Ab Initio Molecular Orbital Study of the Mechanism of H−H, C−H, N−H, O−H, and Si−H Bond Activation on Transient Cyclopentadienylcarbonylrhodium

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Abstract: An ab initio molecular orbital method at the MP2 level of theory in conjunction with a relativistic core potential and valence triple-ζ + polarization basis set for Rh and double-ζ + polarization basis set for other atoms has been applied to the study of the potential energy surface of the oxidative addition reaction $CpRh(CO) + HR \rightarrow CpRh(CO)(H)(R)$, where HR is H_2, CH_4, NH_3, H_2O, and SiH_4. At gas-phase collisionless conditions, the oxidative addition reaction of $H-SiH_3$, $H-H$ and $H-CH_3$ to CpRh(CO) should take place without an activation barrier, while the reaction of $H-NH_2$ and $H-OH$ goes over a barrier about 5 kcal/mol relative to the reactants. The differences in the reactivity of the substrates considered here can be correlated to the H−R bond strength and the Rh−R bond strength as well as the exothermicity of reaction. Going from SiH_4 to H_2, CH_4, NH_3, and H_2O, the H−R bond becomes stronger (88, 99, 108, 109, and 118 kcal/mol, respectively, calculated at the present level), the Rh−R bond becomes weaker (73, 65, 59, 47, and 55 kcal/mol, respectively), the exothermicity becomes smaller (49, 31, 16, 3, and 2 kcal/mol, respectively), and the ease of reaction decreases. In solution or in the gas phase when the collisional energy equilibrium is faster than the reaction itself and reaction should be considered to start from the pre-reaction molecular complex $CpRh(CO)\cdot(HR)$, the oxidative addition reaction of CH_4 requires a small barrier (6 kcal/mol), while that of NH_3 and H_2O requires a large barrier (42 and 26 kcal/mol, respectively) and would not take place easily under normal conditions. The high barrier is essentially determined by the stability of the molecular complex.

I. Introduction

The oxidative addition of the H−H, C−H, N−H, O−H, and Si−H bonds of the H_2, CH_4, NH_3, H_2O, and SiH_4 molecules, respectively, to a transition-metal complex is a important step of many catalytic cycles, and has been a focus of studies for long time.[1−12] It has been found that the activation of the H−R bond in hydrogen-containing compounds, which make up a large percentage of natural materials, occurs on metal surfaces, in several biological systems that contain metal complexes at their active sites, and with transition-metal complexes. Intensive studies of the oxidative addition reaction to transition-metal complexes have shown several marked differences and trends among different H−R bonds.

First, in spite of the similarity of the H−H and C−H bond strengths, the H−H bond of the hydrogen molecule is found to be activated more easily by a large number of transition-metal complexes than by C−H bonds in saturated hydrocarbons. The reason for the difference in the H−H and C−H activation has been explained in terms of the directionality of the bond involving an alkyl group compared to the bond involving hydrogen atoms.[13,14]

Second, a prediction[15,16] of oxidative addition of $H-CH_3$, $H-NH_2$ and $H-OH$ bonds has been made on the basis of a significant attraction that should exist between lone pairs of the ligand R and empty d-orbitals of the transition-metal center. This means that the products of the water and ammonia reaction, where lone-pairs of ligands are involved, should be more strongly bound than that of the methane reaction for the early transition metals. However, for late transition metals, which have more lone-pair d-electrons than empty d-orbitals, the trends of the M-R bonds (where R = CH_3, NH_2 and OH) should be completely different. This difference in trend is further accentuated if the Nyholm−Gillespie rules are applied, which state that the repulsion between d-electrons and lone-pairs of ligands is stronger than repulsion between bond electron pairs. Thus, for late transition metals the products should be less bound for the water and ammonia than for the methane reaction. The linear relationship between the H−R activation barrier on the transition-metal complexes and H−R bond strengths also has been proposed;[17] this means that the activation barrier should increase in the order (C−H) < (N−H) < (O−H). Third, a significant difference between the $H-SiH_3$ and $H-CH_3$ bond activation on transition-metal complexes also has been predicted,

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the origin of which has been explained for $RhCl(PH_3)_2$ complex in terms of the strong Rh−Si bond and the weak Si−H bond compared to Rh−C and C−H bonds, respectively.[18]

Recently, Wasserman, Moore, and Bergman[19,20] have carried out a gas-phase version of the H−H and C−H activation processes by transition-metal complexes. The activation of the strong H−H and C−H bonds in hydrogen and alkanes, respectively, by interaction with the partially "naked" metal center in the coordinatively unsaturated 16-electron d^8 fragment CpRh(CO) readily occurs in the gas phase, producing CpRh(CO)(H)(R) (where R = H, CH_3, and larger alkyls). They proposed the following reaction sequence which involves formation of a weakly bound intermediate:

$$\mathrm{HR + CpRh(CO) \rightarrow (HR)\cdot\cdot RHCP(CO) \rightarrow CpRh(CO)(H)(R)} \quad (1)$$

Since this reaction occurs in the gas phase, free of solvent and support interactions, it is the best example to test, both experimentally and theoretically, the above mentioned trends and predictions for oxidative addition reactions of H−R bonds of H_2, CH_4, NH_3, H_2O, and SiH_4 molecules. Experimentally, however, it is very difficult to detect the assumed intermediate and the transition state, and therefore theoretical studies are needed to clarify the structure and the stability, as well as the nature, of these species.

Thus, the purpose of this paper is to study the potential energy surface of reaction one for the H_2, CH_4, NH_3, H_2O, and SiH_4 molecules in order to (i) clarify the reaction mechanism, and determine the structure and energies of the assumed intermediates and transition states and (ii) test the above mentioned trends and predictions for oxidative addition reactions of the H−R bonds.

The structure and stability of the assumed intermediates and transition states, as well as reactants and products, of reaction 1 have previously been calculated by using a density functional theory with Hartree−Fock−Slater exchange (with Becke nonlocal correction) and Stoll correlation functional for H_2 and CH_4,[21] and RHF and MP2 methods for CH_4.[22] In these calculations relatively small basis sets have been used, and geometries have been fixed for both the Cp ring with the local D_{5h}-symmetry and CO. It has been found that the ground state of CpRh(CO) is the $^1A'$ state with $^3A''$ lying only 1−5 kcal/mol higher.[21] Reaction 1 for H_2 takes place without any energetic barrier and yields only one product, $CpRh(CO)(H)_2$, with about 24−26 kcal/mol energy gain.[21] The reaction 1 for CH_4 yields in the first step a molecular complex, $CpRh(CO){\cdot}CH_4$, with a stabilization energy of 6.9 (ref 21) or 14.8 (ref 22) kcal/mol. Then activation of the C−H bond takes place with an 8.8 (ref 21) or 4.1(ref 22) kcal/mol barrier, which leads to the product $CpRh(CO)(H)(CH_3)$. The whole reaction is calculated to be exothermic by 15 (ref 21) or 31 (ref 22) kcal/mol.

However, in the DFT study[21] an H_2 complex has been reported with an H−H distance of 1.11 Å, and its nature needs to be clarified. The structures of the $CpRh(CO){\cdot}CH_4$ complex reported by Song and Hall[22] by the MP2 method and Ziegler and co-workers[21] by the DFT method are different and also need additional studies.

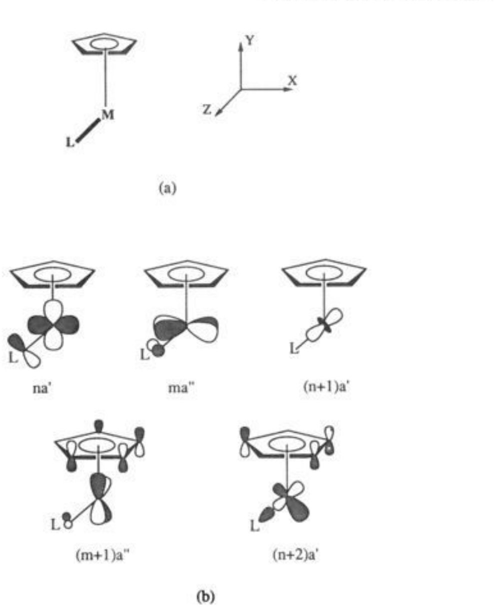

Figure 1. (a) The coordinate system used and (b) the valence molecular orbitals of the CpRhL complex.

The electronic structure of the fragment CpML has been discussed by Hofmann and Padmanabhan[23] for various ligands, L, and M = Co, Rh, and Ir with the extended Hückel method. The valence molecular orbitals are na', ma'', $(n+1)a'$, $(m+1)a''$, and $(n+2)a'$ orbitals under C_s symmetry and the coordinate system given in Figure 1. In Figure 1 one sees that the na' and ma'' orbitals are mainly d_{xx-yy} and d_{xz} orbitals stabilized by interaction with π^* orbitals on L. The occupied metal-based d_{zz} orbital, $(n+1)a'$, is at somewhat higher energy, with a weak M−L antibonding σ interaction. The metal-based $(m+1)a''(d_{yz})$ and $(n+2)a'(d_{xy})$ orbitals are highest by energy, destabilized by interaction with occupied π orbitals on the Cp ring, and, in addition, for $(n+2)a'$ by the σ orbital on L. Thus, it was suggested that the singlet $^1A'$ state with the electronic configuration $(na')^2(ma'')^2((n+1)a')^2((m+1)a'')^2((n+2)a')^0$ and the triplet $^3A''$ state with $(na')^2(ma'')^2((n+1)a')^2((m+1)a'')^1((n+2)a')^1$ are candidates for the ground state of the CpML fragment.

II. Calculation Procedure

The geometries of the reactants, products, intermediates, and transition states of the present reaction 1 for H_2, CH_4, NH_3, H_2O, and SiH_4 have been calculated by using the second-order Møller−Plesset (MP2) pertubation theory in conjunction with the following basis sets. For the Rh atom we use the 17 valence electron relativistic effective core potential of Hay and Wadt and the standard (5s5p4d/3s3p3d) basis set.[24] For C, O, N, and H atoms the standard 6-31G and for Si the 6-31G* basis set[25] are used and identified below as basis set I. All geometry parameters of the present structures are optimized by using the gradient technique with the assumption of the local C_{5v} symmetry for the Cp ring. The reactant CpRh(CO) is calculated under the overall C_s symmetry constraint, and all other structures are calculated under C_1 symmetry. Though the normal coordinate analysis has not been performed, the optimization in C_1 symmetry is likely to have given stationary points with the proper number of imaginary frequencies. Once the stationary points on the PES are determined, the energetics are recalculated at the MP2 level of theory with basis set II, which includes

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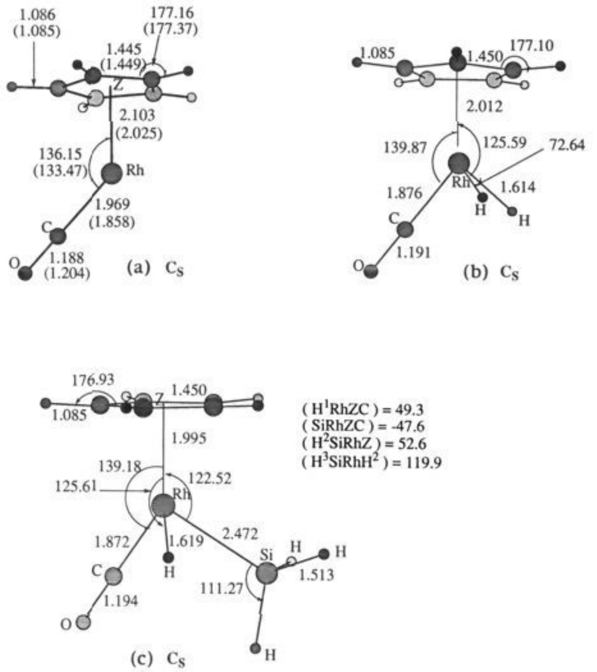


Figure 2. The calculated geometries (distances in Å and angles in deg) (a) of the $^3A''$ and $^1A'$ (in parentheses) states of the reactant CpRh(CO) and (b) the reaction products $CpRh(CO)(H)_2$ and (c) $CpRh(CO)(H)(SiH_3)$, respectively.

polarization $d_{C,O,N}$ ($\alpha = 0.80$, for all these atoms) and p_H ($\alpha = 1.10$) functions on top of basis set I. The Gaussian-92/DFT package has been used.[26]

III. Results and Discussions

The geometries of the critical structures of the present reactions calculated at the MP2/I level are given in Figures 2−5. Their energy parameters calculated at the MP2/II level by using geometries from Figures 2−5 are given in Table 1. In Table 2 we give the results of the Mulliken population analysis calculated at the HF/II level of theory. The profiles of the potential energy surfaces of reaction 1 calculated at the MP2/II level are given in the Figure 6.

A. CpRh(CO). As seen from Table 1, the singlet $^1A'$ state is calculated to be the ground state for the CpRh(CO) complex. The triplet $^3A''$ state lies just 3.9 kcal/mol above. As seen in Figure 2, the distance R(Rh−Z) between the metal atom and the center, Z, of the Cp ring, the distance R(Rh−CO), and the angle ∠(OC)RhZ are larger for the triplet compared with the singlet. This is a result of single occupancy of the $(n+2)a'$ orbital in the $^3A''$ state, which has Rh−CO and Rh−Cp antibonding character. As seen in Figure 1, upon optimization of the geometry of the Cp ring its H atoms bend up about 2°, which makes the interaction between Rh and π-orbitals of the Cp ring more favorable. A qualitatively similar result has been found by Ziegler et al.[21] by a density functional theory (DFT); at the DFT level the singlet−triplet energy gap is estimated to be 1−5 kcal/mol for CpRh(CO). However, the distances R(Rh−Z) and R(Rh−CO) are respectively 0.14 and 0.02 Å shorter and the angle ∠(OC)RhZ is 3−7° larger at the DFT level than at the MP2/I level in this paper. Relaxation of local D_{5h} constraint for the Cp ring in the DFT paper would further shorten the Rh−Z distance. Therefore, these differences must come from the use of different methods.

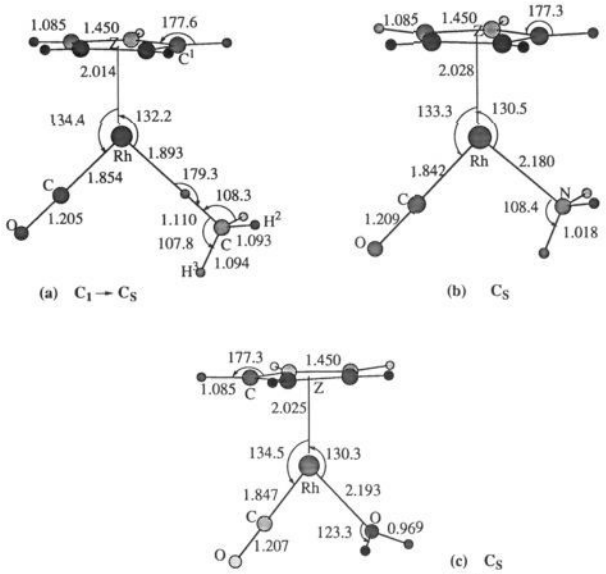
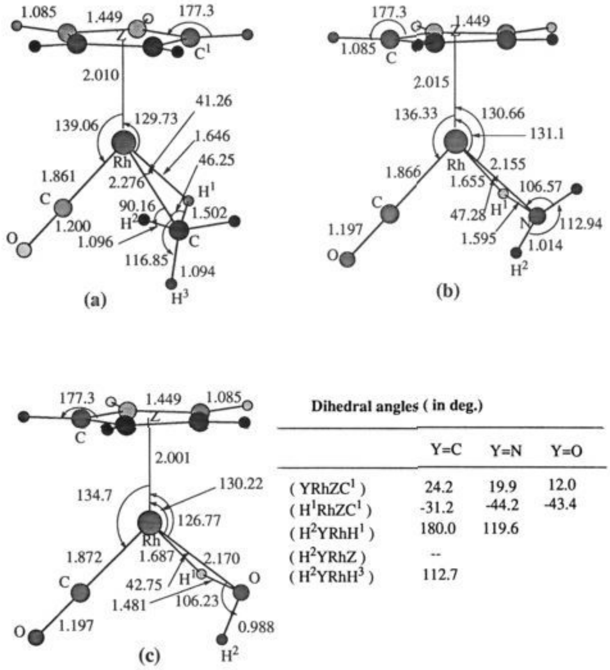


Figure 3. The calculated geometries (distances in Å and angles in deg) of the molecular complexes CpRh(CO)(HR), where HR is (a) CH_4, (b) NH_3, and (c) H_2O.



Dihedral angles (in deg.)

	Y=C	Y=N	Y=O
($YRhZC^1$)	24.2	19.9	12.0
(H^1RhZC^1)	-31.2	-44.2	-43.4
(H^2YRhH^1)	180.0	119.6	
(H^2YRhZ)	--		
(H^2YRhH^3)	112.7		

Figure 4. The calculated geometries (distances in Å and angles in deg) of the transition states of the reaction CpRh(CO) + HR → CpRh(CO)(H)(R), where HR is (a) CH_4, (b) NH_3, and (c) H_2O.

B. Geometries and Energetics of Reaction 1. Since the ground state of CpRh(CO) is calculated to be the singlet $^1A'$ state, and additional ligands will further stabilize of the singlet $^1A'$ state, the reaction of eq 1 is investigated only for the $^1A'$ state. As seen in Table 1 and Figure 6, reaction 1 for molecules H_2 and SiH_4 takes place without barrier and intermediate and directly leads to the products $CpRh(CO)(H)_2$ and $CpRh(CO)(H)SiH_3$, respectively, given in Figure 2. All attempts to find any intermediate led directly to products, and it is certain that an intermediate or a transition state does not exist at the present level of theory. Both reactions are exothermic, by 31.0 and 49.4 kcal/mol for H_2 and SiH_4, respectively.

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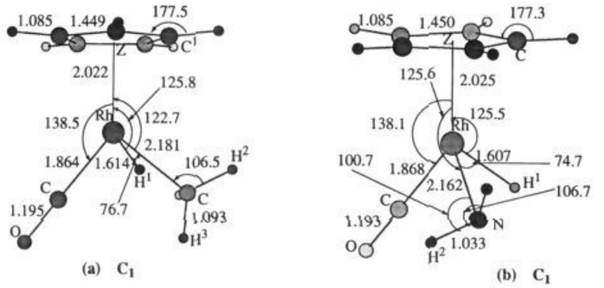

Dihedral angles (in deg.)

	Y=C	Y=N	Y=O
($YRhZC^1$)	-47.5	39.2	36.8
(H^1RhZC^1)	49.7	-57.3	-60.9
(H^2YRhH^1)	--	125.3	147.0
(H^2YRhZ)	46.6		
(H^2YRhH^3)	119.9		

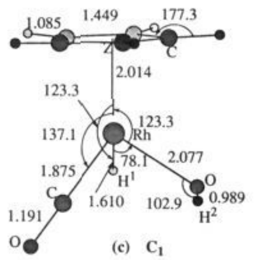

Figure 5. The calculated geometries (distances in Å and angles in deg.) of the products of the reaction CpRh(CO) + HR → CpRh(CO)(H)(R), where HR is (a) CH_4, (b) NH_3, and (c) H_2O.

Generally similar results for reaction 1 with H_2 have been found in the previous DFT study,[21] except the strange "H_2 complex", which seems to be an artifact. All our calculations started from the dihydrogen structure with the short H−H bond converged to the bishydrido complex $CpRh(CO)(H)_2$, indicating that the dihydrogen complex (with the H−H bond) does not exist at the present level of theory. On the other hand, the H−H distance reported in the DFT studies, 1.11 Å, is much longer than the characteristic H−H distance, 0.74−0.85 Å, reported for gas-phase complexes and in the crystal structure.[27,28] We should note that in literature a few "H_2 complexes" with quite long H−H distances, 1.1−1.65 Å, also have been reported.[29] However, all these molecules have a crystal structure having strong steric interaction, and therefore the existence of the real H−H bond in these complexes is doubtful.

The calculated geometries of the products, $CpRh(CO)(H)_2$ and $CpRh(CO)(H)(SiH_3)$ are depicted in Figure 2. As seen from comparison of these data with analogous data for the free CpRh(CO) complex, the addition of two H ligands or H and SiH_3 ligands does not change the geometry of the Cp ring. The distances R(Rh−Cp) and R(Rh−CO) decrease by about 0.01−0.03 Å, while the angle ∠(OC)RhZ increases by about 5°. These changes are maximum for the SiH_3 ligand, since the Rh−SiH_3 bond is stronger compared with the Rh−H bond.

The potential energy surfaces of reaction 1 for CH_4, NH_3, and H_2O are quite different from those for H_2 and SiH_4 molecules, as seen in Table 1 and Figure 6. In the first step the reactants yield a molecular complex, CpRh(CO)•HR, with a stabilization energy of 7.7, 36.8, and 20.5 kcal/mol for CH_4, NH_3, and OH_2, respectively. However, these numbers might be overestimated by up to several kilocalories per mole because of basis set superposition error (BSSE). As seen in Figure 3, in the complex CpRh(CO)•HR, OH_2 and NH_3 coordinate to the metal atom Rh with the lone pair orbitals of the central O and N atoms, respectively. In the complex $CpRh(CO){\cdot}CH_4$, methane coordinates to the metal atom by one of the H atoms, i.e. in the monodentate manner. Its bi- and tridentate structures, with two and three coordinated hydrogen atoms, respectively, lie energetically less than 1 kcal/mol higher but are not local minima and rearrange spontaneously into the monodentate structure. As seen in Figure 3, due to weak interaction between CpRh(CO) and CH_4 fragments, the C−H^1 bond is elongated by 0.02 Å compared to the other C−H bonds in the CH_4 fragment.

As shown in Table 2, the Rh atom has a positive charge and N and O have a negative charge. The Rh−N and Rh−O interaction is mainly electrostatic in nature. On the other hand, the interaction with CH_4 shows a large polarization character; the bridging hydrogen H^1 with +0.12 e charge in free CH_4 is polarized by the positively charged Rh and becomes negatively charged with −0.13 e in the $CpRh(CO){\cdot}CH_4$ complex. The overlap populations Q(Rh−H^1), Q(Rh−N), and Q(Rh−O) are very small (about 0.01−0.02 e).

The next step in the present reaction is the H−R bond activation process, which takes place with a barrier of 5.5, 41.9, and 25.9 kcal/mol, relative to the molecular complex, for CH_4, NH_3, and OH_2, respectively. These barriers also can be influenced by BSSE. The comparison of geometries of the transition state with those of the product CpRh(CO)(H)(R) on one side and of the molecular complex CpRh(CO)·HR on the other side, as given in Figures 3−5, shows that it is a late transition state. Bonds being formed, Rh−R (R = OH, NH_2, and CH_3) and Rh−H^1, are only 0.10, 0.007, 0.095 and 0.077, 0.048, 0.032 Å longer in the TS than in the product. At the same time, the R−H^1 bond being broken is longer by 0.51, 0.58, and 0.41 Å at the TS than at the complex CpRh(CO)•R.

As seen in Table 1, the transition state corresponding to the top of the energetic barrier lies 2.2 kcal/mol lower than reactants for the CH_4 case. Though the BSSE may raise the barrier somewhat, the reaction CpRh(CO) + CH_4 will take place without (or possibly with a very small) a barrier under gas-phase collisionless conditions and will lead to the hydromethyl complex $CpRh(CO)(H)(CH_3)$. However, the TS for NH_2 and OH_2 respectively lies about 5.1 and 5.4 kcal/mol higher than reactants respectively. Thus, even at collisionless conditions the reactions CpRh(CO) + NH_3 and CpRh(CO) + OH_2 need some activation or threshold energy. The entire reaction 1 for CH_4, NH_3, and H_2O is calculated to be exothermic by 16.4, 3.2, and 2.4 kcal/mol, respectively.

The comparison of the geometries of the Cp ring and the CO molecule in the "free" CpRh(CO) complex on one side and in CpRh(CO)·HR, TS, and CpRh(CO)(H)(R) on the other side shows that they are very close. Fixing the geometries of the Cp ring during the PESs calculations at its local C_{5v} symmetry will not change the final conclusions.

As was mentioned above, our calculations show that in $CpRh(CO){\cdot}CH_4$ the CH_4 molecule coordinates to Rh in a monodentate manner, which is consistent with the results of Ziegler et al.[21] but is different from those of Song and Hall (SH).[22] Optimization of geometry from a nearly bidentate structure without symmetry constraint converged to the monodentate structure, indicating that the bidentate structure does not exist at the present level of theory.

Comparison of the geometries obtained by using different methods shows that the largest differences are in the distances R(Rh−Cp), R(Rh−CO), R(Rh−H), and R(Rh−CH_3). The MP2 distance R(Rh−Cp) calculated by us is 0.10−0.12 Å longer than the DFT result, but it is 0.10−0.15 Å shorter than the small basis MP2 result reported by SH. Our result for the R(Rh−CO) distance is close to that obtained at the DFT level (except

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Table 1. The Calculated Energies, at the MP2/II Level, of Critical Points of the Potential Energy Surfaces of the Reaction CpRh(CO) + HR → CpRh(CO)(H)(R), Where R = H, CH_3, NH_2, OH, and SiH_3, as Well as Bond Energies D_e of R−H and Rh−R Bonds[a]

molecule	total energy	D_e(H−R)
H_2	−1.157661	99.00 (104.2)[b]
CH_4	−40.364626	107.9 (104.8)
NH_3	−56.383217	108.7 (107.4)
H_2O	−76.219786	117.8 (119.0)
SiH_4	−291.338997	88.30 (90.3)
CpRh(CO), $^1A'$	−414.782524	
CpRh(CO), $^3A''$	3.9 [1 ~ 5][d]	

system	molecular complex CpRh(CO)·(HR)	TS[c]	product CpRh(CO)(H)(R)	D_e(Rh−R)
CpRh(CO)+ H_2	N	N	−31.0 [−24 to −26]	65.0
CpRh(CO) + CH_4	−7.7 [−6.9; −14.8]	−2.2 [1.1; −10.7]	−16.4 [−15.0; −31.0]	59.3
CpRh(CO) + NH_3	−36.8	5.1	−3.2	46.9
CpRh(CO) + H_2O	−20.5	5.4	−2.4	55.2
CpRh(CO) + SiH_4	N	N	−49.4	72.7

[a] Total energies (italic, in hartrees) are given only for reactants. The relative energies calculated relative to reactants and the bond energies are given in kcal/mol. N indicates that the species does not exist. [b] Experimental values in parentheses. [c] The barrier heights calculated relative to the molecular complex CpRh(CO)·(HR) are 5.5, 41.9, and 25.9 kcal/mol for HR = CH_4, NH_3, and H_2O, respectively. [d] Numbers in brackets were taken from ref 21 (first number) and ref 22 (second number, if given).

Table 2. The Calculated Mulliken Population Analysis for Critical Points of PESs of the Reactions CpRh(CO) + HR → CpRh(CO)(H)(R), Where HR = H_2, CH_4, NH_3, OH_2, and SiH_4[a]

	atomic charges, Z^* (in e)				overlap population, Q (in e)			
molecule	Rh	H^1	X	H	Rh−H^1	Rh−X	X−H^1	X−H
CpRh(CO), $^1A'$	+0.50							
$^3A''$	+0.52							
CH_4			−0.48	+0.12			0.80	0.80
NH_3			−0.79	+0.26			0.70	0.70
H_2O			−0.67	+0.34			0.61	0.61
SiH_4			+0.67	−0.17			0.78	0.78
CpRh(CO)$(H)_2$	+0.37	−0.05			0.24			
CpRh(CO)(CH_4)	+0.48	−0.13	−0.32	+0.14	0.01		0.60	0.80
TS	+0.33	+0.11	−0.54	+0.16	0.22	0.11	0.35	0.79
CpRh(CO)(H)(CH_3)	+0.33	+0.02	−0.49	+0.14	0.44	0.26		0.78
CpRh(CO)(NH_3)	+0.50		−0.88	+0.33		0.01	0.68	0.68
TS	+0.36	+0.31	−0.91	+0.30	0.30	0.02	0.18	0.68
CpRh(CO)(H)(NH_2)	+0.46	+0.06	−0.81	+0.26	0.36	0.30		0.64
CpRh(CO)(H_2O)	+0.52		−0.71	+0.40		0.02	0.62	0.62
TS	+0.40	+0.34	−0.75	+0.35	0.20	0.01	0.25	0.56
CpRh(CO)(H)(OH)	+0.60	+0.06	−0.80	+0.30	0.36	0.26		0.55
CpRh(CO)(H)(SiH_3)	−0.02	+0.03	+0.73	−0.15	0.48	0.41		0.78

[a] Here H^1 and H are bridging and terminal H atoms, respectively, and X = C, N, O, and Si.

complex CpRh(CO)(H)(CH_3), where our result is shorter by 0.07 Å) but 0.10−0.12 Å shorter than the MP2 result reported by SH. The R(Rh−H) and R(Rh−CH_3) distances calculated in this paper are about 0.10−0.26 Å shorter than the DFT results, but about 0.10 Å longer than the SH results. Thus, differences in geometrical parameters of critical points of the PESs of reaction 1 CH_4 and H_2 calculated in this paper and reported by Ziegler et al.[21] with a DFT method and by Song and Hall [22] with a smaller basis set are significant.

C. Comparison of Rh−R Bond Strengths. Here we would like to compare the calculated Rh−R bond strengths using the technique used by Koga and Morokuma.[18] Formally, the energies of reaction 1, ΔE, with a negative value representing an exothermicity, can be represented using bond energies by

$$\Delta E = D_e(\text{H−R}) - D_e(\text{Rh−R}) - D_e(\text{Rh−H}) \quad (2)$$

$$\text{R} = \text{H}, \text{CH}_3, \text{SiH}_3, \text{NH}_2, \text{and OH}$$

where Rh stands for the CpRh(CO) fragment. At first we note that, as shown in Table 1, at the present level of theory, MP2/II//MP2/I, the H−R bond energy is estimated to be 99.0, 107.9, 108.7, 117.8, and 88.3 kcal/mol for the H−H, H−CH_3, H−NH_2, H−OH and H−SiH_3 bond, respectively, vs experimental values

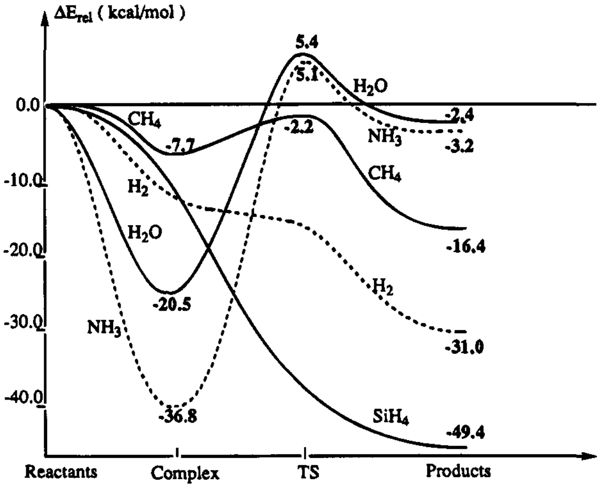

Figure 6. The potential energy profiles of the reaction of CpRh(CO) with H_2, CH_4, NH_3, H_2O, and SiH_4.

of 104.2, 104.8, 107.4, 119, and 90.3 kcal/mol, respectively.[30] So, the H−H, H−CH_3, H−NH_2 and H−OH bonds are calculated to be about 10.7, 19.6, 20.4, and 29.5 kcal/mol stronger than H−SiH_3 vs experimental values of 13.9, 14.5, 17.1, and 28.7 kcal/mol, respectively. Although the calculated absolute values of bond energies are up to 5 kcal/mol different from their experimental values, the trend, H−OH > H−NH_2 > H−CH_3 ≥ H−H > H−SiH_3, is well reproduced. Taking the difference of eq 2 between two reactions, one obtains

$$\Delta E^1 - \Delta E^2 = D_e(\mathrm{H{-}R^1}) - D_e(\mathrm{H{-}R^2}) - [D_e(\mathrm{Rh{-}R^1}) - D_e(\mathrm{Rh{-}R^2})] \quad (3)$$

where E^i is the energy of reaction 1 for the HR^i molecule. Thus, the calculated H−R bond energies and the calculated exothermicities of reaction 1 can be used to estimate the difference between Rh−R^1 and Rh−R^2 bond energies, D_e(Rh−R^1) − D_e(Rh−R^2). An advantage of this method is that the error due to approximations in calculational methods would be largely canceled in taking differences and we can avoid direct calculation of D_e(Rh−R), which is more difficult than calculating D_e(R−H).

For the reaction of H_2, the calculated H_2 bond energy and the calculated exothermicity in Table 1 give the Rh−H bond energy D_e(Rh−H) to be 65.0 kcal/mol. This value is in good agreement with the value of 65.1 kcal/mol obtained by Koga and Morokuma[18] for $RhCl(PH_3)_2(H)_2$ with a large basis set.

For the reaction of other substrates, the application of eq 3 gives the Rh−R bond energy relative to the Rh−H bond energy,

$$D_e(\mathrm{Rh{-}CH_3}) = D_e(\mathrm{Rh{-}H}) - 5.7\ \mathrm{kcal/mol}$$

$$D_e(\mathrm{Rh{-}NH_2}) = D_e(\mathrm{Rh{-}H}) - 18.1\ \mathrm{kcal/mol}$$

$$D_e(\mathrm{Rh{-}OH}) = D_e(\mathrm{Rh{-}H}) - 9.8\ \mathrm{kcal/mol}$$

$$D_e(\mathrm{Rh{-}SiH_3}) = D_e(\mathrm{Rh{-}H}) + 7.7\ \mathrm{kcal/mol}$$

Using the Rh−H bond energy obtained above, one obtains the following order of bond energies at the present MP2/II//MP2/I level of theory: Rh−Si (72.7) > Rh−H (65.0) > Rh−C (59.3) > Rh−O (55.2) > Rh−N (46.9). The Rh−Si bond is about 13 kcal/mol stronger than the Rh−C bond. Koga and Morokuma[18] have shown for $RhCl(PH_3)_2(H)(R)$ with a large basis set that Rh−Si, Rh−H, and Rh−C bond energies are 77.8, 65.1, and 54.6 kcal/mol, respectively, in good agreement with the present results. The reaction of SiH_4 is the most exothermic, because one breaks the weakest H−SiH_3 bond and forms the strongest Rh−SiH_3 bond. The reaction of H_2 is more exothermic than those of CH_4, NH_3, and H_2O because the H−H bond is weaker and the Rh−H bond is stronger. Since the present analysis has been carried out at the relatively low MP2 level with a modest basis set, the absolute value of the Rh−R bond energy may contain some error due to approximate treatment, basis functions, and BSSE.

D. Comparative Discussion of PESs of the Reaction 1 for H_2, CH_4, NH_3, OH_2, and SiH_3. Comparison of the potential energy profiles represented in Figure 6 shows that the barrier height of the H−R bond activation depends on several factors. Here we would like to analyze them carefully.

(i) **Barrier from the Reactants.** We would like to consider the barrier height with respect to the reactants, which is considered to be the threshold energy at gas-phase collisionless conditions. One of the obvious factors is the strength of the H−R bond to be broken. Another would be the strength of the Rh−R bond to be formed, where Rh stands for CpRh(CO). The other bond to be formed, the Rh−H bond, is common to all the substrates and need not be considered explicitly. The exothermicity of the reaction is also another factor one should consider, though the exothermicity is related, as discussed in the preceding section with eq 2, to a difference in bond energies to be formed and to be broken. At first we show the present calculated values (in kilocalories per mole) of them all, truncated at the decimal for a qualitative discussion.

	R =								
	SiH_3		H		CH_3		NH_2		OH
R−H bond energy	88	<	99	<	108	<	109	<	118
	(90)		(104)		(105)		(107)		(119)
Rh−R	73	>	65	>	59	>	47	<	55
exothermicity	49	>	31	>	16	>	3	>	2
activation barrier from reactants	N		N		−2	<	5	~	5

Here numbers in parentheses are experimental values and N indicates that the corresponding species does not exist. One can clearly see a trend going from R = SiH_3 through H and CH_3 to NH_2 and OH. The existence of the barrier and its height is related to both the bond energy of the R−H bond to be broken and the bond energy of the Rh−R bond to be formed. The stronger the bond one breaks and the weaker the bond one forms, the more likely one has a barrier. Among the present substrates the increase in the H−R bond energy is strongly correlated (except for a minor exception) with the decrease in the Rh−R bond energy. The Si−H bond is the weakest and the Rh−Si bond is the strongest, and N−H and O−H bonds are the strongest and Rh−N and Rh−O bonds are the weakest. The relative exothermicity, related to the Rh−R bond energy minus the R−H bond energy, therefore also has a strong correlation with the ease of reaction; the more exothermic the reaction is, the more likely it is to take place without a barrier. These results are consistent with the prediction that the activation barrier should be correlated to the exothermicity for oxidative addition.[18] They are also consistent with the prediction based on the nature of the M−R bond,[15,16] which states that for late transition metals the products should be bound less strongly for water and ammonia than for methane, due to a strong repulsion between lone-pair d-electrons of metal and lone pairs of ligands. One should note, however, this kind of agreement may not hold for early transition metals. Koga and Morokuma[18] have shown for $Cl_2Zr(R)(H)$ that the Zr−SiH_3 bond is weaker than the Zr−CH_3 bond by 14 kcal/mol, opposite to the present trend for Rh.

(ii) **Barrier from the Prereaction Complex.** Next we would like to consider the barrier height with respect to the prereaction molecular complexes, which should be considered to be the activation energy in solution or in the gas phase when collisional energy equilibrium is faster than the reaction itself. Additionally, an obvious factor to be considered is the complexation capability of the RH molecules, which strongly correlates with their Lewis basicity.

	R =				
	SiH_3	H	CH_3	NH_2	OH
complexation energy	N	N	8	37	21
activation barrier (from complex)	N	N	6	42	26

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[30] *CRC Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: Boca Raton−Ann Arbor−Boston, 1991−1992.

It is obvious that the activation barrier from the prereaction complex CpRh(CO)·(HR) is closely related to and essentially determined by the complexation energy; the stronger the complexation energy, the harder it is to get out of the well and the higher the barrier. These results suggest that in solution where the reaction should be considered to start from the prereaction complex, CpRh(CO)·(HR), it will be very difficult to activate R−H bonds of molecules that have a strong Lewis base character, such as NH_3 and H_2O.

In the reactions in solution with transition-metal complexes, O−H and N−H bonds are considered to be more difficult to activate than C−H bonds. This is frequently attributed to the higher bond energies of the former. However, the present study indicates that the difference is more importantly due to the requirement of desolvation energy for activation of strongly coordinated ligands such as O and N; the difference in the barrier is much more pronounced than the difference in the bond energies.

(iii) **General Discussion.** Comparison of the PESs of reaction 1 for H_2 and CH_4 molecules shows that, in spite of the similarity of the H−H and H−CH_3 bond strengths, the H−H bond of the hydrogen molecule is activated without a barrier, while the C−H bond of methane has a small (5.5 kcal/mol) activation barrier calculated relative to the prereaction molecular complex CpRh(CO)·(HR). This difference in the H−H and C−H activation can be explained, besides the above mentioned factors (the H−R bond strength and the exothermicity of the entire oxidative addition reaction), in terms of the directionality of the CH_3 orbital compared to the H orbital, as suggested by Siegbahn et al.,[13,14] as well as in terms of the stronger Rh−H bond compared to the Rh−CH_3 bond. Indeed, due to the spherical nature of the H orbital, the Rh−H bond can start to form at the same time as the H−H bond is weakened and therefore there is no barrier for the breaking of the H−H bond. In contrast, the directionality of the CH_3 unpaired orbital forces the C−H bond to be broken before the new Rh−CH_3 bond is formed, thus leading to a barrier for the reaction. The absolute value of the calculated barrier height for CH_4, 5.5 kcal/mol, may contain some error. The correction for BSSE will raise the energy of the complex (−7.7 kcal/mol) as well as the TS (−2.2 kcal/mol), and the barrier could be affected. The zero-point correction will lower the barrier. More accurate calculations would be required to predict if the CpRh(CO)·CH_4 complex should be detected experimentally.

However, we should note that in a real situation all these factors discussed above act simultaneously and it is not easy to identify the importance of specific factors for the general class of substrates. One would be able to make predictions only for the same class of molecules where one factor would be dominant. For example, since the experimental values[30] of the H−Ge and H−Sn bond strength, 83 ± 2 and 75.0 kcal/mol, in GeH_4 and SnH_4 molecules, respectively, are much weaker than that of H−SiH_3, 90.3 kcal/mol, in SiH_4, one may expect that the former bonds will be activated without barrier by CpRh(CO). Similarly, since the experimental value of the H−SH bond strength,[30] 91.1 ± 1 kcal/mol, in SH_2 is weaker than that of H−OH, 119 kcal/mol, in H_2O, one may expect that H−SH also will be activated easily by CpRh(CO).

IV. Conclusions

The following key conclusions may be drawn from the calculations presented here.

1. At gas-phase collisionless conditions the oxidative addition reaction of H−SiH_3, H−H, and H−CH_3 bonds to CpRh(CO) takes place without barrier, while that of H−NH_2 and H−OH bonds requires an activation energy of about 5 kcal/mol.
2. The Rh−H, Rh−CH_3, Rh−SiH_3, Rh−NH_2, and Rh−OH bond energies are calculated to be 65.0, 59.3, 72.7, 46.9, and 55.2 kcal/mol, respectively. Though some error may be involved in the absolute values, the relative values are expected to be more reliable.
3. The ease of oxidative addition reaction, i.e. existence of an activation barrier and its height, is correlated strongly to the R−H bond strength as well as to the Rh−R bond strength. Going from SiH_4 to H_2, CH_4, NH_3, and H_2O, the R−H bond energy increases and the Rh−R bond energy decreases (except for the Rh−O case), and the oxidative addition becomes more difficult. The exothermicity, related to the Rh−R bond energy minus the R−H bond energy, therefore correlates well with the ease of reaction; the more exothermic the reaction is, the more easily it takes place.
4. In solution or in the gas phase when collisional energy equilibrium is faster than the reaction itself and the reaction should be considered to start from the prereaction complex CpRh(CO)·(HR), the ease of oxidative addition reaction is essentially determined by the depth of the complexation complex. The reaction of H_2 and SiH_4 should take place without barrier, while that of NH_3 and H_2O requires a very high activation barrier, 42 and 26 kcal/mol, respectively. Thus, under these conditions, it will be very difficult to activate R−H bonds of molecules that have a strong Lewis base character. The only product experimentally detectable at not very rigorous conditions would be the molecular complex CpRh(CO)·(RH).

Not only have we given an explanation of the experimental results for the reaction of H_2 and CH_4, but we have also made predictions of the reactivity for SiH_4, NH_3, and H_2O. We encourage experimentalists to carry out experiments to examine our predictions.

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