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Review

Current understanding of the σ-bond metathesis reactions of $L_nMR + R'–H \rightarrow L_nMR' + R–H$

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Contents

Abstract

The metathesis reactions of $L_nMR + R'$-$H \rightarrow L_nMR' + R$–H are important fundamental reactions in organometallic chemistry and catalysis. In this article, we reviewed the current understanding of the reactions from a theoretical point of view. Selected examples of the reactions involved in catalysis were discussed.

Keywords: C–H activation; σ-Bond metathesis; Oxidative addition; Reaction mechanisms

1. Introduction

It is now well known that various metal fragments have the ability to mediate organic reactions involving activation of C–H bonds of saturated and unsaturated hydrocarbons [1]. Representative examples include metal fragments of early ($Cp^*_2ScR(R = Me, Ar)$) [2], lanthanide (Cp^*_2LuMe) [3a,b], actinide ($Cp^*_2Th(CH_2Bu^t)_2$) [3c,d], and late transition metals ($[Cp^*Ir(PMe_3)R]^+$ (R = H, Me, Ar) [4], $[TpIr(PMe_3)Me]^+$ [5] and $[TpRu(PPh_3)H]$) [6]. In these metal-fragment-mediated C–H activation processes, the following σ-bond metathesis reactions are often involved.

$$L_nMR + R'–H \rightarrow L_nMR' + R–H \qquad (1)$$

The generally accepted mechanism related to the above σ-bond metathesis reactions is that the metal fragment first coordinates with R′–H in an η^2 fashion followed by the transfer of H from R′–H to R giving the R–H product. The hydrogen-transfer process, shown in Scheme 1, may occur via either a two-step process with an oxidative addition giving an intermediate followed by a reductive elimination of R–H (path a) or a one-step process with a four-center σ-bond metathesis transition

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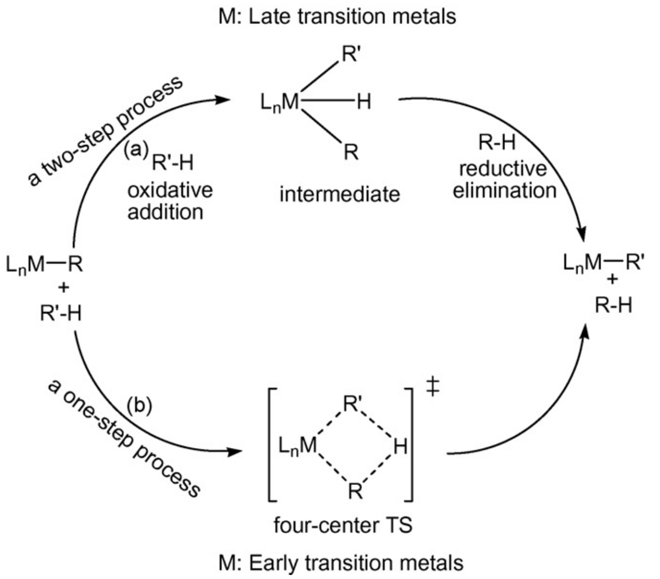
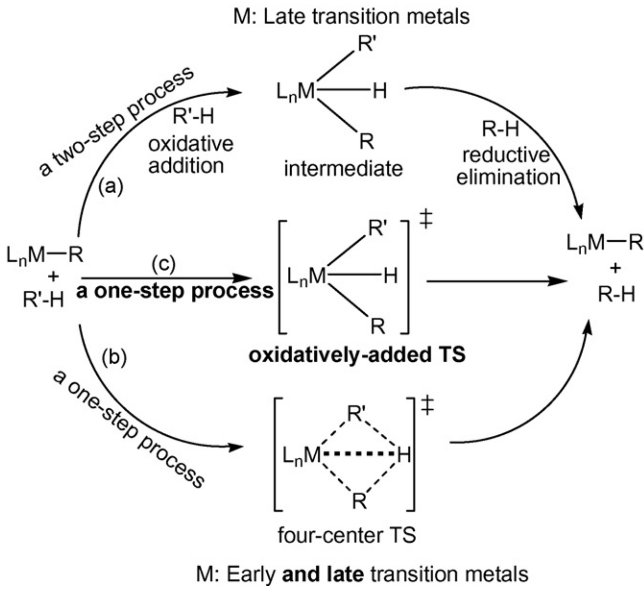


Scheme 1.



Scheme 2.

state (path b) [7a]. Of the two processes, it is well established that path b occurs generally with early, lanthanide and actinide metals while path a is normally associated with late transition metals [7b]. Supporting the general conclusion, many theoretical studies have been carried out. Systematic studies on the σ-bond metathesis reactions of R–H with $Cp_2M–R'$ (M = Sc, Lu; R, R′ = H, Me, CCH, CH=CH_2) using density functional methods showed that all these σ-bond metathesis reactions proceed through a four-center σ-bond metathesis transition state [8]. Previous theoretical studies predicted that a methane metathesis at $[CpIr(PH_3)Me]^+$ proceeds via an oxidative addition through the formation of the $[CpIr(PH_3)Me_2H]^+$ intermediate [9].

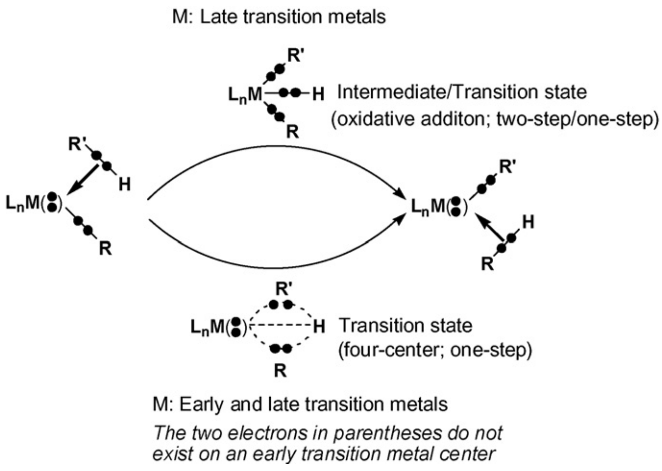
We have recently carried out theoretical calculations on the metathesis reactions of $[TpRu(PH_3)H]$ and R–H (R = Me, Ph), which model the H/D exchange reactions catalyzed by $[TpRu(PPh_3)H]$ [6]. The reactions were found to proceed through an oxidative addition. However, instead of having an oxidatively-added intermediate, we found that the oxidatively-added species is a transition state. This observation prompted us to have systematically calculated the following systems, $[TpM(PH_3)CH_3] + H–CH_3$ (M = Fe, Ru and Os), $[CpM(PH_3)CH_3]^+ + H–CH_3$ (M = Co, Rh and Ir) and $[TpM(PH_3)CH_3]^+ + H–CH_3$ (M = Co, Rh and Ir), and gained deeper insight into the roles played by various metal fragments [10]. Through the systematic study, we proposed a modified scheme, Scheme 2, illustrating the possible processes for the commonly encountered metathesis reactions. In Scheme 2, we purposely use bold letters and lines to highlight the new feature of the modified scheme. In the newly modified 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 addition, the interaction between the metal center and the transferring hydrogen is emphasized in the original one-step pathway with a four-center transition state. We also found that even with the late transition metals, a four-center transition state structure is possible.

It is clear that there are a few mechanistic possibilities for the metathesis reactions shown in Eq. (1). Experimentally, it is, however, very difficult to distinguish among the different mechanisms. The metathesis product would be the same regardless which reaction pathway is operative. Therefore, it is reasonable to question the importance of making a distinction. This review concerns the metathesis reactions shown in Eq. (1). We will focus our discussion on transition-metal mediated/catalyzed reactions relevant to C–H bond activation to illustrate the importance of understanding the reaction mechanisms.

2. Understanding the mechanisms

2.1. Oxidative addition processes

Scheme 3 schematically illustrates the electron redistribution processes relevant to the three mechanistic possibilities mentioned in Section 1. When a metathesis proceeds through one of the two oxidative addition processes, the oxidation state of



Scheme 3.

the metal center increases formally by two from the precursor complex to the intermediate for the two-step process or to the transition state for the one-step process. Therefore, it is expected that metathesis mediated by metal fragments containing late transition metals is more likely to proceed through one of the two oxidative addition processes because the metal centers under consideration have the possibility of being further oxidized. Whether the oxidatively-added species is an intermediate or a transition state depends on the ligand environment and easiness of the metal center under consideration to be in the formally higher oxidation state.

Earlier theoretical calculations show that certain iridium metal centers easily attain the +5 oxidation state and, in a few Ir-mediated/catalyzed C–H activation reactions, were found to shuttle between Ir(III) and Ir(V), where the Ir(V) species are the intermediates [9,11]. If the metal center under consideration cannot easily attain a formally higher oxidation state, the oxidatively-added species having the metal center in the formally higher oxidation state can become a transition state. The Ru(IV) species TpRuL(H)(R)(R′) mentioned above is such an example and is a transition state for the metathesis of TpRuL(R) + R′–H → TpRuL(R′) + R–H (R = R′ = Me; L = PH_3) [6,10].

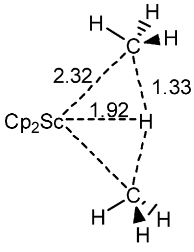
2.2. Four-center processes

When the metathesis proceeds through the four-center process, the oxidation state of the metal center does not change in the transition state. Metathesis mediated by metal fragments containing early transition metals or rare-earth metals normally follows this type of mechanism because the metal centers in these metal fragments normally have a d^0 electron-configuration and cannot be further oxidized [8,12]. However, the four-center transition states are not limited to the d^0 early transition metal centers or rare-earth metal centers [13]. Early work on the metathesis reactions of $(CO)_3Co–C(O)Me + H_2 \rightarrow (CO)_3Co–H + MeC(O)H$, (bipyrimidine)PtX + $H–CH_3$ → (bipyrimidine)$PtCH_3$ + HX (X = $OSO_2(OH)$) and $(PH_3)_4Fe(H)(\eta^2\text{-}H_2) \rightarrow (PH_3)_4Fe(\eta^2\text{-}H_2)(H)$ showed that the relevant transition states have also a four-center structure [14,15]. Our work on TpFeL(R) + R′–H → TpFeL(R′) + R–H (R = R′ = Me; L = PH_3) also demonstrated that the metathesis proceeds through a one-step process with a four-center transition state [10]. In their studies of the mechanisms of the Pd(II) or Ni(II) catalyzed ethylene polymerization reaction, Morokuma and co-workers [16] investigated the chain termination process through hydrogenolysis, a metathesis reaction of $[(\text{diimine})Pd(R)(\eta^2\text{-}H_2)]^+ \rightarrow [(\text{diimine})Pd(H)(\eta^2\text{-}HR)]^+$. They found a four-center transition state for the metathesis reaction. In terms of structural feature, these observations indicate that those late transition metal centers, which do not favor high oxidation states with certain ligand environments, can have a one-step process with a four-center transition state.

Despite the structural similarity in the four-center transition state structures calculated for d^0/f-block metal centers and certain later transition metal centers such as Fe(II), detailed electronic structure analyses on the four-center transition states of the $(PH_3)_4Fe(H)(\eta^2\text{-}H_2) \rightarrow (PH_3)_4Fe(\eta^2\text{-}H_2)(H)$ and $Cl_2Sc(H)(\eta^2\text{-}H_2) \rightarrow Cl_2Sc(\eta^2\text{-}H_2)(H)$ metathesis reactions show that there is a subtle difference in the electron topology between the two transition states [15]. Occupied d orbitals are expected to be involved in the transition state of the former metathesis reaction, causing the subtle difference observed in the electron topology analysis.

2.3. Structural feature of the four-center transition states

A new feature of Scheme 2 is to emphasize the bonding interaction between the metal center and the transferring hydrogen in the four-center transition state in the four-center metathesis process. In 1993, Ziegler et al. calculated the metathesis reaction of $Cp_2Sc\text{-}CH_3 + H\text{–}CH_3 \rightarrow Cp_2Sc\text{-}H + H\text{–}CH_3$ and pointed out that the transferring hydrogen has established a full bond with Sc in the transition state structure **1** [8a]. Similar structural feature has also been found in related systems containing lanthanide metals [12a–c]. For the metathesis mediated by $Tp(PH_3)Fe$ and $(PH_3)_4Fe(H)$, the four-center transition state structures **2** and **3** also show the bonding interaction between Fe and the transferring hydrogen [10,15].



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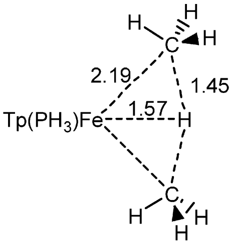

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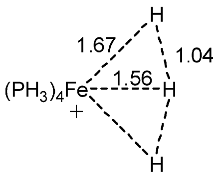

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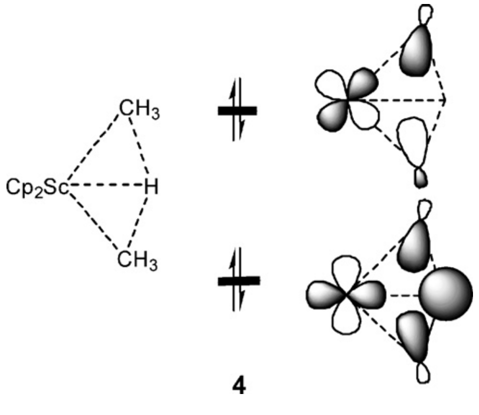
As shown in Scheme 3, there are two pairs of electrons involved in the four-center transition states of systems containing d^0/f-block metal centers. The two pairs of electrons occupy two molecular orbitals shown in **4**, in which the lower-energy orbital shows the bonding interaction between the metal center and the transferring hydrogen in the four-center transition state [8a]. However there is another view regarding the hydrogen transferring process. It was suggested that there is no bond between the metal center and the transferring hydrogen atom in the transition state and the transferring process corresponds to a proton transfer [12a–c]. In systems containing late transition metal centers, participation of occupied d orbitals makes the four-center transition states possess slightly oxidative addition character [15].



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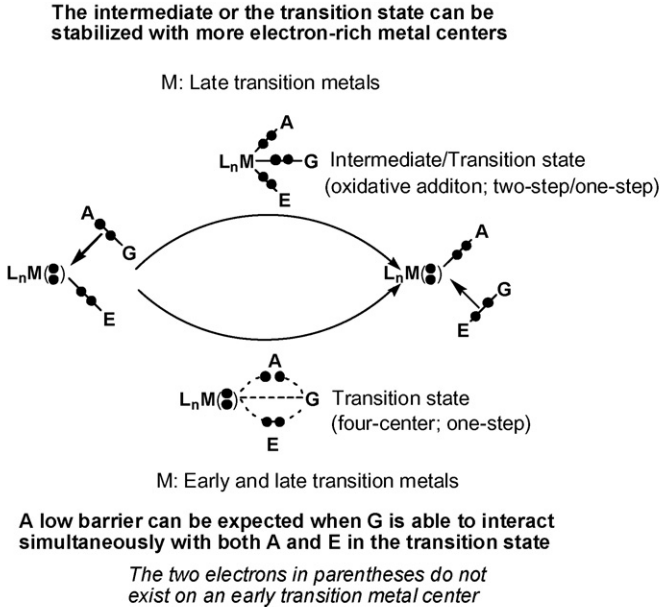


Scheme 4.

2.4. *General trends*

Scheme 4 illustrates the electron redistribution processes for the three possible reaction mechanisms discussed above with a general metathesis reaction of $L_nM–A + G–E \rightarrow L_nM–E + A–G$. On the basis of the electron redistribution processes, one can easily come to the following generalizations. For the oxidative addition processes, one can increase the electron-richness of the metal center to stabilize the intermediate for the two-step process and the transition state for the one-step process. It should be pointed out here that certain metal centers, such as osmium [10], are too electron-rich and the oxidatively-added intermediate becomes too stable, resulting in difficulty with the immediately-followed reductive elimination step. For the one-step four-center process, the metathesis reaction can be promoted when G is able to interact simultaneously with A and E in the transition state. In the following sections, we will provide examples to discuss the implication of the reaction mechanisms and to see how different A, G and E affect the metathesis barrier(s).

3. Oxidatively-added transition states

As mentioned above, with a proper combination of ligands and metal centers, oxidatively-added species can be a transition state instead of an intermediate for the metathesis reactions shown in Eq. (1). Sabo-Etienne, Chaudret and co-workers reported a ruthenium-assisted reversible proton transfer from an aromatic carbon to a hydride (Fig. 1(a)) [17]. DFT calculations on model complexes showed that the proton transfer involves a metathesis process with a one-step oxidative addition (Fig. 1(b)) [17].

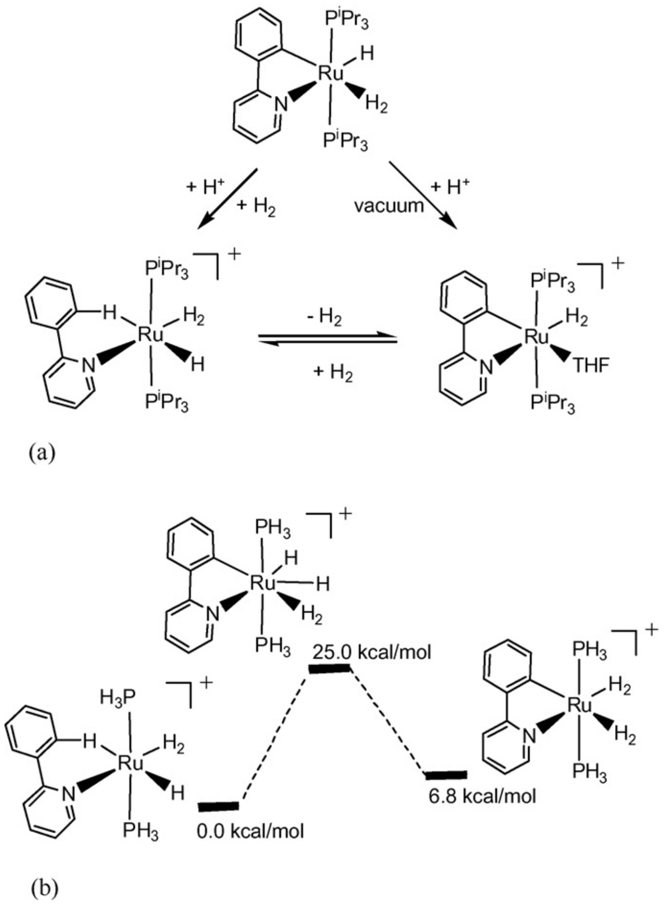


Fig. 1. (a) Protonation of $RuH(H_2)(o\text{-}C_6H_4py)(P^iPr_3)_2$ in THF. (b) The relative electronic energies (ΔE) on the basis of DFT calculations on the model complexes related to the equilibrium step shown in (a).

In our studies on the H/D exchange reactions between CH_4 and some deuterated organic solvents - benzene-d_6, tetrahydrofuran-d_8, diethyl ether-d_{10}, and dioxane-d_8 catalyzed by $[TpRu(PPh_3)H]$, we also found that the mechanism involves a metathesis process with a one-step oxidative addition [6]. Fig. 2 shows the potential energy profiles calculated for the hydrogen exchange processes. The starting σ-complex [Ru](H) (η^2-H–R) (here $[Ru] = TpRu(PH_3)$) undergoes an oxidative addition, giving $[Ru](H)_2R$ as the transition state for the formation of the intermediate η^2-H_2 σ-complex. The rotation of the η^2-H_2 ligand in the intermediate gives the same intermediate by exchanging the positions of the two hydrogen atoms in the η^2-H_2 ligand. The intermediate then passes through the dihydride transition state, completing the hydrogen exchange.

Recently, Periana, Goddard and co-workers reported experimental and theoretical studies on Ru- and Ir-catalyzed arene C–H addition across the double bond of an olefin [18]. A general mechanism, which involves mainly an olefin insertion step and a σ-bond metathesis process, for the metal-catalyzed reactions is illustrated in Fig. 3(a). Fig. 3(b) shows the potential energy profiles related to the metathesis step. Again, we see that both the Ru and Ir systems involve a one-step oxidation addition for the metathesis step. The one-step oxidative addition process has also been referred as oxidative hydrogen migration (OHM) [18]. More recently, the same team reported Ir-catalyzed hydrovinylation of olefins via a mechanism, similar to the one shown in Fig. 3(a), which involves olefin CH bond activation and insertion into a metal-vinyl intermediate [19]. The olefin

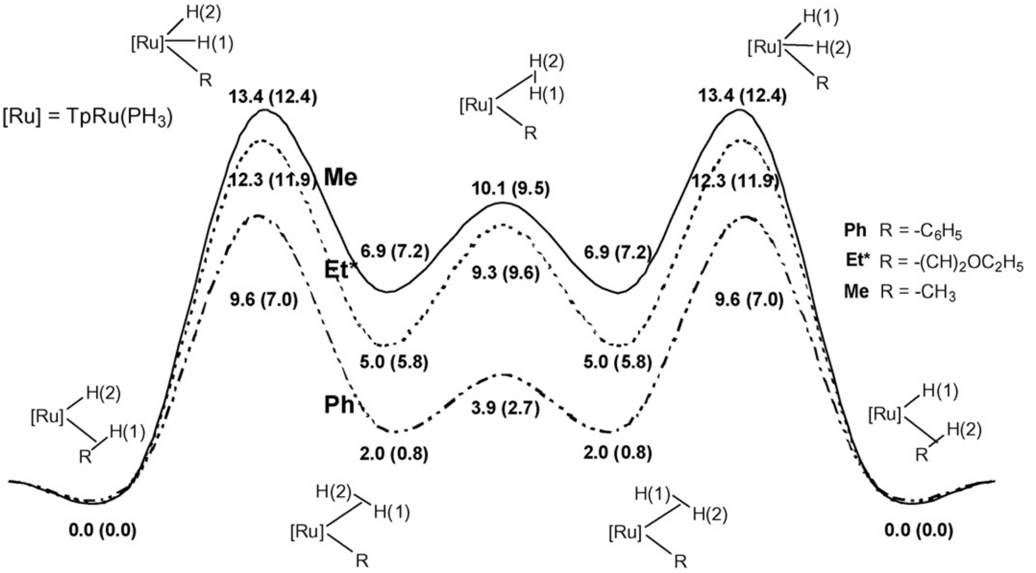


Fig. 2. Potential energy profiles for hydrogen exchange reactions catalyzed by $TpRu(PH_3)H$. Pathway Ph represents the exchange between the hydride and hydrogen atoms of benzene. Pathway Et* is for the exchange between the hydride and hydrogen atoms of diethyl ether. Pathway Me gives the exchange between the hydride and hydrogen atoms of methane. The relative electronic energies (ΔE) are given in kcal/mol. The values in parentheses are relative free energies (ΔG at 298.15 K). (Adapted from ref. [6]).

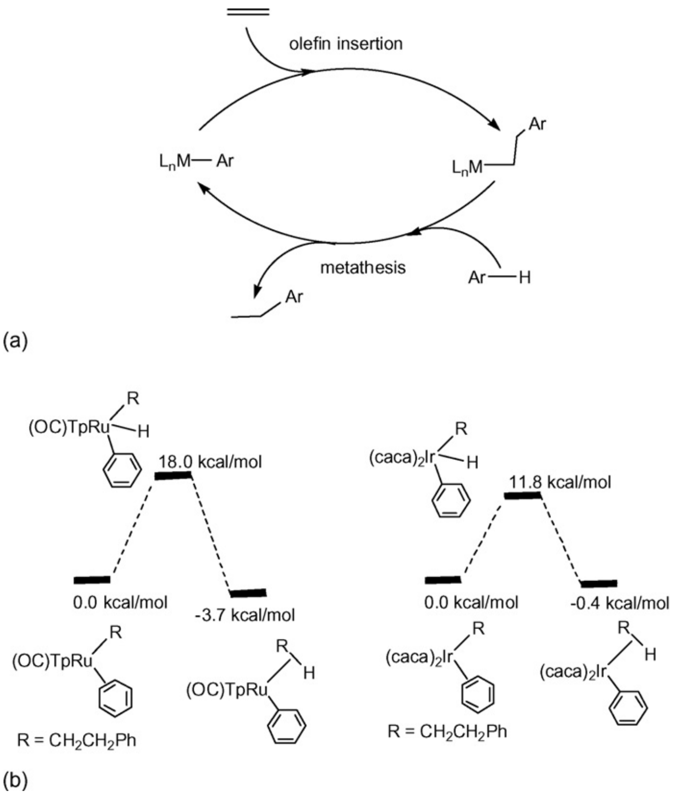


Fig. 3. (a) A general mechanism for metal-catalyzed C–H bond addition across an olefin double bond. (b) Potential energy profiles related to the metathesis step showing the one-step process with oxidatively-added species as the transition states. The energies are solvent corrected enthalpies at 0 K (see ref. [18] for more details).

CH bond activation again involves a σ-bond metathesis that can be characterized as a one-step oxidative addition.

In all the transition state structures discussed above, the hydride–hydride and hydride–alkyl distances are ca. 1.6 Å or greater, suggesting that they are indeed species derived from oxidation addition. Among the four examples shown in Figs. 1–3, three are ruthenium-related. These transition states have Ru(IV) metal centers. The osmium and iron metals do not behave the same because Os(IV) is expected to be relatively more stable while Fe(IV) is expected to be much less stable. The remaining example is iridium-related. In this example, the Ir(V) metal center is present in the transition state. This example is very interesting. It suggests that a proper ligand environment can make Ir(V) present in a transition state instead of an intermediate as found in many other Ir-mediated reactions [9,11].

In the theoretical study of reaction pathways for the rhodium phosphine-catalyzed borylation of C–H bonds with pinacilborane, we also found that the metathesis reaction of $L_2Rh(H)(\eta^2\text{-HBpin}) \rightarrow L_2Rh(Bpin)(\eta^2\text{-}H_2)$ (L = phosphine) proceeds via a one-step process with an oxidatively-added transition state $L_2Rh(H)_2(Bpin)$, which has a Rh(III) metal center [20].

4. Various metathesis processes

4.1. d^0 Early transition metal or rare-earth metal complexes

In the four-center transition states shown in Schemes 1–3, one may notice that the transferring atom is a hydrogen atom. The spherical property of hydrogen 1s orbital allows effective orbital overlap with the orbitals from the other three centers, stabilizing the four-center transition state [8a]. Systematic studies of $Cp_2Ln\text{-}H + H\text{–}AH_3 \rightarrow Cp_2Ln\text{-}AH_3 + H\text{–}H$ versus Cp_2Ln-H

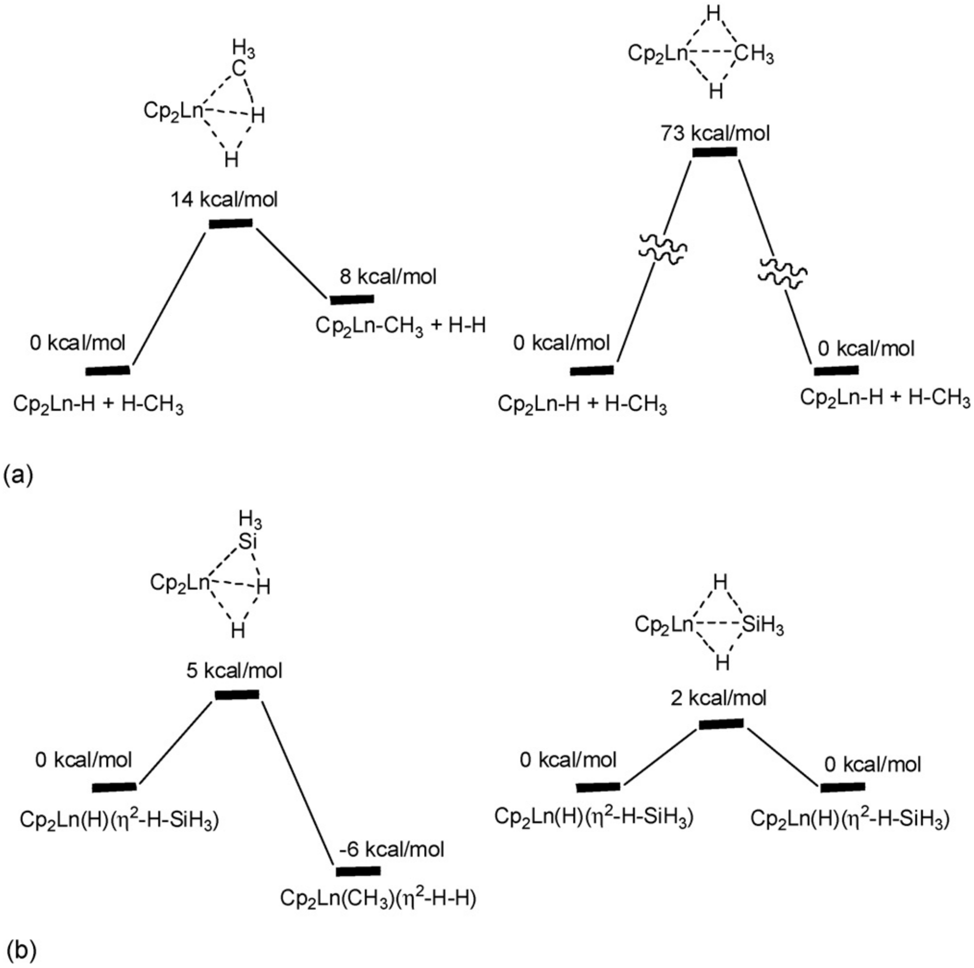
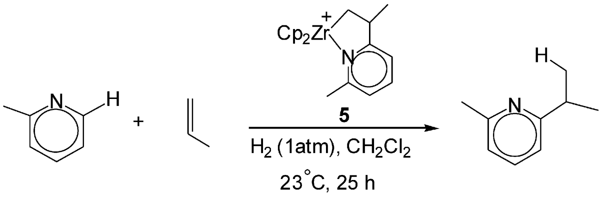


Fig. 4. Comparison between the metathesis barriers of (a) Cp_2Ln-H + H–CH_3 → Cp_2Ln-CH_3 + H–H vs. Cp_2Ln-H + H–CH_3 → Cp_2Ln-H + H–CH_3, and (b) Cp_2Ln-H + H–SiH_3 → Cp_2Ln-SiH_3 + H–H vs. Cp_2Ln-H + H–SiH_3 → Cp_2Ln-H + H–SiH_3. Ln represents a lanthanide metal. The energy data were taken from ref [12a,e]. (a) Gives the relative free energies (ΔG) at 298.15 K [12a] while (b) gives the relative electronic energies (ΔE) [12e]. Entropy contribution is expected to be small in the reactions shown in (b) because number of the reactant and product molecules is equal.

+ H–AH_3 → Cp_2Ln-H + H–AH_3 (Ln = lanthanide metals; A=C, Si) by Eisenstein and co-workers give interesting results [12a,e]. Fig. 4 compares the metathesis barriers. The barrier difference is remarkable between Cp_2Ln–H + H–CH_3 → Cp_2Ln-CH_3 + H–H and Cp_2Ln–H + H–CH_3 → Cp_2Ln-H + H–CH_3. The former has a transferring H atom while the latter has a transferring methyl group. The barrier difference is about 60 kcal/mol in favor of the one having H as the transferring atom (Fig. 4(a)). Interestingly, when the transferring methyl group is replaced with a silyl SiH_3 group, both the metathesis processes are possible and have small barriers (Fig. 4(b)). More interestingly, the reactivity preference has been reversed, favoring SiH_3 as the transferring group. The ability of the silicon center to become hypervalent, which allows the silicon center to interact with both the hydrogen centers in the transition state, explains the considerably low metathesis barrier calculated [12e]. An earlier study of the H/H exchange, Cp_2Ln-H + H–R → Cp_2Ln-H + H–R, on the basis of EHMO calculations concluded that the exchange is easier for R = aryl than for R = alkyl because an sp^2 carbon can better stabilize the [H–R–H] moiety in the assumed four-center transition state [21a]. The π orbitals of the aryl ring in the assumed four-center transition state were expected to interact simultaneously with the two H atoms, stabilizing the four-center transition state. However, a recent DFT study on perfluoroarenes showed that a transition state having an C_6F_5 as the transferring group does not exist, suggesting that this kind of transition state structure is energetically unfavorable [21b].

As mentioned above, the spherical property of hydrogen 1s orbital helps to stabilize a four-center transition state. Introducing an additional hydrogen atom in the four-center transition state also helps significantly. Fig. 5 shows the energy profiles for $Cp_2Sc(Me)(\eta^2$-H–$CH_3)$ → $Cp_2Sc(Me)(\eta^2$-H–$CH_3)$ and $Cp_2Sc(Me)(\eta^2$-H–H) → $Cp_2Sc(H)(\eta^2$-H–$CH_3)$. One can see that introducing an additional hydrogen atom significantly lowers the metathesis barrier.



(2)

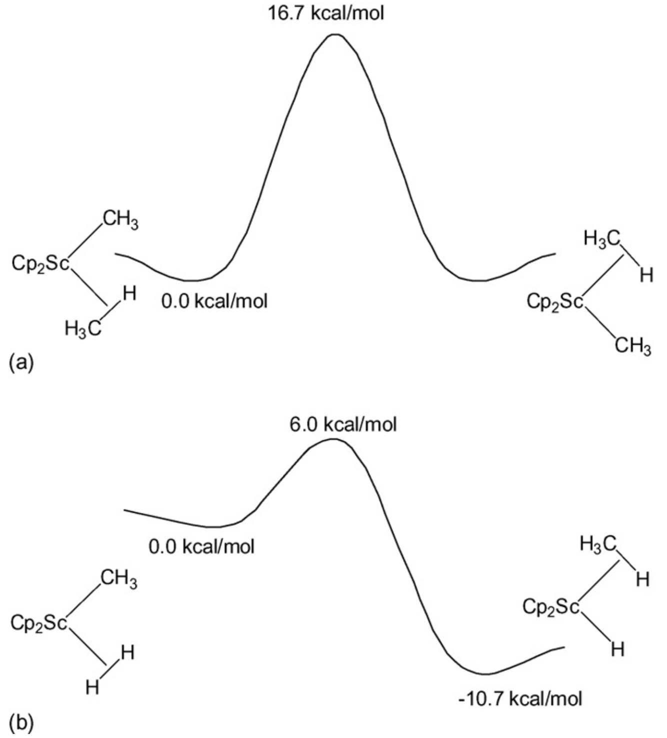
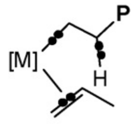


Fig. 5. Energy profiles for (a) $Cp_2Sc(Me)(\eta^2\text{-H–CH}_3) \rightarrow Cp_2Sc(Me)(\eta^2\text{-H–CH}_3)$ and (b) $Cp_2Sc(Me)(\eta^2\text{-H–H}) \rightarrow Cp_2Sc(H)(\eta^2\text{-H–CH}_3)$. The energy data ($\Delta E$) were taken from ref. [8a].

The zirconocene-catalyzed addition of the ortho C–H bond of α-picoline to propene (Eq. (2)) reported by Jordan and co-workers demonstrates the importance of introducing additional hydrogen [22]. In the catalytic reaction, H_2 acts as a co-catalyst, i.e., it is required for the reaction to proceed but it is not consumed. A theoretical study on the reaction mechanism found that H_2 plays a crucial role in this catalytic process [23]. In the absence of H_2, following the insertion of propene into the Zr–C bond of the η^2-pyridyl complex $Cp_2Zr(\eta^2\text{-2-Me-6-pyridyl})^+$, a direct four-center σ-bond metathesis reaction of **5** with α-picoline might proceed to regenerate the η^2-pyridyl complex (Fig. 6(a)). However, the barrier for the metathesis process is inaccessibly high (Fig. 6(a)). Introduction of H_2 splits the inaccessible four-center σ-bond metathesis step involving **5** and α-picoline into two accessible four-center σ-bond metathesis steps, one being the hydrogenolysis of **5** by H_2 and the other being the release of H_2 via C–H activation of a hydride-alkyl complex (Fig. 6(b)). The involvement of H_2 makes these four-center transition states energetically accessible because the spherical character of the H 1s orbital increases the orbital overlap and the small size of H alleviates steric crowding.

In olefin polymerization catalyzed by d^0 early transition metal complexes, the most accepted chain termination mechanism can also be described as a metathesis process involving C–H bond activation (path A of Scheme 5) [24]. The transition state ($\mathbf{TS_A}$) shows a strong bonding interaction between the metal center and the transferring hydrogen, similar to those discussed in Section 2.3. The metathesis processes mediated by d^0 early transition metal complexes discussed in Section 4.1 involve electron redistribution of two pairs of electrons. However, the metathesis process here involves three pairs of electrons (see **6**).



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Possibly because of involvement of an additional electron pair, a very recent study showed existence of a new pathway involving a direct hydrogen transfer without a strong metal-hydrogen bonding interaction (path B of Scheme 5) [25]. The study also showed that path B becomes a strongly preferred path in cases where steric constraints block the “classical” path A [25]. The ligand spread angle formed by the two metal-bonded carbons in $\mathbf{TS_B}$ is smaller than that in $\mathbf{TS_A}$.

4.2. Late transition metal complexes

In 1994, Hartwig et al. reported that addition of catecholborane (HBcat) to $Cp(L_2)RuMe$ in arene solvent at room temperature led to quantitative formation of a ruthenium hydride and methylcatecholborane (MeBcat) in less than 30 min (Eq. (3)) [26]. Careful kinetic studies allowed Hartwig and co-workers to conclude that the transition state involves a four-center structure, analogous to the transition states involved in σ-bond metatheses for d^0 metal centers (Scheme 6). The experimental data also allowed them to rule out the possibility of phosphine dissociation and to argue strongly against a ring slip mechanism. A Lewis structure describing the four-center transition state is presented here in Scheme 6. One very interesting question is: why does not the reaction, shown in Eq. (3), give a metal-boryl complex and CH_4. In the metathesis reaction observed, the transferring group is Bcat not H. The experimental observation indicates that in addition to hydrogen, boryl is also a good transferring group in a four-center transition state. This is because the “vacant” orbital present in a boryl group, providing the situation that the transferring group can interact simultaneously with H and Me in the transition state. Another important reason is as follows. Since, phosphine dissociation has been ruled out [26], the complex $Cp(L_2)RuMe$ is an 18e species and can only interact with the “vacant” orbital on the boron center of HBcat.

$$Cp(PPh_3)_2RuMe + HBcat \rightarrow Cp(PPh_3)_2RuH + MeBcat \tag{3}$$

In 1990s, Hartwig and co-workers found that the transition metal boryl complexes $Cp^*M(CO)_{n+1}(\text{boryl})$ ($n = 1$: M = Fe, Ru; $n = 2$: M = W; boryl = Bcat or Bpin) can efficiently and selectively functionalize alkane C–H bonds after photodissociation of one CO ligand [27] and that $Cp^*Re(CO)_3$ can catalyze borylation of alkanes with B_2pin_2 under photochemical conditions [28]. Photodissociation of one CO ligand from $Cp^*M(CO)_{n+1}(\text{boryl})$ generates a coordinately unsaturated 16e intermediate, which can be trapped with phosphine. In the absence of phosphine, the intermediate readily cleaves and functionalizes a terminal alkane C–H bond or an arene C–H bond (Scheme 7). The

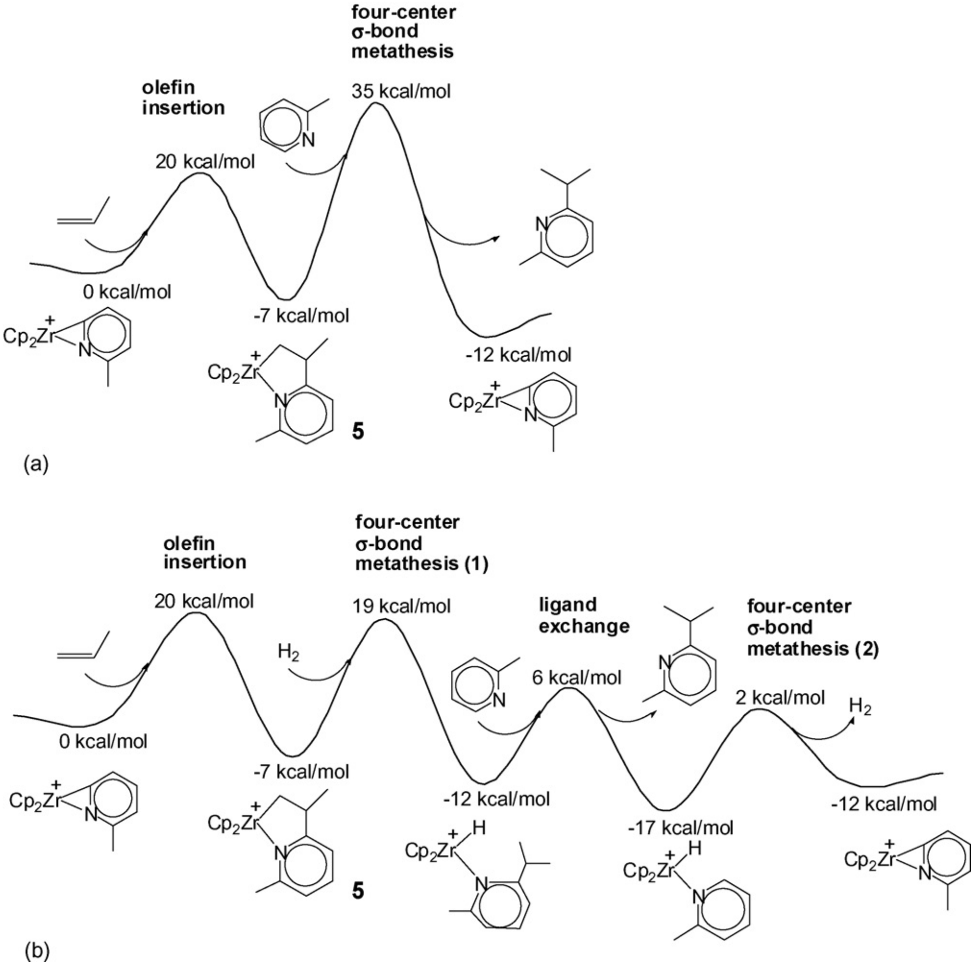
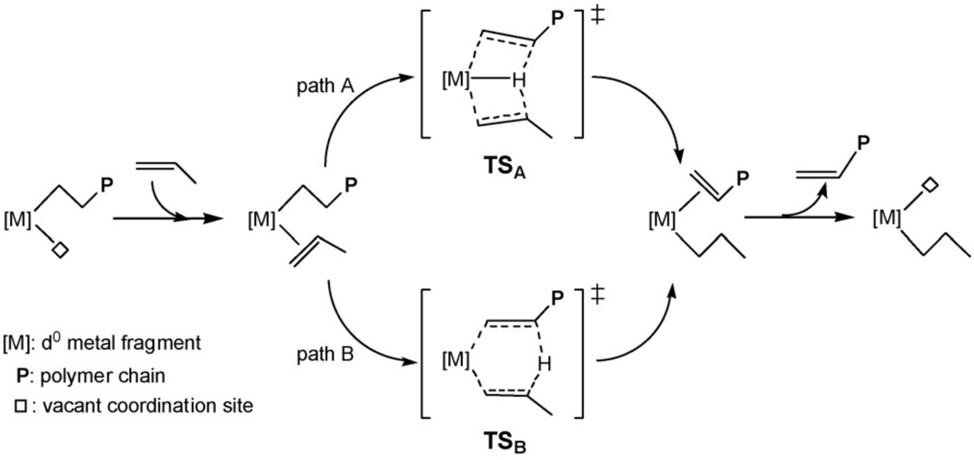
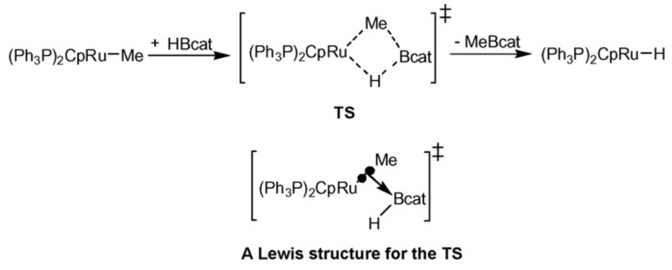


Fig. 6. (a) Energy profile for the catalytic reaction shown in Eq. (2) in the absence of H_2. (b) Energy profile for the catalytic reaction shown in Eq. (2) in the presence of H_2. The energy data (relative free energies ΔG at 298.15 K) were taken from ref. [23].

related complexes of alkyl and aryl ligands, $CpM(CO)_{n+1}R$, do not show a similar reactivity [29]. The boryl ligands are clearly important in the reactions. Theoretical calculations at the B3LYP level of density functional theory allow a reaction mechanism, shown in Scheme 8, to be defined [29]. The reaction mechanism consists of two one-step metathesis processes and σ-borane intermediates play important roles. Interestingly, the first one-step metathesis process involves an oxidatively-added transition state while the second one-step metathesis process involves a four-center transition state (see the structural details given in the supporting information of ref. 29). Different transferring atoms (groups) involved give transition states of different



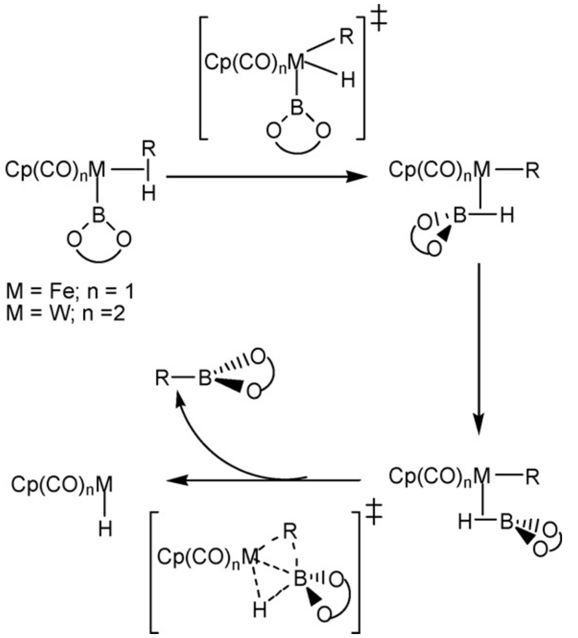
Scheme 5.



Scheme 6.

nature. Clearly, when the boryl ligand acts as the transferring group, a four-center structure is preferred. This feature is closely related to the “empty” p orbital, i.e., the Lewis acidity, of the boron center in the transferring boryl group. The four-center transition state here is different from the four-center transition state shown in Scheme 6. The four-center transition state here is an 18e species while the four-center transition state shown in Scheme 6 is a 20e species when the B–H σ bonding electron pair is included. Metal fragments of tungsten are normally expected to mediate C–H bond activation via oxidative addition followed by reductive elimination. The example given here shows a one-step process having an oxidatively-added transition state and demonstrates that ligands can also play a determining role in the choice of the reaction paths. Presence of the two carbonyl ligands reduces the ability of the tungsten metal center being oxidized, making the oxidatively-added species as a transition state even with a tungsten metal center.

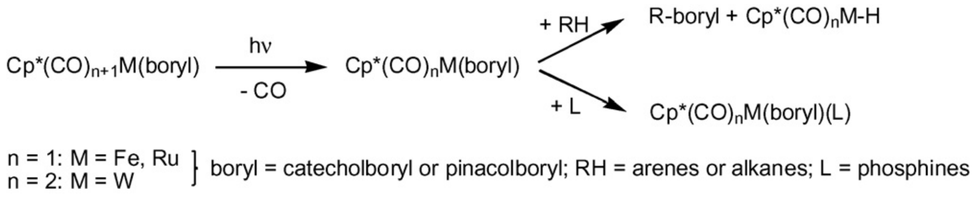
In the photochemical reactions of the metal-boryl complexes with various hydrocarbons [27b–d], the tungsten boryl complexes Cp*W(CO)$_3$Bcat’ are reactive toward both alkanes and arenes. However, the reactivities of the iron boryl complexes Cp*Fe(CO)$_2$(Bcat) and CpFe(CO)$_2$(Bcat) are distinctly different toward the two types of substrates; these complexes are very reactive toward the aromatic C–H bonds of arenes and are unreactive toward the alkane C–H bonds. We carried out DFT studies on the metathesis (borylation) reactions of CpM(CO)$_n$(Bcat)(η^2-HR) → CpM(CO)$_n$(H)(η^2-RBcat) (M = Fe, n = 1; M=W, n = 2; R = Me, Ph) [30] and found that the borylation by the Fe boryl complex favors a one-step mechanism with an oxidatively-added transition state (Fig. 7(a)), while borylation by the tungsten boryl complex only proceeds by a two-step mechanism (Fig. 7(b)). The significant barrier difference between the two Fe systems (Fig. 7(a)) and the small barrier difference between the two W systems (Fig. 7(b)) explain the experimental observations. The distinct barriers between borylation of methane and benzene by the Fe complex have been related to the significant stabilization interaction between the “empty” boron p orbital of the boryl group and the π orbitals, which accommodates the π electrons, of the benzene ring in the oxidatively-added transition state for the iron-benzene system. The type of B–C interaction is not important in the borylation of benzene by the tungsten boryl complex because of the two-step reaction mechanism. The metathesis reactions via the slightly more complicated mechanism, defined as a boron-assisted σ-bond metathesis [29], shown in Scheme 8, were found to have slightly smaller barriers by 2–3 kcal/mol than the direct metathesis shown in Fig. 7. Nevertheless, we believe that the concept of invoking the additional B(boryl)...C(phenyl) interactions to stabilize the transition state should have a significant impact in the future design of effective catalysts.



Scheme 8.

A recent study on the C–H bond activation mediated by the Cp*Rh(X)(Bpin) (X = H, Bpin) fragments showed that various metathesis processes involved are one-step and the relevant transition states are species in between an oxidatively-added structure and a four-center structure [31].

For late transition metal mediated metathesis reactions, another interesting scenario is shown in Scheme 9 in which the lone pair of the ligand X is involved in the metathesis [13]. Siegbahn and Crabtree studied theoretically the mechanism of the Shilov reaction [32] and suggested that the activation of alkane C–H bonds by Pt salts proceeds via transfer of a hydrogen atom from a methane σ complex to a neighboring Cl ligand, described as a σ-bond metathesis [33]. The



Scheme 7.

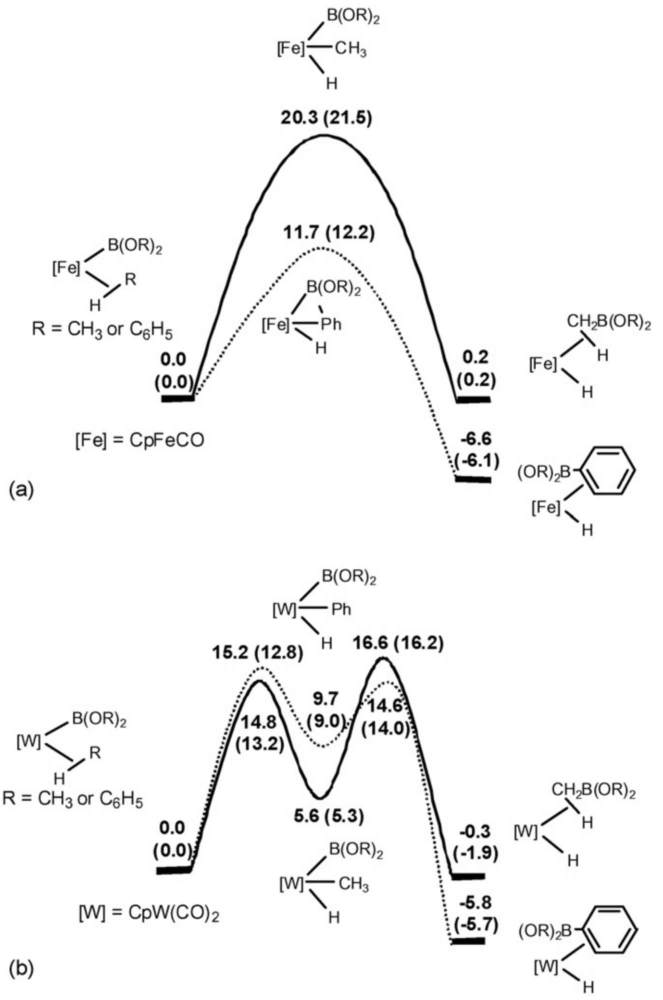
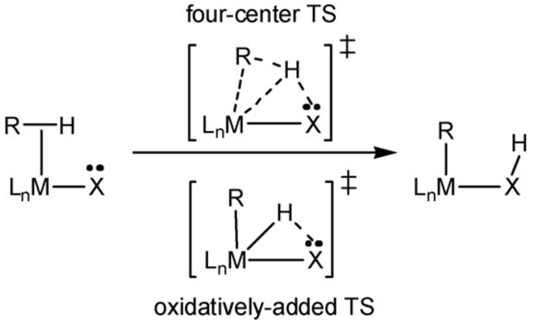
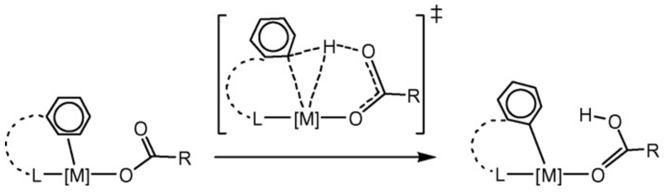


Fig. 7. The relative electronic energies (ΔE) together with the relative free energies (ΔG) at 298.15 K (in parentheses) related to the borylation of methane and benzene by (a) $CpFe(CO)B(OR)_2$ and (b) $CpW(CO)_2B(OR)_2$ $[(OR)_2 = O_2C_2H_2]$. The relative energies are given in kcal/mol. (Adapted from ref. [30]).

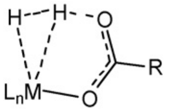
transition state calculated for the σ-bond metathesis [33] has the feature of an oxidatively-added species (see Scheme 9). When related metathesis reactions are mediated by metal fragments having a less electron-rich metal center, four-center transition states (Scheme 9) can be found. For example, four-center transition states were found in the metathesis reactions of $(Me)(NH_3)Pd(CH_4)(OMe) \rightarrow (Me)(NH_3)Pd(CH_3)(HOMe)$ [34a], $(Cl)(NH_3)Pd(H_2)(OH) \rightarrow (Cl)(NH_3)Pd(H)(H_2O)$ [34a], and $(PH_3)_2Rh(H_2)(OAc) \rightarrow (PH_3)_2Rh(H)(HOAc)$ [34b–c,35a]. Recent studies on CH bond activation with an O-donor Iridium methoxo complex [34d] and H/D exchange between $TpRu(PMe_3)_2X$ (X = OH, OPh) and deuterated arene solvents [34e] also suggest that four-center metathesis processes are involved. The metathesis involved the OAc ligand proceeds more favorably via a one-step, six-center σ-bond metathesis transition state shown in **7** [35].



Scheme 9.



Scheme 10.

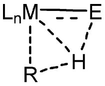


7

Several recent computational studies [36] showed that one-step six-center σ-bond metathesis transition states (Scheme 10) are commonly found in arene C–H bond activation mediated by Pd(II) or Pt(II) or Ir(III) complexes containing carboxylate ligands.

4.3. 1,2-Addition across metal-ligand multiple bonded functionalities

Addition of an alkane to a metal-nonmetal double bond is not an exact metathesis reaction. However, it is one of important strategies that can lead to C–H bond activation reactions [1] and the relevant transition states have four-center structures. An example of methane addition across a Zr–N double bond (Eq. (4)) has been reported [37]. Alkane additions across M=N and M=C bonds of various early and middle transition metal centers are also known [38–41]. Theoretical calculations [40,41] show that the transition states have the four-center structural feature with a transferring hydrogen, shown in **8**.



8

$$(R'NH)_3ZrR \xrightarrow[\Delta]{RH} (R'NH)_2Zr{=}NR' \xrightarrow{CH_4} (R'NH)_3ZrCH_3 \qquad (4)$$

5. Concluding remarks

In this article, we have reviewed the current understanding of the metathesis reactions of $L_nMR + R'–H \rightarrow L_nMR' + R–H$, which are important fundamental reactions in organometallic chemistry and catalysis. Despite the simplicity of the reactions formulated in the chemical equation, there are rich mechanistic features. Early understanding of the reactions, which includes a two-step process with an oxidative addition giving an intermediate followed by a reductive elimination of R–H and a one-step process with a four-center σ-bond metathesis transition state, is apparently incomplete. We expect that there is a monotonous evolution of the mechanisms from one to the other. In this review, we pointed out the existence of another mechanism that has a one-step process with an oxidatively-added transition state. The rich mechanistic features are related to the environment of the metal center. In this review, we have also given several examples, which are related to catalytic reactions, to illustrate the importance of understanding the reaction mechanisms.

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