Ruthenium-Mediated C−C Coupling Reactions of Alkynes − The Key Role of Ruthenacyclopentatriene Complexes

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Keywords: Ruthenium / Cyclopentadienyl Ligands / Acetylenes / Oxidative coupling / Carbenes / Vinylidene ligands

This review describes the highlights of the reactions of the substitutionally labile neutral pseudo 14VE complexes RuCp′(COD)Cl (Cp′ = Cp, Cp*; COD = 1,5-cyclooctadiene) and the cationic complexes $[CpRu(CH_3CN)_2L]^+$ and $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2\text{-}\kappa^1P\text{-}PPh_2)]^+$ with alkynes. The ligand L is a coligand, whose nature turns out to be critical to the outcome of the reaction, and varies from halides to tertiary phosphanes, tertiary stibines, CO, and acetonitrile. Along these lines vast and diversified varieties of rearrangements within and between molecules ligated to the transition-metal center has been discovered. A crucial role in all reactions reported is the intermediacy of electrophilic ruthenacyclopentatriene complexes, an entity featuring a biscarbene functionality.

1. Introduction

Of the diverse elemental combinations, carbon−carbon bond-forming reactions have attracted great interest for their many applications in industrial and synthetic processes. This type of conversion is catalyzed mainly by transition-metal compounds. The basis of the catalytic action is the remarkable ability of transition-metal containing fragments to coordinate organic molecules. Besides the fascinating world of the structural chemistry of these complexes thus generated, a crucial consequence is the essential modification of the chemical behavior through ligation. In fact, some of the most powerful and selective methods for preparing organic molecules involve organometallic catalysis. Specifically of interest to our group are C−C and C−heteroatom bond-forming reactions involving alkynes, such as the cyclotrimerization of alkynes or the cyclocotrimerization of two alkynes with unsaturated organic compounds containing C=X bonds (X = C, O, S, N etc.) for obtaining carbocycle and heterocycle structures as exemplarily shown in Scheme 1.

The development of cyclization methods is 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 the ruthenium chemistry. Lying at the heart of the periodic table, ruthenium combines the valuable properties of both early- and late-transition-metal relatives. Thus, the

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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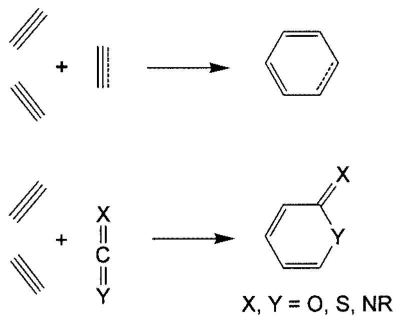
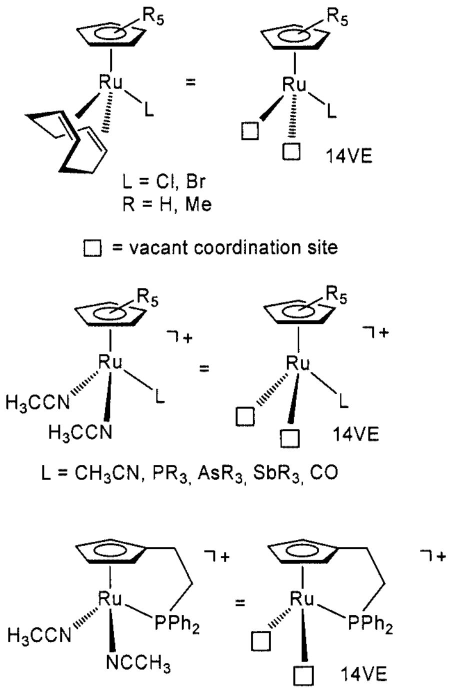


Scheme 1

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.[1] 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,[2,3] while many other transition-metal centers are deactivated because of strong coordination to sulfur compounds.

The elucidation of the mechanistic aspects of homogeneous catalysis has been an ambitious scientific goal from the beginning of the interest in organometal catalysis. Unfortunately, kinetic studies in this field of research are scarce. One of the reasons is the fact that often the rates of the successive steps are too fast to be observed separately, and the diverse reaction intermediates are not stable enough to be characterized. Fortunately, 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, β-hydrogen transfer, σ-bond metathesis, and nucleophilic addition reactions.[4] 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 what follows we cover important results of our recent research in the context of work from others in the field. Specifically, we will describe the highlights of the reactions of the substitutionally labile neutral pseudo 14VE complexes RuCp′(COD)L (Cp′ = Cp, Cp*; COD = 1,5-cyclooctadiene; L = Cl, Br) and the cationic complexes $[CpRu(CH_3CN)_2L]^+$ and $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2\text{-}\kappa^1P\text{-}PPh_2)(CH_3CN)_2]^+$ with various triple and double bonds. The ligand L is a co-ligand, whose nature turns out to be critical to the outcome of the reaction, and varies from halides to tertiary phosphanes, tertiary arsanes, tertiary stibines, CO, and acetonitrile (Scheme 2). Along these lines there are many diverse rearrangements within and between molecules ligated to the transition-metal center.



Scheme 2

2. The Cyclotrimerization of Alkynes Mediated by the Cp′RuCl Fragment

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 ($\Delta H^\circ = -143$ kcal/mol).[5] On the other hand, and contrary to the Hammond postulate, the activation energy is prohibitively high and is calculated to lie in the 60−80 kcal/mol region.[6] Such high barriers arise from 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.[6a] Another contribution to the high barrier stems from closed-shell repulsions between the filled π-orbitals (HOMO−HOMO interactions),[6b] despite some aromatic stabilization of the transition state.[7]

Noteworthy, the activation energy is diminished appreciably through the coordination of the alkynes to the transition-metal centers. Actually, since the pioneering work done in 1948 by Reppe,[8] 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 for synthesizing functionalized arene systems.[9] Subsequently, a wide array of transition-metal containing fragments were found to actively catalyze the reaction. Of these, derivatives of cobalt and ruthenium proved particularly efficient, while tolerating the presence of varied functionality of the alkyne. For the former, the $CpCoL_2$ (L = CO, PR_3, olefin) catalyst family was studied in great detail.[10,11] In recent years, the ruthenium complexes Cp′Ru(COD)L and Ru(η^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,[12] olefins,[13] allylic ethers,[14] dicyanides,[15] nitriles,[16] tricarbonyl compounds,[17] isocyanates,[2] isothiocyanates, and CS_2.[3]

One problem that should be noted is that the reactions rarely proceed with high chemo- and regioselectivity. That is, when the method is to be applied to the preparation of substituted aromatic compounds from three different, unsymmetrical acetylenes, 38 homo- and cross-coupling products may possibly be produced.[18] Thus, the assembly of such acetylenes to form strictly one single aromatic compound is a formidable challenge. For this goal, a knowledge of the detailed mechanism of the catalytic cycles might be very helpful. The issues to be addressed are among others: which intermediate controls the selectivity of the overall cyclotrimerization process or what determines the size of the rings to be formed. Actually, in the development of cyclization methods, facilitating formation of unusual ring sizes represents a significant objective.[19]

There are three recent theoretical examinations of the mechanism of acetylene cyclotrimerization. One is based on $CpCo(L)_2$ complexes,[20] and the other two on the Cp′RuCl fragment.[21,22] The proposal derived from DFT/B3LYP calculations performed by our group is shown in Scheme 3 and reveals a few uncommon intermediates (see also Figure 1, Figure 2, and Figure 3). In the first step, the starting precatalyst Cp′Ru(COD)Cl undergoes two ligand-substitution reactions resulting in the formation of the bis-acetylene complex **A**. Subsequent oxidative coupling of the two acetylene ligands generates the metallapentatriene complex **B**. In the next step, **B** is readily able to coordinate a third acetylene to give the acetylene-coordinated ruthenacycle **C**. No less than three successive intermediates could be found for subsequent arene formation. The first, an unusual ruthenabicyclo[3.2.0]heptatriene **D** rearranges to a very unsymmetrical metallaheptatetraene **E**. Ultimately, an η^2-coordinated benzene ring appears in species **F** through a reductive elimination step. Completion of the cycle is achieved by an exothermic displacement of the arene by two acetylene molecules thereby regenerating **A**.

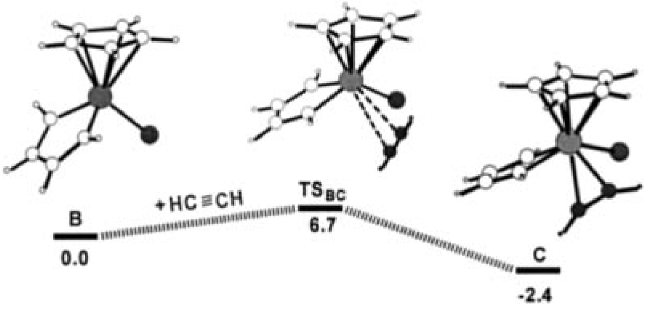
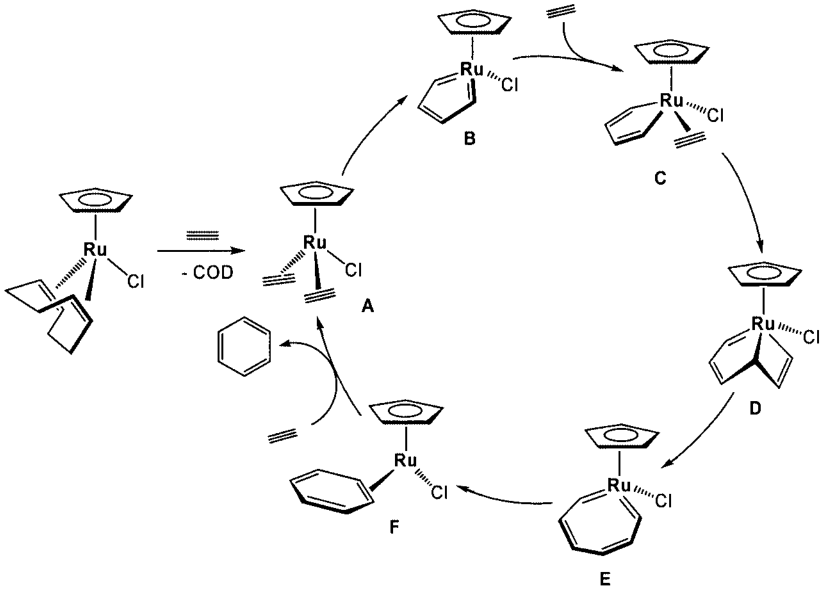


Figure 1. Energy profile for the cyclotrimerization of acetylene (energies in kcal mol^{-1}, relative to the bisacetylene complex **A**)

Some remarks about the key intermediates follows.

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 CpCo system the respective intermediate is better formulated as a metallacyclopentadiene (type **I**), in the RuCp′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 isolated and unequivocally characterized by NMR spectroscopy and X-ray crystallography.[23] Two bi-



Scheme 3

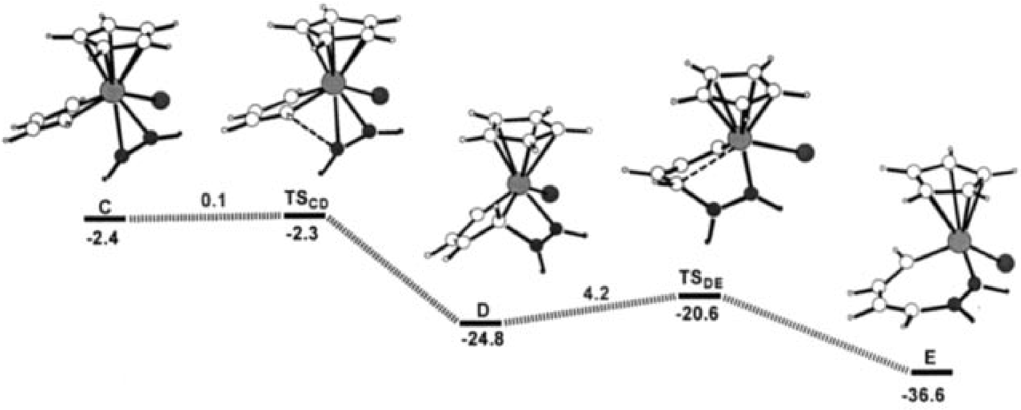


Figure 2. Energy profile for the cyclotrimerization of acetylene (energies in kcal mol^{-1}, relative to the bisacetylene complex **A**)

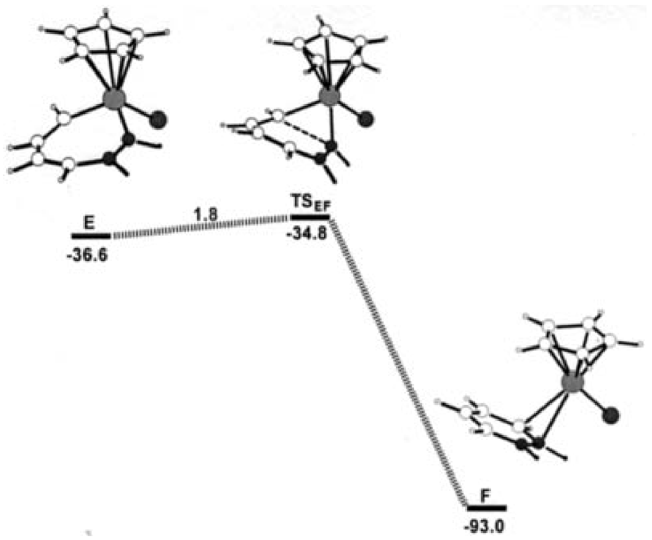
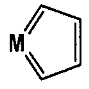


Figure 3. Energy profile for the cyclotrimerization of acetylene (energies in kcal mol^{-1}, relative to the bisacetylene complex **A**)

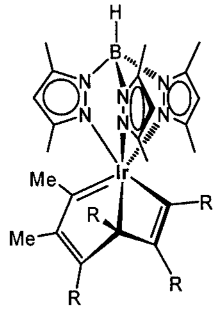
I



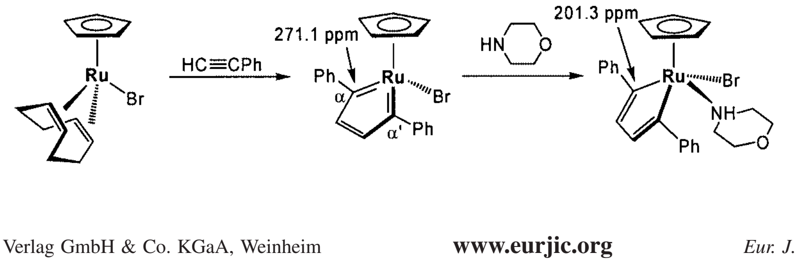
II

cyclic analogues also have been isolated and characterized by X-ray crystallography.[24] In fact RuCp′(COD)L (L = Cl, Br) reacts with aryl acetylenes to give stable ruthenacyclopentatriene complexes (Scheme 4) that exhibit characteristic ^{13}C NMR resonances in the range of about 270−240 ppm. The oxidative coupling takes place regioselectively in a head-to-head fashion with the substituents ending up in the α and α′ position. It should be noted that ruthenacylopentatrienes serve as key intermediates in several catalytic reactions involving alkynes, for example, the double cyclopropanation of 1,6-diynes with strained cyclic olefins,[13a] the reaction of two alkyne molecules with carboxylic acids,[25] the cycloisomerization of alkynes and propargylic alcohols,[26] or the hydrative diyne cyclization.[27] The reactivity of **B** is guided by the possibility of an attack by 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 (Scheme 4).[23a,28] This 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 (see below), as well as bulky substituents in the 1- and 4-positions.

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.[29] The crucial inter-



R = COOMe



Scheme 4

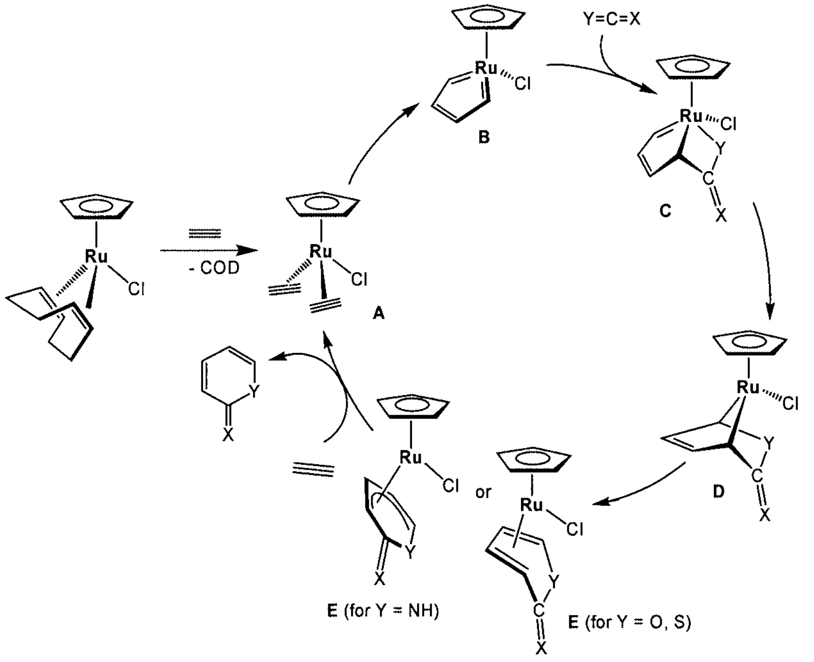
mediate **D** is shown in Figure 2 in order to emphasize the steric constraints between the hydrogen atom of the metallacycle (i.e. from the first two acetylene molecules) and that of the Cp ring. It is easy to see that this intermediate controls the selectivity of the overall cyclotrimerization process. Acetylene molecules carrying two bulky substituents will therefore experience considerable repulsion 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 η^3 and η^5, as is also found in other systems.[30] The asymmetry of **E** removes the symmetry-forbidden character from the final step.

F: This final complex is surprising when considering the 18e rule, because the benzene ring is η^2-bonded rather than η^4 as in the corresponding isoelectronic CpCo 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 be η^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.[31,32]

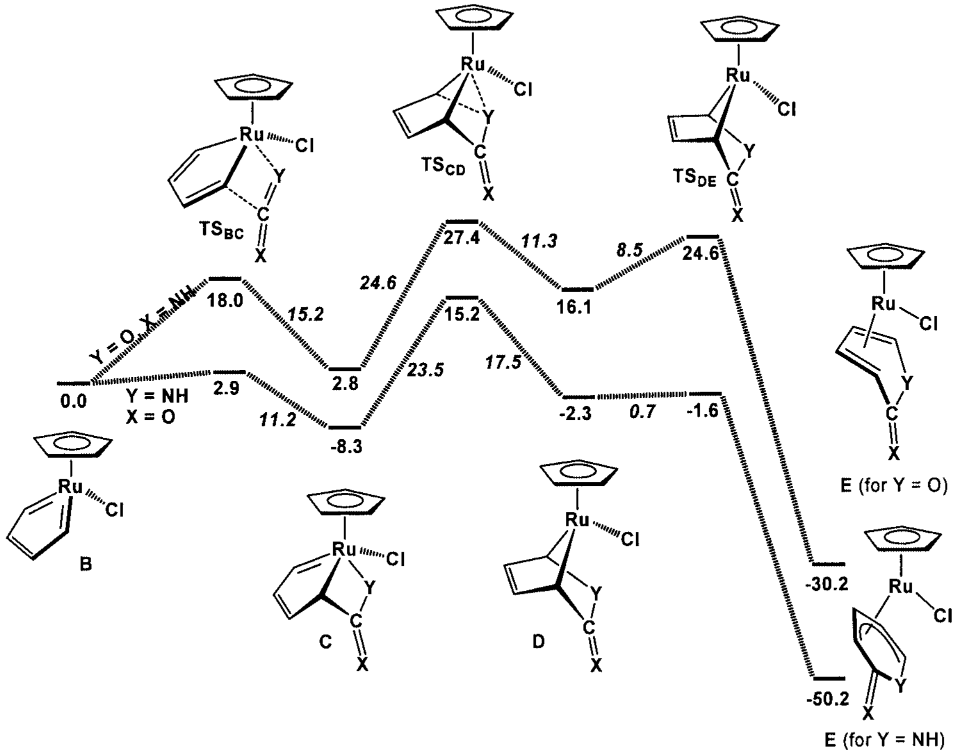
3. The Cyclocotrimerization of Alkynes with Unsaturated Organic Molecules Mediated by the Cp′RuCl Fragment − Chemoselective Formation of Pyridine-2-one and Thiopyran-2-imine from Isocyanates and Thioisocyanates

As mentioned above, the cyclocotrimerization of two alkynes with unsaturated organic compounds containing C=X bonds (X = O, S, N etc.) is a synthetically useful and atom economic process for obtaining a variety of six-membered heterocyclic systems. Here we focus exemplarily on the particularly intriguing case of coupling of diynes with ambidentate molecules RN=C=X (X = O, S). Clearly, there are two different kinds of ring closures possible, which lead to either pyridine-2-ones and pyridine-2-thiones, or to pyran-2-imines and thiopyran-2-imines according to Scheme 1. Experimentally it was found that in the case of X = O, pyridine-2-ones, that is the nitrogen-heterocycle, are exclusively formed, whereas in the case of X = S, the chemoselectivity is reversed to give thiopyran-2-imines, that is the sulfur-heterocycle. Gratifyingly, the different chemoselectivities were reproduced well by the theoretical studies using DFT/B3LYP calculations performed in our laboratory.[33] The course of the reactions is characterized by two intermediates that are not so trivial in addition to the metallacyclopentatriene **B**, viz. the bicyclic carbene **C**, and the coordinatively unsaturated metallaheteronorbornene **D**, according to Scheme 5.

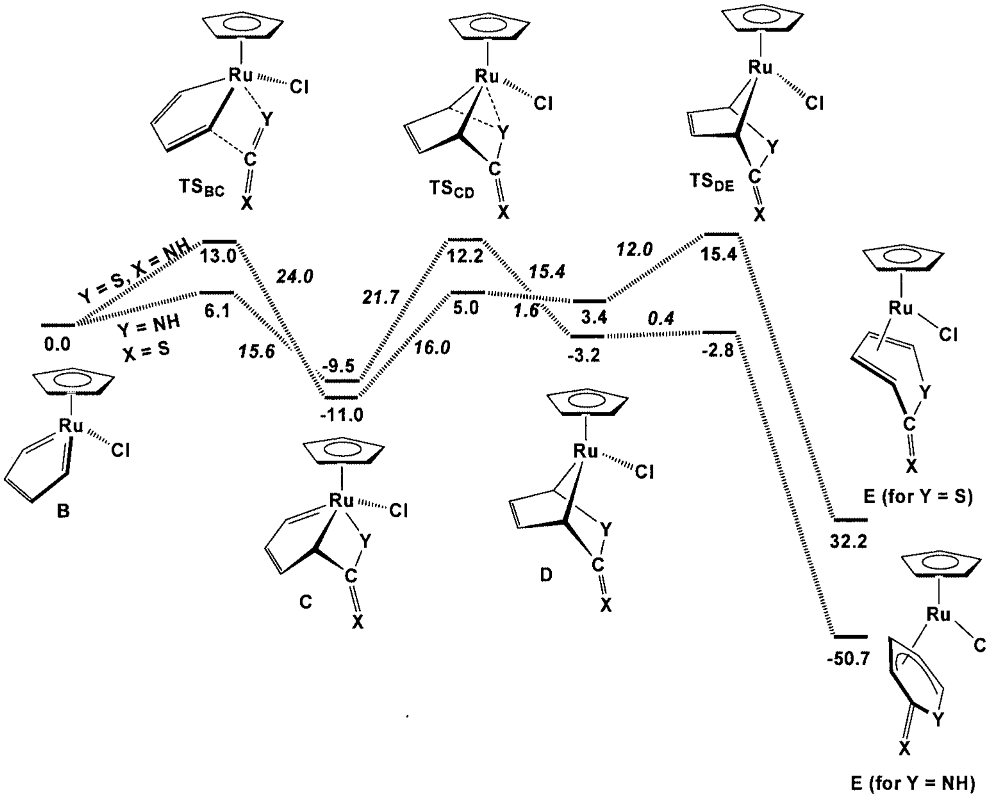


Scheme 5

According to the proposed mechanism, the key reaction step is addition of a double bond to the metallacyclopentatriene to give a bicyclic carbene intermediate. This double-bond-addition is initiated by η^1 attack at the ruthenium center, and it is only the attacking atom that is finally incorporated in the cycle. Thus, the chemoselectivity arises from



Scheme 6



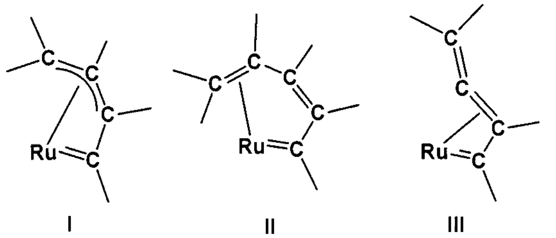
Scheme 7

the fact that, for HNCO, N attack is preferred over O, but for HNCS, S attack is preferred over N. The energy profile for the two alternatives, viz. the orientation of N, O, and S towards the ruthenium center, is shown in Scheme 6 and Scheme 7.

4. Dramatic Changes seen upon Replacement of Cl in Cp′RuCl with ER_3 (P, Sb) and CO

At first glance, the 14-electron fragment $[RuCp(PR_3)]^+$ would seem a promising candidate for mediating cyclization reactions, since it is possible to vary the properties of the phosphane ligand through the substituents. In this way, the regioselectivity of the coupling process might be controlled. However, although this species is catalytically active in the isomerization of allyl alcohols[34] and is a catalyst for the transfer hydrogenation of acetophenone and cyclohexanone as well as the isomerization of allyl ethers,[35] 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.

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 two cases, namely the reactions of $[RuCp(PCy_3)(CH_3CN)_2]^+$ and $[RuCp(SbPh_3)(CH_3CN)_2]^+$ with 2,8-decadiyne, such intermediates have been unequivocally identified by means of $^{13}C\{^1H\}$ NMR spectroscopy. The characteristic resonances in their $^{13}C\{^1H\}$ NMR spectra at $\delta = 325.6$ and 330.0 ppm, respectively, can be associated with the carbene ring carbon atoms. It is also very important to note 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 RuCp′Cl fragment. Thus, the substituents in the cationic metallacyclopentatriene intermediate are exclusively in the α- and β′-position (see Scheme 9). The electrophilicity of the two carbene carbon atoms gives rise to a wide array of inter-ligand transformations, preventing the attack of a third alkyne molecule. Among other structures, ruthenium allyl carbene (**I**), butadienyl carbene (**II**), and allenyl carbene complexes (**III**) are formed (Scheme 8).[36,37]



Scheme 8

4.1. Formation of Ruthenium Allyl Carbenes − Migration of a PR_3 Ligand

As shown in Scheme 9 (and in Scheme 10), the phosphane coligand migrates from Ru to C generating an allyl carbene. In the case of terminal alkynes, C−C coupling is highly selective in a head-to-tail fashion, with the result that the substituents are at the carbene carbon atom and the internal carbon atom of the allylic moiety, whereas with the diynes, the two internal sp carbon atoms 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 RuCp fragment. This reaction proceeds very fast even if bulky phosphanes such as PCy_3 are used and substituents at the α-, α′-carbon atoms of the metallacycle are present. A structural view of $[CpRu(=CH-(\eta^3-CC(CH_2)_3CHPCy_3)]PF_6$ showing the migration of the bulky PCy_3 ligand is depicted in Figure 4.

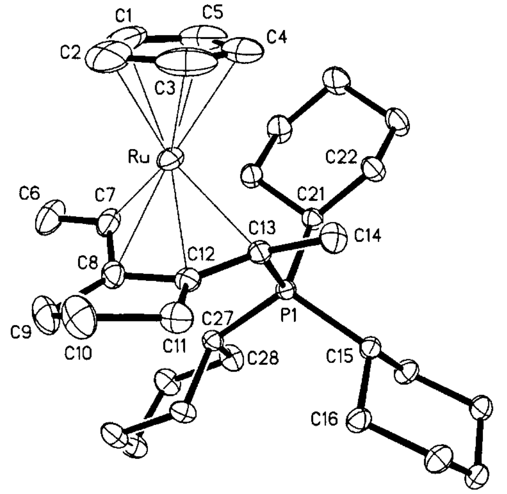
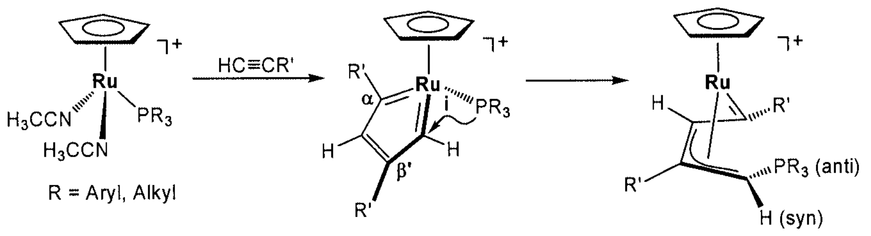


Figure 4. Structural view of $[CpRu(=CH-(\eta^3-CC(CH_2)_3CHPCy_3)]PF_6$ (PF_6^- omitted for clarity)



Scheme 9

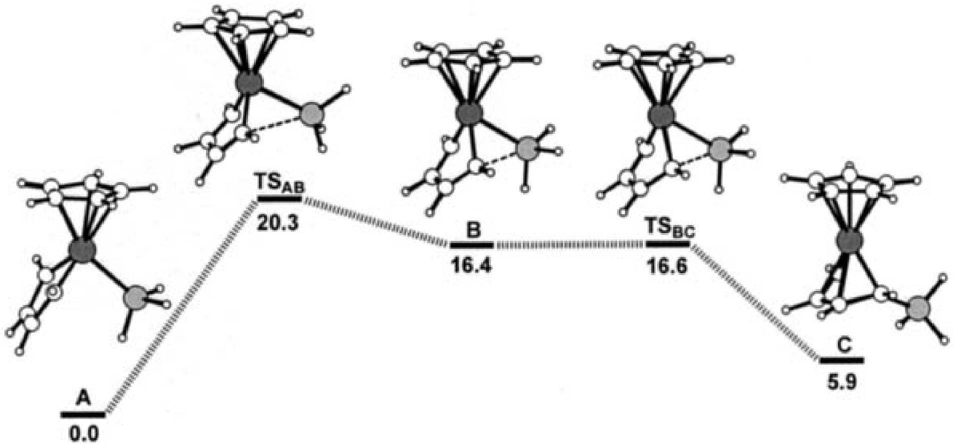
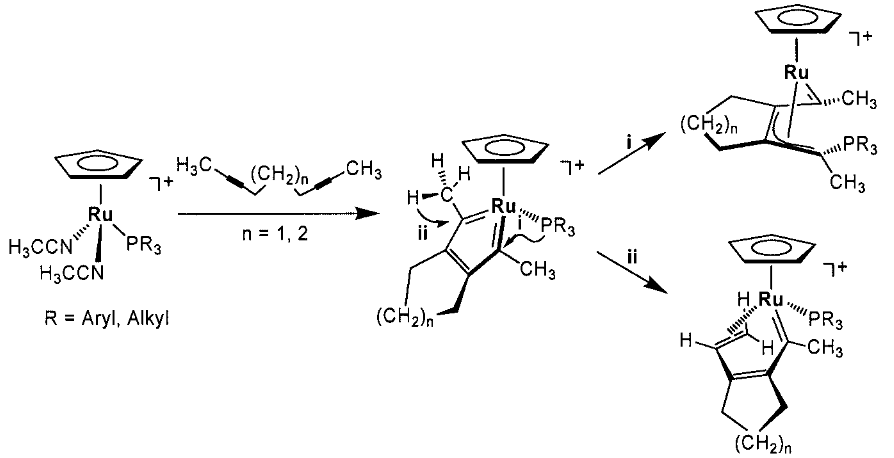


Figure 5. Energy profile of the B3LYP potential energy surfaces for the conversion of the ruthenacyclopentatriene complex **A** into the allyl carbene **C**

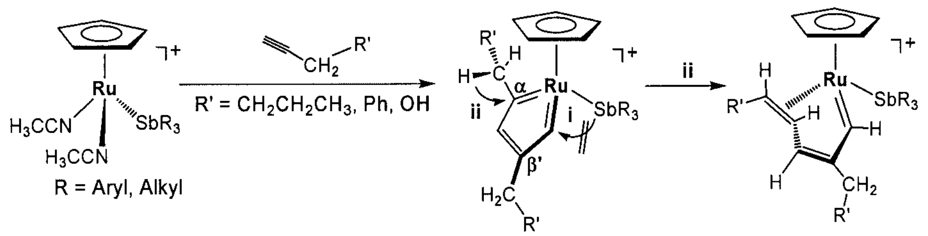
In the absence of kinetic data DFT/B3LYP calculations have been performed to shed light on the mechanism of this unusual phosphane migration process; the results are shown in Figure 5. The conversion of the metallacyclopentatriene **A** into the final allylcarbene complex **C** proceeds with relatively small activation barriers; the rate-limiting step is the initial distortion to produce the intermediate **B**. The metallacycle bends and approaches the C atoms in the β-position 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$_{AB}$**, and the activation energy is 20.3 kcal mol^{-1}. **TS$_{AB}$** is much closer in energy to **B** than to **A**. 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, which involve formation of the Ru$-$C$_{\beta}$ bonds.

4.2. Formation of Ruthenium Butadienyl Carbenes − Carbene to Olefin Interconversion through a 1,2-Hydrogen Shift

If the alkyne has an α-alkyl substituent, in some cases, a competitive intramolecular 1,2-hydrogen migration results in the formation of a butadienyl carbene (Scheme 10). A structural view of [CpRu(=C(CH$_3$)C(CH$_2$)$_4$C-η^2-CH=



Scheme 10



Scheme 11

$CH_2)(PPh_3)]PF_6$ is given in Figure 6. When pathway (i) is preferred over (ii), the phosphane ligand is more nucleophilic. In this respect, the mechanistic change-over from (i) to (ii) is noted when phosphane is replaced by other group 15 ligands AsR_3 and SbR_3 (Scheme 11). Thus, arsane and stibine ligands have no tendency to migrate.[37] Under certain circumstances both allyl carbene and butadienyl carbene complexes can undergo further transformations as follows.

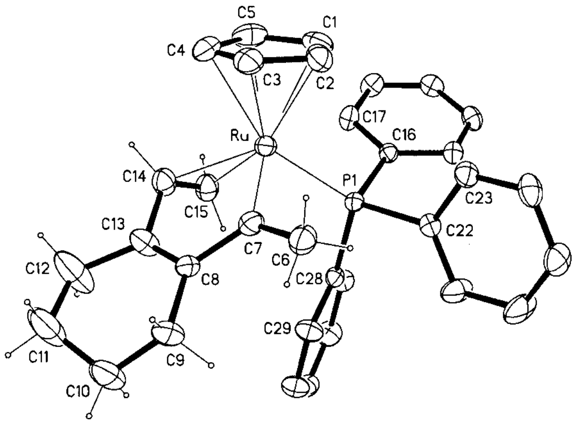
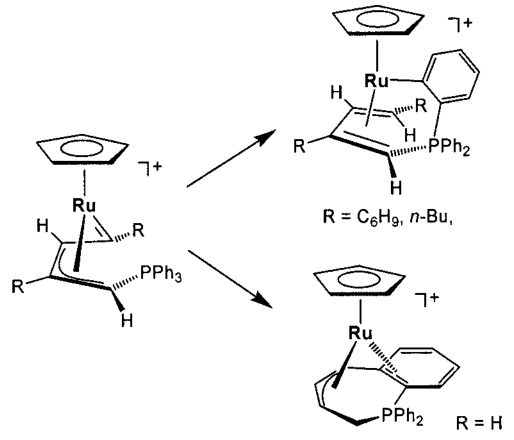


Figure 6. Structural view of $[CpRu(=C(CH_3)C(CH_2)_4C\text{-}\eta^2\text{-}CH=CH_2)(PPh_3)]PF_6$ (PF_6^- omitted for clarity)

4.3. Ruthenium Allyl Carbenes as Masked Coordinatively Unsaturated Complexes − Intramolecular C−H Bond Activation

Ruthenium η^3-allyl carbene complexes act as pseudo-16e species and are capable of activating C−H bonds of aryl and alkyl groups of the phosphane.[38] This occurs if the phosphanes are sufficiently bulky such as PPh_3 or PCy_3, whereas no such reaction is observed with PMe_3. Pertinent reactions are given in Scheme 12 to 14. The initially formed allyl carbene complexes are not stable and, in some cases, transform slowly at room temperature into novel η^4-butadiene complexes featuring an orthometallated arene ligand derived from PPh_3.

A somewhat different reaction takes place when the parent acetylene is used: the allyl carbene intermediate eventually rearranges into $[RuCp(\eta^3\text{-}CHCHCH{-}CH_2PPh_2\text{-}\eta^2\text{-}C_6H_4)]^+$, as shown in Scheme 12. The structure and bonding features of this complex are rather unusual. Firstly, an *ortho* C−H bond of the PPh_3 substituent is activated that results in C−C bond formation between the carbene carbon atom of the allyl carbene moiety and the *ortho* arene carbon atom. In the course of this process the *ortho* hydrogen atom is transferred to the terminal carbon of the allyl carbene unit; this involves carbon $sp^2 \rightarrow sp^3$ rehybridization. Furthermore, besides coordination to an η^3-allyl moiety, the metal center is η^2-coordinated to a double bond of a phenyl ring adjacent to the P-donor of the PPh_3 substituent. This bonding mode is very rare, and thus only a few examples have been reported recently.[39] Molecular structures of $[RuCp(\eta^4\text{-}CH(C_6H_9)CHC(C_6H_9)CH{-}PPh_2(\eta^1\text{-}C_6H_4))]PF_6$ and $[RuCp(\eta^3\text{-}CHCHCH{-}CH_2PPh_2\text{-}\eta^2\text{-}C_6H_4)]PF_6$ are shown in Figure 7 and Figure 8.



Scheme 12

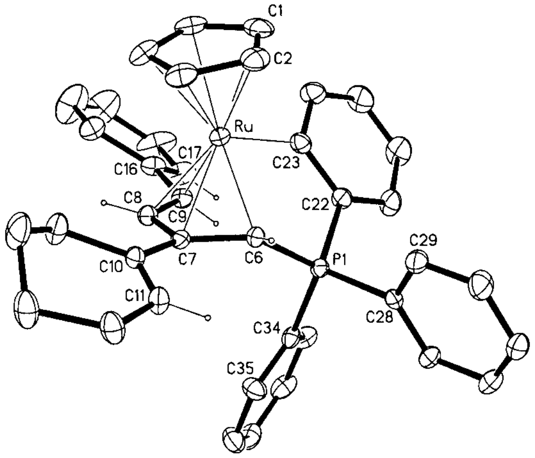


Figure 7. Structural view of $[RuCp(\eta^4\text{-}CH(C_6H_9)CHC(C_6H_9)CH{-}PPh_2(\eta^1\text{-}C_6H_4))]PF_6$ (PF_6^- omitted for clarity)

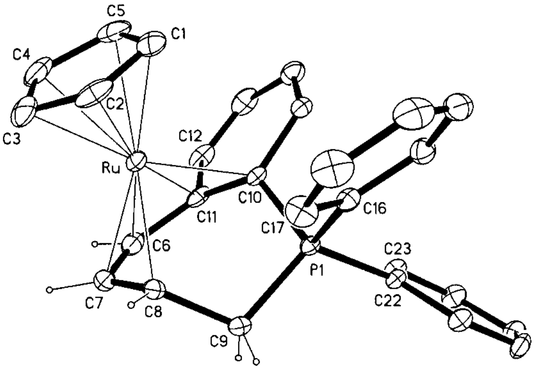
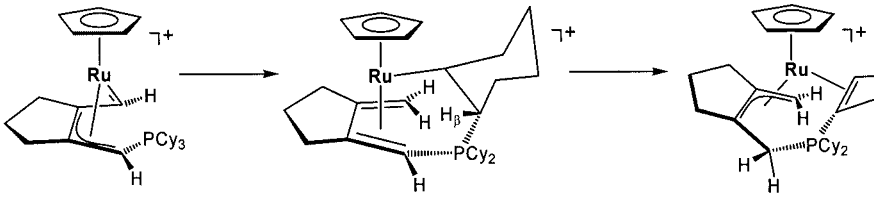


Figure 8. Structural view of $[RuCp(\eta^3\text{-}CHCHCH\text{-}CH_2PPh_2\text{-}\eta^2\text{-}C_6H_4)]PF_6$ (PF_6^- omitted for clarity)

Another example of facile intramolecular C−H bond activation initiated by allyl carbenes is shown in Scheme 13. Here one cyclohexyl substituent of the phosphane ligand is



Scheme 13

converted into an η^2-coordinated cyclohexenyl ligand (Figure 9). The reaction does not stop after the oxidative addition step but β-elimination also takes place The overall transformation involves the transfer of two hydrogen atoms from a cyclohexyl ring of PCy_3 to the C4 chain of the allyl carbene moiety. Notably, related reactions have been reported recently, which in some cases require the addition of olefin as an external hydrogen acceptor.[40]

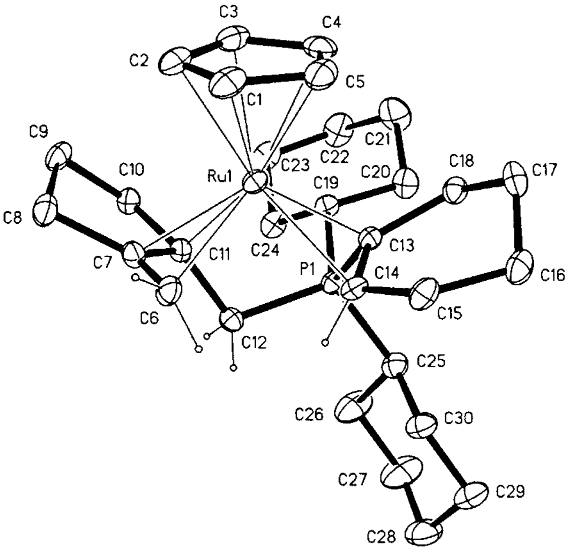


Figure 9. Molecular view of $[CpRu(\eta^3\text{-}CH_2C(CH_2)_3CCH_2PCy_2(\eta^2\text{-}C_6H_9)]PF_6$ (PF_6^- omitted for clarity)

In analogous fashion to RuCp complexes, reactions of acetylenes with the Cp* analogue $[RuCp^*(PEt_3)(CH_3CN)_2]^+$ have been performed. Scheme 14 summarizes the reactions of $[RuCp^*(PEt_3)(CH_3CN)_2]^+$ with the alkynes HC≡CR (R = COOMe, *n*Bu) and 1,6-heptadiyne. The η^3-allyl carbene complexes were obtained in high isolated yields. However, in contrast to the RuCp analog η^3-allyl carbene complexes, these compounds are unstable in solution and react slowly at room temperature to afford $[Ru(\eta^6\text{-}C_5Me_4CH_2)(\eta^4\text{-}CH(R){=}CH{-}C(R){=}CHPEt_3)]PF_6$ and $[Ru(\eta^6\text{-}C_5Me_4CH_2)(\eta^4\text{-}CH_2{=}C(CH_2)_3C{=}CH{-}PEt_3)]PF_6$, respectively. In both, one of the ring methyl C−H bonds

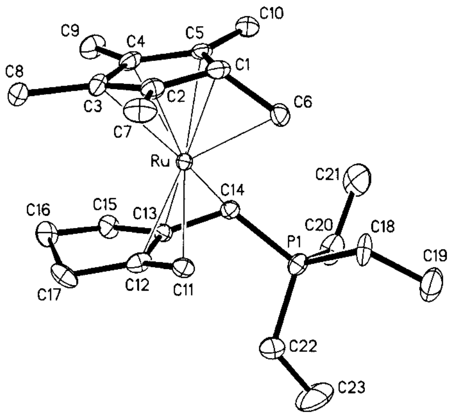
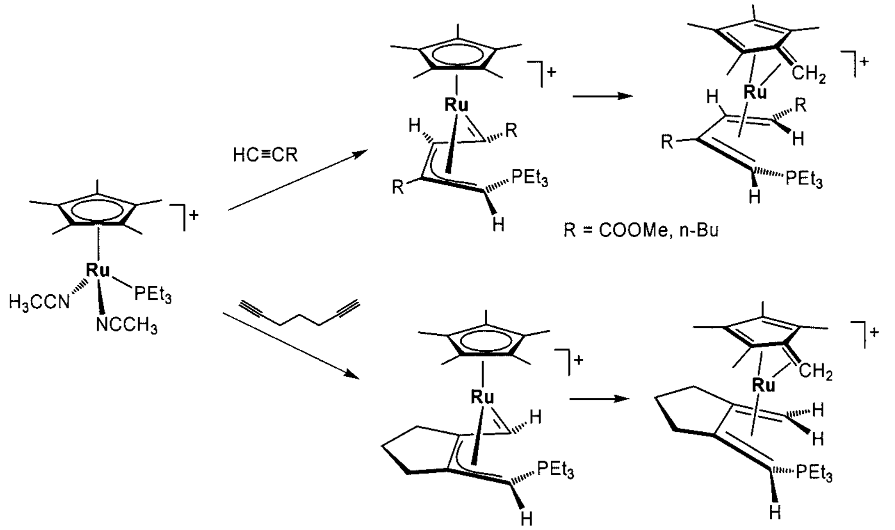


Figure 10. Structural view of $[Ru(\eta^6\text{-}C_5Me_4CH_2)(\eta^4\text{-}CH_2{=}C(CH_2)_3C{=}CHPEt_3)]PF_6$ (PF_6^- omitted for clarity)

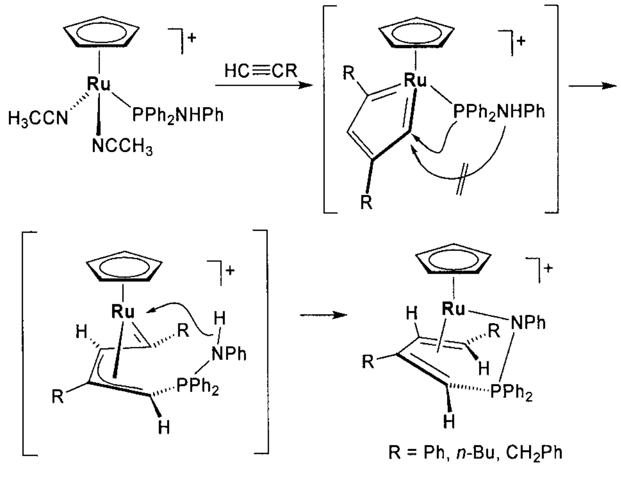


Scheme 14

of the Cp* ligand has been cleaved (Scheme 14). In these transformations, the hydrogen atom is transferred to the carbene carbon atom at the inside face of the molecule to form an η^4-diene unit. Based on the NMR spectroscopic data, the newly formed η^6-$C_5Me_4CH_2$ ligand may be envisioned as a tetramethylfulvene rather than a tetramethylcyclopentadienyl-σ-alkyl ligand. The X-ray data are also consistent with a tetramethylfulvene rather than an η^1:η^5-$CH_2C_5Me_4$ (σ:η^5-$CH_2C_5Me_4$) description. A structural view of $[Ru(\eta^6\text{-}C_5Me_4CH_2)(\eta^4\text{-}CH_2{=}C(CH_2)_3\text{-}C{=}CHPEt_3)]PF_6$ is depicted in Figure 10. Related methyl C−H activation processes of transition-metal coordinated C_5Me_5 and C_6Me_6 ligands have been reported previously.[41,42]

4.4. Formation of Ruthenium Butadiene Amido Complexes

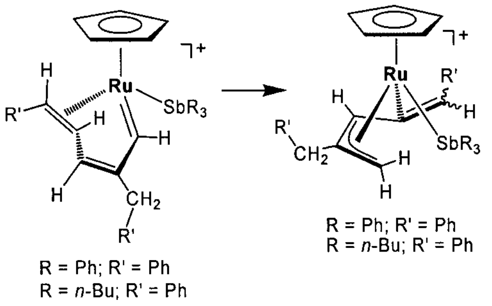
The above reactions of $[RuCp(PR_3)(CH_3CN)_2]PF_6$ with alkynes all involve phosphane migration and subsequent C−H bond activation at either the phosphane substituent or the Cp* ligand. In this respect it is interesting to switch over to the phosphanyl-amine ligand PPh_2NHPh from PR_3 in order to see whether migration appears at the P or the N site, and whether there will be N−H or C−H bond activation. Accordingly, the reaction of $[RuCp(PPh_2NHPh)(CH_3CN)_2]PF_6$ with HC=CR (R = Ph, *n*Bu, CH_2Ph), 1,6-heptadiyne, and 1,7-octadiyne results in the formation of the η^4-butadiene amido complexes $[RuCp(\eta^4\text{-}C_4H_3(R)_2{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$, $[RuCp(\eta^4\text{-}C_4H_3(CH_2)_3{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$, and $[RuCp(\eta^4\text{-}C_4H_3(CH_2)_4{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ in good yields (Scheme 15).[43] Thus, migration of the κ^1(P)-coordinated PPh_2NHPh ligand occurs through P rather than N in an analogous manner to that in the η^3-allyl carbene complexes already described. In contrast, however, instead of activation of a C−H bond involving the phenyl substituents of the PPh_2NHPh ligand, facile N−H activation of the NHPh-moiety occurs. In this way, RuCp η^4-butadiene amido complexes are afforded. This is noteworthy in view of the comparatively strained four-membered Ru-*N*−P−C ring system formed, in contrast to a five-membered Ru−C−C−P−C ring system in case of C−H bond activation.



Scheme 15

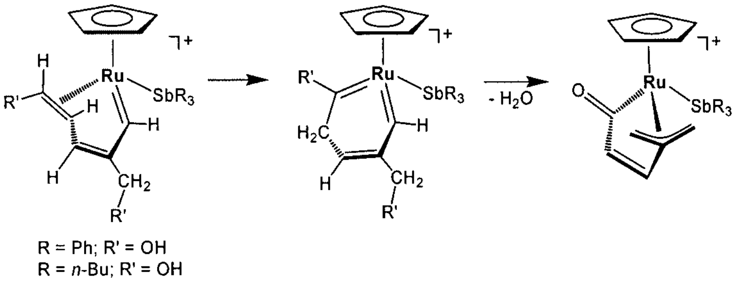
4.5. Reactivity of Ruthenium Butadienyl Carbenes

In special cases, butadienyl carbene complexes undergo further rearrangement such as in the reaction of $[RuCp(SbR_3)(CH_3CN)_2]^+$ with $HC{\equiv}CCH_2Ph$,[37] to give an η^3-allyl-vinyl complex (Scheme 16). When $HC{\equiv}CCH_2OH$ is the alkyne, an η^3-allyl-acyl complex is obtained as illustrated in Scheme 17.

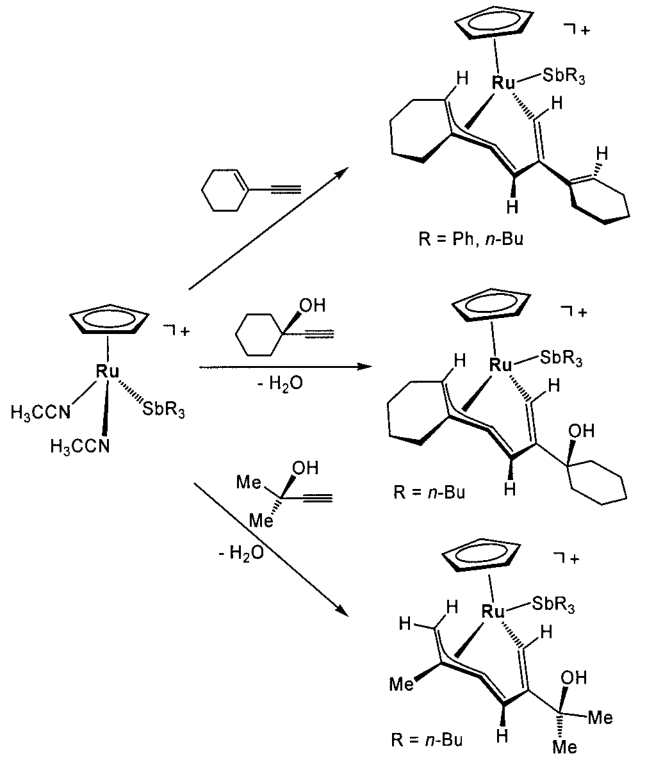


Scheme 16

The alkynes utilized above contain an α-alkyl substituent that is capable of facile 1,2-hydrogen shift. With alkynes lacking α-C−H bonds, namely $HC{\equiv}CC_6H_9$ and the propargylic alcohols $HC{\equiv}CC_6H_{10}OH$ and $HC{\equiv}CCMe_2OH$, η^3-butadienylvinyl complexes are formed as presented in Scheme 18.



Scheme 17



Scheme 18

4.6. Formation of Ruthenium Allenyl Carbenes

The formation of allenyl carbene complexes has also been observed in the reaction of $[RuCp(PR_3)(CH_3CN)_2]^+$ with a very atypical alkyne, viz. ferrocenyl and ruthenocenyl acetylene (see Scheme 19 and Figure 11).[36] This new type of C−C bond formation is affected by the strong electronic coupling between the ferrocenyl moiety and the conjugated

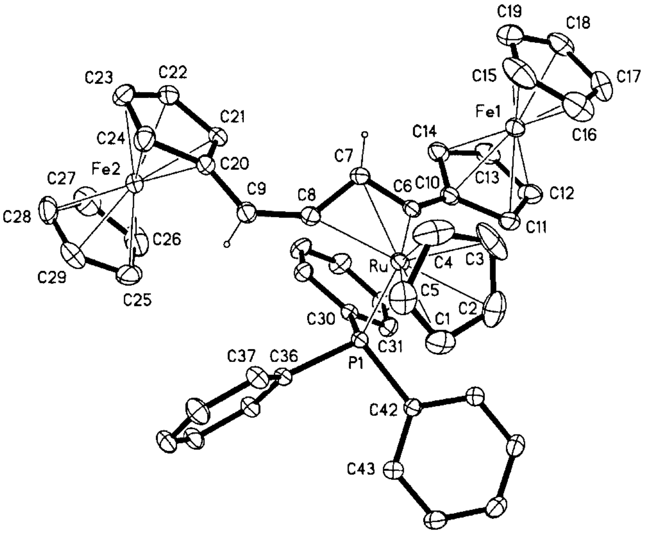


Figure 11. Structural view of $[CpRu(=C(Fc)\text{-}\eta^2\text{-}CH=C=CH\text{-}(Fc))(PR_3)]PF_6$ (PF_6^- omitted for clarity)

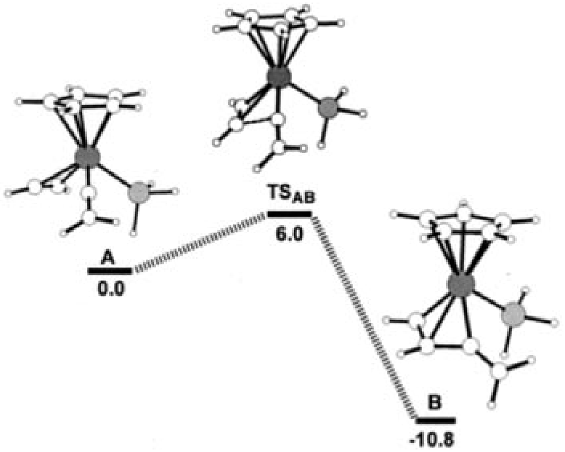
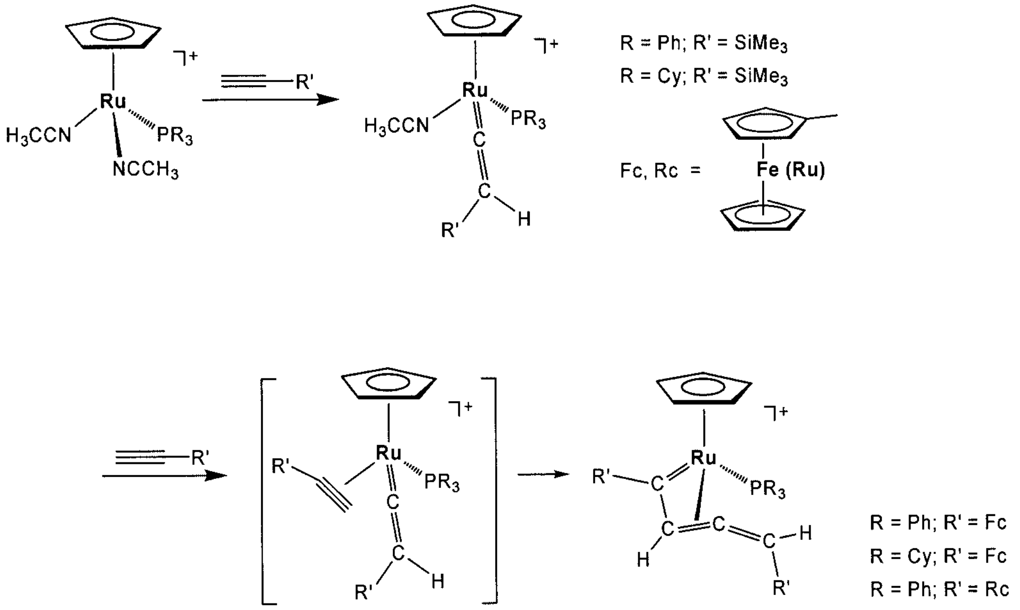
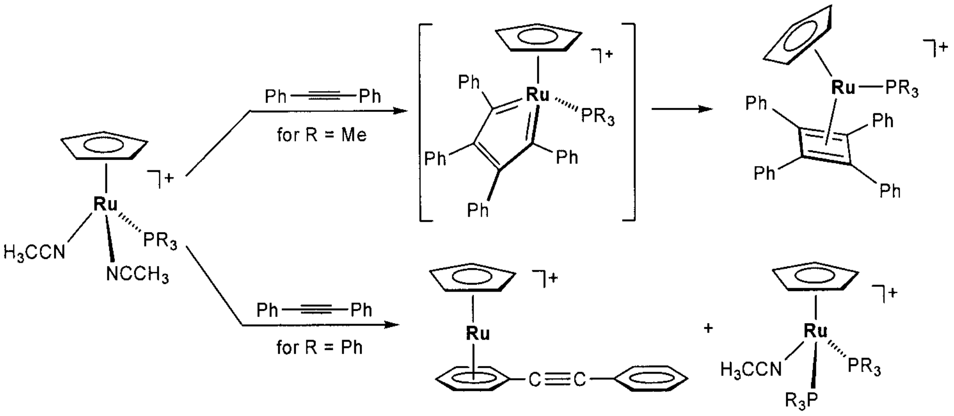


Figure 12. Energy profile of the B3LYP potential energy surface for the conversion of the vinylidene-acetylene complex **A** into the allenyl carbene **B**



Scheme 19



Scheme 20

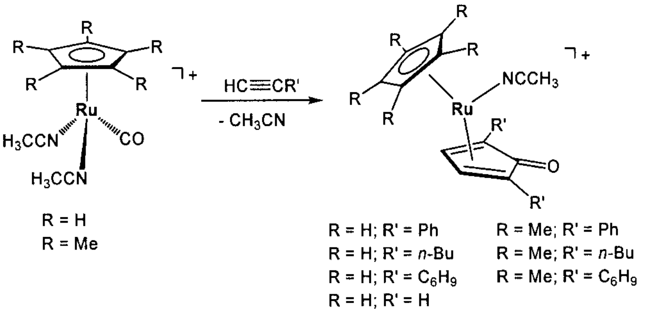
allenyl carbene unit, which facilitates transient vinylidene formation with subsequent alkyne insertion into the Ru=C double bond. The strong electronic coupling is also apparent from the X-ray structures of the products. The alkyne-vinylidene coupling reaction is extremely facile requiring merely 6 kcal/mol according to recent DFT/B3LYP calculations performed with the model complexes $[RuCp(PH_3)(\eta^2\text{-}HC{\equiv}CH)(=CCH_2)]^+$ (Figure 12).

4.7. Formation of Ruthenium Cyclobutadiene Complexes

Under particular instances the metallacyclopentatriene can transform into an η^4-cyclobutadiene complex. This outcome has been observed in the reaction of $[RuCp(PMe_3)(CH_3CN)_2]^+$ with PhC≡CPh as shown in Scheme 20. Theoretical calculations reveal that this transformation is actually symmetry forbidden that involves HOMO/LUMO crossing. Thus, the kinetic barrier becomes prohibitively high, albeit the reaction appears to be energetically favorable. Any cyclobutadiene complexes known hitherto are derived from acetylenes with bulky substituents, such as phenyl or trimethylsilyl.[44,23b] There is obviously a subtle balance of factors that influence the availability of the cyclobutadiene pathway. In fact, in the above example, on switching from $[RuCp(PMe_3)(CH_3CN)_2]^+$ to $[RuCp(PPh_3)(CH_3CN)_2]^+$, a completely different reaction outcome is observed: sandwich complexes are formed. In a forthcoming paper we will investigate the detailed mechanism of the cyclobutadiene pathway, of which to date very little is known.

4.8. Formation of Ruthenium Cyclopentadienone Complexes

Similarly to tertiary phosphanes, in the present type of conversions, carbon monoxide is also not a spectator ligand, but instead functions as an active ligand. Thus the mono-carbonyl complex $[RuCp'(CO)(CH_3CN)_2]^+$ reacts with terminal and internal alkynes to afford ruthenium cyclopentadienone complexes (Scheme 21 and Scheme 22).[45]



Scheme 21

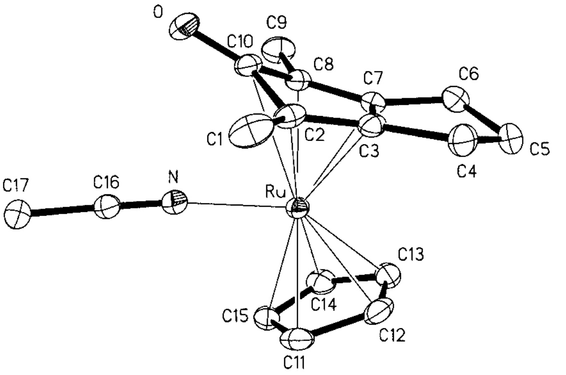
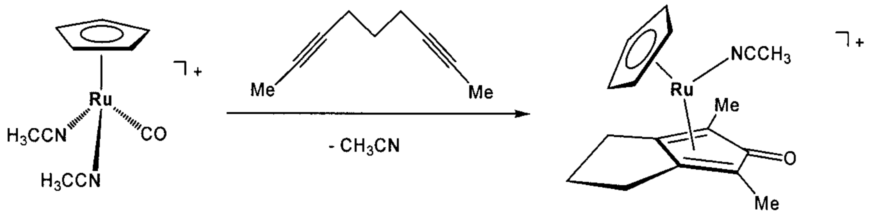
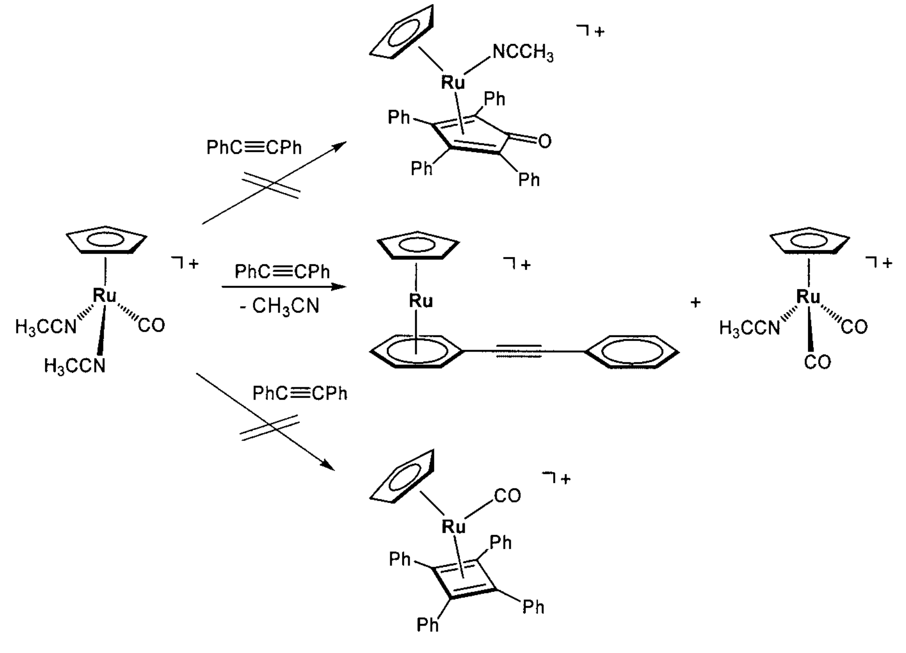


Figure 13. Molecular structure of $[RuCp(\eta^4\text{-}OC_5Me_2C_3H_6)(CH_3CN)]PF_6$ (PF_6^- omitted for clarity)



Scheme 22

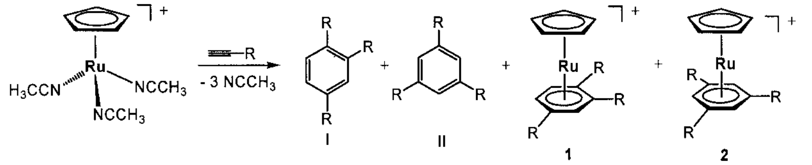


Scheme 23

A structural view of [RuCp(η^4-$OC_5Me_2C_3H_6$)(CH_3CN)]PF_6 is depicted in Figure 13.

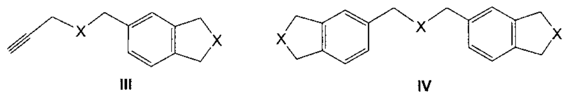
These reactions are highly selective, yielding, in the case of terminal alkynes, only one regioisomer with the substituents exclusively in the α,α′-positions of the cyclopentadienone moiety. Further, in this case the substituent on the alkyne is of critical importance to the outcome of the reaction. Specifically, the reaction with PhC≡CPh does not yield the cyclopentadienone complex, but rather the sandwich complex [RuCp(η^6-C_6H_5PhC≡CPh)]$^+$ and a biscarbonyl complex [RuCp$(CO)_2$(CH_3CN)]$^+$ in a 1:1 ratio (Scheme 23). Other reactions are also known in which

Table 1. Cyclotrimerization of alkynes mediated by [RuCp$(CH_3CN)_3$]$^+$



Alkynes	[2 + 2 + 2] Cycloadduct			Arene complexes		
	Conversion (%)[a]	**I** (%)	**II** (%)	Conversion (%)[b]	**1** (%)	**2** (%)
1-hexyne	45	75	25	88	75	25
3-phenylprop-1-yne	30	75	25	86	75	25
ethyl propiolate	85	75	25			
phenylacetylene				80	100	
1-ethynylcyclohexene				90	100	
1,6-heptadiyne	38	100[c]		83	100	
1,7-octadiyne	52	100[d]		89	100	

[a] With respect to substrate. [b] With respect to catalyst. [c] A mixture of dimers **III** and trimer **IV** by was obtained in ca. 38 and 52% yield, respectively:



III IV

X = CH_2, CH_2CH_2

[d] A mixture of arene complexes with **III** and **IV** (X = CH_2CH_2) as ligands were formed in ca. 80% overall yield.

cyclopentadienone complexes are formed from carbonyls and acetylenes. The first reported cyclopentadienone complex, Fe(η^4-C_5H_4O)$(CO)_3$, was obtained by treating $Fe(CO)_5$ with an excess of HC≡CH.[46] Other examples are complexes of the types M(η^4-C_5H_4O)$(CO)_3$ (M = Fe, Ru),[47] MCp(η^4-C_5H_4O) (M = Co, Rh),[48] and V(η^4-C_5H_4O)(CO)(PMe_3).[23f]

4.9. Formation of Arenes and Arene Complexes − Cyclotrimerization of Alkynes

In contrast to the above systems, if $[RuCp(L)(CH_3CN)_3]^+$ is used when L = CH_3CN, the catalytic cyclotrimerization of alkynes is promoted as shown in Table 1, although, this does not occur in a selective manner, and 1,2,4- as well as 1,3,5-trisubstituted arenes are formed in most cases.[31] However, in the course of the catalytic process, several pathways that form stable and inert sandwich complexes of the type $[RuCp(\eta^6\text{-arene})]^+$ become readily available. In this way the catalytically active intermediates are consumed and the catalytic cycle is gradually quenched. Therefore, albeit active in various other C−C bond coupling reactions, involving even alkynes, $[RuCp(CH_3CN)_3]^+$ is an unsuitable catalyst for the cyclotrimerization of alkynes. The formation of arene complexes may be prevented under photochemical conditions since the arene ligands in $[RuCp(\eta^6\text{-arene})]^+$ are known to be photo-labile.[49]

5. What Happens if the Phosphane Ligand is Tethered?

What is the reason for the extraordinary difference in behavior between the two fragments RuCpCl and $[RuCp(PR_3)]^+$? There are at least two reasons for this: the first is the charge on the complex: clearly, a cationic complex will be more electrophilic than a neutral complex; the other is the greater steric requirements of the tertiary phosphane ligand than the chloride ligand. To elucidate this point further, we tethered the phosphane ligand onto the Cp ring via a two-carbon linker under, otherwise, the same

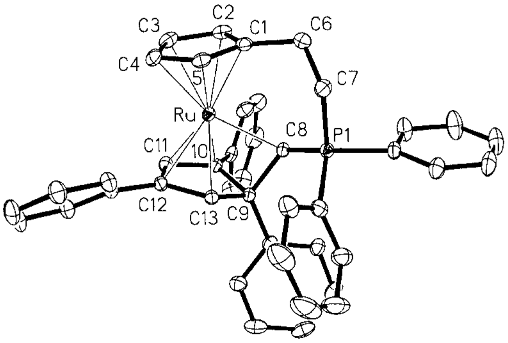
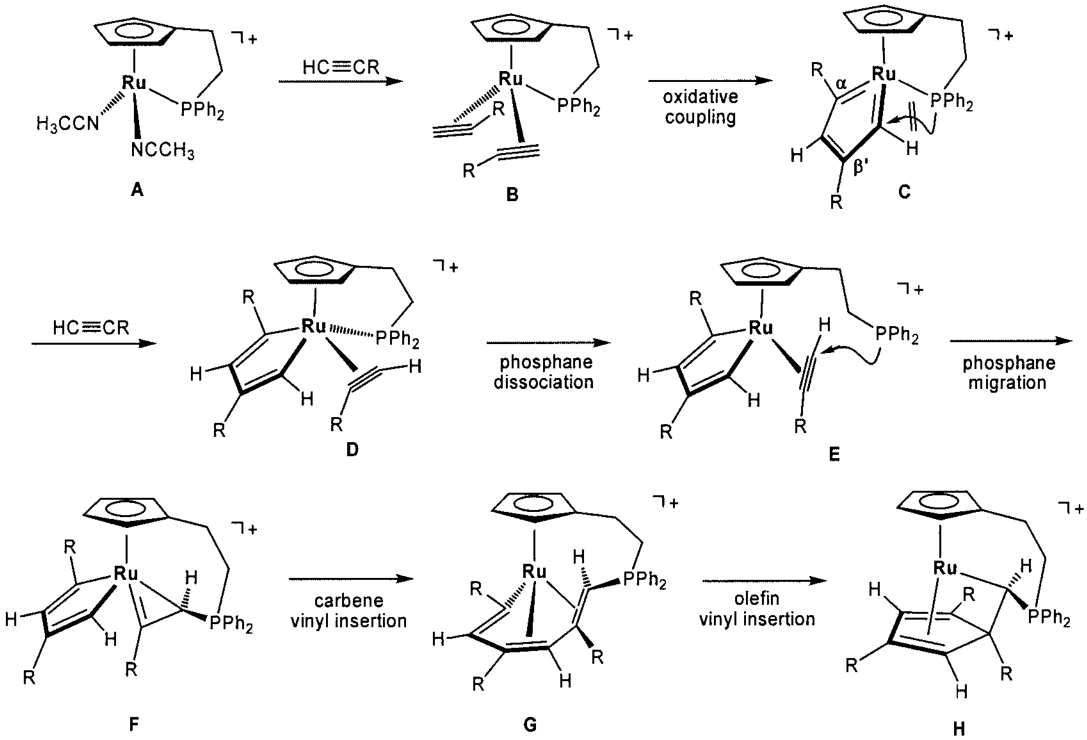


Figure 14. Structural view of [Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1*C*-CH-η^4-$C_5Ph_3H_2$)]PF_6 (PF_6^- omitted for clarity)



Scheme 24

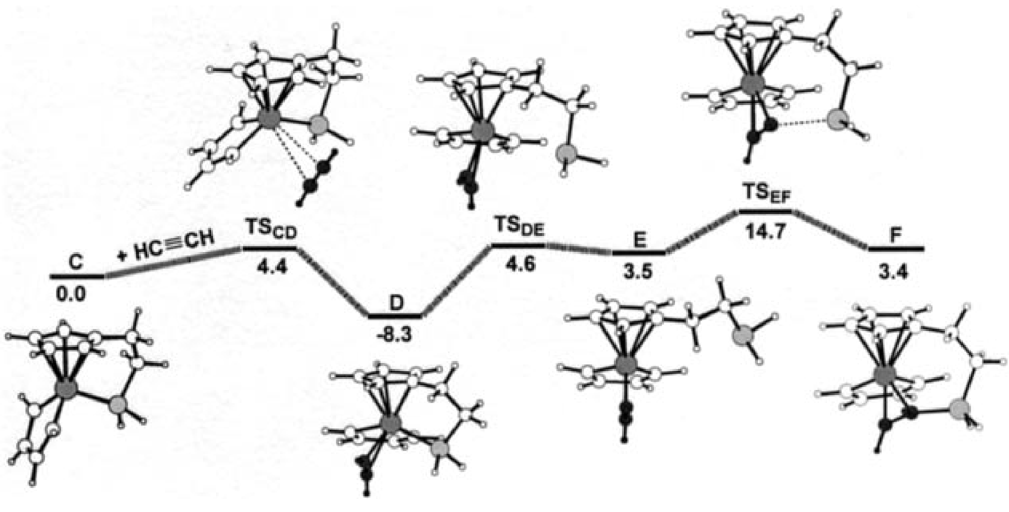


Figure 15. Energy profile of the B3LYP potential energy surfaces for the conversion of the ruthenacyclopentatriene complex **C** into the 1-metallacyclopropene **F**

reaction conditions.[50] In fact, the arrested phosphorus moiety diverts the previously direct nucleophilic attack of the coordinated trialkylphosphane to the α-carbon atom of the metallacyclopentatriene. Instead, a third alkyne molecule is added, which finally leads to an unusual C−C coupling process that involves three alkynes and the tethered phosphane, to give the cycloaddition product **H** as shown in Scheme 24. A structural view of $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2\text{-}\kappa^1C{-}CH\text{-}\eta^4\text{-}C_5Ph_3H_2)]PF_6$ is given in Figure 14.

According to DFT/B3LYP calculations (Figure 15 and Figure 16), this intriguing [2+2+1] alkyne cyclotrimerization proceeds through Ru−P bond dissociation, phosphane attack at the coordinated acetylene to yield the 1-metallacyclopropene **F**, carbene vinyl insertion, and olefin vinyl insertion processes. Thus, in the present case, tethering can be considered to delay phosphane migration. The tethering of the phosphane ligand opens the interligand space between the metallacycle plane and the Ru−P vector and is depicted in Scheme 25. It is interesting to note that the corresponding angle of 103° in the tethered complex parallels that in RuCpCl, which mediates the cyclotrimerization of alkynes (vide supra).

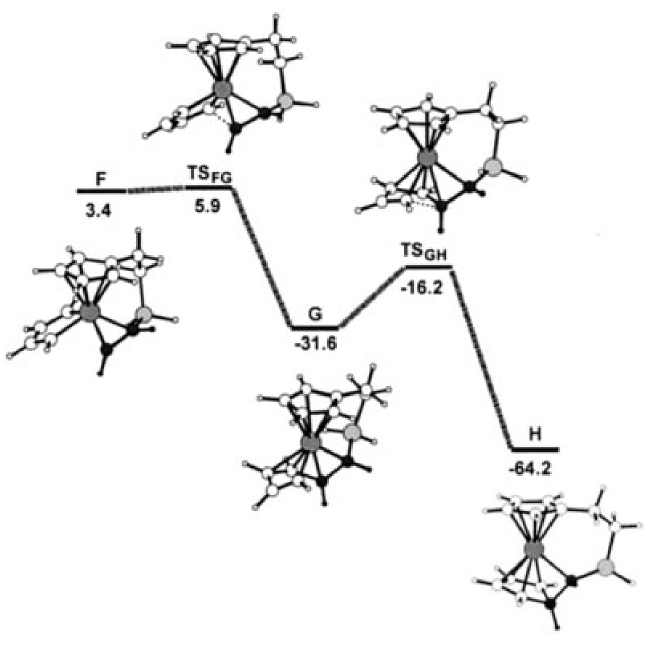
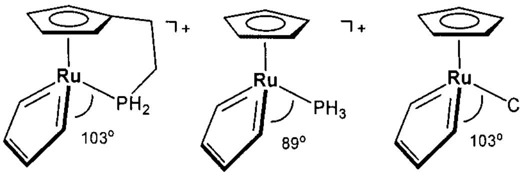


Figure 16. Energy profile of the B3LYP potential energy surfaces for the conversion of the 1-metallacyclopropene **F** into the final cyclotrimerization product **H**



Scheme 25

Complex **C** is easily able to accommodate a third alkyne to afford the metallacyclopentadiene acetylene complex **D**. In the crowded complex **D**, the Ru−P bond is labilized, giving a free phosphane arm in **E** through an endothermic reaction,. The effect of ring strain introduced by a two-carbon tether has been demonstrated recently by Casey et al.[51] The subsequent reaction steps are quite straightforward: Nucleophilic attack of the pendant phosphane ligand at the coordinated acetylene results in the formation of the novel metallacyclopentadiene 1-metallacyclopropene complex **F**. The activation energy for this intramolecular process is 11.2 kcal/mol. It should be noted that related coupling reactions between a coordinated alkyne and a coordinated phosphane to yield 1-metallacyclopropenes and vinyl complexes have been reported in the literature.[52,53] Further, intermolecular nucleophilic additions of phosphanes and phosphites to alkyne ligands are feasible.[54] Complex **F** is prone to C−C coupling between the carbene carbon atom of the 1-metallacyclopropene moiety and the α-carbon atom of the metallacyclopentadiene unit bearing no substituent, to give **G**. This reaction requires an activation energy of only 2.5 kcal/mol and is energetically very favorable releasing 35.0 kcal/mol. The final and rate-determining step is the insertion of the vinyl moiety into the η^2-olefin unit to give **H**, thus completing the [2+2+1] cyclotrimerization.

6. Outlook

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 carbon monoxide, which ordinarily are spectator ligands, function here as active ligands and give rise to a wide array of scenarios that compete with the process of trimerization. This may be compared with the behavior of other metal centers so as to arrive at a deeper understanding of the individuality of the various transition metals. Unfortunately, experimental results are often difficult to compare directly because of the variable reactions conditions applied. The better choice may involve the use of reliable theoretical studies which, however, are still in their infancy and hence scarce.

The reactions surveyed here may be compared with the theoretical study of acetylene trimerization with $CpCoL_2$ (L = CO, PR_3, olefin). At least two fundamental differences are obvious: (i) for $CpCoL_2$, the coligands L serve as leaving ligands only, that give way to the incoming acetylenes; (ii) there is a larger variety of intermediates for the ruthenium system. This may partly be related to the atomic radii; the smaller radius of Co (1.09 vs. 1.21 Å for Ru)[55] may control interligand interactions (through-space coupling)[56] in a different way. In this respect, it might be relevant to undertake investigations of the rhodium analog CpRh.

We can be convinced that in the future an ever-increasing number of theoretical treatments will follow, which ultimately will help us understand chemical periodicity from first principles.

Acknowledgments

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