Oxidative Addition of Methane to Rhodium(I) and Ruthenium(II) Complexes of Particular Interest

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The oxidative addition reaction of methane to some model Rh(I) and Ru(II) complexes has been studied in order to suggest directions for new experiments. The Rh(I) model complexes are of the general form RhXL where X is either a hydrogen or a chlorine and where L stands for a lone-pair ligand. Lone-pair ligands with a varying amount of π-bonding were investigated. It is suggested that a combination of hydride and lone-pair ligands with a minimum of π-bonding should be an optimal combination for the methane reaction. Of the systems studied here, $RhH(NH_3)$ thus gives the most stable products and the lowest transition state energy. The trends of the results are analyzed and compared to the results for the corresponding Ru(I) complexes. In a previous study it was found that RuH_2 has a very low barrier for the methane reaction. In order to approach more realistic systems the reactant RuH_2 is modified in various ways in the present study. First, the hydrides are substituted by methyl groups and halides. Secondly, lone-pair ligands are added. The conclusions are that it should be advantageous for the methane reaction to have methyl (or more general R groups) and lone-pair ligands with as small a covalent bonding as possible. To make a Ru(II) complex activate methane, which has not yet been done experimentally, halide ligands and lone-pair ligands with strong π-bonding should be avoided.

I. Introduction

The main electronic structure effects involved in the oxidative addition reaction for second row transition metal complexes have recently been systematically investigated. In the first step of this approach the reaction between the bare metal atoms and methane was studied.[1] The second step was a similar study for the metal cations.[2] Covalent ligand effects were studied in the third step by gradually saturating all covalencies of the metal by hydrogen atoms.[3] More electronegative ligands with lone pairs were studied in the fourth step where the hydride ligands from ref 3 were substituted by halide ligands.[4] Finally, in the fifth step lone-pair ligands were added.[5] In all these studies the entire second row of the transition metals from yttrium to palladium were compared for the methane reaction. In most cases comparisons were also made to the corresponding hydrogen molecule reaction. In the course of this project a large number of different systems have been studied and some of these have turned out to be particularly interesting. First, rhodium complexes and especially Rh(I) complexes have been found to have low barriers for the C–H activation of methane. This finding is in general agreement with what has been found experimentally, where so far only Rh(I) complexes from the second transition row have been found to activate methane.[6,7] However, of all the systems studied in this project the lowest barrier for the methane reaction has not been found for a Rh(I) complex but for a simple Ru(II) complex, that of RuH_2.[3] In the present paper a deviation is made from the general systematic strategy and focus is instead put on the two groups of systems, Rh(I) and Ru(II) complexes, found to have the lowest barriers for the methane reaction. The main points of interest will be the effect of different types of lone-pair ligands and for the case of the Ru(II) complexes also the effect of substituting the hydride ligands with other R groups. It should be noted that the present project is not at a stage where fully realistic systems can be studied with high accuracy. Instead, the complexes chosen for this and the other studies should be regarded as model complexes. Ideally, the results for these model systems can give suggestions of directions to go for new experiments.

Only a few transition metals are represented among the 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 IrCp*L (L = CO, PR_3).[8,9] Shortly afterward the analogous rhodium fragment (RhCp*L) was found to be active[6] and later on also the $RhClL_2$ (L = PPh_3) fragment.[7] 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 and lone-pair ligands like CO or PPh_3 are present for all these complexes.

Two recent reviews of theoretical studies of the oxidative addition reaction to metal centers have appeared; one is

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written by Koga and Morokuma[10] and the other is written by Hay.[11] Kitaura, Obara, and Morokuma have studied the oxidative addition of H_2 to $Pt(PH_3)_2$ and determined the three-centered transition state using energy gradient methods.[12] This was the first theoretical determination of the transition state structure for an organotransition-metal reaction.[13] The same reaction was studied by Noell and Hay.[14] Koga and Morokuma[15] have investigated the details of the C–H activation in methane using the model complex $ClRh(PH_3)_2$. They showed that this complex dissociates the C–H bond of methane without any barrier. Low and Goddard[15] studied the methane activation by palladium and platinum complexes. Methane activation by the oxidative addition mechanism has also been studied by Ziegler and co-workers, who investigated the methane activation by the CpML complex, with M = Ir, Rh and L = CO, PH_3, and also by $M(CO)_4$ complexes for M = Ru, Os.[16] One of the results in that study is that the complex RhCp(CO) has only a very small barrier for the methane activation. Both these studies also found important precursors with molecularly bound methane. Quite recently, Song and Hall[17] studied the reaction path between RhCp(CO) and methane.

In the previous studies of the C–H activation of methane, reactions for the following simple Rh(I) complexes have been studied; Rh^+, RhH, RhCl, RhF, RhH(CO), and RhCl(CO). The largest of these systems, RhCl(CO), can be characterized as RhClL and is smaller than the Rh(I) complexes studied experimentally which are of the general structure $RhClL_2$ (see above). However, it is still argued that since there is a halide and a lone-pair ligand present in the RhCl(CO) system, the main electronic structure effects of the experimental systems are present. In line with this idea, the energetics of the RhCl(CO) system is roughly what is expected for the systems studied experimentally. With corrections for systematic errors and zero-point vibrational effects (see Appendix) the exothermicity of the methane reaction with RhCl(CO) is predicted to be 22 kcal/mol and there should be essentially no barrier for the reaction.[5] The previous studies on the Rh(I) complexes are in the present study extended by an investigation of lone-pair ligands other than the carbonyl ligand. The systems studied here are also of the general structure RhXL where X is a chloride or a hydride and where the lone-pair ligand L is CO, PH_3, NH_3, and H_2O. All combinations of X and L are considered. The choice of model lone-pair ligands is made according to the varying degree of π-bonding. The carbonyl group is most covalently bound with a large amount of π-bonding followed by the phosphine group. The ammonia and water ligands are essentially without π-bonding. The main difference between ammonia and water in the present context is that ammonia has only one lone pair but water has two which are lower in energy than the one in ammonia. This difference between ammonia and water has substantial effects on the metal–ligand bond strengths, as shown in two previous studies.[18,19] For the metals to the right the higher energy of the ammonia lone pair than of the water lone pairs leads to much stronger $M-NH_3$ bonds than $M-H_2O$ bonds.

Of all the metal complexes previously studied, the one that gave the lowest barrier for the C–H activation of methane was RuH_2. This result is by itself of a rather academic interest since this complex cannot be studied under realistic conditions. However, if RuH_2 is regarded as a model complex, the result can have consequences for the possibility of activating methane using Ru(II) complexes. One immediate question in this context is to what extent ligands will destroy the properties of RuH_2. To study this problem, a lone-pair ligand was added to form the complex RuX_2L. Three different lone-pair ligands were added, carbonyl, phosphine, and ammonia, to find out whether a ligand with large or small π-bonding is advantageous for the methane reaction. Also, the methane reaction for the bare RuX_2 system, which has previously been studied where X is a hydride or a halide, is also studied here for the case where X is a methyl group. The reactions for both $RuHCH_3$ and $Ru(CH_3)_2$ are investigated.

In the previous studies of the methane reaction a few important effects have been noted which are useful to keep in mind when the present results are analyzed. First, of the bare metal atoms rhodium has the lowest barrier. The reason for this is that for rhodium both the s^1 and the s^0 states are low-lying states. The bonds in the product of the reaction are best formed using the s^1 state, whereas the s^0 state is used in the entrance channel since this is the state with the least repulsion toward methane. There are two reasons why the s^1 state is better for forming bonds than the s^0 state. First, the s-orbital is much larger than the d-orbitals and therefore has a better overlap with incoming orbitals. Secondly, and more importantly, the s-orbital in the s^1 state can mix with the d-orbitals and form optimal hybrids. The hybridization using only d-orbitals is much less efficient. When the results for the bare neutral metal atoms are compared to the results for the cations to the right, a characteristic feature is that the cations form substantially weaker bonds in the product of the methane reaction. This result can be understood from differences of the ground states of the cations and the neutral metal atoms. The cations of the metals to the right have s^0 ground states which thus have to be promoted to the s^1 state to form the bonds in the product. In contrast, for the neutral metal atoms to the right, like rhodium and ruthenium, no promotion is needed since these atoms have s^1 ground states. These results have direct bearings on the properties of hydride and halide ligands. It is found that when a hydride ligand is exchanged with a halide ligand for complexes of the atoms to the right, there is a destabilizing effect on the methane reaction. The reason for this is simply that with a halide ligand the metal is more cationic and the metal therefore needs to be promoted to form the bonds in the product. This halide ligand effect will in the following be called the cationic promotion effect. Another important ligand effect was found in the previous

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study where lone-pair ligands were added;[5] see also ref 20. It was found that for the atoms to the right carbonyl ligands in general have a stabilizing effect that increases the exothermicity and lowers the barrier for the methane reaction. The origin of this effect is sd hybridization. When the sd hybrids are formed to make optimal M–R bonds, an sd hybrid pointing perpendicularly to the R–M–R plane is automatically formed at the same time. If this hybrid is made empty, holes in the electron density will be created that can be used to improve the bonding to lone-pair ligands. During the reaction between methane and RhCl(CO), for example, the Rh–CO bond distance is shortened by more than 0.1 Å and the bond is strengthened by 7 kcal/mol. In general, ligand effects are much less pronounced for complexes of the metals to the left, which is one reason the present study only concerns metals to the right. First, the cationic promotion effect is essentially missing to the left since neither the cations nor the neutral atoms have s^0 ground states as the cations have to the right. Secondly, the attractive lone-pair ligand effect is also missing for most systems to the left since this effect requires sd hybridization and covalency in the M–R bonding. The metal atoms to the left prefer ionic bonding, since the ionization potentials are so low, and sp hybridization since the s^2 state is the ground state or a low-lying state.

The geometry optimization for the present systems has been done at the SCF level. The correlation energy is obtained using double ζ plus polarization basis sets and the underlying correlation method is the modified coupled pair functional (MCPF) method, just like in the previous studies of similar type.[1–5] An important difference compared to the previous studies is that the correlation effects are extrapolated using the recently suggested PCI-80 method. This method uses the fact that 80% of the correlation effects are obtained using the present basis sets and methods; see further in the Appendix.

II. Results and Discussion

The results of the present study are discussed in three different subsections. In the first subsection the methane reaction for different Rh(I) complexes is discussed. These complexes are of the general type RhXL, where X is either hydrogen or chlorine and L stands for a lone-pair ligand which is either H_2O, NH_3, PH_3, or CO. In the second subsection the results for the corresponding Ru(I) complexes are presented and compared to the results for the Rh(I) complexes. Finally, in the third subsection the methane reaction for different Ru(II) complexes is discussed. These complexes are of the general form RuXYL, where X and Y are hydrogen, methyl, or chlorine groups and L are the same lone-pair ligands as discussed for the Rh(I) and Ru(I) complexes except for H_2O, which was not studied.

a. Rh(I) Complexes. The product equilibrium and transition state geometries for the reaction between different Rh(I) complexes and methane are given in Tables 1 and 2 together with the corresponding PCI-80 energies. Typical transition state structures are given in Figure 1 for the case of the $RhH(PH_3)$ reactant and for $RhCl(PH_3)$ in Figure 2. Before the results of these reactions are discussed, it is important to note that the ground states of most of the reactants have triplet spin. The notable exceptions are RhH(CO) and $RhH(PH_3)$, where the strong π-bonding has led to singlet ground states. For $RhH(NH_3)$ the singlet and triplet states are almost degenerate. All products of the methane reaction are singlet states.

The main results in Tables 1 and 2 can be described in the following way. Most of the PCI-80 reaction energies are in the range 16–22 kcal/mol. The barrier heights are generally lower for the case when X is hydrogen than when X is chlorine. The lone-pair ligand effects on the transition

Table 1. Geometries and Energies for the Products of the Oxidative Addition Reaction: $RhXL + CH_4 + \Delta E \rightarrow RhXLHCH_3$[a]

X	L	Rh–X	Rh–L	Rh–C	Rh–H	ΔE(PCI-80)
H	H_2O	1.52	2.30	2.04	1.52	−20.5
H	NH_3	1.52	2.31	2.05	1.52	−24.8
H[b]	PH_3	1.52	2.63	2.04	1.52	−15.9
H[b]	CO	1.52	2.13	2.04	1.52	−2.9
Cl	H_2O	2.37	2.15	2.02	1.51	−16.7
Cl	NH_3	2.39	2.16	2.02	1.51	−18.6
Cl	PH_3	2.38	2.49	2.03	1.51	−22.4
Cl	CO	2.36	2.00	2.04	1.51	−22.1

[a] The PCI-80 energies are calculated relative to ground state RhXL systems and methane and include zero-point vibrational effects. [b] Singlet ground state reactant.

Table 2. Geometries and Energies for the Transition State of the Oxidative Addition Reaction: $RhXL + CH_4 + \Delta E^{\ddagger} \rightarrow RhXLHCH_3$[a]

X	L	Rh–X	Rh–L	Rh–C	Rh–H	C–H	$\Delta E^{\ddagger}$(PCI-80)
H	H_2O	1.56	2.23	2.13	1.54	1.60	−9.4
H	NH_3	1.56	2.26	2.13	1.54	1.63	−14.8
H	PH_3	1.55	2.55	2.13	1.55	1.64	−5.4
H	CO	1.53	2.05	2.12	1.54	1.70	4.2
Cl	H_2O	2.40	2.17	2.12	1.55	1.67	0.3
Cl	NH_3	2.41	2.19	2.13	1.55	1.66	−0.4
Cl	PH_3	2.40	2.52	2.13	1.54	1.68	−4.9
Cl	CO	2.37	2.00	2.14	1.54	1.71	−7.2

[a] The PCI-80 energies are calculated relative to ground state RhXL systems and methane and include zero-point vibrational effects.

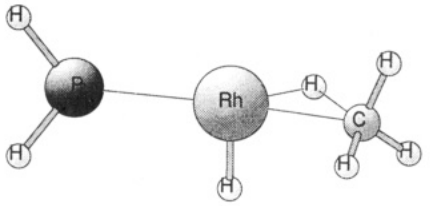

Figure 1. Transition state for the reaction between $RhH(PH_3)$ and methane.

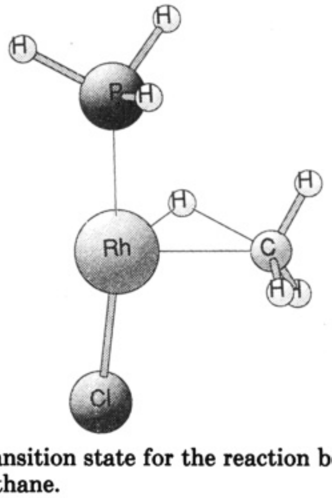

Figure 2. Transition state for the reaction between $RhCl(PH_3)$ and methane.

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state energies have an opposite trend for the hydrides compared to the chlorides. For the hydrides the transition state energies increase with lone-pair ligands having more π-bonding. The highest transition state energy is thus obtained for a carbonyl ligand L in the RhHL complex, and the lowest transition state energy is obtained for the ammonia ligand. For the chlorides the lowest transition state energy is obtained for the carbonyl and the highest one for the water ligand, closely followed by the one for the ammonia ligand.

In order to understand the results in Tables 1 and 2 it is useful to go back to the results obtained for the methane reaction with RhH[3] and RhCl[4] without lone-pair ligands. The calculated PCI-80 reaction energy for methane and RhH is −22.0 kcal/mol, and the transition state energy, −3.6 kcal/mol. The corresponding results for RhCl are −14.6 and +2.4 kcal/mol, respectively. The effect of exchanging a hydride with a halide is thus strongly destabilizing for the methane reaction for the atoms to the right. The origin of this destabilization is the cationic promotion effect; see above. With respect to these results, the addition of a pure lone-pair ligand like water and ammonia, without π-bonding, leads to a significant lowering of the barrier for RhH but has essentially no effect on the reaction energy. For RhCl, on the other hand, the addition of the same pure lone-pair ligands has a slightly larger stabilizing effect for the product than for the transition state. These quite different effects of lone-pair ligands can be rationalized on the basis of the understanding of the lone-pair ligand effect reached in the previous study.[5] The lone-pair ligand stabilization of the methane reaction is due to the sd hybridization caused by the formation of the metal–R bonds. As the sd hybrids making up these M–R bonds are formed, another hybrid pointing perpendicularly to the R–M–R plane will automatically be formed. If this hybrid is made empty, the hole in the electron cloud can be used by lone-pair ligands to stabilize their bonding. If the results for the RhClL systems are analyzed first, it is clear that the sd hybridization is strongest when the M–R bonds are fully formed for the product. Therefore, the product is slightly more stabilized than the transition state. For RhCl(NH_3), the product is stabilized by 4.0 kcal/mol and the transition state by 2.8 kcal/mol due to the addition of the ammonia ligand. For RhH the addition of ammonia stabilizes the transition state by as much as 11.2 kcal/mol but the product is only slightly stabilized by 2.8 kcal/mol. The main difference between the RhClL and RhHL systems is that the RhHL systems have a covalently bound ligand before the reaction. The covalent Rh–H bond therefore induces some sd hybridization already before the reaction. At the end of the reaction the covalency instead becomes a competing factor for the three different covalent M–R bonds. The bonds which are most covalent of these bonds are the two Rh–H bonds, and the lone-pair ligand is therefore oriented perpendicularly to the H–Rh–H plane; see Figure 1. In contrast, the lone-pair ligand in the RhClL reaction is oriented perpendicularly to the H–Rh–C plane; see Figure 2. With three covalent bonds as in the RhHL reaction, it is perhaps not surprising that the lone-pair ligand effect can reach its maximum in the transition state region rather than for the product. When the three covalent bonds are fully formed, the formation of the empty sd hybrid, which is essential for the lone-pair ligand effect, will not be as clean as when only two covalent bonds are formed as in the RhClL reactions.

The different lone-pair ligand effects discussed above for the RhHL and the RhClL systems are nicely illustrated by the detailed geometries. For the RhClL systems the Rh–L distances are about the same for the equilibrium and the transition states, in line with the similar effects on the energies found at these geometries. For the RhH systems, on the other hand, the Rh–L distances are substantially shorter by 0.05–0.10 Å at the transition state than at the equilibrium geometry, in line with the larger energetic effect at the transition state. At the product equilibrium geometries, the total Rh–L contraction effect compared to that of the reactants is about 0.15 Å for the RhClL systems but only about 0.05 Å for the RhHL systems.

The sd hybridization effect occurring during the methane reaction also has a contraction effect on the Rh–X bonds in the RhXL systems. For the Rh–Cl distance there is a shortening between the reactant and the product of about 0.10 Å, and for the Rh–H distance the shortening is about 0.20 Å. For both the Rh–Cl and the Rh–H distance, the shortening effect is slightly larger at the product equilibrium than at the transition state. For the RhHL systems, the Rh–H and the Rh–L bonds thus behave quite differently during the reaction.

The effects on the methane reaction of having π-bonding to the ligands are cleanest for the case of the RhClL systems since there is no change of ground states during the reactions for these systems. The carbonyl ligand has the most π-bonding followed by the phosphine group. For the water and ammonia ligands there is essentially no π-bonding. At the transition states of the RhClL reactions there is a clear correlation between the amount of π-bonding and the barrier height. The calculated transition state energies for the water and ammonia ligands are about the same with +0.3 and −0.4 kcal/mol, respectively. Increasing the amount of π-bonding, as for the phosphine ligand, lowers the calculated transition state energy to −4.9 kcal/mol. Finally, when the π-bonding is increased still further, as for the carbonyl ligand, the calculated transition state energy is down to −7.2 kcal/mol. The effect of π-bonding on the products of the methane reaction with RhClL follows almost the same trend. The least stable product is found for the water ligand with a calculated energy of −16.7 kcal/mol. The products with the most π-bonding, the phosphine and the carbonyl ligands, are almost equally stable with −22.4 and −22.1 kcal/mol, respectively. There are two, essentially equivalent, ways to explain this trend. The first explanation is most obvious. The shortening of the Rh–L distance, which is about the same for all lone-pair ligands, is most beneficial for the carbonyl and phosphine ligands since the π-bonding can then be improved. The amount of π-bonding is known to be strongly distance dependent. The second explanation of the π-bonding effect focuses on the sd hybridization which is the key for the lone-pair ligand effect. This type of hybridization goes hand in hand with the amount of covalency in the system. It is clear that π-bonding is a type of covalent effect which should therefore increase the sd hybridization. For the RhClL systems, where the covalency is not very strong, π-bonding therefore improves the lone-pair ligand effect during the methane reaction.

The lone-pair ligand effect on the RhHL reactions is somewhat obscured by the fact that for two of the systems

Table 3. Geometries and Energies for the Products of the Oxidative Addition Reaction: $RuXL + CH_4 + \Delta E \rightarrow RhXLHCH_3$[a]

X	L	Ru–X	Ru–L	Ru–C	Ru–H	ΔE(PCI-80)
H	H_2O	1.57	2.28	2.08	1.57	−15.9
H	NH_3	1.57	2.34	2.10	1.57	−14.1
H	PH_3	1.56	2.72	2.08	1.57	−11.5
H[b]	CO	1.59	2.18	2.08	1.59	8.7
Cl	H_2O	2.40	2.16	2.04	1.57	−11.3
Cl	NH_3	2.41	2.19	2.07	1.57	−10.0
Cl	PH_3	2.42	2.54	2.06	1.56	−12.9
Cl	CO	2.41	2.00	2.07	1.57	−9.0

[a] The PCI-80 energies are calculated relative to ground state RuXL systems and methane and include zero-point vibrational effects. [b] Doublet ground state reactant.

Table 4. Geometries and Energies for the Transition State of the Oxidative Addition Reaction: $RuXL + CH_4 + \Delta E^{\ddagger} \rightarrow RuXLHCH_3$[a]

X	L	Ru–X	Ru–L	Ru–C	Ru–H	C–H	$\Delta E^{\ddagger}$(PCI-80)
H	H_2O	1.63	2.24	2.15	1.58	1.61	−6.5
H	NH_3	1.63	2.30	2.15	1.58	1.65	−6.6
H	PH_3	1.61	2.62	2.14	1.57	1.68	−5.9
H	CO	1.72	2.00	2.26	1.70	1.61	15.3
Cl	H_2O	2.46	2.23	2.13	1.59	1.68	10.4
Cl	NH_3	2.46	2.25	2.13	1.59	1.67	8.0
Cl	PH_3	2.45	2.56	2.13	1.58	1.71	−2.1
Cl	CO	2.42	2.00	2.13	1.58	1.77	−2.0

[a] The PCI-80 energies are calculated relative to ground state RuXL systems and methane and include zero-point vibrational effects.

there is a change of ground state during the reaction. Both RhH(CO) and RhH(PH_3) have bent singlet ground states and therefore need to be promoted to the triplet state to form the bonds in the product of the methane reaction. The fact that the *triplet* state of the reactant forms the bonds in the product is analogous to the fact that the bonds in the water molecule are formed between the triplet oxygen atom and two doublet hydrogen atoms. For RhH(CO) the adiabatic excitation energy to the linear triplet state is 22.6 kcal/mol and for RhH(PH_3) this excitation energy is 9.7 kcal/mol. If this excitation energy is subtracted from the calculated RhHL reaction energies in Table 1, quite stable product energies are obtained for the four different lone-pair ligands. For water and ammonia, where there is no promotion, the calculated reaction energies are −20.5 and −24.8 kcal/mol, respectively. With the subtracted promotion energies the reaction energy for RhH(PH_3) becomes −25.6 kcal/mol and for RhH(CO) it becomes −25.5 kcal/mol. It thus appears as if the amount of π-bonding does not affect the reaction energies at all for the RhHL systems. One way to view the situation is that with three covalent M–R bonds the covalency in these systems is already saturated. The amount of sd hybridization is therefore not affected by additional covalencies coming from the Rh–L bonding. In accord with the discussion above, it is perhaps more adequate to describe this saturation as a balance of two effects. One effect is the competition for the available covalency, and the other effect is the increased π-bonding due to the shortening of the Rh–L bonds. The situation is very similar at the transition state for the RhHL reactions. With correction for promotion effects, the calculated transition state energies are for water −9.4 kcal/mol, for ammonia −14.8 kcal/mol, for phosphine −15.1 kcal/mol, and for carbonyl −18.4 kcal/mol. A slight correlation between the amount of π-bonding and the barrier height can thus be noted. However, this advantage of having π-bonding to the ligands is more than compensated for by the fact that a promotion is needed to form the M–R bonds. It is this promotion which leads to the opposite trend of the barriers and reaction energies for the RhHL systems compared to the RhClL systems.

In some of the previous studies of the methane reaction[1–5] it was pointed out that a low-lying low-spin state is an advantage for a low barrier. The low barrier for the reaction with the bare rhodium atom was, for example, partly rationalized on the basis of the presence of the low-lying doublet state for rhodium. It could therefore be of some interest to try to relate the barrier heights in Table 2 to the corresponding high-spin to low-spin excitation energies for the reactants. This comparison can only be made in a meaningful way for the RhClL systems since two of the RhHL systems have low-spin ground states. It turns out that there is indeed a correlation between these excitation energies and the barrier heights. The adiabatic excitation energies are 13.6 kcal/mol for RhCl(H_2O), 12.6 kcal/mol for RhCl(NH_3), 10.4 kcal/mol for RhCl(PH_3), and 8.5 kcal/mol for RhCl(CO). The corresponding calculated transition state energies in Table 2 are +0.3, −0.4, −4.9, and −7.2 kcal/mol. The value of the adiabatic excitation energy is thus a rather useful way to identify whether a triplet state reactant will have a low or a high barrier for the oxidative addition reaction with methane.

b. Ru(I) Complexes. As a comparison to the above results for the reaction between methane and the Rh(I) complexes, calculations were also performed for the reaction with the corresponding Ru(I) complexes. The results are given in Tables 3 and 4. These results are to a large extent parallel to those for the Rh(I) complexes. A characteristic difference, which holds for all the presently studied reactions, is that the products are less stable and the barrier heights higher for the Ru(I) complexes than for the Rh(I) complexes. The major reason for this difference is that the exchange energy loss is larger for the Ru(I) complexes since the spin is higher.

The trends of the results for the Ru(I) complexes are in most cases the same as for the Rh(I) complexes. Starting with the RuClL reactions, the barrier heights decrease when ligands with more π-bonding are present. The barriers are about 10 kcal/mol lower for RuCl(CO) and RuCl(PH_3) than they are for RuCl(NH_3) and RuCl(H_2O). This is a larger effect than was found for the Rh(I) complexes, where the difference in barrier heights is about 5 kcal/mol. For the product energies of the Ru(I) reactions there is a more irregular variation with the amount of π-bonding than was found for the Rh(I) reactions. In particular, the product energy for RuCl(CO) is 4 kcal/mol less stable than the one for RuCl(PH_3). It appears that the carbonyl system experiences a situation of oversaturated covalency, just like the case was for the RhHL product systems, where competition for the available covalency also was a destabilizing effect. The origin of this effect can be traced down to the binding in the RuCl(CO) reactant. This is a linear system with a $^4\Sigma^-$ ground state. Since the two π-orbitals are doubly occupied and the δ-orbitals singly occupied, the π-bonding is saturated, leading to a very strong Ru–CO bond of 45.6 kcal/mol. As a comparison the Rh–CO bond strength in RhCl(CO) is only 37.7 kcal/mol. The increase of the d repulsion in RhCl(CO) actually leads to a longer Rh–CO bond distance of 2.12 Å than for the Ru–CO bond distance of 2.06 Å in RuCl(CO), although the rhodium atom has a smaller radius than the ruthenium atom. In general, covalent oversaturation occurs easier for Ru complexes than for Rh complexes due to the lower ionization potential for ruthenium; see more below.

When the RuHL reactions are analyzed, it should be noted that RuH(CO) has a doublet ground state in contrast to the quartet ground state for all the other Ru(I) reactants studied here. The adiabatic excitation energy for RuH(CO) to reach the quartet state is 14.5 kcal/mol, and this energy should thus be subtracted from the results in the tables before the lone-pair ligand effects are compared for the RuHL systems. For the RhHL systems promotion energies were subtracted for both RhH(CO) and RhH(PH_3); see above. When the promotion corrected product energies are compared for the RuHL and RhHL systems, it can be noted that the difference between these energies increases markedly for the ligands with more π-bonding. The product energy difference between RuH(H_2O) and RhH(H_2O) is 4.6 kcal/mol, while the corresponding (promotion corrected) difference for the carbonyl systems is as large as 19.8 kcal/mol. This leads to an overall trend for the different lone-pair ligands for RuHL which is opposite to the one for the RuClL systems. The most stable product for the RuHL systems is thus found for RuH(H_2O). The oversaturation of the covalency pointed out for the RhHL products is thus even more pronounced for the RuHL systems. This effect is present also at the transition states for the RuHL systems where the lowest barrier is found for RuH(H_2O). This is contrary to the RhHL systems where no oversaturation of the covalency could be noted at the transition state and the lowest (promotion corrected) barrier height thus was found for RhH(CO). The reason the covalency is more easily saturated for the Ru complexes than for the Rh complexes is that ruthenium has a lower ionization potential than rhodium. The amount of covalency in the bonding decreases rapidly to the left in the periodic table, and already from technetium and to the left, ionicity strongly dominates the bonding. This has the effect that hydrides and halides are to a large extent exchangeable for the complexes of the metals to the left since the M–H and M–Cl bonds are both quite ionic.

Just as for the case of the Rh(I) complexes discussed in the previous subsection, the high-spin to low-spin excitation energies have been calculated for the Ru(I) reactants in Tables 3 and 4, trying to relate them to the calculated transition state energies for the methane reaction. The adiabatic excitation energies for the RuClL systems are 30.5 kcal/mol for RuCl(H_2O), 29.3 kcal/mol for RuCl(NH_3), 19.6 kcal/mol for RuCl(PH_3), and 19.0 kcal/mol for RuCl(CO). The corresponding transition state energies in Table 4 are +10.4, +8.0, −2.1, and −2.0 kcal/mol. For the RuClL systems there is thus also a very good correlation between excitation energies and transition state energies, like that found for the Rh(I) complexes. Another positive aspect of this analysis is that the excitation energies are higher for the Ru(I) systems than for the Rh(I) systems, in line with the larger barrier heights for the Ru(I) complexes. The only problem noted for the present systems concerns a comparison of some of the RuHL systems. The excitation energy for RuH(PH_3) of 1.2 kcal/mol is thus much lower than the one for RuH(NH_3) of 11.3 kcal/mol, but the barrier height is actually lower for RuH(NH_3) by 0.7 kcal/mol. In summary, the adiabatic excitation energies contain quite useful information but they cannot be used alone to identify whether a system should have a low or a high barrier for the methane reaction.

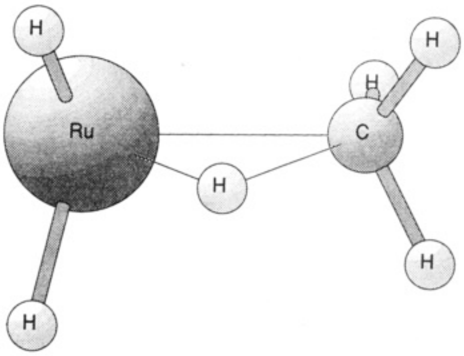

Figure 3. Transition state for the reaction between RuH_2 and methane.

Table 5. Geometries and Energies for the Products of the Oxidative Addition Reaction: RuXYL + CH_4 + $\Delta E \rightarrow$ $RuXYLHCH_3$[a]

reactant	Ru–X	Ru–Y	Ru–L	Ru–C	Ru–H	ΔE(PCI-80)
RuH_2	1.58	1.58		2.03	1.58	−11.7
$RuHCH_3$	1.58	2.01		2.01	1.58	−21.3
$Ru(CH_3)_2$	2.02	2.02		2.02	1.59	−24.1
RuHCl	1.56	2.44		2.07	1.56	−9.7
$RuCl_2$	2.35	2.35		2.07	1.54	−1.0
$RuH_2(NH_3)$	1.59	1.59	2.31	2.09	1.53	−20.4
$RuH_2(PH_3)$[b]	1.58	1.58	2.63	2.08	1.53	−10.8
RuH_2(CO)[b]	1.58	1.58	2.10	2.09	1.53	6.3

[a] The PCI-80 energies are calculated relative to ground state RuXYL systems and methane and include zero-point vibrational effects. [b] Singlet ground state reactant.

Table 6. Geometries and Energies for the Transition States of the Oxidative Addition Reaction: RuXYL + CH_4 + $\Delta E^{\ddagger} \rightarrow$ $RuXYLHCH_3$[a]

reactant	Ru–X	Ru–Y	Ru–L	Ru–C	Ru–H	C–H	$\Delta E^{\ddagger}$(PCI-80)
RuH_2	1.58	1.58		2.13	1.54	1.64	−6.8
$RuHCH_3$	1.59	2.06		2.11	1.54	1.66	−8.1
$Ru(CH_3)_2$	2.06	2.06		2.12	1.54	1.64	−4.7
RuHCl	1.57	2.42		2.15	1.58	1.75	−3.7
$RuCl_2$	2.36	2.36		2.19	1.58	1.72	16.3
$RuH_2(NH_3)$	1.59	1.59	2.27	2.13	1.54	1.76	−17.8
$RuH_2(PH_3)$	1.59	1.59	2.57	2.12	1.54	1.77	−8.6
RuH_2(CO)	1.58	1.58	2.09	2.10	1.53	1.97	6.7

[a] The PCI-80 energies are calculated relative to ground state RuXYL systems and methane and include zero-point vibrational effects.

c. Ru(II) Complexes. One of the most interesting results in the previous studies of the methane reaction is that, of all the hydrides studied, the lowest barrier was obtained for RuH_2.[3] This is interesting since no ruthenium complex that can activate methane has so far been found experimentally. Another interesting finding was the rather awkward geometry found for the C–H activation, with methane coming in perpendicularly to the H–Ru–H plane; see Figure 3. In the present study it was therefore decided to investigate the reaction between methane and Ru(II) complexes further. In the first step of this investigation the hydrogen atoms in the reactant RuH_2 were substituted by methyl groups. In the second step the hydrides were substituted by chlorides. Finally, a lone pair ligand L was added to RuH_2. The results are collected in Tables 5 and 6.

The calculated transition state energy for RuH_2 is 6.8 kcal/mol below the reactant asymptote. The energy difference between the product equilibrium geometry and the optimized transition state geometry is surprisingly small, only 4.9 kcal/mol. This is much smaller than the corresponding differences found for both the Rh(I) and Ru(I) complexes discussed in the previous subsections. The small energy difference between the product and transition state geometry is a general finding for most of the Ru(II) complexes in Tables 5 and 6. For RuH_2, this means that the stability of the product is rather low. The calculated reaction energy is only −11.7 kcal/mol. This could be a problem for the possibility of observing C–H activation for Ru(II) complexes under realistic conditions since the binding energy to other ligands present in the solution could be larger than what it is for the products of the methane reaction.

When the hydrides in RuH_2 are substituted by methyl groups, there is a significant effect on the methane reaction energy. With one methyl substituted, the energy of the product of the methane reaction goes from −11.7 down to −21.3 kcal/mol. When both hydrides are substituted by methyl groups, there is a further stabilization of the product down to −24.1 kcal/mol. The origin of this trend is competition for the available covalency. Since the Ru–H bond is more covalent than the Ru–CH_3 bond, the competition for covalency is largest for RuH_2 and smallest for $Ru(CH_3)_2$. It was noted already in the comparison of the results for the Rh(I) and Ru(I) reactions above that the ruthenium complexes are more sensitive to competition for covalency than the rhodium complexes. The reason for this is that the bonding quickly becomes more ionic going to the left in the periodic table due to the lower ionization potentials to the left. The trend of the reaction energies as the hydrides are substituted by methyl groups is one way to note the larger covalency in the methyl–hydrogen than in the metal–methyl bonds. Another aspect of this difference in covalency was noted above in the comparison of the geometries shown in Figures 1 and 2. In that case the lone-pair ligand prefers to bind perpendicularly to the plane with the largest covalency, which for the product of the RhClL reaction is the H–Rh–C plane and for the product of the RhHL reaction is the H–Rh–H plane. The barrier height for the methane reaction with RuH_2 is less affected than the reaction energy by the substitution of the hydrides by methyl groups. Substituting one hydrogen by a methyl group slightly lowers the transition state energy from −6.8 to −8.1 kcal/mol. Substituting also the other hydrogen by a methyl group to an increase of the transition state energy to −4.7 kcal/mol. One reason for the similarity of these transition state energies is that the competition for the available covalency is somewhat less severe at the transition state than at the equilibrium geometry, where the bonds are fully formed. It is also possible that differences in hybridization and steric effects to some extent counteract the effects of the oversaturation in the covalency. In summary, the substitution of the hydrides by methyl groups should be an advantage for the methane reaction since it stabilizes the product and does not significantly change the barrier height. On the basis of the present calculations, the barriers should anyway be below the reactant asymptote.

The effects on the methane reaction of substituting hydrides with halides were studied in detail in ref 4. The results for the $RuCl_2$ reaction were presented already in that study, whereas the results for RuHCl are new. The main conclusions from ref 4 remain the same. Halides thus have a destabilizing effect on the reaction for complexes of the metals to the right in the periodic table. The energy of the product of the methane reaction goes from −11.7 kcal/mol for RuH_2 to −9.7 kcal/mol for RuHCl up to −1.0 kcal/mol for $RuCl_2$. Similarly, the transition state energies increase from −6.8 kcal/mol for RuH_2 to −3.7 kcal/mol for RuHCl all the way up to 16.3 kcal/mol for $RuCl_2$. The origin of the halide destabilization of the products is the cationic promotion effect, described in the Introduction. The cations to the right have s^0 ground states and need to be promoted to the s^1 state to form the bonds in the products of the methane reaction.[2] In contrast, the neutral metal atoms to the right already have s^1 ground states and do not need to be promoted.[1] Since the metal atoms become more cationic as halide ligands are present, the binding in the product of the methane reaction is therefore destabilized as hydrides are substituted by halides. This effect is only present to the right in the periodic table. In summary, it is thus a disadvantage for the methane reaction when the Ru(II) complexes have strongly electronegative ligands like halides present.

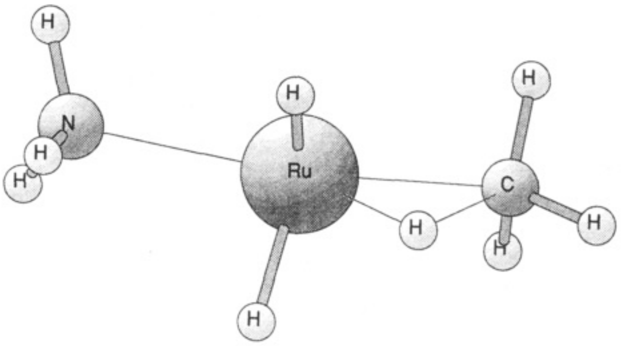

Figure 4. Transition state for the reaction between $RuH_2(NH_3)$ and methane.

The final investigation of the methane reaction with Ru(II) complexes concerns the effect of adding lone-pair ligands to the RuH_2 reactant. One lone-pair ligand without π-bonding, ammonia, was added and one ligand with substantial π-bonding, carbonyl, was also investigated. As an intermediate case a phosphine ligand was studied. The effects on the methane reaction are very clearly seen on the results in Tables 5 and 6. The addition of a lone-pair ligand without π-bonding has a very positive effect on the methane reaction. Adding ammonia leads to a stabilization of the product by 8.7 kcal/mol, and for the transition state the stabilization is as large as 11.0 kcal/mol. Since the lone-pair ligand makes use of the sd hybridization effect perpendicularly to the plane with the most covalent bonds (see above) the ammonia ligand will be situated perpendicularly to the H–Ru–H plane during the reaction. The incoming methane also makes use of the same effect; see below. This leads to a rather strange structure of the transition state of the reaction; see Figure 4. The sd hybridization effect on the lone-pair ligand should be present already before the reaction but from the calculated energies it is clear that the sd hybridization increases in the reaction with methane. When ligands with more π-bonding are added to RuH_2, this leads to a change of the reactant ground state. Both $RuH_2(PH_3)$ and $RuH_2(CO)$ have singlet ground states. This means that an electronic promotion is needed in order to bind the products of the methane reaction. For $RuH_2(PH_3)$ the adiabatic excitation energy to reach the binding triplet state is 10.9 kcal/mol and for $RuH_2(CO)$ the excitation energy is as high as 32.5 kcal/mol. The destabilizations compared to the case with the ammonia ligand, which does not need any promotion, correspond rather well to these excitation energies. The product of the reaction with $RuH_2(PH_3)$ is thus 9.6 kcal/mol less stable than for the reaction with $RuH_2(NH_3)$, and for $RuH_2(CO)$ the corresponding destabilization is 26.7 kcal/mol. At the transition state the energy differences are quite similar. In summary it is thus very important for the methane reaction that strongly π-bonding ligands which change the ground state of the reactant to a stable singlet state are avoided.

There are two rather curious aspects of the RuH_2L reactions with methane. One of these was already mentioned, and this is the geometry. The geometry where all the ligands are compressed on one side [see Figure 4 (the equilibrium geometry is quite similar)] is apparently necessary to make full use of the sd hybridization effect. More reasonably looking structures of, for example, trigonal bipyramidal form were tried but were found to be less stable by 5–10 kcal/mol than the structure in Figure 4. The second curious aspect of the RuH_2L results is the very flat nature of the potential surface. In fact, the energies of the products and of the transition states differ by only 1–2 kcal/mol. From a practical viewpoint this does not mean that the elimination barrier for methane is small since the product is bound by as much as 20 kcal/mol in the ammonia case. Neither does it mean that the transition state region has been missed in the geometry search since the local geometry of this region is extremely characteristic. For almost all systems studied in the present study the C–H bond length is in the range 1.6–1.8 Å, the Ru–H bond in the range 1.5–1.6 Å, and Ru–C bond in the range 2.1–2.2 Å.

A general comment can finally be given on why the present RuH_2 type complexes have such low barriers for the methane reaction. It is clear, especially from the geometries in Figures 3 and 4, that the reaction mechanism is related to the sd hybridization effect discussed above for the lone-pair ligands. The strong covalencies in the Ru–H bonds create an empty sd hybrid pointing perpendicularly to the H–Ru–H plane. By using this hole in the electron cloud, methane is able to approach ruthenium quite closely for a very favorable interaction leading to the C–H activation.

III. Conclusions

The present study has focused on some Rh(I) and Ru(II) complexes found in the previous studies to be particularly interesting for the oxidative addition reaction with methane. The Rh(I) complexes studied have the general form RhXL where X is either hydrogen or chlorine and L stands for a lone-pair ligand. Of the Rh(I) complexes experimentally found to activate alkanes, the present type of model complex is most closely related to the $RhCl(PPh_3)_2$ complex.[7] The present study suggests that it might be possible to find Rh(I) complexes which for the reaction with methane lead to products that are more stable than those studied so far experimentally and which also could have lower C–H activation transition state energies. This could be the case if the chloride is substituted by a hydride, or other R group, and the lone-pair ligands are simultaneously chosen to minimize π-bonding. This conclusion is based on model calculations which, for example, give a calculated stability of the product for the $RhH(NH_3)$ reaction which is a few kcal/mol more stable than the product of the $RhCl(PH_3)$ reaction. For the corresponding transition state structures the energy difference is much larger in favor of the ammonia system. In general, the RhClL systems have lower barriers the stronger the π-bonding is to the lone-pair ligand. For the RhHL systems the trend is opposite. The reasons for these different trends are the following. For the RhClL systems an sd hybridization is induced by the formation of the M–R bonds in the methane reaction. This sd hybridization automatically creates an empty sd hybrid pointing perpendicularly to the H–Rh–C plane, and this empty sd hybrid can be used by the lone-pair ligand to approach closer to the metal. In particular if there is a large amount of π-bonding to the ligand, the Rh–L bonding will then improve substantially. Of the RhClL systems presently studied, this leads to a trend of higher stabilities and lower barriers going from lone-pair ligands of ammonia and water over to phosphine and to carbonyl, which has the highest stability. For the RhHL systems, the fact that the $RhH(PH_3)$ and RhH(CO) systems are singlet states has a decisive effect on the methane reaction. This means that these two systems have to be promoted to form the bonds in the product which leads to higher barriers and less stable products than for the $RuH(H_2O)$ and $RhH(NH_3)$ systems. The fact that there is already a strongly covalent Rh–H bond before the reaction also leads to some oversaturation of the covalency during the reaction. This latter effect is even more evident for the methane reaction with the same model Ru(I) complexes. Since ruthenium has a lower ionization potential than rhodium, the bonding tends to be more ionic and oversaturation of the covalency occurs easier. In the products of the RhHL reaction there are three strongly covalent bonds in contrast to the case for the RhClL reaction, where there are only two covalent bonds in the product. This leads to an interesting geometric difference between these products. For the RhHL reaction the lone-pair ligand will be oriented perpendicularly to the H–Rh–H plane since these are the two strongest covalent bonds. In contrast, the lone-pair ligand in the product of the RhClL reaction will be oriented perpendicularly to the H–Rh–C plane.

No ruthenium complex has yet been found experimentally that can activate the C–H bond in methane. Following the previous finding that RuH_2 has a low activation barrier for the methane reaction,[3] several other Ru(II) model complexes have been investigated in the present study. Several of these are found not to have any barrier for the C–H activation reaction. Starting out from RuH_2, it is found that substituting the hydrides with methyl (or more general alkyl) groups significantly stabilizes the product and should thus be an advantage for the methane reaction. The stabilities of the methane products follow a trend of decreasing competition for the available covalency. The Ru–H bond is more covalent than the Ru–CH_3 bond and the competition for the covalency, which is a destabilizing factor, is therefore largest for RuH_2 and smallest for $Ru(CH_3)_2$. There is no similar stabilization effect of substituting hydrides with R groups at the transition state since the product bonds are not yet formed, but this should not matter since the energy at the transition state should anyway be below the reactant asymptote. In line with the results of a previous detailed investigation,[4] it is furthermore found that substituting the hydrides in RuH_2 with halides is a disadvantage for the methane reaction. This is due to the cationic promotion effect present to the right in the periodic table.[2]. The cations to the right have s^0 ground states and since the metal becomes more cationic with halides present an electronic promotion is needed to the bonding s^1 state in order to bind the products of the methane reaction. In contrast, the neutral metal atoms to the right already have s^1 ground states. This leads to more weakly bound products when halide ligands are present. Finally, the effects on the methane reaction of adding more or less covalently bound lone-pair ligands to RuH_2 were investigated. The conclusions from the model calculations are very clear. It is a definite advantage to have lone-pair ligands with a minimum of π-bonding present. The addition of ammonia thus leads to a significant stabilization both of the product, with 8 kcal/mol, and of the transition state, with 11 kcal/mol. This stabilization is due to sd hybridization and the attractive lone-pair ligand effect; see above. In contrast, if a lone-pair ligand with strong π-bonding is added, like carbonyl, there is instead a large destabilization for both the product and the transition state. The reason for this effect is that the $RuH_2(CO)$ reactant becomes a singlet due to the large π-bonding effect. This means that a large promotion energy has to be paid for $RuH_2(CO)$, which leads to a corresponding destabilization of the products of the reaction. In summary, for future investigations of the reaction between methane and Ru(II) complexes, it is suggested that complexes with alkyl R groups and lone-pair ligands with as small a π-bonding as possible are chosen. Halide ligands and lone-pair ligands with π-bonding should be avoided.

Appendix A. Computational Details

In the calculations reported in the present paper on the oxidative addition reaction of methane to selected Rh(I) and Ru(II) complexes, reasonably large basis sets were used in a generalized contraction scheme. All valence electrons, except the chlorine 3s electrons, were correlated using size consistent methods. The basis sets and methods are identical to those used in the previous studies of the same type.[1-5] In short, the geometry optimizations are performed at the SCF level using the GAMESS set of programs[21] using double ζ quality basis sets. Computed Hessians were always used to locate the transition states and were also determined whenever this was felt motivated. The accuracy of the geometry optimization step has recently been systematically tested and found to be adequate for both equilibrium and transition state geometries for cases where no coefficient in the configuration expansion of the preceding correlation calculation is larger than 0.20.[25] This criterion holds for all systems studied in this paper. The correlated calculations are performed using the modified coupled pair functional (MCPF) method,[22] which is a size consistent, single reference state method. The zeroth order wave functions are in these cases determined at the SCF level. The basis sets in these calculations are larger than those used in the geometry optimization, with polarization functions on all atoms including an f-set on the metal. Because rotation between valence and core orbitals sometimes occurs, 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.[23] 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.[24]

Even though the absolute accuracy of the MCPF calculations is not very high, the fact that the errors are highly systematic can be used to significantly reduce the relative errors. The accuracy is mainly limited by the basis set size, but the lack of triples is another rather important factor. In comparison to these other errors, the error in geometry optimization step can normally be neglected. On the basis of comparisons to calculations of high accuracy[26] and of comparisons to experiments, it can be concluded that the present type of treatment gives about 80% of the valence correlation effects. A simple estimate of the remaining correlation effects is then obtained by simply adding 20% correlation energy to each system. This is the general idea behind the PCI-80 (parametrized configuration interaction with parameter 80) method which has recently been proposed.[27] It was shown in ref 27 that this parametrization gives a major improvement of the results compared to an unparametrized treatment. For a benchmark test consisting of the atomization energies of 32 neutral first row systems the PCI-80 method gives an average absolute deviation compared to experiments of only 2.3 kcal/mol. Pople et al.[28] have shown that for the same systems the MP2 method gives an average absolute deviation of 22 kcal/mol using polarized basis sets. This means that the PCI-80 method should be a significant improvement compared to the MP2 method, which has up til now with a few exceptions been the highest level of treatment used for the present size of transition metal complexes; see the reviews in refs 10 and 11. For transition metal systems the improvement at the PCI-80 level compared to an unparametrized treatment is sometimes quite dramatic. Tests against essentially all experimentally studied small second row transition metal complexes show that the accuracy of the PCI-80 method for bond strengths is probably at least as high as that available from experiments for these systems.[27] For several first row systems it was shown in ref 27 that a Hartree–Fock limit correction is also needed. This correction is usually small for transition metal systems. In fact, a useful approximation is to assume that these effects roughly cancel basis set superposition errors and 4s,4p correlation effects. This approximation has been used in the present study. In order to be directly comparable to experiments the calculated energies have to be corrected for zero-point vibrational effects. However, it turns out that these effects make a negligible contribution to the energies for the present systems. This is qualitatively different from what has previously been found for the methane reaction with naked transition metal atoms or cations where zero-point vibrational effects contribute the significant amount

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of about −5 kcal/mol both at the equilibrium geometry and at the transition state.

Some of the energies for the transition states in the tables are negative. A negative barrier height should simply be interpreted as a reaction without a barrier. The question whether the transition state obtained at the SCF level remains a true transition state after correlation effects are included is not addressed in the present study. It is possible that the transition state is simply converted to a point along the reaction path. It is also possible that the point remains a true transition state even if the energy is negative. This can happen if the reaction passes over a precursor state which energetically is below the transition state. Precursor states will be investigated in a separate paper.[29]

Finally, all the results reported here are for the ground state of each system. It should be noted that since in most cases the ground state of the reactants has a different total spin than the ground state of the products, for a particular reaction the energies are given for different spin states in the beginning and at the end of the reaction. This procedure is partly motivated by the need to conveniently define what has been done. However, it is also motivated by what actually happens in these reactions involving the relatively heavy second row transition metal atoms. It has been shown in detail by Mitchell[30] that, in the case of the association reaction between the nickel atom and carbon monoxide, the crossing probability between different spin surfaces is near unity due to the large spin–orbit coupling. 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.[31] The crossing probability should be even larger for the present second row transition metal systems.

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