Density Functional Study of the Mechanisms and the Potential Energy Surfaces of $MCH_2^+ + H_2$ Reactions. The Case of Cobalt and Rhodium (M = Co, Rh)

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Received: February 19, 1997; In Final Form: July 23, 1997[⊗]

The potential energy surfaces for the reactions $MCH_2^+ + H_2 \rightarrow M^+ + CH_4$ (M = Co, Rh) have been studied by means of a density functional approach in which we considered both the singlet and triplet state channels. The H−H bond cleavage in the singlet state follows a stepwise H_2 splitting corresponding to an oxidative hydrogen addition mechanism; while for the triplet state only a concerted mechanism with the formation of a four-center transition state structure is possible. For the reaction involving Co^+ cation, the triplet channel is energetically favored at the beginning and at the end of the reaction, although the barrier height for the H_2 activation is much lower in the excited singlet path. However, the energetic penalty required to obtain the singlet excited state is prohibitive and precludes this pathway as a channel for this reaction. Thus, we conclude that this reaction ($M = Co^+$) follows a four-center mechanism in the triplet state. On the basis of our results we conclude that the $RhCH_2^+ + H_2 \rightarrow Rh^+ + CH_4$ reaction should be a spin-forbidden process. The reaction starts in the singlet ground state and follows through an oxidative addition mechanism of H_2 to the Rh^+ moiety of the $RhCH_2^+$ compound. Further shift of the hydrogen atom toward the carbon leads to formation of the hydrido−methyl complex ($HRhCH_3^+$). Changing of the singlet spin state probably occurs immediately after formation of the $HRhCH_3^+$ intermediate. This intermediate in the triplet state is metastable and collapses to the final complex without any barrier. Our results for both considered reactions are in good agreement with available experimental data.

Introduction

Understanding the mechanisms of reactions taking place at transition metal sites is of fundamental and practical importance in inorganic[1−7] and bioinorganic chemistry.[8,9] The complexity of these processes necessitates the use of a wide variety of experimental and theoretical approaches to characterize geometries, transition states, energy surfaces, and reaction mechanisms of transition metal mediated catalysis. The reaction of carbine complexes MCH_2^+ with hydrogen and small alkanes is one example of recent experimental and theoretical efforts to obtain insight into the mode of action of transition metals as catalysts. Because of their significance as possible intermediates and reactive species in many important homogeneous and heterogeneous catalytic reactions, the cations formed by transition metal atoms and methylene-like ligands are subjects of increasing experimental study.[10−26] In addition, the relatively small size compounds that are involved in the reaction make them attractive targets for rigorous theoretical calculations.[27−35] The abundance of data from both experimental and theoretical efforts provides insight into reaction mechanisms and, furthermore, allows an estimation of the accuracy of different theoretical schemes by comparing the results of calculations with available experimental data.

In this paper we report a density functional study of the mechanisms and the potential energy surfaces for the reaction

$$MCH_2^+ + H_2 \rightarrow M^+ + CH_4 \qquad (1)$$

in which M^+ is cobalt or rhodium. As we discuss below, despite several experimental and theoretical efforts,[11,15,16,26,31] the catalytic mode of action of MCH_2^+ (M = Co, Rh) with hydrogen has not been unambiguously established.

In addition, the distinguishably different catalytic activity of $CoCH_2^+$ (the reaction needs ~8 kcal/mol of activation energy[25]) and $RhCH_2^+$ (reaction occurs spontaneously[26]) prompted us to perform comparative analysis of these reactions with the aim to find out the reason(s) for such different catalytic behavior. The first possible explanation is that the different nature of metal ions changes the reaction profiles in the framework of the same catalytic mechanism. The second possible explanation may be that the different nature of metal ions also results in a different catalytic mechanism. To answer these questions, and keeping in mind that previous works[29,31] indicated different spin states for $CoCH_2^+$ (triplet) and $RhCH_2^+$ (singlet), we decided to investigate possible reaction mechanisms for reaction 1 for both singlet and triplet states.

Two different mechanisms have been considered (Scheme 1). In the case of the first mechanism, the splitting of the hydrogen molecule proceeds through a four-center transition state, **TS_{fc}**, that directly leads to the intermediate $HMCH_3^+$ (Scheme 1a). Alternatively, the same intermediate can be obtained after an oxidative H_2 addition to the M^+ moiety followed by the shift of the hydrogen atom from the metal to the ligand (Scheme 1b). For both mechanisms the second stage of reaction 1 is identical and assumes that the intermediate $HMCH_3^+$ collapses to the M^+CH_4 final complex through a H migration from the metal atom to the carbon.

The Case of Cobalt. The gas-phase reaction between $CoCH_2^+$ and H_2 has been investigated experimentally by using Fourier transform mass and guided beam techniques.[10,15,25] On

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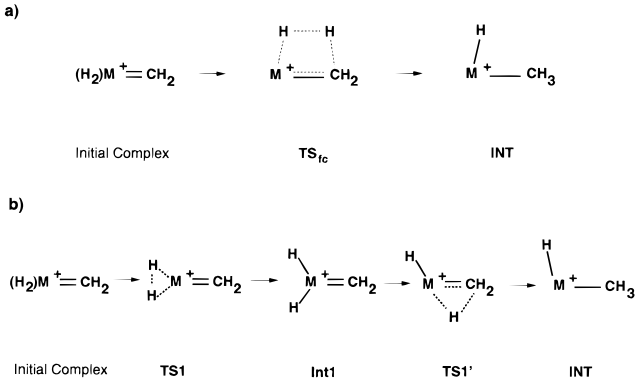
[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S1089-5639(97)00611-7 CCC: $14.00

SCHEME 1



the basis of these studies, $CoCH_2^+$ was found to exhibit small reactivity with H_2. It was also found that the formation of the cobalt cation and methane from $CoCH_2^+$ and dihydrogen is an exothermic process (25.0 ± 7 kcal/mol[15]). Experimental evidence has determined the presence of the $CoCH_2^+$ complex, but the presence of the $HCoCH_3^+$ has not been determined. This has led to the proposal that $HCoCH_3^+$ does not exist as a stable compound.[15,18] Recently, the reaction between $CoCH_2^+$ and H_2 was reinvestigated by Armentrout and co-workers[25] in order to experimentally characterize the reaction's potential energy surface and quantitatively measure the reaction barrier.

The $CoCH_2^+ + H_2$ reaction has also been studied theoretically by applying both the CASSCF and MR-SDCI-CASSCF levels of theory.[29] Musaev et al. investigated the potential energy surface for the case of the triplet state and concluded that the reaction proceeds via a four-center transition state. The conclusions of this study are qualitatively consistent with available experimental results; however, the theoretically predicted value of the four-center transition state barrier is three times larger than the experimental value (8.1 ± 1.9 kcal/mol).[25]

The Case of Rhodium. A four-center transition state mechanism of H_2 splitting on $RhCH_2^+$ was proposed by Jacobson and Freiser.[15] This mechanism is considered by many experimentalists as the most favorable one in such kinds of processes, and it is believed to be consistent with the observation that the reaction proceeds downhill without an activation barrier.[15,26] However, the results of recent theoretical calculations of Musaev et al.,[31] within the framework of a four-center transition state mechanism, predict that an essential activation barrier of approximately 16 kcal/mol must be overcome in order to initiate the hydration of the carbine complex $RhCH_2^+$. One possible explanation for this apparent inconsistency is that the ab initio method used by Musaev et al. was not accurate enough to describe the reaction barrier. A second possible explanation is that there exists an alternative reaction pathway that was not considered in the previous theoretical studies. We will show that an alternative mechanism does exist and is a dihydride reaction path (Scheme 1b), corresponding to oxidative addition of H_2 to the Rh^+ moiety of $RhCH_2^+$ followed by formation of the intermediate $H_2RhCH_2^+$ (**Int1**).

To our knowledge, this reaction mechanism has not been given much attention. Jacobson and Freiser[15] considered this pathway to be unlikely, and Musaev et al.,[31] following the same logic, elected not to investigate this pathway in their theoretical study. Jacobson and Freiser arguments against this mechanism were based on the different dissociation energy values of the H−H bond dissociation, D°(H−H) = 104 kcal/mol, and Rh−H bond formation, $D°(Rh^+{-}H) = 42$ kcal/mol. The bond dissociation energy $D°(Rh^+{-}H)$ was obtained as a result of the experimental study of the reaction:[12]

$$Rh^+ + D_2 \rightarrow RhD^+ + D \qquad (2)$$

Using these data in a formal way, one must conclude that oxidative addition of H_2 to the Rh^+ cation yields formation of **Int1** as endothermic by approximately 20 kcal/mol. This would require an activation energy that is more than 20 kcal/mol. Since a high barrier is contrary to experimental observation, they concluded that the reaction cannot follow this path. Such a conclusion might be possible if some evidence were available that Rh^+ as a separate cation or as a moiety of the $RhCH_2^+$ compound had approximately the same chemical activity. In general, this is not the case, and two different catalytic sites involving the same transition metal can be chemically quite different. For example, Irikura and Beauchmap[21] showed that the number of oxo ligands of osmium (OsO_n^+) has a striking effect on the chemistry. In particular, Os^+ is unreactive with H_2, but OsO_4^+ can split a hydrogen molecule with relative ease. On the basis of the above example, one can conclude that the environment of the cation can significantly influence its chemical properties or catalytic activity, and thus thermodynamic data for the separated cation might not be appropriate to describe chemical characteristics in the case of the complex. Therefore, we argue that one cannot a priori exclude the dihydride path in the case of the $RhCH_2^+$ compound and that a theoretical study should include the investigation of both possible mechanisms for reaction 1.

The large discrepancies between the previous high-level ab initio theoretical results and experiment prompted us to investigate the $MCH_2^+ + H_2$ reaction (where M = Co and Rh) by means of density functional theory (DFT) as an alternative theoretical approach for investigations of the reaction of carbine complexes MCH_2^+ with hydrogen and small alkanes.[35] DFT is well-known for its ability to accurately describe systems involving heavy transition metals.[9,36]

Thus, the purpose of our study is to perform comparative analysis of the four-center transition mechanism and the oxidative addition mechanism for reaction 1 (M = Co,Rh) for both singlet and triplet spin states using DFT and to see if our investigations can resolve discrepancies between the theoretical and experimental results.

Method

The Dgauss package[37,38] has been employed in all the calculations. The nonlocal corrections using the Becke exchange[39] and Perdew correlation[40] potentials (NLSD approximation) have been obtained starting from the Vosko, Wilk, and Nuisar local potential.[41] The calculations were performed using the DZVP basis set, which is (621/41/1) for carbon, (41) for hydrogen, (63321/531/41) for cobalt, and (633321/53211/531) for rhodium atoms.[42] The convergence of geometry optimization was less than 0.005 hartree/bohr for the largest Cartesian energy gradient component. The matrix of second derivatives was evaluated by a finite difference scheme using analytical first derivatives. A step size of 0.03 bohr was used in the numerical scheme.

In some cases localization of the saddle points was done with the Abashkin and Russo algorithm[43] incorporated into the deMon program.[44] As we have shown in previous work[43,45] this new transition state searching algorithm provides us the opportunity for efficient investigation of various possible mechanisms of reactions. Using initial guesses found by this algorithm, refinement of the saddle point geometries was realized by applying the TS searching procedure[46] incorporated in the Dgauss code.

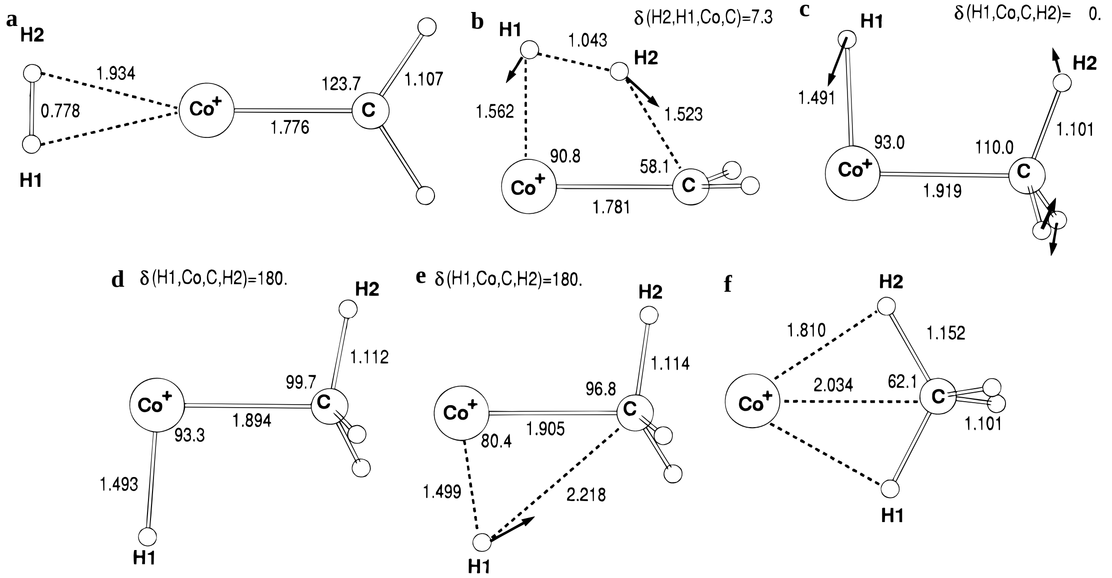


Figure 1. Geometrical parameters for structures corresponding to critical points along the reaction path of the $CoCH_2^+ + H_2 \rightarrow Co^+ + CH_4$ reaction for *the triplet state*. Bond lengths are in angstroms, and bond angles are in degrees. Arrows represent the Hessian matrix eigenvector components with a negative eigenvalue at transition state geometries. (a) Initial complex − $(H_2)CoCH_2^+$, (b) TS_{fc} ($\nu_i = 1105$ cm^{-1}), (c) TS_{rot} ($\nu_i = 372$ cm^{-1}), (d) intermediate(**INT**), $HCoCH_3^+$, (e) TS2 ($\nu_i = 387$ cm^{-1}), (f) final complex, Co^+CH_4.

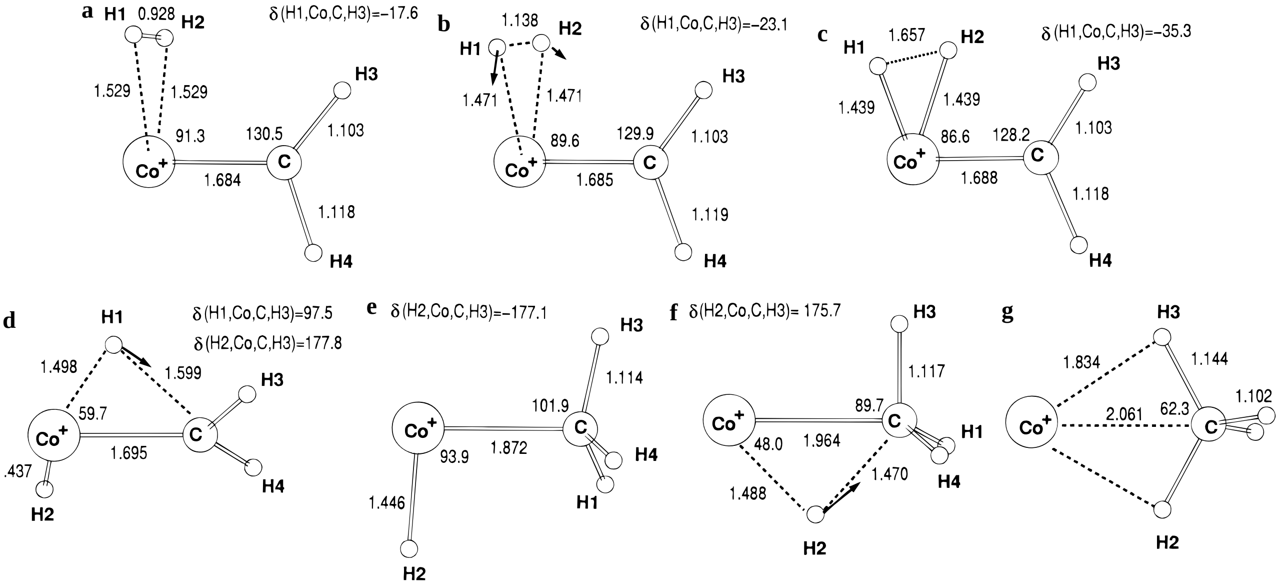


Figure 2. Geometrical parameters for structures corresponding to critical points along the reaction path of the $CoCH_2^+ + H_2 \rightarrow Co^+ + CH_4$ reaction for *the singlet state*. Bond lengths are in angstroms and bond angles are in degrees. Arrows represent the Hessian matrix eigenvector components with a negative eigenvalue at transition state geometries. (a) initial complex, $(H_2)CoCH_2^+$, (b) TS1 ($\nu_i = 728$ cm^{-1}), (c) intermidiate (**Int1**), $H_2CoCH_2^+$, (d) TS1′ ($\nu_i = 662$ cm^{-1}), (e) intermediate (**INT1**), $HCoCH_3^+$, (f) TS2 (ν_i =780 cm^{-1}), (g) final complex, Co^+CH_4.

The bonding patterns during the course of the reaction (1) were characterized using the formulation of bond order analysis suggested by Mayer.[47] This method is especially useful for DFT calculations since it links the details of the density matrixes with qualitative chemical concepts such as valence indices of atoms and bond orders.

Results and Discussion

We have considered both mechanisms (Scheme 1) for the singlet and the triplet states for both cobalt and rhodium catalytic cations (M = Co, Rh). The four-center TS path has been found only for the triplet state, while the oxidative addition path was found to be possible only for the singlet state. The structures of the minima and transition states are reported in Figures 1, 2 and 4, 5 for the triplet and singlet states of Co compounds and for the singlet and triplet states of Rh compounds, respectively. The internal energy profiles of the Co reaction are shown in Figure 3. Figure 6 presents the internal energy profiles for reaction 1 involving Rh cation. Mayer bond orders for critical points along the reaction are presented in Tables 1 and 2 for the triplet and singlet states for the cobalt reaction and in Tables 4 and 5 for the singlet and triplet states for the rhodium reaction, respectively.

Before comparing the results of the two reactions (eq 1) (M = Co,Rh) and drawing general conclusions, we present an analysis of our results for the case of cobalt and rhodium separately.

The Case of Co. As evident from the presented data (Figures 1, 2, and 3), the features of the potential energy surface and geometrical parameters of the stationary points of the triplet reaction path are quite different from the corresponding points of the singlet. First of all, for the $CoCH_2^+$ compound, the most

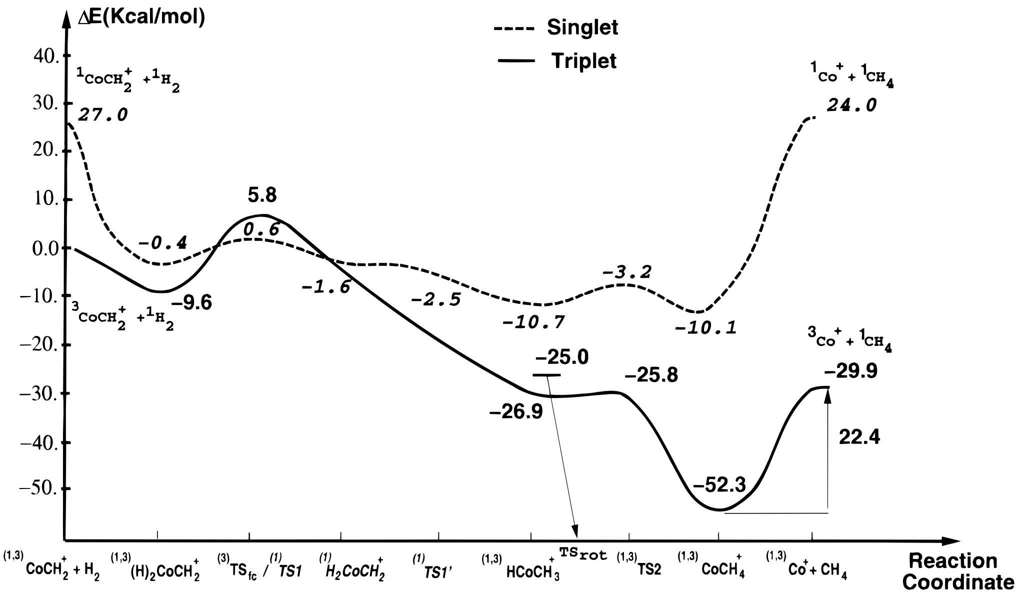


Figure 3. Energetic profiles of the $CoCH_2^+ + H_2 \rightarrow Co^+ + CH_4$ reaction for the singlet and triplet states.

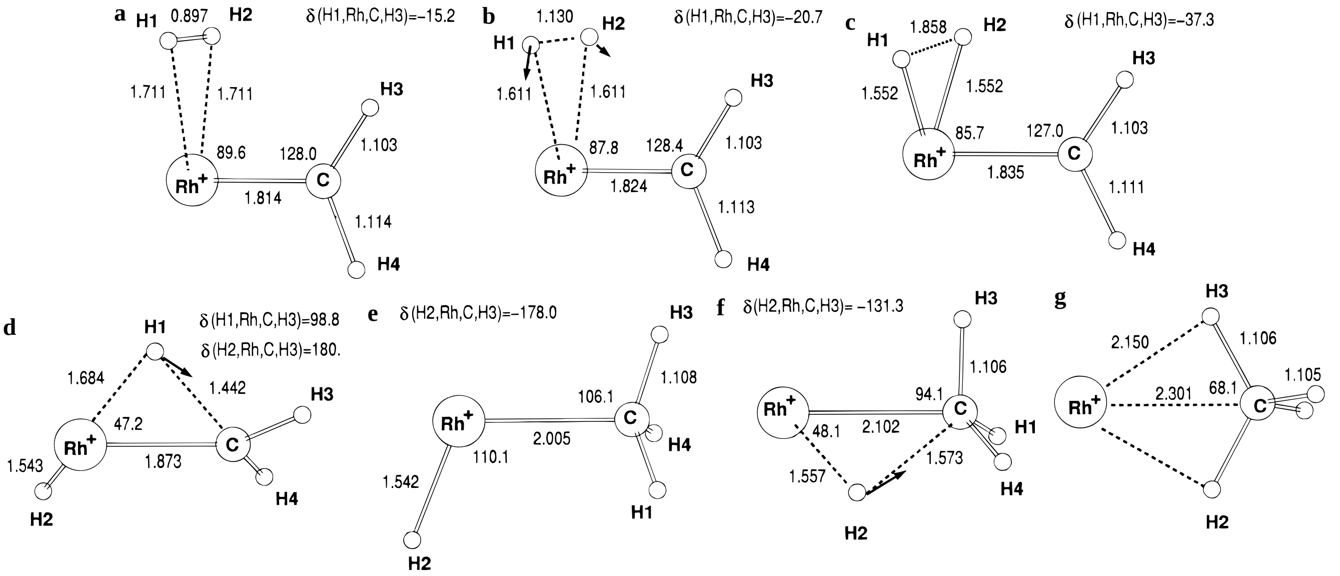


Figure 4. Geometrical parameters for structures corresponding to critical points along the reaction path of the $RhCH_2^+ + H_2 \rightarrow Rh^+ + CH_4$ reaction for *the singlet state*. Bond lengths are in angstroms, and bond angles are in degrees. Arrows represent the Hessian matrix eigenvector components with a negative eigenvalue at transition state geometries. (a) Initial complex, $(H_2)RhCH_2^+$, (b) TS1 ($\nu_i = 782$ cm^{-1}), (c) intermediate (**Int1**), $H_2RhCH_2^+$, (d) TS1′ ($\nu_i = 764$ cm^{-1}), (e) intermediate (INT), $HRhCH_3^+$, (f) TS2 ($\nu_i = 727$ cm^{-1}), (g) final complex, Rh^+CH_4.

stable conformation appears to be that of the cobalt cation linked to the carbon atom of CH_2 with a double bond (Tables 1 and 2). The ground state is the triplet ($E_{tot} = -1421.6892$ au; H_2 total energy $-$ $E_{tot} = -1.176\,89$), and the singlet ($E_{tot} = -1421.7324$ au) lies higher in energy by 27 kcal/mol. Such a large energetic gap between the singlet and triplet states led Musaev et al.[29] to conclude that it is unlikely that the singlet channel of the reaction plays any significant practical role. As a result of that speculation the authors did not consider this pathway. We should note, however, that in our calculations the energy difference between the singlet and triplet states for the $(H_2)CoCH_2^+$ complex decreases dramatically with respect to the separated reactants and appears to be 9.2 kcal/mol. In contrast to the conclusion made by Musaev et al.[29] that was based on energy differences between the singlet and triplet states for separated reactants, our result cannot a priori exclude the practical importance of the singlet reaction pathway.

For the $(H_2)CoCH_2^+$ complex, different geometries have been considered. The most stable conformation of the complex appears to be a planar one (C_{2v}) for the triplet state, while in the singlet state the H_2 group is out of the $CoCH_2^+$ plane (Figures 1 and 2). In addition, some differences can be noted especially for the Co−H and Co−C bond lengths. The Co−C bond is stronger in the case of the singlet (bond order, 1.95) than for the triplet state (bond order, 1.68). In the initial complexes the H_2 molecule is coordinated more strongly to the Co^+ moiety in the singlet state (effective bond order of 0.63) than the triplet state (0.26). This relatively small interaction in the triplet state between the metal cation and the hydrogen molecule does not practically affect the H−H distance (0.778 Å) compared to the H−H distance in isolated H_2. For the singlet electronic configuration (Table 2), the qualitative picture for H_2 binding to $CoCH_2^+$ is different. In the singlet state the Co−H interaction corresponds to a bond order value of 0.63, which is comparable to a strong covalent C−H bond (0.84). Such strong interaction between hydrogen atoms and the metal leads to weakening of the H−H bond and a large increase in

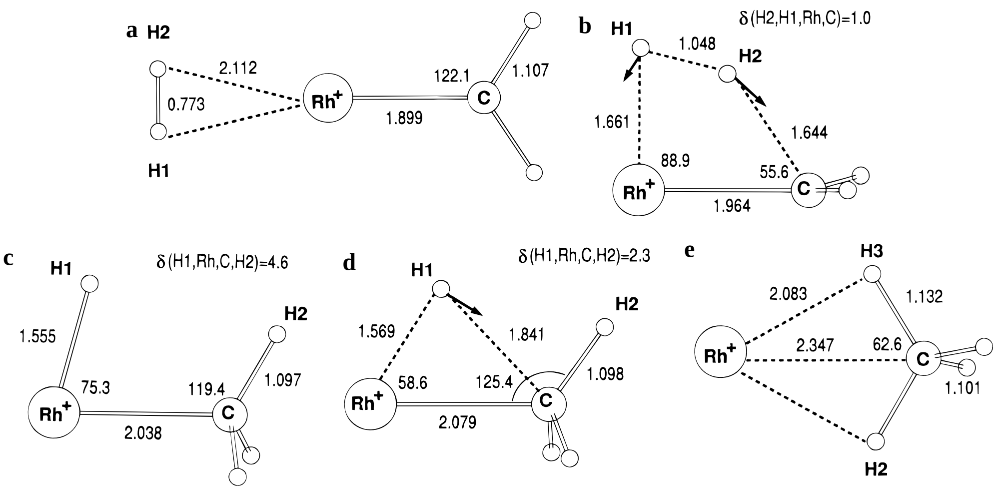


Figure 5. Geometrical parameters for structures corresponding to critical points along the reaction path of the $RhCH_2^+ + H_2 \rightarrow Rh^+ + CH_4$ reaction for *the triplet state*. Bond lengths are in angstroms, and bond angles are in degrees. Arrows represent the Hessian matrix eigenvector components with a negative eigenvalue at transition state geometries. (a) Initial complex, $(H_2)RhCH_2^+$, (b) TS_{fc} ($\nu_i = 1045$ cm^{-1}), (c) intermediate (**INT**), $HRhCH_3^+$, (d) TS2 ($\nu_i = 504$ cm^{-1}), (e) final complex, Rh^+CH_4.

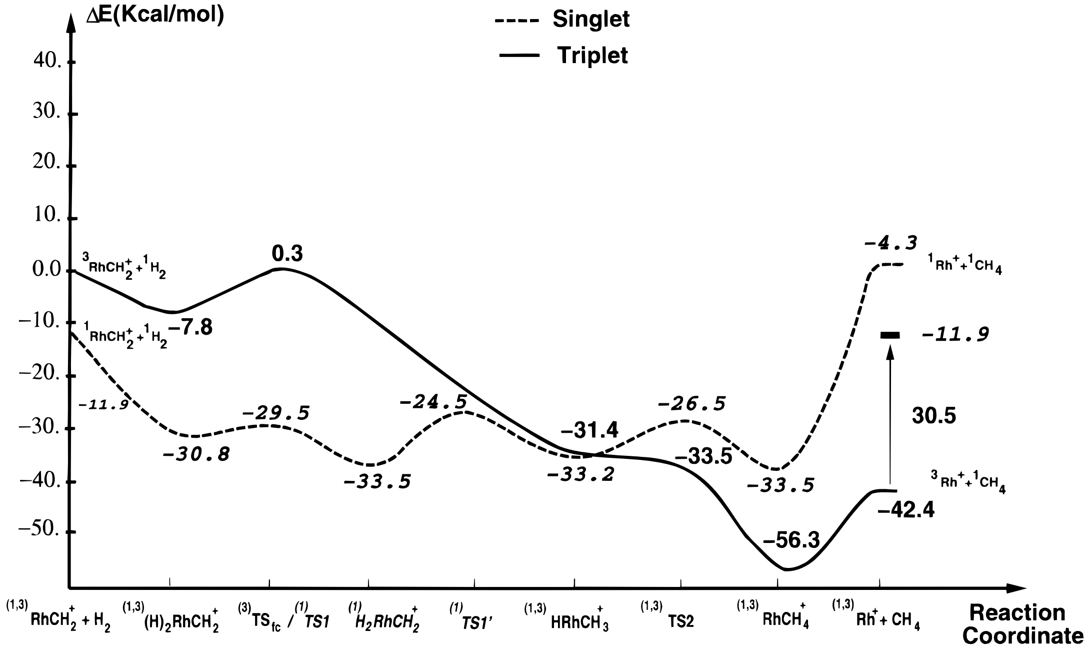


Figure 6. Energetic profiles of the $RhCH_2^+ + H_2 \rightarrow Rh^+ + CH_4$ reaction for the singlet and triplet states.

TABLE 1: Mayer Bond Order Analysis for Structures Corresponding to Critical Points along the Reaction Path of $CoCH_2^+ + H_2 \rightarrow Co^+ + CH_4$ Reaction for the Triplet State[a]

structures	Co−C	Co−H1	Co−H2	C−H1	C−H2	C−H3/H4
$CoCH_2^+$	1.72					0.84
initial complex	1.68	0.26	0.26			0.85
TS_{fc}	1.50	0.71	0.46		0.22	0.82
INT	1.21	0.92			0.82	0.82
TS_{rot}	1.07	0.93			0.83	0.83
TS2	1.18	0.89			0.82	0.83
final complex	0.63	0.24	0.24	0.67	0.67	0.85

[a] The values are presented only for bonds that have a bond order of 0.1 or more.

the H−H distance 0.928 Å. This results in a predisposition of the H_2 molecule to dissociate easily in the singlet complex.

As we previously pointed out, despite extensive searching of the potential energy surface only one mechanism of H−H bond activation was found for each spin state. Namely, in the triplet state the reaction proceeds through a four-center transition state path (**TS_{fc}** in Figure 1), while only oxidative addition of H_2 (**TS1**, **Int1**, and **TS1'** in Figure 2) is possible for the singlet state. The **TS_{fc}** structure shows a H−H bond (1.043 Å) that is in the "breaking phase" and Co−H and C−H distances that are similar (1.562 versus 1.523 Å). The two hydrogens atoms of the H_2 molecule along with the Co and C atoms create an approximately planar structure. Significant changes in the bonding pattern are needed to obtain the configuration of the **TS_{fc}** transition state with respect to the initial complex (Table 1). The activation energy associated with this change is quite high, 15.4 kcal/mol. On the contrary, oxidative addition of H_2 to Co^+ requires only 1 kcal/mol of activation energy, and the corresponding **TS1** transition state structure is geometrically close to the initial complex. We should stress that the absolute energy barrier for the triplet (**TS_{fc}**) is higher than the singlet H_2 oxidative **TS1** by 5.2 kcal/mol (Figure 3).

Following the triplet path we found the $HCoCH_3^+$ intermediate at 26.9 kcal/mol below the reactants. The intermediate corresponds to a trans position of the hydrogen atoms bound to the Co and C atoms (Figure 1). Our numerous attempts to find

TABLE 2: Mayer Bond Order Analysis for Structures Corresponding to Critical Points along the Reaction Path of $CoCH_2^+ + H_2 \rightarrow Co^+ + CH_4$ Reaction for the Singlet State[a]

structures	Co−C	Co−H1	Co−H2	Co−H3	C−H1	C−H2	C−H3	C−H4
$CoCH_2^+$	2.00						0.82	0.82
initial complex	1.95	0.63	0.63				0.84	0.80
TS1	1.91	0.76	0.76				0.84	0.80
Int1	1.83	0.87	0.87				0.84	0.80
TS1′	1.66	0.70	0.91		0.19		0.83	0.80
INT	1.20		0.93		0.85		0.85	0.83
TS2	0.90		0.67		0.85	0.23	0.85	0.81
final complex	0.60		0.23	0.23	0.85	0.67	0.67	0.85

[a] The values are presented only for bonds that have a bond order 0.1 or more.

TABLE 3: Relative Energies (kcal/mol) from DFT, ab Initio, and Experimental Studies of Stationary Points on the Potential Energy Surface of the $CoCH_2^+ + H_2 \rightarrow Co^+ + CH_4$ Reaction for the Triplet State

species	DFT (this work) NLSD	ab initio MR-SDCI CASSCF-(8/8)SKBJ[a] 3A″/3A′ States	experiment
$CoCH_2^+ + H_2$	0.0	0.0 /0.0	
$(H_2)CoCH_2^+$	−9.6	−8.4/−8.6	
TS_{fc}	5.8	25.9/22.1	8.1 ± 1.9 [b]
$HCoCH_3^+$	−26.9	−23.4/−22.4	
TS_{rot}	−25.0		
TS2	−25.8	−20.8/−24.6	
Co^+CH_4	−52.3	−45.6/−49.0	
$Co^+ + CH_4$	−29.9	−23.9/−27.7	−25.0 ± 7.0[c] −34.6 ± 1.4[b]

[a] The highest level of the calculations in ref 29. [b] Reference 25. [c] Reference 15.

an equilibrium conformation of $HCoCH_3^+$ with the hydrogen atoms in the cis position failed. In fact, all trial cis configurations rapidly collapsed to the final complex Co^+CH_4. This forced us to conclude that the **TS_{fc}** can directly lead to the final complex. However, in the cis conformation there exists a saddle point with one imaginary frequency that corresponds to a rotational TS leading to the highly metastable intermediate $HCoCH_3^+$ in the trans conformation (Figure 1). We will discuss a transformation of this species later.

TS1 of the singlet reaction path first leads to the $H_2CoCH_2^+$ intermediate, **Int1** (Figure 2), that rearranges, without an energy barrier, through a H shift from Co to C (**TS1′**). This results in the hydrido-methyl intermediate **INT,** which is, however, characterized with different energetic parameters with respect to a similar triplet analogue. The singlet intermediate $HCoCH_3^+$ lies at 10.7 kcal/mol below the reactants and 16 kcal/mol above the corresponding triplet state structure.

A further H shift is necessary to give the final Co^+CH_4 complex. In the case of the triplet state, the $HCoCH_3^+$ intermediate collapses to the final complex, practically, without a barrier (1 kcal/mol). The corresponding transition state structure (**TS2** Figure 1) has an imaginary frequency of 387 cm^{-1} and lies at 25.8 kcal/mol below the reactants. The Co^+-CH_4 complex is the absolute minimum and lies at −52.3 kcal/mol with respect to the reactant energy. The dissociation into Co^+ and CH_4 requires 22.4 kcal/mol.

Following the singlet reaction path, we found that the barrier (**TS2**, Figure 2) for the migration of H resulting in the formation of the final complex is 7.5 kcal/mol, and the Co^+CH_4 minimum is practically isoenergetic with intermediate $HCoCH_3^+$. A large amount of energy (34.1 kcal/mol) is required to obtain the singlet state reaction products. Thus, for the singlet state the reaction is practically thermoneutral, while the exothermicity of the triplet state path reaction was found to be 29.9 kcal/mol.

It is important to stress that the triplet and singlet reaction paths are very different in prediction of the characteristics of the $HCoCH_3^+$ intermediate. In the triplet path the **INT** easily collapses in the Co^+CH_4 minima, and its existence is not "real". In the case of the singlet, the existence of the hydrido−methyl complex can be postulated. It is also important to point out that despite the fact that the singlet state is an excited state, some activation barriers are lower in the singlet mechanism than the corresponding ones in the triplet mechanism. The energy required to generate the singlet $CoCH_2^+$ system is 27 kcal/mol. However, the activation barrier for H_2 activation with respect to the initial complex is only 1 kcal/mol, whereas H_2 activation in the triplet mechanism is 15 kcal/mol.

Table 3 summarizes our DFT results and available theoretical and experimental data for energetic parameters for critical points of the reaction in the case of the triplet state. Comparing our data with the results of Musaev et al.[29] obtained from an ab initio correlated method, we, first of all, mention that they qualitatively give the same reaction profile. Quantitative agreement is also observed for the energetic characteristics of the local minimum structures and for the estimation of the stability of an intermediate complex $HCoCH_3^+$.

The ground state of $CoCH_2^+$ is the triplet, and the singlet lies higher in energy by 27 kcal/mol, in agreement with previous calculations (27.6 kcal/mol).[29] This observation is consistent with the conclusion[48] on the reliability of DFT in predicting the singlet−triplet energy gap. The $(H_2)CoCH_2^+$ complex in the triplet state configuration has a structure comparable with that found at the CASCFF level[29] as well. The stabilization energy of the initial complex with respect to reactants is quite similar by both DFT (−9.6 kcal/mol) and ab initio (−8.4/8.6 kcal/mol) levels. We found that dissociation into Co^+ and CH_4 requires 22.4 kcal/mol. This value is in excellent agreement with the experimental values of 22.9 ± 0.7 kcal/mol[23] and 21.4 ± 1.2 kcal/mol.[24] Our value of the dissociation energy also agrees well with that suggested on the basis of the highest level of theory employed in the work of Musaev et al.[29] (21.7/21.3 kcal/mol) and theoretical results of Perry et al. (21.4 kcal/mol).[33] The exothermicity of the reaction is found to be 29.9 kcal/mol by our calculations versus 25.0 ± 7 kcal/mol[15] and 34.6 ± 1.4 kcal/mol[25] determined by experiment and 23.9 and 27.7 kcal/mol obtained for the $^3A'$ and $^3A''$ states, respectively, at the MR-SDCI-CASSCF(8/8)IIf(HW) level of theory.[29]

Among differences between the results of DFT and ab initio studies of the investigated reaction, the following should be mentioned. We predict the geometrical configuration of the $HCoCH_3^+$ intermediate as a trans conformation in contrast to the cis conformation obtained in ref 29. In fact, in our case the cis conformation corresponds to a rotational TS structure. Our planar **TS2** structure does not coincide with the C_1 symmetry geometry of the transition state conformation from the ab initio calculations.

The principal difference between our results and the results of Musaev et al. concerns the value of the four-center transition state (**TS_{fc}**) that essentially determines the overall rate of reaction

TABLE 4: Mayer Bond Order Analysis for Structures Corresponding to Critical Points along the Reaction Path of $RhCH_2^+ + H_2 \rightarrow Rh^+ + CH_4$ Reaction for the Singlet State[a]

structures	Rh−C	Rh−H1	Rh−H2	Rh−H3	C−H1	C−H2	C−H3	C−H4
initial complex	1.78	0.41	0.41				0.85	0.85
TS1	1.72	0.53	0.53				0.85	0.85
Int1	1.63	0.84	0.84				0.85	0.85
TS1′	1.32	0.50	0.88		0.43		0.83	0.83
INT	1.07		0.94		0.86		0.86	0.86
TS2	0.81		0.69		0.85	0.27	0.85	0.85
final complex	0.49		0.15	0.15	0.84	0.75	0.75	0.84

[a] The values are presented only for bonds that have a bond order of 0.1 or more.

TABLE 5: Mayer Bond Order Analysis for Structures Corresponding to Critical Points along the Reaction Path of $RhCH_2^+ + H_2 \rightarrow Rh^+ + CH_4$ Reaction for the Triplet State[a]

structures	Rh−C	Rh−H1	Rh−H2	C−H1	C−H2	C−H3/H4
initial complex	1.51	0.24	0.24			0.86
TS$_{\mathrm{fc}}$	1.16	0.62	0.37		0.25	0.83
INT	1.05	0.85		0.13	0.86	0.83
TS$_{\mathrm{rot}}$	1.10	0.88			0.86	0.83
TS2	0.91	0.73		0.24	0.86	0.83
final complex	0.43	0.15	0.15	0.76	0.76	0.85

[a] The values are presented only for bonds that have a bond order of 0.1 or more.

1. They predicted that the value is more than 20 kcal/mol with respect to reactants at all levels of theory used in their work. Such a high activation barrier assumes that the reaction does occur at elevated energies. This strongly contradicts our results that show the process of H−H bond activation can be performed relatively easily and needs 5.8 kcal/mol with respect to reactants and 15.4 kcal/mol (more than 30 kcal/mol in the ab initio calculations) with respect to the initial complex. The recent experimental data[25] on the activation barrier that appeared at the same time we finished our calculation suggests that the TS estimation is 8.1 ± 1.9 kcal/mol. Thus, the density functional level of theory employed in our computations only slightly underestimates the energy barrier. Possible sources of discrepancies between the DFT and the ab initio results can be ascribed to the different treatment of the cobalt atom (all electron versus model core potential) and to the different type and amount of correlation energy taken into account.

The Case of Rh. We first consider the reaction profile corresponding to the singlet state potential energy surface. In agreement with previous theoretical calculations,[31,49] we found that the ground state of $RhCH_2^+$ is the singlet ($E_{\mathrm{tot}} = -4727.0815$ au for the singlet state; $E_{\mathrm{tot}} = -4727.0625$ au for the triplet state, and H_2 total energy $-E_{\mathrm{tot}} = -1.17689$). This implies that the ground state of the isolated reactants, $RhCH_2^+ + H_2$, is also the singlet. Following the reaction path we found that the most stable conformation of the $(H_2)RhCH_2^+$ complex appears to be nonplanar (Figure 4), and the energy of the complex lies 18.9 kcal/mol lower than the energy of the isolated reactants (Figure 6). Significant energetic stabilization of the complex with respect to the reactants indicates a strong interaction between the H_2 and $RhCH_2$ compounds. The bond analysis (Table 4) confirms this conclusion. The Rh−H interaction corresponds to a bond order value of 0.41, which equals half of the value for a strong covalent C−H bond (0.84). Such a strong interaction between hydrogen atoms and the metal leads to weakening of the H−H bond and a large increase in the H−H distance (0.897 Å) with respect to the undisturbed hydrogen molecule (0.772 Å). This results in a predisposition of the H_2 molecule to dissociate easily in the singlet complex.

Starting from the $(H_2)RhCH_2^+$ complex, only 1.3 kcal/mol (**TS1**) is needed to split the H_2 molecule. This oxidative addition of the hydrogen molecule results in the formation of the $H_2RhCH_2^+$ intermediate (**Int1**). The intermediate further rearranges through a H shift from Rh to C (**TS1′**). This leads to a hydrido−methyl intermediate $HRhCH_3^+$ (**INT**). **TS1** and **TS1′** energy values lie below the energy of the reactants (Figure 4). Thus, in the framework of the oxidative addition mechanism, no activation energy is needed to obtain the hydrido−methyl intermediate in the case of the singlet state.

As we previously pointed out, activation of the H−H bond, resulting in an intermediate $HRhCH_3^+$, can be accomplished by an alternative path—a four-center transition state mechanism. We performed intensive searching of the singlet state potential energy surface in order to locate the four-center transition state, **TS$_{\mathrm{fc}}$**. However, only the second-order saddle point was found. The existence of the second imaginary frequency indicates that the true TS structure must exist and lies below the second-order saddle point. Optimization of the second-order saddle point toward this TS structure results in **TS1** for the stepwise mechanism described above. Thus, we conclude that in the case of the singlet state the only feasible mechanism of H_2 splitting appears to be oxidative addition of the hydrogen molecule.

Our calculations show that the $HRhCH_3^+$ intermediate is a relatively stable compound, since ~7 kcal/mol is needed to activate the hydrogen atom transfer from the metal to the carbon in order to form the final complex, $RhCH_4^+$. The final step of the reaction, obtaining the products Rh^+ and CH_4, requires 29.2 kcal/mol in the singlet state.

Summarizing our results on the reaction of carbine complex $RhCH_2^+$ with hydrogen in the case of the singlet state, we conclude that the reaction is endothermic (7.6 kcal/mol). The first part of the reaction—formation of the $HRhCH_3^+$ intermediate—occurs without an activation barrier. However, the second part of the reaction—releasing the products—needs a significant energetic contribution (29 kcal/mol).

The features of the potential energy surface and geometric parameters of the stationary points of the triplet reaction path (Figures 5 and 6) are quite different from the corresponding points of the singlet. First of all, the triplet state for the $RhCH_2^+$ compound is the excited state, and the singlet lies lower in energy by 11.9 kcal/mol. In contrast to the singlet case, the most stable conformation of the complex for the triplet appears to be a planar one (C_{2v}). In addition, the relatively small interaction between the metal cation and the hydrogen molecule (Table 5; bond order, 0.24) practically does not disturb the H−H distance(0.773 Å) compared to the H−H distance in isolated H_2.

Despite extensive searching of the triplet state potential energy surface, only one mechanism of H1−H2 bond activation was found. Namely, the reaction proceeds through a four-center transition state. This **TS$_{\mathrm{fc}}$** has approximately a planar structure (Figure 5), which is characterized by practically equal Rh−H1 (1.661 Å) and C−H2 (1.644 Å) distances. The activation energy for this process is only 0.3 kcal/mol with respect to the reactants and 8.1 kcal/mol with respect to the initial complex. However, due to the excited nature of the triplet state on that part of the potential energy surface, the absolute energy of $\mathbf{TS_{fc}}$ is much higher (by 30 kcal/mol) than the corresponding value for **TS1** found for the singlet. Following the reaction path we found the $HRhCH_3^+$ metastable intermediate, which collapses without a barrier (**TS2**) to the $RhCH_4^+$ final complex. The complex is the absolute minimum with respect to all reaction critical points for both spin states and lies 56.3 kcal/mol below the reactants in the triplet state. Further dissociation into the products, Rh^+ and CH_4, requires 13.9 kcal/mol.

It should be pointed out that the triplet reaction pathway lies considerably higher in energy (up to 30 kcal/mol) for the first stage of the reaction, which represents the formation of the $HRhCH_3^+$ intermediate. However, this energetic difference diminishes in the vicinity of the intermediate so that the singlet state of the hydrido−methyl intermediate is only 2 kcal/mol more stable than the triplet. In the case of the triplet state the pathway from the $HRhCH_3^+$ intermediate to the final complex is more energeticly favorable than in the singlet case. The triplet state final complex is 23 kcal/mol more stable than the singlet state final one. In addition, the products of the reaction in the triplet state lie 38.0 kcal/mol lower than in the case of the singlet.

Thus, on the first step of the reaction the singlet state is the ground state, while the formation of the final complex and its dissociation into products corresponds to a triplet ground state. In other words, there is a crossing of the singlet and triplet reaction pathways (Figure 6) in the vicinity of the $HRhCH_3^+$ intermediate. Analyzing the results of our calculations, we have to conclude that the reaction 1 is a spin-forbidden reaction, i.e., it starts in the singlet state and should be finished in the triplet. In the framework of this assumption we conclude that $RhCH_2^+$ reacts with H_2 with no activation barrier to form $Rh^+ + CH_4$. The exothermicity of the spin-forbidden reaction is 30.5 kcal/mol. Our conclusions are in excellent qualitative and quantitative agreement with experimental data. First of all, Jacobson and Freiser found experimentally that $RhCH_2^+$ reacts very rapidly at thermal energies with H_2^+ to form $Rh^+ + CH_4$. Further, our conclusion on the spin-forbidden nature of the reaction and the calculated reaction profiles coincide with the results of a guided ion beam mass spectrometry study by Chen and Armentrout,[26] who constructed a quantitative potential surface for this reaction and found no barrier in excess of the endothermicity for the reaction of dehydrogenation of methane by ground-state Rh^+(i.e., the inverse reaction with respect to reaction 1). They also concluded that this process is a spin-forbidden one and the change of the spin likely occurs immediately after formation of the hydrido−methyl intermediate. Finally, our estimation of the reaction exothermicity, 30.5 kcal/mol, is very close to the experimental measurements by Chen and Armentrout, 23.5 ± 2.1 kcal/mol.

Despite an agreement between our results and experimental observations, one can notice the difference between our conclusions on the mechanism for the investigated reaction and the catalytic scheme considered in a number of experimental papers. We first note that there are not, to our knowledge, any direct experimental studies of the reaction mechanism. Jacobson and Freiser[15] first postulated the four-center transition state mechanism of hydrogen molecule splitting. Their consideration was based on thermodynamic arguments that allowed them to reject the oxidative addition of a hydrogen molecule to an Rh^+ moiety. Thus, the four-center TS mechanism was considered as the most probable one. Chen and Armentrout pointed out that the four-center mechanism did not contradict their experimental observations. However, guided ion beam mass spectrometry cannot reveal the details of the reaction mechanism. It is the task of theory to investigate the details of possible mechanisms based on experimental data. As we already noticed above, simplified thermodynamic analysis by Jacobson and Freiser cannot a priori exclude the oxidative addition of H_2 to the Rh^+ moiety of the $RhCH_2^+$ compound. In fact, our findings show that oxidative addition of H_2^+ is the only possible mechanism for reaction 1 ($M = Rh$) since the four-center TS mechanism can be performed only in the excited triplet state.

Our results and conclusions dramatically differ from the results of Musaev et al. According to the calculations of Musaev et al., a four-center transition state exists on both the singlet and triplet state potential energy surface of reaction 1 ($M = Rh^+$). They also predicted that the behaviors of the potential energy surfaces of the reaction for the ground singlet state and excited triplet state are very similar and that on both reaction paths significant activation energy (by 16 kcal/mol) is needed to split the H−H bond. All these predictions completely contradict our conclusions that there are two different mechanisms for the two spin states and no activation barrier exists for the spin-forbidden reaction 1. As we mentioned above, our results are supported by direct experimental observations of the absence of a barrier for reaction 1[15] and a quantitative potential energy surface for this reaction constructed by Chen and Armentrout.[26] Moreover, as simple molecular orbital consideration showed,[26] it seems plausible that the singlet and the triplet states of $RhCH_2^+$ should have different transition state energies for addition of H_2. We did obtain large differences between transition state barriers for H−H splitting in different spin states. From our point of view, further studies are needed to understand the sources of inconsistency between the ab initio approach of Musaev et al. and our theoretical calculations and available experimental results.

Conclusions

The potential energy surfaces for the $MCH_2^+ + H_2 \rightarrow M^+ + CH_4$ ($M = Co$, Rh) reactions have been studied by means of a Gaussian density functional approach in which we considered both the singlet and triplet state channels. Two different mechanisms—a four-center transition state mechanism of H_2 splitting on MCH_2^+ and oxidative H_2 addition to the M^+ moiety—have been considered for both electronic states. The singlet and triplet reaction paths are very different. The H−H bond cleavage in the singlet state follows a stepwise H_2 splitting corresponding to an oxidative hydrogen addition mechanism, while for the triplet state only a concerted mechanism with the formation of a four-center transition state ($\mathbf{TS_{fc}}$) structure is possible. In agreement with experimental and previous theoretical indications, the hydrido−methyl complex ($HMCH_3^+$) does not exist (or it is very metastable) on the triplet state reaction pathway. It can exist in the singlet state.

Despite the fact that oxidative addition of H_2 to the M^+ (Co^+, Rh^+) moiety for the singlet spin state of MCH_2^+ is more favorable than the four-center TS mechanism splitting of H_2 with respect to the initial complexes, the energetic penalty required to obtain the singlet excited state of $CoCH_2^+$ is prohibitive and precludes this pathway as a channel for Co reaction. Thus, only the four-center TS mechanism can be performed in the case of Co. This process needs 5.8 kcal/mol to be activated and results in the $HCoCH_3^+$ intermediate. Since the intermediate is metastable for the triplet channel, the final complex can be easily obtained.

In contrast to $CoCH_2^+$, the singlet state is the ground state for $RhCH_2^+$ compound and the H_2 splitting can be performed in the framework of the oxidative addition mechanism. This reaction step does not require an activation energy with respect to the reactants. The triplet channel becomes more energetically favorable for the second part of the reaction. Our results suggest that the changing of the singlet spin state occurs immediately after formation of the hydrido−methyl intermediate ($HRhCH_3^+$). As in the case of Co, this intermediate in the triplet state is metastable and collapses to the final complex without any barrier. We conclude that the $RhCH_2^+ + H_2 \rightarrow Rh^+ + CH_4$ reaction should be a spin-forbidden process.

As mentioned in the Introduction, one of the goals of this work is to answer the question about the distinguishably different catalytic activity of $CoCH_2^+$ and $RhCH_2^+$ compounds. On the basis of our findings, we conclude that the different nature of the metal cations leads not only to qualitative change in the reaction energy profiles but to a fundamental difference in the mechanism itself.

Our results and conclusions dramatically differ from the results of ab initio calculations by Musaev et al.[31] in the case of Rh. The principal disagreements include their predictions that a four-center transition state exists on both the singlet and the triplet state potential energy surfaces and that the behavior of the potential energy surfaces of the reaction for the ground singlet state and excited triplet state are very similar. In addition, the high activation barrier value for H−H splitting (by 16 kcal/mol) obtained by the authors is contrary to our conclusion of a barrierless reaction profile and to available experimental data.

Overall, the results of our calculations show that DFT is a reliable tool to study the reactions of carbine complexes MCH_2^+ with hydrogen and small alkanes. This method has been shown to provide both qualitative and quantitative agreement with experimental data and provide details of catalytic mechanisms that are not directly available from experimental studies.

Acknowledgment. We are grateful to the Frederick Biomedical Supercomputing Center of the National Cancer Institute for computer support and to MURST and CNR (Commitato Scienze Chimiche) for their financial contributions. The content of this publication does not necessary reflects the views or policies of the Department of Health and Human Services, nor does mention of trade names, commercial products, or organizations imply endorsement by U.S. Government.

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