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Comparison of the C−H Activation of Methane by $M(C_5H_5)(CO)$ for M = Cobalt, Rhodium, and Iridium

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Abstract: The C−H activation reactions of methane by MCp(CO) (Cp = C_5H_5) for the metals cobalt, rhodium, and iridium have been studied using a variety of methods including a recently developed scaling scheme, different perturbation theory methods, and also hybrid density functional theory methods. The main chemical problems investigated include the recent finding that CoCp(CO) is entirely inert toward alkanes in contrast to the corresponding rhodium and iridium systems. Comparisons are made for CoCp(CO) between the reaction with methane and the reaction with CO, which is found experimentally to proceed fast. Also studied are the isotope effects on the reaction in relation to other recent experiments. At the highest level of treatment, good agreement is found with all present observations for these systems, but it should be pointed out that precise experimental information is lacking for many of the systems studied. Severe deviations between the results obtained at different computational levels are pointed out.

Introduction

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. Most notably, rhodium and iridium complexes have been found to activate C−H bonds of alkanes, and these complexes were also the first ones to be observed to have this ability 10−15 years ago.[1−4] These complexes have the general formula MCp*L (L = CO, PR_3) or $MClL_2$ (L = PPh_3). The small number of metals observed to be active must imply very special electronic structure requirements for oxidative addition of alkanes. Since complexes of rhodium and iridium are among these complexes, a natural step is to investigate also complexes of the first-transition row member of this triad, cobalt, in their reaction with alkanes. This was done recently experimentally by Bergman et al.[5] who found that the CoCp(CO) complex is totally inert to reactions with alkanes. In fact, the experiments indicated not only that C−H insertion did not take place but also that molecular complexes of the type $CoCp(CO)(CH_4)$ were not formed. This surprising finding was one of the main motivations to start the present study of the reactions between methane and MCp(CO) for cobalt, rhodium, and iridium. It can be added that the addition reaction between CoCp(CO) and CO is found to occur much in the same way as it occurs for rhodium and iridium. In the present study this reaction is therefore studied as a comparison to the methane reaction. In recent research on the C−H activation reaction, Bergman et al.[6] have also obtained another rather surprising result, and this is that there is a large inverse isotope effect on the preequilibrium constant for the reaction between cyclohexane and RhCp(CO), implying that C_6D_{12} binds more strongly than C_6H_{12} to the rhodium center. This effect will also be investigated in the present study.

A third major reason to study the reactions between MCp(CO) and methane is that this is a representative realistic model reaction for comparing different electronic structure methods. It has recently been shown that by using the effect that the errors obtained in standard *ab initio* methods are highly systematic, much improved results can be obtained by a simple scaling procedure using a single empirical parameter.[7,8] This scaling scheme was termed PCI-*X* (parametrized configuration interaction with parameter *X*), where the parameter *X* is the fraction of the correlation energy obtained in the *ab initio* treatment. Using standard double-ζ plus polarization basis sets and coupled cluster or coupled pair functional type methods, the parameter *X* takes a value close to 80, and this is the value used in the present study. It was shown in ref 7 that for a large number of small second-transition row systems the accuracy for the energetics is as high as that obtained experimentally. However, no tests for larger realistic systems have so far been made even though one of the main objectives for the development of this scheme was that small enough basis sets can be used so that also rather large more realistic systems can be studied. Another point of interest is to study the accuracy for first- and third-transition row complexes where the PCI-80 scheme has hardly been applied yet. In density functional theory (DFT), very large progress on the accuracy has also recently been made.[9] The introduction of gradient corrections and semiempirical parameters has made the accuracy for methods of this type as high as for the PCI-80 scheme for common benchmark tests of first- and second-row systems.[9] Much less is known about the accuracy for transition metal complexes, and an important part of the present study is therefore to compare

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the PCI-80 results with those of these DFT methods. The third type of method investigated here is the complete active space second-order perturbation theory (CASPT2) method.[10] This is a method designed to be able to treat systems with close lying states and is therefore of special interest for transition metal complexes where near degeneracies are common. This is particularly true for the first transition row where reliable quantum chemical methods are not well established yet.

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. It has, for example, been shown that the reaction proceeds via a molecular precursor state. For the RhCp(CO) complex, Bergman et al.[11] predicted the energy profile for the gas-phase methane reaction to be the following. First, on the basis of previous experimental work[12−14] 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 molecular methane and RhCp(CO) should be about 10 kcal/mol. From this precursor state, the C−H activation barrier was assumed to be the same as that measured for cyclohexane in liquid phase, i.e., 4.5 kcal/mol.[15] 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. Even though these detailed energies are not directly measured for the gas-phase RhCp(CO) system, they are of sufficient accuracy to be of very large importance when the accuracy of the methods described above is evaluated.

There are several theoretical studies in the literature of the oxidative addition reaction between methane and transition metal complexes.[16−18] Musaev and Morokuma[16] studied the reaction between RhCp(CO) and methane at the MP2 (Møller−Plesset second-order perturbation theory) level using polarized basis sets. They found a reaction energy profile in good agreement with the one suggested based on experiments.[11] A molecular precursor was found to be bound by 7.7 kcal/mol, the barrier was found to be 5.5 kcal/mol above the precursor, and the exothermicity was 16.4 kcal/mol. Song and Hall[17] also studied the same reaction at the MP2 level, but they used unpolarized basis sets, and quite different results were obtained. 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 as large as 30.6 kcal/mol. Ziegler et al.[18] also studied this reaction but using density functional methods including gradient corrections. The molecular precursor was found to be bound by 7 kcal/mol, and the transition state was found to be 9 kcal/mol above the precursor, which is thus 2 kcal/mol above the reactants. This result is thus in contrast to the other studies which found the transition state below the reactants. The reaction exothermicity was found to be 15 kcal/mol. In the same study the methane reaction was studied also for different ruthenium, osmium, and iridium complexes. For iridium the precursor was found to be bound by 14 kcal/mol, and the reaction exothermicity was 33 kcal/mol. The activation barrier was found to be as small as 2 kcal/mol.

Recent systematic theoretical studies on the oxidative addition between small second-row transition metal model complexes and methane have given detailed information on the electronic structure factors of importance for this reaction.[19−21] These studies focused on the transition state and the product equilibrium of the oxidative addition, but in a recent paper these investigations were extended to include also the molecular precursor complex.[22] The electronic structure requirements for strongly bound precursors and insertion products for the oxidative addition were found to be quite different. It was found that only the singlet state forms significantly bound precursors. A ground or a low-lying singlet state is thus required for a large binding energy of the precursor with respect to the ground state reactant. A ground or a low-lying triplet state is, on the other hand, required for a strongly bound insertion product. The size of the barrier for C−H activation will thus depend on a combination of these requirements and is therefore to a large extent determined by the reactant singlet−triplet splitting.

Computational Details

The first method used for the study of the reactions between methane and the MCp(CO) complexes was the recently developed PCI-80 scheme.[7,8] This parametrized scheme is based on calculations performed using the modified coupled pair functional (MCPF) method,[23] which is a standard quantum chemical, size-consistent, single reference state method. The zeroth-order wave functions were determined at the SCF level. All valence electrons were correlated including the nd and $(n + 1)$s electrons on the metal atom. If standard double-ζ plus polarization (DZP) basis sets are used, it has been shown that about 80% of the correlation effects on bond strengths are obtained quite surprisingly 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.[7] The parameter 80 is thus an empirical parameter, which is not fitted but still chosen to give agreement with experiment for a common bench-mark test[24] consisting of experimental heats of formation of 32 first-row molecules. The use of a single scaling parameter for the entire periodic table is the key feature of the PCI-80 scheme. Other scaling schemes exist, such as those due to Truhlar et al.[25] In those schemes different parameters are used for different systems. For several first-row systems, it was shown in refs 7 and 8 that a Hartree−Fock limit correction is also strictly needed in the PCI-80 scheme. However, this correction is usually small for transition metal systems, and a useful procedure is to consider these effects together with basis set superposition errors and core correlation effects as included in the parametrization. This procedure has been used in the present study. In the PCI-80 calculations relativistic effects were added using perturbation theory for the mass-velocity and Darwin terms.[26] The PCI-80 calculations were performed using the STOCKHOLM set of programs.[27]

The second set of methods used in the present study are two different empirically parametrized DFT methods. These methods are hereafter

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termed B3LYP and B3P86. The B3LYP functional can be written as $F^{\mathrm{B3LYP}} = (1 - A)*F_x^{\mathrm{Slater}} + A*F_x^{\mathrm{HF}} + B*F_x^{\mathrm{Becke}} + C*F_c^{\mathrm{LYP}} + (1 - C)\, F_c^{\mathrm{VWN}}$, where F_x^{Slater} is the Slater exchange, F_x^{HF} is the Hartree−Fock exchange, F_x^{Becke} is the exchange functional of Becke,[9] F_c^{LYP} is the correlation functional of Lee, Yang, and Parr,[28] and F_c^{VWN} is the correlation functional of Vosko, Wilk, and Nusair.[29] In the B3P86 method the correlation functional of Perdew[30] is used instead of F_c^{LYP} and F_c^{VWN}. *A*, *B*, and *C* are the coefficients determined by Becke[9] using a fit to experimental heats of formation for a similar bench-mark test as the one used for the PCI-80 scheme.[24] However, it should be noted that Becke did not use F_c^{LYP} in the expression above when the coefficients were determined but used the correlation functional of Perdew and Wang instead.[31] The introduction of gradient corrections, Hartree−Fock exchange, and empirical parameters has made this type of hybrid DFT approach highly competitive in accuracy with the most accurate standard quantum chemical methods. The DFT and MP2 calculations were carried out using the GAUSSIAN92/DFT package.[32]

The final type of method used in the present study is the CASPT2 method.[10] In this method a complete active space SCF (CASSCF)[33] calculation is first performed. This part of the calculation should take care of the most important near-degeneracy effects. Using the CASSCF wave function in an internal contraction scheme for a second-order perturbation theory calculation, the remaining part of the dynamical correlation energy is obtained in the final CASPT2 step. A fundamental problem in this type of approach is to find a proper active space in a general and unbiased way. However, for closed shell transition metal complexes to the right, a standard choice is to have an active space consisting of five d-dominated strongly occupied orbitals and five weakly occupied d-orbitals. This is the choice made for the present calculations. The same or a similar active space was used for the triplet states. The CASPT2 calculations were performed using the MOLCAS program package.[34]

Essentially the same standard DZP basis sets were used for the most important part of the molecules in both the DFT and the PCI-80 calculations. Exactly the same basis sets were used for the PCI-80 and CASPT2 calculations. For first-row atoms the primitive (9s,5p) basis of Huzinaga[35] was used, contracted according to the generalized contraction scheme to [3s,2p], and one d function was added. For hydrogen the primitive (5s) basis from ref 35 was used in the PCI-80 calculations, augmented with one p function and contracted to [3s,1p]. In the PCI-80 and CASPT2 calculations, the polarization functions were taken away for the Cp and CO ligands. For the DFT calculations a primitive (4s,1p) basis contracted to [2s,1p] was used instead. In the PCI-80 and CASPT2 calculations, an all-electron description was used for the first-transition row metal atoms using the Wachters primitive basis[36] and for the second-transition row using the Huzinaga primitive basis[37] extended by adding one diffuse d function, two p functions in the $(n + 1)$p region, and three f functions. The core orbitals were totally contracted except for the *n*s- and *n*p-orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects. The $(n + 1)$s- and $(n + 1)$p-orbitals were described by a double-ζ contraction and the *n*d by a triple-ζ contraction. The f functions were contracted to one function. Relativistic effects were accounted for using first-order perturbation theory.[26] For iridium a relativistic ECP (RECP) was used with the same type of contraction.[38] For the DFT and MP2 calculations, on the other hand, the RECP's of Hay and Wadt[39] were used for the metal. In this RECP, the *n*s- and *n*p-orbitals are described by a single-ζ contraction, the valence $(n + 1)$s- and $(n + 1)$p-orbitals by a double-ζ basis, and the *n*d-orbital also by a double-ζ basis, including one diffuse function. No f function was used for this ECP. The ECP's of Hay and Wadt are nonrelativistic for the first transition row, and in this case the relativistic effects were taken from the MCPF calculations.

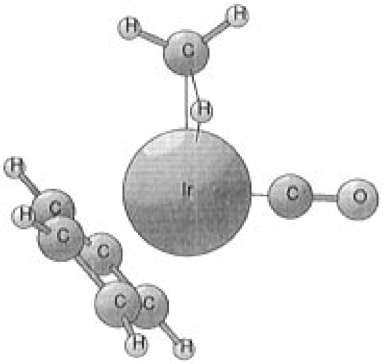

Figure 1. Transition state for the reaction between IrCp(CO) and methane.

All the geometries of the present study have been optimized at both the MP2 and B3LYP levels using the above basis sets without polarization functions. The geometries obtained at the MP2 and B3LYP levels were found to be very similar for the present rhodium and iridium systems, while for cobalt some marked differences were found. According to previous experience, the B3LYP geometries should be more reliable for cases where the MP2 and B3LYP geometries differ, and for this reason B3LYP geometries were used for the energy evaluation for the cobalt reaction. For rhodium and iridium, the MP2 geometries were used. All degrees of freedom, including those of the Cp and CO ligands, were optimized. SCF level zero-point vibrational effects for the methane reaction were finally added taken from the reaction between RhH(CO) and methane and used also for the other metals. For the binding of CO the zero-point vibrational effects were taken from RhH(CO).

Results and Discussion

The discussion of the results of the calculations for the reaction between the MCp(CO) complexes and methane will be divided into four subsections. In the first subsection the PCI-80 results for the three different metals, cobalt, rhodium, and iridium, will be compared. A structure illustrating the methane reaction is shown in Figure 1 for the case of the transition state for C−H activation for the iridium system. In the second subsection the rhodium results will be compared to the reaction profile derived from experiments by Bergman et al.[11] In the third subsection the results for cobalt will be discussed in relation to recent experiments.[5] In particular, an explanation will be suggested for the finding that the cobalt complex is totally unreactive and does not even form molecular precursor complexes with methane. In the fourth subsection, finally, the results of the different computational methods will be compared.

1. Comparison of the Results for Cobalt, Rhodium, and Iridium. The PCI-80 results for the reaction between MCp-

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Table 1. PCI-80 Results for the Reactions between MCp(CO) and Methane for the Metals Cobalt, Rhodium, and Iridium[a]

metal	ΔE(S−T)	ΔE(Prec)	$\Delta E^{\#}$	ΔE(Prod)
Co	−11.2	17.1	23.1	34.1
Rh	5.9	12.5	6.6	17.2
Ir	−0.3	6.5	8.3	29.2

[a] Energies are given in kcal/mol. ΔE(S−T) is the singlet to triplet excitation energy, ΔE(Prec) and ΔE(Prod) are the binding energies of the precursor and the insertion product, and $\Delta E^{\#}$ is the barrier height. All energies are given with respect to the singlet reactant.

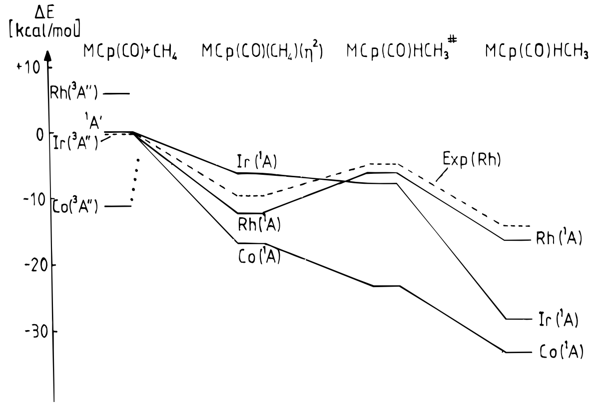

Figure 2. PCI-80 results for the reactions between $M(C_5H_5)(CO)$ and methane for cobalt, rhodium, and iridium. The experimentally suggested curve for the rhodium−cyclohexane system[11] is also given for comparison.

(CO) and methane for the metals cobalt, rhodium, and iridium are collected in Table 1 and also displayed in Figure 2. In this subsection only the PCI-80 results will be discussed. As suggested by Bergman et al.[11] the three main features of the reactions are the formation of a molecular precursor, the passage over a C−H insertion transition state, and the formation of the product insertion complex,

$$M(C_5H_5) + CH_4 \rightarrow M(C_5H_5)(CO)(CH_4) \rightarrow M(C_5H_5)(CO)HCH_3^{\#} \rightarrow M(C_5H_5)(CO)HCH_3$$

The results for the three different metals are qualitatively similar, but the energies shift somewhat from cobalt to rhodium to iridium. On the singlet surface the molecular precursor complex is bound by as much as 17.1 kcal/mol for cobalt, 12.5 kcal/mol for rhodium, and only 6.5 kcal/mol for iridium. On the same singlet surface the insertion product is bound by 34.1 kcal/mol for cobalt, 17.2 kcal/mol for rhodium, and 29.2 kcal/mol for iridium. The transition state energies on the singlet surface are 6.6 kcal/mol below the reactants for rhodium, 8.3 kcal/mol below for iridium, and as much as 23.1 kcal/mol below for cobalt. This leads to a barrier height with respect to the molecular precursor of 5.9 kcal/mol for rhodium and actually negative barriers for both iridium and cobalt of −1.8 and −6.0 kcal/mol, respectively. The main reason for the negative barrier for iridium is that zero-point vibrational effects (taken from $RhH(CO) + CH_4$) decrease the precursor binding energy by 2.0 kcal/mol and lower the transition state by 0.7 kcal/mol. Without these effects included, there is thus a true minimum for the molecular precursor. For cobalt, the major reason for the negative barrier is that the geometries were not obtained at the PCI-80 level but at the B3LYP level.

The singlet−triplet splittings of the MCp(CO) reactants differ in a marked way between the three metals. For rhodium the singlet state is the ground state for the reactant. The excitation energy to the triplet state is low with only 5.9 kcal/mol. For iridium the singlet and triplet states are almost degenerate with a splitting favoring the triplet by only 0.3 kcal/mol. In fact, this splitting is so low and the spin−orbit effects so large that it is meaningless to assign a singlet or triplet spin to the IrCp(CO) system. In contrast to the rhodium reactant, the CoCp(CO) reactant is a triplet state with an excitation energy to the singlet state as high as 11.2 kcal/mol. An important origin for the difference of spin states of the MCp(CO) systems can be traced to a difference already for the isolated atoms. The cobalt atom has a quartet d^7s^2 ground state with a high excitation energy to the doublet d^9 state of 77.5 kcal/mol. For the iridium atom the ground state is again a quartet d^7s^2 state but with a slightly lower excitation energy to the doublet d^9 state of 60.7 kcal/mol. Rhodium finally has a quartet d^8s^1 ground state with a quite low excitation energy of only 7.8 kcal/mol to the d^9 state. Since a molecular surrounding will always favor a low spin state for these systems as the metal orbitals can then freely mix with the ligand orbitals, the ligands in MCp(CO) are able to convert the rhodium system to low spin but are not quite able to convert the cobalt system with its high excitation energy to low spin. The difference in the singlet−triplet splittings for the MCp(CO) systems has large consequences for the methane reaction as will be discussed below.

It is difficult to draw general conclusions about trends based only on three numbers as in the present comparison of the cobalt, rhodium, and iridium reactions. Eventually many more results of the same type will become available, but until then a few factors which contribute to the trends can be discussed. For the precursor complexes, the relative size of the d-orbitals, the occupation of the d-orbitals, and the position of the lowest singlet and triplet states are of importance for the binding energy. The main origin of the large precursor binding energy for cobalt on its singlet surface is that the triplet state is so low, implying that also the singlet has large open shell character. An open shell singlet can be considered to be composed of two closed shell configurations with equal weights. One of these configurations will have a doubly occupied sd-hybrid pointing away from methane and an empty sd-hybrid pointing toward methane. The second singlet configuration will have the opposite occupation. The first one of these will have a favorable interaction with methane and is the one that dominates in the molecular region leading to a large binding energy. A complicating factor here is that the same type of effect is present also for the other ligands, and it is not always clear that precisely the interaction with methane can be optimized. Rhodium on the other hand has a large precursor binding energy because of its easy access to states with high d-occupation (see the discussion of the atoms above). Since the d-orbitals are smaller than the valence s- and p-orbitals, the repulsion to a ligand like methane will be smaller for states with high d-occupation. The Rh d-population for the precursor is 8.26, while it is 8.07 for iridium and 8.01 for cobalt. The rather low precursor binding energy for iridium is somewhat surprising, but a relatively low d-occupation and a low amount of open shell character in the singlet state are two contributing factors for this result. A third factor of importance is the relative size of the d-orbitals. The iridium d-orbitals are relatively larger compared to the s- and p-orbitals than they are for rhodium and cobalt, and the iridium d-orbitals are therefore also more repulsive toward ligands.

The main factor of importance for the bond strength in the insertion complex is the position of the triplet state for the MCp(CO) reactant. Since two new covalent bonds have to be formed in the product, the bond-prepared MCp(CO) state has to have at least two open shells, and the lowest state of this type is the triplet state. The bonding in the product can thus be viewed as

Table 2. Geometries (Å) Obtained at the MP2 Level for the Singlet and Triplet States of the Reactant MCp(CO) Systems[a]

metal	state	M−Z	M−CO	∠(CO−M−Z)
Co	$^1A'$	1.75 (1.75)	1.73 (1.75)	136.0 (137.6)
	$^3A''$	1.96 (1.93)	1.83 (1.80)	146.4 (139.8)
Rh	$^1A'$	1.99 (2.03)	1.83 (1.85)	133.3 (136.0)
	$^3A''$	2.08 (2.09)	1.91 (1.90)	135.7 (136.0)
Ir	$^1A'$	1.99 (2.01)	1.83 (1.83)	137.2 (140.3)
	$^3A''$	2.06 (2.07)	1.85 (1.85)	135.7 (138.2)

[a] Z denotes the midpoint of the Cp ring. Results in parentheses were obtained at the B3LYP level.

Table 3. Geometries (Å) Obtained at the MP2 Level for the Different Systems Involved in the Reactions between MCp(CO) and Methane[a]

metal	description	M−Z	M−CO	∠(CO−M−Z)	∠(C_x−M−H_x)
Co	reactant	1.75 (1.75)	1.73 (1.75)	136.0 (137.6)	
	precursor	1.72 (1.81)	1.69 (1.75)	133.8 (134.1)	
	tr state	1.70 (1.82)	1.66 (1.75)	133.3 (133.1)	40.7 (50.8)
	product	1.67 (1.83)	1.59 (1.74)	137.5 (135.3)	71.8 (81.2)
Rh	reactant	1.99 (2.03)	1.83 (1.85)	133.3 (136.0)	
	precursor	2.01 (2.05)	1.83 (1.85)	133.9 (135.0)	
	tr state	1.99 (2.05)	1.84 (1.85)	136.6 (135.5)	40.5 (44.2)
	product	2.03 (2.07)	1.84 (1.85)	138.5 (138.0)	78.4 (80.5)
Ir	reactant	1.99 (2.01)	1.83 (1.83)	137.2 (140.3)	
	precursor	2.01 (2.04)	1.83 (1.83)	137.0 (138.2)	
	tr state	2.01 (2.05)	1.83 (1.83)	136.6 (136.1)	32.1 (34.2)
	product	2.03 (2.06)	1.83 (1.84)	136.6 (136.4)	79.9 (81.0)

[a] All the systems are singlets. Z denotes the midpoint of the Cp ring. C_x and H_x are the atoms in the CH bond that is dissociated. Results in parentheses were obtained at the B3LYP level.

bonds formed between the triplet MCp(CO) state and the two doublet radicals, the methyl radical, and the hydrogen atom, much in the same way as the bonding in water can be viewed as bonds formed between the oxygen triplet state and the two hydrogen atoms. The binding energy of the product with respect to the triplet reactant is thus much more similar for the three metals than the binding energy with respect to the singlet asymptote. Since CoCp(CO) has a triplet ground state, the binding energy of the insertion product on the singlet surface is quite high. IrCp(CO) also has a triplet ground state but with a much lower excitation energy to the singlet state and will therefore form somewhat weaker bonds in the product. RhCp(CO) finally has a singlet ground state and will therefore form the weakest product bonds. The ease of forming good bonding hybrids is also a contributing factor, and here iridium has an advantage with its more similar size of the valence s-, p-, and d-orbitals.

The position of the transition state for the C−H insertion will depend on the binding energies both of the precursor and of the insertion product. Iridium with its low precursor binding energy and its large product binding energy will therefore have a lower barrier than rhodium. This follows directly if the reductive elimination barriers are considered to be the same for the different metals. As seen in Table 1 and Figure 2, this is not quite so with a somewhat higher elimination barrier for iridium due to its larger bond strengths of the product. However, the product bonds for iridium are not strong enough to lead to a higher transition state than for rhodium.

Finally, the most important geometrical parameters are given in Table 2 for the singlet and triplet reactants and for the other singlet systems in Table 3. Concerning the singlet and triplet reactants, it can be noted that the metal−ligand bond distances are longer for the triplet states. This is a general effect, and the origin of it is that a triplet state has a poorer ability to form hybridized orbitals. This is because singly occupied orbitals to a first approximation only can mix with other singly occupied orbitals and not with the large number of doubly occupied orbitals. The electronic structure of triplet states is therefore frozen to a certain extent. In particular for the σ-interaction it is extremely important to introduce sd-hybridization to avoid σ-repulsion. This inability to form hybridized orbitals is also the reason triplet states have low binding energies for the molecular precursors; see above. When the geometric structures for the singlet states in Table 3 are studied, the most striking result is the very small geometric change these systems undergo during the reaction. For the rhodium and iridium systems, the metal to ligand distances change only by 0.02 Å and the ligand angle only by a few degrees. These geometric changes probably contribute <1 kcal/mol to the reaction energies, which should be seen in contrast to the large C−H bond energy in methane of 103 kcal/mol. These results imply that the major factor that allows the MCp(CO) to break C−H bonds of unsaturated alkanes is the electronic structure of the metal itself. The main effect of the Cp ligand is to affect the singlet−triplet splitting of the system and also not to be in the way for the incoming methane. In line with these conclusions, the ligand-free rhodium atom, which has a suitable singlet−triplet splitting, is found to break C−H bonds in alkanes much in the same way as the RhCp(CO) system does.[40] As a final technical comment, the MP2 geometries in Tables 2 and 3 are very similar to the B3LYP-optimized geometries for the rhodium and iridium systems. For the cobalt reaction, the C_x−M−H_x angle for the transition state and the product is 10° larger at the B3LYP level. For the triplet cobalt reactant, the CO−M−Z angle is 10° larger at the MP2 level. As shown previously,[22] the Hartree−Fock level is in general inadequate for obtaining geometries of the precursors. It also leads to too long M−Cp distances.

2. Reaction Profile for the Rhodium Complex. As already mentioned in the Introduction, Bergman et al.[11] have derived a reaction profile for the reaction between RhCp(CO) and alkanes based on different experimental results. From measured binding energies for alkanes with $W(CO)_5$, for example, a conservative estimate of 10 kcal/mol is made for the cyclohexane molecule to RhCp(CO). The barrier height from the precursor to the C−H insertion transition state was measured for cyclohexane in a rare gas solvent and found to be 4.5 kcal/mol. Finally, the reaction exothermicity for the total reaction is estimated to be at least 15 kcal/mol based on the minimum lifetime of the product insertion RhCp(CO)RH complex. In qualitative terms these results agree quite well with the present PCI-80 results in Table 1. The calculated binding energy of the molecular complex is 12.5 kcal/mol compared to the experimental estimate of 10 kcal/mol. The computed barrier height is 5.9 kcal/mol compared to the experimental value of 4.5 kcal/mol, and finally the calculated exothermicity of 17.2 kcal/mol agrees with the experimental lower bound of 15 kcal/mol. These comparisons thus support the previous conclusions drawn from comparisons to experiments for smaller transition metal systems, that the PCI-80 bond strengths for the second transition row agree with experiments generally to 3−4 kcal/mol.[7,40] In the previous comparisons, the accuracy of the experiments is not higher than this discrepancy, and it was in fact concluded that the PCI-80 results are probably at least as accurate as experiments for those systems. In the present case, with the indirect nature of the experimental estimates, a better agreement than what is found can not be expected.

Even though the PCI-80 results are highly satisfactory in comparisons to the experimental estimates, there are still a few minor question marks. For example, the estimate of the molecular precursor binding energy for cyclohexane of 10 kcal/

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[40] Carroll, J. J.; Weisshaar, J. C.; Haug, K. L.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Svenson, M. *J. Phys. Chem.* **1995**, *99*, 13955.

mol is somewhat smaller than the presently calculated value of 12.5 kcal/mol for methane. This is in contrast to experiments done for W(CO)$_5$ which in that case show that molecular methane is much less strongly bound than cyclohexane.[12] The experimental binding energies given are <5 kcal/mol for methane and 11.6 kcal/mol for cyclohexane. Since very little experience is available for calculations on this type of molecular complexes, the possibility that the calculated result at the PCI-80 level could be too large has to be taken seriously. However, the results in Table 1 reveal that the molecular precursor binding energies to third-row transition metal centers are considerably weaker than those to second-row metals. The binding energy of methane to IrCp(CO) is only 6.5 kcal/mol, which is not much larger than the 5 kcal/mol upper limit for methane to W(CO)$_5$. A second fact of interest appears when calculations are made for Mo(CO)$_5$, and this is that for this system the methane binding energy is found to be 8.0 kcal/mol which is substantially smaller than the 12.5 kcal/mol found for methane to RhCp(CO). When these results are combined, the fact that methane is bound by <5 kcal/mol for W(CO)$_5$ does not appear to be in obvious disagreement with a value of 12.5 kcal/mol for RhCp(CO). Basis set superposition errors and other effects, like increasing the basis set on the other ligands, were finally also checked, but these investigations did not reveal any unusual problem. At this stage there are therefore no obvious indications that the PCI-80 results for these precursor binding energies should be much too large. An overestimation by 2−3 kcal/mol is clearly still possible.

An interesting question in relation to the precursor binding energy of methane is exactly how the size of the binding energy affects the reactivity. It is found experimentally that methane is much less reactive than larger alkanes like cyclohexane.[11] From an experimental point of view, it is quite reasonable to connect this finding with the experiment for W(CO)$_5$ discussed above and conclude that the reason methane has such a low reactivity with RhCp(CO) is that methane is hardly able to bind as a precursor to the rhodium center. Therefore, the present result with a precursor binding energy as high as 12.5 kcal/mol is again somewhat surprising. However, in the experiments on RhCp(CO), this reactant is not in the gas phase but is solvated in a rare gas like krypton or xenon. Therefore, the most relevant energy in this context is not the total binding energy of methane but the difference between the methane and the rare gas atom binding energies. If methane binds more weakly or about equally as strong as the rare gas atoms do, this should affect the reactivity with methane considerably. The binding energies for both krypton and xenon to RhCp(CO) were therefore also calculated. This was done at the MP2 level since this level was found to give quite reasonable binding energies for the methane precursor; see further below. The result is that krypton binds 4.0 kcal/mol weaker than methane and xenon only 0.7 kcal/mol more weakly. These results are somewhat uncertain, since there is at present not much experience on the basis set dependence for the bond strengths for these heavy rare gas atoms. It is therefore at least conceivable that both these rare gases in fact will have binding energies to RhCp(CO) which are comparable to the one for methane. These rare gases could thus constitute a hindrance for the reaction with methane.

A few minor comments can also be made concerning the fact that the PCI-80 result for the methane barrier height of 5.9 kcal/mol is somewhat higher than the measured value for cyclohexane of 4.5 kcal/mol. This difference appears quite reasonable. Even though it is expected that additional agostic interactions for the molecular precursor should make the binding energy larger for cyclohexane than for methane, β-agostic interactions at the transition state, which are not present for methane, are expected to be at least as important. It is also of importance in this context that the C−H bond in cyclohexane is substantially weaker (by 3−5 kcal/mol) than the C−H bond in methane. The sum of these effects should thus tend to make the barrier lower for cyclohexane than for methane.

In recent experiments on the C−H activation of cyclohexane by RhCp*(CO), Bergman et al.[6] found a large normal kinetic isotope effect on the C−H activation step but a large inverse isotope effect on the preequilibrium constant, implying that C_6D_{12} binds more strongly than C_6H_{12}. From the temperature dependence, activation energies of 4.2 ± 0.5 kcal/mol for C−H activation and 5.3 ± 0.5 kcal/mol for C−D activation were derived. Some simple model calculations were performed for the methane reaction with RhH(CO) and RhCl(CO) for comparisons to the experiments and to see whether these effects are general. In the present type of calculations, zero-point vibrational effects are added at the end, and it is instructive to consider the situation before and after these effects are added. Zero-point vibrational effects will raise the energies everywhere but by different amounts. For the reaction between a free metal atom and methane, it is expected that zero-point vibration will have the following main effects. The vibrational energy of a C−H bond is quite high, and dissociation of CH_4 into CH_3 and H leads to a decrease of the zero-point vibrational energy by as much as 10.3 kcal/mol. This decrease should be higher than the gain of zero-point vibration due to the formation of the M−H and M−CH_3 bonds in the oxidative addition reaction. It is therefore expected that zero-point vibration will *decrease* for both the transition state and the product compared to the reactants, giving both a higher reaction exothermicity and a lower barrier for the C−H activation of methane. This is also what is found with an increased exothermicity by 2.7 kcal/mol and a decreased barrier by 3.0 kcal/mol for the reaction between the Rh atom and methane due to zero-point vibrational effects. Since the zero-point vibrational energy is 30% smaller for CD_4 than for CH_4, the lowering of the zero-point energy is also about 30% smaller, 7.3 kcal/mol, when CD_4 is broken up into CD_3 and D, compared to 10.3 kcal/mol for CH_4. It is therefore expected that the increase of the exothermicity and the lowering of the barrier height will be smaller for CD_4 roughly by the same fraction. In line with these expectations, for RhH(CO) the transition state energy (counted from the reactants) is lower by 0.4 kcal/mol for CH_4 than for CD_4. For RhCl(CO) the corresponding value is only 0.1 kcal/mol, which shows that ligands can affect zero-point effects slightly differently. For the molecular precursor, zero-point vibration has an opposite effect. Since no bond is broken, there should be only a small loss of zero-point vibration due to the slight weakening of the C−H bonds involved in agostic bonding. Instead, a few new degrees of freedom are formed for the precursor that should give some *increase* of the zero-point vibration. For CD_4 this increase should be smaller than for CH_4. This is also what happens. For RhH(CO), CD_4 is therefore more strongly bound by 0.6 kcal/mol than CH_4. For RhCl(CO) this difference is also 0.6 kcal/mol. For the C−H activation step, from precursor to the activation, the barrier for RhH(CO) is therefore higher by 1.0 kcal/mol (0.4 + 0.6 kcal/mol) for CD_4 than for CH_4. For RhCl(CO) the difference is 0.7 kcal/mol. For the reaction between ethane and RhH(CO) the activation step is 1.0 kcal/mol lower for C_2H_6 than for C_2D_6. For the activation step all these results are in good agreement with the experimental result for cyclohexane that breaking the C−H bond in C_6H_{12} has a 1.1 kcal/mol lower barrier than breaking a C−D bond in C_6D_{12}. There is also agreement between the calculations and the experiments concerning the fact that the deuterated species should bind stronger than the undeuterated one in the precursor region. However, the experimental difference is suggested to be 1.1 kcal/mol, while the calculated results are smaller, about 0.6 kcal/mol. Temperature dependent enthalpy effects do not change these results significantly. As discussed in the experimental paper,[41] entropy effects, which are difficult to estimate correctly for the present systems solvated in rare gases, could be important. The slight deviation between theory and experiments could also be due to a difference between the systems actually studied.

3. Reactions Involving CoCp(CO). Recently Bergman et al.[5] studied the reaction between CoCp(CO) and alkanes experimentally. Their results were quite surprising. They found that unlike the analogous rhodium and iridium complexes, the CoCp(CO) complex does not bind detectably to either a noble gas or an alkane. In quantitative terms they estimate the cobalt−xenon interaction energy that exists in solutions of CoCp(CO) in liquid Xe to be at most 2 kcal/mol. On the other hand, they find that CoCp(CO) reacts rapidly with CO and $CoCp(CO)_2$, actually much faster than the corresponding rhodium complex does. In order to find an explanation for these results, calculations were performed for the association reactions for CoCp(CO) with both methane and CO.

The results for the reaction between CoCp(CO) and methane were already discussed in section 1. These results, shown in Table 1 and Figure 2, indicate one marked difference between CoCp(CO) and the corresponding rhodium and iridium complexes, and this is that CoCp(CO) has a triplet ground state whereas the other complexes have singlet ground states. In previous studies on small transition metal complexes, it has always been found that high-spin states bind alkanes very poorly.[19,22,40] The origin of this behavior has already been mentioned above, and this is the poor ability of high-spin states to form sd-hybridized orbitals. Singly occupied orbitals can not mix well with doubly occupied orbitals, and this leads to a partly locked electronic configuration for high-spin states. The sd-hybridization is absolutely essential for allowing the alkane to approach the metal center close enough for an attractive interaction. The main origin of the binding is the interaction between an unshielded metal nucleus and the electrons on the alkane. This type of interaction is quite analogous to the interaction between the σ-lone pair of CO and a metal center, which actually does not require any electron donation from the ligand to be attractive as is normally assumed in the donation−back-donation picture. The main difference between CO and methane is that for methane there can not be any back-donation. When the geometry was optimized at the B3LYP level for the triplet state of $CoCp(CO)(CH_4)$, a very long $Co-CH_4$ distance was found of 3.71 Å, compared to only 2.40 Å for the singlet state. The interaction energy for the triplet is 2.0 kcal/mol at the PCI-80 level. At the DFT and CASPT2 levels, binding energies of <1 kcal/mol were obtained.

Since isolated CoCp(CO) has a triplet ground state while the inserted complex has a singlet ground state, a spin−orbit-induced crossing is required for a reaction to occur. The height of this crossing point is important for the reaction rate. It is not possible with present methodology to locate this crossing point for the present type of reaction, but an estimate can be made. In this connection it should be pointed out that a one-dimensional picture can be quite misleading for a system with many degrees of freedom. It might be argued in a one-dimensional picture that since methane addition to the Co center is exothermic (by 17 and 2 kcal/mol for the singlet and triplet states, respectively) and downhill, the crossing point should be lower in energy than the reactant triplet ground state. This is not correct. Instead, the following information is relevant. Although the adiabatic excitation energy between the triplet and singlet states of the CoCp(CO) reactant is 11.2 kcal/mol, the vertical excitation energy at the triplet minimum is as high as 25.0 kcal/mol. This difference is due to the quite different geometries for the singlet and triplet states; see Table 2. The vertical excitation energy at the singlet minimum is 10.3 kcal/mol, which as expected is lower than the adiabatic excitation energy but not by much. From these numbers it is clear that the singlet−triplet crossing for the isolated CoCp(CO) reactant should be substantially higher than the adiabatic excitation energy of 11.2 kcal/mol. The next question is whether the interaction with methane could bring down this crossing point significantly. This is unlikely for the following reason. At the triplet minimum for the $CoCp(CO)(CH_4)$ complex (at a $Co-CH_4$ distance of 3.71 Å), the vertical excitation energy to the singlet is as high as 23.9 kcal/mol. At the singlet minimum of this complex (at a $Co-CH_4$ distance of 2.40 Å), the vertical excitation energy from the singlet to the triplet is 31.4 kcal/mol. The singlet and triplet states thus prefer very different geometries. A linear extrapolation between these points leads to an estimated crossing point for a $Co-CH_4$ distance of 3.15 Å at a height of about 10 kcal/mol above the triplet reactant. It should furthermore be added that on the basis of comparisons to the results of the other methods (see below), the PCI-80 crossing point should be regarded as a lower bound. The true crossing point is therefore probably 13−15 kcal/mol higher than the triplet reactant. Due to the rapidly varying energy of both these states around the crossing point, the crossing should occur with high slopes of the potential surfaces which decrease the crossing probability still further. It is therefore clear that the required spin−crossing explains why CoCp(CO) is unreactive toward alkanes. The system should first reach the high singlet−triplet crossing point, and at this point spin−orbit interaction is required to actually cross to the singlet surface, which makes the effective barrier height appear even higher.

Table 4. Comparisons of Different Methods for Reactions Involving CoCp(CO)[a]

method	ΔE(S−T)	ΔE(CO,S)	ΔE(CO,T)	ΔE(Prec)	ΔE(Prod)
MCPF	−21.6	54.1	8.4	13.3	22.0
PCI-80	−11.2	65.0	12.9	17.1	34.1
MP2	1.3	71.2	22.6	19.5	35.7
CASPT2	−21.5	64.7	11.5	15.4	23.0
B3LYP	−27.8	54.2	11.5	9.0	7.7
B3P86	−26.7	59.6	13.6	11.5	11.8

[a] Energies are given in kcal/mol. ΔE(S−T) is the singlet to triplet excitation energy, and ΔE(Prec) and ΔE(Prod) are the binding energies of the precursor and the insertion product of the methane reaction given with respect to the singlet reactant. ΔE(CO,S) and ΔE(CO,T) are the binding energies of CO on the singlet and triplet surfaces, respectively.

The experimental result that CoCp(CO) does not bind detectably to either a noble gas or cyclohexane is particularly surprising in light of its fast reaction with CO. The results of the calculations for the association reaction between the triplet and singlet states of CoCp(CO) and CO are given in Table 4. These results are totally consistent with the experimental observations. An appreciable binding energy of 12.9 kcal/mol is found at the PCI-80 level for the binding of CO to the triplet state. For the singlet state an unusually large binding energy of 65.0 kcal/mol is found. The Co−CO bond distances for the triplet and singlet states are quite similar, 1.90 and 1.75 Å, respectively. The association reaction between CoCp(CO) and CO will therefore proceed in the following way. The ground

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(41) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019.

state triplet of CoCp(CO) will first bind to CO following a pathway which is attractive all the way. The reason CoCp(CO) reacts faster with CO than the rhodium complex does is most likely a result of the very weak binding energy to the rare gas atom for the cobalt complex. For rhodium the metal−rare gas interaction will constitute some hindrance and slow down the reaction. Once the $CoCp(CO)_2$ complex has reached its triplet minimum, it can eventually cross over to the singlet ground state by a spin−orbit-induced crossing. There are thus two main differences between the methane and the CO reaction that leads to the large difference observed in their reactions. First, the binding energy of the alkane is very small. Second, and perhaps even more importantly, the cobalt−methane distances are quite different for the triplet and singlet minima which makes a curve crossing appear at energies higher than those of the reactants, which will make the crossing quite difficult. In contrast, for CO the cobalt−carbonyl distances for these minima are quite similar and the crossing will occur for energies lower than the reactants.

The origin of the very large binding energy for CO in the singlet state is the open shell character of the singlet state already discussed above. This open shell character leads to a very efficient sd-hybridization which unshields the metal nucleus and forms a strong attractive interaction between the metal and the CO σ-lone pair. The binding energy of 65.0 kcal/mol can be compared to the average CO binding energy of 35 kcal/mol found for the more normal carbonyl complex $Ni(CO)_4$.

4. Comparisons of Different Methods. During the course of this project it became evident that the results using different methods commonly used were sometimes quite different. Since these results should be of general interest for future work on quantum chemical methods, the results are listed in Tables 4−6. It should be emphasized that this method comparison is not made in order to conclusively decide which method is most reliable in all cases. This obviously has to be decided for a much larger and more broadly chosen set of systems. Also, since very few experimental results are available for the present systems, such a comparison is better made for other systems. For transition metal-containing systems, bench-mark tests have, for example, recently been made by Ricca and Bauschlicher[42] for the first-transition row MCH_2^+ systems showing overall quite good agreement with experiments for the B3LYP method, in particular. The first method used in the present study was the MCPF method on which the PCI-80 scaling scheme is built. Second, the PCI-80 scheme itself and, third, the MP2 method were used, which has until recently been the most commonly used method for transition metal complexes. Fourth, the CASPT2 method was tested with an active space consisting of the nd- and $(n + 1)$d-orbitals. Finally, as the fifth and sixth methods, two different versions of the DFT approach were used. These methods are the B3LYP and B3P86 methods which both use gradient corrections, include part of the Hartree−Fock exchange, and are empirically parametrized. The same set of geometries was used for all methods, and the basis sets were chosen to be as similar as possible. More details can be found in the computational section.

Even though the present basis sets were chosen to be as similar as possible between the different methods, there can be a few question marks in this connection. The first question concerns the use of ECP's for the DFT calculations. In order to test these ECP's, all-electron B3LYP calculations were also performed for the cobalt reaction. Using ECP's the reaction exothermicity was found to be 7.7 kcal/mol (see Table 4). At the all-electron level using Wachter's basis set[36] including diffuse p and d functions and a set of f functions (as described in Computational Details), the result is 10.0 kcal/mol. The singlet−triplet splitting of the reactant using ECP's is 27.8 kcal/mol, while the all-electron result is 25.0 kcal/mol. The second major question in the present comparison of methods concerns the neglect of polarization functions on the Cp and CO ligands in the *ab initio* type calculations. This procedure has been tested for many systems, such as $PdCl(H_2O) + CH_3$, $PdCl + C_3H_7$, $RhCl(PH_3)_2 + CH_4$, etc., and the errors in these reaction energies were found to be at most 1−2 kcal/mol. It can not be tested for the present methane reactions since they are too large, but it can be tested for quite similar H_2 reactions. The exothermicity for the reaction between RhCp and H_2 is 42.1 kcal/mol when polarization was used also on the Cp ligand. When these functions were removed, the exothermicity became 41.9 kcal/mol. For the RhCp(CO) reaction with H_2, the exothermicity was found to be 46.0 kcal/mol without polarization functions on the ligands. With polarization added on the CO ligand, the exothermicity decreased to 45.4 kcal/mol. The remaining differences in the basis sets in this method comparison are truly minor and should have very small effects on the general conclusions.

Table 5. Comparisons of Different Methods for Reactions Involving RhCp(CO)[a]

method	ΔE(S−T)	ΔE(Prec)	$\Delta E^{\#}$	ΔE(Prod)
MCPF	−0.3	10.1	1.7	11.5
PCI-80	5.9	12.5	6.6	17.2
MP2	1.1	12.3	6.2	18.8
CASPT2	−0.6	11.7	9.6	21.9
B3LYP	−1.5	5.6	−3.1	5.8
B3P86	−4.4	8.0	2.0	9.9

[a] Energies are given in kcal/mol. ΔE(S−T) is the singlet to triplet excitation energy, ΔE(Prec) and ΔE(Prod) are the binding energies of the precursor and the insertion product, and $\Delta E^{\#}$ is the barrier height for the methane reaction. All energies are given with respect to the singlet reactant.

Starting with the rhodium reaction, the PCI-80 scheme can be used as a reasonable reference point since this method has been extensively tested and shown to perform well for this transition row. The PCI-80 results are also in quite good agreement with the experimental estimates for the present rhodium reaction. If the MCPF results are compared to the PCI-80 results, it can be concluded that scaling does not change the result significantly for the precursor but has a substantial effect in the right direction (compared to experiments) for both the product and the transition state. Another important effect is that the ground state of the reactant is changed from a triplet to a singlet due to the scaling.

The results of the MP2 method are in remarkable agreement with the PCI-80 results for the rhodium reaction, which is gratifying since this method has been used extensively for this type of system. However, this is to some extent due to a fortuitous cancellation of errors for the present particular system. This is clear when the C−H bond energy of methane itself is considered. The MP2 result with the present DZP basis sets has for this bond an error as large as 7.2 kcal/mol. The corresponding error for the PCI-80 scheme is 0.4 kcal/mol. For the MCPF method the error of 5.5 kcal/mol on the C−H bond in methane is smaller than for the MP2 method, and still the results for the reaction deviate much more for the rhodium reaction. The same conclusion about cancellation of errors can also be drawn about the present CASPT2 results since the error on the C−H bond energy of methane of 8.4 kcal/mol is about the same as for the MP2 method. This error is not surprising since only the d-orbitals were chosen as active in the calculation, which means that only inactive orbitals were used for methane.

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[42] Ricca, A.; Bauschlicher, C. W. *Chem. Phys. Lett.* **1995**, *245*, 150.

Table 6. Comparisons of Different Methods for Reactions Involving IrCp(CO)[a]

method	Δ*E*(S−T)	Δ*E*(Prec)	Δ*E*[#]	Δ*E*(Prod)
MCPF	−5.1	4.5	5.7	26.4
PCI-80	−0.3	6.5	8.3	29.2
MP2	−4.8	17.6	20.7	46.3
B3LYP	−4.6	9.8	11.7	33.7
B3P86	−4.0	13.7	16.6	38.8

[a] Energies are given in kcal/mol. Δ*E*(S−T) is the singlet to triplet excitation energy, Δ*E*(Prec) and Δ*E*(Prod) are the binding energies of the precursor and the insertion product, and Δ*E*[#] is the barrier height for the methane reaction. All energies are given with respect to the singlet reactant.

The reason the result is not exactly the same as for MP2 is that ROHF orbitals are used and that a slightly different zeroth-order Hamiltonian is used in the CASPT2 method, which affects the energy of the open shell CH_3 system slightly. It could be argued that a larger active space should have been used for the CASPT2 calculations since the C−H bond of methane can hardly be claimed to be inert in this reaction. However, this immediately leads to severe difficulties in defining the appropriate orbitals for the different complexes apart from the fact that the calculations become very much more expensive. The advantage with the present choice of active space is that it is reasonably well defined from system to system and still manageable computationally for the present systems. The present MP2 results for the rhodium reaction are very close to the results of Musaev and Morokuma,[16] as they should be since very similar basis sets were used. There is one notable exception, and this is that Musaev and Morokuma found a much smaller precursor binding energy of only 7.7 kcal/mol, compared to 12.3 kcal/mol found here. No explanation for this difference can be suggested here at present. The MP2 results of Song and Hall[17] are similar to the present ones for the precursor and for the transition state but rather different for the exothermicity, which must be due to the use of a smaller basis set without polarization functions in their case.

For the DFT methods B3LYP and B3P86, finally, surprisingly large deviations compared to the PCI-80 results were found for the rhodium reaction. This is surprising since we have found quite good agreement between these methods (using the same basis sets and ECP's as here) for the first-transition row MH^+, MCH_3^+, and MCH_2^+ systems. Both the B3LYP and B3P86 methods predict a triplet ground state for the reactant and much smaller reaction exothermicities than the PCI-80 scheme does and also from what is indicated based on experiments. The PCI-80 exothermicity is 17.2 kcal/mol, and the experimental estimate is >15 kcal/mol, while the B3LYP value is 5.8 kcal/mol and the B3P86 value 9.9 kcal/mol. Increasing the basis set on the metal by adding an f function gave only a slight improvement to 6.4 kcal/mol at the B3LYP level, while instead splitting the s,p,d basis further increased the exothermicity to 8.8 kcal/mol. These values are still much lower than the value of 14.8 kcal/mol found previously using a DFT method by Ziegler et al.[18] Since Ziegler et al. obtained a better agreement with experiments and did not use any Hartree−Fock exchange, this could indicate a problem with this type of procedure. On the other hand, Ziegler et al. also found the transition state higher than the reactants as is found here at the B3LYP level. These results are rather far away from the PCI-80 results. Another possible problem with the B3LYP and B3P86 methods as used here is that the parameters were actually determined for a different functional (see Computational Details).

The fortuitous aspect of the MP2 results for the rhodium reaction can clearly be seen on the results for the cobalt and iridium systems. For the cobalt reaction, the MP2 method is the only one which actually predicts a ground state singlet for the reactant. For iridium, the MP2 method gives a precursor binding energy 2−3 times larger than the one found at the PCI-80 level and an exothermicity which is 17 kcal/mol larger than the PCI-80 exothermicity. For the iridium reaction, on the other hand, the B3LYP results are in quite good agreement with the PCI-80 results. In fact, in the reaction region the curves are almost perfectly parallel with a constant deviation of 3−4 kcal/mol. This deviation is consistent with a very similar deviation for the singlet−triplet splitting of the reactant since there should be a relationship between the exothermicity and the position of the triplet state; see further above. The B3P86 results are somewhere in between the PCI-80 and MP2 results.

The cobalt reaction is the one where the PCI-80 results can be most seriously questioned. This is due to the near-degeneracies present for this reaction. These near-degeneracies are also the origin of the even more severe problems found at the MP2 level. It has previously been found[8] that the PCI-80 scheme can tend to overestimate correlation effects when there are near-degeneracies. Ideally, the dynamical and nondynamical correlation energies should be scaled using different scale factors, and the choice of 80 as scale factor is an optimal compromise which works well in normal situations. Work to extend the scaling scheme to use two different scale factors is in progress. For the PCI-80 results in Table 4 for the cobalt reaction, it can probably be concluded that they should be upper bounds, i.e., the true reaction exothermicity should probably be lower than 34.1 kcal/mol by 3−5 kcal/mol, and the precursor binding energy should be lower than 17.1 kcal/mol. In this context it is useful to consider the results at the CASPT2 level where all the near-degeneracy problems have been removed. In particular, the exothermicity is much smaller at the CASPT2 level which is a clear indication that the PCI-80 value is too high. Also, the singlet−triplet splitting is much higher at the CASPT2 level indicating that the true splitting should probably be about 15 kcal/mol. It should again be emphasized that to definitely draw these quantitative conclusions requires additional work.

It is somewhat frustrating that the B3LYP results differ so much from the PCI-80 results for the cobalt reaction, in particular since the B3LYP method has been shown to perform quite well for other systems of the first transition row.[42−44] The reaction exothermicity, for example, is only 7.7 kcal/mol at the B3LYP level, while it is 34.1 kcal/mol at the PCI-80 level. Also, the singlet−triplet splitting is 27.8 kcal/mol compared to only 11.2 kcal/mol at the PCI-80 level. With the limited experience available of the PCI-80 scheme for the first transition row and with the presence of rather large near-degeneracy effects, this could have indicated a case of severe breakdown of this scheme. However, the CASPT2 results are strong indications that the errors of the PCI-80 scheme could not be very severe. The CASPT2 method has no problem with near-degeneracy situations, and still the results are not too far away from the PCI-80 results. It should be remembered that the CASPT2 method suffers from the limited basis set size, whereas this defect has been corrected in the PCI-80 scheme. Previous experience strongly suggests that increasing the basis set should increase the bond strengths and thus move the CASPT2 results closer to those of the PCI-80 scheme. The very good experience with the CASPT2 method for first-row transition metal systems once large enough basis sets are used is another important factor in this context.[45] However, as already indicated above, corrections of 3−5 kcal/mol of the PCI-80 results in the direction toward the CASPT2 results could very well be motivated. It should be emphasized that this size of correction does not modify any of the chemical conclusions drawn in the previous sections. It can finally, in relation to the large deviation between the PCI-80 and DFT results, be noted that for the binding of CO to CoCp(CO) the results are rather similar and that this association reaction is more similar to the previous comparative studies that have been done using the B3LYP method.[43,44] Since the PCI-80 result should be overestimated due to near-degeneracies, in particular for the singlet state, the true result should be somewhere in between those of the PCI-80 and B3LYP results. It must finally be kept as an open possibility that any one of the methods used, including the PCI-80 scheme, in a more thorough and general test is shown to have severe and unexpected errors in some cases.

Conclusions

In the present study of the C−H activation of methane for the MCp(CO) complexes of cobalt, rhodium, and iridium, a few main conclusions have been drawn. First, the origin of the quite different behavior found experimentally for the cobalt reaction in comparison to the rhodium and iridium reactions is the ground state triplet spin of the CoCp(CO) reactant. It is important to note that this conclusion can be drawn almost irrespective of which computational method has been used. The only exception is the MP2 method which breaks down for the cobalt complex due to the strong near-degeneracies and therefore predicts a ground state singlet for this system. The DFT methods used, which for the rest of the reaction give very different results compared to the PCI-80 scheme, also give triplet ground states like the MCPF and CASPT2 methods. All these latter methods actually give a larger preference for the triplet state than the PCI-80 scheme. On the basis of the PCI-80 results and a linear extrapolation of vertical excitation energies, the spin−crossing should occur at an energy of 13−15 kcal/mol above the triplet ground state for the cobalt reaction. There is also agreement among all the methods used that the binding of molecular methane on the triplet surface is very weak at a long Co−CH_4 distance, while the binding of CO is relatively large at a rather short Co−CO distance in $CoCp(CO)_2$. The spin−orbit-induced crossing can thus occur for the CO reaction but will not occur for the methane reaction. These results explain the experimental findings that the association reaction between CO and CpCo(CO) is fast while there is no C−H insertion reaction with methane.

For the RhCp(CO) reaction there are in general good agreement with experimental results. The C−H activation barrier is, for example, found to be 5.9 kcal/mol for methane, while the one measured for cyclohexane is 4.2 kcal/mol. A slightly lower barrier is expected for cyclohexane due to β-agostic effects at the transition state and due to the weaker C−H bond. The C−D activation of CD_4 is calculated to be 0.7−1.0 kcal/mol higher than the C−H activation of methane for a few model complexes, while the corresponding difference found experimentally for C_6D_{12} is 1.1 kcal/mol. There is also agreement between the calculations and the experimental finding that a deuterated precursor binds more strongly than an undeuterated one. The experimental difference is 1.1 kcal/mol, while the calculated results are about 0.6 kcal/mol for the model complexes. It is suggested that the low reactivity for methane found experimentally is not due to a low precursor binding energy but rather due to a small difference between the methane binding energy and those of the solvent rare gas atoms used in the experiment. In particular, the binding energy of xenon is very close to the one for methane, and the presence of xenon in the experiments should constitute a hindrance for the C−H activation reaction.

Several different commonly used methods have been applied to the MCp(CO) reactions, and surprisingly large differences were found. The differences are largest for the cobalt reaction, mostly due to the presence of near-degeneracies but also because of the intricate balance of exchange loss effects and promotion effects which exists as the bonds are formed. The difference between the PCI-80 results and the DFT results are as large as 22−26 kcal/mol for the exothermicity, and the singlet−triplet splittings of the reactant differ by 16 kcal/mol. It is reasonable that the PCI-80 results should be too large for the exothermicity and too small for the splitting due to near-degeneracy effects but not by that much. On the basis of the CASPT2 results, where near-degeneracy problems have been removed but where the basis set problem still remains, the PCI-80 results should probably be corrected by 3−5 kcal/mol in the direction toward the CASPT2 results. For the rhodium reaction the deviation between the PCI-80 results and the DFT results is still significant, but for iridium the agreement is quite good, in particular for the B3LYP results. Further investigations on similar systems, preferably with direct comparisons to experiments, are needed to entirely understand and resolve these deviations.

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