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Ruthenium-mediated cyclotrimerization of alkynes utilizing the cationic complex $[RuCp(CH_3CN)_3]PF_6$

Eva Rüba [a], Roland Schmid [a], Karl Kirchner [a,*], Maria José Calhorda [b,c]

[a] Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria
[b] ITQB, Av. da República, EAN, Apart. 127, 2781-901 Oeiras, Portugal
[c] Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

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Abstract

The substitutionally labile cationic complex $[RuCp(CH_3CN)_3]^+$ (as the PF_6^- salt) was tested with respect to its ability to catalyze the cyclotrimerization of terminal alkynes and diynes to afford benzene derivatives. Whereas $[RuCp(CH_3CN)_3]^+$ is in fact promoting the catalytic cyclotrimerization of alkynes, the formation of stable and inert sandwich complexes of the type $[RuCp(\eta^6\text{-arene})]^+$ deactivates the catalyst and thus quenches the catalytic cycle. All new sandwich complexes were isolated and characterized spectroscopically. A proposal for a plausible catalytic cycle including possible degradation pathways of the catalyst is presented based on DFT calculations. As key intermediates several novel carbene complexes have been identified including metallacyclopentatriene and metallaheptatetraene species.

Keywords: Ruthenium; Alkynes; Cyclotrimerization; Arene Complexes; DFT calculations

1. Introduction

The transition-metal mediated [2+2+2] cycloaddition of alkynes is a very efficient method to synthesize functionalized arene systems [1]. Particularly appealing is the intrinsic atom-economical nature of these reactions, although the chemo- and regioselectivity still remains a problem. These transformations occur both in stoichiometric and catalytic fashion depending on the transition metal complexes. In the first case, the arene ring frequently remains coordinated to the metal fragment. Recent stoichiometric examples include alkyne coupling reactions mediated by $(\eta^2\text{-propene})Ti(O\text{-}i\text{-}Pr)_2$ [2], $[Cp^*Fe(CH_3CN)_3]^+$ [3], and $ZrCp_2(C_4Et_4)$ [4]. Metal-catalyzed cyclotrimerizations have also been reported using, for instance, the complexes $CpCo(CO)_2$ [5], $Ni(acac)_2/PPh_3$ [6], $RhCl_2(PPh_3)_3$ [7], $(\eta^5\text{-}C_9H_7)Ru(cod)Cl$ [8], CpRu(cod)Cl, and Cp*Ru(cod)Cl [9] as precatalysts. Accordingly, a large body of experimental results has been accumulated containing vast and widely diversified information. Nevertheless, in order to systematize the manifold observations further experimental data and theoretical studies are of vital importance [10]. Important issues to be addressed are: What intermediates are involved, e.g. metallacyclopentadienes, metallacyclopentatrienes, metallaheptatrienes, or metallanorbornadienes? What is the origin of the chemo- and regioselectivity, and what determines whether sometimes five- [11] and four-membered rings, instead of six membered rings are formed, i.e. why [2+2+1] and [2+2] cycloadditions take place? In the present work we focus, experimentally and theoretically, on the reaction of $[CpRu(CH_3CN)_3]^+$ (**1**) with terminal alkynes and diynes. Despite the fact that the CH_3CN ligands of $[RuCp(CH_3CN)_3]^+$ are substitutionally labile [12], one cannot *a priori* surmise that this complex is not suitable for promoting the cyclotrimerization of alkynes in catalytic fashion due to facile arene coordination, a process requiring the dissociation of all three CH_3CN ligands. It has been shown [13] that as soon as one CH_3CN ligand is replaced by another ligand such as CO or PR_3, the exchange rate of the remaining two CH_3CN

* Corresponding author. Tel.: +43-1-5880115341; fax: +43-1-5880115499.
E-mail address: kkirch@mail.zserv.tuwien.ac.at (K. Kirchner).

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ligands drops by several orders of magnitude. Moreover, it may be noted that complex **1** is active also with respect to alkene–alkyne and alkyne–alkyne coupling [14,15] and the cyclization of yne-enones [16].

2. Results and discussion

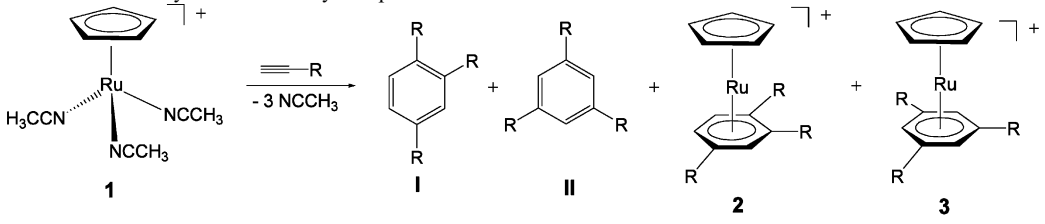
2.1. Reactions of $[RuCp(CH_3CN)_3]PF_6$ (1) with terminal alkynes and diynes

Treatment of **1** with an excess of terminal alkynes HC≡CR (R = *n*-Bu, CH_2Ph, COOEt, Ph, C_6H_9) at 80 °C afforded on work-up a mixture of both organic cyclotrimerization products as well as metal complexes of the type $[RuCp(\eta^6\text{-}C_6H_3R_3)]PF_6$ containing η^6-coordinated arene ligands.

The organic products could be separated by extraction with Et_2O with the product distribution determined by ^{1}H-NMR spectroscopy. The results are summarized in Table 1. With the terminal alkynes HC≡CBu^n, HC≡CCH_2Ph, and HC≡CCOOEt, isomeric mixtures of cyclotrimerization products viz 1,2,4- and 1,3,5-substituted benzenes **I** and **II** were isolated in low to medium yields. Only in the case of HC≡CCOOEt the yield was as high as about 85%. With HC≡CPh and HC≡CC_6H_9, on the other hand, surprisingly no cyclotrimerization products were formed at all. It is interesting to note that the two possible isomers were exclusively obtained in a 3:1 ratio which may be explained by the intermediates shown in Scheme 1. This finding may also suggest that there is no steric or electronic preference for any of these pathways. A detailed mechanistic study based on DFT/B3LYP calculations is presented in the following section.

In a fashion similar to terminal alkynes, also the diynes 1,6-heptadiyne and 1,7-hexadiyne afforded cyclotrimierzation products isolated as mixtures of the dimers **III** and **IV** in moderate to medium yields (Table 1). With most alkynes, complex **1** reacted to give sandwich

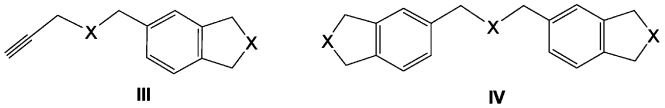
Table 1
Cyclotrimerization of alkynes mediated by complex **1**



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

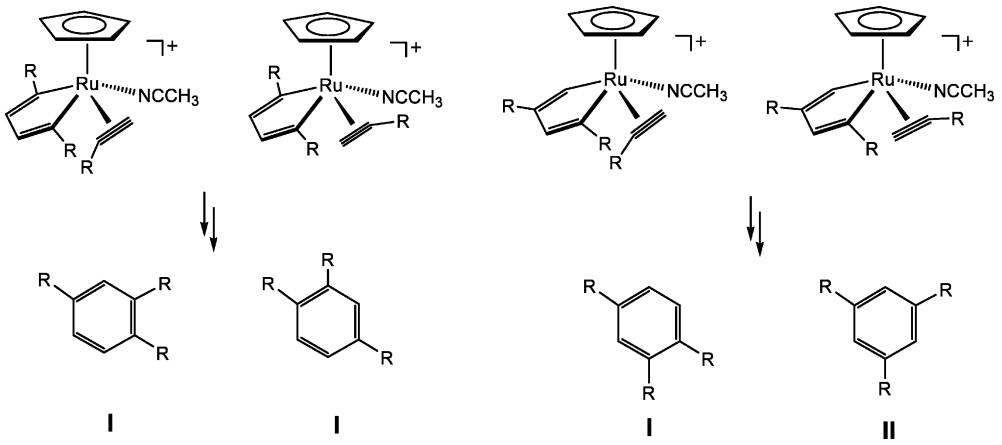
[a] With respect to Substrate, [b] With respect to Catalyst

[c] A mixture of two dimers **III** and **IV** by was obtained in ca. 38 and 52% yield, respectively



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.



Scheme 1.

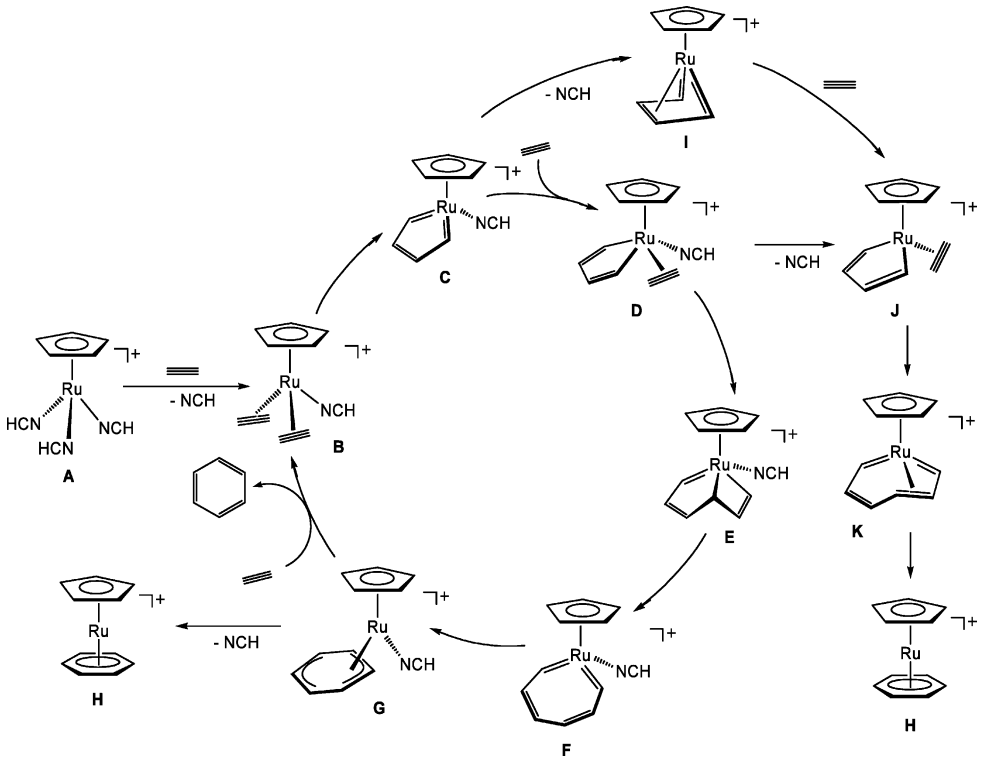
complexes $[RuCp(\eta^6\text{-}C_6H_3R_3)]PF_6$ in high yields (Table 1). Only in the case of HC≡CCOOEt no metal complex formation has been observed. All complexes were characterized by ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy. The complexes with R = *n*-Bu and CH_2Ph were 3:1 mixtures of the 1,2,4- and the 1,3,5-substituted arene complexes **2a**, **2b**, **3a**, and **3b** and could not separated. With HC≡CPh and $HC{\equiv}CC_6H_9$ exclusively the η^6-1,2,4-substituted benzene complexes **2c** and **2b** were formed. The ^1H-NMR spectrum typically showed one characteristic signal for the three protons of the η^6-coordinated 1,3,5-substituted benzene and two doublets and one singlet for the protons of the 1,2,4-substituted product in the range of 6.3 to 5.9 ppm. The signal of the protons of the Cp ligand gives rise to a singlet between 5.4 and 5.2 ppm. In the $^{13}C\{^1H\}$-NMR spectra the coordinated benzene ligand exhibits characteristic resonances in the range of 100 to 80 ppm.

2.2. Theoretical study. Formation of benzene and benzene complexes

A general pathway for the conversion of the labile tris-acetonitrile complex $[CpRu(NCCH)_3]^+$ (**1**) (the model with NCH will be called **A**), into benzene complex **H** and free benzene is schematically shown in Scheme 2 as a result of DFT/B3LYP [17] calculations using Gaussian98 [18]. The potential energy surface (in kcal mol^{-1}) for a catalytic cycle including possible side reactions is given in Fig. 1.

The first step consists of the substitution of acetonitrile by acetylene which by experiment is known to proceed via a dissociative mechanism [12], leading to the bis-acetylene complex **B**. The associative alternative for which the coordination of acetylene is accompanied by $\eta^5 \rightarrow \eta^3$ ring slippage to preserve the 18-electron count can be excluded. The overall substitution reaction is endothermic by 10.2 kcal mol^{-1} (Fig. 1). Bis-acetylene complexes have been proposed as intermediates in several conversions such as in cyclotrimerizations, but surprisingly no representative of Ru is known. Oxidative coupling of the acetylene ligands in **B** results in the formation the coordinatively saturated metallacyclopentatriene **C**, a symmetry allowed process if C_s symmetry is preserved. Location of the transition state $\mathbf{TS_{BC}}$ for this reaction revealed a moderate activation barrier of 10.0 kcal mol^{-1}. The detailed structures of **B**, **C**, and the transition state $\mathbf{TS_{BC}}$ are shown in Fig. 2. As the reaction proceeds, the new C···C bond starts to form noted by the decrease in the C···C distance from 2.787 in **B** to 2.106 in $\mathbf{TS_{BC}}$, to reach 1.390 Å in species **C**, characteristic of a C=C bond. At the same time, the two acetylene groups must reorient themselves, so that two of the Ru–C bonds become stronger (distances decrease from 2.252 (**B**), via 2.104 $\mathbf{TS_{BC}}$ to 1.946 (**C**), and the other two weaker (2.240, 2.368, 2.883 Å, respectively). These changes occur smoothly. The transition state occupies an intermediate position, lying closer to the bisacetylene complex than to the metallacycle. Note that the C_α–C_β distances are still rather short exhibiting triple bond character (1.243 compared to 1.270 Å in the starting structure **B**), while C_β–$C_{\beta'}$ is still away from a bonding distance (2.106 Å). The calculated structure **C** compares well with the X-ray structures of the related species containing CpRuBr and RuCp* fragments [19].

The metallacyclopentatriene **C** readily adds a third acetylene molecule to give the metallacyclopentadiene **D** (Fig. 3). In the absence of α-substituents there are no severe steric restrictions for an incoming third alkyne, since the nitrile co-ligand is a sterically little demanding molecule. This is in contrast to related RuCp systems containing the more bulky PR_3 or SbR_3 co-ligands where no catalytic activity towards cyclotrimerization has been observed [20]. A comparison of the optimized geometry of **C** with that of **D** shows that the C–C and Ru–C bond distances within the metallacycle are very different and coordination of a third alkyne severely perturbs the metallacycle framework. In contrast to



Scheme 2.

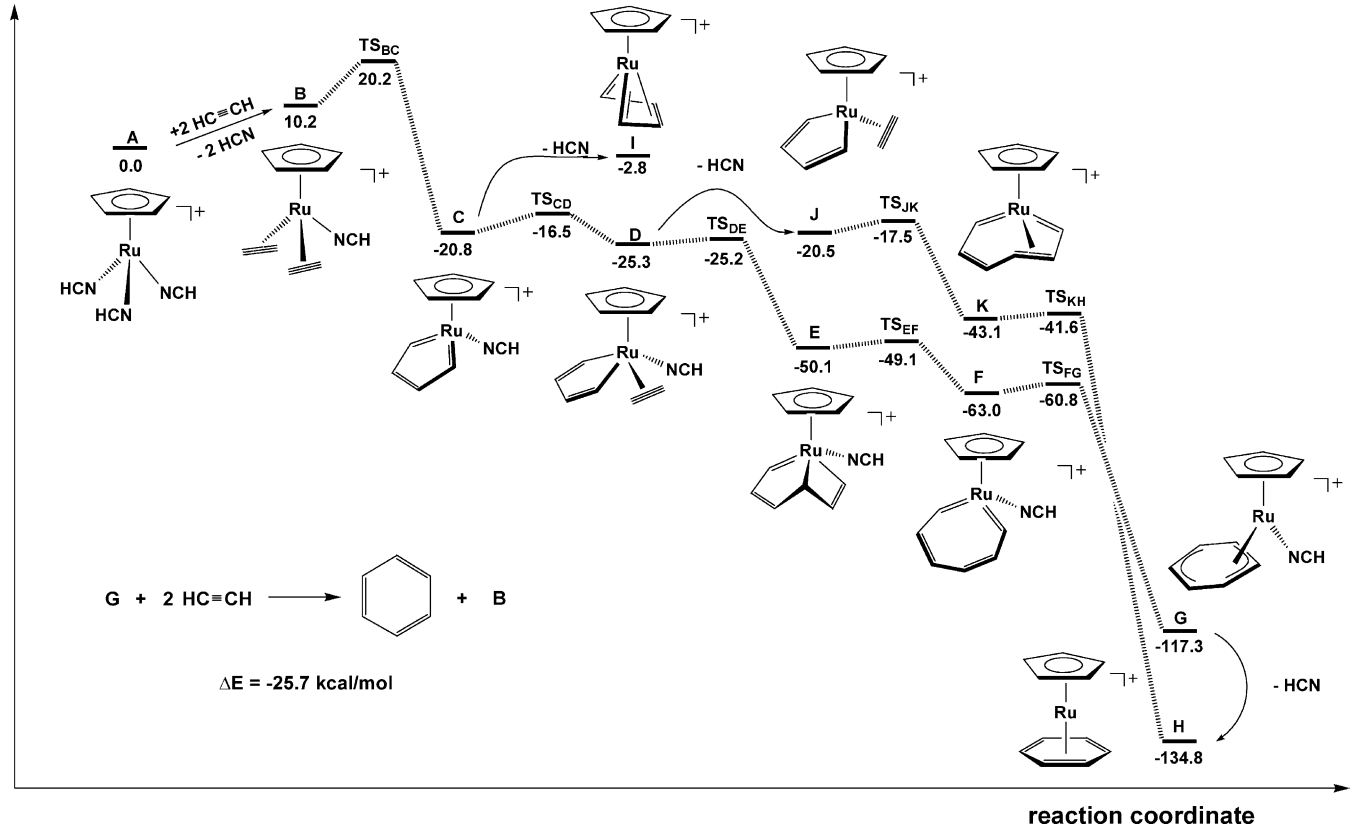


Fig. 1. Profile of the B3LYP potential energy surfaces for the formation of benzene catalyzed by the ruthenium bisacetylene complex **B** and formation of the benzene complex **H**.

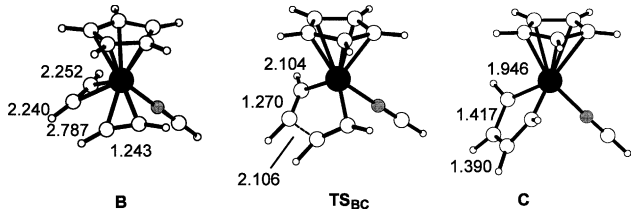


Fig. 2. Relevant distances (Å) in the optimized B3LYP geometries of the ruthenium bisacetylene complex **B**, the metallacyclotpentatriene **C**, and the transition state $\mathbf{TS_{BC}}$.

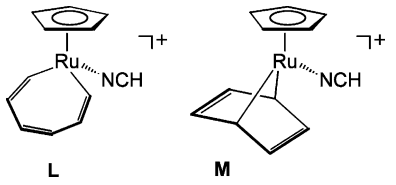


Chart 1.

complex **C** the C–C bond distances of **D** exhibit a short–long–short pattern with the C_α–C_β, $C_{\alpha'}$–$C_{\beta'}$ and C_β–$C_{\beta'}$ bonds being 1.350, 1.348, and 1.444 Å, respectively, while the Ru–C distances are elongated being 2.077 and 2.124 Å. Energetically, **D** lies 4.8 kcal mol^{-1} lower in energy than **C** and free acetylene. The activation energy required for this addition is rather small being merely 4.3 kcal mol^{-1}. Complex **D** undergoes subsequently facile C–C bond coupling to give the novel bicyclic carbene complex **E** releasing thereby 24.8 kcal mol^{-1}. The transition state for this process, $\mathbf{TS_{DE}}$, is very similar to the structure of **D** coupled with the long 2.161 Å C_α–$C_{acetylene}$ bond distance indicating that the transition state structure occurs quite early along the reaction coordinate. The only noticeable change from **D** is rotation of the acetylene ligand by ca. 5°. Energetically this transition state lies merely 0.1 kcal mol^{-1} higher in energy than **D** (Fig. 2). Complex **E** contains an unusual five- and four-membered bicyclic ring system with one short and two long Ru–C bonds (1.959, 2.240, and 2.067 Å). It is very important to mention that addition of a third alkyne to form **D** does not result in a classical insertion of an alkyne into the Ru–C_α single bond of **D** to give the coordinatively unsaturated metallacycloheptatriene **L** as shown in Chart 1. Metallacycloheptatrienes are indeed frequently proposed intermediates [21] in cyclotrimerization reactions of alkynes referred to as Schore's mechanism [1b]. However, as the reaction proceeds and the new C–C bond starts to form, the Ru–C_α bond which is directly involved in the C–C coupling process increases from 2.124 in **D** to 2.134 in $\mathbf{TS_{DE}}$ and 2.240 Å in **E** but is not being cleaved, while the other one decreases from 2.077 to 2.071 and 1.959 Å, respectively. The detailed structures of **D**, **E**, and the transition states $\mathbf{TS_{CD}}$ and $\mathbf{TS_{DE}}$ are given in Fig. 3.

It is very important to note, however, that the transformation of **D** to **E** via $\mathbf{TS_{DE}}$ is difficult if **C** and **D** bear α-substituents since after C_α–$C_{acetylene}$ coupling the substituent (in the model system a hydrogen atom, complex **E**) is pointing towards the Cp ligand giving rise to repulsive interactions (Fig. 3). In fact, as has been shown [9], the catalytic cyclotrimerizations of alkynes by RuCp(COD)Cl takes place only if one of the alkynes to be coupled is a 1,6-diyne.

Another intermediate to be envisaged in the formation of arenes is the metallanorbornadiene **M** (Chart 1). For the present system we were unable, however, to locate neither a stationary point for **L** nor **M**. Notwithstanding this, even if **L** and **M** had been located at the density functional level, the reductive elimination carrying both a metallacycloheptatriene and a metallanorbornadiene to benzene is actually symmetry forbidden thus implying a prohibitively large activation barrier.

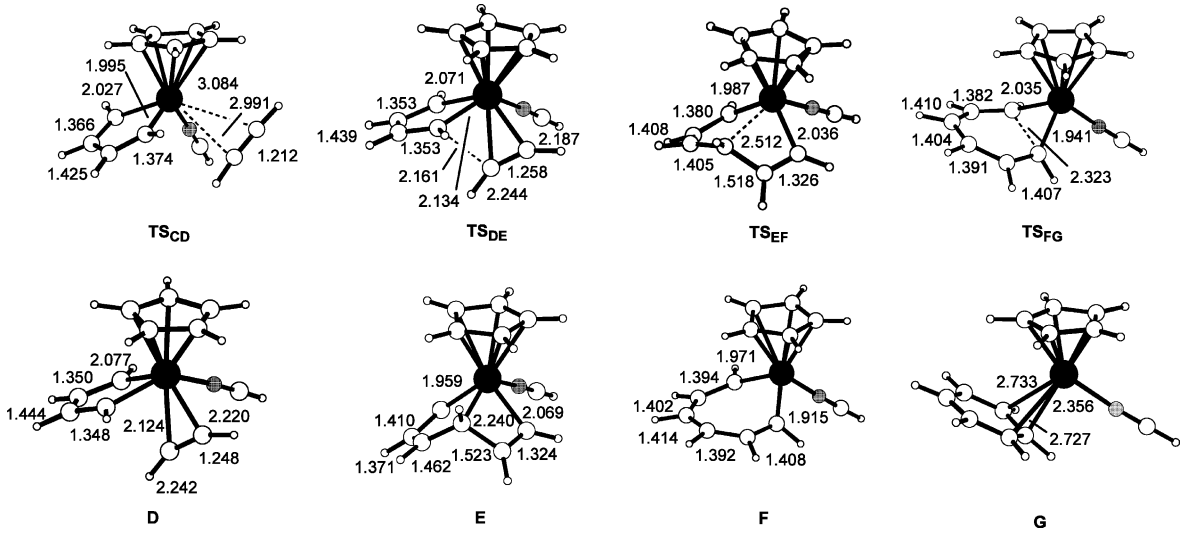


Fig. 3. Relevant distances (Å) in the optimized B3LYP geometries of complexes **D**, **E**, **F**, **G** and the transition states $\mathbf{TS_{CD}}$, $\mathbf{TS_{DE}}$, $\mathbf{TS_{EF}}$, and $\mathbf{TS_{FG}}$.

Similar results have been reported recently for the related CoCp system [10b].

Complex **E** rearranges easily via transition state $\mathbf{TS_{DE}}$ to afford the novel metallacycle **F**. In the course of this process the internal Ru–C single is cleaved. This reaction requires merely 1.0 kcal mol^{-1} activation energy and is energetically very favorable releasing 12.9 kcal mol^{-1}. Complex **F** features an unusual non-planar asymmetric seven-membered metallacyclic moiety with two short Ru–C bonds (1.971 and 1.915 Å). The C–C bond distances within the metallacycle are very similar ranging from 1.392 to 1.402 Å. In simplified **F** may be described as a metallacycloheptatetraene species.

The final intermediate in the catalytic cycle of Scheme 2 is complex **G** featuring a weakly bound η^3-coordinated benzene ligand. The release of the resonance stabilization energy upon arene formation combines with the construction of two new carbon carbon σ-bonds releasing 64.0 kcal mol^{-1}. The arene ligand is only weakly coordinated noting the two rather long Ru–C bonds (2.733 and 2.727 Å). This reaction is unusual, however, since a new C–C bond is formed via a reductive elimination process involving a biscarbene complex, a species that contains two metal carbon double bonds. In the course of this reductive elimination the carbon carbon distance decreases from 2.774 in **F** to 2.323 in $\mathbf{TS_{FG}}$ eventually to 1.416 Å in **G**.

Completing the catalytic cycle in Scheme 2 requires displacement of the arene ligand in **G** by a pair of alkynes ligands. Thermodynamically, the barrier to overcome this process is the Ru-arene binding energy which appears to be small (weak Ru–C bonds). The energetic consequences of the displacement of benzene by two alkynes to give benzene and **B** is exothermic by 25.7 kcal mol^{-1} showing that arene displacement is thermodynamically accessible (Fig. 1).

Experimentally it has been found that the formation of arene complexes gradually quenches the catalytic cycle of Scheme 2 due the formation of sandwich complexes of type **H**. This process requires at some stage the liberation of HCN for which several dissociation scenarios are conceivable. If HCN dissociates already from **C**, metallacycle **I** is formed (Fig. 1). This reaction is endothermic by 18.0 kcal and not very likely. On the other hand, if HCN is liberated from **D**, the metallacyclopentadiene acetylene complex **J** is formed. This reaction is only moderately endothermic by 4.8 kcal mol^{-1}. Once formed, **J** rearranges quite easily to afford the cyclic biscarbene **K** and eventually via $\mathbf{TS_{KH}}$ to give the sandwich complex **H**. The activation energies to convert **J** into **K** and **K** into **H** are rather small being 3.0 and 1.5 kcal mol^{-1}, respectively. The small kinetic barrier may be attributed to the large thermodynamic driving force associated with the conversion of **K** into **H** releasing 91.7 kcal mol^{-1}. Finally, complex **H** may be easily formed upon release of HCN from **G**. This reaction is exothermic by 17.5 kcal. The detailed structures of **J**, **K**, and the transition states $\mathbf{TS_{JK}}$ and $\mathbf{TS_{KH}}$ are given in Fig. 4. Accordingly, the two most likely reactions to form the arene complex **H** may originate from **D** and/or **G** via dissociation of HCN.

3. Conclusion

We have shown here that $[RuCp(CH_3CN)_3]^+$ indeed promotes the catalytic cyclotrimerization of alkynes, but not in a selective manner with 1,2,4- as well as 1,3,5-trisubstituted arenes formed in most cases. However, in the course of the catalytic process several pathways to 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, although 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 [23].

4. Experimental

4.1. General information

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [22]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$ (**1**) [23] was prepared according to the literature. ^{1}H-, and

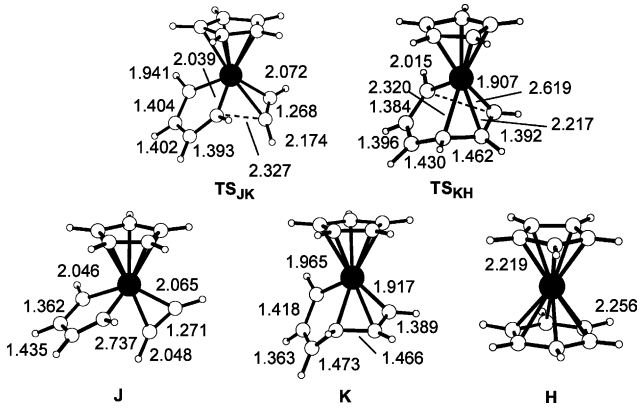


Fig. 4. Relevant distances (Å) in the optimized B3LYP geometries of complexes **J**, **K**, **H** and the transition states $\mathbf{TS_{JK}}$ and $\mathbf{TS_{KH}}$.

$^{13}C\{^1H\}$-NMR spectra were recorded on Bruker AVANCE-250 spectrometer and were referenced to $SiMe_4$.

4.2. Reactions of $[RuCp(CH_3CN)_3]PF_6$ (**1**) with alkynes

In a typical procedure, 100 μl of HC≡CR (R = *n*-Bu, CH_2Ph, COOEt, Ph, C_6H_9) and 1,6-heptadiyne and 1,7-octadiyne) were added to a solution of **1** (20 mg, 0.046 mmol) in 3 ml CH_3NO_2. The solution was heated to 80 °C for 24 h. After that time the reaction mixture was evaporated to dryness under vacuum and the products were extracted with Et_2O. The solvent was again removed under vacuum affording mixtures of coupling products. The product distribution was determined by NMR spectroscopy. The residues, which were insoluble in Et_2O, were filtrated, dried under vacuum and characterized by NMR spectroscopy.

4.2.1. $[RuCp(\eta^6\text{-}C_6H_3(n\text{-}Bu)_3)]PF_6$ (**2a**, **3a**)

The residue is a mixture of 1,2,4- and the 1,3,5-substituted benzene complexes at a ratio of 3:1. The two compounds were not separated. Yield: 23 mg (88%). ^{1}H-NMR (δ, $CDCl_3$, 20 °C): 6.19 (s, 3H, η^6-Bz^{sym}), 6.05 (s, 1H, η^6-Bz^{asym}), 6.00 (s, 1H, η^6-Bz^{asym}), 5.98 (s, 1H, η^6-Bz^{asym}), 5.24 (s, 5H, Cp^{sym}), 5.23 (s, 5H, Cp^{asym}), 2.72-2.36 (m, 6H, CH_2), 1.71-1.27 (m, 12H, CH_2), 1.06-0.83 (m, 9H, CH_3). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20 °C): 106.8 (1C, η^6-Bz^{asym}), 106.5 (s, 1C, η^6-Bz^{asym}), 106.0 (3C, η^6-Bz^{sym}), 105.3 (η^6-Bz^{asym}), 88.1 (3C, η^6-Bz^{sym}), 87.0 (1C, η^6-Bz^{asym}), 86.7 (1C, η^6-Bz^{asym}), 86.0 (1C, η^6-Bz^{asym}), 81.6 (5C, $Cp^{sym+asym}$), 34.5, 34.3, 34.2, 34.1, 34.0, 31.9, 31.6, 23.3, 23.2, 22.9, 22.8 (Bu^n), 14.0 (CH^3).

4.2.2. $[RuCp(\eta^6\text{-}C_6H_3(CH_2Ph)_3)]PF_6$ (**2b**, **3b**)

The residue is a mixture of 1,2,4- and the 1,3,5-substituted benzene complexes at a ratio of 3:1. The two compounds were not separated. Yield: 26 mg (86%). ^{1}H-NMR (δ, acetone-d_6, 20 °C): 7.59-7.00 (m, 15H, Ph), 6.34-5.99 (m, 3H, Bz), 5.34 (s, 5H, Cp), 4.20-3.80 (m, 6H, CH_2). $^{13}C\{^1H\}$-NMR (δ, acetone-d_6, 20 °C): 139.4, 138.4, 138.3 (3C, Ph), 129.5, 129.4, 129.2, 129.1, 128.9, 128.7, 127.6, 127.5 (15C, Ph), 106.0, 104.9, 104.4 (3C, η^6-Bz), 88.4, 86.9, 85.8 (3C, η^6-Bz), 81.9 (5C, Cp), 39.4, 37.3, 36.9 (3C, CH_2).

4.2.3. $[RuCp(\eta^6\text{-}C_6H_3(1,2,4\text{-}Ph)_3)]PF_6$ (**2c**)

Only one isomer and no cyclotrimerization products have been observed [24]. Yield: 23 mg (80%). ^{1}H-NMR (δ, CD_3CN, 20 °C): 7.76 (m, 2H, Ph), 7.50 (m, 4H, Ph), 7.40-7.12 (m, 9H, Ph), 6.79 (s, 1H, η^6-Bz), 6.76 (d, $J_{HH} = 6.0$ Hz, 1H, η^6-Bz), 6.53 (d, $J_{HH} = 6.0$ Hz, 1H, η^6-Bz), 5.36 (s, 5H, Cp). $^{13}C\{^1H\}$-NMR (δ, CD_3CN, 20 °C): 134.8, 133.9, 133.8, 130.7, 130.1, 129.8, 129.6, 129.5, 129.0, 128.9, 128.8, 128.2 (18C, Ph), 106.1, 106.0, 103.9 (3C, η^6-Bz), 89.0, 86.6, 86.3 (3C, η^6-Bz), 83.5 (s, 5C, Cp).

4.2.4. $[RuCp(\eta^6\text{-}C_6H_3(1,2,4\text{-}C_6H_9)_3)]PF_6$ (**2d**)

Only one isomer and no cyclotrimerization products have been observed. Yield: 26 mg (90%). ^{1}H-NMR (δ, $CDCl_3$, 20 °C): 6.41 (m, 1H, C_6H_9), 6.35 (d, $^3J_{HH} = 6.5$ Hz, 1H, η^6-Bz), 6.13 (d, $^3J_{HH} = 6.5$ Hz, 1H, η^6-Bz), 6.05 (s, 1H, η^6-Bz), 5.94 (m, 2H, C_6H_9), 5.29 (s, 5H, Cp), 2.32-1.48 (m, 24H, C_6H_9). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20 °C): 133.4, 133.2, 133.0, 132.6, 133.4 (6C, C_6H_9), 108.4, 108.3, 105.4 (3C, η^6-Bz), 86.0, 82.7, 81.5 (3C, η^6-Bz), 80.9 (5C, Cp), 30.6, 30.3, 27.1, 26.2, 26.0, 22.9, 22.6, 21.8, 21.7, 21.6 (12C, C_6H_9).

4.2.5. $[RuCp(\eta^6\text{-}C_{14}H_{16}]PF_6$ (**2e**)

Yield: 19 mg (83%). ^{1}H-NMR (δ, $CDCl_3$, 20 °C): 6.32 (s, 1H, η^6-C_6H_3), 6.27 (d, $^3J_{HH} = 6.0$ Hz, η^6-C_6H_3), 5.99 (d, $^3J_{HH} = 6.0$ Hz, η^6-C_6H_3), 5.29 (s, 5H, Cp), 2.90 (t, $^3J_{HH} = 7.5$ Hz, 4H, CH_2), 2.73 (t, $^3J_{HH} = 7.5$ Hz, 2H, CH_2), 2.23 (dt, $^3J_{HH} = 7.0$ Hz, $^3J_{HH} = 2.4$ Hz, 2H, CH_2), 2.09 (t, $^3J_{HH} = 7.4$ Hz, 2H, CH_2), 2.02 (t, $^4J_{HH} = 2.4$ Hz, 1H, CCH), 1.85 (m, 2H, CH_2). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20 °C): 109.1, 108.3, 104.7 (3C, η^6-Bz), 85.2, 83.7, 82.1 (3C, η^6-Bz), 81.2 (5C, Cp), 70.2, 65.6 (2C, CCH), 35.5, 34.6, 33.2, 31.2, 30.9, 24.6, 17.7 (6C, CH_2).

4.2.6. $[RuCp(\eta^6\text{-}C_{16}H_{20})]PF_6$ (**2f**) and $[RuCp(\eta^6\text{-}C_{24}H_{30})]PF_6$ (**2g**)

The compounds **2f** and **2g** could not separated, but their ratio was determined by NMR spectroscopy and is 7:4 (**2f**:**2g**). Yield: 23 mg (89%). ^{1}H-NMR (δ, $CDCl_3$, 20 °C): 7.04-6.83 (m, 3H, Bz (non-coord., trimer)), 6.25-5.99 (m, 3H, Bz (coord., dimer + trimer)), 5.30 (s, 5H, Cp(dimer)), 5.25 (s, 5H, Cp (trimer)), 2.88-2.69 (m, 4H, CH_2), 2.64-2.43 (m, 2H, CH_2), 2.27 (dt, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 2.6$ Hz, 2H, CH_2 (dimer)), 2.00 (t, $^4J_{HH} = 2.6$ Hz, CH (dimer)), 1.92-1.50 (m, 12H, CH_2). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20 °C): 138.6, 136.2, 132.4 (3C, Bz (non-coord., trimer)), 129.5, 129.4, 124.3 (3C, Bz (non-coord., Trimer)), 112.8, 103.3, 102.7 (3C, Bz (coord., dimer + trimer)), 87.3, 86.5, 85.4 (3C, Bz (coord., dimer + trimer)), 81.4 (5C, Cp, dimer), 81.2 (5C, Cp, trimer), 78.5, 69.3 (2C, CCH), 30.9, 30.1, 22.5, 19.5, 18.4, 14.1 (8C, CH_2 (dimer + trimer).

4.3. Computational techniques

All calculations were performed using the Gaussian98 software package [18] on the Silicon Graphics Cray Origin 2000 of the Vienna University of Technology. The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level [17] with the Stuttgart/Dresden ECP (sdd) basis set [25] to describe the electrons of the ruthenium atom. For all other atoms the 6–31g** basis set was employed [26].

Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides, and obtaining the minima presented on the reactions energy profile. All geometries were optimized without constraints (C_1 symmetry) and the energies were zero point corrected.

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