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# Ruthenium-mediated C–C coupling reactions of alkynes – mechanistic investigations based on DFT calculations

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**Abstract** This article describes the highlights of the reactions of the substitutionally labile neutral pseudo 14VE complexes Ru*Cp*(*COD*)Cl (*COD* = 1,5-cyclooctadiene) and the cationic complexes $[Ru\mathit{Cp}(CH_3CN)_2\mathit{L}]^+$ with alkynes. The ligand *L* is a co-ligand, whose nature turns out to be critical to the reaction's outcome being tertiary phosphines ($PR_3$) and the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (*IPr*). A crucial role in all reactions reported is the intermediacy of electrophilic ruthenacyclopentatriene complexes, an entity featuring a biscarbene functionality. While with Ru*Cp*(*COD*)Cl the catalytic cylcotrimerization of alkynes is achieved, $[Ru\mathit{Cp}(CH_3CN)_2(\mathit{L})]^+$ complexes are catalytically inactive for this process. These compounds undergo selective head-to-tail coupling of two alkynes. However, addition of a third alkyne is precluded due to an unusual migratory insertion of the $PR_3$ and the N-heterocyclic carbene, respectively, into the Ru–C carbon double bond of a ruthenacyclopentatriene intermediate to afford stable allyl carbenes. With parent acetylene, on the other hand, an unusual C–C coupling process takes place involving three acetylene molecules and migration of the *NHC* ligand to give formal [2 + 2 + 1] cycloaddition products. Conceivable mechanisms for all these reactions are established by means of DFT/*B3LYP* calculations.

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**Keywords** Ruthenium complexes; Phosphines; N-Heterocyclic carbenes; Oxidative coupling; DFT calculations.

## Introduction

The thermal cyclotrimerization of acetylene to benzene is an intriguing process. Based on experimental heats of formation of benzene and acetylene this trimerization is extremely exothermic ($\Delta H^\circ = -598\,\mathrm{kJ/mol}$) [1]. On the other hand, and contrary to the *Hammond* postulate, the activation energy is prohibitively high, calculated to lie in the 250–335 kJ/mol regime [2]. Such high barrier originates in the fact that some bonding orbitals of the reactants have to become antibonding orbitals in the product and vice versa. Therefore substantial distortions of the acetylenes have to occur so as to switch electron density from bonding regions in the reactants to bonding regions in the product [2a]. Another contribution to the barrier stems from closed-shell repulsions between the filled $\pi$ orbitals (*HOMO–HOMO* interactions) [2b] despite some aromatic stabilization of the transition state [3].

Noteworthy, the barrier is diminished appreciably through the coordination of the alkynes at transition metal centers. Actually, since the pioneering work done in 1948 by *Reppe et al.* [4], who found that low-valent nickel complexes catalyze alkyne cyclooligomerization, the transition-metal mediated [2 + 2 + 2] cycloaddition of alkynes has developed as a very efficient method to synthesize functionalized

arene systems [5]. Subsequently, a wide array of transition metal containing fragments was found to actively catalyze the reaction. In recent years, the ruthenium complexes Ru*Cp**(*COD*)Cl and Ru($\eta^5$-$C_9H_7$)(*COD*)Cl were found to promote the cyclotrimerization of 1,6-diynes as well as the cyclocotrimerization of 1,6-diynes with terminal alkynes [6], olefins [7], allylic ethers [8], dicyanides [9], nitriles [10], tricarbonyl compounds [11], isocyanates [12], isothiocyanates, and $CS_2$ [13].

Specifically of interest are C–C and C-heteroatom bond-forming reactions involving alkynes such as the cyclotrimerization of alkynes (a) and the cyclocotrimerization of two alkynes with unsaturated organic compounds containing C=*X* and C≡N bonds (b–d) for obtaining carbocycle and heterocycle structures as exemplarily shown in Chart 1. The development of catalytic cyclization methods constitutes a continuing challenge because of the ubiquitous occurrence of cyclic structures, especially among bioactive targets. For instance, the vast majority of pharmaceuticals in use today contain either one or two 5 or 6 membered rings. Among the wide range of transition metal compounds that were found to actively catalyze cyclizations we have focused particularly on ruthenium chemistry. Lying at the heart of the periodic table, ruthenium combines indeed valuable properties of both early- and late-transition-metal relatives. Thus, the high reactivity of elements to its left and the less oxophilic and *Lewis* acidic nature of those to its right results in a special array of desirable properties [14]. Accordingly, ruthenium is characterized by a high capacity of multiple metal bonding on the one hand and functional group tolerance on the other. For instance, even the formation of cyclic organosulfur compounds is mediated by appropriate ruthenium complexes [12, 13] while many other transition metal centers are deactivated because of strong coordination to sulfur compounds.

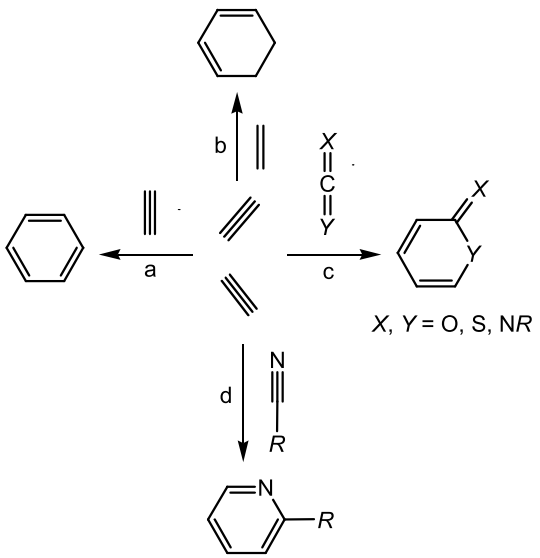
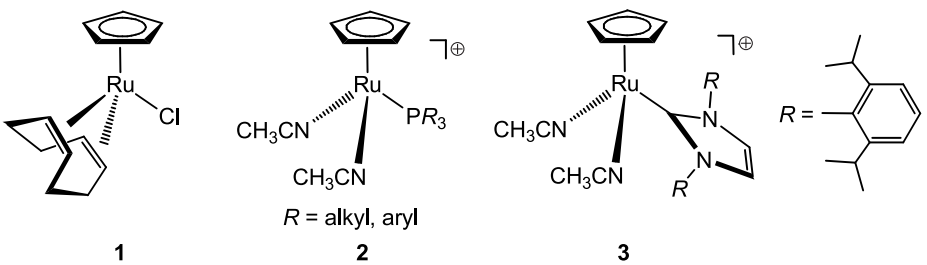



**Chart 1**

The elucidation of the mechanistic aspects of homogeneous catalysis has been an ambitious scientific goal from the beginning of the awareness of organometal catalysis. Due to the enormous progress in computational chemistry in the last several years, theoretical methods are playing an increasingly important role in identifying possible elementary reactions. These may be substitution, oxidative addition, reductive elimination, migratory insertion, hydrogen exchange, $\beta$-hydrogen transfer, $\sigma$-bond metathesis, and nucleophilic addition [15]. Ultimately, one would like to understand these fundamental transformations to be able to monitor and tune changes in reactivity toward an obvious synthetic purpose. Thus it has become very useful for us to combine, whenever possible, experimental work with theoretical studies based on density functional theory (DFT) calculations.

In this article we describe the recent highlights of the reactions of the substitutionally labile neutral pseudo 14VE complexes Ru*C*p(*COD*)Cl (**1**) and




**1** **2** **3**

**Chart 2**

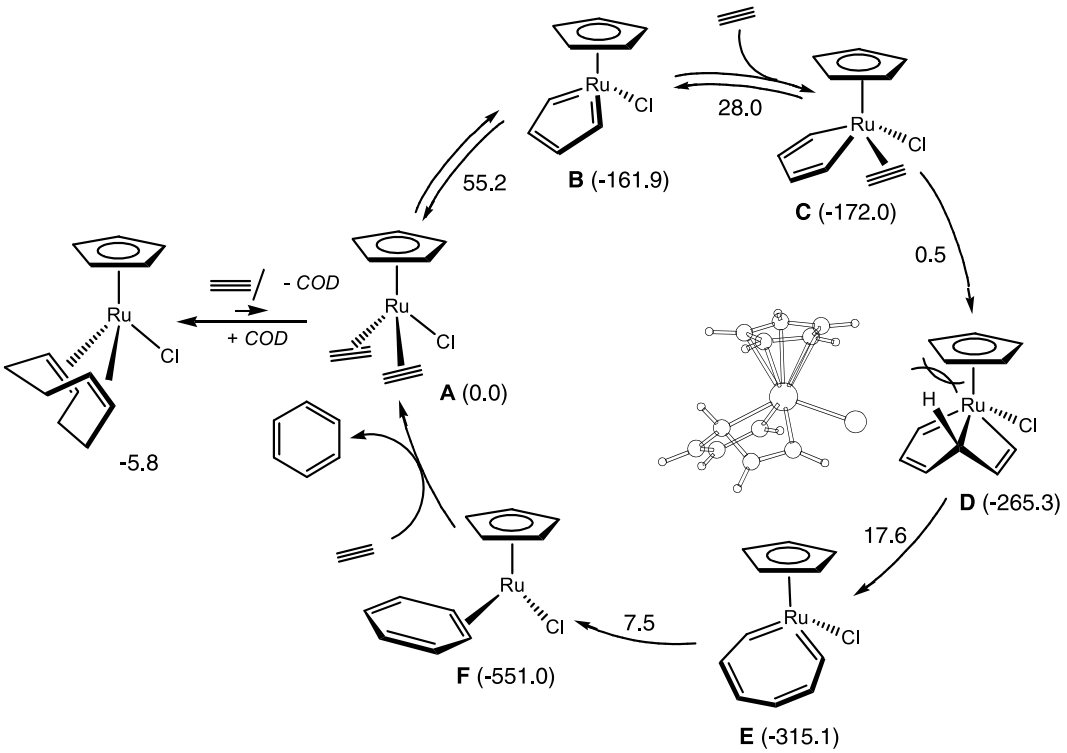
the cationic complexes $[RuCp(CH_3CN)_2(L)]^+$ (**2**, **3**) with alkynes (Chart 2). The neutral ligand *L* is a co-ligand, whose nature turns out to be critical to the reaction's outcome, vary from several tertiary phosphines ($PR_3$) to the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (*IPr*).

## Results and discussion

### *The cyclotrimerization of alkynes mediated by the CpRuCl fragment*

There are two recent theoretical examinations of the mechanism of acetylene cyclotrimerization based on the *Cp**RuCl fragment [16, 17]. The proposal derived from DFT calculations performed by our group is shown in Scheme 1 (energies of intermediates and transition states in kJ/mol), revealing a couple of uncommon intermediates. In the first step, the starting precatalyst Ru*Cp*(*COD*)Cl undergoes a pair of ligand-substitution reactions resulting in the formation of the bis-acetylene complex **A**. Subsequent oxidative coupling of the two acetylene ligands generates the metallacyclopentatriene complex **B**. In the next step, **B** is readily capable of coordinating a third acetylene molecule to give the acetylene-coordinated ruthenacycle **C**. No less than three successive intermediates could be located for subsequent arene formation. The first, an unusual ruthenabicyclo[3.2.0]-heptatriene **D** rearranges to a very unsymmetrical metallaheptatetraene **E**. Ultimately an $\eta^2$-coordinated benzene ring appears in species **F** *via* a reductive elimination step. Completion of the cycle is achieved by an exothermic displacement of the arene by two acetylene molecules regenerating **A**. The overall process is exothermic by 89.5 kJ/mol. Experimentally, the reaction proceeds under mild conditions, namely at, or event below, room temperature.

Some remarks about the key intermediates are in order here: **B**: It is now safe to assume that all cyclization processes are initiated by a metallacycle as the first key intermediate. However, the bonding modes in **B** can vary with the metal fragment. While in the similar *Cp*Co system the respective intermediate is better formulated as a metallacyclopentadiene (type I), in the Ru*Cp*Cl case **B** is clearly a metallacylopentatriene complex (type II) featuring a bis-carbene functionality. In recent years several ruthanacyclopentatriene complexes (and metallacylopentatriene complexes in general) have been iso-

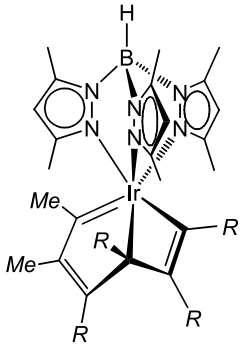



**Scheme 1**

lated and unequivocally characterized by NMR and X-ray crystallography [18]. Two bicyclic analogues also have been isolated and characterized by X-ray crystallography [19]. In fact Ru*Cp*(*COD*)Cl and Ru*Cp**(*COD*)Cl react with arylacetylenes to give stable ruthenacyclopentatriene complexes exhibiting characteristic $^{13}$C NMR resonances in the range of about 270–240 ppm. The oxidative coupling takes place regioselectively in head-to-head fashion with the substituents ending up in the 1 and 4 position. It has to be mentioned that ruthenacylopentatrienes have been invoked as key intermediates in several catalytic reactions involving alkynes, *e.g.*, in the double cyclopropanation of 1,6-diynes with strained cyclic olefins [7a], in the reaction of two alkyne molecules with carboxylic acids [20], in the cycloisomerization of alkynes and propargylic alcohols [21], or in the hydrative diyne cyclization [22]. The reactivity of **B** is guided by the availability of the attack of another alkyne (or a nucleophile in general). It has been demonstrated that these species behave as masked coordinatively unsaturated complexes and react readily with donor ligands such as tertiary phosphanes, phosphites, or amines to give ''normal'' metallacyclopentadiene complexes [18a, 23], which is not a simple nucleophilic addition at the metal center but involves severe changes in the bonding mode. Addition of substrates to **B** becomes increasingly difficult in the case of a bulky co-ligand as well as bulky substituents in the 1,4 positions.


I II

**D**: It may be noted that very recently such a structure could indeed be isolated for the first time, *viz* a stable iridabicyclo[3.2.0]hepta-1,3,6-triene, which is reversibly transformed into an iridacycloheptatriene [24]. The crucial intermediate **D** is shown in Scheme 1 in order to emphasize the steric constraints between the hydrogen of the metallacycle (*i.e.*, from the first two acetylene molecules) and that of the *Cp* ring. It is easy to see that this intermediate controls the selectivity of the overall cyclotrimerization process. Acetylene molecules carrying two bulky substituents will therefore experience considerable repulsions at this stage. In fact, cyclotrimerization is found to work well only when parent 1,6-diynes or unsymmetrical 1,6-diynes react with terminal alkynes.




**E**: This intermediate is most interesting as it reveals a notable asymmetry of the *Cp*-bonding or, in other words, ring slippage. The *Cp* ring can be considered as having a hapticity between $\eta^3$ and $\eta^5$, as is also described in other systems [25]. The asymmetry of **E** removes the symmetry-forbidden character from the final step.

**F**: This final complex looks surprising with respect to the 18e rule, because the benzene ring is $\eta^2$-bonded rather than $\eta^4$ as in the corresponding isoelectronic *Cp*Co system. This becomes possible because of significant contraction of all of the five Ru–C(*Cp*) bonds. In this respect the particular role played by the other co-ligand (in our case chloride) is worth emphasizing. If it were labile, the arene would become $\eta^6$-coordinated. The resulting stable and inert sandwich complexes would deactivate the catalyst and thus quench the catalytic cycle. This is exemplified when the complexes $[RuCp(CH_3CN)_3]^+$ or $[FeCp^*(CH_3CN)_3]^+$ are used as mediators for alkyne coupling reactions [26, 27].

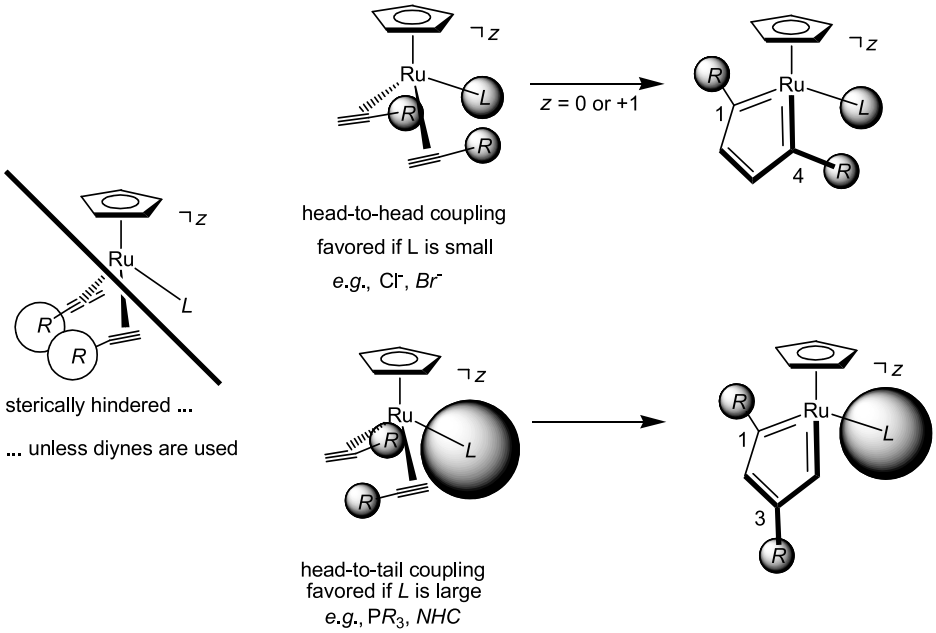
### *Dramatic reactivity changes upon replacement of Cl in CpRuCl with $PR_3$ and NHC ligands*

One severe problem may be mentioned in that the reactions with Ru*Cp*Cl systems rarely proceed with high chemo- and regioselectivity. Moreover, the catalytic process is limited to alkynes where at least on substituent is small, *i.e.*, preferably hydrogen. Accordingly, the catalytic process is successful only when parent 1,6-diynes or unsymmetrical 1,6-diynes react with terminal alkynes. Therefore, the development of alternative catalysts is highly desirable.

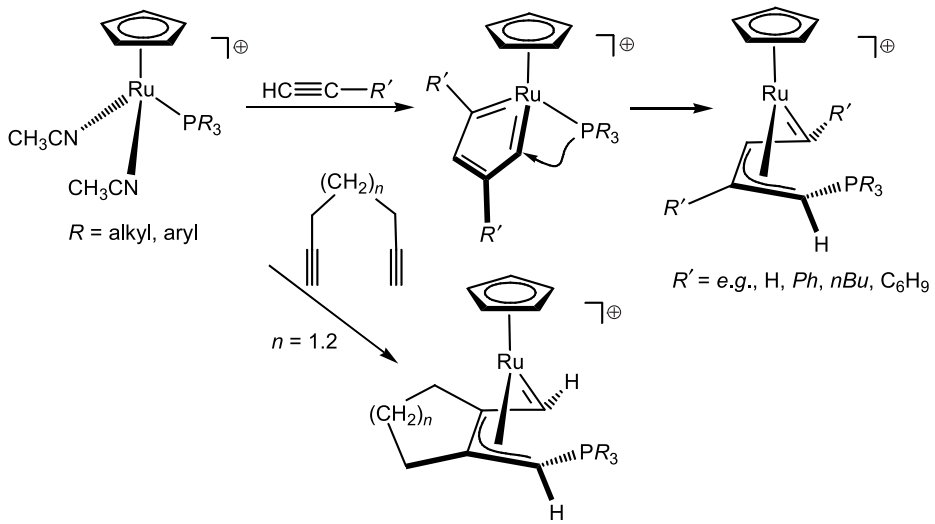
At first glance, the 14-electron fragment $[RuCp(PR_3)]^+$ (**2**) would seem a promising candidate for mediating cyclization reactions, since it is possible to vary the electronic and steric properties of the phosphine ligand through the substituents. In

this way the chemo- and regioselectivity of the coupling process might be controlled. However, despite of the fact that **2** is catalytically active in the isomerization of allyl alcohols [28] and is also a catalyst for the transfer hydrogenation of acetophenone and cyclohexanone as well as the isomerization of allyl ethers [29], the cyclotrimerization of alkynes is not initiated. Instead, a number of unusual and interesting products are obtained, depending on the structure of the alkyne and the substituent of the phosphane ligand [30].

In most reactions of the $[RuCp(PR_3)]^+$ fragment with alkynes the key intermediate is a cationic metallacyclopentatriene – in contrast to a metallacyclopentadiene – featuring two highly electrophilic carbene carbon atoms. In one case, namely the reaction of $[RuCp(PCy_3)(CH_3CN)_2]^+$ with 2,8-decadiyne, such an intermediate has been unequivocally identified by means of $^{13}C\{^1H\}$ NMR spectroscopy. The characteristic resonance in the $^{13}C\{^1H\}$ NMR spectrum at 325.6 ppm can be associated with the carbene ring carbon atoms. The formation of a simi-




**Scheme 2**




**Scheme 3**

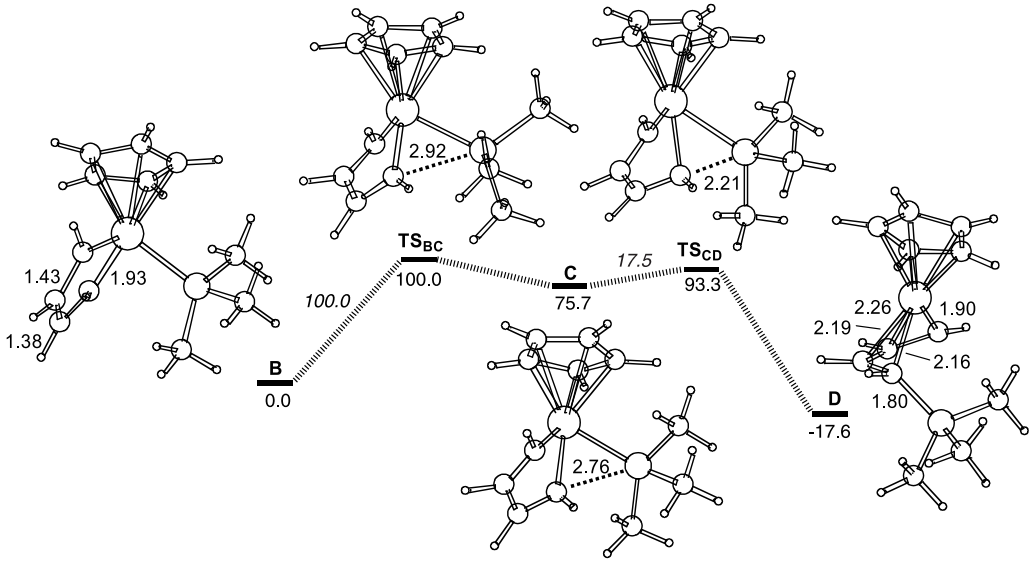



**Fig. 1** Reaction profile of the computed relative *Gibbs* free energies/kJ/mol for the migratory insertion of a P*Me*$_3$ ligand into the Ru–C double bond of the ruthenacyclopentatriene intermediate **B** to give the allyl carbene complex **D** (bond distances/Å)

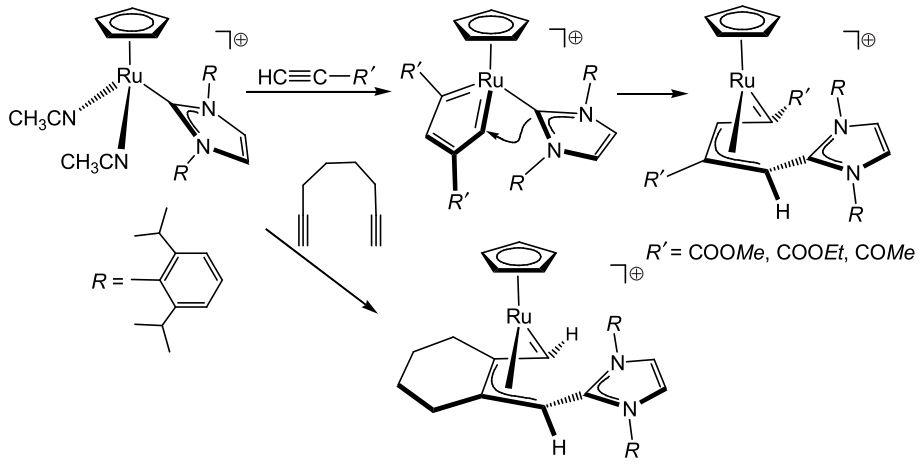
lar metallacyclopentatriene complex has been observed when [Ru*Cp*(Sb*Ph*$_3$)(CH$_3$CN)$_2$]$^+$ is reacted with 2,8-decadiyne [31]. It is also very important to notice that the initial oxidative coupling step with terminal alkynes takes place selectively in a head-to-tail rather than in head-to-head fashion as observed for the Ru*Cp*Cl fragment. Thus the substituents in the cationic metallacyclopentatriene intermediate end up exclusively in the 1 and 3 positions (Scheme 2).

However, the electrophilicity of the two carbene carbon atoms gives rise to a wide array of interligand transformations, preventing the attack of a third alkyne molecule. Among other structures, ruthenium allyl carbene complexes are typically formed (Scheme 3). In the case of terminal alkynes C–C coupling is highly selective in a head-to-tail fashion with the substituents ending up at the carbene carbon atom and the internal carbon atom of the allylic moiety, whereas with the diynes the two internal sp carbons are involved. In the allyl carbene systems formed in both cases all four carbon atoms of the C$_{1-4}$ chain are bonded to the Ru*Cp* fragment. This reaction proceeds very fast even if bulky phosphanes such as P*Cy*$_3$ are used and substituents at the $\alpha$,$\alpha'$ carbon atoms of the metallacycle are present.

In the absence of kinetic data, DFT/*B3LYP* calculations have been performed to shed light on the mechanism of this unusual phosphane migration process with the results shown in Fig. 1. As model system the [Ru*Cp*(P*Me*$_3$)]$^+$ fragment has been choosen.

The conversion of the metallacyclopentatriene **B** into the final allylcarbene complex **D** proceeds with relatively small activation barriers, the rate limiting step being an initial distortion to produce the intermediate **C**. What happens is bending of the metallacycle, approaching the C$_\beta$ carbon atoms to the metal. Conversely, at the other side of the molecule, the Ru–C$_\alpha$ bond stretches and this carbon atom starts to form a new C$_\alpha$–P bond. This feature is already obvious in the transition state **TS$_{BC}$** and the activation energy is 100.0 kJ/mol. **TS$_{BC}$** is much closer to **C** than **B**. The final transformation involves complete Ru–P bond breaking and formation of the C$_\alpha$–P bond, with simultaneous formation of the allylcarbene, and the adjustments of the carbon chain, namely formation of the Ru–C$_\beta$ bonds.

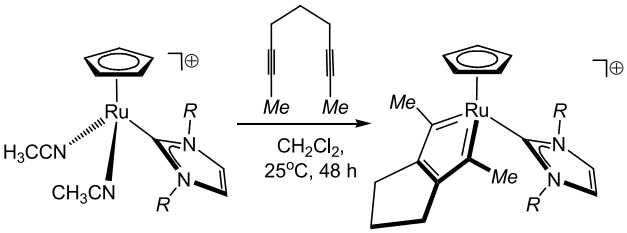
N-heterocyclic carbenes (*NHC*) play an important role as ''noninterfering'' supporting ligands in many stoichiometric and catalyzed reactions of transition metal complexes [32]. The role of the carbene ligands is similar to that of tertiary phosphine ligands but they are in general much more strongly bound to a metal center than phosphines and thus less likely to be replaced by other ligands [33]. On the other hand, due the obvious electronic differences between *NHC* ligands and tertiary phosphines it is not surprising that *NHC* ligands are much more likely to participate




**Scheme 4**

in rearrangement reactions within the metal coordination sphere. In fact, several recent reports clearly show that *NHC*-metal bonds are kinetically not inert and are able to participate in various intramolecular reactions [34] This includes migration of a methyl group to a coordinated *NHC* ligand and the reductive elimination of alkylimidazolium salts from *NHC* alkyl complexes. Since our studies of the interactions between the $[RuCp(PR_3)]^+$ moiety and alkynes have revealed that the $PR_3$ ligand rapidly migrates onto the carbene carbon atom of a highly electrophilic biscarbene intermediate affording allyl carbene complexes (Scheme 3) it was obvious to switch over to the bulky *NHC* ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (*IPr*) in order to see whether similar transformations take place [35, 36].

Treatment of $[RuCp(IPr)(CH_3CN)_2]PF_6$ with 2 equiv of the terminal alkynes HC≡C*R* (*R* = COO*Me*, COO*Et*, CO*Me*) and 1,7-octadiyene results in the formation of allyl carbene complexes $[RuCp(=C(R)–\eta^3–CHC(R)CH–IPr)]PF_6$ and $[RuCp(=CH–\eta^3–C(CH_2)_4CCH–IPr)]PF_6$ in essentially quantitative yield (Scheme 4). These reactions proceed also *via* an electrophilic metallacyclopentatriene similarly to the reactions with $PR_3$ and $SbR_3$ as co-ligands [30, 31]. The involvement of such an intermediate was evident from $^1H$ and $^1H–^{13}C–$HSQC NMR measurements at −20°C in $CD_2Cl_2$. While with teminal alkynes no intermediates could be detected, with 1,7-octadiyene a characteristic low-field resonance at 17.08 ppm was observed assignable to the carbene hydrogens of a metallacyclopentatriene intermediate. This resonance is correlated with a signal at 298.0 ppm, which can be associated with the $C_\alpha$ ring




**Scheme 5**

carbons. In this context it has to be noted that recently we were even able to structurally characterize the first cationic metallacyclopentatriene from the reaction of $[RuCp(IPr)(CH_3CN)_2]PF_6$ with 2,7-nonadiyne featuring two electrophilic alkylidene moieties and one nucleophilic N-heterocyclic carbene [37] (Scheme 5).

A reasonable mechanism for this unusual *NHC* migration has been established by DFT/*B3LYP* calculations. The results of this study are shown in Fig. 2. Based on our experimental findings, starting point and key intermediate is obviously the metallacyclopentatriene complex **B** (with 1,3-dimethylimidazol-2-ylidene as model *NHC* ligand). The conversion of the metallacyclopentatriene **B** into the final allylcarbene complex **D** proceeds with relatively small activation barriers, the rate limiting step being an initial distortion to produce the intermediate **C**. What happens is bending of the metallacycle, approaching the $C_\beta$ carbon atoms to the metal. Conversely, at the other side of the molecule, the Ru–$C_\alpha$ bond stretches and this carbon atom starts to form a new $C_\alpha$–C(*NHC*) bond. This feature is already obvious in the transition state $\mathbf{TS_{BC}}$ where the C–C(*NHC*) distances

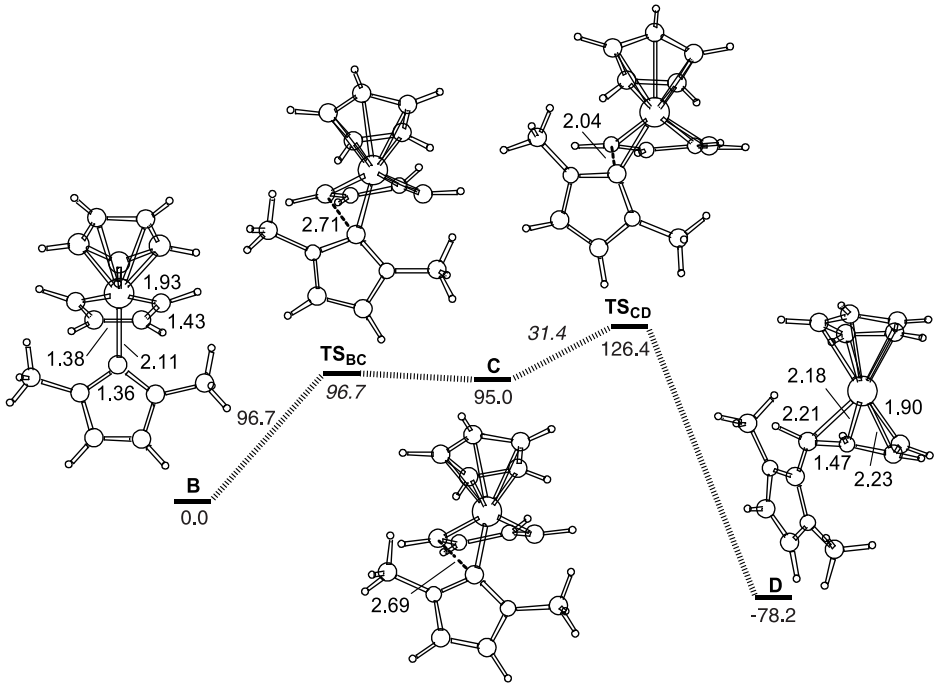
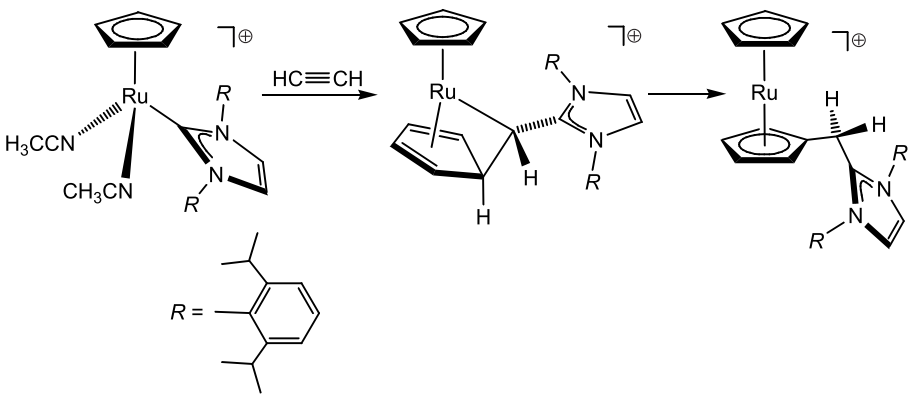



**Fig. 2** Reaction profile of the computed relative *Gibbs* free energies/kJ/mol for the migratory insertion of a 1,3-dimethylimidazol-2-ylidene ligand into the Ru–C double bond of the ruthenacyclopentatriene intermediate **B** to give the allyl carbene complex **D** (bond distances/Å)

is 2.71 Å. The free activation energy is 96.7 kJ/mol. $\mathbf{TS_{BC}}$ is much closer to **C** than **B**. The final transformation involves complete Ru–C(*NHC*) bond breaking and formation of the $C_\alpha$–C(*NHC*) bond, with simultaneous formation of the allyl carbene, and the adjustments of the carbon chain, namely formation of the Ru–$C_\beta$ bonds. The overall reaction from **B** to **D** is exergonic by −78.2 kJ/mol. The energy profiles of P$R_3$ and *NHC* migration (Figs. 1 and 2) are very similar emphasizing the similarities of these ligand systems in this particular reaction.

*Migratory insertion of acetylene in N-heterocyclic carbene complexes of ruthenium: formation of (ruthenocenylmethyl)imidazolium salts*

With parent acetylene and [Ru*Cp*(*IPr*)$(CH_3CN)_2$]-$PF_6$ an unusual C–C coupling process takes place involving three acetylene molecules and migration of the *NHC* ligand to give the formal [2 + 2 + 1] cycloaddition products [Ru*Cp*($\eta^4$–$C_5H_5$-$\eta^1$–CH–*IPr*)]$PF_6$ (Scheme 6). This complex undergoes a facile 1,2–H shift to afford the (ruthenocenylmethyl) imidazolium salt [Ru*Cp*($\eta^5$–$C_5H_4$–$CH_2$–*IPr*)]$PF_6$.




**Scheme 6**

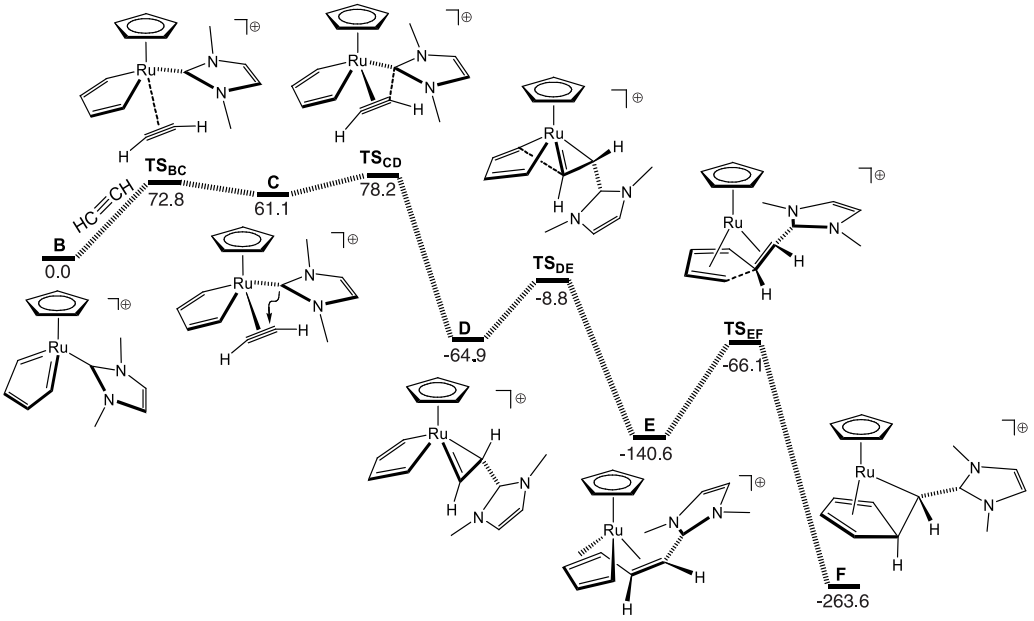



**Fig. 3** Reaction profile of the computed relative *Gibbs* free energies/kJ/mol for the reaction of the ruthenacyclopentatriene **B** with acetylene to give the formal [2 + 2 + 1] cycloaddition product **F** (bond distances/Å) with 1,3-dimethylimidazol-2-ylidene as model *NHC* ligand

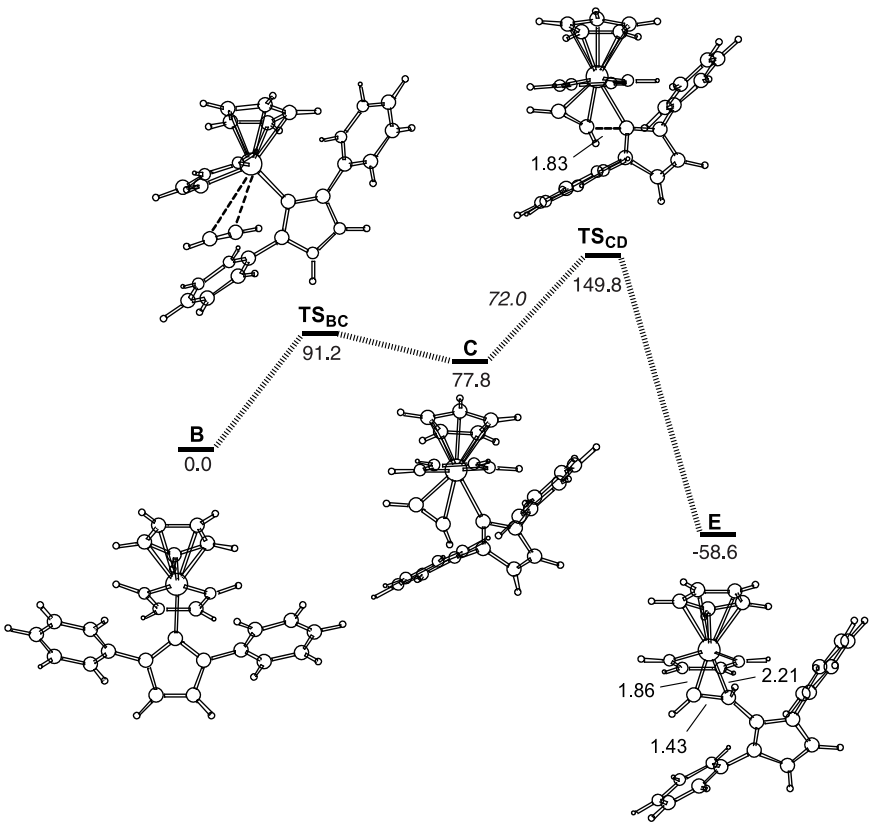



**Fig. 4** Reaction profile of the computed relative *Gibbs* free energies/kJ/mol for the reaction of the ruthenacyclopentatriene **B** with acetylene to give the 1-metallacyclopropene intermediate **D** (bond distances/Å) with 1,3-diphenylimidazol-2-ylidene as model *NHC* ligand

A conceivable mechanism for this reaction sequence is established by means of DFT calculations. A free energy profile for the conversion of **B** to the [2 + 2 + 1] cycloaddition product (**F** in the model) is depicted in Fig. 3 with 1,3-dimethylimidazol-2-ylidene ($R = Me$) as model *NHC* ligand. Additionally, the free energy profile for the most crucial conversion of **B**–**D** has been calculated with the bulkier *NHC* ligand 1,3-diphenylimidazol-2-ylidene ($R = Ph$) (Fig. 4) since it has been shown that aromatic and aliphatic imidazolium compounds exhibit different electronics and particularly significant steric differences [38]. Starting point and key intermediate is again the ruthenacyclopentatriene complex **B** which is able to accommodate a third acetylene molecule to afford the metallacyclopendiene acetylene complex **C**. This step requires an free activation energy of 72.8 and 91.2 kJ/mol for $R = Me$ and $Ph$. The most remarkable step is the insertion of acetylene into the Ru–C bond of **C** resulting in the formation of the novel metallacyclopentadiene 1-metallacyclopropene complex **D**. The free activation energy for this intramolecular process is very low for $R = Me$ requiring merely 17.2 kJ/mol but 72.0 kJ/mol for $R = Ph$ and may be largely attributed to the increased steric bulk of the 1,3-diphenylimidazol-2-ylidene ligand. In fact, *Nolan et al*. have demonstrated that the electronic differences for *NHC* ligands are relatively small when moving from alkyl- to aryl-substituted ligands, especially, compared to the substantial electronic differences seen in phosphine ligands [38]. It should be noted that coupling reactions between a coordinated alkyne and coordinated phosphines to yield 1-metallacyclopropenes have been reported in the literature [39, 40]. In all of these cases, however, the ''formal'' insertion of alkynes into metal-P bonds appears to be a nucleophilic addition at the coordinated alkyne requiring prior dissociation of the phosphine. In fact, intermolecular nucleophilic additions of phosphines and phosphites to alkyne ligands are feasible and well established [41] complex **C** is prone to C–C coupling between the carbene carbon atom of the 1-metallacyclopropene moiety and the $\alpha$-carbon of the metallacyclopentadiene unit to give **E**. This reaction requires a free activation energy of 56.1 kJ/mol and is energetically very favorable releasing 146.4 kJ/mol. The final step is the insertion of the vinyl moiety into the $\eta^2$-olefin unit giving **F**, thus completing the [2 + 2 + 1] cyclotrimerization. The overall reaction from **B** to **F** is strongly exergonic by −263.6 kJ/mol.

## Conclusion

It is highly fascinating to witness the vast and diversified varieties of rearrangements within and between molecules ligated to the ruthenium(II) center. Tertiary phosphanes and *NHC* ligands, which ordinarily are held to be spectator ligands, function here as acting ligands, giving rise to a wide array of scenarios competing with the process of cyclotrimerization. Our experimental and theoretical data provide for the first time clear evidence that $PR_3$ as well as N-heterocyclic carbenes are able to migrate from a ruthenium center to an electrophilic alkylidene ligand (metallacyclopentatriene). These processes are accompanied by Ru–P and Ru–C bond cleavage. Moreover, acetylene is able to undergo facile migratory insertion into the Ru–C bond of *NHC* ligands which has not been observed before in N-heterocyclic carbene complexes and contrasts the behavior of related phosphine systems.

## Computational details

All calculations were performed using the Gaussian98 software package [42] on the Silicon Graphics Power Challenge of the Vienna University of Technology. The geometry and energy of the complexes (298 K, 1 atm) were optimized at the *B3LYP* level [43] with the Stuttgart/Dresden ECP (sdd) basis set [44] to describe the electrons of the ruthenium atom. For the C, H, N, and P atoms the 6–31 g** basis set was employed [45]. A vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequency. Zero-point vibration energy (*ZPVE*) and thermal corrections (at 298 K) to the energy have been estimated on the basis of the frequency calculations at the optimization level and were not scaled. The geometries were optimized without constraints ($C_1$ symmetry). The vibrational eigenvectors corresponding to the reaction coordinate (with imaginary frequency) of all transition states were visually checked to confirm the connectivity of transition states with the reactants and the products. Crucial transition states have been confirmed by *IRC* calculations.

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