Theoretical Studies on the Metathesis Processes, [Tp(PH_3)MR(η^2-H–CH_3)] → [Tp(PH_3)M(CH_3)(η^2-H–R)] (M = Fe, Ru, and Os; R = H and CH_3)

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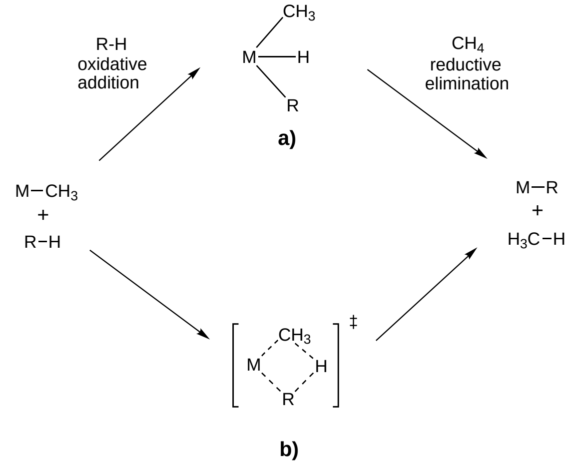
Abstract: Theoretical calculations on the metathesis process, [Tp(PH_3)MR(η^2-H–CH_3)] → [Tp(PH_3)M(CH_3)(η^2-H–R)] (M = Fe, Ru, and Os; R = H and CH_3), have been systematically carried out to study their detailed reaction mechanisms. Other than the one-step mechanism via a four-center transition state and the two-step mechanism through an oxidative addition/reductive elimination pathway, a new one-step mechanism, with a transition state formed under oxidative addition, has been found. Based on the intrinsic reaction coordinate calculations, we found that the trajectories of the transferring hydrogen atom in the metathesis processes studied are similar to each other regardless of the nature of reaction mechanisms.

Keywords: C–H activation · DFT calculations · metathesis · reaction mechanisms

Introduction

σ-Bond metathesis is an important organometallic reaction for the activation of unreactive C–H bonds.[1–3] Bergman et al. recently reported several Ir^{III} compounds, such as [Tp^{Me2}(PMe_3)IrMe(L)][BAr_F] (Tp^{Me2} = hydridotris(3,5-dimethylpyrazolyl)borate, L = CH_2Cl_2 and N_2, BAr_F = B[3,5-C_6H_3-$(CF_3)_2]_4$),[4] [Cp*(PMe_3)Ir(Me)]OTf (Cp* = C_5Me_5, OTf = O-SO_2CF_3), and [Cp*(PMe_3)Ir(Me)($ClCH_2Cl$)][BAr_F],[5] which are capable of selectively cleaving carbon-hydrogen bonds in hydrocarbons. In these activation reactions, it is believed that the hydrocarbon molecule (HR) is first coordinated to the cationic metal fragments, $[Cp^*(PMe_3)IrMe]^+$ and $[Tp^{Me2}(PMe_3)IrMe]^+$, through the Ir-η^2-H-R interaction, and the hydrogen from the η^2 ligand is then transferred to the Me group in the cationic metal fragment, giving methane as the product. The hydrogen-transfer process, which is a metathesis process of [L_nMR(η^2-H-R')] → [L_nMR'(η^2-H-R)], can proceed either via a four-center transition state or by oxidative addition then reductive elimination (see Scheme 1). Previous theoretical studies showed that the cationic Ir^{III} fragment $[Cp(PH_3)IrMe]^+$ favored the oxidative addition/reductive elimination (OA/RE) pathway (a two-step mechanism) with the formation of an intermediate Ir^V complex (Scheme 1a).[6, 7] Theoretical studies on the C–H activation mechanisms by analogous complexes $[Cp(PH_3)MCH_3]^+$ (M = Rh and Co) have also been carried out.[8] The results showed that the C–H activation of methane by $[Cp(PH_3)CoCH_3]^+$ proceeded via a four-center transition state (a one-step mechanism) with a high activation barrier (Scheme 1b); on



Scheme 1.

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the other hand, the reaction seemed to adopt a mechanism somewhere in between the OA/RE and the four-center process with $[Cp(PH_3)RhCH_3]^+$, since the relative energies of its intermediate and the transition state in the energy profile are very close to each other. Here, it should be noted that on the basis of mass spectrometric work on $[Cp^*(PMe_3)Ir(CH_3)]^+$ an entirely different reaction mechanism that involves the dissociation of CH_4 through the formation of a cyclometalated intermediate, $[Cp^*Ir(\eta^2\text{-}CH_2PMe_2)]$, has been proposed.[9] The proposed activation was later calculated to have much higher reaction barriers relative to the oxidative addition/reductive elimination pathway.[10]

Our recent study on the mechanism of H/D exchange between methane and some common deuterated organic solvents catalyzed by the Ru^{II} system $[Tp(PPh_3)Ru(CH_3CN)H]$ (Tp = hydrotris(pyrazolyl)borate) gives some interesting results.[11] The H/D exchange process, resulting from C–H(D) activation of methane and the deuterated solvent, involves transformation of the σ-complex $[Tp(PPh_3)Ru(\eta^2\text{-H–R})H]$, which is generated by the displacement of CH_3CN with H–R, to an η^2-dihydrogen species $[Tp(PPh_3)Ru(\eta^2\text{-}H_2)R]$. The transformation passes through a one-step mechanism with a seven-coordinate pentagonal-bipyramidal $[Tp(PPh_3)Ru(R)(H)(H)]$ transition state. This type of seven-coordinate species usually appears as intermediate resulting from an oxidative addition step.

There is a common belief that the activation of a C–H bond by a $L_nM\text{–}H$ complex would involve either a one-step mechanism with a four-center transition state or a two-step mechanism with a species formed under oxidative addition as the intermediate. This point of view ignores the continuous aspect of chemistry whereby one mechanism can gradually change into the others. One can thus wonder whether a two-step mechanism could have an intermediate with the structural characteristics of a four-center species or if a one-step mechanism could have a transition state with the structural characteristics of a species formed under oxidative addition. To study these interesting problems, we were prompted to systematically study the following metathesis process, $[Tp(PH_3)MR(\eta^2\text{-H–}CH_3)] \rightarrow [Tp(PH_3)M(CH_3)(\eta^2\text{-H–R})]$ (M = Fe, Ru, and Os; R = H and CH_3). We are interested to know how the metal center and Tp ligand affect the mechanistic pathway for C–H activation, that is, whether a two- (OA/RE) or one-step reaction mechanism is favorable. Furthermore, we would also like to find out, for those metathesis processes that proceed through a one-step mechanism, whether the transition states possess a four-center character or are purely species formed under oxidative addition. Similar mechanistic studies with the Cp analogues have also been carried out for comparison purpose.

Computational Details

Density functional theory calculations at the Becke3LYP (B3LYP) level[12] have been used to perform the geometry optimizations for all reactive species in the metathesis process. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ)[13] was used to describe P atoms, while the Couty and Hall's modified version of LANL2DZ basis set[13c, 14] has been chosen for transition metals. Standard 6-31G basis set[15] was used for all other atoms, except the uncoordinated C and H atoms in the Tp ligand, for which a STO-3G basis set[16] was used. To increase the accuracy, polarization functions have been added for hydride ligands, migrating hydrogen atoms, and carbon atoms ($\zeta_p(H) = 1.0$ and $\zeta_d(C) = 0.8$) that are directly coordinated to the metal center and involved in the metathesis processes.

All calculations were performed with the use of Gaussian 98 package[17] on Silicon Graphics Indigo^2 workstations and PC Pentium IV computers. The electron density analysis was carried out with MOPLOT 2.4.[18]

Result and Discussion

As mentioned in the introduction, the following metathesis processes, $[Tp(PH_3)MR(\eta^2\text{-H–}CH_3) \rightarrow Tp(PH_3)M(CH_3)(\eta^2\text{-H–R})]$ (M = Fe, Ru, and Os; R = H and CH_3), will be studied. For convenience, the reactive species in these metathesis processes will be labeled as **TpMH** and **TpMMe** followed by either **(CH_4)** or **(H_2)** to denote the methane σ-complexes and the η^2-H_2 complexes, respectively. **TS** stands for transition states and **INT** for intermediates.

$[Tp(PH_3)MH]$ (M = Fe, Ru, and Os): The metathesis process of $[Tp(PH_3)MH]$ and methane starts with the formation of a σ-complex $[Tp(PH_3)MH(\eta^2\text{-H–}CH_3)]$, followed by either a two-step mechanism (OA/RE) with the formation under oxidative addition of an M^{IV} intermediate, or a one-step mechanism, giving the dihydrogen complexes $[Tp(PH_3)M(CH_3)(\eta^2\text{-}H_2)]$. Figure 1 shows the energetics related to the metathesis processes of $[Tp(PH_3)MH] + CH_4$ (M = Fe, Ru, and Os). For both the Fe and Ru systems, the metathesis reactions proceed by a one-step mechanism. The activation energy for the Fe system is higher than that for the Ru system by 4.1 (4.2) kcal mol^{-1}; the value in the parentheses is the activation free energy. In the text below, we will give free energies in parentheses whenever the energies are mentioned.

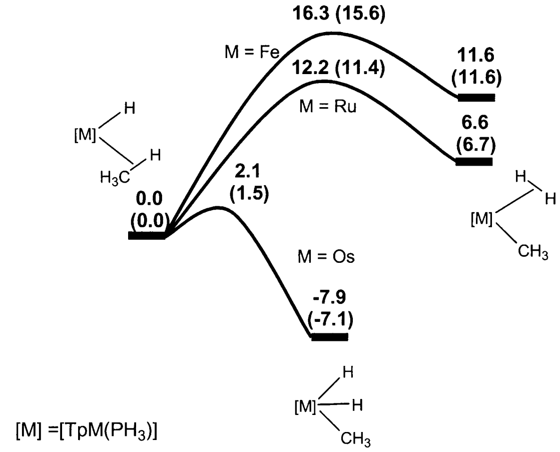


Figure 1. The relative reaction energies together with the relative free energies (in parentheses) related to the metathesis process $[Tp(PH_3)MH] + CH_4$ (M = Fe, Ru, and Os). The energies are given in kcal mol^{-1}.

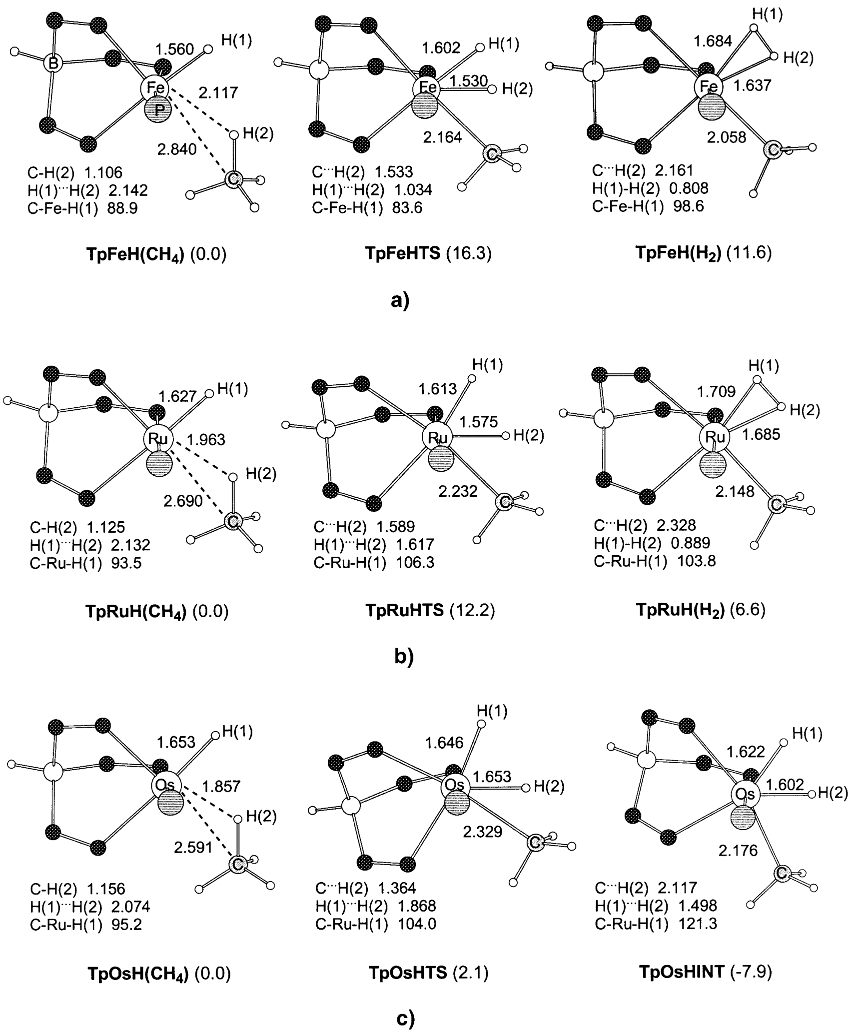


Figure 2. The relative reaction energies (kcal mol^{-1}) and selected structural parameters of B3LYP optimized species in the metathesis process [Tp(PH$_3$)MH] + CH$_4$, for a) M = Fe, b) M = Ru, and c) M = Os; these parameters correspond to the stationary points of Figure 1. For the purpose of clarity, the hydrogen atoms in the PH$_3$ group and the carbon and hydrogen atoms of the pyrazolyl groups in Tp are omitted. The bond lengths and angles are given in Å and °, respectively.

For [Tp(PH$_3$)OsH], the energy profile ends with a formally Os^{IV} dihydride complex, rather than an Os^{II} dihydrogen complex. Attempted optimization of the η^2-dihydrogen complex [Tp(PH$_3$)OsH(η^2-H$_2$)] was unsuccessful. The optimization starting with a dihydrogen complex returns back to the formally Os^{IV} complex. The activation of the C–H bond by [Tp(PH$_3$)OsH] exhibits a small barrier (2.1 (1.5) kcal mol^{-1}) and is exothermal (7.9 (7.1) kcal mol^{-1}). It is worth noting that the Os^{IV} dihydride complex is a seven-coordinate species supported by a Tp ligand, which is well-known for enforcing octahedral geometry about metal center.[19] We have reported that the protonation of the Tp osmium hydride complex [Tp(PPh$_3$)$_2$OsH] gives the cationic six-coordinate η^2-dihydrogen complex [Tp(PPh$_3$)$_2$Os(η^2-H$_2$)]$^+$ rather than the seven-coordinate dihydride species [Tp(PPh$_3$)$_2$OsH$_2$]$^+$.[20] The seven-coordinate Os^{IV} dihydride complex studied in this paper is neutral, while that reported in the literature is cationic. The positive charge carried by the reported complex may have the significant effect in stabilizing the η^2-dihydrogen form. Geometry optimization on model cationic complex [Tp(PH$_3$)$_2$Os(η^2-H$_2$)]$^+$ indeed gives a six-coordinate η^2-dihydrogen species with the H···H distance being 0.956 Å, supporting the positive charge argument and indicating that the level of theory is reliable.

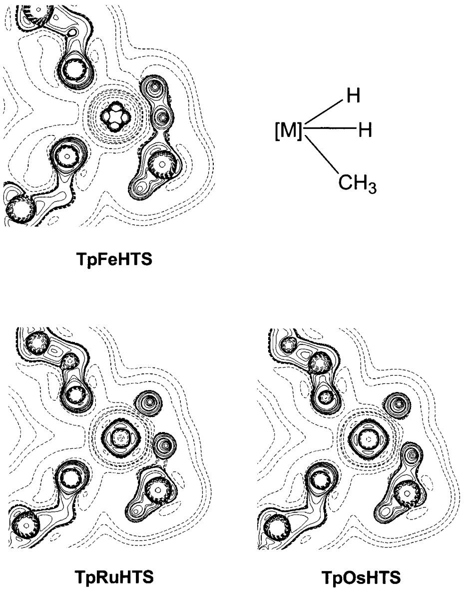
The relative reaction energies and selected structural parameters of the species, which correspond to the stationary points of Figure 1, are shown in Figure 2. For the Fe system, **TpFeHTS** is a late transition state; this is in agreement with the process being endothermal, as the H(1)···H(2) distance (1.034 Å) in **TpFeHTS** is quite close to that in the dihydrogen complex (0.808 Å) **TpFeH(H$_2$)**. Even though there is an interaction between H(1) and H(2) in **TpFeHTS**, the transferring hydrogen atom H(2) has a short contact with the metal center (1.530 Å), indicating the hydride character of the former. It can be explained in terms of the spherical nature of the 1s orbital in hydrogen, which allows good overlaps with the metal and neighboring atoms.[21] The C-M-H(1) angle in **TpFeHTS** is 83.6°, which is similar to those four-center transition states in the activation of saturated C–H bonds by early transition metal systems.[21, 22]

For the Ru system, whose endothermicity is lower than that for Fe system, a relatively long H(1)···H(2) distance (1.617 Å) and a large C-M-H(1) angle (106.3°) are found in the transition state **TpRuHTS**. The C···H(2) distance in **TpRuHTS** is also quite long (1.589 Å). These structural features suggest unambiguously that the metathesis is a one-step process and that the transition state has the features of oxidative addition of the methane C–H bond.

For the Os system, the structure of transition state **TpOsHTS** is reached early in the process; this is in agreement with its exothermicity, as it resembles the C–H σ-complex **TpOsH(CH$_4$)**. The short C···H(2) distance (1.364 Å) in the transition state **TpOsHTS** implies that the C–H bond of the entering methane has not yet been broken in the transition state. [Tp(PH$_3$)OsH(η^2-H–CH$_3$)] is a local minimum while [Tp(PH$_3$)Os(CH$_3$)(η^2-H$_2$)] is not. The stronger [Os]–H ([Os] = Tp(PH$_3$)Os) interaction, relative to [Os]–CH$_3$, weakens the Os(d)-to-σ*(C–H) backdonation interactions, giving a stable [Os](H)(η^2-H-CH$_3$) structure. The weaker [Os]–CH$_3$

interaction facilitates the Os(d)-to-σ*(H–H) backdonation interaction, giving a classical dihydride structure.

Figure 3 shows the Laplacian plots of the electron density, $-\nabla^2\rho$, for the transition states **TpMHTS** (M = Os, Ru, Fe) in a plane defined by the metal center, the hydrides, and the carbon atom in the methyl group. In the contour plots, solid lines denote $-\nabla^2\rho > 0$, at which the electron density is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, at which the electron density is locally depleted. The four concentrated areas of electron density around the metal center for each transition structure can be associated with the electron density contributed from a metal d orbital.[23] Significant electron density concentrations can be found in **TpFeHTS** between the transferring hydrogen atom and the methyl group, and also the hydride. Evidently, a four-center character is present in **TpFeHTS**. Similar electron density concentrations are not found in **TpRuHTS**. The Laplacian plot for **TpRuHTS** (Figure 3) provides an additional support for a one-step process with a transition state formed under oxidative addition. Electron density concentrations between the transferring hydrogen atom and the methyl group of the entering methane can be found in **TpOsHTS**. This Os-η^2-(H–C) three-center interaction indicates that the C–H bond of the entering methane is not completely broken in the transition state.



TpFeHTS

TpRuHTS **TpOsHTS**

Figure 3. Plots of the Laplacian of electron density for the transition states **TpMHTS** (M = Fe, Ru, and Os) in a plane defined by the metal center, hydride, and the carbon atom in the methyl group.

These results show that the metathesis process of [Tp(PH$_3$)FeH] and methane favors a one-step mechanism via a four-center transition state (**TpFeHTS**), in which the transferring hydrogen atom has an interaction with the metal center. The metathesis process of [Tp(PH$_3$)RuH] and methane also proceeds by a one-step mechanism, not via a four-center transition state, but through one in which the C–H bond of methane is oxidatively added to the metal center. Finally, for the Os system, the C–H bond is oxidatively added to the metal center with a low barrier, and the reaction ends with a formally Os^{IV} dihydride complex, instead of a η^2-dihydrogen species. The different mechanistic behavior among the three systems may also be related to the different sizes of the metal centers. The transition state **TpFeHINT** does not exist as a minimum because Fe^{IV} is too small to be stable in the ligand environment.

In order to investigate the role of the metal center in the hydrogen-transfer process, intrinsic reaction coordinate (IRC) calculations[24] were carried out to trace the change in the distances between the metal center and the transferring hydrogen atom in the metathesis process. Starting from the transition state **TpMHTS**, structures along each reaction path are obtained through the IRC calculations. Figure 4 shows the changes in distance between the metal and transferring

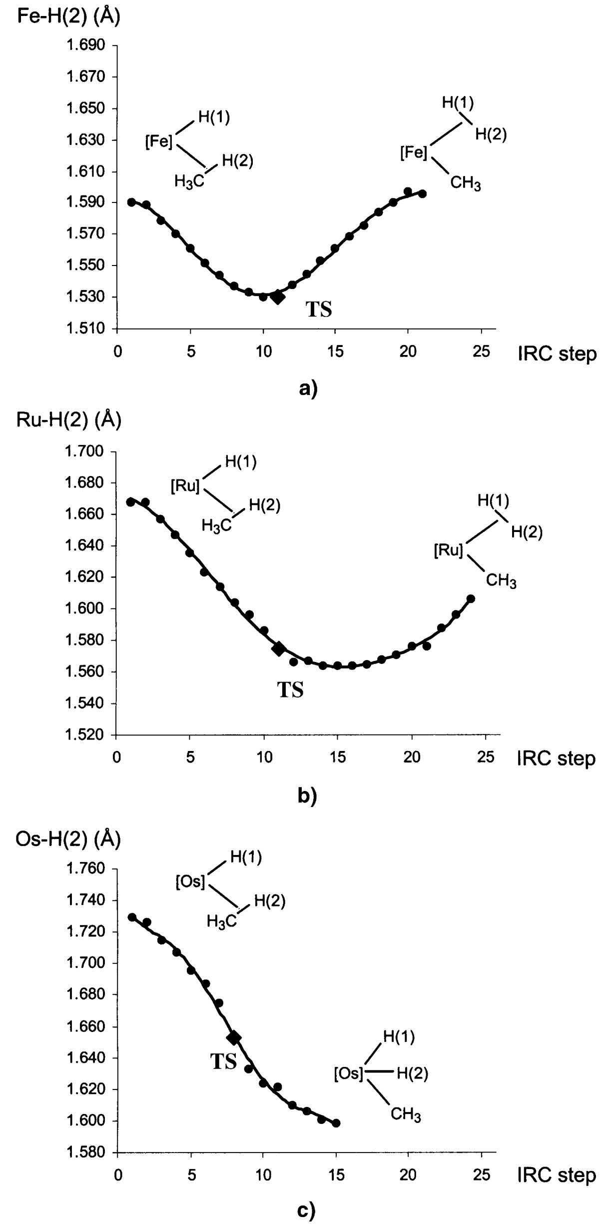


Figure 4. The change in the distance between the metal and transferring hydrogen atom along the metathesis path, [Tp(PH$_3$)MH] + CH$_4$, for a) Fe, b) Ru, and c) Os.

hydrogen atom (M–H) along the reaction paths. For the Fe and Ru systems, the M–H distances decrease along the path from **TpMH(CH$_4$)** to the transition state **TpMHTS** and increase from **TpMHTS** to **TpMH(H$_2$)**. For the Os system, the Os–H(2) distances decrease in the path from **TpOsH(CH$_4$)** to **TpMHINT**. The path of the transferring hydrogen atom in each of the metathesis processes is curved inward towards the metal center. Evidently, the metal centers provide a stabilizing interaction to the transferring hydrogen atom during the transfer process. In other words, the trajectories of the transferring hydrogen atom are similar in the metathesis processes studied regardless of the types of transition states we have.

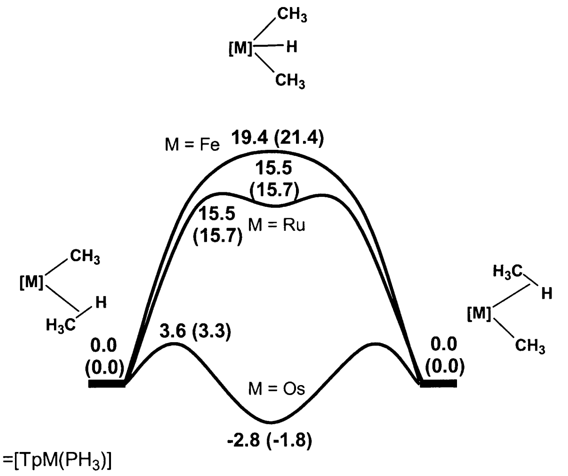
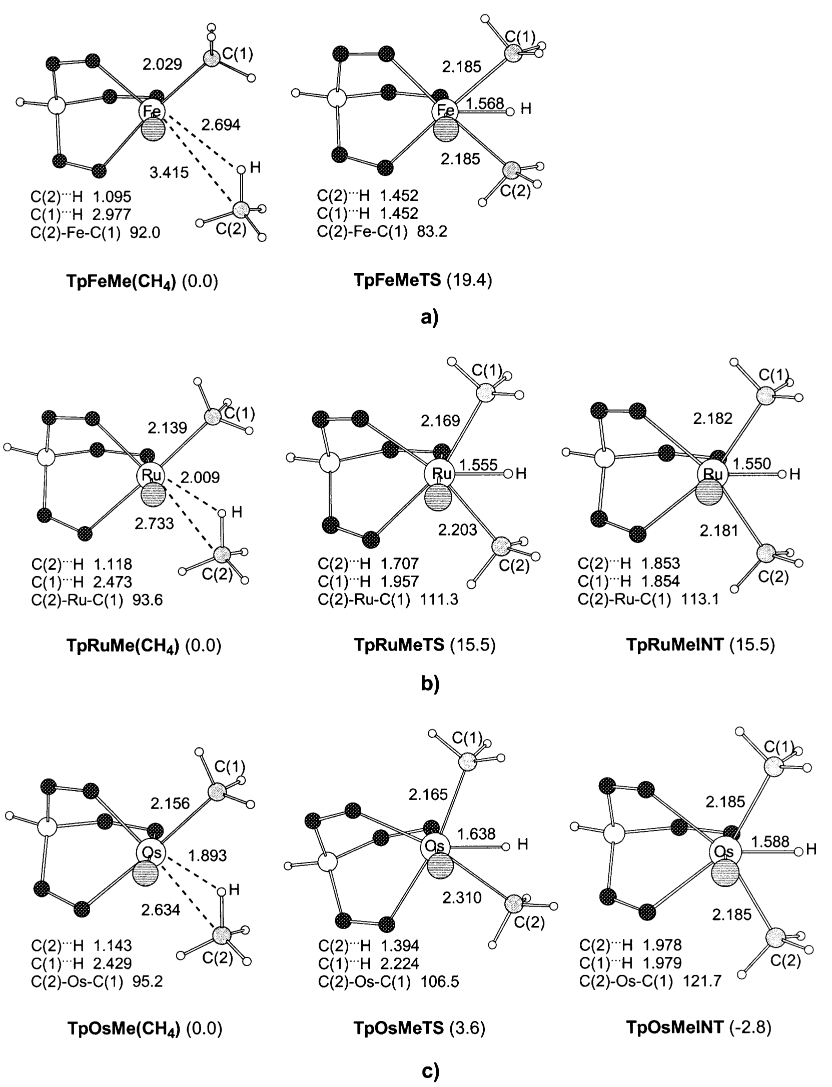


Figure 5. The relative reaction energies together with the relative free energies (in parentheses) related to the metathesis process [Tp(PH$_3$)MCH$_3$] + CH$_4$ (M = Fe, Ru, and Os). The energies are given in kcal mol^{-1}.

[Tp(PH$_3$)MMe] (M = Fe, Ru, and Os): The methane metathesis processes of [Tp(PH$_3$)MCH$_3$] have also been studied. In these metathesis processes, the starting complexes and the final products are identical. Figure 5 shows the energetics related to each metathesis process. Interestingly, previous studies on the methane metathesis processes at [Cp(PH$_3$)MCH$_3$]$^+$ (M = Co, Rh and Ir) gave similar energy profiles.[8] Similar to the [Cp(PH$_3$)IrCH$_3$]$^+$ + CH$_4$ system,[6, 7] the Os system goes through a two-step mechanism with the lowest C–H activation barrier; the reaction in the Fe system proceeds by a one-step mechanism with the highest activation barrier, and the Ru system is somewhere in between. In the Ru system, the intermediate and the transition states are structurally and energetically similar. One can consider the metathesis as a one-step process. The unusual flatness of potential-energy surfaces was also found in the case of stretched dihydrogen complexes.[25]

The relative reaction energies and selected structural parameters of species that correspond to the stationary points of Figure 5 are shown in Figure 6. For the structure of **TpFeMeTS**, the transferring hydrogen atom maintains a short contact with the two methyl groups and the metal center. The C(2)-Fe-C(1) angle 83.2°, which is small, implies a four-center structure close to that found in previous theoretical work on scandium.[21, 26] The C(2)···H distance in **TpRuMeTS** is significantly longer



TpFeMe(CH$_4$) (0.0) **TpFeMeTS** (19.4)

a)

TpRuMe(CH$_4$) (0.0) **TpRuMeTS** (15.5) **TpRuMeINT** (15.5)

b)

TpOsMe(CH$_4$) (0.0) **TpOsMeTS** (3.6) **TpOsMeINT** (-2.8)

c)

Figure 6. The relative reaction energies (kcal mol^{-1}) and selected structural parameters of B3LYP optimized species in the metathesis process [Tp(PH$_3$)MMe] + CH$_4$, for a) M = Fe, b) M = Ru, and c) M = Os; these parameters correspond to the stationary points of Figure 5. The Tp ligand in each structure is simplified (see the caption of Figure 2 for details) for the purpose of clarity. The bond lengths and angles are given in Å and °, respectively.

than that in **TpOsMeTS**. The former is 1.707 Å and the latter is 1.394 Å. Thus, the geometrical pattern at the top of the energy curve for **TpRuMeTS** corresponds to a species formed under oxidative addition.

The Laplacian plots of the electron density for each of the transition states on a plane defined by the metal center and the two methyl groups are shown in Figure 7. For **TpFeMeTS**, significant concentrations of electron density can be found between the transferring hydrogen atom and the two methyl groups. Apparently, a four-center transition state is again present in the Fe system. On the other hand, for **TpRuMeTS**, electron density concentrations are not found between the transferring hydrogen atom and the two methyl groups, indicating that the coordinated C–H bond of the entering methane is broken in the transition state. However, some electron density concentrations can be found between transferring hydrogen atom and one of the two methyl groups in **TpOsMeTS**, similar to the situation in **TpOsHTS**.

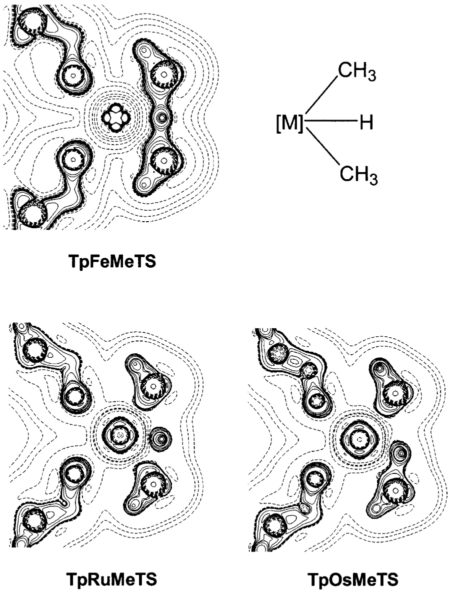


Figure 7. Plots of the Laplacian of electron density for the transition states **TpMMeTS** (M = Fe, Ru, and Os) in a plane defined by the metal center and the two methyl groups.

These results show that the metathesis process between [Tp(PH$_3$)FeMe] and methane favors a one-step mechanism via a four-center transition state, and the transferring hydrogen atom again has a strong interaction with the metal center in the transition state **TpFeMeTS**. The metathesis process of [Tp(PH$_3$)RuMe] and methane can be more or less viewed as passing through a one-step mechanism, via a transition state formed under oxidative addition, because both the energy and structural differences between **TpRuMeTS** and **TpRuMeINT** are very small (see Figure 6b). For the Os system, the metathesis process favors a two-step mechanism with the formation of an Os^{IV} intermediate. Similar to the Os^{IV} species **TpOsHINT**, the intermediate **TpOsMeINT** is also the most stable structure along the metathesis reaction path.

IRC calculations have also been carried out. Figure 8 shows the change in the distances between the metal and transferring hydrogen atom (M–H) along the reaction paths. Since the products and the reactants are identical in each metathesis process, the curves are symmetrical. For the Fe system, the distance between the metal and transferring hydrogen atom decreases in the direction from **TpFeMe(CH$_4$)** to the **TpFeMeTS**. For the Ru and Os systems, the M–H distances decrease along the reaction path and reach their minima at **TpMMeINT**. The path of the transferring hydrogen atom in each of the metathesis process is again curved inward towards the metal center. These results further demonstrate that the metal centers have interaction with the transferring hydrogen atom even in processes that involve a one-step mechanism with a four-center transition state.

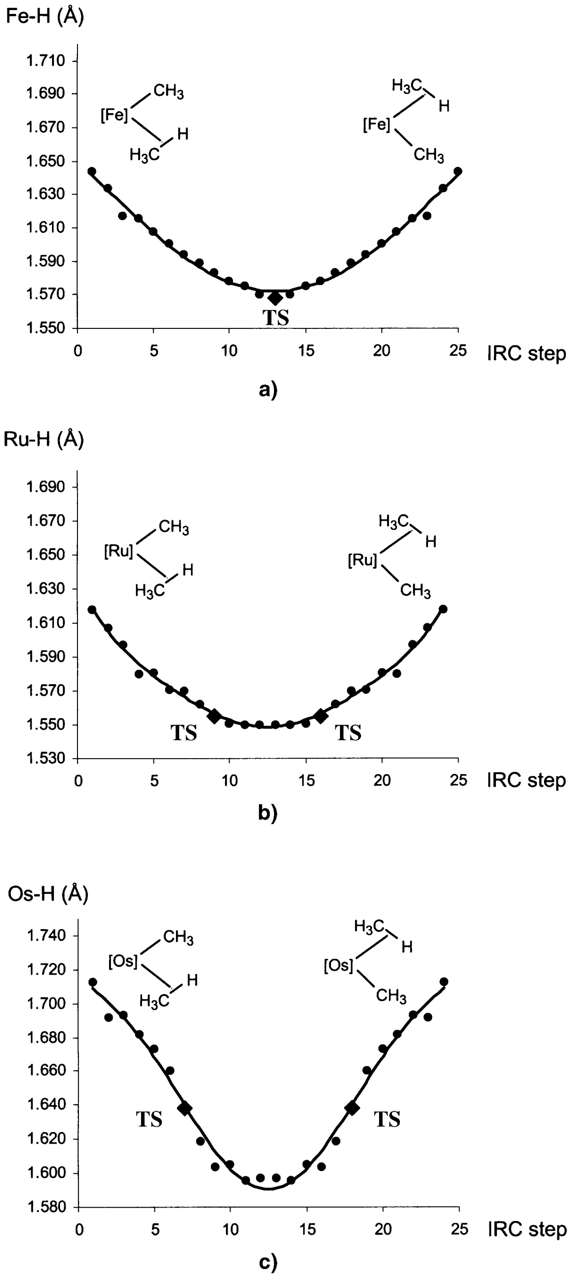


Figure 8. The change in the distance between the metal and transferring hydrogen atom along the metathesis path, [Tp(PH$_3$)MMe] + CH$_4$, for a) Fe, b) Ru, and c) Os.

Periodic trends and comparison with the Cp-containing analogues: The barriers for the metathesis of $[Tp(PH_3)MR] + CH_4$ ($R = H$ or CH_3, $M = Os$, Ru and Fe) decrease down the group of the transition metals. In comparison with the Fe and Ru systems, the incomplete breaking of the C–H bond in the transition states of the Os systems does not cause excessive destabilization; this leads to small activation energies in these systems. The calculations show that the intermediates **TpOsMeINT** and **TpOsHINT** are even more stable than the corresponding η^2-H–C and η^2-H_2 complexes. These results are related to the fact that the electron-richer Os metal center has a greater tendency for higher oxidation state. A previous theoretical study on the hydrogen exchange between the hydride and methyl ligands in $[Cp^*(dmpm)Os(CH_3)H]^+$ also showed that an Os^{IV} complex was the most stable point on the reaction profile.[27] Indeed, several relevant Os^{IV} complexes have been structurally characterized.[28, 29] Although the barriers for the oxidation addition of the C–H bond of methane at $[Tp(PH_3)OsH]$ and $[Tp(PH_3)OsMe]$ are very low, the metathesis processes may not be able to proceed to completion owing to the high stability of the intermediate Os^{IV} complexes which renders the reductive elimination step unfavorable.

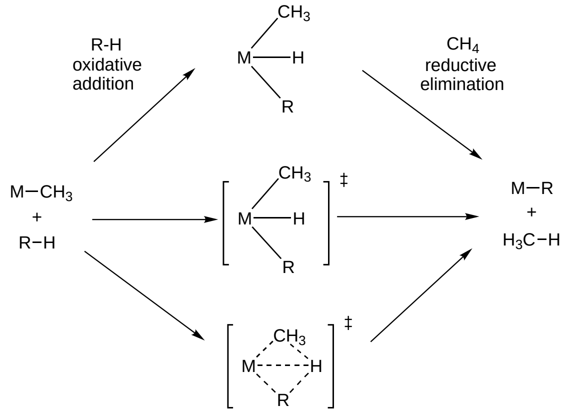
The metathesis process for $[Tp(PH_3)FeR]$ ($R = H$ or CH_3) can only proceed by a one-step mechanism via a four-center transition state; this is similar to the metathesis processes with the early-transition-metal systems.[21, 22, 26] Although Fe is a late transition metal, the metal does not favor a high oxidation state. For comparison, we have also studied the metathesis processes with the analogous complexes $[Cp(PH_3)FeR]$ ($R = H$ or CH_3). As expected, the metathesis processes with the Cp-containing $[Cp(PH_3)FeR]$ ($R = H$ or CH_3) complexes also proceed by a one-step mechanism via a four-center transition state. Moreover, the metathesis processes of the Cp-containing systems have lower barriers, 12.1 (10.6) and 16.6 (16.8) $kcal\,mol^{-1}$ for the CpFeH and CpFeMe systems, respectively, than those of the Tp-containing systems; this is probably due to the fact that the Cp ligand is believed to be more electron-donating, although exceptions have been found for Fe complexes.[30–32]

The metathesis processes of the Ru systems have adopted a mechanism somewhere in between the one- and two-step ones. The reaction of $[Tp(PH_3)RuH]$ with CH_4 proceeds by a one-step mechanism in which the transition state is a dihydride species $[Tp(PH_3)Ru(H)_2(CH_3)]$ formed under oxidative addition. Similarly, the reaction of $Tp(PH_3)RuCH_3$ with CH_4 also proceeds approximately by a one-step mechanism. While the metathesis reactions of the Fe systems prefer to proceed by a one-step mechanism with a four-center transition state that involves significant interactions between the Fe and transferring hydrogen atoms, the reactions of the Os systems in contrast go by a two-step mechanism with an intermediate formed under oxidative addition. The intermediate behavior of the Ru systems reflects the periodic trend of the triad. Because of the special feature in the reaction mechanisms of the Ru systems, the ancillary ligands are expected to play an important role in determining the mechanistic pathway. More electron-rich ancillary ligands may be able to promote the Ru systems in favor of a two-step mechanism. Indeed, studies of the C–H activation by $[Cp(PH_3)RuR]$ ($R = H$ or CH_3) show that the C–H activation of methane by $[Cp(PH_3)RuR]$ ($R = H$ or CH_3) passes through a two-step mechanism with a formally Ru^{IV} intermediate. The Ru^{IV} intermediates are 6.8 (5.3) $kcal\,mol^{-1}$ for $R = H$ and 5.0 (3.6) $kcal\,mol^{-1}$ for $R = CH_3$ more stable than their transition states. These results imply that the Cp ligand can stabilize the intermediate Ru^{IV} complexes and that a two-step mechanism is more favorable. The ability of stabilizing Ru^{IV} oxidation state has been demonstrated by the characterization of $[Cp(PPh_3)_2RuH_2]^+$ and $[Tp(PPh_3)_2Ru(\eta^2\text{-}H_2)]^+$ complexes;[33, 34] the Cp complex is a dihydride species, whereas the Tp complex is a η^2-dihydrogen one.,

Conclusion

Theoretical calculations on the metathesis process $[Tp(PH_3)MR(\eta^2\text{-}H\text{–}CH_3)] \rightarrow [Tp(PH_3)M(CH_3)(\eta^2\text{-}H\text{–}R)]$ ($M = Fe$, Ru, and Os; $R = H$ and CH_3) have been systematically carried out. This work illustrates a monotonous evolution of mechanisms that go from a one-step four-center transition state mechanism to a two-step mechanism with an intermediate formed under oxidative addition via a one-step transition state, also formed under oxidative addition. Metal centers from the first period, which in general do not favor high oxidation states, prefer the one-step process with a four-center transition state regardless the nature of ligands. Metal centers from the third period favor, as expected, the two-step process with an intermediate formed under oxidative addition. A special situation is obtained for the second period metal centers, for which a one-step transition state formed under oxidative addition or a two-step intermediate, also formed under oxidative addition, are both possible. This is paradoxical in part, because it is just not in the usual thinking of a chemist to have species with geometries formed under oxidative addition not being intermediates. The uniqueness of this work is that we find it possible. The situation is related just to the environment of the metal center, which does not stabilize a sufficiently high oxidation state. This is why changes in ligand appear to have a strong influence for this family of metal centers. Better donating ligand turns the transition state, formed under oxidative addition, into an intermediate of variable stability. It is worth mentioning that the four-center transition state will never turn into an intermediate in the late-transition-metal systems, because the stabilization from the metal center is always provided by an occupied d orbital, thus turning a four-electron transition state into a six-electron transition state, which is a characteristic of a structure formed under oxidative addition.

Intrinsic reaction coordinate calculations of the systems studied show that the movements of hydrogen transfer in the metathesis processes are very similar; in each of the processes the transferring hydrogen atom approaches the metal center before completing the metathesis process. Scheme 2 summarizes the findings we have in this study. In the newly established scheme, a new one-step mechanistic pathway in which the transition state corresponds to the oxidative addition of the C–H bond to the metal center is added. In



Scheme 2.

addition, the interaction between the metal center and the transferring hydrogen atom is emphasized in the original one-step pathway with a four-center transition state.

It cannot be excluded that the potential-energy surface for these metal systems may be influenced by the use of the different model ligands. However, the main idea, which has not been emphasized before, is that a species formed under oxidative addition can be a transition state under an appropriate electronic environment. It is not intuitive that electronic factors leading to a species, formed under oxidative addition, can be present in a transition state and be not sufficient important to change a transition state into an intermediate. The idea of looking at the geometric change by appropriate chemical modification has been at the heart of the studies of crystal structures.[35]

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