Different Electronic Structure Requirements on Precursors and Transition States for the Oxidative Addition Reaction with Methane

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Abstract: Molecular precursor complexes for the reaction between methane and a systematically selected set of second-row transition metal complexes are studied using methods of high accuracy. Comparisons are made to previous detailed studies of the transition states and product complexes of the oxidative addition reaction. The electronic structure requirements for a strongly bound precursor and for a low barrier for the oxidative addition are compared and found to be quite different. A ground or a low-lying singlet state is required for the formation of a strongly bound precursor. A ground or a low-lying triplet state is required for a low reaction barrier. The barrier counted from the precursor is thus to a large extent determined by the reactant singlet–triplet splitting. Comparisons are made to experimentally derived results for RhCp(CO). The levels of accuracy needed for the energy evaluation and for the geometry optimization are tested. It is found that for the precursors the inclusion of van der Waals attraction is needed in the geometry optimization.

I. Introduction

Experiments on the oxidative addition reaction between transition metal complexes and methane have given considerable detailed insight into the mechanism of this potentially important reaction. Most notably in the present context is that it has been shown that the reaction proceeds via a molecular precursor state. For the RhCp(CO) complex, Bergman et al.[1] predicted the energy profile for the gas phase methane reaction to be the following. First, based on previous experimental work,[2–4] for gas phase equilibrium constants for, for example, the reaction between alkanes and $W(CO)_5$, they conclude that the stability of the precursor complex between a molecular alkane and RhCp(CO) should be about 10 kcal/mol. From this precursor state the C–H activation barrier was predicted to be the same as that measured for cyclohexane in the liquid phase, i.e., 4.5 kcal/mol.[5] This means that the gas phase transition state should lie below the reactant asymptote. Finally, the exothermicity is predicted to be larger than 15 kcal/mol based on the minimum lifetime of the product RhCp(CO)RH. In previous papers on the methane reaction we have considered electronic structure effects in detail for both the transition state and the product equilibrium of the oxidative addition.[6–8] In the present paper we extend these investigations to include also the precursor complex. In particular, we consider two alternative possibilities concerning the role of the precursor state for the bond-breaking in methane. The first possibility, which is perhaps intuitively most appealing, is that the C–H bond breaking has already started in the precursor region and there should therefore be a relationship between the stability of the precursor and the height of the barrier. The second possibility is that there is no such relationship and that the precursor state is just a different, electronically unrelated, point on the potential surface for this reaction. In other words, is it possible to find systems with a low barrier for the oxidative addition reaction but only weakly bound precursors or to find systems with strongly bound precursors but still with high barriers for the oxidative addition reaction?

Recent systematic theoretical studies on the oxidative addition between second-row transition metal complexes and methane have given detailed information on the electronic structure factors of importance for this reaction.[6–8] For example, when the reactions for several different metal atoms are compared, the dominating atomic state in the products for metals to the right can be identified as the s^1 state. One way to see this is that when systems which do not have s^1 ground states, like the palladium atom or most of the metal cations to the right, react with methane a promotion energy has to be paid with a corresponding destabilization of the product as a result. This result for the cations has direct bearing also on ligated complexes where, as a consequence of this promotion effect, the presence of strongly electronegative ligands destabilizes the product of the methane reaction.[8] The electronic structure requirements at the transition state for the reaction have until recently been less clear. For the bare metal atoms it has been noted that low-lying s^0 states are an advantage so some mixing with this state clearly occurs in the transition state region. On the other hand a mixing with the s^1 state also has to be present so that the bonds in the product can start to form. For realistic ligated complexes the bonding state that corresponds to the s^1 state of the atom is the high-spin triplet state. The state corresponding to the atomic s^0 state is the low-spin singlet state of the metal complex. A quite surprising finding in a recent study, where the methane reactions for several RhXL complexes were compared, was that it appears as if the same electronic structure requirements apply to the transition state region as to the products.[9] This means that a triplet ground state, or at least a low-lying triplet state, is an advantage for a low barrier. For a ground state singlet like RhH(CO) essentially the full promotion energy to the triplet state has to be paid already to reach the transition state. This finding raises questions concerning the role of the molecular precursor state for the C–H bond-breaking

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process, since for the precursor it is an advantage to have a low-spin ground state. On the basis of this result it is thus expected that the singlet RhH(CO) should have a strongly bound precursor but a high transition state. For the triplet RhCl(CO), the situation should be opposite with a weakly bound precursor and a low transition state. These expectations are tested in this paper.

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).[10,11] Shortly afterwards, the analogous rhodium fragment (RhCp*L) was found to be active[12] and later on also the $RhClL_2$ (L = PPh_3) fragment.[13] 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.

There are several theoretical studies in the literature of the oxidative addition reaction between methane and transition metal complexes.[14–17] Morokuma et al.[14] studied the reaction between $RhCl(PH_3)_2$ and methane at the MP4 level using unpolarized basis sets. They found a reaction energy profile in reasonable agreement with what is expected based on experiments. A molecular precursor was found to be bound by 17 kcal/mol, the barrier was found to be 3 kcal/mol above the precursor, and the exothermicity was 24 kcal/mol. Song and Hall[15] studied the above-mentioned reaction between RhCp(CO) and methane at the MP2 level using unpolarized basis sets. The precursor was found to be bound by 14.8 kcal/mol, the transition state was found to be 4.1 kcal/mol above the precursor, and the exothermicity was found to be 30.6 kcal/mol. Ziegler et al.[16] also studied the RhCp(CO) reaction using density functional methods including gradient corrections. Results rather different from those reported by Song and Hall were found. The molecular precursor was found to be bound by 6.9 kcal/mol, and the transition state was found to be 8.8 kcal/mol above the precursor, which is thus 1.9 kcal/mol above the reactants. The reaction exothermicity was found to be only 14.8 kcal/mol. In the same study the methane reaction was studied also for different ruthenium, osmium, and iridium complexes. Finally, Low and Goddard[17] studied the reaction between the palladium atom and methane. They found a transition state 31 kcal/mol above the reactants and an endothermicity for this reaction of 20 kcal/mol.

Besides the specific questions mentioned above concerning the role of the precursor for the methane reaction, there are two additional points of interest in the present work. First, the present work is one of the first studies where the recently suggested PCI-X (parametrized configuration interaction with parameter X) scheme[18] is used. The parameter X corresponds to the percentage of the correlation effects obtained using a specified basis set and correlation treatment. The remaining percentage of the correlation effects are extrapolated. It was shown in ref 18 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 3.2 kcal/mol. Pople et al.[19] 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 until now with a few exceptions been the highest level of treatment used for the present size of transition metal complexes; see, for example, ref 15. For transition metal complexes the use of density functional methods including gradient corrections appear promising, but any systematic test of these methods for this type of systems has not yet been performed, and it is therefore too early to draw any conclusions concerning the accuracy of these methods for the present systems. For these 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.[18]

The second additional point of interest of the present work concerns the chemical models used. The present models of type RhXL are not identical to those studied experimentally. In fact, it is part of the purpose of a theoretical study to use as simple models as possible since the results can then be generalized to a larger group of systems. A condition for such a generalization is, of course, that the results for the simple model fall in line with those known for experimentally relevant systems. In the present work several interesting comparisons can be made to the experimentally suggested energy profile for the methane oxidative addition reaction, mentioned above.[1] It should be emphasized that this experimental result is also a deduction based on several similar systems and not a result for a single system and should thus have a similar generality. One question raised in the present paper is, for example, if the present simple models give precursor complexes bound by as much as 10 kcal/mol, as suggested experimentally. Other questions are if the present models have transition states below the reactant asymptote, in line with experiments, and if the exothermicity is as high or higher than 15 kcal/mol as suggested experimentally. If that is so, it can be concluded that the present models adequately model the electronic structure effects present in realistic systems. Other effects, such as steric constraints, can naturally not be modeled by the present small ligands.

II. Computational Details

The underlying calculations of the present paper are the same as have been described in detail in several previous papers.[6–9] In the present context it is of particular importance that the basis sets are well balanced. They were chosen to be of double ζ plus polarization type and can be described in the following way. For the metals the Huzinaga primitive basis[20] 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 except for the 4s and 4p orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects. The 5s and 5p orbitals were described by a double ζ contraction and the 4d by a triple ζ contraction. The f functions were contracted to one function giving a (7s,6p,4d,1f) contracted basis. For first row atoms the primitive (9s,5p) basis of Huzinaga[21] was used, contracted according to the generalized contraction scheme to [3s,2p], and one d function was added. For second-row atoms a similarly contracted basis was used based on the primitive (12s,9p) basis of Huzinaga[22] and including one set of d-functions. For hydrogen the primitive (5s) basis from ref 21 was used, augmented with one p function, and contracted to [3s,1p].

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The correlation method chosen was the modified coupled pair functional (MCPF) method,[23] which is a size-consistent, single reference state method. The zeroth order wavefunctions were determined at the SCF level. All valence electrons were correlated including the 4d and 5s electrons on the metal atoms. Using the above basis sets and the MCPF method it has been shown that about 80% of the correlation effects on bond strengths are obtained irrespective of the system studied. A good estimate of a bond strength is thus obtained by simply adding 20% of the correlation effects, and this is what is done in the PCI-80 scheme.[18] For several first-row systems it was shown in ref 18 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. Before the correlation treatment the core orbitals were localized using an r^2 minimization procedure. Relativistic effects were accounted for using first order perturbation theory including the mass–velocity and Darwin terms.[24] The calculations were performed using the STOCKHOLM set of programs.[25]

The geometries of the present systems have in most cases been fully optimized at the SCF level using valence double ζ basis sets. It may appear that this type of low-level geometry optimization is not in balance with the accurate method used for the energy evaluation at the optimized geometries, described above. However, it has been shown both that the geometries obtained at this level are surprisingly accurate and also that the energetics is rather insensitive to small deviations from exact geometries for second-row transition metal complexes.[26] The same conclusion has also been drawn by Cundari in several comparisons to experiments.[27] These conclusions concern both equilibrium geometries and transition states. An additional comment is necessary for the case of transition states. In some cases the PCI-80 energy at the SCF transition state is below the precursor. These structures are obviously no longer true transition states but should be regarded as characteristic points on the reaction pathway in the bond-breaking region. The conclusion in these cases is that the barrier is low, probably with an energy at the transition state which is only slightly above the precursor. In the present study also the geometries of molecular precursor complexes are needed. Even though van der Waals forces are known not to be fully responsible for the binding in these systems it cannot be ruled out at this stage that such forces play a qualitative role for the geometry. For this reason the precursor geometries were determined at the MP2 level and the energetic result is compared to that obtained at the standard SCF geometries. The SCF geometries were determined using the GAMESS set of programs[28] and the MP2 geometries using GAUSSIAN-92.[29] 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 of about −5 kcal/mol both at the equilibrium geometry and at the transition state. In the process of the geometry optimization and the evaluation of zero-point vibrational effects, it was further found from the computed Hessians that the optimized geometries are true equilibria and transition states, respectively. This was a rather unsurprising finding, since the geometries determined are extremely similar to those obtained for unligated systems, where the conclusion of the character of the geometry is rather trivial and obvious. In fact, a comparison to simpler systems is probably in general a better way to decide whether a correct transition state has been reached than to elucidate the Hessian. One imaginary frequency is not a proof that the lowest transition state has been reached. Nor is the absence of imaginary frequencies a proof that the best equilibrium geometry is reached. To properly decide these questions, chemical intuition based on comparisons to similar systems has to be used and plausible geometries have to be investigated.

Table 1. PCI-80 Energies (kcal/mol) at Different Points on the Singlet Potential Surface for the Reaction between Methane and Different Reactants (The Energies (D_0) are Calculated Relative to the Ground State of the Reactants and Methane)

reactant	precursor	transition state	product
RhCl(CO)[a]	−3.4	−7.2[c]	−22.1
RhH(CO)	−10.8	+4.2	−2.9
$\mathrm{RhH(NH_3)}$	−14.5	−14.8[c]	−24.8
$\mathrm{RuH_2}$[a]	+4.0[b]	−6.8[c]	−11.7

[a] Triplet state reactant. [b] Triplet bound by 1 kcal/mol. [c] Characteristic point on the reaction pathway in the bond-breaking region but no longer a true transition state, see Section II.

Results and Discussion

In the present study the energy profile for the oxidative addition reaction between methane and different transition metal complexes is investigated. These transition metal complexes were selected out of a large body of systems recently studied,[6–9] as models including different representative types of ligand effects. First, RhCl(CO) includes both a strongly electronegative ligand and a lone-pair ligand. In this way it should include all the electronic structure effects present in the class of molecules found experimentally to activate the C–H bond in alkanes. These experimental second-row transition metal complexes are either of type RhCpL or $\mathrm{RhClL_2}$.[12,13] The second reactant complex chosen for the present study is RhH(CO), where the strongly electronegative ligand chlorine has been exchanged with the covalently bound hydrogen. In the third complex, $\mathrm{RhH(NH_3)}$, the strongly π-bonding carbonyl ligand, has been exchanged with an ammonia ligand which is essentially without π-bonding. Finally, a quite different type of reactant, $\mathrm{RuH_2}$, was selected. This type of complex has previously been found to have unusual and interesting properties for the methane reaction.[9] The energetic results for the methane reactions for these different reactants are given in Table 1 at three different points on the potential surface. The first point is the molecular precursor complex, the second point is the transition state of the reaction, and the third point is the product complex. The energies are given for points on the singlet potential energy surface and are given with respect to the ground state asymptotes, which have different spin for the different reactants. Apart from at the asymptotes, the singlet states have the lowest energy for most of these points. The exception is the molecular precursor complexes for $\mathrm{RuH_2}$, where the singlet state is unbound and the triplet state is slightly bound and is thus lower in energy.

In order to understand the results of the present reactions, the electronic and geometric structure of the reactants first has to be described. RhCl(CO) has a linear triplet ground state with an adiabatic excitation energy to the bent singlet of 5 kcal/mol. In contrast, RhH(CO) has a bent singlet ground state with an adiabatic excitation energy to the linear triplet of 23 kcal/mol. For $\mathrm{RhH(NH_3)}$ the bent singlet and the linear triplet are almost perfectly degenerate with an excitation energy of less than 1 kcal/mol. The ruthenium complex $\mathrm{RuH_2}$ finally has a bent triplet ground state with a high excitation energy of 18 kcal/mol to the bent singlet state. The extrapolation of the correlation effects as done in the PCI-80 scheme is rather important for these excitation energies. For RhCl(CO) the unparametrized result for the excitation energy is 13 kcal/mol (the PCI-80 result is 5 kcal/mol), for RhH(CO) it is 13 kcal/mol (23 kcal/mol), for $\mathrm{RhH(NH_3)}$ it is 7 kcal/mol (0 kcal/mol) favoring the triplet, and finally, for $\mathrm{RuH_2}$ it is 20 kcal/mol (18 kcal/mol).

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Table 2. Geometries and Energies for the Precursor of the Oxidative Addition Reaction: $RhXL + CH_4 + \Delta E \rightarrow RhXLCH_4$ (The Energies at the PCI-80 Level Are Calculated Relative to Ground State RhXL Systems and Methane)

reactant	method[a]	Rh–C	Rh–H_1[b]	Rh–$H_{2,3}$[b]	C–H_1[b]	C–$H_{2,3}$[b]	∠(X–Rh–L)	ΔE
RhClCO	MP2	2.58	2.20	2.66	1.115	1.104	103.9	−3.4
RhClCO	SCF	2.87	2.37	2.94	1.089	1.083	99.2	+3.8
RhHCO	MP2	2.47	2.12	2.55	1.122	1.105	110.7	−10.8
RhHCO	SCF	2.80	2.24	2.90	1.093	1.083	100.4	−8.6
$RhHNH_3$	MP2	2.49	1.88	2.71	1.138	1.102	102.4	−14.5
$RhHNH_3$	SCF	2.91	2.26	3.05	1.090	1.082	97.5	−7.1

[a] Method indicates the geometry optimization method. [b] H_1 and $H_{2,3}$ are the hydrogens closest to rhodium.

The most clear-cut example of how the electronic structure affects the precursor and the transition state of the methane reaction is seen in a comparison of the results for RhCl(CO) and RhH(CO). As mentioned above, RhCl(CO) is a triplet and RhH(CO) is a singlet. It is expected that singlet state reactants should form stronger molecular adducts than triplet states since singlets should hybridize better.[6] The open shells of a triplet cannot easily mix with the closed shells, and the electronic structure is therefore locked to a certain extent for a triplet. The hybridization is expected to be critical since this allows the systems to approach each other close enough for an efficient interaction. In line with this expectation the RhH(CO) system forms a much stronger bound molecular precursor with methane than RhCl(CO). The predicted binding energy of the precursor for RhH(CO) is 10.8 kcal/mol, in very good agreement with the prediction from experiment of about 10 kcal/mol for this type of complex. RhCl(CO), on the other hand, forms a singlet precursor complex which is only bound by 3.4 kcal/mol with respect to the triplet asymptote. A dominating part of the reason for this is that the adiabatic excitation of 5 kcal/mol to reach the singlet has to be paid for the RhCl(CO) reactant. There are obviously also other minor differences between RhH(CO) and RhCl(CO) which contribute to the difference in the precursor region as seen on the final binding energies. On the triplet surface RhCl(CO) forms a very weakly bound complex by 1 kcal/mol, as expected.

On the basis of the fact that RhH(CO) forms a much more strongly bound precursor than RhCl(CO) it might be expected that the energy at the SCF-optimized transition state should be lower for RhH(CO). As seen in Table 1 this is not the case. Instead, the transition state is 11 kcal/mol lower for RhCl(CO) than for RhH(CO). The lower energy obtained for the transition state than for the precursor for RhCl(CO) indicates in fact that there might not be a true C–H bond-breaking transition state for this reaction, but the energy could be downhill throughout this region. Since the precursor geometry was obtained at the MP2 level including correlation, this minimum should in that case be due to a too high transition state at this level which prevents the system from going all the way to the products. For RhH(CO) on the other hand the energy at the transition state is 15 kcal/mol higher than for the precursor. By comparison to other similar systems it can be shown that one of the main reasons for the higher barrier for the RhH(CO) system than for the RhCl(CO) system is that essentially the full promotion energy to reach the triplet state has to be paid for RhH(CO) to reach the transition state. The best evidence for this is that the transition state for the $RhH(PH_3)$ reaction is 9 kcal/mol lower than for RhH(CO), and at the same time the adiabatic excitation energy to reach the triplet state is 13 kcal/mol lower for the phosphine system.[9] For the stability of the products the full promotion energy enters and the product for $RhH(PH_3)$ is thus 13 kcal/mol more stable than for RhH(CO). Further evidence for the importance of the promotion energy is given for the $RhH(NH_3)$ and $RhH(H_2O)$ systems which have triplet ground states and where the transition state region for the methane reaction is very low. It can be added that the fact that the full promotion energy enters at the transition state does not mean that the barrier has to be equal to the promotion energy. Other attractive effects, such as the start of bond formation, clearly also contribute to the barrier height. A simple parallel can be found for the bond formation in methane between the carbon atom and the four hydrogen atoms. In this case it is clear that for the carbon atom the full promotion energy to go from the s^2p^2 state to the sp^3 state is paid and this does still not mean that there should be a very high barrier for the bond formation. The promotion energy will only give a negative contribution to the final bond strengths.

The present results thus indicate that there are entirely different requirements on the reactant to form a stable precursor and to obtain a low transition state for the oxidative addition reaction with methane. For a strongly bound precursor a ground state, or a low-lying, singlet of the reactant is an advantage, while for a low transition state a ground state, or a low-lying, triplet is an advantage. This means that the barrier from the precursor to the transition state is not expected to be characteristic for the methane dissociation reaction, but is expected to be different from system to system depending on the singlet–triplet splittings of the individual reactants. As seen in Table 1, the energy at the transition state for RhH(CO) is 15.0 kcal/mol higher than for the precursor, which in line with this expectation is not very similar to the 4.5 kcal/mol measured experimentally for the RhCp(CO) system in the liquid phase.[5] A very similar result between these two systems would require very similar singlet–triplet splittings. In fact, calculations performed show that the singlet–triplet splitting for RhCp(CO) is 12 kcal/mol which is thus lower than the 23 kcal/mol obtained for RhH(CO), by a similar amount as the difference in barrier heights counted from the precursors.

In order to show that also other effects enter the detailed energetics of the methane reaction, results are given in Table 1 for $RhH(NH_3)$ and for RuH_2. Since $RhH(NH_3)$ has a very small singlet–triplet splitting, $RhH(NH_3)$ both forms a strong precursor and has a low energy in the C–H bond-breaking region. The difference in energy compared to RhH(CO) in the precursor region shows that the covalent π-bonding to carbonyl competes somewhat with the precursor bond. The ruthenium complex RuH_2 finally, which has a ground state triplet and a high excitation energy to the singlet state, forms a precursor on the singlet surface that is not bound with respect to the asymptote. The transition state region is low in energy but the product is not very stable since in this case a large geometrical distortion is needed.[9]

In Table 2 the geometries obtained both at the MP2 and at the SCF level for the precursor complexes are given. The structure of the precursor for RhH(CO) is shown in Figure 1. As seen in this figure, methane is best described as η^3 coordinated trans to the carbonyl. The RhH(CO) unit has almost the same structure as it has in the singlet reactant. The H–Rh–CO angle increases from 90° for the reactant to 104° for the precursor. The changes for the other systems are rather similar to the one for RhH(CO). As seen in Table 2, the η^3-coordination does not have three exactly equal distances, but one Rh–H distance is somewhat shorter. As the reaction for RhH(CO) proceeds, basically the same type of geometry is kept. In contrast, the transition state for RhCl(CO) has the chloride trans to the carbonyl. The difference in geometries between these systems can be explained by a stronger covalency in the metal–hydrogen than in the metal–methyl bonds and an increased lone-pair attraction due to sd-hybridization.[9]

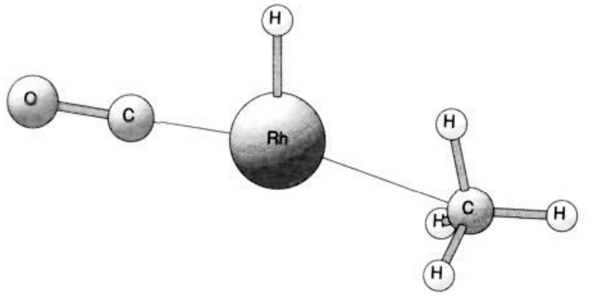

Figure 1. Molecular precursor complex for the reaction between RhH(CO) and methane.

Table 3. Energies at the MCPF and PCI-80 Level for the Precursor of the Oxidative Addition Reaction: $RhXL + CH_4 + \Delta E \rightarrow RhXLCH_4$ (The Energies Are Calculated Relative to Ground State RhXL Systems and Methane)

reactant	ΔE(MCPF)	ΔE(PCI-80)
RhClCO	+6.1	−3.4
RhHCO	−9.0	−10.8
$RhHNH_3$	−11.6	−14.5
RhH_2	+8.3	+4.0

The energies given in Table 2 show that it can be very important to optimize the structure of the precursor at a correlated level. The precursors for both RhCl(CO) and $RhH(NH_3)$ are stabilized by about 7 kcal/mol at the MP2 geometry compared to the SCF geometry. This energy change is mainly due to a significant shortening of the rhodium to methane distance. Both the Rh–C and the $Rh–H_{2,3}$ distances are shortened by 0.3–0.4 Å. The shortening of the closest $Rh–H_1$ distance is somewhat smaller with 0.1–0.2 Å, but this is still significant. Also, the characteristic long C–H bonds in the range 1.12–1.14 Å, which are typically observed experimentally for methane precursors, are only obtained at the MP2 level (the C–H bond in free methane is 1.08 Å). It is thus clear that it is necessary to include van der Waals attraction in the geometry optimization for a qualitatively correct treatment of the precursors. It should finally be noted that the C–H bonds for the precursor in the range 1.12–1.14 Å are still very far away from the C–H bonds typical at the transition state for the oxidative addition, which are in the range 1.5–1.7 Å. When attempts have been made experimentally to map the potential surface for the oxidative addition reaction of alkanes by using precursor geometries,[30] it is thus clear that a very large and uncertain extrapolation is needed to reach the transition state region. Since the electronic structure requirement at the transition state also is quite different from what it is in the precursor region, deviations between theoretical and experimental reaction trajectories must be expected.[15]

In Table 3 the effect of the PCI-80 extrapolation procedure is shown for the precursor systems. These effects are all significant and vary between the systems. The smallest effect is found for RhH(CO) with 1.8 kcal/mol followed by $RhH(NH_3)$ where the effect is 2.9 kcal/mol. It is interesting to note that the results for the RhH(CO) precursor were also stable to the level of geometry optimization, as shown in Table 2. If this system alone would have been chosen to test the accuracy of the computational procedures very different conclusions would have been reached than when several systems are studied. This illustrates the danger of being to restricted in the comparisons. It is also, in our opinion, quite dangerous to base any conclusions on the reliability of a theoretical treatment on randomly selected comparisons to what happens to be available experimentally. Some type of systematic selection of systems is a much preferred procedure. The largest effect of using the PCI-80 scheme is found for RhCl(CO) with 9.5 kcal/mol, which leads to a qualitatively different picture at this level. The large effect for this system is partly expected since this system changes spin from long distance to the precursor minimum. The correlation effects on singlet–triplet splittings are well known to be quite large.

IV. Conclusions

The electronic structure requirements are quite different to form a strong precursor and to obtain a low barrier for the oxidative addition reaction with methane. For the formation of a strong precursor a ground state singlet is important, as expected. Furthermore, the precursor binding energy will be larger if the complex does not have π-bonding ligands. The precursor binding for RhH(CO) with 10.8 kcal/mol is thus smaller than the precursor binding for $RhH(NH_3)$ with 14.5 kcal/mol. The binding energy found for RhH(CO) is quite similar to the one estimated from experiments for RhCp(CO) of about 10 kcal/mol, which is reasonable since both systems have π-bonding ligands. For RhCl(CO) the precursor binding energy is quite small with 3.4 kcal/mol since the promotion energy of 5 kcal/mol from the ground state triplet to the excited singlet has to be paid.

In contrast, a low barrier for the oxidative addition reaction with methane requires a low-lying triplet state of the reactant. Both RhCl(CO) and RuH_2, which are ground state triplets, thus have low barriers for the reaction. The transition states for both these systems are found to be about 7 kcal/mol below the reactant asymptote. For $RhH(NH_3)$, which is a ground state singlet but has a very low excitation energy to the singlet of less than 1 kcal/mol, the transition state is even lower than for the triplet systems. Again, for $RhH(NH_3)$ it is an advantage not to have π-bonding ligands that will compete with the bond formation in the oxidative addition process. For RhH(CO), which has a ground state singlet with a rather high excitation energy to the triplet, the transition state is highest of the systems studied with an energy which is 4 kcal/mol above the reactant asymptote. It is interesting to note that for the experimentally studied system RhCp(CO), which is also a singlet, the excitation energy to the triplet is only about half of that for RhH(CO). A much lower transition state for RhCp(CO) than for RhH(CO) is thus expected. On the basis of experiments the transition state for RhCp(CO) is estimated to be below the asymptote by 5 kcal/mol,[1] which is thus in line with this expectation.

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(30) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.