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Mechanistic aspects regarding the formation of metal vinylidenes from alkynes and related reactions

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Abstract

This review focuses on the tautomerization mechanism between alkynes and vinylidene units taking place in the coordination sphere of transition metal fragments. Reactions of vinylidene complexes as well as catalytic reactions involving a metal-vinylidene intermediate are also reviewed from the mechanistic point of view.
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1. Introduction

Metal vinylidenes are easily accessible by addition of alkynes to appropriate metal complexes, and this provides one of the easiest routes to species with a metal carbon double bond. Indeed, vinylidene complexes have been claimed to be easily available and active precursors that trigger catalytic olefin metathesis reactions [1–4]. Also, a number of catalytic reactions involving alkyne reactants have been suggested to proceed via metal vinylidene intermediates [5]: for example, regio- and stereo-specific dimerization [5], polymerization [6], addition of various nucleophiles [7], insertion into aromatic C–H bond [8], and dienone-electrocyclizations [9].

Successful use of metal vinylidenes or vinylidene intermediates in synthetic organic chemistry has been promoted by the organometallic chemistry of vinylidene complexes. Synthesis and reactions of metal vinylidene complexes have shown a great deal of development during the past few decades. After publication of the early review by Bruce [10], many researchers including Werner's group have further explored a variety of vinylidene complexes of different metals with various kinds of auxiliary ligands [11]. Among several known means to prepare metal vinylidene complexes, the isomerization of an

η^2-alkyne to vinylidene ligand has attracted particular interest as a model for key steps occurring in a number of catalytic reactions, but it is also interesting in its own light from the perspective of organometallic reactions of simple unsaturated molecules. A modern trend in such research activity appears to be increasing attention to mechanistic feature of the reactions, probably encouraged by recent rapid growth of computational and theoretical chemistries. In the present article, we survey mechanistic and theoretical investigations of alkyne to vinylidene tautomerization taking place on various metal fragments and further reactions of thus formed metal vinylidenes. This review, however, will not discuss dinuclear and polynuclear μ-vinylidene complexes.

2. Bonding

Based on molecular orbital calculations performed on d^6-electron metal complexes $[CpFe(CO)_2(=C=CH_2)]^+$, $[CpFe(PH_3)_2(=C=CH_2)]^+$, and $CpMn(CO)_2(=C=CH_2)$ [12,13], and additionally on d^8-electron $IrCl(PH_3)_2(=C=CH_2)$ and $CpRh(PH_3)(=C=CH_2)$ complexes [14], a schematic drawing of frontier orbital interactions between a metal fragment and its vinylidene ligand may be deduced as presented in Fig. 1. The interaction diagram in $TpRuCl(PPh_3)(=C=CHPh)$
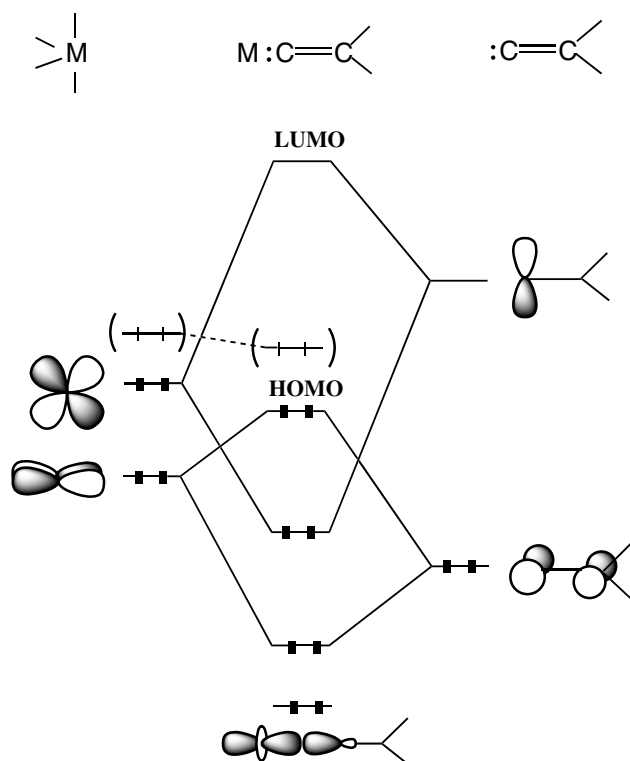
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Fig. 1. Simplified interaction diagram for vinylidene complexes.

(Tp = hidrotris(pyrazolyl)borate) calculated by Kirchner and coworkers [15] was essentially similar. In these cases, the LUMO has exclusively large contribution from the empty p orbital located at the vinylidene Cα with some portion of the metal dπ-orbital, interacting each other in anti-bonding manner as a counterpart of the back-donation interaction. Together with low-lying σ-donative interaction of lone-pair electrons at Cα with the metal dσ-orbital, the metal-Cα local bonding scheme is similar to those of metal-CO and metal-carbene bonds. The HOMO is in most cases derived from four-electron interaction between a filled metal dπ-orbital and the π-orbital of CC double bond of the vinylidene fragment. However, when the central metal has enough d-electrons (e.g., some low-valent late transition metals), the HOMO might well be a non-bonding metal d-orbital as shown by parenthesis in Fig. 1. This situation sometimes gives rise to complicated regio-selectivity in electrophilic addition to vinylidene complexes as will be discussed later.

According to DFT calculations of trans-[RhF(PMe$_3$)$_2$(=C=CH$_2$)], LUMO in this complex is pz of Cα, as expected, with small anti-bonding contribution from a Rh dπ-orbital, whereas the HOMO is mainly composed of dz^2 orbital of Rh [16]. Examination of the ν(Rh=C) band at around 570 cm^{-1} in FT-Raman spectroscopy of a series of similar complexes has shown that the vinylidene group is a better σ-donor and less effective π-acceptor as compared to CO ligand.

Using quantum mechanical ab initio methods, Frenking analyzed the C$_2$H$_2$ unit ligating to a high oxidation state metal, i.e., the bonding in MX$_4$(C$_2$H$_2$) complexes (M = Mo, W, X = F, Cl) [17]. The results suggest that the vinylidene ligand is a stronger acceptor (weak donor) than chlorine and the metal can be viewed to have d^0 electron configuration, i.e., in +VI formal oxidation state rather than +IV. The metal carbon bond here and probably those in electron poor early transition metal vinylidene complexes in general, may better be regarded as a double bond in a literal sense rather than donation and back-donation interaction shown in Fig. 1.

## 3. Interconversion between a coordinated alkyne and vinylidene

It has been well known that in the coordination sphere of transition metals, one of the hydrogens or substituents of an η^2-coordinated alkyne can undergo 1,2-shift to generate a vinylidene ligand. Often, the backword reaction is also observed (Scheme 1). The most common migrating species is hydrogen, but regarding the alkyne to vinylidene isomerization, migration of SiR$_3$ [18–22], SnPh$_3$ [23], SMe [24], and iodine [25] have also been known. The irreversible isomerization of vinylidene ligand in [CpFe(CO)$_2$(=C=CR^{1}R^2)]$^+$(R^1, R^2 = Me, Ph) to form the corresponding η^2-alkyne complex [CpFe(CO)$_2$ (R^{1}C≡CR^2)]$^+$ was observed by means of NMR spectroscopy above −50 °C, where the higher migrating ability of the Ph than Me group was noted [26].

The vast majorities of the studies carried out to examine the mechanism of this interesting rearrangement are concerned with terminal alkynes and unsubstituted parent acetylene. The isomerization routes commonly discussed in the literature are summarized in Scheme 2(a). For concerted migration of the hydrogen atom, two alternative pathways have been proposed: either direct 1,2-hydrogen shift over the CC triple bond (A ⇌ T$_{12}$ ⇌ V) or 1,3-hydrogen shift from the metal to Cβ via a hydride–alkynylmetal intermediate (A ⇌ B ⇌ T$_{13}$ ⇌ V). A stepwise deprotonation/protonation process (dashed straight arrows in Scheme 2(a)) should also be taken into consideration particularly in protic solvents.

In a specific case where the central metal bears hydride, a new route to vinylidene from coordinated 1-alkyne was observed (Scheme 2(b)) [27]. The initially
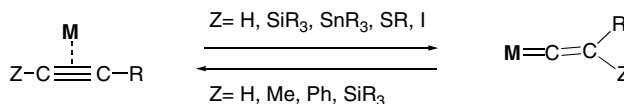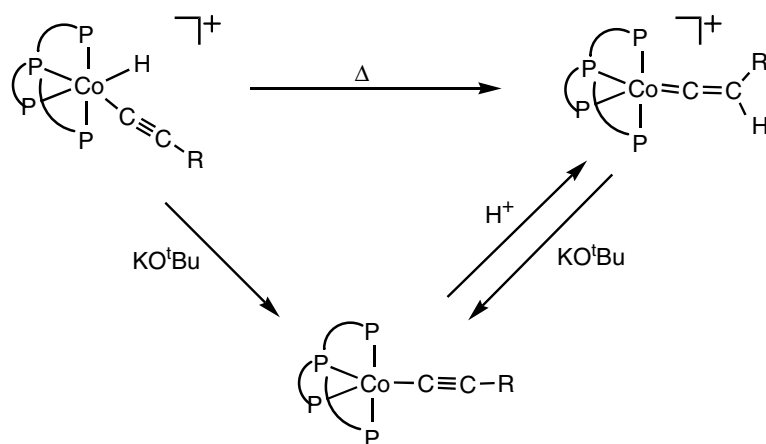

Scheme 1.
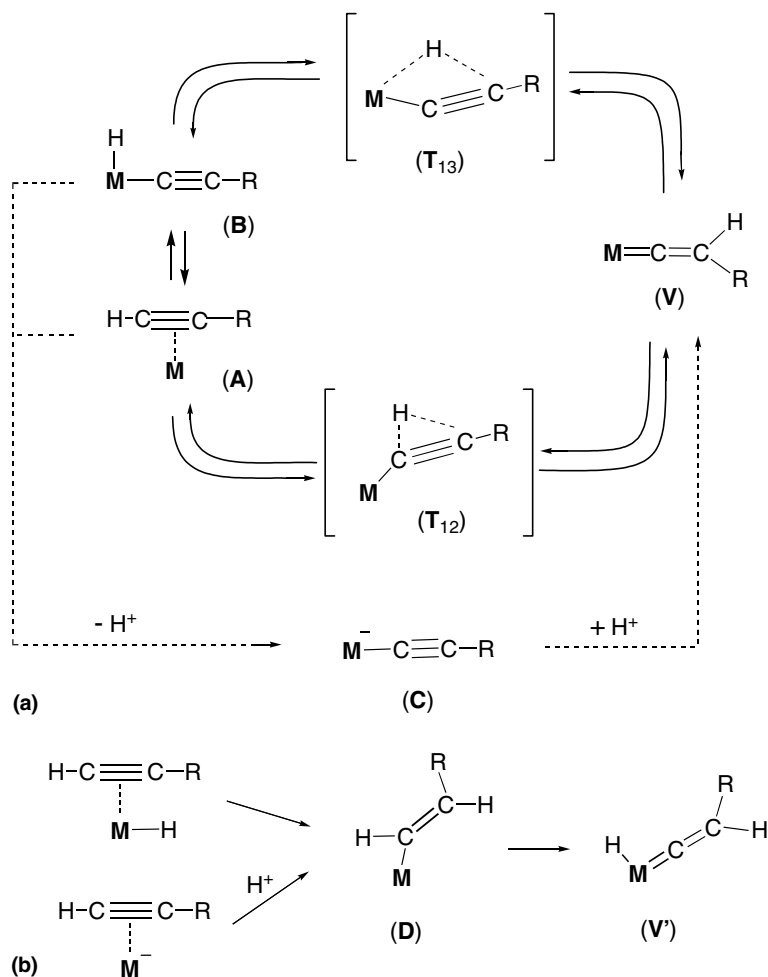
Scheme 2.

η^2-coordinated 1-alkyne inserts into the M–H bond to form the vinyl complex **D**, the α-hydrogen of which then migrates to the metal center to give eventually hydride–vinylidene complex **V'**. Alternatively, **D** may be formed by direct protonation of the coordinated 1-alkyne.

3.1. Isolation or detection of complexes that have mechanistic implications

The dinitrogen Co(I) complex $[Co(PP_3)(N_2)]^+(PP_3 = P(CH_2CH_2PPh_2)_3)$ was reacted with 1-alkynes $HC{\equiv}CR$ to give two different products depending on R. With R = SiMe$_3$, the reaction gives exclusively a stable oxidative addition product cis-$[Co(PP_3)(H)(CCR)]^+$, whereas the same reaction gives vinylidene complexes $[Co(PP_3)({=}C{=}CHR)]^+$ when R = H and Ph [28]. If R = alkyls, a mixture of the oxidative addition product and the vinylidene complex was obtained. Besides, some η^2-alkyne complexes were detected spectroscopically. On heating (16–40 °C) acetone solutions, the hydride–alkynyl complexes isomerize to vinylidenes, showing

that the lattes are the thermodynamic products. The temperature at which this rearrangement occurs increases in the order R = SiMe$_3$ > Ph > H $\gg$ ^{t}Bu > ^{n}C$_3$H$_7$ $\cong$ ^{n}C$_5$H$_{11}$ and accordingly the electronic effects seem to prevail over steric ones in governing the tautomerization. This tautomerization was also found in the solid state at 30–90 °C, where a similar dependency of the necessary temperatures on the substituents R was noted. Deprotonation of the hydride–alkynyl complexes, as well as of vinylidene complexes was easily achieved by adding stoichiometric amount of KO^{t}Bu to give neutral σ-alkynyl complexes, which in turn, were protonated at the β-carbon with triflic acid to re-generate the vinylidene complexes. The reactions are summarized in Scheme 3. Taken these observations together, as well as the measured largely positive $\Delta S^{\ddagger}$ value (see Section 3.2) for the tautomerization of the hydride–alkynyl to vinylidene complexes, the most reasonable mechanism for the transformation seems to be the metal-proton dissociation in $[Co(PP_3)(H)(C{\equiv}CR)]^+$ and successive intra molecular migration of the proton to the Cβ of the alkynyl group. Analogous Rh fragment

Scheme 3.

$[Rh(PP_3)]^+$ reacted similarly with HC≡CR to give hydride–alkynyl complexes, but no further conversion to Rh(I)–vinylidene complexes was observed. This has been attributed to the greater strength of the Rh–H bond as compared to the Co–H bond.

In contrast to the ready oxidative addition of the acetylenic C–H bond across the d^8-electron Co(I) and Rh(I) metal centers as above, a similar reaction with d^6-electron metal center has been believed to be much more difficult. However, a Ru(II) system developed by Puerta and Valerga [29] with strongly electron donating ancillary ligands is able to afford hydride–alkynyl complexes of Ru(IV) when reacted with 1-alkynes. Thus, by the reaction of $Cp^*RuCl(PEt_3)_2$ with HC≡CH ($Cp^* = \eta^5\text{-}C_5 Me_5$), all three related complexes, i.e., $[Cp^*Ru(PEt_3)_2(\eta^2\text{-}HC\equiv CH)]^+$, trans-$[Cp^*Ru(PEt_3)_2(H)(C\equiv CH)]^+$, and $[Cp^*Ru(PEt_3)_2(=C=CH_2)]^+$ were isolated and spontaneous rearrangement of the former two to the most stable vinylidene complex could be monitored. But the easier way of converting the ligating η^2-alkyne to vinylidene form was deprotonation/protonation cycle (Scheme 4(a)). The reaction of mono-substituted alkynes HC≡CR gave the hydride–alkynyl complexes without detection of η^2-alkyne complexes. The rate of their successive isomarization to vinylidenes were in the order R = ^tBu > $SiMe_3$ > Ph > CO_2Me. The spontaneous rearrangement to vinylidene was also observed in the solid state.

A similar chemistry of the complex with a different phosphine ligand was studied by the same group [29]. Isolated hydride–alkynyl complexes trans-$[Cp^*Ru(dippe)(H)(C\equiv CR)]^+$, where R = $CO_2 Me$, Ph, $SiMe_3$ and dippe = 1,2-bis(diisopropylphosphino)ethane, isomerize to their vinylidene form in acetone solution at room temperature as in the analogous PEt_3 complexes. An important observation here has been that addition of small amounts of strong acids such as HBF_4 inhibits this spontaneous isomerization. This provides supporting evidence that the mechanism of the isomerization to

the vinylidene complex is initiated by dissociative deprotonation of the metal hydride followed by protonation at Cβ. The situation, however, is different in the rearrangement of acetylene HC≡CH: ^{31}P NMR monitoring has lead to the conclusion that the hydride–ethynyl complex first undergoes reductive elimination back to the η^2-HC≡CH complex, which directly isomerizes (via 1,2-H shift) to the stable vinylidene complex (Scheme 4(b)). In accord with this proposal, this isomerization does not seem to be inhibited by strong acids. Substitution of Cp^* by less electron-donating Cp, as expected, does not give any hydride–alkynyl complex but only the η^2-alkyne complexes. The isomerization of $[CpRu(dippe)(\eta^2\text{-}HC\equiv CR)]^+$ to $[CpRu(dippe)(=C=C(H)R)]^+$ observed by NMR was again not inhibited by strong acid. Hence, a direct 1,2-hydrogen shift in the coordinated alkyne unit appears to be operating in this standard complex.

When the coordinated 1-alkyne to vinylidene rearrangement takes place on $Os(H)Cl(CO)(P^iPr_3)_2$ moiety, scrambling of hydrogens accompanies [30]. Thus the reaction of $Os(D)Cl(CO)(P^iPr_3)_2$ with cyclohexylacetylene, HC≡C-Cy, gave a 1:1 mixture of $Os(D)Cl(CO)(P^iPr_3)_2(=C=CHCy)$ and $Os(H)Cl(CO)(P^iPr_3)_2(=C=CDCy)$. This phenomenon has been interpreted as indicated in Scheme 5.

While some complexes have been known to isomerize to vinylidenes in the solid state [28,31], the isomerization in low-temperature matrix has also been reported. Thus $Mo(CO)_5(\eta^2\text{-}HC\equiv CR)$ (R = H or Me) generated by photochemical reaction on Ar or CH_4 matrix, undergoes rearrangement to give what is believed to be a vinylidene complex $Mo(CO)_5(=C=C(H)R)$ [32].

In some cases, a metal σ-vinyl can be transformed to a metal η^1-vinylidene unit by transferring the hydrogen at Cα onto the metal. In an Ar matrix, photolysis of $CpIr(H_2C=CH_2)_2$ gave primarily the oxidative addition product $CpIr(H)(HC=CH_2)(H_2C=CH_2)$, which on further photolysis released free ethylene and the result-

Scheme 4.

[Os] : OsCl(CO)(PiPr₃)₂

Scheme 5.

L = P^{t}Bu₂Me
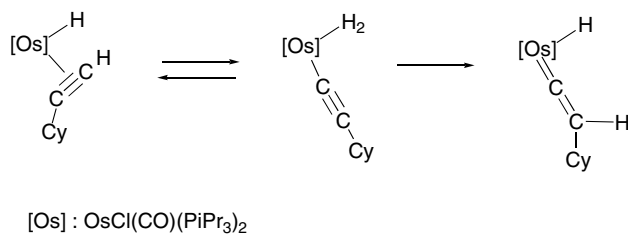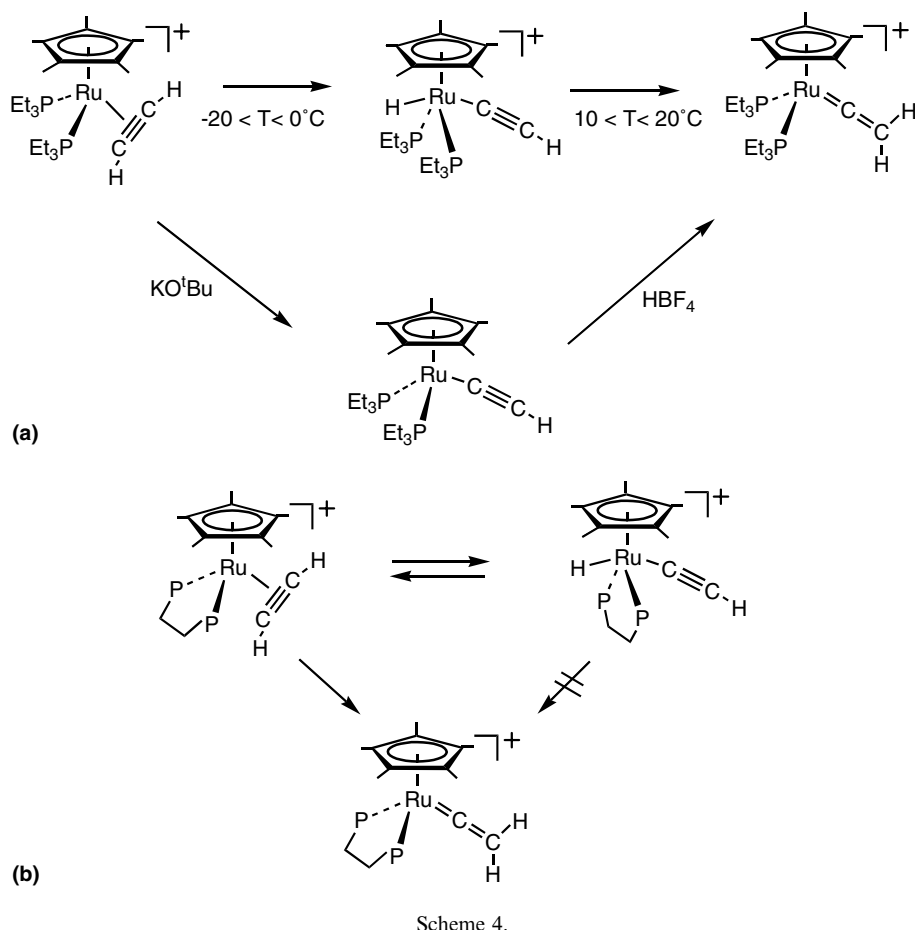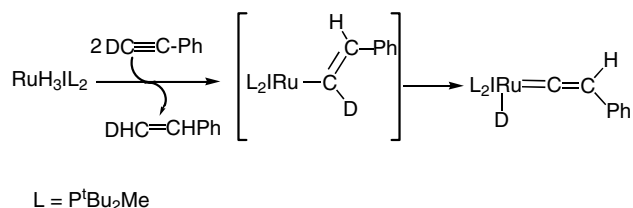
Scheme 6.

ing complex was identified as CpIr(H)₂(=C=CH₂) by IR spectra [33]. A similar transformation appears to be more common in early transition metal complexes [34]. Caulton and coworkers [27] have provided a proof for the mechanism of a similar rearrangement occurring in their Ru polyhydride complex: the reaction of Ru (H₃)I(P^{t}Bu₂Me)₂ with DC≡CPh yields exclusively Ru (D)I(P^{t}Bu₂Me)₂(=C=CHPh) through a pathway shown in Scheme 6.

3.2. Kinetics

In 1989, Bullock [35] reported the kinetic data for a 1-alkyne to vinylidene isomerization on ruthenium, i.e. the rearrangement of [CpRu(PMe₃)₂(HC≡CMe)]⁺ to [CpRu(PMe₃)₂(=C=CHMe)]⁺ in acetonitrile, which was monitored with absorption spectroscopy. The reaction was first-order at temperatures from 15 to 40 °C and gave parameters shown in Scheme 7(a). A closely related complex with chelating alkylphosphine ligand [CpRu(dippe)(HC≡CCO₂Me)]⁺ has parameters shown in Scheme 7b as determined by NMR spectroscopy. A large positive $\Delta S^{\ddagger}$ value was not discussed [29].

Ozawa and coworkers [36] were able to measure the activation parameters for both the forward and backward reactions between η^2-(silyl)(ferrocenyl)acetylene complex of square planar Rh(I) and its η^1-vinylidene isomer. Judging from the reasonably negative values of activation entropies along the reaction coordinate (Scheme 7(c)), the mechanism appears to involve direct 1,2-shift of the

(a) $\Delta H^{\ddagger} = 23.4 \pm 0.3$ Kcal/mol
$\Delta S^{\ddagger} = 3.9 \pm 0.9$ cal/mol·K

(b) $\Delta H^{\ddagger} = 26.6 \pm 0.5$ Kcal/mol
$\Delta S^{\ddagger} = 21 \pm 1$ cal/mol·K
R = CO₂Me

(c) $\Delta H^{\ddagger} = 19.8 \pm 0.2$ Kcal/mol
$\Delta S^{\ddagger} = -4.8 \pm 0.7$ cal/mol·K
$\Delta H^{\ddagger} = 22.7 \pm 0.1$ Kcal/mol
$\Delta S^{\ddagger} = -8.6 \pm 0.4$ cal/mol·K
ΔG 21.4
4.2
Fc: Ferrocenyl

(d) $\Delta H^{\ddagger} = 27.2 \pm 0.4$ Kcal/mol
$\Delta S^{\ddagger} = -9.7 \pm 0.9$ cal/mol·K
R = SiMe₂^{i}Pr

(e) $\Delta H^{\ddagger} = 23.2 \pm 0.2$ Kcal/mol
$\Delta S^{\ddagger} = 20.0 \pm 1.0$ cal/mol·K
R = SiMe₃
Oxidation
$\Delta H^{\ddagger} = 14.6 \pm 0.7$ Kcal/mol
$\Delta S^{\ddagger} = -1.4 \pm 3$ cal/mol·K
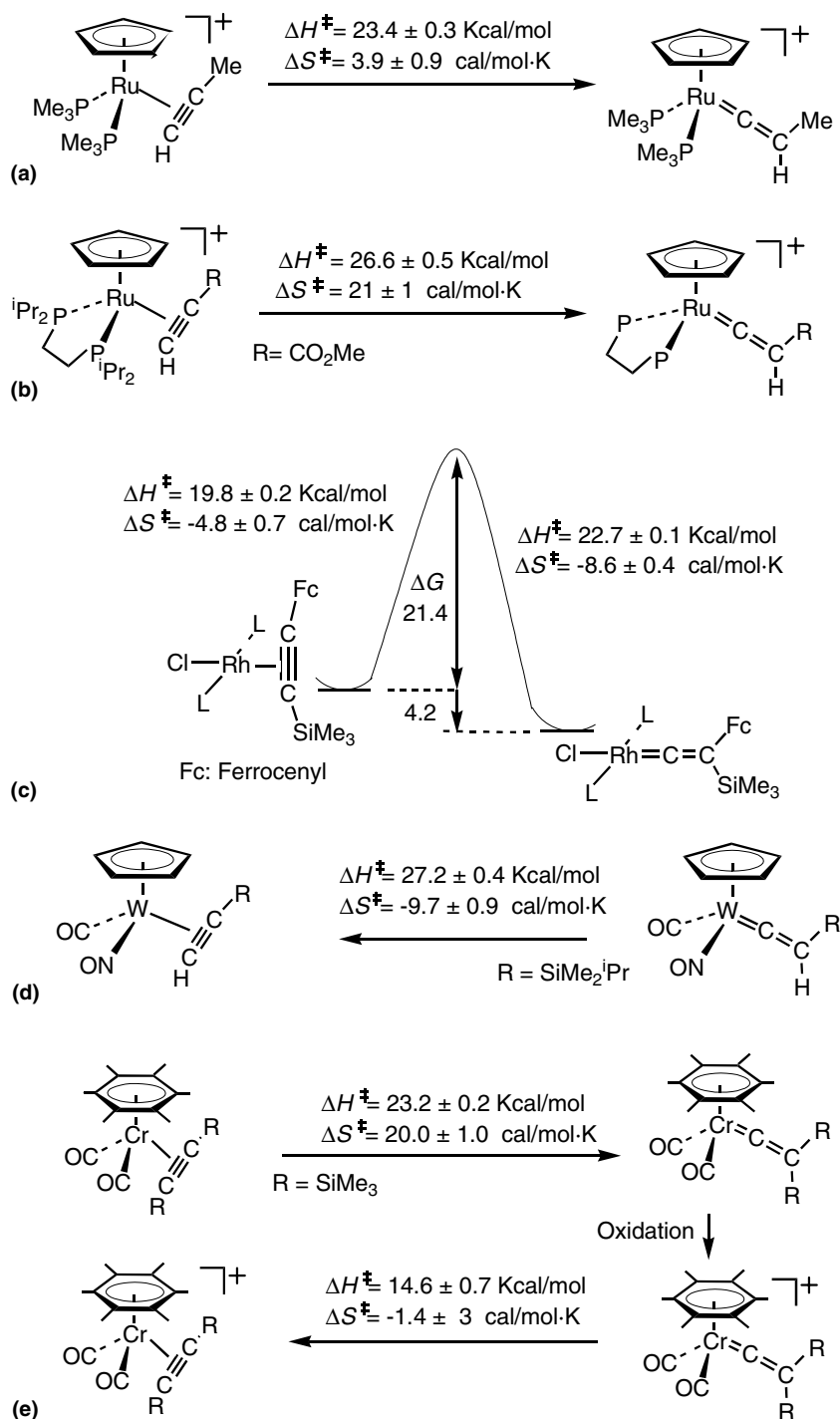
Scheme 7.

silyl group (cf. T_{12} in Scheme 2). The exchange equilibrium of the vinylidene ligand with other alkynes have suggested that the thermodynamic stability of *trans*-RhCl(P^{i}Pr₃)₂[C≡C(R)(SiMe₃)] depends on the substituent R and increases in the order SiMe₃ > Fc > Ph.

Recently, the η^1-vinylidene (=C=CHR) to η^2-alkyne (HC≡CR) conversion in the coordination sphere of CpM(CO)(NO) fragment, where M = Mo or W, was measured at 130–150 °C in aromatic solvents (Scheme 7(d)) [37]. Relatively small isotope effect of $k_H/k_D = 1.2$ found for R = SiMe₂^{i}Pr as compared to that for R = ^{t}Bu ($k_H/k_D = 2.00$) has lead to the conclusion that the migrating species is the silyl group in the rearrangement of CpW(CO)(NO)[C=C(H)(SiMe₂^{i}Pr)] to CpW(CO)(NO)[(^{i}PrMe₂ Si)C≡CH], while it is hydrogen in the case of the R = ^{t}Bu analog.

Parameters for the redox-induced vinylidene-to-alkyne isomerization on a Cr(0) fragment (C₆Me₆)Cr(CO)₂,

were reported [38]. The thermodynamically favored isomers are vinylidene in the case of the neutral 18-electron complexes but it is alkyne in the case of the 17-electron cations. Apparently, occupation of the HOMO is the controlling factor to determine the relative thermodynamics. As shown in Scheme 7(e), the isomerization of cationic vinylidene complex to the corresponding cationic alkyne form is enthalpy-driven whereas the isomerization of neutral alkyne complex to vinylidene is driven largely by the increase in entropy. The latter is presumably related to steric inhibition of internal motion, i.e., moving the bulky $SiMe_3$ group away from the metal center allows for greater freedom of motion for the C_6Me_6 ring.

The hydride–alkynyl Co(I) complexes with Bianchini's tetrapod phosphine ligand showed large positive $\Delta S^{\ddagger}$ values (Scheme 8(a)) in their unimolecular isomerization to the vinylidene structure [28]. Therefore, dissociative cleavage of the Co–H bond, followed by a migration of the hydrogen to the alkynyl Cβ carbon was postulated. The process may be viewed as deprotonation/protonation pathway (cf. dashed arrows in Scheme 2(a)) occurring in an intra molecular manner.
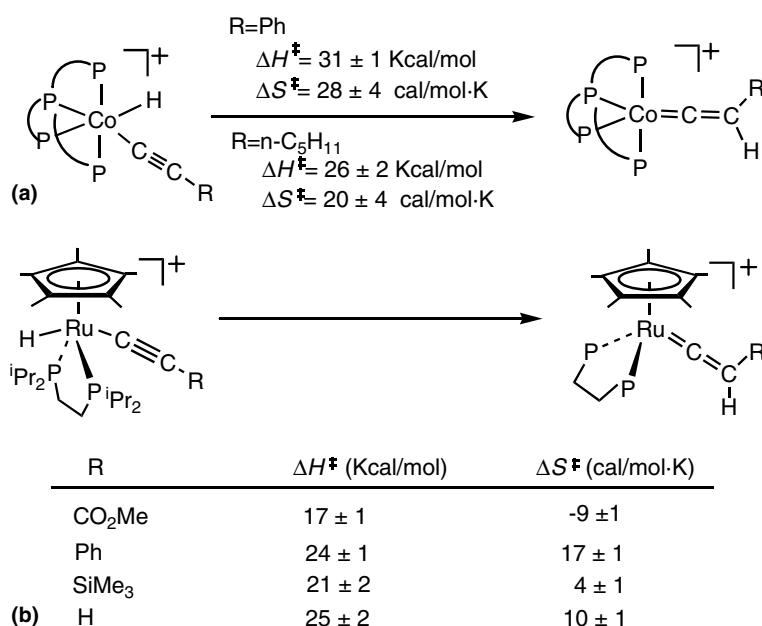
The *trans*-hydride–alkynyl complexes of Ru(IV) with electron-rich spectator ligands [Cp*Ru(dippe)(H)(C≡CR)]+, rearrange to vinylidenes with the activation parameters listed in Scheme 8(b) [29]. With the exception of the small negative $\Delta S^{\ddagger}$ for R = CO$_2$Me, which could be a consequence of experimental error, the positive activation entropy values are consistent with dissociative nature of the isomerization reaction, as in the case of the isomerization of hydride–alkynyl Co(I) complex to vinylidene.

3.3. Theoretical calculations

The first theoretical calculations to compare transition energies for the two alternative routes (T_{12} and T_{13}) depicted in Scheme 2(a), was performed by Hoffmann in 1985 [13]. The EHMO analysis on the reaction of $CpMn(CO)_2(C_2H_2)$ resulted in the conclusion that the route via T_{12} is much more feasible than the other.

Detailed ab initio calculations on $RuCl_2$-$(PH_3)_2(C_2H_2)$ have reveled that the η^2-acetylene complex and its vinylidene tautomer are essentially isothermal as illustrated in Fig. 2. The oxidative addition reaction of acetylene to form a hexagonal Ru(IV) hydride–ethynyl complex costs too much energy. While the isomerization of coordinated acetylene to vinylidene is intraligand 1,2-H shift (TS_2) as in the $CpMn(CO)_2$ system, the transition state is preceded by a slippage motion of the acetylene unit from η^2-(C≡C) to η^2-(C–H) coordination [39]. The transition state TS_1 that lead to this intermediate has the η^1-(C≡C) coordinated acetylene with weak metal-Cα bonding (Ru–C: 2.4 Å). Another important information obtained from contour diagrams of relevant localized molecular orbitals is that the migrating hydrogen in TS_2 behaves as a proton rather than a hydride. The migrating hydrogen leaves behind the lone pair of electrons, which is originally accommodated in the Cα–H σ-bond orbital, so that Cα can donate these electrons to the metal after the rearrangement.

The intraligand 1,2-H shift is also the calculated pathway for the interconversion between the niobocene complexes $[Cp_2Nb(L)(HC≡CMe)]^+/[Cp_2Nb(L)(=C=CHMe)]^+$ (Fig. 3; L = CO or PH_3) [40]. The hydride–

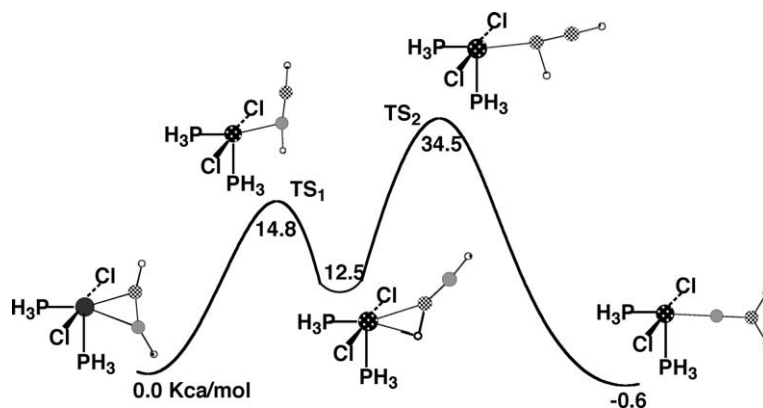| R	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·K)
CO$_2$Me	17 ± 1	-9 ±1
Ph	24 ± 1	17 ± 1
SiMe$_3$	21 ± 2	4 ± 1
H	25 ± 2	10 ± 1

Scheme 8.

Fig. 2. Tautomerization of C_2H_2 unit in $RuCl_2(PH_3)_2(C_2H_2)$.

alkynyl complex **A** was able to be located, but that for L = CO was found to be too high in energy above the vinylidene complex. In contrast, the oxidative addition product with more electron-donating L (PH$_3$) is only 25.6 kcal/mol above the corresponding vinylidene complex, though the 1,3-H shift transition state (**TS3**) between the hydride–alkynyl and vinylidene complexes has too high energy-barrier for their interconversion. Consequently, the 1,2-H migration via **TS1** and η^2-(C–H) intermediate **B** is more likely. Since **TS4** that connects **A** and **B** causes only a small barrier, and the energy level of **A** is lower than that for **TS1**, the hydride–alkynyl species **A** in small amount may coexist in the reaction mixture as a resting state when the isomerization 1-alkyne → vinylidene is to be carried out with this complex.

A number of experimental examples indicate that oxidative addition of acetylenic C–H to a d^8-electron metal center should be fairly easy and in such cases, the hydride–alkynyl intermediate should be operating in the
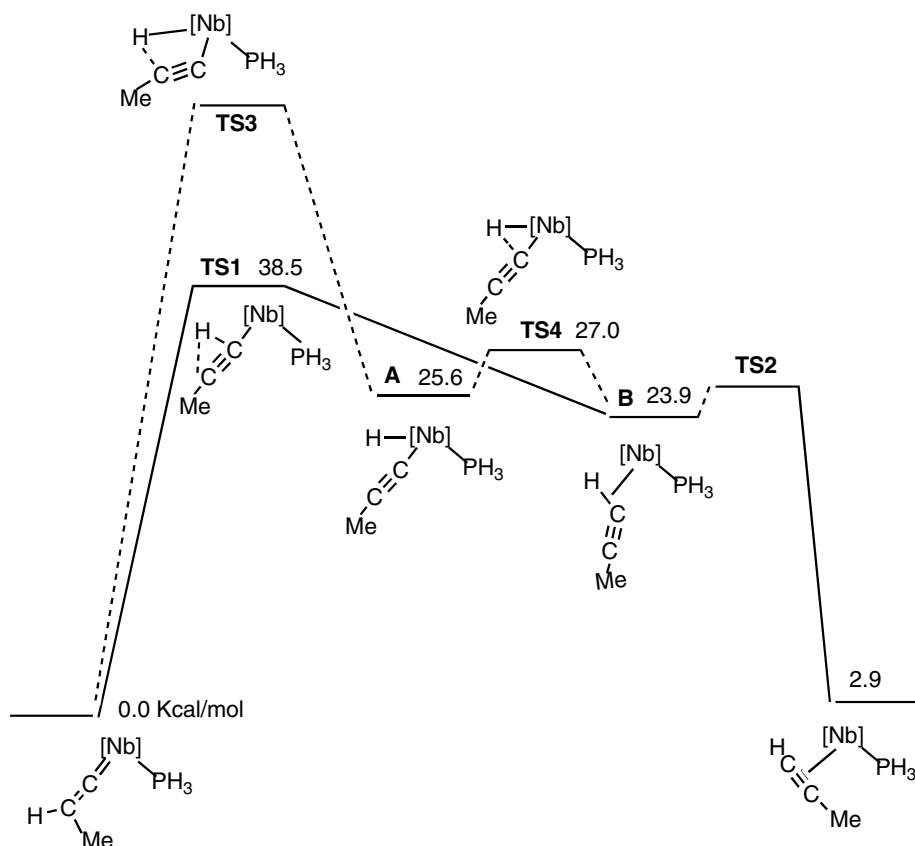

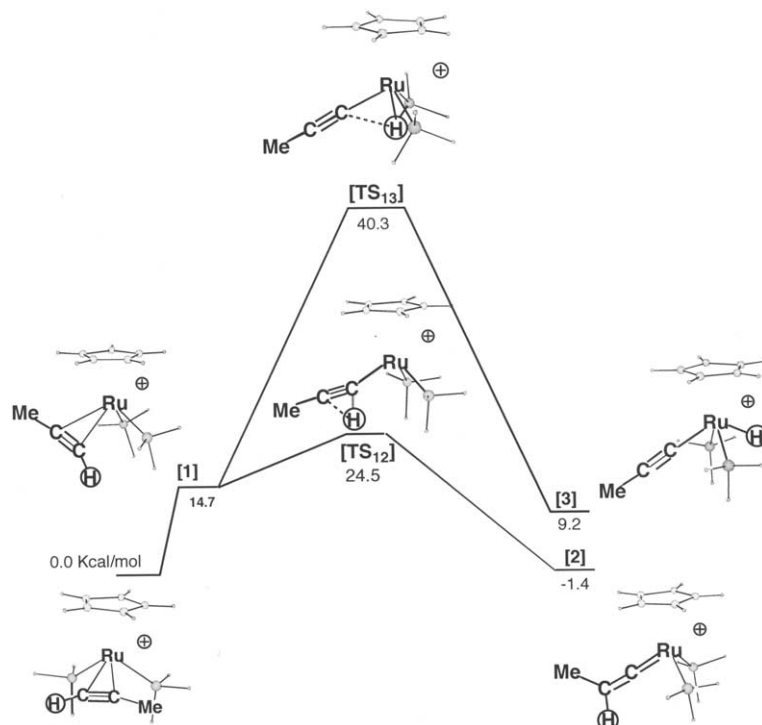Fig. 3. Tautomerization on niobocene fragment: [Nb] = Cp_2Nb^+.

tautomerization process of a coordinated 1-alkyne to vinylidene. Indeed, the ab initio MO study on the reaction of $RhCl(PH_3)_2(C_2H_2)$ revealed the energy profile depicted in Fig. 4(a) [41]. As in the case of the corresponding d^6-electron Ru(II) complexes $RuCl_2(PH_3)_2(C_2H_2)$ shown in Fig. 2, the η^2-(C≡C) coordinated acetylene (**A**) undergoes slippage to a η^1-(C–H) species (**Bts**). In striking contrast to the Ru(II) system where the η^1-(C–H) species is an intermediate to climb the slope towards 1,2-H shift transition state (Fig. 2), **Bts** here itself is a transition state which has a steep down-slope to the hydride–ethynyl complex **C**. A route from **A** to vinylidene **E** via direct 1,2-H migration was, therefore, not found. Instead, the transition state (**Dts**) for the concerted 1,3-H migration, where the shifting hydrogen has concomitant interactions with Rh, Cα, and Cβ, has been found, which lies 33.5 kcal/mol above the level of **C**. Another route from **C** to **E** was found to be a bimolecular path shown in Fig. 4(b). Even the complex with bulkier phosphine ligand, $RhCl(PiPr_3)_2(H)(C≡CH)$, can adopt such bimolecular association

and has barrier (ca. 17 kcal/mol at 25 °C) lower than the intramolecular 1,3-H shift process. In several transformations of hydride–alkynyl complexes into vinylidenes (see Section 3.1), the ease of deprotonation by base and successive protonation at Cβ (cf. Scheme 2(a)) has been pointed out. In the present bimolecular process, the Cβ of the second molecule itself acts as the hydrogen-extracting base. In accord with this perspective, the character of the migrating H has been concluded to be protic based on localized molecular orbital analysis.

The oxidative addition of HC≡CH and the role of the resulting hydride–ethynyl complex on the way from η^2-alkyne complex $[Co(PP_3)(HC≡CH)]^+$ to ultimate vinylidene complex $[Co(PP_3)(=C=CH_2)]^+$ was analyzed by ab initio MO calculations [42]. Participating three reactants or intermediate, and two transition states between them have been found to be essentially similar to those in Fig. 4(a) in terms of the metal–C_2H_2 interactions. However, the transition state that connects the hydride–ethynyl and the vinylidene complexes is at rather

Fig. 4. Formation of hydride–alkynyl intermediate and intra (a) and inter (b) molecular H-migration.

Fig. 5. Oxidative addition vs. 1,2-H shift pathways in [CpRu(PH$_3$)$_2$(HCCMe)]$^+$ complex.

low energy, being only 20.6 kcal/mol higher than that of the hydride–ethynyl complex. Thus, concerted 1,3-H migration process from the metal to Cβ appears feasible in this system. Further, qualitative analysis of this system with the help of EHMO has lead to an interesting conclusion that the hydrogen moving from the metal to Cβ should initially be regarded as a hydride since it abstracts lone pair electron from the metal. As the hy-

dride moves toward Cβ, the four-electron repulsion with the coplanar C–C π-bond is maximized at some point to the transition state and the hydride electron pair is returned to a metal orbital. The final stage of the pathway then corresponds to the simple protonation of the acetylide Cβ atom.

Last few years, alkyne/vinylidene complexes of half-metallocene d^6-electron metals including Mn(I) [43],

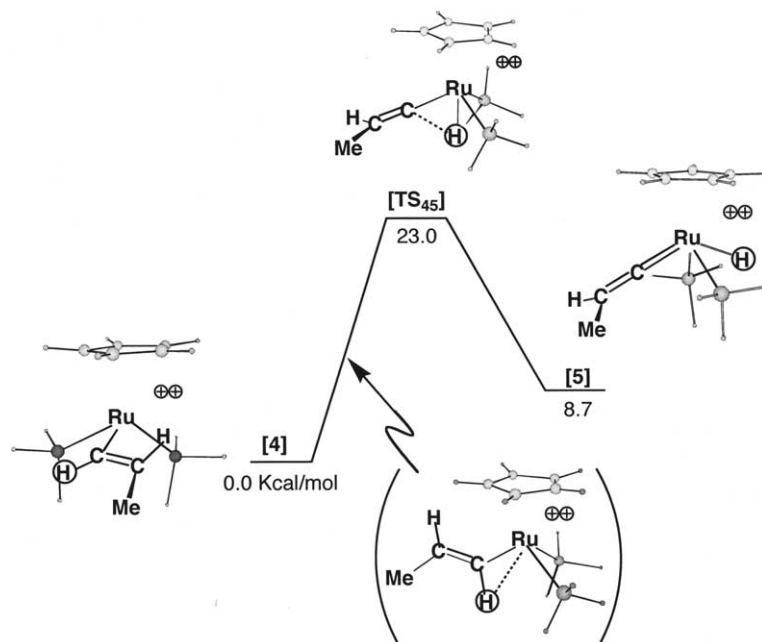Fig. 6. Vinylic α-H migration to the metal after protonation of [CpRu(PH$_3$)$_2$(HCCMe)]$^+$.

Os(II) [44], and in particular Ru(II), have been the subjects of many theoretical studies. For example, the DFT calculations on [CpRu(PH$_3$)$_2$(C$_2$HMe)]$^+$ complexes gave the energy diagram shown in Fig. 5 that compares preference for the formation of hydride–alkynyl (**3**) with that of vinylidene complex (**2**) [45]. Unlike more symmetric RuCl$_2$ (PH$_3$)$_2$ fragment system, the oxidative addition product **3** in the half metallocene complex was calculated to be rather stable. However, the transition state **TS13** leading to it is still at quite high energy level and the vinylidene complex **2** via this route is unlikely. Consequently, **2** has been predicted to form dominantly via the direct 1,2-H migration (**TS12**). Using the same model, protonated species was examined (Fig. 6). Protonation at the β-carbon of alkyne complex **1** gives a σ-vinyl complex of Ru(IV) (**4**), which can rearrange to form *trans*-hydride–vinylidene complex **5** via the α-hydrogen migration to the metal center. This α-hydrogen migration takes place through transition state **TS45** located at 23 kcal/mol above the σ-vinyl complex. To reach this transition state from **4**, rotational motion of the vinyl group accompanies. According to the localized MO analysis, the migrating hydrogen is best regarded as a hydride when it migrates through this transition state.

The DFT calculations were also reported, which employ similar but more realistic models [CpRu(PMe$_3$)$_2$(HC≡CR)]$^+$ and [CpRu(PMe$_3$)$_2$ (=C=CHR)]$^+$, where R = H or Me [46]. Calculated structures and energy changes on going from η^2-alkyne to the final vinylidene complex via slippage and 1,2-H shift processes are illustrated in Fig. 7(a). Although alternative intramolecular 1,3-H shift can be ruled out due to its computed high energy transition state, the prior oxidative addition reaction has a relatively low barrier (31.7 and 29.0 kcal/mol above the η^2-alkyne complex for R = H and Me, respectively), and might become a competitive process in HC≡CR rearrangement on this electron-rich fragment. The easier oxidative addition here as compared to that shown in Fig. 5 (40 kcal/mol) may be the result of replacement of PH$_3$ by more electron-releasing PMe$_3$ ligand.

The electronic and steric influence of spectator ligands in [CpRuL$_2$(C$_2$H$_2$)]$^+$ and [Cp*RuL$_2$(C$_2$H$_2$)]$^+$ complexes (L = PH$_3$, PMe$_3$, PEt$_3$) was estimated by the combinations of QM and MM computations [29]. Full ab initio calculations on the optimized QM/MM geometries of model [Cp*Ru(PEt$_3$)$_2$(C$_2$H$_2$)]$^+$ can mimic the experimentally suggested very similar relative energies of the η^2-acetylene and hydride–ethynyl isomers.

Energy diagrams for the interconversion of η^2-HC≡CH and η^1-C=CH$_2$ on (Indenyl)Ru(PH$_3$)L fragment (L = PH$_3$, CO) were calculated (Fig. 7(b)) [47]. The vinylidene to alkyne tautomerization is more accessible both thermodynamically and kinetically for the carbonyl complex (L = CO).

Recently, the isomerization of CpMn(CO)$_2$(C$_2$H$_2$) was revisited using dynamical DFT approach and preference for the 1,2-H shift mechanism was confirmed [48]. The energy profile along the reaction coordinate, with a free energy barrier of 27.3 kcal/mol, was similar to that for isoelectronic Ru(II) half metallocene cation (cf. Fig. 7(a)). The higher barrier computed for the oxidative addition leading to the corresponding hydride–ethynyl complex (35.0 kcal/mol), rules out the intermediacy of such a species in the rearrangement process.

As described in this section so far, vinylidene complexes are thermodynamically more stable than, or almost equal to corresponding η^2-alkyne complexes with d^6 and d^8 electron metal centers. In contrast, quantum mechanical calculations at the CCSD(T) level indicated that the high-valent tungsten–acetylene complex
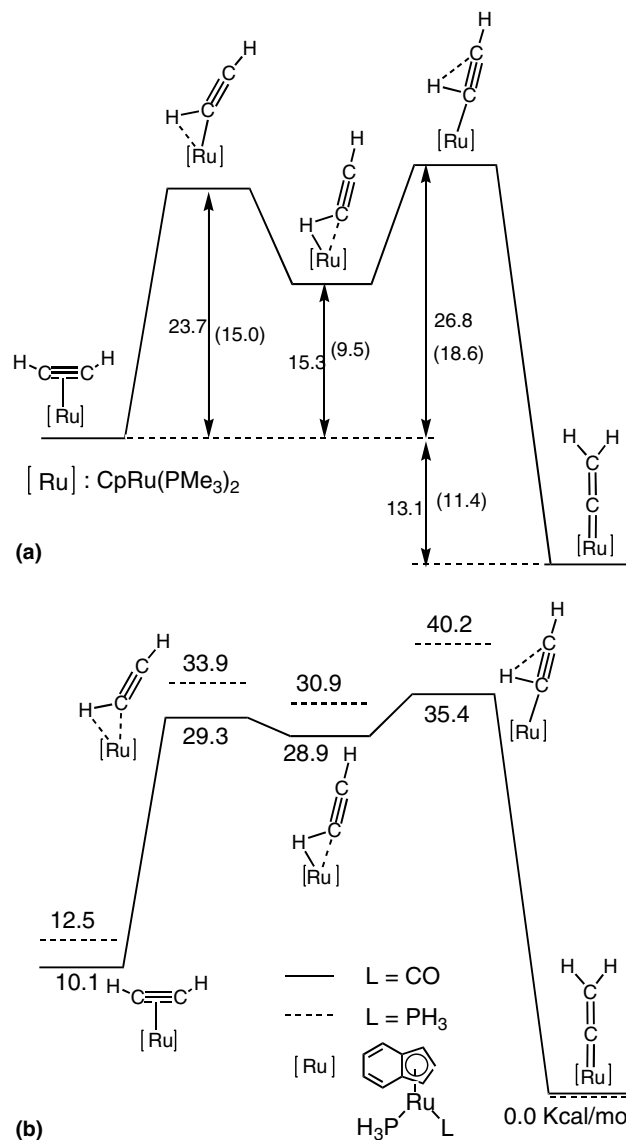

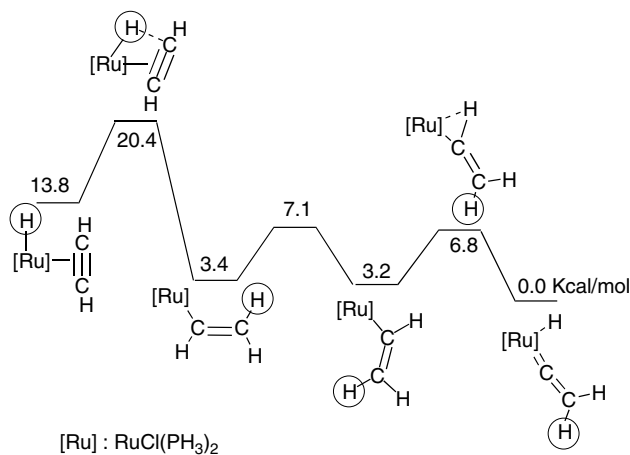Fig. 7. (a) Tautomerization of C$_2$H$_2$ and C$_2$HMe (values in parenthesis). (b) Tautomerization in (Indenyl)ruthenium complexes.

Fig. 8. Insertion of HCCH ligand to Ru–H and successive vinylic α-H migration to the metal.

F₄W(HC≡CH) is 10.4 kcal/mol lower in energy than the isomeric vinylidene complex [49]. The direct 1,2-H migration has a barrier as high as 84.8 kcal/mol and the transition state has non-planar C_2H_2 moiety. This transition state geometry resembles that for the tautomerization of free C_2H_2 anion in its triplet state. The oxidative addition product, hydride–ethynyl complex, has 50.5 kcal/mol higher energy and successive 1,3-H migration has barrier of 85.5 kcal/mol with respect to the starting acetylene complex. The high barriers for both of the two alternative pathways strongly suggest that such isomerization would not take place in this d^2-electron complex under normal reaction conditions.

The route to vinylidene shown in Scheme 2(b) was verified by DFT simulations for the intramolecular reaction of M(H)Cl(PH₃)₂(HC≡CH), where M = Ru and Os [50]. It was shown that the path starting with insertion into the Ru–H bond is more favorable than 1,2-H migration within the coordinated acetylene. The highest barrier in the transformation of Ru complex is the insertion step: the next step, i.e. the α-H migration to form a 16-electron hydride–vinylidene complex from 14-electron σ-vinyl intermediate is much easier (Fig. 8). The latter process includes rotation of the metal-vinyl bond so that the activation of the Cα-H bond can occur at the site *trans* to the Cl ligand. In the case of Os, the general reaction path is similar to that for the Ru complex, but the vinyl intermediate adopts η²-vinyl bonding conformation.

4. Reactions of vinylidene complexes

### 4.1. Stoichiometric reactions with electrophiles or nucleophiles

Since one of the preparative methods to obtain metal vinylidenes is protonation of Cβ in metal alkynyl com-

plexes (Scheme 2(a)), the first paper introduced in this section is concerned with DFT analysis of early and late transition metal ethynyl bond [51]. Based on the calculations on CpFe(CO)₂(C≡CH), the well known regioselectivity for electrophilic attack at Cβ in late transition metal acetylides was explained by much higher negative charge at Cβ and also by larger contribution of Cβ in the HOMO. On the other hand, calculations on M(HO)₃(C≡CH) (M = Ti, V, Cr) have indicated that the Cα bears higher negative charge than Cβ, which gives rise to electrophilic attck at Cα by charge factors. This could be the general tendency in high valent early and middle transition metal acetylide complexes.

Electrophilic and nucleophilic additions to vinylidene complexes were theoretically examined. As we have seen already (Section 2), nucleophilic attack at Cα in late transition metal vinylidene complexes is easily be understood whereas electrophilic attack is more complicated (Fig. 1). EHMO analysis of model complexes CpMn(CO)₂(=C=CH₂), [CpFe(CO)₂(=C=CH₂)]⁺, IrCl(PH₃)₂(=C=CH₂), and CpRh(PH₃)(=C=CH₂) predicts that while electrophilic attack at Cβ is the general trend, an electrophile will attack to the metal in the case of the Ir complex but to Cα in the case of the Rh complex [14].

Mechanism of H⁺ addition to rhenium vinylidene complexes was studied by stopped-flow spectrophotometry [52]. The reactions of *trans*-[ReX(dppe)₂(=C=CHR)] with [NHEt₃][BPh₄] to form the carbine complex [Re-X(dppe)₂(≡C-CH₂R)]⁺ (X = Cl; R = Ph, ᵗBu, CO₂Me, CO₂Et; X = F; R = CO₂Et) were found to proceed via three pathways whose relative contribution depends on the nature of R and X (Scheme 9). For the R = Ph, all three pathways occur whereas the pathways that involve direct addition to the vinylidene ligand do not operate for the bulky R = ᵗBu, the reaction proceeding exclusively by the intramolecular hydride migration path (k_4-route). For the R = CO₂R′, the strong electron-withdrawing effect of the ester group results in the formation of adduct, where [NHEt₃]⁺ is hydrogen-bonded to the β-carbon of the vinylidene ligand.

The reaction of Ru–vinylidene complexes with water, the simplest nucleophile, has been known to give Ru–acyl complexes or its decarbonylation products, i.e., Ru(CO)(alkyl) species [53]. Accordingly, metal-assisted CC triple bond cleavage of 1-alkynes by water to give a metal-carbonyl and one-carbon-short alkane had been postulated to involve metal-vinylidene intermediates. The detailed mechanistic study on the Ru-promoted C≡C bond cleavage of phenyl acetylene on hydration in the presence of (PNP)RuCl₂ (PNP = ⁿPrN(CH₂CH₂CH₂PPh₂)₂) has confirmed that this is indeed the case (Scheme 10) [54]. Vinylidene complex **2** was isolated in high yield in the absence of water. The process **2 → 3 → 4** was postulated because the experiment using D₂O has indicated that

[Re] : ReCl(dppe)$_2$
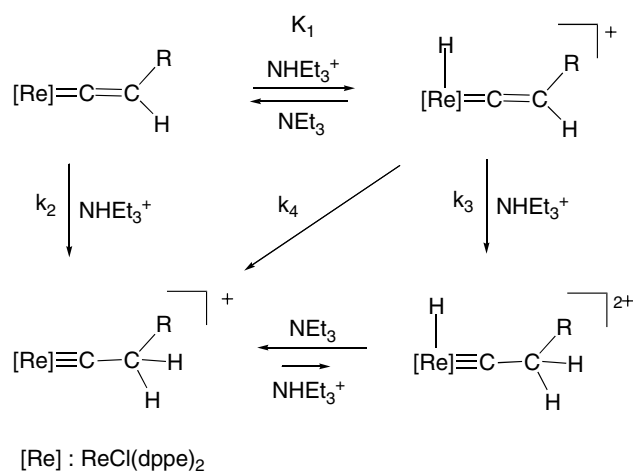
Scheme 9.

the vinylidene hydrogen at Cβ is exchanging rapidly with water hydrogen. Complex **4** with coordinated water was isolated. Taken together these observations and other model reactions, the process shown in Scheme 10 was derived.

### 4.2. Catalytic reactions that involve nucleophilic addition to vinylidene intermediates

As nucleophilic attack to a vinylidene intermediate should occur at the α-carbon, a catalytic addition of

nucleophiles to 1-alkynes would give rise to *anti*-Markovnikov addition products if the alkyne to vinylidene tautomerization could take place prior to the net addition reaction. Indeed, such a reaction pathway was proposed for the synthesis of vinylic carbamates $R^1CH=CH(OCONR^2)$ from 1-alkynes $R^1 C\equiv CH$ and ammonium carbamates HCO_2NR^2 in the presence of a ruthenium catalyst [55]. Similarly, a certain class of ruthenium complexes, Ru(diphos)(2-methylprope-nyl)$_2$, are able to catalyze addition of carboxylic acids to 1-alkynes in *anti*-Markovnikov manner with (Z) stereoselectivity [56,57].

With respect to addition of water, it has been believed that acid or metal-catalyzed hydration of 1-alkynes follows exclusively Markvnikov's rule and yields ketones. Principally, *anti*-Markovnikov hydration should be possible if a vinylidene intermediate can be invoked. However, Scheme 10 tells us that such a process may often end up cleavage of the CC bond and yield simply a stable metal carbonyl complex. Despite this anticipated difficulty, the first *anti*-Markovnikov hydration of 1-alkynes to give aldehyds was found in 1998 using ruthenium catalysts [58]. Besides, it was found later that rather ubiquitous ruthenium half-metallocene complexes of the type CpRuCl(PR$_3$)$_2$ are excellent catalyst [59,60]. Detailed mechanistic investigation on this system has strongly suggested the catalytic cycle in Scheme 11, where the key-intermediate is the Ru(IV)–vinylidene (**C**) formed via α-hydrogen migration in the σ-vinyl
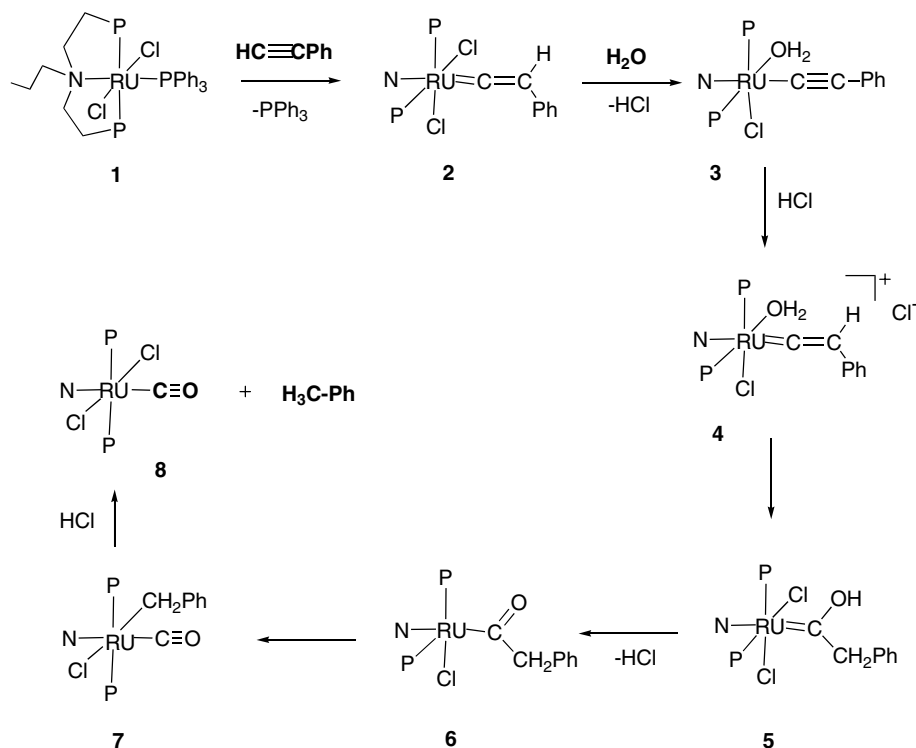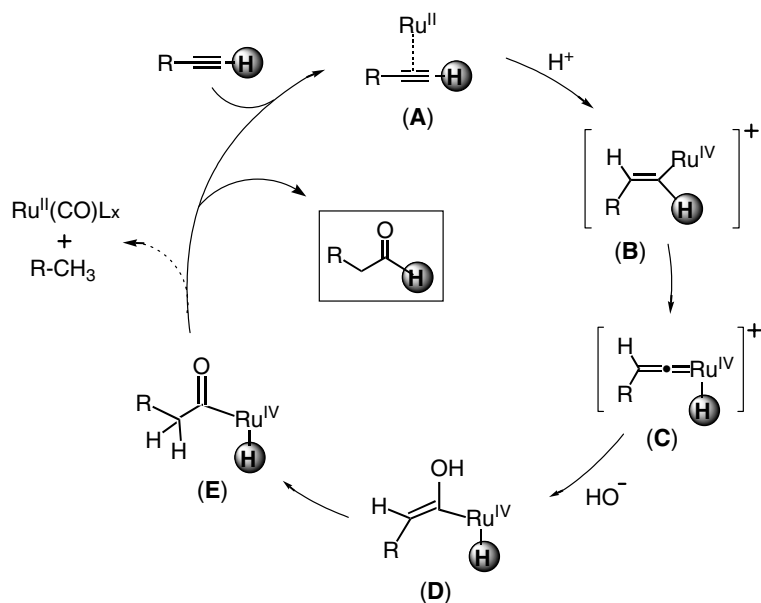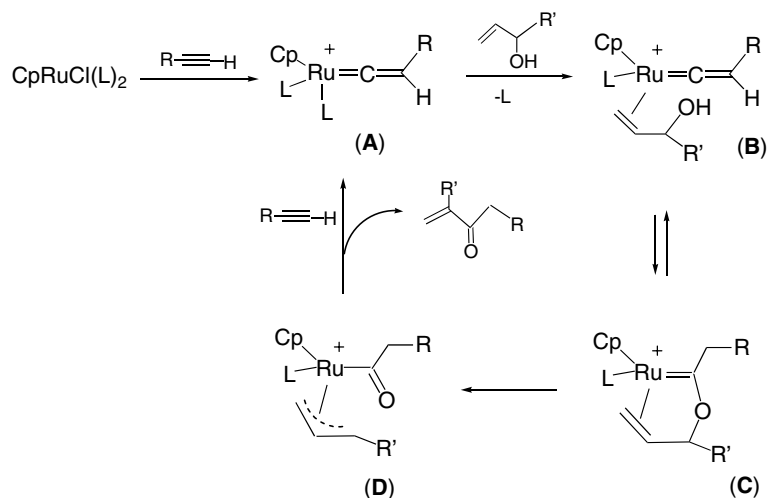

Scheme 10.

Scheme 11.

complex (**B**) (cf. Scheme 2(b)) [45]. The supporting evidence for this mechanism is: (1) the hydration of DC≡CR gives exclusively RCH$_2$ CDO; (2) the Ru(II)–vinylidene complex [CpRu(dppe)(=C=CHPh)]$^+$ does not react with H$_2$O under the same conditions where the precursor CpRuCl(dppe) can initiate efficient catalytic hydration of PhCCH furnishing PhCH$_2$CHO. A Ru(II)–vinylidene intermediate, therefore, is not involved in the reaction; (3) DFT calculations gave the energy diagram shown in Fig. 5. Since the much easily formed Ru(II)–vinylidene does not play a role in the reaction, Ru(IV) hydride–alkynyl intermediate would not be involved either; (4) The energy barrier for the step (**B**) → (**C**) was estimated reasonable (Fig. 6). Finally, it has been mentioned: (1) the Cα of Ru(IV)–vinylidene

(**C**) is more susceptible to nucleophilic attack as compared to the corresponding Ru(II)–vinylidene due to less efficient back-donation from the metal. (2) The reductive elimination from Ru(IV) hydride-acyl (**E**) should be much faster than the corresponding reaction of more electron-rich Ru(II) hydride-acyl so that the competitive decarbonylation reaction can be almost ignored.

Another case that involve a Ru(IV)-acyl intermediate was presented by Trost and coworkers [61,62] in their catalytic reconstitutive condensation of allylic alcohols and 1-alkynes, whose mechanistic rationale is illustrated in Scheme 12. Preformed vinylidene complex (**A**) was proved to be a good catalyst. The observations that addition of PPh$_3$ retarded the rate of the condensation reaction and chelating diphosphine ligands completely

Scheme 12.
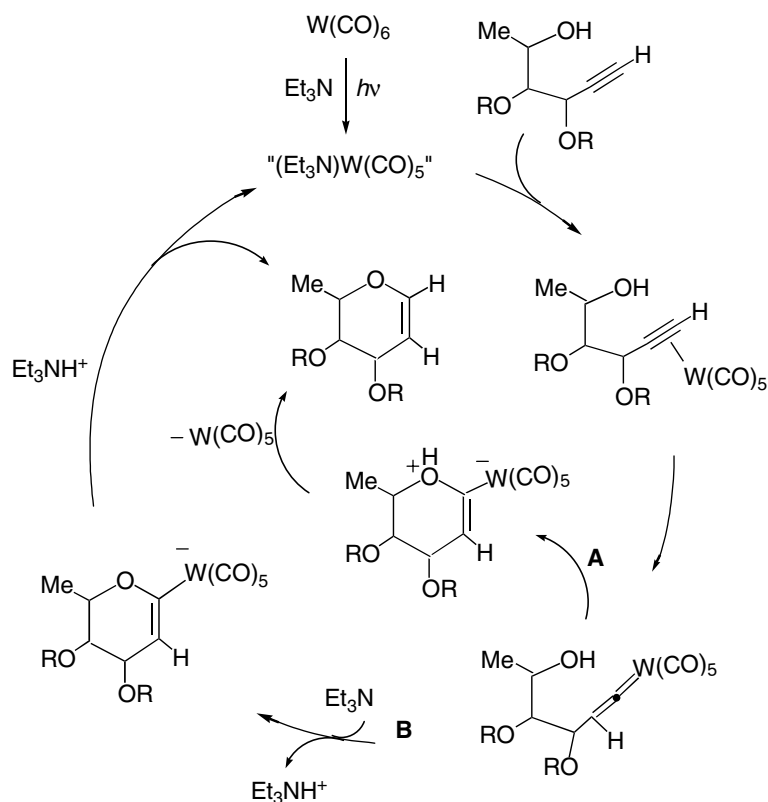
Scheme 13.

inhibited it, have suggested the phosphine replacement step (**A**) → (**B**). The reaction of preformed (**A**) with ethanol virtually does not take place but *intra* molecular nature of the nucleophilic addition (**B**) → (**C**) makes the reaction of allylic alcohol easy. Interestingly, the reaction with $H_2C=CH-CD_2(OH)$ indicated that reductive elimination of the allyl and acyl fragments in (**D**) occurs with retention of the positional identity of the $CH_2CH_2CD_2$ moiety, the coupling being faster than allyl rotation. In intermediate (**D**), the presence of the strongly electron-withdrawing acyl group on an already electron-poor Ru(IV) species should sufficiently destabilize the intermediate to ensure rapid reductive elimination.

A tungsten catalyzed intramolecular attack of oxygen nucleophile to 1-alkyne was computationally analyzed by Morokuma and coworkers [63]. The DFT calculations on the cyclotrimerization of 4-pentyn-1-ol with tungsten pentacarbonyl catalyst reproduced the experimentally observed *endo*-selectivity to form six-membered cyclic ether (Scheme 13). The rate-determining barrier of the entire catalytic process is 26 kcal/mol at the 1,2-hydrogen migration step to form a W-vinylidene intermediate, which is considerably lower than *exo*-cycloisomerization to give five-membered oxacycle. In the real reactions, amine appears to work as a cocatalyst (path **B**) but even when amine does not participate (path

A), each of the successive steps has low energy barrier. In this route after the cyclization, the hydride moves from the hydroxy group initially to the carbonyl ligand, then to W, and finally to Cα eventually releasing the final product.

4.3. Stoichiometric CC bond formation

A cationic half-ruthenocene complex with readily replaceable MeCN ligand gives allenyl carbenes when reacted with excess HC≡CR (R = ferrocenyl or ruthenocenyl) and the model reaction, $[CpRu(PH_3)(HCN)_2]^+$ + HC≡CH, has been analyzed with DFT calculations [64]. The acetylene η^2-coordinated to the metal by substitution of the first HCN rapidly isomerizes to vinylidene and subsequent substitution of another HCN by the second acetylene yields $[CpRu(PH_3)(=C=CH_2)(\eta^2-HC\equiv CH)]^+$. The calculated transition state for the new C–C bond formation, between Cα of the vinylidene and one of the acetylene carbon, is 6 kcal/mol above the (vinylidene)(acetylene) complex and has geometry similar to the starting π-complex except for closer orientation of the two coupling ligands. Over this rather early transition state, formation of the allenyl carbene complex $[CpRu=CH-(\eta^2-CH=C=CH_2)(PH_3)]^+$ is exothermic.

4.4. Catalytic dimerization of 1-alkynes

In 1991, two groups reported regio and stereospecific dimerization of 1-alkynes, common feature of which is involvement of Ru(II)–vinylidene intermediates. Generalized reaction pathways are given in Scheme 14. In one case, [RuH(N$_2$)P(CH$_2$CH$_2$PPh$_2$)$_3$]$^+$ initiates catalytic dimerization of HC≡CSiMe$_3$ or HCCPh to their (Z)-1,4-disubstituted-1,3-enynes in 92–95% selectivity [65], while in the other, HC≡C^{t}Bu gives (Z)-1,4-di-*tert*-butylbutatriene in 96% selectivity by employing the catalyst precursor [Ru(CO)(PPh$_3$)$_3$(H)(C≡C^{t}Bu)]/P^{i}Pr$_3$ [66]. The branching point is the enynyl intermediate **D**, which is formed by migration of the alkynyl in **C** to the adjacent α-carbon of the vinylidene ligand. If **D** has space to accommodate an incoming free 1-alkyne molecule, the hydrogen transfer will give rise to release of the 1,3-enyne and re-generation of alkynyl complex **A**. On the other hand, if **D** has no room for free alkyne and the hydrogen-transfer is slow enough, 1,3-migration of the metal to terminal carbon of the C4 unit to form **E** will become a predominant reaction path, which eventually releases butatriene and regenerates **A** via **F**. The preference for the butatriene route has been proposed to be of steric origin: two bulky phosphine ligands bound at axial positions and the enynyl backbone with two bulky substituents at both terminals prevent access of free alkyne to the metal center. As modeling study has shown, the hydrogen from free alkyne is available after the butatrienyl intermediates **E** and **F** are formed. Steric

factor also plays a critical role in the observed stereo selectivity of enyne and butatriene products. The (Z)-selectivity of the products can be traced back to step **C → D**: as the repulsion between the metal fragment [Ru] and substituent R becomes more severe, the mutual *trans*-orientation of them with respect to the CC double bond should become more preferred because it puts R away from the metal fragment.

5. Concluding remarks

We have focused on the most widely studied method of obtaining metal vinylidene species, i.e., isomerization of coordinated 1-alkynes, as well as subsequent reactions of thus formed vinylidenes hoping that mechanistic consideration would help to organize ideas behind a number of experimental examples. In the case of 1-alkyne to vinylidene isomerization, the three hydrogen-migration pathways depicted in Scheme 2(a) may be generalized in effect as the shift of proton from the α to β-carbon regardless of the path it takes. Since a proton does not carry any electrons, the newly formed Cβ-Hσ-bond consumes two electrons that have originally occupied in-plane π-orbital of the C≡C. Within this π-orbital, the in-plane p-atomic orbital at the β-carbon turns into the Cβ–Hσ-bond orbital using these electrons, whereas its partner, the one at Cα, is left empty. The empty p thus formed at Cα of vinylidene plays important roles in accepting back-donation from the metal and accepting nucleophiles in further reactions of metal vinylidenes. The major role of the metal in the tautomerization is to accept lone pair electrons that grow at the σ-orbital of Cα during the proton migration process. Although much less popular, the formation of a metal vinylidene complex via a σ-vinyl intermediate (Scheme 2(b)) can also be a key-step in catalytic reactions as proposed recently [45]. In this case, the hydrogen migrates as a hydride by taking two electrons that have been used for the Cα(vinyl)-Hσ-bond, so that empty p-orbital forms on Cα (vinylidene). The donation/back-donation bonding scheme in metal vinylidenes thus fits well the fact that the tautomerization of an η^2-alkyne ligand to vinylidene is most familiar in late transition metal complexes with d^8 and d^6 valence electrons.

Since the 1-alkyne to vinylidene isomerization on a metal fragment was postulated more than 30 years ago [67], researchers in this area would have viewed the reaction qualitatively as mentioned above. However, it is rather recent that such a reaction scheme taking place in realistic complexes rather than simplified model complexes has become quantitatively understood based on molecular orbital discussions. Recent experimental and theoretical reports are noteworthy, that demonstrate significant electronic effect of ancillary ligands on the
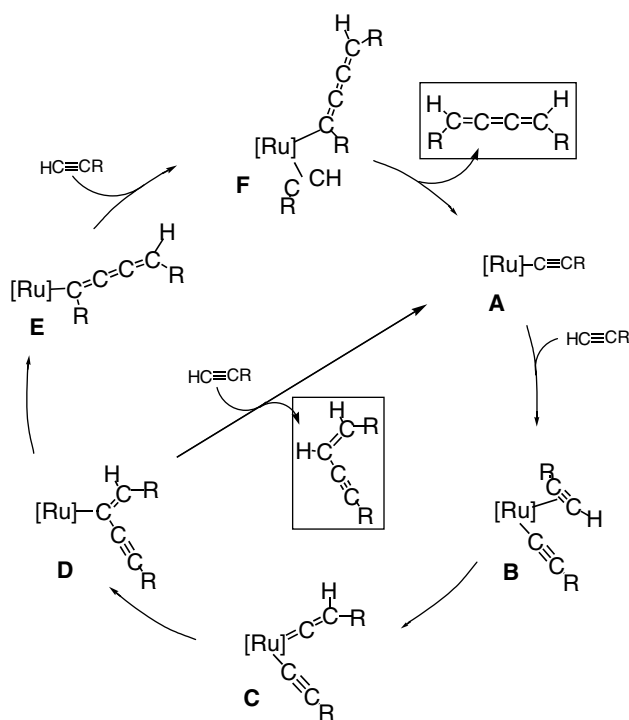
Scheme 14.

behavior of metal-bound 1-alkynes. Studies on detailed mechanisms of these rather simple organometallic reactions could in near future give rise to a number of useful catalytic reactions designed beforehand.

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