5.74	0.43	0.26	–0.29	–0.34	+0.01	–0.56
Ru(^{3}A”)	+0.46	6.84	0.38	0.27	–0.30	–0.33	+0.07	–0.58
Rh(^{2}A’)	+0.36	7.96	0.35	0.27	–0.32	–0.27	+0.11	–0.59
Pd(^{1}A’)	+0.35	8.97	0.36	0.25	–0.31	–0.24	+0.10	–0.62

TABLE 7. Geometries and energies for the olefin addition reaction: $MCl + C_2H_4 + \Delta E \rightarrow MClC_2H_4$. The energies are calculated relative to ground state metal chlorides and ethylene. ΔE(H) is the corresponding result for MH

M	State	M–C	M–Cl	C–C	ΔE	ΔE(H)
Y	^{1}A’	2.27	2.60	1.56	–15.6	–15.1
Zr	^{2}A’	2.20	2.52	1.52	–42.3	–43.3
Nb	^{3}A”	2.18	2.49	1.48	–36.0	–30.9
Mo	^{4}A”	2.20	2.51	1.44	–11.7	–10.6
Tc	$^5B_1$	2.27	2.48	1.40	–31.1	–33.1
Ru	$^4B_1$	2.45	2.48	1.36	–33.6	–21.4
Rh	$^3A_2$	2.53	2.46	1.35	–26.0	–27.5
Pd	$^2A_1$	2.56	2.43	1.35	–22.6	–17.8

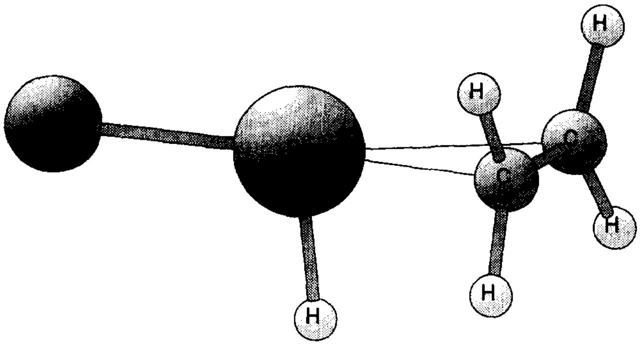

Fig. 1. The π-complex between RhHCl and ethylene.

state for $ZrHCl(C_2H_4)$ in Fig. 2. The energetic data given in the Tables are also displayed in Figs. 3 and 4. Before the results are discussed in detail below, it is useful to consider the exothermicity of the olefin insertion into a metal–hydrogen bond. This exothermicity is to a large extent insensitive to the particular additional ligands in the complex, but depends mostly on the carbon–carbon σ-bond formed and π-bond broken. There is also a contribution from the difference in the metal–hydrogen bond broken and metal–carbon bond formed, which leads to some slight variation in the exothermicities between the metals. In the previous study [5] the calculated exothermicities were found to decrease more or less monotonically from yttrium at 30 kcal/mol to palladium at 25 kcal/mol.

Of the results obtained in the present study there are a few which are especially remarkable. These concern the halide ligand effect on the olefin insertion barrier for the complexes to the right in the periodic table. For the MH_2 systems the barrier height for olefin insertion compared to free MH_2 and C_2H_4 is for ruthenium −2.4 kcal/mol, for rhodium −0.9 kcal/mol and for palladium −1.4 kcal/mol. When a

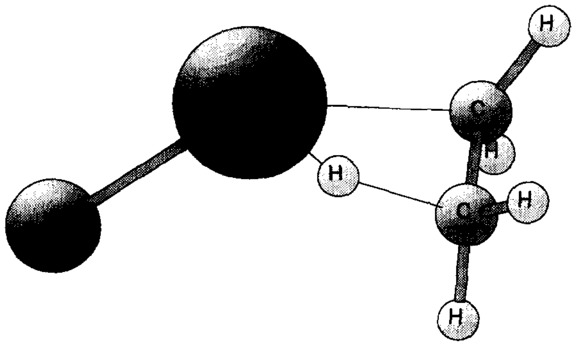

Fig. 2. The transition state structure for the olefin insertion into the Zr–H bond of ZrHCl.

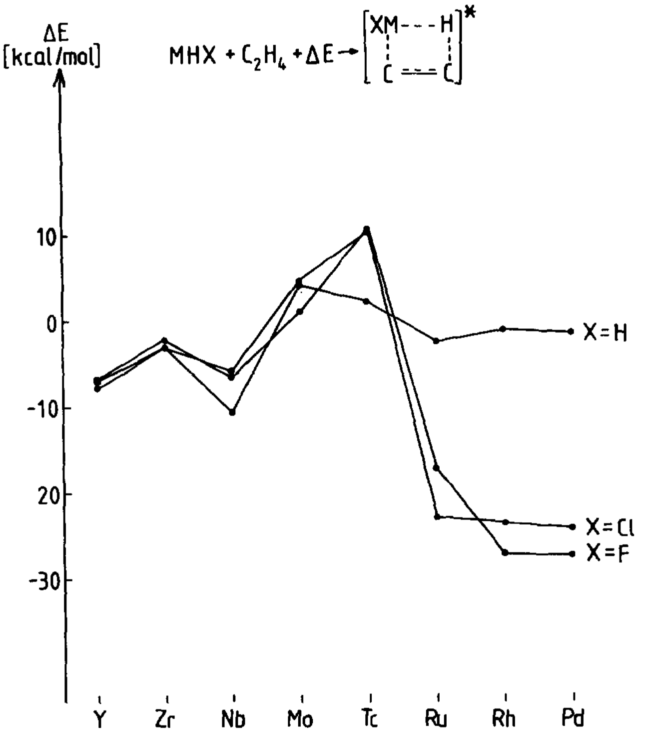

Fig. 3. Transition state energies for the olefin insertion reaction with MHCl, MHF and MH_2. The energies are calculated relative to an asymptote with a free ethylene.

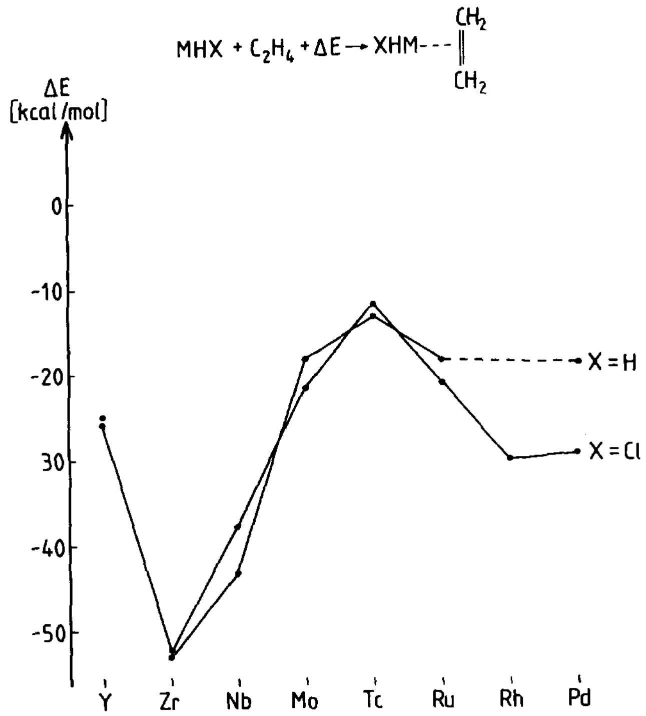

Fig. 4. π-complex energies for the addition reaction between ethylene and MHCl, MHF and MH_2. The energies are calculated relative to an asymptote with a free ethylene.

hydride is replaced by a chloride the barrier heights are decreased by the significant amount of 20 kcal/mol for all three of these metals. These results are particularly striking in view of the quite small effects of only a few kcal/mol found for the complexes to the left caused by the same ligand exchange. The strong stabilization of the transition states for the complexes to the right by replacing a hydride with a halide can be understood in the following way. First, one of the main conclusions previously drawn in earlier studies of the olefin insertion reaction [5,6] was that repulsive effects between non-bonding metal electrons and the olefin electrons are of key importance for the size of the barrier. This repulsion is particularly large for the metal 4s,4p electrons. The best example of this effect is the low insertion barrier found for RhH relative to those for RuH and PdH [5]. At the transition state, where the formation of a single d-bond is required, rhodium can use its low-lying s^0-state. In contrast, the s^0-state of palladium cannot form a d-bond, and for ruthenium this state is much higher in energy. When there is a halide ligand in the complex the metal will resemble a metal cation, whereas with only hydride ligands the metal will be more neutral [15,16]. This has direct consequences on the spectrum for the metal atoms, in particular for those to the right in the Periodic Table. Most of the metal cations to the right have s^0 ground states whereas most of the neutral atoms have s^1 ground states. This means that the metal-halides to the right will have easy access to s^0-states and will, just as in the case of the neutral rhodium atom, form stable transition state complexes. In contrast, without halides present as for MH_2, there will in general be higher excitation energies to s^0-states and the barriers for olefin insertion will be higher. This change in the atomic spectrum is the most important effect when halide ligands are added. There is also another quite important effect and that is the direct charge-induced dipole effect, which is enhanced for the metals to the right when halide ligands are present. With halide ligands present the metal will generally be more positive than when they are absent. It was shown in a previous paper [10] that even non-transition metal cations tend to have low barriers for olefin insertion, which must to a large extent be due to attractive electrostatic effects. However, it should in this context be remembered that this electrostatic effect is much smaller when counterions are present than it is for isolated cations.

The second most interesting finding from the present calculations is that the halide ligand effects are much smaller for metals to the left than for those to the right in the Periodic Table. This does not require different explanations than those used above for the effects found to the right. First, the differences in the metal spectra between cations and neutral atoms noted above for the atoms to the right do not appear for the atoms to the left. Neither the cations nor the neutral metal atoms to the left have s^0 ground states. Also, the requirement for s^0 ground states for the metal atoms is not as strong for the atoms to the left since the repulsive metal electrons can be hybridized away by using a mixing with empty d-orbitals. The importance of this hybridization effect was best demonstrated in the previous studies [5,6] by the sudden large increase in barrier height going from niobium, which has empty d-orbitals, to molybdenum, which does not have empty d-orbitals in its ground state. Another difference between the atoms to the left and those to the right occurs for the charge induced dipole effect. Since the ionization energies for the atoms to the left are smaller than they are to the right, already the metal–hydrogen bond is quite ionic for the atoms to the left. The ionicity will therefore not increase much when the hydride is exchanged with a halide for these atoms. These similarities and differences between metals to the right and to the left were discussed in detail recently in a comparison of the bonding in the MHCl and MH_2 systems [15]. The larger degree of ionicity in the bonding to the left leads to very similar M–H bonds for MHCl and MH_2. On the other hand, for the atoms to the right where covalency is more important, the M–H bonds are much weaker in the MHCl systems than they are in the MH_2 systems.

The data in Tables 1 and 2 show that there are qualitative differences between the potential surfaces for the metals to the left and to the right for the present systems. For the metals to the right the π-binding energies are in the range 20–30 kcal/mol and the transition states in the range 23–24 kcal/mol. Since the exothermicity of the olefin insertion into a metal–hydrogen bond should be in the range 25–30 kcal/mol irrespective of the particular ligands in the complex [5], the potential surfaces for the metals to the right are extremely flat all the way from the π-complexes to the insertion products. In contrast, the potential surfaces for the metals to the left are much more irregular. In particular, the π-complexes (except for yttrium) are very strongly bound. The largest binding energy is obtained for zirconium with 52.6 kcal/mol. In spite of these large binding energies for the π-complexes, the energies at the transition states are higher than they are to the right. One reason for these differences between the metals to the left and those to the right is that the π-complexes to the left form metallacycles with the olefin. This requires two free covalencies in addition to those needed for the hydride and the halide. Since yttrium has only three covalencies in total, the metallacyclic bonding cannot be formed and the π-complex binding energy is therefore much smaller than it is for zirconium and niobium. For the metals towards the middle of the row the exchange loss when the metallacycle is formed is an important factor, and the π-complex binding energy is therefore only 22 kcal/mol for molybdenum. The π-complexes for the metals to the right have predominantly electrostatic bonding, which can be seen from the resulting C–C bond distances. For the complexes of ruthenium, rhodium and palladium the C–C bond distance is 1.36 Å, which is close to the C–C bond distance of 1.33 Å in free ethylene. In contrast, the C–C bond distance for the zirconium π-complex is 1.50 Å, not far from the value for ethane of 1.54 Å, which is typical for a single bond. An additional covalent ligand changes the potential surface markedly for zirconium. The results from the previous study on olefin insertion into ZrH_3 gave a π-complex binding energy of only 18.6 kcal/mol and a barrier height of -15.9 kcal/mol [5]. It is therefore clear that the present large π-complex binding energies, leading to the irregular forms of the potential surfaces for zirconium and niobium, are not typical for saturated realistic metal complexes to the left, but can only be related to very unsaturated systems. However, the energies for both the insertion products and the transition states are expected to change much less with the addition of more ligands.

The binding energy of the π-complex for ruthenium is 8–9 kcal/mol smaller than it is for rhodium and palladium. The origin of this difference is not a different type of binding for ruthenium. Instead, the binding energy difference is a result of a different ground state for RuHCl. Both RhHCl and PdHCl have bent low spin ground states while RuHCl has a linear high-spin quintet ground state. In order to bind the olefin a promotion to the triplet is needed for the ruthenium system and this costs 7.4 kcal/mol [16]. It is noteworthy that this promotion energy is higher for RuHF by 5.3 kcal/mol than it is for RuHCl. In line with this, the π-complex binding energy is 8.8 kcal/mol smaller for RuHF than for RuHCl. The origin of the small difference between these numbers is that the geometry optimization partly failed for the RuHF system and the rhodium geometry had to be used. Partial failure of SCF geometry optimizations for weakly bound π-complexes to the right has in several cases previously been observed [5].

The ruthenium and technetium systems are somewhat special cases in the present comparison between olefin insertion for the MHX and the MH_2 systems. The MHX system for ruthenium is the only one in which the ground state structure is different from that for MH_2 [16], and TcH_2 is the only linear high-spin dihydride [15]. This means that the ground state of the π-complex has a lower spin than the ground state of the inserted complex for RuHX, TcHX and TcH_2. The insertion process will therefore to some extent occur on an excited state surface, either for the reactant or for the product. In the present study the same spin state has been assumed as the one studied previously [5,6]. This is the triplet spin for ruthenium, which is undoubtedly the lowest surface in the transition state region, and it is the quartet state for technetium. When the quartet state is used for technetium, the promotion energy for the product from the ground state sextet to the lowest quartet state will to some extent contribute to the barrier height for the insertion reaction. Since the ground state of RuHX is high-spin and that for RuH_2 low-spin, the promotion energy between these states is probably larger for TcHX than it is for TcH_2. This has the effect that the barrier heights are somewhat higher, by about 8 kcal/mol, for the TcHX than they are for the TcH_2 systems. The same argument would have held also for the ruthenium systems but in this case the cationic metal effect for the MHX systems, discussed in detail above, is much more important and leads to substantially lower barriers for RuHX than for RuH_2. In connection with this discussion of spin states it can be added that spin-orbit coupling effects are so strong for transition metal complexes that spin-crossings normally occur with very high probability [17]. This means that the best way to think about these systems is to consider them as always occurring on the potential surface with lowest energy at that point. As an example, the oxidative addition reaction between the nickel atom and water, which was recently studied in a combined experimental and theoretical effort [18], proceeds through two subsequent crossings between surfaces of different spin.

It is of interest to compare the halide ligand effect for the π-complexes and for the transition states for the systems to the right. As already discussed above, exchanging a hydride with a halide has a dramatic lowering effect at the transition states for these atoms of about 20 kcal/mol. This was mainly attributed to the cationic nature of the metal when the halide is present, leading to important contributions of the s^0-state, which has a very low repulsion towards the olefin. The direct charge-induced dipole effect from a more positive metal was judged to have a smaller influence. One reason for this conclusion was that if this effect were dominant it would be expected to be similar for the binding of the π-complex. Unfortunately, a direct measure of the halide stabilization effect cannot be obtained, since the corresponding π-complexes for the MH_2 systems of rhodium and palladium adopt a different type of geometry, with an

η^2-coordinated hydrogen molecule. Based on the results for the π-complex binding energy for ruthenium, including a consideration of the promotion effect, and of results for the smaller metal-hydrides, an estimated stabilization of less than 10 kcal/mol of the hydride–halide exchange can be estimated (see also arguments in next paragraph). This binding energy increase includes both the direct charge effect and the reduction of repulsion from the s^0-state of the metal. It can thus be concluded that the total halide effect is much larger at the transition state. On the basis of these results, the direct reduction of the repulsion towards the olefin is considered to be the most important effect at the transition state, in line with the conclusions previously drawn [5,6].

When the effect of halides on the π-complexes is considered, it is interesting to compare the π-binding energies for MH taken from ref. 5 with the corresponding binding energies for MCl given in Table 7. Support for the above assignment of a rather small halide effect for the π-complexes of the MHCl systems is found, since the binding energies between MCl and C_2H_4 are not particularly large even for the metals to the right. They are, except for ruthenium, very close to those for MH. In fact, on the basis of the binding energies of Table 6 alone, exchanging a hydride with a halide would not be expected to have any effect at all for the π-complexes. However, it should be noted that for the systems to the right the binding has a somewhat changed character. As seen from the C–C bond distances for these systems, with values in the range 1.35–1.36 Å close to that in ethylene, the bonding is predominantly electrostatic. For the binding between MH and ethylene there are large covalent contributions in terms of donation and back-donation, leading to somewhat longer C–C bonds of about 1.40 Å.

An interesting geometric effect in the transition states of the olefin insertion has already been noted [5]. The transition states for the systems to the right from technetium to palladium all have C_s symmetry, with the halide in the MCC-plane. For the systems to the left the halide moves out of the MCC-plane and the systems no longer have any symmetry; see Fig. 1. The origin of this difference has been assigned to sd-hybridization to the left and sp-polarization to the right [5]. The importance of sd-hybridization to the left was best seen in the previous study from the large difference in barrier heights between the niobium and molybdenum systems. Niobium has empty d-orbitals and can therefore mix empty and occupied orbitals to reduce the repulsion at the transition state. For molybdenum all non-bonding d-orbitals are singly occupied and high-spin coupled, and these orbitals can therefore not be used in any effective way for hybridization. The energetic effect of moving the halide out of the plane is quite significant. For example, for ZrHCl the transition state is lowered by 7.7 kcal/mol when the halide moves out of the plane. It should be added that the geometry change for the halide is accompanied by other significant changes, such as an increase of the C–C bond length from 1.41 to 1.47 Å. A contributing factor in this energy gain could be that the halide finds a more favourable position for interacting with the empty d-orbitals of the metal when it is out of the MCC-plane. However, this effect cannot predominate since exactly the same preference is found when the halide is exchanged with a hydride. In connection with the discussion of the geometries of these catalytic systems it can be added that the qualitative geometrical structure of the catalysts for the Ziegler-Natta reaction has been discussed intensively recently in connection with the stereospecificity in syndiotactic polymerizations [7–9]. This discussion is often based on a model in which the stereospecificity is determined by the planar or non-planar nature of the starting catalyst. The results of the present study indicate that the qualitative nature of the geometry is often quite different for the reactant and the transition state, and this could also have effects that can influence the stereospecificity.

For comparison, calculations were also performed for the reaction between MHF and C_2H_4, with the results shown in Tables 4–6. These results provided no surprises but were extremely useful as a test of the corresponding chlorine results, as discussed further below. The most notable difference between the fluorine and chlorine results has already been mentioned, namely the binding energy of the π-complexes for ruthenium. This is a special case, since the RuHX system has to be promoted and RuHF has a slightly higher promotion energy than RuHCl. There are also slight differences in the energies of the transition states to the right between the fluorine and the chlorine systems. The best way to rationalize differences between fluoride and chloride ligands is normally to consider them as point charges [19]. In this picture the differences appear because the bond distances for fluoride ligands are much shorter than for chloride ligands. A discussion of this point is not pursued further here since the differences between the systems are too small.

Halide ligand effects have recently been studied also for the oxidative addition of C–H and H–H bonds [19] and there are interesting parallels between the results of that study and of this one. For both the olefin insertion and the oxidative addition reaction the effects for the systems to the left are very small when hydrides are exchanged with halides. For both these reactions there are also large effects of hydride-halide exchange for the systems to the right. However, for the oxidative addition reaction the barrier heights are much higher for the halide than for the hydride case, in contrast to the olefin insertion reaction where the opposite applies. However, the explanation of these different effects is the same. When halides are present as ligands the metal will be more cationic for the metals to the right. This leads to a dominant contribution of the metal s^0-state. For the olefin insertion reaction this is a big advantage since the important repulsion of the olefin will be reduced and the barriers will therefore be low for the metals to the right. In contrast, for the oxidative addition reaction this will be a disadvantage since the s^0-state needs to be promoted to form the bonds in the product of the reaction. The promotion energy to the s^1-state will therefore enter more or less directly for the barrier heights, which will then be higher for the halide than for the hydride case.

Theoretical aspects of the olefin insertion reaction, also called hydride migration to a coordinated olefin, have recently been reviewed by Koga and Morokuma [4]. References to earlier *ab initio* work on this reaction can be found in this review and in refs. 5 and 6. Of the work discussed in Ref. 4 there is one study by Koga *et al.* [20] which is more directly concerned with the subject dealt with in the present paper, that is with halide ligand effects. Ethylene insertion for $H_2RhCl(C_2H_4)(PH_3)_2$ and a corresponding complex in which the chloride has been exchanged with a hydride, $H_2RhH(C_2H_4)(PH_3)_2$, was compared, and it was found that chlorine makes the ethylene insertion more endothermic. This reaction is considered to be an internal rearrangement reaction and the reaction energy is therefore counted relative to the π-complex. It should be recalled that the present energies are always expressed relative to an asymptote with a free ethylene. Since no energies were given in ref. 20 with respect to this asymptote, the results in the present tables and those of ref. 20 are not directly comparable. The energies for the inserted products in the present work should be about 25 kcal/mol [5] for the atoms to the right. The π-complexes of MH_2 for the atoms to the right should have energies of about 20 kcal/mol and those of MHCl about 30 kcal/mol for rhodium and palladium. This means that the rearrangement reaction is indeed more endothermic for MHCl than for MH_2, in line with the results found by Koga *et al.*, However, it should be noted that this finding does not alter the fact that the presence of halide ligands dramatically lowers the barrier for the olefin insertion even counted from the π-complex for the atoms to the right. Therefore, the present results do not support the conclusion drawn by Koga *et al.*, that chloride ligands play a key role in making olefin insertion rate-determining in the hydrogenation of alkenes. On the contrary, if halide ligands were exchanged with hydride ligands the insertion process should be made more difficult, at least for the present systems. Another comment can also be made in this context. The π-complex binding energies are likely to be quite sensitive to the presence of other ligands, particularly if they are sterically demanding. The transition state energies and the product energies should be much less sensitive. The present model results for the insertion barrier and reaction energies are therefore much more reliable if they are counted from the asymptote with a free ethylene than if they are counted from the π-complex.

An important aspect of the present approach could be of some general interest. During the course of the study it became increasingly evident that a comparison with previous results is not only interesting but is also necessary in order to obtain correct results. This is exemplified by the calculations on the transition states for the olefin insertion for the metals to the left. All the geometry optimizations for the transition states converged to structures with the halide in or close to the MCC-plane. As noted above it is quite important energetically that the halide is out of the MCC-plane for the systems to the left. The energy differences at the MCPF level between the planar and the optimal structure are 5–10 kcal/mol. When the resulting barrier heights for the planar structures to the left were compared with those obtained in the previous study for the MH_2 systems it was immediately clear that there was something wrong. This was mainly based on the results from the previous study in which the MHCl and MH_2 systems were compared and the bonding was found to be extremely similar for the metals to the left [16]. Therefore, a situation where the transition states for olefin insertion was qualitatively different for these systems, both in terms of geometry and energy, is unreasonable. This led to an investigation of non-planar geometries for the MHCl olefin insertion transition states which eventually led to the results presented here. It should be added that the large preference for the out of plane geometries to the left is mainly a correlation effect. With the small basis sets used in the geometry optimization, the planar geometry is actually slightly preferred for both zirconium and niobium. Therefore, any information available from the computed Hessian at this level will not help to resolve this problem. With the larger basis sets used in the final energy evaluation, the non-planar geometry for zirconium is preferred by only 0.6 kcal/mol at the SCF level, and is increased to 7.7 kcal/mol at the MCPF level. These examples are only a few of a large number found so far in which a crosswise comparison of results has been shown to be absolutely necessary before the results can be relied upon.

3. Conclusions

Halide ligands can sometimes have very large effects on insertion reactions. These effects only occur for metals to the right in the Periodic Table. When an olefin is inserted into a metal–hydrogen or metal–alkyl bond the barrier height is quite sensitive to direct repulsive effects between non-bonding metal electrons and the olefin electrons. It was noted in the previous studies that if a metal to the right can utilize the s^0-state to form the required single d-bond at the transition state, the barrier for the insertion is very low [5,6]. The best example of this was provided by the insertion into RhH where the low-lying d^9-state of rhodium can form the d-bond at the transition state with a resulting very low barrier. When a halide is present as a ligand the metal will be more cationic. The ground states of the cations to the right have s^0 ground states, and thus there will be larger contributions from this state when halide ligands are present. In contrast, when there are only hydride ligands the metal will be more neutral. Since the ground states of the neutral atoms to the right in most cases are s^1-states, the promotion energy to the s^0-state will be higher in these cases and the barrier for the olefin insertion higher. Quantitatively this means that when a hydride in MH_2 is exchanged with a halide the barrier for olefin insertion is lowered by as much as 20 kcal/mol.

The second most interesting result of the present study is that the effect of exchanging a hydride with a halide ligand for the complexes of metals to the left is remarkably small. In fact, for modelling purposes, the use of a simple hydride ligand in place of a halide ligand for these complexes provides a very good model. This finding is not unique for the present systems but is true for most systems studied so far. It is therefore not correct to describe halides as generally more electron-withdrawing than hydrides, since this depends very much on whether the systems are to the left or to the right. A major difference between the systems to the left and to the right is that for those to the left ionic effects dominate, while for those to the right there are much stronger covalent components in the bonding. The origin of this difference is, of course, that the ionization energies are higher to the right than to the left.

In a recent study on the oxidative additions of C–H and H–H bonds it was found that for metals to the right halide ligands have a destabilizing effect. For those to the left, hydrides and halides are again remarkably similar for this reaction. The origin of the destabilization to the right is that the cationic s^0-state forms weaker bonds than the neutral s^1-state. This leads to lower exothermicities for the oxidative addition reaction when hydrides are exchanged with halides. The smaller exothermicities in turn, lead to higher barriers for the halide case. These differences between complexes with halide and hydride ligands are quite similar to the differences for the reactions between the naked neutral and cationic metals themselves [21].

This work is part of a systematic study of trends for second row transition metal complexes. An aspect of this type of study that has not been emphasized much before is that the reliability of the results is made much higher by a comparison between different systems following different trends. In fact, a significant portion of the observations for the present systems was initially wrong, but the errors were identified and corrected after detailed comparisons with other similar systems. It may even be argued that this is the most important aspect of this type of study on such relatively complicated transition metal complexes, where the possibility of selecting a state of wrong spin or spatial symmetry or to converge to a non-optimal geometry is quite high.

References

1 K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, *67* (1955) 541.
2 G. Natta, *Macromol. Chem.*, *16* (1955) 213.
3 R. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 1988.
4 N. Koga and K. Morokuma, in A. Zedien (ed.), *Transition Metal Hydrides*, Ch. 6, VCH Publishers, New York, 1992.
5 P.E.M. Siegbahn, *J. Am. Chem. Soc.*, *115* (1993) 5803.
6 P.E.M. Siegbahn, *Chem. Phys. Lett.*, *205* (1993) 290.
7 L.A. Castonguay and A.K. Rappe', *J. Am. Chem. Soc.*, *114* (1992) 5832.
8 H. Kawamura-Kuribayashi, N. Koga and K. Morokuma, *J. Am. Chem. Soc.*, *114* (1992) 8687.
9 H. Kawamura-Kuribayashi, N. Koga and K. Morokuma, *J. Am. Chem. Soc.*, *114* (1992) 2359.
10 V.R. Jensen and P.E.M. Siegbahn, *Chem. Phys. Lett.*, *212* (1993) 353.
11 X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc.*, *113* (1991) 3623.
12 Y.W. Alelyunas, R.F. Jordan, S.F. Echols, S.L. Borkowsky and P.K. Bradley, *Organometallics*, *10* (1991) 1406.
13 O. Novaro, E. Blaisten-Barojas, E. Clementi, G. Giunchi and M.E. Ruiz-Vizcaya, *J. Chem. Phys.*, *68* (1978) 2337.
14 M. Brookhart, A.F. Volpe, Jr. and D.M. Lincoln, *J. Am. Chem. Soc.*, *112* (1990) 5634.
15 P.E.M. Siegbahn, *Theor. Chim. Acta*, *87* (1994) 441.
16 P.E.M. Siegbahn, *Theoret. Chim. Acta*, in press.
17 S.A. Mitchell, in A. Fontijn (ed.), *Gas-Phase Metal Reactions*, Ch. 12, Elsevier, Amsterdam, 1992.
18 S.A. Mitchell, M.A. Blitz, P.E.M. Siegbahn and M. Svensson, *J. Chem. Phys.*, *100* (1994) 423.
19 P.E.M. Siegbahn and M.R.A. Blomberg, *Organometallics*, *13* (1994) 354.
20 (a) N. Koga, C. Daniel, J. Han, X.Y. Fu and K. Morokuma, *J. Am. Chem. Soc.*, *109* (1987) 3455; (b) C. Daniel, N. Koga, J. Han, X.Y. Fu and K. Morokuma, *J. Am. Chem. Soc.*, *110* (1988) 3773.
21 M.R.A. Blomberg, P.E.M. Siegbahn and M. Svensson, *J. Phys. Chem.*, in press.

22 S. Huzinaga, *J. Chem. Phys., 66* (1977) 4245.
23 (a) J. Almlöf and P.R. Taylor, *J. Chem. Phys., 86* (1987) 4070; (b) R.C. Raffenetti, *J. Chem. Phys., 58* (1973) 4452.
24 S. Huzinaga, *Approximate Atomic Functions, II*, Department of Chemistry Report, University of Alberta, Canada, 1971.
25 L.G.M. Pettersson and P.E.M. Siegbahn, *J. Chem. Phys., 83* (1985) 3538.
26 S. Huzinaga, *J. Chem. Phys., 42* (1965) 1293.
27 GAMESS (General Atomic and Molecular Electronic Structure System): M.W. Schmidt, K.K. Baldrigde, J.A. Boatz, J.H. Jensen, S. Koseki, M.S. Gordon, K.A. Nguyen, T.L. Windus and S.T. Elbert, *OCPE Bulletin, 10* (1990) 52.
28 P.J. Hay and W.R. Wadt, *J. Chem. Phys., 82* (1985) 299.
29 P.J. Hay and W.R. Wadt, *J. Chem. Phys., 82* (1985) 270.
30 P.E.M. Siegbahn and M. Svensson, *Chem. Phys. Lett., 216* (1993) 147.
31 D.P. Chong and S.R. Langhoff, *J. Chem. Phys., 84* (1986) 5606.
32 R.L. Martin, *J. Phys. Chem., 87* (1983) 750; see also R.D. Cowan and D.C. Griffin, *J. Opt. Soc. Am., 66* (1976) 1010.
33 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.

Appendix A. Computational details

In the calculations reported in the present paper on the olefin insertion for the MHCl and MHF systems 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 [22] 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 [23] 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 zeta contraction and the 4d by a triple zeta 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 [24] 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 [24], and including an even-tempered diffuse p-function with exponent 0.044. One d-function with exponent 0.54 was added [25]. For hydrogen the primitive (5s) basis from Ref. 26 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 [27], somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt [28] was used. The frozen 4s and 4p orbitals are described by a single zeta contraction and the valence 5s and 5p orbitals are described by a double zeta basis and the 4d 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 [29]. For more details of the accuracy of the present type of geometry optimization, see ref. 30.

The correlated calculations were in all cases performed using the Modified Coupled Pair Functional (MCPF) method [31], which is a size-consistent, single reference state method. The zero-th order wave-function is 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 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 [32].

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 [33].