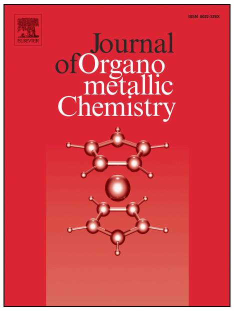

Synthesis of cyclohexadienyl ruthenium complexes by replacement of the naphthalene ligand in $[(\eta^5\text{-}C_6H_3Me_4)Ru(\eta^6\text{-}C_{10}H_8)]^+$

Evgeniya A. Trifonova, Dmitry S. Perekalin, Natalia L. Loskutova, Yulia V. Nelyubina, Alexander R. Kudinov

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Graphical abstract: synopsis

Half-sandwich cyclohexadienyl ruthenium complexes were synthesized by replacement of the naphthalene ligand in the readily available complex $[(\eta^5\text{-}C_6H_3Me_4)Ru(\eta^6\text{-}C_{10}H_8)]^+$.

Synthesis of cyclohexadienyl ruthenium complexes by replacement of the naphthalene ligand in $[(\eta^5\text{-}C_6H_3Me_4)Ru(\eta^6\text{-}C_{10}H_8)]^+$

Evgeniya A. Trifonova, Dmitry S. Perekalin, Natalia L. Loskutova, Yulia V. Nelyubina, Alexander R. Kudinov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: arkudinov@ineos.ac.ru

Abstract

Reactions of the cyclohexadienyl ruthenium complex $[(\eta^5\text{-}C_6H_3Me_4)Ru(C_{10}H_8)]^+$ (**1**) with 2-electron ligands L lead to replacement of the naphthalene ligand with formation of the half-sandwich complexes $[(\eta^5\text{-}C_6H_3Me_4)RuL_3]^+$ (L = MeCN, ^{t}BuNC, $P(OEt)_3$, 1,3,5-triaza-7-phosphaadamantane). Similar reactions with $P(OMe)_3$ or dppe in the presence of $Cl^–$ give the neutral complexes $(\eta^5\text{-}C_6H_3Me_4)Ru(P(OMe)_3)_2Cl$ or $(\eta^5\text{-}C_6H_3Me_4)Ru(dppe)Cl$, respectively. Cation **1** also exchanges the naphthalene ligand for other arenes producing the corresponding sandwich compounds $[(\eta^5\text{-}C_6H_3Me_4)Ru(arene)]^+$ (arene = C_6H_6, 1,4-$C_6H_4(OMe)_2$). Complex **1** catalyzes cyclotrimerization of N,N-di(propargyl)tosylamide with 1-octyne or 4-pentynol, but less effectively than $[CpRu(C_{10}H_8)]^+$. The mechanism of the naphthalene replacement in **1** was studied by DFT calculations.

Keywords: Cyclohexadienyl / Ruthenium / Naphthalene / Cyclotrimerization / Alkynes / DFT calculations

Introduction

Cyclopentadienyl ruthenium complexes $(C_5R_5)RuL_2X$ and $[(C_5R_5)RuL_3]^+$ are widely used in organometallic synthesis and catalysis [1]. Although analogous cyclohexadienyl complexes can find similar application, their chemistry is notably less developed. Several compounds with the unsubstituted cyclohexadienyl ligand $[(C_6H_7)RuL_3]^+$ were obtained by nucleophilic addition of hydride to the corresponding benzene complexes [2]. Complexes with 6,6-dimethyl-cyclohexadienyl ligand $(\eta^5\text{-}C_6H_5Me_2)RuL_2Cl$ have been synthesized by reaction of the sandwich compound $(\eta^5\text{-}C_6H_5Me_2)_2Ru$ with HCl followed by addition of 2-electron ligands L [3]. Similar reaction of $(\eta^5\text{-}C_6H_5Me_2)_2Ru$ with HBF_4 in MeCN has given cationic complex $[(\eta^5\text{-}$

$C_6H_5Me_2)Ru(MeCN)_3]^+$, in which two acetonitrile ligands can be replaced for PMe_3 or dppe. Some related pentadienyl compounds were also obtained by this protonation-substitution approach [4]. To the best of our knowledge, the catalytic activity of the cyclohexadienyl complexes was not investigated.

Recently it has been shown that the cyclopentadienyl ruthenium complexes $(C_5R_5)RuL_2X$, $[(C_5R_5)RuL_3]^+$ and $[(C_5R_5)Ru(arene)]^+$ can be conveniently synthesized by replacement of the naphthalene ligand in the cationic complexes $[(C_5R_5)Ru(C_{10}H_8)]^+$ [5,6,7]. Herein we describe a similar synthesis of the cyclohexadienyl complexes by naphthalene replacement in the readily available cation $[(\eta^5\text{-}C_6H_3Me_4)Ru(C_{10}H_8)]^+$ [8]. DFT calculations on the mechanism of naphthalene replacement in **1** as well as investigation of the catalytic activity of **1** are also reported.

Results and Discussion

We found that cation $[(\eta^5\text{-}C_6H_3Me_4)Ru(C_{10}H_8)]^+$ (**1**) reacts with 2-electron ligands L giving cationic complexes $[(\eta^5\text{-}C_6H_3Me_4)RuL_3]^+$ (**2a–d**; L = MeCN, ^{t}BuNC, $P(OEt)_3$, 1,3,5-triaza-7-phosphaadamantane) in 68–97% yields (Scheme 1).[*] The reaction rate depended on the ligand size: small MeCN and ^{t}BuNC reacted at room temperature, while heating at 60 °C was required for bulky $P(OEt)_3$ and 1,3,5-triaza-7-phosphaadamantane. Even more bulky ligands, Ph_3P and Ph_3Sb, replaced naphthalene ligand in **1** at 60 °C giving mixtures of unidentified products instead of the expected tris-ligand complexes [9]. Regardless the nature of the ligand, the naphthalene replacement in **1** proceeded faster than in its cyclopentadienyl analogue $[CpRu(C_{10}H_8)]^+$ [5a, 6b]. This tendency was previously observed for other dienyl complexes $[(\eta^5\text{-}C_6H_7)Ru(C_{10}H_8)]^+$ [10] and $[(\eta^5\text{-}C_8H_{11})Ru(C_{10}H_8)]^+$ [11].

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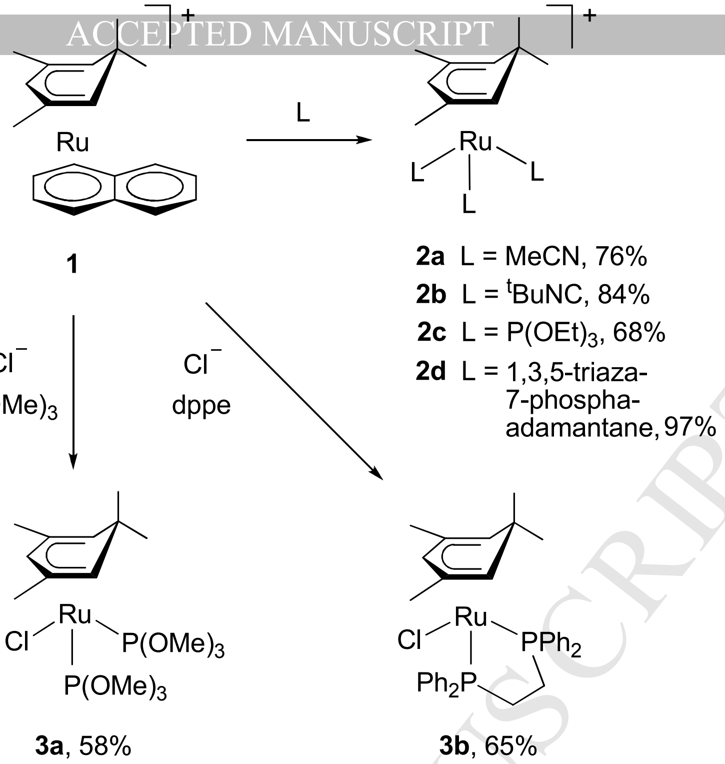
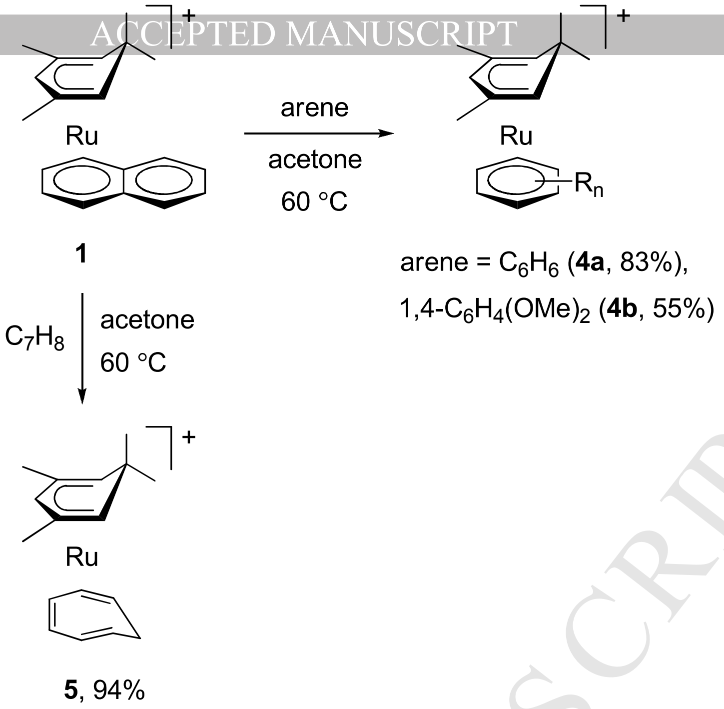
[*] All cationic complexes described in this paper were isolated and used as salts with PF_6^- anions.



Scheme 1

Cation **1** also reacted with chloride anion in the presence of $P(OMe)_3$ or dppe in CH_2Cl_2 at room temperature giving neutral complexes (η^5-$C_6H_3Me_4$)Ru($P(OMe)_3$)$_2$Cl (**3a**) or (η^5-$C_6H_3Me_4$)Ru(dppe)Cl (**3b**), respectively. The conversion of **1** into **3a**,**b** was quantitative according to ^{1}H NMR, but the isolated yields were only ca. 60% since high solubility of the products led to losses during work-up.

The naphthalene ligand in cation **1** can be exchanged for 6-electron ligands, *viz.* benzene, 1,4-dimethoxybenzene or cycloheptatriene, providing complexes $[(\eta^5\text{-}C_6H_3Me_4)Ru(C_6H_6)]^+$ (**4a**), $[(\eta^5\text{-}C_6H_3Me_4)Ru(1,4\text{-}C_6H_4(OMe)_2)]^+$ (**4b**) or $[(\eta^5\text{-}C_6H_3Me_4)Ru(C_7H_8)]^+$ (**5**), respectively (Scheme 2). The replacement of naphthalene by benzene in acetone solution was slow at room temperature (50% conversion in a week) and reasonably fast at 60 °C (100% conversion in 24 h). However, similar reaction with a sterically hindered durene did not reach the complete conversion even after 96 h of heating at 60 °C. An attempt to accelerate the reaction by visible light irradiation was unsuccessful. Therefore, we concluded that the arene complexes $[(\eta^5\text{-}C_6H_3Me_4)Ru(arene)]^+$ are more conveniently prepared from dimethyloctadienyl ruthenium chloride $[(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ [8] rather than from **1**.



Scheme 2

All new compounds were characterized by ^{1}H and ^{13}C NMR spectra as well as elemental analysis. The structures of complexes [**2d**]PF$_6$ and **3a** were established by X-ray diffraction (Fig. 1 and 2). The coordination of the cyclohexadienyl ligand in the chloride **3a** is unsymmetrical apparently due to the trans-influence of the phosphite ligand. In particular, the Ru1–C6 bond (2.358 Å), which is located opposite to the P2 atom, is longer than the formally equivalent Ru–C2 bond (2.203 Å). More symmetrical coordination was observed for the cyclohexadienyl ligand in **2d** where the Ru–C bonds had fallen into a narrow range of 2.260–2.281 Å.

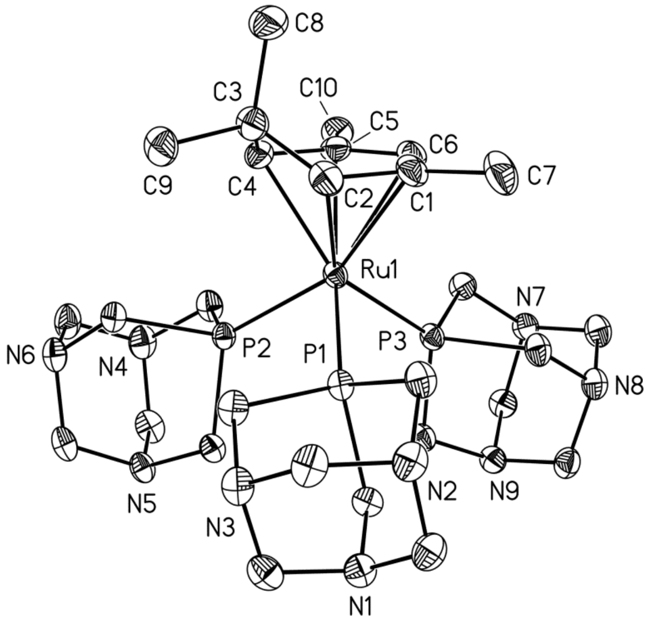


Fig. 1. The structure of complex [**2d**]PF_6 in 50% thermal ellipsoids. All hydrogen atoms and the counter-anion are omitted for clarity. Selected interatomic distances (Å): Ru1–C1 2.281(4), Ru1–C2 2.260(4), Ru1–C4 2.274(4), Ru1–C5 2.263(4), Ru1–C6 2.261(4), Ru1–P1 2.3054(10), Ru1–P2 2.3018(10), Ru1–P3 2.3271(10).

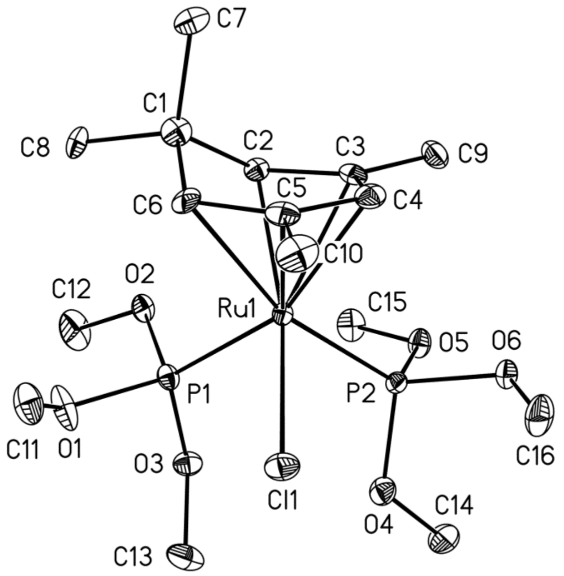
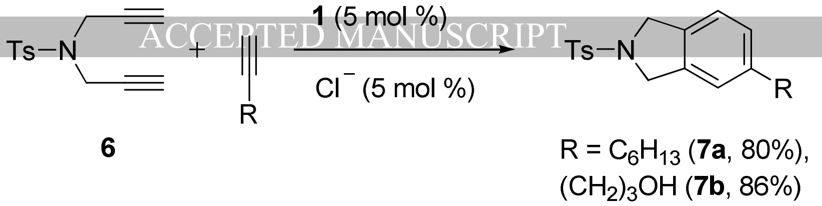


Fig. 2. The structure of **3a** in 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru1–C2 2.203(4), Ru1–C3 2.183(4), Ru1–C4 2.217(4), Ru1–C5 2.290(4), Ru1–C6 2.358(4), Ru1–P1 2.2654(11), Ru1–P2 2.2448(10), Ru1–Cl1 2.4556(10).

It has been recently shown that the cyclopentadienyl ruthenium naphthalene complexes $[(C_5R_5)Ru(C_{10}H_8)]^+$ are efficient catalysts for various transformations of alkynes due to their ability to generate active species $[(C_5R_5)Ru]^+$ [5a,6b,12]. In contrast, we found that the cyclohexadienyl complexes **1** and **2a** were generally inactive in such catalytic reactions. In particular, they did not promote Alder-ene reaction between 3-hexyne and N-tosyl-allylamine [13], addition of acetic acid to phenylacetylene [14,15], as well as anti-Markovnikov hydration of phenylacetylene in the presence of bipyridine [12b]. In the presence of Cl^- anion complex **1** catalyzed cyclotrimerization of N,N-di(propargyl)tosylamide (**6**) with 1-octyne or 4-pentynol giving isoindoline derivatives **7a**,**b** in good yields (Scheme 3). However, compared to the cyclopentadienyl analogue $[CpRu(C_{10}H_8)]^+$, higher loading of catalyst **1** (5%) and longer reaction times (2–6 h) were required to achieve full conversion of **6**.



Scheme 3

It was mentioned above that the naphthalene replacement in the cyclohexadienyl complexes $[(\eta^5\text{-}C_6H_3R_4)Ru(C_{10}H_8)]^+$ (R = H, Me) proceeds faster than in the cyclopentadienyl analogue $[CpRu(C_{10}H_8)]^+$. We have studied the mechanism of naphthalene replacement by MeCN in the parent complexes $[(\eta^5\text{-}C_6H_7)Ru(C_{10}H_8)]^+$ and $[CpRu(C_{10}H_8)]^+$ by DFT computation. Figure 3 shows the intrinsic reaction coordinates (IRC) for the primary step, at which these species are attacked by the first MeCN molecule. This step has maximal activation energy, since it is changes the coordination mode of the naphthalene ligand from η^6 in complex to η^4 in transition state **TS** and intermediate **IM** (Figure 4). It is in accordance with general tendency established earlier both experimentally [16] and theoretically [6b] for chromium and ruthenium naphthalene complexes. The activation energy of naphthalene replacement in the cyclohexadienyl complex is considerably lower than for the cyclopentadienyl analogue (Table 1). These results correlate with previous EDA calculations [8] indicating that stronger Ru–C_6H_7 bond (vs Ru–Cp) leads to weaker Ru–arene bond in cyclohexadienyl complexes.

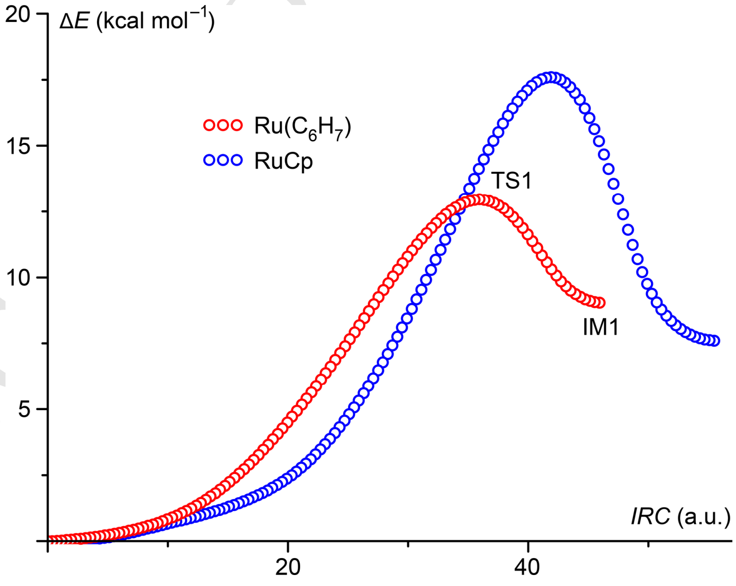


Figure 3. Intrinsic reaction coordinates for the primary step of naphthalene replacement by acetonitrile in $[(\eta^5\text{-}C_6H_7)Ru(C_{10}H_8)]^+$ and $[CpRu(C_{10}H_8)]^+$ (at PBE/L2 level).

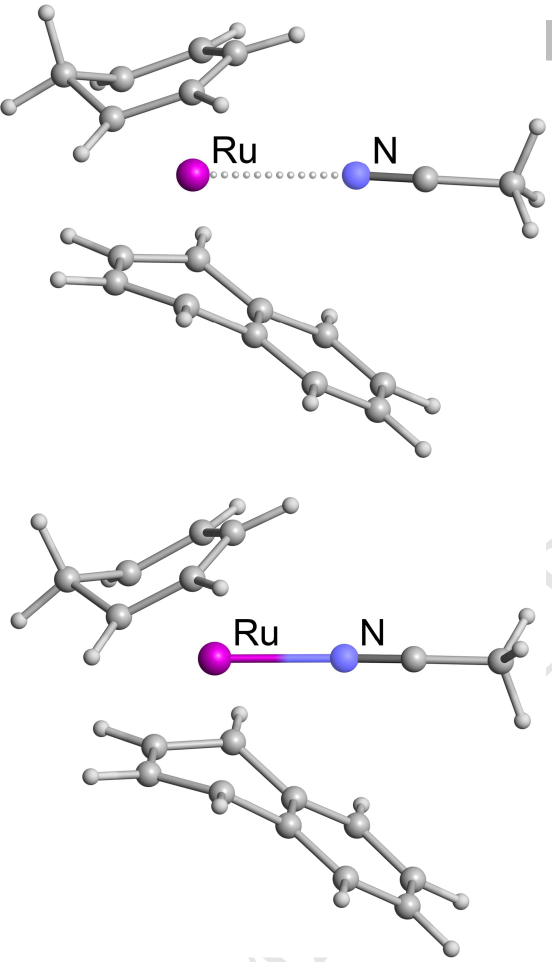


Figure 4. Optimized structures of the transition state **TS** (above) and the intermediate **IM** (below) for the primary step of naphthalene replacement by acetonitrile in cation $[(\eta^5\text{-}C_6H_7)Ru(C_{10}H_8)]^+$ (at BPBE/L2 level).

Table 1. Activation enthalpies H_a and free energies G_a for the primary step of naphthalene replacement in $[(\eta^5\text{-}C_6H_7)Ru(C_{10}H_8)]^+$ and $[CpRu(C_{10}H_8)]^+$ complexes by MeCN. Energies are given at BPBE/def2-TZVPP//BPBE/L2 level with PCM solvation energy corrections for MeCN (in kcal mol^{-1} at 298.15 K).

Complex	H_a	G_a
$[(\eta^5\text{-}C_6H_7)Ru(C_{10}H_8)]^+$	16.6	26.2
$[CpRu(C_{10}H_8)]^+$	20.7	31.5

Conclusion

To conclude, we have developed a general method for the synthesis of various cyclohexadienyl ruthenium complexes via naphthalene replacement in the readily available cation $[(\eta^5\text{-}C_6H_3Me_4)Ru(C_{10}H_8)]^+$ (**1**). Both experiment and computation indicate that the naphthalene replacement in the cyclohexadienyl complexes is faster than in cyclopentadienyl analogues. At the same time the catalytic activity of **1** in alkyne transformations is lower than that of $[CpRu(C_{10}H_8)]^+$.

Experimental section

General

All reactions were carried out under argon in anhydrous solvents, which were purified and dried using standard procedures. Isolation of products was conducted in air. ^1H, ^{13}C and ^{31}P NMR spectra were measured with a Bruker Avance 400 spectrometer at 20°C from $[D_6]$-acetone solutions of complexes, unless otherwise stated. Complex [**1**]PF_6 was synthesized according to the published procedure [8].

Synthesis of $[(\eta^5\text{-}C_6H_3Me_4)Ru(MeCN)_3]PF_6$ *([**2a**]PF_6)*

A solution of [**1**]PF_6 (51 mg, 0.10 mmol) in acetonitrile (1 ml) was stirred overnight. Then hexane (10 mL) was added to extract the liberated naphthalene. The mixture was vigorously stirred for 5 minutes and the upper phase of the biphasic system was removed. Another portion of hexane (10 ml) was added to a reaction mixture, it was left stirring for 5 hours. This process was repeated twice. After a total of 44 h stirring, the acetonitrile solution was evaporated in vacuum and the resulting green-yellow solid was washed with hexane (3×5 mL) to give [**2a**]PF_6 as a yellow-green solid (38 mg, 0.075 mmol, 76% yield). In order to avoid possible oxidation of [**2a**]PF_6 its isolation was carried out under argon atmosphere.

^1H NMR (400 MHz, CD_2Cl_2): δ = 5.23 (s, 1H, $C_6H_3Me_4$), 2.17 (s, 2H, $C_6H_3Me_4$), 2.12 (s, 9H, MeCN), 1.65 (s, 6H, Me), 1.32 (s, 3H, Me), 0.29 (s, 3H, Me). ^{13}C NMR (101 MHz): δ = 99.28, 70.20, 44.25, 37.52, 27.65, 19.76, 2.11 (*Me*CN). Anal. Calc. for $C_{16}H_{24}F_6N_3PRu$: C 38.10, H 4.80; found C 38.24, H 4.57.

Synthesis of $[(\eta^5\text{-}C_6H_3Me_4)Ru(^tBuNC)_3]PF_6$ *([**2b**]PF_6)*

A solution of [**1**]PF_6 (20 mg, 0.04 mmol) and ^tBuNC (0.224 mL, 2.00 mmol) was stirred in THF (2 ml) for 24 hours. The solvent was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short alumina column (3 cm) with acetone-CH_2Cl_2 mixture (1:1). Resulting solution was evaporated, the residue was washed with Et_2O-pentane mixture (1:1) and reprecipitated from CH_2Cl_2 by Et_2O-pentane mixture (1:4) to give white crystals of [**2b**]PF_6 (20 mg, 0.032 mmol, 84% yield).

^1H NMR (400 MHz): δ = 5.81 (s, 1H, $C_6H_3Me_4$) 3.12 (d, *J* = 1 Hz, 2H, $C_6H_3Me_4$), 1.94 (s, 6H, Me), 1.59 (s, 9H, ^tBu), 1.37 (s, 3H, Me), 0.55 (s, 3H, Me). ^{13}C NMR (101 MHz): δ = 143.26

(CN), 122.20, 112.82, 78.67, 61.81 ($C\mathrm{Me}_3$), 37.09, 35.76, 34.39, 25.27, 21.26 ($\mathrm{C}Me_3$). Anal. Calc. for $C_{25}H_{42}F_6N_3PRu \times CH_2Cl_2$: C 43.64, H 6.20; found C 43.86, H 6.07.

Synthesis of $[(\eta^5\text{-}C_6H_3Me_4)Ru(P(OEt)_3)_3]PF_6$ *([**2c**]PF₆)*

A solution of [**1**]PF_6 (25 mg, 0.050 mmol) and $P(OEt)_3$ (0.05 mL, 0.30 mmol) in acetone (2 ml) was heated at 60 ºC for 10 hours. The solvent was evaporated and the solid was washed with Et_2O (2×7ml). The residue was dissolved in CH_2Cl_2, filtered through a piece of cotton wool and reprecipitated from CH_2Cl_2 by petroleum ether to give [**2c**]PF_6 (30 mg, 0.034 mmol, 68% yield) as white solid.

^{1}H NMR (400 MHz): δ = 5.52 (s, 1H, $C_6H_3Me_4$), 4.18 (dt, J = 7, 5 Hz, 18H, $OC\underline{H}_2CH_3$), 2.96 (s, 2H, $C_6H_3Me_4$), 2.02 (s, 6H, Me), 1.36 (s, 3H, Me) 1.33 (t, J = 7 Hz, 27H, $OCH_2C\underline{H}_3$), 0.49 (s, 3H, Me). ^{31}P NMR (162 MHz): δ = 137.93 (s), −144.05 (sept, J = 708 Hz, PF_6). ^{13}C NMR (101 MHz): δ = 113.71, 80.69, 62.60 – 62.07 (m), 37.55, 36.76, 20.31, 15.50. Anal. Calc. for $C_{28}H_{60}F_6O_9P_4Ru$: C 38.23, H 6.87; found C 37.92, H 6.88.

Synthesis of $[(\eta^5\text{-}C_6H_3Me_4)Ru(\text{1,3,5-triaza-7-phosphaadamantane})_3]PF_6$ *([**2d**]PF₆)*

A solution of [**1**]PF_6 (25 mg, 0.050 mmol) and 1,3,5-triaza-7-phosphaadamantane (39 mg, 0.25 mmol) in acetone (2 mL) was heated at 60 ºC for 10 hours. The solvent was evaporated and the solid was washed with Et_2O-petroleum ether mixture (1:1). The residue was dissolved in acetone, filtered through a piece of cotton wool and reprecipitated from acetone by petroleum ether to give [**2d**]PF_6 (41 mg, 0.048 mmol, 97% yield) as white solid.

^{1}H NMR (400 MHz): δ = 6.01 (s, 1H, $C_6H_3Me_4$), 4.66 (d, J = 13 Hz, 9H, CH_2), 4.54 (d, J = 13 Hz, 9H, CH_2), 4.25 (s, 18H, CH_2), 3.09 (s, 2H, $C_6H_3Me_4$), 2.28 (s, 6H, Me), 1.48 (s, 3H, Me), 0.51 (s, 3H, Me). ^{31}P NMR (162 MHz): δ = –42.99 (s), −144.05 (sept, J = 708 Hz, PF_6). ^{13}C NMR (101 MHz): δ = 108.80, 81.64, 72.32, 57.76 (m), 55.07 (m), 39.91, 21.89. Anal. Calc. for $C_{28}H_{51}F_6N_9P_4Ru$: C 39.44, H 6.03; found C 39.98, H 6.31.

Synthesis of $(\eta^5\text{-}C_6H_3Me_4)Ru(P(OMe_3)_2Cl$ *(**3a**)*

A solution of [**1**]PF_6 (51 mg, 0.10 mmol), $P(OMe)_3$ (0.1 mL, 0.80 mmol), and $[Et_3NBn]Cl$ (23 mg, 0.10 mmol) in CH_2Cl_2 (2 mL) was stirred overnight. The solvent was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short alumina column (3 cm) with petroleum ether-CH_2Cl_2 mixture (1:1). Resulting solution was evaporated and the residue was washed with cold pentane (2 ml) to give **3a** (30 mg, 0.058 mmol, 58% yield) as yellow solid.

^{1}H NMR (400 MHz): δ = 5.45 (s, 1H, $C_6H_3Me_4$), 3.73 (m, 18H, OMe), 2.49 (br. s, 2H, $C_6H_3Me_4$), 1.79 (s, 6H, Me), 1.22 (s, 3H, Me), 0.42 (s, 3H, Me). ^{13}C NMR (101 MHz): δ = 79.84

(m), 52.38, 37.07, 35.83 (m), 27.78, 20.85. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 153.23 (s). Anal. Calc. for $C_{16}H_{33}ClO_6P_2Ru$: C 36.96, H 6.40; found C 36.95, H 6.42.

*Synthesis of (η^5-$C_6H_3Me_4$)Ru(dppe)Cl (**3b**)*

A solution of [**1**]PF_6 (51 mg, 0.10 mmol), dppe (40 mg, 0.10 mmol), and [Et_3NBn]Cl (23 mg, 0.10 mmol) in CH_2Cl_2 (2 mL) was stirred overnight. The solvent was evaporated and the residue was extracted with Et_2O (2×3 ml). Yellow extract was evaporated and the residue was washed with cold pentane (2 ml) to give **3b** (42 mg, 0.063 mmol, 65% yield) as bright yellow solid.

^{1}H NMR (400 MHz): δ = 7.98 (s, 4H, Ph), 7.41 (m, 6H, Ph), 7.37 (m, 6H, Ph), 7.33-7.25 (m, 4H, Ph), 5.91 (br. s, 1H, $C_6H_3Me_4$), 2.98 (dd, *J* = 13, 6 Hz, 2H, dppe), 2.39 (br. s, 2H, $C_6H_3Me_4$), 2.14 (br. s, 2H, dppe), 1.42 (s, 6H, Me), 1.16 (s, 3H, Me), 0.43 (s, 3H, Me). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 68.71 (s). Anal. Calc. for $C_{36}H_{39}ClP_2Ru$: C 64.52, H 5.87; found C 65.06, H 6.02.

*Synthesis of [(η^5-$C_6H_3Me_4$)Ru(C_6H_6)]PF_6 ([**4a**]PF_6)*

A solution of [**1**]PF_6 (51 mg, 0.10 mmol) and benzene (0.027 ml, 0.30 mmol) in acetone (3 ml) was heated at 60 ºC for 24 hours. The solvent was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short alumina column (3 cm) with acetone-CH_2Cl_2 mixture (1:1). Resulting solution was evaporated, the solid was washed with Et_2O (3×5 ml) and reprecipitated from CH_2Cl_2 by Et_2O to give white microcrystals of [**4a**]PF_6 (38 mg, 0.083 mmol, 83% yield).

^{1}H NMR (400 MHz): δ = 6.62 (s, 1H, $C_6H_3Me_4$), 6.36 (s, 6H, C_6H_6), 3.71 (s, 2H, $C_6H_3Me_4$), 1.99 (s, 6H, Me), 1.31 (s, 3H, Me), 0.41 (s, 3H, Me). The spectrum is similar to that described in ref. [8].

*Synthesis of [(η^5-$C_6H_3Me_4$)Ru(1,4-$C_6H_4(OMe)_2$)]PF_6 ([**4b**]PF_6)*

A solution of [**1**]PF_6 (44 mg, 0.090 mmol) and p-dimetoxybenzene (36 mg, 0.27 mmol) in acetone (3 ml) was heated at 60 ºC for 24 hours. The solvent was evaporated and the solid was washed with diethyl ether (3×2ml). The residue was dissolved in CH_2Cl_2, filtered, and the product was crystallized by slow diffusion of Et_2O vapors into solution to give white crystals of [**4b**]PF_6 (25 mg, 0.048 mmol, 55% yield).

^{1}H NMR (400 MHz): δ = 6.60 (s, 1H, $C_6H_3Me_4$), 6.22 (s, 4H, C_6H_4), 3.90 (s, 6H, OMe), 3.47 (s, 2H, $C_6H_3Me_4$), 1.90 (s, 6H, Me), 1.34 (s, 3H, Me), 0.42 (s, 3H, Me). ^{13}C NMR (101 MHz): δ = 134.49, 101.13, 88.18, 75.74, 56.76, 54.21, 37.28, 32.94, 19.84. Anal. Calc. for $C_{18}H_{25}F_6O_2PRu$: C 41.62, H 4.85; found C 40.97, H 4.96.

*Synthesis of [(η^5-$C_6H_3Me_4$)Ru(C_7H_8)]PF_6 ([**5**]PF_6)*

A solution of [**1**]PF_6 (51 mg, 0.10 mmol) and cycloheptatriene (0.031 ml, 0.30 mmol) in acetone (3 ml) was heated at 60 ºC for 24 hours. The solvent was evaporated and the solid was washed with Et_2O (3×2 ml). The residue was reprecipitated from CH_2Cl_2 by Et_2O to give yellow crystals of [**5**]PF_6 (44 mg, 0.093 mmol, 94% yield).

^{1}H NMR (400 MHz): δ = 6.40 (br. s, 2H, C_7H_8), 6.25 (s, 1H, $C_6H_3Me_4$) 5.80 (br. s, 2H, C_7H_8), 4.09 (br. s, 2H, C_7H_8), 3.95 (s, 2H, $C_6H_3Me_4$), 3.21 (m, 1H, C_7H_8), 1.86 (s, 6H, Me), 1.67 (m, 1H, C_7H_8), 1.24 (s, 3H, Me), 0.47 (s, 3H, Me). ^{13}C NMR (101 MHz): δ = 107.21, 98.63, 96.40, 88.04, 60.44, 42.71, 38.35, 34.15, 28.06, 22.96, 19.37. Anal. Calc. for $C_{17}H_{23}F_6PRu$: C 43.13, H 4.90; found C42.63, H 5.01.

*Cyclotrimerization of Diyne **6** with 1-octyne*

To a solution of [**1**]PF_6 (5 mg, 0.01 mmol), [Et_3NBn]Cl (2.3 mg, 0.01 mmol), and 1-octyne (0.117 ml, 0.80 mmol) in CH_2Cl_2 (1 ml) a solution of diyne (50 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added dropwise within 30 min. The reaction mixture was stirred for 6 h. After complete consumption of diyne (by TLC), the solvent was evaporated, and the crude product was purified by flash column chromatography on silica gel (gradient elution with hexane-EtOAc, from 10:1 to 1:1) to afford pure isoindoline derivative **7a** (58 mg, 0.16 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8 Hz, 2H, Ts), 7.30 (d, *J* = 8 Hz, 2H, Ts), 7.07 (d, *J* = 8 Hz, 2H, CH),7.04 (d, *J* = 8 Hz, 2H, CH), 6.97 (s, 1H, CH), 4.58 (s, 4H, CH_2), 2.55 (t, *J* = 7 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 1.55 (m, 2H, CH_2), 1.27 (m, 6H, CH_2), 0.87 (t, *J* = 7 Hz, 3H, CH_3). The spectrum is similar to that described in ref. [17].

*Cyclotrimerization of Diyne **6** with 4-pentynol*

To a solution of [**1**]PF_6 (5 mg, 0.01 mmol), Et_3NBnCl (2.3 mg, 0.01 mmol), and 4-pentynol (0.074 ml, 0.8 mmol) in CH_2Cl_2 (1 ml) a solution of diyne (50 mg, 0.20 mmol) in CH_2Cl_2 (1 ml) was added dropwise within 30 min. The reaction mixture was stirred for 2 h. After complete consumption of diyne (by TLC), the solvent was evaporated, and the crude product was purified by flash column chromatography on silica gel (gradient elution with hexane-EtOAc, from 9:1 to 1:1) to afford pure isoindoline derivative **7b** (57 mg, 0.17 mmol, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8 Hz, 2H, Ts), 7.30 (d, *J* = 8 Hz, 2H, Ts), 7.06 (br. s, 2H, CH), 6.99 (br. s, 1H, CH), 4.56 (s, 4H, CH_2), 3.62 (t, *J* = 6 Hz, 2H, CH_2), 2.72–2.60 (m, 2H, CH_2), 2.38 (s, 3H, CH_3), 1.98 (br. s., 1H, OH), 1.86–1.77 (m, 2H, CH_2). The spectrum is similar to that described in ref. [18].

Crystallographic data

Crystals of [**2d**]PF_6 ($C_{28}H_{51}F_6N_9P_4Ru \times 1.4[CH_2Cl_2]$, M = 971.62) were triclinic, space group P-1, at 120K: a = 12.6225(5), b = 12.6611(5), c = 14.2864(5) Å, α = 88.6570(10), β = 72.6870(10), γ = 68.2030(10)°, V = 2014.11(13) $Å^3$, Z = 2 (Z' = 2), d_{calc} = 1.602 g cm^{-3}, μ(MoKα) = 7.98 cm^{-1}, F(000) = 998. Crystals of **3a** ($C_{16}H_{33}ClO_6P_2Ru$, M = 519.88) were monoclinic, space group C2/c, at 120K: a = 16.2380(10), b = 10.2996(6), c = 25.8352(16) Å, β = 96.5950(10)°, V = 4292.2(5) $Å^3$, Z = 8 (Z' = 1), d_{calc} = 1.609 g cm^{-3}, μ(MoKα) = 10.32 cm^{-1}, F(000) = 2144. Intensities of 20883 and 14298 reflections for [**2d**]PF_6 and **3a**, respectively, were measured with a Bruker APEX2 CCD diffractometers [λ(MoKα) = 0.71072Å, ω-scans, $2\theta<54°$]. 8794 and 4674 independent reflections [R_{int} 0.0390 and 0.0261] were used in further refinement for [**2d**]PF_6 and **3a**, respectively. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H(C) atom positions were calculated, and they were refined in the isotropic approximation within riding model. For [**2d**]PF_6, the refinement converged to wR2 = 0.1634 and GOF = 1.206 for all the independent reflections (R1 = 0.0545 was calculated against F for 7561 observed reflections with $I>2\sigma(I)$)**.** For **3a**, the refinement converged to wR2 = 0.1243 and GOF = 1.005 for all the independent reflections (R1 = 0.0446 was calculated against F for 4046 observed reflections with $I>2\sigma(I)$)**.** All calculations were performed using SHELXTL PLUS 5.0 [19].

Computation details

Geometry optimizations were performed without constraints using PBE and BPBE exchange-correlation functionals [20], the scalar-relativistic Hamiltonian [21], atomic basis sets of generally-contracted Gaussian functions [22] and a density-fitting technique [23] as implemented in a recent version of Priroda code [24]. The all-electron triple-ζ basis set L2 (similar to cc-pVTZ) [25] augmented by two polarization functions was used [26]. Frequency calculations were performed to confirm the nature of the stationary points to yield one imaginary frequency for the transition states and none for the minima. The path of the reaction was traced from the transition state to the product and back to the reactant by using the Intrinsic Reaction Coordinate method (IRC) [27]. The Gibbs free energy values were obtained from frequency calculation using BPBE functional, triple-ζ basis set augmented by two polarization functions def2-TZVPP [28] and solvent corrections for MeCN according to PCM model [29] as implemented in Gaussian 09 software [30]. The ChemCraft software [31] was used for molecular modeling and visualization.

Acknowledgments

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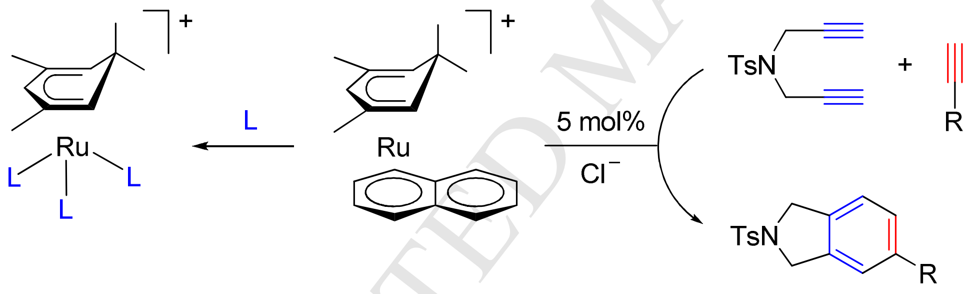
Appendix A. Supplementary material

CCDC 1046330 ([**2d**]PF_6) and 1046331 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data associated with this article can be found online.

Graphical abstract



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Highlights

Cyclohexadienyl ruthenium complexes were synthesized by naphthalene replacement

The mechanism of naphthalene replacement was studied by DFT calculations

Cyclohexadienyl ruthenium naphthalene complex catalyzes cyclotrimerization of alkynes

SUPPORTING INFORMATION

Synthesis of cyclohexadienyl ruthenium complexes by replacement of the naphthalene ligand in $[(\eta^5\text{-}C_6H_3Me_4)Ru(\eta^6\text{-}C_{10}H_8)]^+$

Evgeniya A. Trifonova, Dmitry S. Perekalin, Natalia L. Loskutova, Yulia V. Nelyubina,
Alexander R. Kudinov

Cartesian coordinates and energies for structures optimized at PBE/L2 and BPBE/L2.

$[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}C_{10}H_8)]^+$

PBE/L2				BPBE/L2			
E = -5149.543778 a.u. E_0 = -5149.287801 a.u. ZPVE = 0.255977 a.u. = 160.6281 kcal/mol T = 298.150 K: H = 169.8031 kcal/mol, G = 135.4871 kcal/mol				E = -5149.910251 a.u. E_0 = -5149.654595 a.u. ZPVE = 0.255656 a.u. = 160.4266 kcal/mol T = 298.150 K: H = 169.6298 kcal/mol, G = 135.2675 kcal/mol			
6	-2.35380489	0.31837586	-1.16316602	6	-2.36782928	0.30840113	-1.16531808
6	-2.35384197	0.31832693	1.16315128	6	-2.36788240	0.30828081	1.16531600
6	-1.48362336	1.44248767	1.22731385	6	-1.50267385	1.43956739	1.22938280
6	-1.48358119	1.44253843	-1.22727281	6	-1.50262531	1.43969952	-1.22923855
6	-1.07214080	2.04510828	0.00004093	6	-1.09392393	2.04574602	0.00011295
6	-3.31316043	0.18610840	-0.00002733	6	-3.32894502	0.16918773	-0.00003039
1	-4.13421588	0.92581537	-0.00002548	1	-4.15519951	0.90376425	-0.00001157
1	-1.04100354	1.77396312	2.16688614	1	-1.06411600	1.77548754	2.16960764
1	-0.35923161	2.86937225	0.00007690	1	-0.38755309	2.87595004	0.00017639
1	-1.04089241	1.77400805	-2.16681386	1	-1.06402888	1.77571372	-2.16941159
1	-3.76910797	-0.81134970	-0.00005637	1	-3.77866221	-0.83152304	-0.00009857
1	-2.54802248	-0.22843912	-2.08728406	1	-2.56010183	-0.23807571	-2.09040011
1	-2.54811398	-0.22850827	2.08724533	1	-2.56018916	-0.23830328	2.09032977
44	-0.53946346	-0.09802808	0.00001014	44	-0.54578306	-0.09890142	0.00001103
6	-0.13205977	-2.18396383	0.70772095	6	-0.12366418	-2.18856928	0.70882904
6	0.70622653	-1.27720681	-1.40962777	6	0.71211009	-1.27649515	-1.41175104
6	1.68386413	-0.47619001	-0.72444163	6	1.69109623	-0.47250999	-0.72580060
6	1.68386046	-0.47616466	0.72442976	6	1.69109947	-0.47248820	0.72577204
6	-0.13206897	-2.18397484	-0.70768325	6	-0.12370089	-2.18855838	-0.70881436
6	0.70625030	-1.27719376	1.40964260	6	0.71211672	-1.27646059	1.41174702
6	2.62185767	0.34649108	1.41544321	6	2.63478995	0.34801703	1.41804586
6	3.53052697	1.09794233	0.71078351	6	3.54862703	1.09637690	0.71210588
6	2.62183439	0.34647891	-1.41547514	6	2.63495949	0.34774575	-1.41812988
6	3.53053139	1.09791626	-0.71083556	6	3.54873447	1.09621668	-0.71223183
1	-0.81826461	-2.82955565	-1.25378260	1	-0.80551348	-2.83885140	-1.25534353
1	0.66339970	-1.23720080	-2.49833127	1	0.66958919	-1.23895249	-2.50065762
1	0.66344388	-1.23717570	2.49834647	1	0.66964094	-1.23896006	2.50065693
1	-0.81824219	-2.82954771	1.25383329	1	-0.80545839	-2.83886547	1.25537733
1	4.26415436	1.70256121	1.24405908	1	4.28572217	1.69729030	1.24558972
1	2.62338006	0.34371558	2.50604577	1	2.63780726	0.34555356	2.50882298
1	4.26414441	1.70253733	-1.24412847	1	4.28594714	1.69696398	-1.24573976
1	2.62339143	0.34363558	-2.50607758	1	2.63807622	0.34509038	-2.50890593

$[CpRu(\eta^6\text{-}C_{10}H_8)]^+$

PBE/L2				BPBE/L2			
E = -5110.275598 a.u. E_0 = -5110.047484 a.u. ZPVE = 0.228114 a.u. = 143.1435 kcal/mol T = 298.150 K: H = 151.6292 kcal/mol, G = 118.4103 kcal/mol				E = -5110.622792 a.u. E_0 = -5110.395002 a.u. ZPVE = 0.227791 a.u. = 142.9409 kcal/mol T = 298.150 K: H = 151.4534 kcal/mol, G = 118.1614 kcal/mol			
6	-2.62466012	0.45857505	-0.71905723	6	-2.63883091	0.44245383	-0.72028964
6	-2.62481562	0.45843875	0.71877701	6	-2.63887719	0.44244754	0.72023090
6	-1.68568271	1.44768073	1.16112581	6	-1.70737855	1.44223947	1.16312915
6	-1.68542127	1.44788969	-1.16101124	6	-1.70733187	1.44227748	-1.16312124
6	-1.10547444	2.05192659	0.00018013	6	-1.13224834	2.05296412	0.00002570
1	-1.45630736	1.69647493	2.19305328	1	-1.48168247	1.69471968	2.19529377
1	-3.24079723	-0.16858675	-1.35696140	1	-3.25062809	-0.18940435	-1.35827774
1	-0.34191280	2.82506271	0.00033344	1	-0.37765361	2.83509777	0.00005672
1	-1.45585724	1.69692081	-2.19283968	1	-1.48155479	1.69475586	-2.19526847
1	-3.24109169	-0.16883462	1.35643734	1	-3.25066875	-0.18946175	1.35817354
44	-0.65079565	-0.10560396	0.00002193	44	-0.65638488	-0.10654814	0.00000457
6	-0.31589217	-2.17632404	0.71207096	6	-0.30719029	-2.18021761	0.71315883
6	0.55150416	-1.30712587	-1.41769543	6	0.55739344	-1.30501003	-1.41999234
6	1.51293429	-0.49425729	-0.72592021	6	1.52006190	-0.48909723	-0.72728670
6	1.51295813	-0.49420190	0.72591341	6	1.52011770	-0.48914335	0.72728444
6	-0.31591651	-2.17637631	-0.71188800	6	-0.30719789	-2.18022599	-0.71312140
6	0.55156209	-1.30703059	1.41778296	6	0.55737433	-1.30494972	1.42000725
6	2.44271288	0.34703956	1.41560118	6	2.45551881	0.35007363	1.41830223
6	3.33529653	1.11280994	0.71254765	6	3.35376855	1.11238196	0.71398298
6	2.44264017	0.34695867	-1.41570433	6	2.45549433	0.35007793	-1.41831842
6	3.33526180	1.11276712	-0.71274028	6	3.35375574	1.11238318	-0.71401178
1	-1.02584484	-2.79795070	-1.25560577	1	-1.01314941	-2.80654217	-1.25719373
1	0.51297560	-1.26802235	-2.50625691	1	0.51836429	-1.26771794	-2.50873918
1	0.51307972	-1.26784979	2.50634340	1	0.51842626	-1.26772166	2.50875869
1	-1.02578820	-2.79787265	1.25586005	1	-1.01313565	-2.80650821	1.25726835
1	4.06161515	1.72662319	1.24528703	1	4.08376140	1.72232273	1.24695005

1	2.44932394	0.33686935	2.50611847	1	2.46305296	0.34076062	2.50899228
1	4.06153767	1.72656791	-1.24555227	1	4.08375499	1.72230651	-1.24698994
1	2.44920463	0.33671538	-2.50622132	1	2.46299125	0.34079412	-2.50900886

$[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}C_{10}H_8)]^+$ + MeCN **TS1**

PBE/L2 ν = 82.19i cm^{-1}				BPBE/L2 ν = 80.57i cm^{-1}			
E = -5282.238664 a.u. E_0 = -5281.938476 a.u. ZPVE = 0.300188 a.u. = 188.3709 kcal/mol T = 298.150 K: H = 200.6511 kcal/mol, G = 157.4322 kcal/mol				E = -5282.665424 a.u. E_0 = -5282.365562 a.u. ZPVE = 0.299862 a.u. = 188.1662 kcal/mol T = 298.150 K: H = 200.4815 kcal/mol, G = 157.2142 kcal/mol			
6	-1.68077598	-1.23042382	0.59759496	6	-1.68973375	-1.22760408	0.57894896
6	-1.69888834	1.02215952	1.14131989	6	-1.70785051	1.02849942	1.12281122
6	-1.80428042	1.42188548	-0.22667731	6	-1.81811376	1.42895476	-0.24730795
6	-1.78510644	-0.96367991	-0.80250356	6	-1.79894096	-0.96147339	-0.82357244
6	-1.92580559	0.39416419	-1.20278749	6	-1.94376303	0.39868391	-1.22420328
6	-2.33172970	-0.28102511	1.58091817	6	-2.34293613	-0.27685232	1.56490527
1	-3.43691131	-0.28515029	1.56119880	1	-3.44847825	-0.28056965	1.54353769
1	-1.72113432	2.46430609	-0.53324801	1	-1.73972565	2.47203548	-0.55398143
1	-1.94678088	0.64934337	-2.26065495	1	-1.97559508	0.65346170	-2.28214774
1	-1.68727394	-1.75009515	-1.55051397	1	-1.70594782	-1.74896936	-1.57151394
1	-2.02343133	-0.52583204	2.60538613	1	-2.03632740	-0.52153375	2.59008467
1	-1.47132929	-2.25829688	0.90090843	1	-1.48139556	-2.25606343	0.88151566
1	-1.50396655	1.80155722	1.88087019	1	-1.51398272	1.80917645	1.86148542
44	-0.07568944	0.10605080	0.05243201	44	-0.08325631	0.11281562	0.02358542
6	1.18945087	0.41209228	1.84623389	6	1.17991005	0.41766687	1.82844332
6	1.71804036	-1.34141900	0.24862434	6	1.73505666	-1.33883302	0.23894866
6	2.63716844	-0.48183011	-0.46691714	6	2.69419593	-0.48819455	-0.44194333
6	2.62600784	0.90723981	-0.13157786	6	2.68311934	0.90207063	-0.10619440
6	1.20052517	-0.96537775	1.51369900	6	1.19096853	-0.96271563	1.49514623
6	1.69655894	1.33166453	0.89393416	6	1.71371142	1.33371436	0.88427101
6	3.47665587	1.79365718	-0.81606567	6	3.57697162	1.78039624	-0.74905608
6	4.33915537	1.31066900	-1.79043933	6	4.48339151	1.28625117	-1.68168242
6	3.49866207	-0.94532971	-1.47729220	6	3.59883973	-0.96281130	-1.41151565
6	4.35015024	-0.05798168	-2.12085122	6	4.49431467	-0.08392866	-2.01256832
1	0.76883327	-1.70178196	2.18956620	1	0.74918235	-1.69883958	2.16479045
1	1.63805551	-2.38511757	-0.05916716	1	1.65418438	-2.38168914	-0.07217644
1	1.59960340	2.39949206	1.09588412	1	1.61591275	2.40229244	1.08291844
1	0.74910525	0.75241482	2.78203389	1	0.72934092	0.76036279	2.75851181
1	5.02138122	1.99378422	-2.29730378	1	5.19666572	1.96202358	-2.15519851
1	3.46737239	2.85394544	-0.55948762	1	3.56882278	2.84120993	-0.49342766
1	5.04080075	-0.42418311	-2.88104013	1	5.21596551	-0.45831446	-2.73968669
1	3.50642027	-2.00590871	-1.73271695	1	3.60761870	-2.02337130	-1.66817247
7	0.62177750	0.73972475	-2.54863237	7	0.64630676	0.73867665	-2.54088064
6	1.09493612	0.99204561	-3.57887069	6	1.01721412	0.99990924	-3.61153025
6	1.68517508	1.30699790	-4.86472018	6	1.48110583	1.32654577	-4.95022100
1	2.31559151	0.47465719	-5.20470829	1	2.09645666	0.50752511	-5.34655843
1	0.89844733	1.48251736	-5.61067172	1	0.62436227	1.48202887	-5.62014952
1	2.30452988	2.21021283	-4.78466623	1	2.08372983	2.24461142	-4.92712528

$[CpRu(\eta^6\text{-}C_{10}H_8)]^+$ + MeCN **TS1**

PBE/L2 ν = 107.41i cm^{-1}				BPBE/L2 ν = 104.19i cm^{-1}			
E = -5242.963459 a.u. E_0 = -5242.691203 a.u. ZPVE = 0.272256 a.u. = 170.8430 kcal/mol T = 298.150 K: H = 182.4572 kcal/mol, G = 140.5142 kcal/mol				E = -5243.371261 a.u. E_0 = -5243.099365 a.u. ZPVE = 0.271896 a.u. = 170.6175 kcal/mol T = 298.150 K: H = 182.2801 kcal/mol, G = 140.2889 kcal/mol			
6	-1.80948543	-0.73517196	0.85221586	6	-1.81961675	-0.70755573	0.84220949
6	-1.83197359	0.70950619	0.85717243	6	-1.83916218	0.73925271	0.81427837
6	-1.81208051	1.15330779	-0.50173666	6	-1.81262303	1.15244695	-0.55589927
6	-1.80290605	-1.17597823	-0.51738055	6	-1.80981629	-1.18106717	-0.51957566
6	-1.80846969	-0.01590692	-1.33670265	6	-1.80892006	-0.03831510	-1.36655676
1	-1.82229911	2.18427924	-0.84090229	1	-1.82105166	2.17612013	-0.91748782
1	-1.84804228	-1.37606787	1.72924834	1	-1.86628281	-1.32822611	1.73346234
1	-1.75551583	-0.01437689	-2.42045123	1	-1.75864439	-0.06298493	-2.45035193
1	-1.80339596	-2.20602159	-0.86079013	1	-1.81371886	-2.21908298	-0.83927951
1	-1.87431057	1.34350771	1.73866195	1	-1.88461950	1.39368541	1.68081673
44	0.00175458	-0.00275946	-0.00181133	44	-0.00025623	-0.00064355	-0.02729301
6	1.20601526	0.27024583	1.79926999	6	1.19479657	0.26591875	1.78973694
6	1.78946079	-1.44755743	0.17070440	6	1.80368056	-1.45665294	0.17076223
6	2.68550981	-0.54722047	-0.52168512	6	2.73681211	-0.56567722	-0.49112152
6	2.66827372	0.83157305	-0.13641043	6	2.72062816	0.81490671	-0.10538581
6	1.24148147	-1.10518218	1.42830298	6	1.22763274	-1.11224771	1.41743921
6	1.73761233	1.22344272	0.89778366	6	1.75629068	1.21524274	0.89918784
6	3.51389718	1.74552453	-0.79357781	6	3.60609574	1.71993623	-0.72643859
6	4.37447120	1.30251311	-1.78621637	6	4.50607362	1.26475388	-1.68203421
6	3.54201195	-0.96647739	-1.55801846	6	3.63288131	-0.99684618	-1.49159711
6	4.38614631	-0.05347948	-2.17096911	6	4.51754612	-0.09318582	-2.06673302

1	0.79695080	-1.86282318	2.07193667	1	0.76826763	-1.86861835	2.05235416
1	1.73312800	-2.48392722	-0.16429439	1	1.74496225	-2.49229410	-0.16684417
1	1.63686489	2.28383974	1.13243830	1	1.65694812	2.27641017	1.13205104
1	0.73344495	0.57934972	2.73060091	1	0.70952496	0.57839633	2.71358821
1	5.05552287	2.00534993	-2.26714662	1	5.21508364	1.95950386	-2.13405190
1	3.50117808	2.79536313	-0.49742867	1	3.59501462	2.77044226	-0.43167826
1	5.07381554	-0.38783904	-2.94821502	1	5.23357372	-0.43635310	-2.81442954
1	3.55284416	-2.01681372	-1.85240200	1	3.64373685	-2.04706264	-1.78731820
7	0.71000371	0.85521892	-2.49165776	7	0.74810960	0.85080846	-2.51132360
6	1.12018840	1.19952876	-3.52210013	6	1.04889982	1.22663501	-3.56978945
6	1.63464960	1.63260874	-4.80603732	6	1.42701064	1.69744290	-4.89249740
1	2.01140233	0.77103501	-5.37325831	1	1.76970227	0.85576227	-5.50969707
1	0.84065117	2.11924411	-5.38823714	1	0.56708872	2.17123470	-5.38552788
1	2.45538990	2.34761207	-4.66098971	1	2.23854132	2.43336138	-4.81305853

$[(\eta^5\text{-}C_6H_7)Ru(\eta^4\text{-}C_{10}H_8)(MeCN)]^+$ **IM1**

PBE/L2				BPBE/L2			
E = -5282.245169 a.u. E$_0$ = -5281.944196 a.u. ZPVE = 0.300973 a.u. = 188.8637 kcal/mol T = 298.150 K: H = 201.3066 kcal/mol, G = 158.5207 kcal/mol				E = -5282.670205 a.u. E$_0$ = -5282.369693 a.u. ZPVE = 0.300512 a.u. = 188.5743 kcal/mol T = 298.150 K: H = 201.1221 kcal/mol, G = 157.6944 kcal/mol			
6	-1.66531541	-1.26676062	0.67913312	6	-1.66848850	-1.26795154	0.66486366
6	-1.71233580	0.99874052	1.19376502	6	-1.71465647	0.99797122	1.18952427
6	-1.98459160	1.37045960	-0.15206808	6	-1.97765722	1.37738271	-0.15916021
6	-1.93552290	-1.03190197	-0.69799874	6	-1.92904504	-1.02632005	-0.71578898
6	-2.15261903	0.31843116	-1.09995717	6	-2.14512723	0.32807154	-1.11337513
6	-2.23075823	-0.32334468	1.72040495	6	-2.24513748	-0.32682643	1.70699927
1	-3.32817955	-0.37241028	1.83707812	1	-3.34461758	-0.37277118	1.80896219
1	-1.97625785	2.40928482	-0.47961100	1	-1.96827251	2.41817957	-0.48158303
1	-2.29796388	0.55488310	-2.15387210	1	-2.28981412	0.56899091	-2.16649008
1	-1.89099225	-1.82663703	-1.44158983	1	-1.88293416	-1.81853050	-1.46250420
1	-1.78998311	-0.53741020	2.70245224	1	-1.81790835	-0.54666513	2.69383335
1	-1.37857654	-2.27873844	0.96995452	1	-1.38747701	-2.28237129	0.95352404
1	-1.46207014	1.79628174	1.89535815	1	-1.47008944	1.79240888	1.89692177
44	-0.15935684	0.13352568	-0.10381772	44	-0.15085144	0.13496419	-0.10414308
6	1.17837980	0.48879441	1.61764763	6	1.18748180	0.48788554	1.62725812
6	1.72802818	-1.24337402	0.01853087	6	1.74852701	-1.24868855	0.03000618
6	2.78618542	-0.42450776	-0.57263522	6	2.81512856	-0.42938491	-0.55191793
6	2.75758240	0.95559223	-0.25134270	6	2.78678465	0.95316340	-0.22910115
6	1.20784684	-0.89301285	1.29629175	6	1.21608592	-0.89635028	1.30413262
6	1.67296780	1.38708833	0.63017662	6	1.69414840	1.38811935	0.64528562
6	3.70399192	1.82025159	-0.80831772	6	3.75327835	1.81479371	-0.76419404
6	4.68779333	1.31501207	-1.66284255	6	4.75635992	1.30335440	-1.59538711
6	3.76057853	-0.91643265	-1.44561780	6	3.80955982	-0.92687986	-1.40424893
6	4.71587304	-0.04757640	-1.98026473	6	4.78440802	-0.06177710	-1.91405451
1	0.80171952	-1.63559462	1.98069062	1	0.80692654	-1.63911452	1.98659078
1	1.64035631	-2.28197370	-0.30479271	1	1.66110625	-2.28722480	-0.29408354
1	1.54063454	2.45746202	0.79662314	1	1.56360523	2.45857824	0.81356090
1	0.74926589	0.83648236	2.55561765	1	0.75608586	0.83536067	2.56428936
1	5.43940651	1.98606565	-2.07935351	1	5.52198950	1.97054431	-1.99316891
1	3.68023780	2.88359977	-0.56363425	1	3.73189132	2.87812491	-0.51815796
1	5.48922107	-0.43563018	-2.64362813	1	5.57185920	-0.45366333	-2.55896390
1	3.78073662	-1.97853390	-1.69596992	1	3.83195921	-1.98926802	-1.65424303
7	0.51248395	0.61059589	-2.08326144	7	0.52382030	0.61662262	-2.10681867
6	0.95352415	0.86143899	-3.12621760	6	0.90584684	0.87101603	-3.17356738
6	1.53141195	1.17224769	-4.41456667	6	1.39685708	1.18804142	-4.50130464
1	1.23568612	0.41870536	-5.15727582	1	1.06116068	0.42861034	-5.22123399
1	1.19455560	2.16060345	-4.75587771	1	1.02287826	2.17124461	-4.81938464
1	2.62700312	1.17777146	-4.32759943	1	2.49527512	1.20983757	-4.49126519

$[CpRu(\eta^4\text{-}C_{10}H_8)(MeCN)]^+$ **IM1**

PBE/L2				BPBE/L2			
E = -5242.979377 a.u. E$_0$ = -5242.706294 a.u. ZPVE = 0.273082 a.u. = 171.3619 kcal/mol T = 298.150 K: H = 183.1527 kcal/mol, G = 140.9376 kcal/mol				E = -5243.385375 a.u. E$_0$ = -5243.112785 a.u. ZPVE = 0.272589 a.u. = 171.0525 kcal/mol T = 298.150 K: H = 182.9488 kcal/mol, G = 140.8882 kcal/mol			
6	-1.80866791	-0.74426156	1.01219523	6	-1.81490638	-0.45766438	1.15371898
6	-1.87548551	0.68657601	1.00470356	6	-1.90767984	0.92852068	0.78089807
6	-2.04559337	1.12292813	-0.34893821	6	-2.06786421	0.99362605	-0.63777265
6	-1.93705115	-1.20769072	-0.34371651	6	-1.91379894	-1.25052507	-0.04250418
6	-2.09280834	-0.05770338	-1.17311745	6	-2.07194846	-0.36028417	-1.14916333
1	-2.15414196	2.14998306	-0.68325271	1	-2.17045992	1.90250881	-1.22374854
1	-1.70040710	-1.37263270	1.89169411	1	-1.71142686	-0.84027401	2.16546692
1	-2.19396047	-0.07231100	-2.25475784	1	-2.17712857	-0.65400793	-2.18966621
1	-1.93995013	-2.24206807	-0.67393657	1	-1.88255130	-2.33533745	-0.09776379
1	-1.81368705	1.33370859	1.87538581	1	-1.87076231	1.77863926	1.45677085

44	-0.14839628	0.05549048	-0.17527092	44	-0.14778418	0.04551105	-0.18981903
6	1.24310491	0.31378007	1.53478341	6	1.26134682	0.16208124	1.53320702
6	1.87962443	-1.35980821	-0.10950938	6	1.88306720	-1.42104514	-0.21039994
6	2.90342153	-0.48821369	-0.65630849	6	2.92389670	-0.53161819	-0.69858175
6	2.88648588	0.87217752	-0.24158589	6	2.92671871	0.80312045	-0.19897742
6	1.26470958	-1.05487885	1.12204452	6	1.25859393	-1.17939666	1.03112417
6	1.84687495	1.26590321	0.68990826	6	1.88852711	1.15723597	0.75469244
6	3.82414443	1.77014263	-0.76832708	6	3.89561600	1.71263662	-0.65298856
6	4.78879367	1.32209171	-1.67086691	6	4.87000940	1.29878371	-1.56443514
6	3.85843183	-0.91656241	-1.58726677	6	3.88997341	-0.92306977	-1.63963124
6	4.80568195	-0.01820539	-2.07930392	6	4.86718717	-0.01609950	-2.05665834
1	0.81377050	-1.83165572	1.73695348	1	0.78229192	-1.98376057	1.58997293
1	1.80999425	-2.37989797	-0.49003544	1	1.79549550	-2.41355912	-0.65546185
1	1.74187875	2.32404547	0.93461263	1	1.80525979	2.19835477	1.07087389
1	0.76648997	0.60721702	2.46885478	1	0.78737686	0.40353976	2.48359819
1	5.53443936	2.01746709	-2.05689698	1	5.63812103	2.00018641	-1.89225132
1	3.80718976	2.81519104	-0.45413282	1	3.89682632	2.73635161	-0.27402796
1	5.56454784	-0.36242601	-2.78234274	1	5.63309486	-0.33269042	-2.76558785
1	3.86881708	-1.95903959	-1.91008605	1	3.88676932	-1.94397471	-2.02608482
7	0.62804285	0.63083070	-1.97079042	7	0.62527023	0.70986235	-1.96977420
6	1.03227965	0.96055720	-3.00804960	6	0.97829937	1.09724083	-3.00752075
6	1.55715635	1.37003343	-4.29123552	6	1.42441826	1.57995371	-4.30049932
1	1.23392437	0.67468665	-5.07826641	1	1.05402175	0.92414866	-5.10114519
1	1.20670255	2.38031001	-4.54412891	1	1.05333417	2.59969547	-4.47580724
1	2.65572921	1.37474221	-4.25002914	1	2.52288152	1.59181665	-4.33106973