

Reactions of RuCp and RuCp* Allyl Carbene Complexes: Products Derived from Activation of Phenyl, Cyclohexyl, and Methyl C–H Bonds in PPh₃, PCy₃, and Cp* Ligands

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Ruthenium allyl carbene complexes of the type [RuCp(=C(R)-(η³-CHC(R)CHPR'₃))]PF₆ (R, R' = aryl, alkyl substituents) are characterized by two reaction modes. (i) They behave as masked coordinatively unsaturated complexes and react readily with the donor ligands PR₃ and P(OR)₃ to give η³-butadienyl complexes. This is not a simple nucleophilic addition at the metal center but involves changes in both the bonding mode and the stereochemistry of the allyl carbene C₄-chain. The incoming nucleophile induces C–H bond activation effecting formally a 1,4 hydrogen shift. (ii) They are capable of activating C–H bonds of aryl and alkyl groups in the bulky tertiary phosphine ligands PPh₃ and PCy₃ to give novel η⁴-butadiene complexes. In these, one R of PR₃ is σ-bonded to the metal center. A divergent rearrangement results if the allyl carbene complex derives from parent acetylene (instead of a terminal alkyne). In this case the C₄-unit features a η³-allyl moiety and the metal center is η²-coordinated to an arene ring of the PPh₃ substituent. Finally, RuCp* allyl carbene complexes have been prepared for the first time. They are reactive entities and react slowly with cleavage of one of the ring methyl C–H bonds of the Cp* ligand to give tetramethylfulvene-type complexes.

Introduction

Coordinatively unsaturated complexes and complexes with labile ligands are the most promising candidates for catalytic activity. Clearly, the availability of a vacant coordination site is prerequisite to both stoichiometric and catalytic molecular transformations of organic molecules at a transition metal center. A particularly notable situation is encountered with ligands that are capable of reversibly changing their bonding mode. Examples include η⁵ ↔ η³ ring slippage of Cp and indenyl ligands¹ as well as η¹-vinyl ↔ η²-vinyl or η¹-vinylcarbene ↔ η³-vinylcarbene rearrangements.² Similarly, a few years ago Green et al. reported^{3,4} that ruthenium η³-allyl carbene (structure **A** in Scheme 1) can convert into the η³-butadienyl species (structure **B**). Accordingly, allyl carbenes may be considered as masked coordinatively unsaturated complexes that can accommodate an attacking nucleophile at the metal center (Scheme 1).

This feature is worthy of consideration since quite recently⁵ a large variety of ruthenium allyl carbene complexes became readily available by the reaction of labile [RuCp(PR₃)(CH₃CN)₂]PF₆ (R = tertiary phosphines)⁶ with alkynes. In a preliminary communication^{5a} we have reported that allyl carbenes are reactive species that are able not only to add nucleophiles to the metal center but also to dehydrogenate a cyclohexyl group of the bulky PCy₃ ligand initiated by C–H bond activation.

In the present paper we shall investigate the reactivity of ruthenium allyl carbenes in more detail. It will be seen that nucleophiles are accommodated with formation of η³-butadienyl complexes. In addition, C–H bonds of bulky tertiary substituents are activated under mild conditions. This leads to the formation of novel η⁴-diene complexes with σ-bonded arene and cyclohexyl ligands. We will also examine in what ways the reactivity is changed if the Cp* ligand is substituted for Cp. Included are also the X-ray structures of representative reaction products.

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(1) For a review on Cp ring slippage reactions see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(2) For a review on η¹/η³-vinyl carbene complexes see: Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1525.

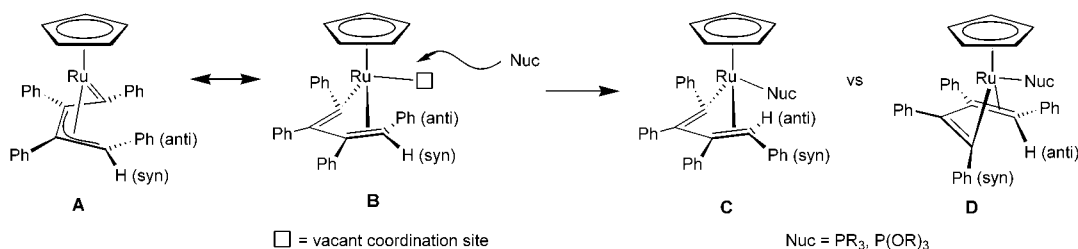
(3) Crocker, M.; Green, M.; Nagle, K. R.; Orpen, A. G.; Neumann, H. P.; Morton, C. E.; Schaverin, C. J. *Organometallics* **1990**, *9*, 1422.

(4) Crocker, M.; Dunne, B. J.; Green, M.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1589.

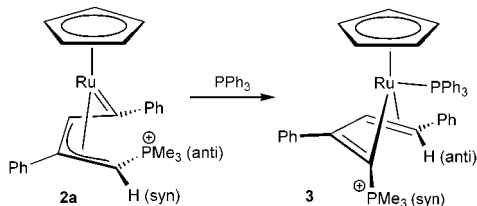
(5) (a) Mauthner, K.; Soldouzi, K. M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 4681. (b) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K.; Schottenberger, H. *J. Organomet. Chem.* **2001**, *637–639*, 70. (c) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K. *Chem. Commun.* **2001**, 1996. (d) Rüba, E.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K.; Schottenberger, H.; Calhorda, M. J. Veiros, L. F. *Eur. J. Chem.*, in press.

(6) Rüba, E.; Simanko, W.; Mauthner, K.; Soldouzi, K. M.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 3843.

Scheme 1



Scheme 2



Results and Discussion

The reaction sequence presented in Scheme 1 applies to using tertiary phosphines and phosphites as the nucleophile. This type of reaction is intriguing since not only a change in the bonding mode of the allyl carbene fragment is involved but also a change in stereochemistry of substituents on the terminal carbon of the allyl moiety. In precursor **A** the hydrogen occupies a pseudo *syn* position, whereas in the butadienyl complex **C** the stereochemistry is reversed with the hydrogen in the pseudo *anti* position and the phenyl substituent in the pseudo *syn* site. Such a stereomutation has been proposed to occur via a ring-opening/ring-flip mechanism.³

In the present work we have treated complex **2a** with 1 equiv of PPh₃. According to Scheme 2, the η³-butadienyl complex [RuCp(CPMe₃=CPh-η²-CH=CHPh)-(PPh₃)]PF₆ (**3**) is formed, whose molecular structure from X-ray crystallography is depicted in Figure 1. In contrast to allyl carbenes the butadienyl ligand in complex **3** binds with σ-vinyl and η²-alkene functions. The σ-bonding of the butadienyl ligand is reflected in the Ru–C(9) bond distance of 2.139(4) Å, while the C(6) and C(7) comprise an olefinic unit bound to the metal with Ru–C(6) and Ru–C(7) distances of 2.292(4) and 2.197(4) Å, respectively. The butadienyl C–C bond distances adopt a typical short–long–short pattern (the C(6)–C(7), C(7)–C(8), and C(8)–C(9) bond distances are 1.399(5), 1.489(5), and 1.334(5) Å, respectively). The asymmetric manner in which the butadienyl unit is coordinated to the ruthenium center is demonstrated by the respective Ru–C(9)–C(8) and Ru–C(6)–C(7) angles of 99.9(2)° and 68.2(2)°. The atoms Ru, C(7), C(8), and C(9) are approximately coplanar, showing an rms deviation from planarity of 0.031 Å. Ru and C(8) deviate from this plane by 0.019(1) and 0.042(2) Å bent toward P(2).

Unfortunately, no intermediate formation could be detected by NMR monitoring, although, as remarked above, the reaction is not a simple nucleophilic addition of PPh₃ at the metal center.

Note that the hydrogen of the terminal allyl carbon atom of **2a** which occupies a pseudo *syn* position migrates to the carbene carbon atom, then adopting an *anti* position, while the PMe₃ substituent ends up in a

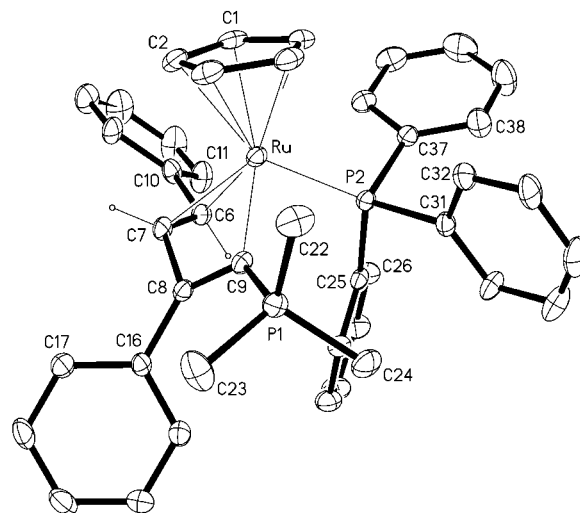


Figure 1. Structural view of [RuCp(CPMe₃=CPh-η²-CH=CHPh)(PPh₃)]PF₆ (**3**) showing 20% thermal ellipsoids (PF₆[−] omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru–C(1–5)_{av} 2.220(4), Ru–C(6) 2.292(4), Ru–C(7) 2.197(4), Ru–C(9) 2.139(4), Ru–P(2) 2.326(2), P(1)–C(9) 1.786(4), C(6)–C(7) 1.399(5), C(7)–C(8) 1.489(5), C(8)–C(9) 1.334(5), C(6)–C(7)–C(8) 123.0(3), C(9)–C(8)–C(7) 104.9(3).

syn site. It may be speculated that such a formal 1,4 hydrogen shift reaction proceeds most likely via an initial C–H activation step induced by the incoming nucleophile PPh₃. The hydrogen is then delivered through the metal center to the carbene carbon atom via the inside face of the molecule to give **3**. According to this finding, the mechanism of the reaction shown in Scheme 1 has to be reconsidered. We believe that this reaction also involves a C–H activation step, and consequently complex **D** should be obtained rather than the isomeric **C**.

Apart from their reactions with simple donor ligands, ruthenium allyl carbene complexes are capable of activating nearby C–H bonds of aryl and alkyl groups in tertiary phosphine ligands. This occurs if the latter are sufficiently bulky such as PPh₃ and PCy₃, whereas no such reaction is observed with PMe₃. A pertinent reaction is given in Scheme 3 for the reaction of **1a** with terminal alkynes HC≡CR (R = C₆H₅, *n*-Bu, Ph-*p*-NO₂, [Ce]⁺ (cobaltocenium), H). The initially formed allyl carbene complexes **2b–e** are not stable and transform slowly at room temperature into the novel η⁴-butadiene complexes [RuCp(η⁴-CHRCHCCH–PPh₂(η¹-C₆H₄)]PF₆ (**4a–d**) featuring an orthometalated arene ligand derived from PPh₃ (an exception is the reaction involving the parent acetylene, see below). The complexes **4** are air-stable in the solid state and were characterized by a combination of elemental analysis and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy.

Scheme 3

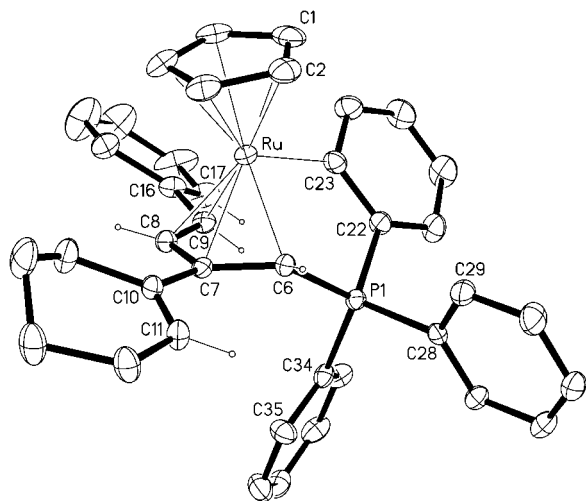
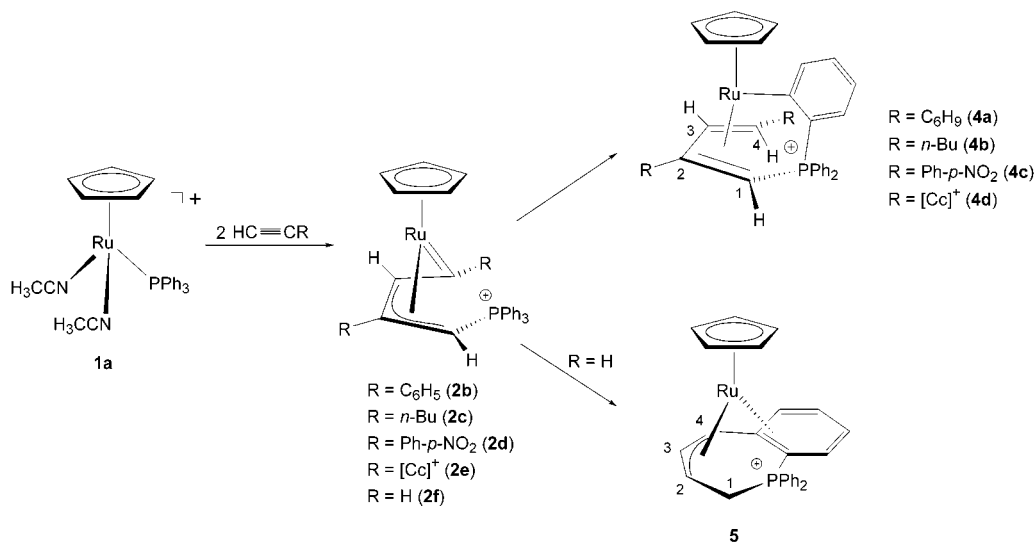


Figure 2. Structural view of $[\text{RuCp}(\eta^4\text{-CH}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{CH-PPh}_2)(\eta^1\text{-C}_6\text{H}_4)]\text{PF}_6$ (**4a**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru–C(1–5)_{av} 2.217 (7), Ru–C(6) 2.141(5), Ru–C(7) 2.181(4), Ru–C(8) 2.176(6), Ru–C(9) 2.297(6), Ru–C(23) 2.112(5), P(1)–C(6) 1.778(5), C(6)–C(7) 1.439(6), C(7)–C(8) 1.432(7), C(8)–C(9) 1.392(7), C(6)–C(7)–C(8) 120.5(4), C(7)–C(8)–C(9) 124.1(6).

Thus, in the ^1H NMR spectrum of **4a** the Cp ring gives rise to a singlet at 5.33 ppm. The diene moiety exhibits three characteristic doublets centered at 5.99, 4.75, and 1.97 ppm assignable to H^3 , H^1 , and H^4 respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the orthometalated carbon atom displays a characteristic singlet at 181.9 ppm, while the carbon atoms of the diene unit are observed at 99.9, 85.9, 76.3, and 36.5 (d, $J_{\text{CP}} = 78.1$ Hz), assignable to C^2 , C^4 , C^3 , and C^1 , respectively. The Cp ligand shows a singlet at 89.2 ppm. The NMR spectra of **4b–d** are analogous and are not described here. In addition to spectroscopic and analytical characterizations of **4a–d**, the solid state structure of **4a** was determined by single-crystal X-ray diffraction. An ORTEP diagram is shown in Figure 2, with selected bond distances and angles reported in the caption. Accordingly, the complex adopts a three-legged piano stool conformation with the orthometalated phenyl substituent and the two C=C bonds of the diene moiety as the

legs. The Ru–C(23) bond distance is 2.112(5) Å. The Ru–C(6), Ru–C(7), Ru–C(8), and Ru–C(9) bond distances are 2.141(5), 2.181(4), 2.176(6), and 2.297(6) Å, respectively. The C–C distances within the diene fragment are very similar, ranging from 1.439 to 1.392 Å.

A somewhat different reaction takes place when **1a** is treated with parent acetylene in that the allyl carbene intermediate **2f** eventually rearranges into $[\text{RuCp}(\eta^3\text{-CHCHCH-CH}_2\text{PPh}_2)(\eta^2\text{-C}_6\text{H}_4)]\text{PF}_6$ (**5**), shown in Scheme 3, in 89% isolated yield. The structure and bonding features of **5** are rather unusual. First, an *ortho* C–H bond of the PPh_3 substituent has been activated, resulting 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 has been transferred to the terminal carbon of the allyl carbene unit involving carbon $\text{sp}^2 \rightarrow \text{sp}^3$ 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.⁷ Complex **5** was fully characterized by elemental analysis and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Characteristic are the ^1H NMR resonances of the CH_2 moiety giving rise to resonances at 3.59 and 1.84 ppm with a geminal coupling constant $^2J_{\text{HH}}$ of 16.3 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the sp^3 carbon atom C^1 shows a doublet resonance centered at 28.8 ppm ($J_{\text{CP}} = 67.3$ Hz).

The structure of **5** as determined from a single-crystal X-ray study is shown in Figure 3, with selected bond distances and angles reported in the caption. Clearly, one phenyl substituent of PPh_3 forms a C–C bond with the original carbene carbon atom and is bound in η^2 -fashion to the metal center. The allyl functionality is asymmetrically bonded to the metal with the Ru–C bond distance to the central allyl carbon atom C(7) (2.133(4) Å) slightly shorter than the Ru–C bonds to

(7) For related $\text{PAr}_2(\eta^2\text{-arene})$ complexes see: (a) Feiken, N.; Pregosin, P. S.; Trabesinger, G.; Scalone, M. *Organometallics* **1997**, *16*, 537. (b) Feiken, N.; Pregosin, P. S.; Trabesinger, G.; Albinati, A.; Evoli, G. L. *Organometallics* **1997**, *16*, 5756. (c) Cheng, T.-Y.; Szalda, D. J.; Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1999**, 1629. (d) Aneetha, H.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Mereiter, K. *Organometallics* **2002**, in press.

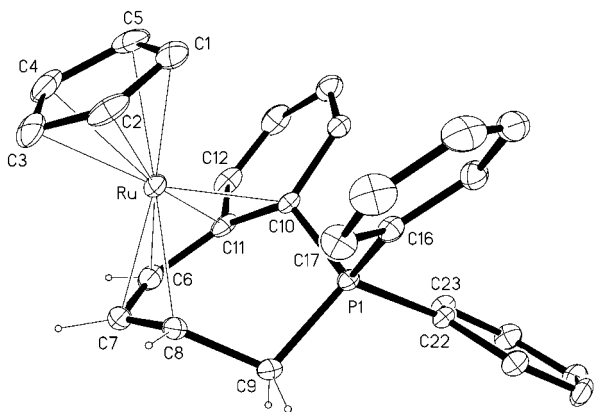


Figure 3. Structural view of $[\text{RuCp}(\eta^3\text{-CHCHCH-CH}_2\text{-PPh}_2\text{-}\eta^2\text{-C}_6\text{H}_4)]\text{PF}_6$ (**5**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru–C(1–5)_{av} 2.188(4), Ru–C(6) 2.192(4), Ru–C(7) 2.133(4), Ru–C(8) 2.222(4), Ru–C(10) 2.198(3), Ru–C(11) 2.207(3), P(1)–C(9) 1.778(3), P(1)–C(10) 1.787(3), C(6)–C(7) 1.393(7), C(6)–C(11) 1.441(6), C(7)–C(8) 1.412(5), C(8)–C(9) 1.525(5), C(10)–C(11) 1.476(4), C(6)–C(7)–C(8) 121.7(4).

the outer carbon atoms C(6) and C(8) (2.192(4) and 2.222(4) Å, respectively). The phenyl moiety of the PPh_3 ligand is bonded to the metal center with the Ru–C bonds to the carbon atoms C(10) and C(11) being 2.198(3) and 2.207(3) Å, respectively. The C(10)–C(11) bond distance is 1.474(4) Å and thus slightly longer than the other C–C bond distances within the phenyl substituent. For comparison,^{7b} in $[\text{RuCp}(\text{MeO-Bihp})]^+$ ($\text{MeO-Bihp} = 6,6'$ -dimethoxybiphenyl-2,2'-diyl)bis(bis(3,5-*tert*-butylphenyl)phosphine)), where a biaryl double bond adjacent to the P-donor atom coordinates to the ruthenium atom in η^2 -fashion, the respective Ru–C(aryl) bond distances are longer, being 2.38(1) and 2.31(1) Å. Similarly, also in $[\text{RuCp}(\text{PPr}^i_2\text{Me})(\text{PPh}_2\text{-}\eta^2\text{-C}_6\text{H}_5)]^+$, where one phenyl double bond of the PPh_3 ligand is η^2 -coordinated, the Ru–C(aryl) bond lengths are considerably longer, being 2.371(3) and 2.459(3) Å.^{7d}

We then repeated the reaction of Scheme 3, but used PCy_3 instead of PPh_3 . Our motive was to see whether the presence of β -hydrogen atoms imposes any mechanistic changes. However, it is noteworthy that no β -elimination occurred. Instead, the reaction taking place is identical to that using PPh_3 ; that is, one Cy group of the PCy_3 ligand becomes σ -bonded to the metal center (Scheme 4). The only difference from Scheme 3 is that no allyl carbene intermediate could be detected.

The lack of β -elimination contrasts with our recent observation that the analogous reaction of **1b** with 1,6-heptadiyne did not stop after the oxidative addition step, but β -elimination took place to give complex **7**, where eventually one cyclohexyl substituent of the phosphine ligand features an η^2 -coordinated cyclohexenyl ligand (Scheme 5).⁸

The identity of **6a** was proven by NMR spectroscopic and analytical characterization as well as by single-crystal X-ray diffraction. A structural view is depicted in Figure 3, with selected bond distances and angles reported in the caption. It is seen that the structures of **6a** and **4a** are very similar, both adopting a three-legged piano stool conformation. The Ru–C(23) bond distance is 2.214(2) Å. The Ru–C(6), Ru–C(7), Ru–C(8), and Ru–C(9) bond distances are 2.258(2), 2.154(2), 2.182-

(2), and 2.250(2) Å, respectively. Further, the C–C distances within the diene fragment are rather uniform, ranging between 1.437 and 1.391 Å.

In the present work we include also experiments with the first Cp* analogue $[\text{RuCp}^*(\text{PEt}_3)(\text{CH}_3\text{CN})_2]^+$ (**1c**). This complex is obtained in essentially quantitative yields (as monitored by ^1H NMR spectroscopy) by the treatment of $[\text{RuCp}^*(\text{CH}_3\text{CN})_3]\text{PF}_6$ ⁹ with 1 equiv of the PEt_3 at room temperature. The complex is stable to air in the solid state but decomposes slowly in solutions exposed to air.

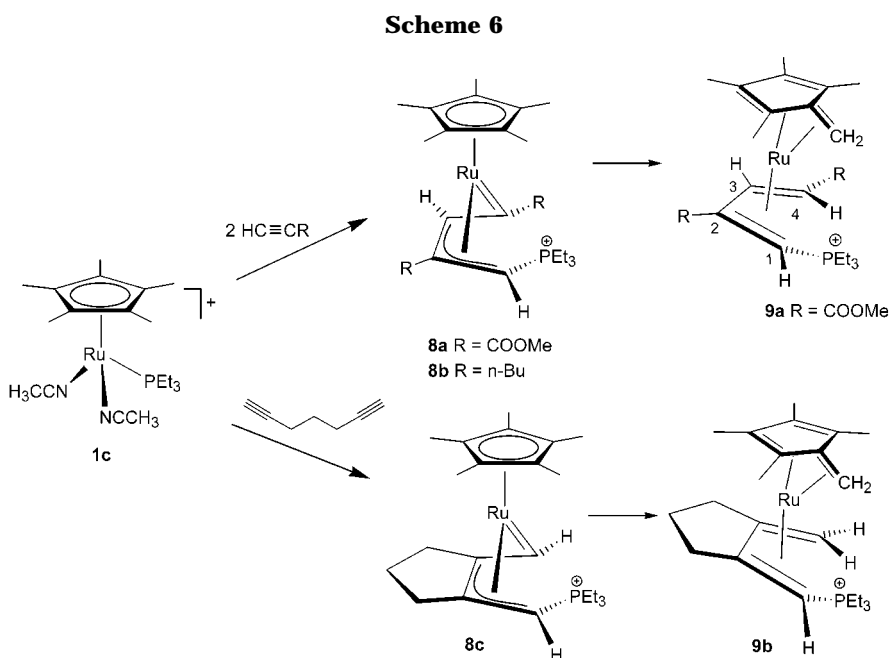
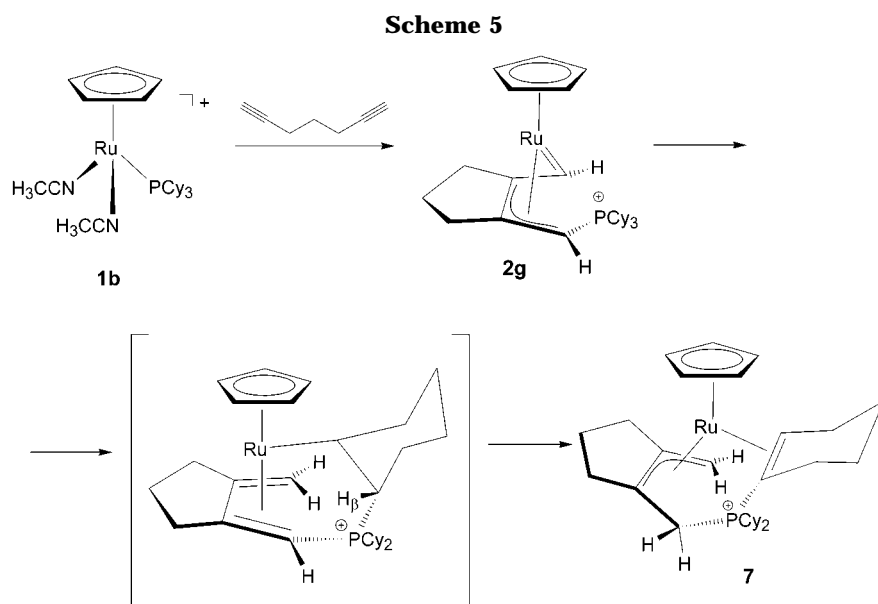
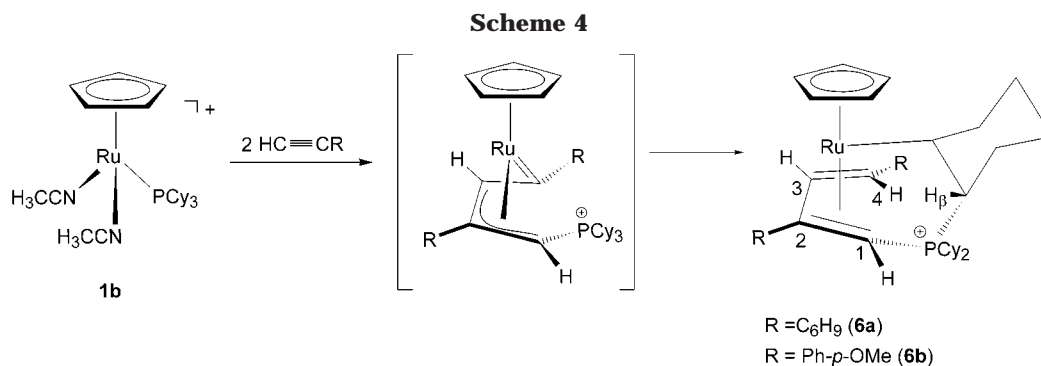
Scheme 6 summarizes the reactions of **1c** with the alkynes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{COOMe}$, *n*-Bu) and 1,6-heptadiyne. The η^3 -allyl carbene complexes **8a–c**, respectively, were obtained in high isolated yields. The identity of these compounds follows from ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and elemental analysis. Characteristic is the low-field signal of the carbene hydrogen atom giving rise to a signal at 11.71 ppm in the ^1H NMR spectrum of **8c** and doublet resonances at 256.3 and 227.1 ppm ($J_{\text{CP}} = 7\text{--}6$ Hz) and a doublet in the range 32.2–28.6 ppm ($J_{\text{CP}} = 66\text{--}55$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **8a–c**, which are assigned to the carbene carbon atoms and the terminal allyl carbon atom bearing the phosphine substituent, respectively. It may be mentioned that no isomers were obtained, meaning that C–C coupling is highly selective in a head-to-tail fashion (for terminal alkynes) with the substituents ending up in the 1 and 3 position. Noteworthy, RuCp^* allyl carbene complexes have been also prepared recently by the reaction of RuCp^* metallacyclopentatriene complexes with tertiary phosphines and phosphites, respectively.¹⁰

In contrast to **8b**, both complexes **8a** and **8c** are unstable in solution and react slowly at room temperature to $[\text{Ru}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\eta^4\text{-CH}(\text{COOMe})=\text{CH}-\text{C}(\text{COOMe})=\text{CHPET}_3)]\text{PF}_6$ (**9a**) and $[\text{Ru}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\eta^4\text{-CH}_2=\text{C}(\text{CH}_2)_3\text{C}=\text{CH}-\text{PET}_3)]\text{PF}_6$ (**9b**), respectively. In both, one of the ring methyl C–H bonds of the Cp* ligand has been cleaved (Scheme 6). In these transformations, the hydrogen atom is transferred to the carbene carbon atom at the inside face of the molecule, forming an η^4 -diene unit. The methylene protons of **9a** exhibit two characteristic singlets at 5.05 and 4.75 ppm in the ^1H NMR spectrum. The small coupling constant (0–3 Hz) is typical of geminal hydrogens attached to sp^2 -hybridized carbons (whereas those attached to sp^3 -hybridized carbon exhibit typical coupling constants in the range 12–15 Hz). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the methylene carbon atom gives rise to a doublet centered at 51.8 ppm ($J_{\text{CP}} = 3.1$ Hz). Of course, the NMR spectra of **9b** are very similar. On the basis of the NMR spectroscopic data the newly formed $\eta^6\text{-C}_5\text{Me}_4\text{CH}_2$ ligand may be envisioned as tetramethylfulvene rather than a tetramethylcyclopentadienyl- σ -alkyl ligand. X-ray data are also consistent with a tetramethylfulvene rather than an $\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4$ ($\sigma:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4$) description

(8) Dehydrogenation of cyclohexyl groups in monodentate PCy_3 to give η^2 - and η^3 -cyclohexyl units: (a) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082. (b) Borowski, A. F.; Sabo-Etienne, S.; Christ, M. L.; Donnadieu, B.; Chaudret, B. *Organometallics* **1996**, *15*, 1427. (c) Chaudret, B.; Dagnac, P.; Labroue, D.; Sabo-Etienne, S. *New J. Chem.* **1996**, *20*, 1137. (d) Six, C.; Gabor, B.; Görls, H.; Mynott, R.; Philipps, P.; Leitner, W. *Organometallics* **1999**, *18*, 3316.

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(vide infra). Related methyl C–H activation processes of transition metal coordinated C_5Me_5 and C_6Me_6 ligands have been reported previously.^{11,12}

To gain further insight into the bonding of the $\text{C}_5\text{-Me}_4\text{CH}_2$ ligand, for **9a** also a single-crystal diffraction study has been performed. A structural view is shown in Figure 5, with selected bond distances and angles

reported in the caption. Most notably, the CH_2 group of the η^6 -bonded $\text{C}_5\text{Me}_4\text{CH}_2$ ligand is bent toward the metal by about 0.92(1) Å from the C_5 plane, corresponding to an angle of about 38.4°. The Ru–C(6) bond distance is comparable (2.298(7) Å) to those of other ruthenium complexes containing the $\eta^6\text{-C}_5\text{Me}_4\text{CH}_2$ ligand (cf. 2.301(2), 2.268(4) (2.271(4)), and 2.430(11) Å in Ru-

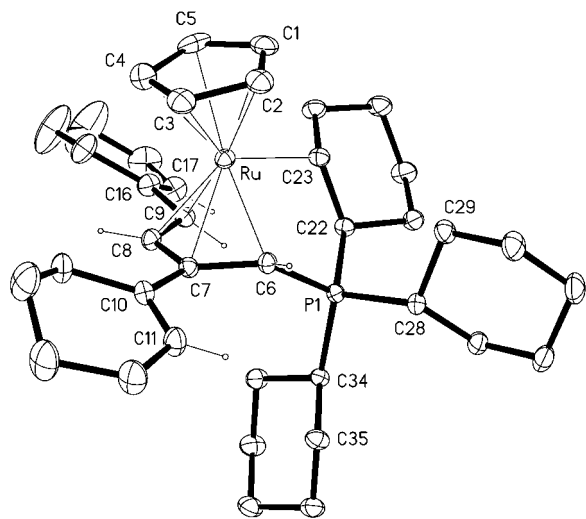


Figure 4. Structural view of $[\text{RuCp}(\eta^4\text{-CH}(\text{C}_6\text{H}_9)\text{CHC}(\text{C}_6\text{H}_9)\text{CH-PCy}_2(\eta^1\text{-C}_6\text{H}_{10}))\text{PF}_6$ (**6a**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru–C(1) 2.070(7), Ru–C(2) 2.197(7), Ru–C(3) 2.267(7), Ru–C(4) 2.280(7), Ru–C(5) 2.183(6), Ru–C(6) 2.297(7), Ru–C(11) 2.147(7), Ru–C(12) 2.156(8), Ru–C(13) 2.143(7), Ru–C(14) 2.147(7), C(1)–C(2) 1.420(11), C(1)–C(6) 1.426(11), C(1)–C(5) 1.436(10), C(2)–C(3) 1.408(11), C(3)–C(4) 1.444(11), C(4)–C(5) 1.412(11), C(11)–C(12) 1.423(10), C(12)–C(13) 1.437(19), C(13)–C(14) 1.448(10), P(1)–C(14) 1.778(7), C(11)–C(12)–C(13) 121.2(7), C(12)–C(13)–C(14) 119.3(6).

$(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{COD})$,^{12a} $[\text{Ru}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Cl}_2]_2$,^{12b,c} and $[\text{Ru}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{OH})]\text{PF}_6$,^{12e} respectively).

In summary, we have shown that allyl carbene complexes indeed behave as reactive masked 16e species which are able to accommodate nucleophiles at the metal center to give η^3 -butadienyl complexes. In the course of this process a C–H bond activation takes place resulting in an overall 1,4 hydrogen shift. Moreover, we have demonstrated that intramolecular C–H activation reactions are a very prominent feature of allyl carbenes, and C–H bonds of both aryl and alkyl substituents of tertiary phosphine ligands as well as methyl C–H bonds of the Cp* ligand are readily activated and cleaved to give novel η^4 -butadiene complexes featuring metal carbon σ -bonds.

Experimental Section

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.¹³ The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[\text{RuCp}^*(\text{CH}_3\text{CN})_3]\text{PF}_6$,⁹ $[\text{RuCp}(\text{PPh}_3)(\text{CH}_3\text{CN})_2]\text{PF}_6$ (**1a**), and

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(13) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

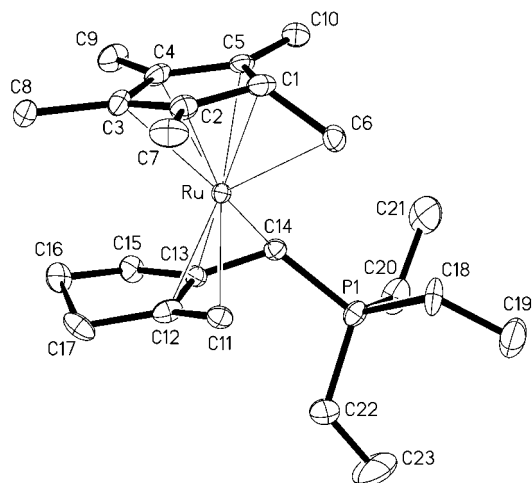


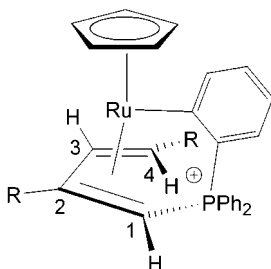
Figure 5. Structural view of $[\text{Ru}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\eta^4\text{-CH}_2=\text{C}(\text{CH}_2)_3\text{C}=\text{CHPEt}_3)]\text{PF}_6$ (**9b**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru–C(1) 2.070(7), Ru–C(2) 2.197(7), Ru–C(3) 2.267(7), Ru–C(4) 2.280(7), Ru–C(5) 2.183(6), Ru–C(6) 2.297(7), Ru–C(11) 2.147(7), Ru–C(12) 2.156(8), Ru–C(13) 2.143(7), Ru–C(14) 2.147(7), C(1)–C(2) 1.420(11), C(1)–C(6) 1.426(11), C(1)–C(5) 1.436(10), C(2)–C(3) 1.408(11), C(3)–C(4) 1.444(11), C(4)–C(5) 1.412(11), C(11)–C(12) 1.423(10), C(12)–C(13) 1.437(19), C(13)–C(14) 1.448(10), P(1)–C(14) 1.778(7), C(11)–C(12)–C(13) 121.2(7), C(12)–C(13)–C(14) 119.3(6).

$[\text{RuCp}(\text{PCy}_3)(\text{CH}_3\text{CN})_2]\text{PF}_6$ (**1b**) were prepared according to the literature.⁶ Synthetic and spectroscopic details of complexes $[\text{RuCp}(\text{C}(\text{Ph})(\eta^3\text{-CHC}(\text{Ph})\text{CHPMe}_3)]\text{PF}_6$ (**2a**), $[\text{RuCp}(\text{C}(\text{C}_6\text{H}_9)(\eta^3\text{-CHC}(\text{C}_6\text{H}_9)\text{CHPPPh}_3)]\text{PF}_6$ (**2b**), $[\text{RuCp}(\text{C}(\textit{n}\text{-Bu})(\eta^3\text{-CHC}(\textit{n}\text{-Bu})\text{CHPPPh}_3)]\text{PF}_6$ (**2c**), $[\text{RuCp}(\text{C}(\text{H})(\eta^3\text{-CHC}(\text{H})\text{CHPPPh}_3)]\text{PF}_6$ (**2f**), and $[\text{RuCp}(\text{C}(\text{H})(\eta^3\text{-CC}(\text{CH}_2)_3\text{CHPCy}_3)]\text{PF}_6$ (**2g**), which are intermediates of the reactions presented in this paper, as well as of complexes $[\text{RuCp}(\text{C}(\text{PMe}_3)=\text{CPh}-\eta^2\text{-CH}=\text{CHPh})(\text{PPh}_3)]\text{PF}_6$ (**3**) and $[\text{RuCp}(\eta^3\text{-CH}_2\text{C}(\text{CH}_2)_3\text{CCH}_2\text{PCy}_2(\eta^2\text{-C}_6\text{H}_9)]\text{PF}_6$ (**7**) have been reported previously.^{5a} IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Bruker AVANCE-250, Varian Unity 400 MHz, or Varian Gemini 200 MHz spectrometers and were referenced to SiMe_4 and H_3PO_4 (85%), respectively. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signal assignments were confirmed by ^1H -COSY, 135-DEPT, and HMQC(^1H - ^{13}C) experiments. Microanalysis was performed by the Serveis Científico-Tècnics, Universitat of Barcelona.

$[\text{RuCp}^*(\text{PEt}_3)(\text{CH}_3\text{CN})_2]\text{PF}_6$ (1c**).** A solution of $[\text{RuCp}^*(\text{CH}_3\text{CN})_3]\text{PF}_6$ (504 mg, 1.00 mmol) in CH_3CN (5 mL) was treated with 1 equiv of PEt_3 (148.4 μL , 1.00 mmol) and stirred for 2 h at room temperature. The solvent was then removed under vacuum, and the residue was washed with Et_2O and dried under vacuum. Yield: 512 mg (88%). Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{F}_6\text{N}_2\text{P}_2\text{Ru}$: C, 41.9; H, 6.28. Found: C, 41.9; H, 6.29. ^1H NMR (δ , CDCl_3 , 20 °C): 2.41 (bs, 6H, CH_3CN), 1.64 (m, 6H, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 1.57 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 0.95 (dt, 9H, $^3J_{\text{HP}} = 17.7$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, $\text{P}(\text{CH}_2\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 124.5 (s, CH_3CN), 85.0 (d, $^2J_{\text{CP}} = 2.1$ Hz, $\text{C}_5(\text{CH}_3)_5$), 18.0 (d, $^1J_{\text{CP}} = 23.0$ Hz, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 9.33 (s, $\text{C}_5(\text{CH}_3)_5$), 6.72 (s, PCH_2CH_3), 4.08 (s, CH_3CN). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 32.1 (s). IR (Nujol, cm^{-1}): 2269 (m, ν_{CN}).

$[\text{RuCp}(\eta^4\text{-CH}(\text{C}_6\text{H}_9)\text{CHC}(\text{C}_6\text{H}_9)\text{CH-PPh}_2(\eta^1\text{-C}_6\text{H}_4))]\text{PF}_6$ (4a**).** A solution of **1a** (200 mg, 0.319 mmol) and 1-ethynylcyclohexene (83 μL , 0.701 mmol) in CH_3NO_2 (5 mL) was stirred for 20 h at room temperature. The color of the solution changed from yellow via violet to brown. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (2 mL) and Et_2O (10 mL) was added. A yellow

precipitate was formed, which was collected on a glass frit, washed with Et₂O, and dried under vacuum. Yield: 120.3 mg (48%). Anal. Calcd for C₃₉H₄₀P₂F₆Ru: C, 59.62; H, 5.13. Found: C, 59.43; H, 5.09. ¹H NMR (δ, acetone-*d*₆, 20 °C): 8.53–8.33 (m, 1H, Ph), 8.06–6.89 (m, 13H, Ph), 6.61 (m, 1H, C₆H₆), 5.99 (d, ³J_{HH} = 9.3 Hz, 1H, H³), 5.33 (s, 5H, Cp), 4.75 (d, ²J_{PH} = 5.1 Hz, 1H, H¹), 4.56 (m, 1H, C₆H₆), 2.67–2.11 (m, 4H, CH₂), 1.97 (d, ³J_{HH} = 9.3 Hz, 1H, H⁴), 1.91–1.33 (m, 12H, CH₂). ¹³C{¹H} NMR (δ, acetone-*d*₆, 20 °C): 181.9 (d, J_{CP} = 32.3 Hz, 1C, Ph_m²), 144.9, 144.6, 142.4, 137.2, 137.1, 135.4, 134.9, 134.8, 134.7, 133.6, 133.5, 133.3, 133.0, 132.8, 132.7, 132.6, 131.9, 131.1, 131.0, 130.9, 130.8, 130.7, 130.5, 128.3, 127.8, 126.3, 125.2, 124.6, 124.4 (21C, Ph, C₆H₆), 99.9 (1C, C²), 89.2 (5C, Cp), 85.9 (1C, C⁴), 76.3 (1C, C³), 36.5 (d, ¹J_{CP} = 78.1 Hz, 1C, C¹), 26.9, 26.5, 24.2, 23.2, 23.0, 22.9, 22.7, 22.6 (16C, CH₂). ³¹P{¹H} NMR (δ, acetone-*d*₆, 20 °C): 48.7 (PPh₂), –142.7 (J_{PF} = 707.8 Hz, PF₆[–]).



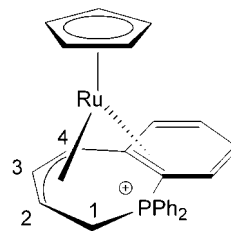
[RuCp(η⁴-CH(*n*-Bu)CHC(*n*-Bu)CH–PPh₂(η¹-C₆H₄))]-PF₆ (4b). A solution of **2b** (40 mg, 0.136 mmol) in acetone-*d*₆ was kept at room temperature for 31 days. During that time the color of the solution changed gradually from red to orange. ¹H NMR (δ, acetone-*d*₆, 20 °C): 8.58 (d, J_{HH} = 7.3 Hz, 1H, C₆H₄), 8.53 (d, J_{HH} = 7.3 Hz, 1H, C₆H₄), 8.10–7.24 (m, 10H, Ph), 7.11 (m, 1H, C₆H₄), 6.85 (m, 1H, C₆H₄), 4.34 (s, 5H, Cp), 4.25 (d, J_{HH} = 4.9 Hz, H³), 4.12 (d, J_{PH} = 13.4 Hz, H¹), 2.46–2.28 (m, 1H, CH₂), 2.23–1.96 (m, 4H, CH₂), 1.93–1.63 (m, 4H, CH₂, H⁴), 1.59–1.36 (m, 2H, CH₂), 1.29–1.05 (m, 2H, CH₂), 0.94 (t, ³J_{HH} = 7.3 Hz, CH₃), 0.64 (t, ³J_{HH} = 7.3 Hz, CH₃). ³¹P{¹H} NMR (δ, acetone-*d*₆, 20 °C): 30.3 (PPh₂), –142.7 (PF₆[–], J_{PF} = 707.8 Hz).

[RuCp(η⁴-CH(Ph-*p*-NO₂)CHC(Ph-*p*-NO₂)CH–PPh₂(η¹-C₆H₄))]-PF₆ (4c). A solution of **1a** (30 mg, 0.048 mmol) and *p*-nitrophenylacetylene (15 mg, 0.100 mmol) in CD₃NO₂ (0.4 mL) was kept at room temperature for 4 days. The color of the solution changed from yellow to dark green and eventually to dark orange. The reaction was monitored by NMR spectroscopy, revealing the intermediacy of the allyl carbene complex [RuCp(=C(Ph-*p*-NO₂)-η³-CH–C(Ph-*p*-NO₂)CHPPh₃)-PF₆ (**2d**). ¹H NMR (δ, CD₃NO₂, 20 °C): 8.31–8.16 (m, 4H, NO₂-C₆H₄), 7.81–7.68 (m, 4H, NO₂-C₆H₄), 7.65–7.35 (m, 15H, PPh₃), 6.32 (d, ²J_{HP} = 8.5 Hz, 1H, H⁴), 5.89 (s, 1H, H²), 5.32 (s, 5H, Cp). ³¹P{¹H} NMR (δ, CD₃NO₂, 20 °C): 31.8 (PPh₃), –143.4 (¹J_{PF} = 706.9 Hz, PF₆[–]). **1a** was quantitatively converted to **4c** after about 4 days. ¹H NMR (δ, CD₃NO₂, 20 °C): 8.74–8.55 (m, 1H, PPh₂C₆H₄), 8.38–7.16 (m, 19H, PPh₃, *p*-NO₂-C₆H₄), 7.08 (d, ³J_{HH} = 8.5 Hz, H³), 6.96 (d, ³J_{HH} = 8.6 Hz, 2H, *p*-NO₂-C₆H₄), 5.26 (s, 5H, Cp), 5.17 (d, ²J_{HP} = 3.8 Hz, H¹), 2.46 (d, ³J_{HH} = 8.5 Hz, H⁴). ¹³C{¹H} NMR (δ, acetone-*d*₆, 20 °C): 175.6 (d, J_{CP} = 30.5 Hz, Ph_m²), 149.3, 148.11, 147.5, 147.0, 144.9, 144.6, 142.8, 141.0, 135.8, 135.4, 135.2, 134.9, 134.7, 133.6, 133.3, 133.2, 133.0, 131.4, 131.2, 131.0, 130.8, 130.6, 130.4, 129.6, 127.1, 125.6, 124.9, 124.8, 124.6, 124.3 (28C, PPh₃, *p*-NO₂-C₆H₄), 97.9 (1C, C²), 93.0 (5C, Cp), 87.7 (1C, C⁴), 72.8 (1C, C³), 44.4 (d, ¹J_{CP} = 77.7 Hz, 1C, C¹). ³¹P{¹H} NMR (δ, acetone-*d*₆, 20 °C): 49.0 (PPh₂), –142.6 (¹J_{PF} = 707.8 Hz, PF₆[–]).

[RuCp(η⁴-CH(Cc)CHC(Cc)CH–PPh₂(η¹-C₆H₄))](PF₆)₃ (4d). To a solution of **1a** (58 mg, 0.094 mmol) in CH₃NO₂ (5 mL) 1-ethynyl cobaltocenium hexafluorophosphate, [C]PF₆

(70 mg, 0.100 mmol), was added. The reaction mixture was stirred at room temperature for 20 h, whereupon the color of the solution changed from yellow to green and finally to dark orange. After that the solvent was removed under vacuum, the residue was redissolved in CH₂Cl₂ (0.5 mL), and Et₂O (10 mL) was added. An orange precipitate was formed, which was collected on a glass frit, washed with Et₂O, and dried under vacuum. Yield: 103 mg (85%). Anal. Calcd for C₄₇H₄₀F₁₈P₄-Co₂Ru: C, 43.77; H, 3.13. Found: C, 43.62; H, 3.15. ¹H NMR (δ, acetone-*d*₆, 20 °C): 8.26–7.27 (m, 14H, Ph), 7.19 (d, J_{HH} = 8.7 Hz, H³), 6.72 (m, 1H, Cc), 6.56 (m, 1H, Cc), 6.16 (m, 2H, Cc), 6.06 (m, 1H, Cc), 5.99 (s, 5H, Cp^{Co}), 5.86 (m, 1H, Cc), 5.78 (m, 2H, Cc), 5.56 (d, J_{HP} = 4.0 Hz, H¹), 5.45 (s, 5H, Cp^{Co}), 5.35 (s, 5H, Cp^{Ru}), 5.04 (m, 1H, Cc), 2.37 (d, J_{HH} = 8.7 Hz, H⁴). ¹³C{¹H} NMR (δ, CD₃NO₂, 20 °C): 170.9 (d, J_{CP} = 28.7 Hz, 1C, Ph_m²), 144.2, 143.9, 142.5, 140.6, 135.5, 134.5, 134.3, 134.0, 133.9, 133.8, 133.2, 133.1, 132.8, 132.7, 131.9, 131.7, 131.1, 130.9, 126.5, 126.4 (17C, PPh₃), 106.5 (d, J_{CP} = 5.3 Hz, 1C, C²), 104.1 (1C, Cc), 92.8 (5C, Cp^{Ru}), 90.3 (1C, C⁴), 86.4 (5C, Cp^{Co}), 85.9 (2C, Cc), 85.8 (2C, Cc), 85.4 (5C, Cp^{Co}), 84.9 (2C, Cc), 84.6 (1C, Cc), 82.8 (1C, Cc), 80.0 (1C, Cc), 77.8 (1C, C³), 44.9 (d, J_{CP} = 77.0 Hz, 1C, C¹). ³¹P{¹H} NMR (δ, acetone-*d*₆, 20 °C): 47.5 (PPh₂), –142.6 (J_{PF} = 711.2 Hz, PF₆[–]).

[RuCp(η³-CHCHCH–CH₂PPh₂-η²-C₆H₄)]PF₆ (5). A solution of **1a** (100 mg, 0.159 mmol) in CH₃NO₂ (4 mL) was stirred under an atmosphere of acetylene at room temperature for 30 min. The color changed from yellow to red. The solvent was removed under reduced pressure. The remaining residue was dissolved in CH₂Cl₂ (3 mL) and was stirred for 1 h at room temperature, whereupon the color of the solution became orange. After removal of the solvent under reduced pressure, the remaining solid was washed with petroleum ether and dried under vacuum. Yield: 88 mg (89%). Anal. Calcd for C₂₇H₂₄F₆P₂Ru: C, 51.85; H, 3.87. Found: C, 51.81; H, 3.84. ¹H NMR (δ, acetone-*d*₆, 20 °C): 8.42–8.26 (m, 2H, PPh₂(C₆H₄)), 8.09–7.79 (m, 4H, PPh₂(C₆H₄)), 7.74–7.62 (m, 1H, PPh₂(C₆H₄)), 7.57–7.44 (m, 2H, PPh₂(C₆H₄)), 7.16–6.88 (m, 5H, PPh₂(C₆H₄)), 6.85 (dd, ³J_{HH} = 6.0 Hz, ⁴J_{HP} = 2.0 Hz, 1H, H⁴), 5.65 (ddd, ³J_{HH} = 7.4 Hz, ³J_{HH} = 6.0 Hz, J_{HH} = 2.8 Hz, 1H, H³), 4.79–4.46 (m, 1H, H²), 4.54 (s, 5H, Cp), 3.59 (ddd, ²J_{HH} = 16.3 Hz, ³J_{HH} = 16.1 Hz, ²J_{HP} = 9.5 Hz, 1H, H¹), 1.84 (ddd, ²J_{HH} = 16.3 Hz, ³J_{HH} = 4.0 Hz, ²J_{HP} = 2.8 Hz, 1H, H¹). ¹³C{¹H} NMR (δ, CDCl₃, 20 °C): 135.4, 135.3, 135.2, 134.8, 134.7, 134.6, 134.3, 134.2, 134.1, 133.7, 133.6, 133.5, 132.4, 132.1, 132.0, 131.9, 131.7, 130.5, 130.1, 129.9, 128.8, 128.7, 128.6, 128.5, 127.5, 127.4, 123.8, 122.8, 121.9, 121.7, 121.4 (15C, PPh₂(C₆H₄)), 91.6 (1C, C⁴), 82.5 (d, J_{CP} = 1.8 Hz, 1C, C³), 81.1 (5C, Cp), 42.4 (1C, C²), 28.8 (d, J_{CP} = 67.3 Hz, 1C, C¹). ³¹P{¹H} NMR (δ, CDCl₃, 20 °C): 63.7 (PPh₂), –143.4 (J_{PF} = 712.1 Hz, PF₆[–]).



[RuCp(η⁴-CH(C₆H₅)CHC(C₆H₅)CH–PCy₂(η¹-C₆H₁₀))]-PF₆ (6a). A solution of **1b** (100 mg, 0.148 mmol) and 1-ethynylcyclohexene (40 μL, 0.341 mmol) in CH₂Cl₂ (4 mL) was stirred at room temperature for 20 h. After removal of the solvent under reduced pressure, the dark yellow solid was obtained, which was washed with Et₂O (5 mL) and dried under vacuum. The crude product was purified by column chromatography (neutral Al₂O₃/acetone). The yellow band was collected. Yield: 105 mg (88%). Anal. Calcd for C₃₉H₅₈F₆P₂Ru: C, 58.27; H, 7.27. Found: C, 58.31; H, 7.29. ¹H NMR (δ, CDCl₃,

Table 1. Crystallographic Data for 3, 4a, 5, 6a, and 9b

	3	4a	5	6a	9b	
formula	C ₄₂ H ₄₁ F ₆ P ₃ Ru	C ₃₉ H ₄₀ F ₆ P ₂ Ru	C ₂₇ H ₂₄ F ₆ P ₂ Ru	C ₃₉ H ₅₈ F ₆ P ₂ Ru	C ₂₃ H ₃₈ F ₆ P ₂ Ru	
fw	853.73	785.72	625.47	803.86	591.54	
cryst size, mm	0.40 × 0.20 × 0.04	0.40 × 0.24 × 0.06	0.50 × 0.40 × 0.35	0.65 × 0.24 × 0.12	0.84 × 0.18 × 0.12	
space group	P1̄ (no. 2)	P2 ₁ (no. 4)	P2 ₁ (no. 4)	Pca2 ₁ (no. 29)	P1̄ (no. 2)	
a, Å	10.007(5)	10.007(4)	8.138(3)	20.101(4)	8.032(3)	
b, Å	10.727(6)	17.243(6)	10.724(4)	10.857(3)	8.888(3)	
c, Å	20.578(9)	10.643(4)	14.922(6)	17.249(4)	18.442(7)	
α, deg	75.14(2)	90	90	90	85.38(2)	
β, deg	82.54(2)	104.21(1)	104.23(2)	90	79.46(2)	
γ, deg	65.72(2)	90	90	90	86.59(2)	
V, Å ³	1946(2)	1780.3(12)	1262.3(8)	3764(2)	1288.8(8)	
Z	2	2	2	4	2	
ρ _{calc} , g cm ⁻³	1.457	1.466	1.646	1.418	1.524	
T, K	296(2)	297(2)	297(2)	297(2)	297(2)	
μ, mm ⁻¹ (Mo Kα)	0.585	0.589	0.807	0.558	0.785	
abs corr	multiscan		multiscan		multiscan	
F(000)	872	804	628	1680	608	
transmn factor min./max.	0.75/0.96	0.79/0.93	0.79/1.00	0.71/0.89	0.76/1.00	
θ _{max} , deg	25	25	30	30	25	
index ranges	-11 ≤ h ≤ 11 -12 ≤ k ≤ 12 -24 ≤ l ≤ 24	-11 ≤ h ≤ 11 -20 ≤ k ≤ 20 -12 ≤ l ≤ 12	-11 ≤ h ≤ 11 14 ≤ k ≤ 14 20 ≤ l ≤ 20	-26 ≤ h ≤ 28 -15 ≤ k ≤ 15 -24 ≤ l ≤ 24	-9 ≤ h ≤ 9 -10 ≤ k ≤ 10 -21 ≤ l ≤ 21	
no. of reflns measd	21 495	18 502	32 734	52 744	9650	
no. of unique reflns	6807	6257	7088	10 825	3467	
no. of reflns I > 2σ(I)	4751	5273	6435	9246	3125	
no. of params	470	442	335	438	289	
R ₁ (I > 2σ(I)) ^a	0.042	0.038	0.034	0.028	0.062	
R ₁ (all data) ^a	0.074	0.050	0.042	0.037	0.069	
wR ₂ (all data) ^b	0.097	0.097	0.079	0.071	0.151	
diff Fourier peaks min./max., e Å ⁻³	-0.70/0.58	-0.29/0.64	-0.84/0.92	-0.35/0.37	-0.90/1.11	

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}.$$

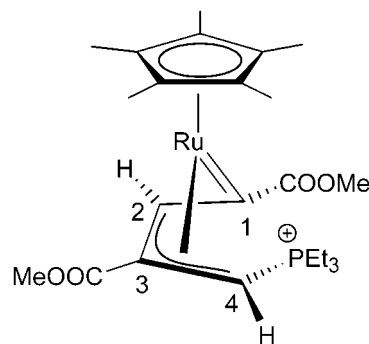
20 °C): 6.20 (m, 1H, C₆H₆), 5.76 (m, 1H, C₆H₆), 5.50 (d, ³J_{HH,trans} = 8.2 Hz, 1H, H³), 4.76 (s, 5H, Cp), 4.55 (vt, ³J_{HH} = 10.6 Hz, 1H, Cy_m²), 3.44 (d, ²J_{HP} = 3.5 Hz, 1H, H¹), 2.73–2.50 (m, 1H, Cy_m¹), 2.40–0.90 (m, 48 H, Cy, Cy_m, C₆H₉), 1.50 (s, 1H, H⁴). ¹³C{¹H} NMR (δ, CDCl₃, 20 °C): 138.5 (1C, C₆H₆), 137.1 (d, J_{CP} = 4.8 Hz, 1C, C₆H₆¹), 130.9 (1C, C₆H₉), 127.1 (1C, C₆H₉²), 97.0 (1C, C²), 88.0 (5C, Cp), 73.9 (1C, C³), 69.5 (1C, C⁴), 53.5 (d, ¹J_{CP} = 56.5 Hz, 1C, PCy_m¹), 35.4 (d, ¹J_{CP} = 31.3 Hz, 1C, PCy¹), 33.7 (d, ¹J_{CP} = 43.2 Hz, 1C, PCy¹), 32.2 (1C, CH₂), 30.3 (1C, PCy_m²), 30.2 (1C, CH₂), 29.2 (d, ¹J_{CP} = 64.3 Hz, 1C, C¹), 28.3, 28.2, 27.6, 27.5, 27.3, 26.7, 26.6, 26.6, 26.5, 26.4, 26.2, 25.7, 25.6, 23.0, 22.9, 22.8, 22.4 (20C, CH₂). ³¹P{¹H} NMR (δ, CDCl₃, 20 °C): 61.2 (PCy₂), -143.1 (J_{PF} = 705.3 Hz, PF₆⁻).

[RuCp(η⁴-CH(Ph-p-OMe)CHC(Ph-p-OMe)CH-PCy₂(η¹-C₆H₁₀))]PF₆ (6b). A solution of **1b** (285 mg, 0.423 mmol) and *p*-methoxyphenylacetylene (137 μL, 1.058 mmol) in CH₂Cl₂ (3 mL) was stirred for 20 h at room temperature. The solvent was removed under vacuum, and the dark brown residue was purified by column chromatography (neutral Al₂O₃/CH₂Cl₂). The second brown fraction was collected. After removal of the solvent, the dark brown solid was washed with Et₂O and dried under vacuum. Yield: 290 mg (80%). Anal. Calcd for C₄₁H₅₄F₆O₂P₂Ru: C, 57.54; H, 6.36. Found: C, 57.48; H, 6.24. ¹H NMR (δ, CDCl₃, 20 °C): 7.57 (d, ³J_{HH} = 8.9 Hz, 2H, CH₃-OC₆H₄), 7.24 (d, ³J_{HH} = 8.9 Hz, 2H, CH₃OC₆H₄), 7.05 (d, ³J_{HH} = 8.9 Hz, 2H, CH₃OC₆H₄), 6.91 (d, ³J_{HH} = 8.9 Hz, 2H, CH₃-OC₆H₄), 6.31 (d, ³J_{HH} = 7.9 Hz, 1H, H³), 4.74 (s, 5H, Cp), 4.74 (vt, ³J_{HH} = 10.3 Hz, 1H, Cy_m²), 3.88 (s, 3H, CH₃OC₆H₄), 3.85 (s, 3H, CH₃OC₆H₄), 3.62 (d, ²J_{HP} = 3.6 Hz, H¹), 2.95–2.71 (m, 1H, PCy_m¹), 2.48–1.23 (m, 32H, Cy, H⁴). ¹³C{¹H} NMR (δ, CDCl₃, 20 °C): 160.9 (1C, CH₃OC₆H₄⁴), 158.6 (1C, CH₃OC₆H₄⁴), 135.4 (1C, CH₃OC₆H₄¹), 132.6 (d, ³J_{CP} = 5.4 Hz, 1C, CH₃-OC₆H₄¹), 129.2 (2C, CH₃OC₆H₄^{2,6}), 127.8 (2C, CH₃OC₆H₄^{2,6}), 115.0 (2C, CH₃OC₆H₄^{3,5}), 114.6 (2C, CH₃OC₆H₄^{3,5}), 96.0 (1C, C²), 90.4 (5C, Cp), 81.6 (1C, C³), 63.4 (1C, C⁴), 55.8, 55.6 (2C, OCH₃), 53.2 (d, ¹J_{CP} = 55.7 Hz, 1C, PCy_m¹), 41.8 (d, J_{CP} = 12.6 Hz, 1C, CH₂), 35.3, 34.8, 33.7, 32.9, 32.7, 31.1, 30.7 (d, ¹J_{CP} = 62.8 Hz, 1C, C¹), 28.2, 28.0, 27.2, 26.6, 26.5, 26.4, 26.3, 26.1,

26.0, 25.6, 25.4 (16C, Cy). ³¹P{¹H} NMR (δ, CDCl₃, 20 °C): 61.2 (PCy₂), -143.4 (J_{PF} = 713.4 Hz, PF₆⁻).

[RuCp*(=C(COOMe)-η³-CHC(COOMe)CHPET₃)]PF₆ (8a).

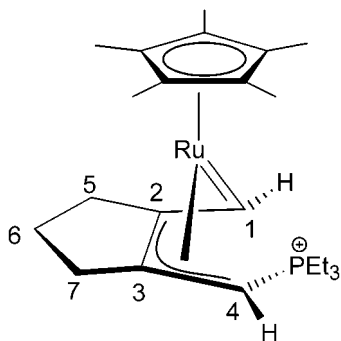
A solution of **1c** (200 mg, 0.344 mmol) in acetone (5 mL) was treated with a slight excess of HC≡CCOOCH₃ (70.0 μL, 0.787 mmol). The color changed to dark green after stirring for 5 min. The solvent was then removed under vacuum and the residue washed with petroleum ether and Et₂O and dried, obtaining a dark green solid. Yield: 196 mg (87%). Anal. Calcd for C₂₄H₃₈F₆O₄P₂Ru: C, 44.0; H, 5.80. Found: C, 43.9; H, 5.80. ¹H NMR (δ, acetone-*d*₆, 0 °C): 6.15 (s, 1H, H²), 4.98 (d, 1H, ²J_{HP} = 6.3 Hz, H¹), 3.87 and 3.83 (both s, 3H each, COOCH₃), 1.89 (m, 6H, P(CH₂CH₃)₃), 1.76 (s, 15H, C₅(CH₃)₅), 1.11 (dt, 9H, ³J_{HP} = 18.0 Hz, ²J_{HH} = 7.6 Hz, P(CH₂CH₃)₃). ¹³C{¹H} (δ, acetone-*d*₆, 0 °C): 227.1 (d, ³J_{CP} = 7.2 Hz, C¹), 172.0 (s, COOCH₃), 168.5 (d, ²J_{CP} = 5.5 Hz, COOCH₃), 100.3 (s, C²), 94.8 (s, C₅(CH₃)₅), 90.5 (d, ²J_{CP} = 2.5 Hz, C³), 53.1 and 52.4 (s, COOCH₃), 32.2 (d, ¹J_{CP} = 66.6 Hz, C⁴), 14.0 and 13.5 (s, P(CH₂CH₃)₃), 10.1 (s, C₅(CH₃)₅), 5.0 (d, ²J_{CP} = 5.0 Hz, P(CH₂CH₃)₃). ³¹P{¹H} NMR (δ, acetone-*d*₆, 0 °C): 47.4 (PET₃). IR (Nujol, cm⁻¹): 1713 (s, ν_{COOMe}), 1632 (m, ν_{C=C}).



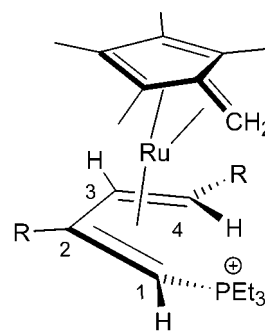
[RuCp*(=C(*n*-Bu)-η³-CHC(*n*-Bu)CHPET₃)]PF₆ (8b). This complex has been prepared analogously to **8a** with **1c** (200

mg, 0.344 mmol) and 2 equiv of 1-hexyne (81.2 μ L, 0.688 mmol) as the starting materials. Yield: 212 mg (94%). Anal. Calcd for $C_{28}H_{50}F_6P_2Ru$: C, 51.3; H, 7.63. Found: C, 51.3; H, 7.64. 1H NMR (δ , acetone- d_6 , 25 $^\circ$ C): 4.87 (s, 1H, H^2), 3.89 (d, $^2J_{HP}$ = 10.0 Hz, 1H, H^4), 3.17 (m, 1H, H^{5b}), 2.35 (t, $^3J_{HH}$ = 8.1 Hz, 2H, H^9), 2.12 (m, 1H, H^{5a}), 1.85 (s, 15H, $C_5(CH_3)_5$), 1.91, 1.72, and 1.51 (m, 14H, H^6 , H^7 , H^{10} , H^{11} + $P(CH_2CH_3)_3$), 1.14 (dt, $^3J_{HP}$ = 17.2 Hz, $^3J_{HH}$ = 7.5 Hz, 9H, $P(CH_2CH_3)_3$), 0.98 and 0.97 (both t, $^3J_{HH}$ = 7.4 Hz, 6H, $-CH_3$). $^{13}C\{^1H\}$ NMR (δ , acetone- d_6 , 25 $^\circ$ C): 256.3 (d, $^3J_{CP}$ = 6.0 Hz, C^1), 106.7 (d, $^2J_{CP}$ = 5.1 Hz, C^3), 94.7 (s, $C_5(CH_3)_5$), 84.4 (s, C^2), 42.8 (s, C^5), 38.6 (d, $^3J_{CP}$ = 4.5 Hz, C^9), 34.7 (s, C^6), 31.4 (d, $^1J_{CP}$ = 67.1 Hz, C^4), 29.9 (s, C^{10}), 23.5 and 23.6 (s, C^7 and C^{11}), 15.2 and 15.7 (s, $P(CH_2CH_3)_3$), 14.1 and 14.2 (s, C^8 and C^{12}), 11.0 (s, $C_5(CH_3)_5$), 6.4 (d, $^2J_{CP}$ = 5.1 Hz, $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (δ , acetone- d_6 , 25 $^\circ$ C): 43.8 (s). IR (Nujol, cm^{-1}): 1605 (m, $\nu_{C=C}$).

[RuCp*(=CH- η^3 -C(CH $_2$) $_3$ CCHPEt $_3$)]PF $_6$ (8c). A solution of **1c** (200 mg, 0.344 mmol) in acetone (5 mL) was treated with 1,6-heptadiyne (39.4 μ L, 0.344 mmol). An immediate color change from pale yellow to dark violet was observed. The solvent was removed under vacuum and the residue washed with petroleum ether (3 \times 5 mL) and dried, obtaining a violet solid. Yield: 191 mg (94%). Anal. Calcd for $C_{23}H_{38}F_6P_2Ru$: C, 46.70; H, 6.47. Found: C, 46.50; H, 6.47. 1H NMR (δ , acetone- d_6 , 0 $^\circ$ C): 11.71 (bs, 1H, H^1), 4.29 (d, 1H, $^2J_{HP}$ = 7.4 Hz, H^4), 2.84 (m, 2H, CH_2), 2.03 (m, 4H, CH_2), 1.84 (s, 15H, $C_5(CH_3)_5$), 1.59 (m, 6H, $P(CH_2CH_3)_3$), 1.07 (dt, 9H, $^3J_{HP}$ = 17.3 Hz, $^2J_{HH}$ = 7.9 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (δ , acetone- d_6 , 0 $^\circ$ C): 227.1 (d, $^3J_{CP}$ = 6.9 Hz, C^1), 114.7 (d, $^2J_{CP}$ = 5.5 Hz, C^3), 110.3 (s, C^2), 95.7 (s, $C_5(CH_3)_5$), 33.8 (d, $^3J_{CP}$ = 4.1 Hz, C^7), 28.6 (d, $^1J_{CP}$ = 68.6 Hz, C^4), 28.1 and 25.0 (s, C^5 and C^6), 14.3 and 13.7 (s, $P(CH_2CH_3)_3$), 10.9 (s, $C_5(CH_3)_5$), 5.9 (d, $^2J_{CP}$ = 5.5 Hz, $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (δ , acetone- d_6 , 0 $^\circ$ C): 43.1 (PEt $_3$). IR (Nujol, cm^{-1}): 1642 (m, $\nu_{C=C}$).



[Ru(η^6 -C $_5$ Me $_4$ CH $_2$)(η^4 -CH(COOME)=CH-C(COOME)=CHPEt $_3$)]PF $_6$ (9a). A solution of **8a** (150 mg, 0.258 mmol) in acetone (5 mL) was stirred at room temperature for 18 h. The solvent was removed under vacuum and the residue washed with petroleum ether (2 \times 5 mL) and dried. Slow recrystallization from a acetone/petroleum ether (1:3) mixture gave orange crystals. Yield: 144 mg (96%). Anal. Calcd for $C_{24}H_{38}F_6O_4P_2Ru$: C, 44.00; H, 5.80. Found: C, 44.10; H, 5.80. 1H NMR (δ , acetone- d_6 , 25 $^\circ$ C): 5.98 (d, 1H, $^2J_{HH}$ = 6.7 Hz, H^4), 5.05 and 4.75 (both s, 1H each, $H_2C=$), 3.88 and 3.61 (both s, 3H each, COOCH $_3$), 2.46 (d, 1H, $^2J_{HP}$ = 3.1 Hz, H^1), 2.25–2.10 (m, 7 H, H^3 + $P(CH_2CH_3)_3$), 1.68, 1.64, 1.48, and 1.41 (all s, 3H each, $C_5(CH_3)_4$), 1.25 (dt, 9H, $^3J_{HP}$ = 17.6 Hz, $^2J_{HH}$ = 7.7 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (δ , acetone- d_6 , 25 $^\circ$ C): 172.5 (s, COOCH $_3$), 169.7 (d, $^3J_{CP}$ = 3.4 Hz, COOCH $_3$), 106.3, 104.0, 103.3, 100.8, and 80.9 (s, $C_5(CH_3)_4$), 95.6 (s, C^2), 90.4 (s, C^4), 57.9 (s, CH_2), 53.0 and 51.4 (s, COOCH $_3$), 45.8 (s, C^3), 25.9 (d, $^1J_{CP}$ = 63.1 Hz, C^1), 17.5 and 17.0 (s, $P(CH_2CH_3)_3$), 9.1, 9.0, 7.1, and 6.2 (s, $C_4(CH_3)_4$), 6.3 (d, $^2J_{CP}$ = 5.5 Hz, $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (δ , acetone- d_6 , 25 $^\circ$ C): 42.6 (PEt $_3$). IR (Nujol, cm^{-1}): 1715 (s, ν_{COOME}), 1587 (s, $\nu_{C=C}$).



[Ru(η^6 -C $_5$ Me $_4$ CH $_2$)(η^4 -CH $_2$ =C(CH $_2$) $_3$ C=CHPEt $_3$)]PF $_6$ (9b). A solution of **8b** (150 mg, 0.254 mmol) in acetone (5 mL) was stirred at room temperature for 18 h. The solvent was removed under vacuum and the residue washed with petroleum ether (2 \times 5 mL) and dried. Slow recrystallization from a acetone/petroleum ether (1:3) mixture gave orange crystals. Yield: 143 mg (95%). Anal. Calcd for $C_{23}H_{38}F_6P_2Ru$: C, 46.7; H, 6.47. Found: C, 46.7; H, 6.47. 1H NMR (δ , acetone- d_6 , 25 $^\circ$ C): 4.83 and 4.67 (both s, 1H each, H_2C), 3.12 (m, 1H, H^{7b}), 2.92 (m, 1H, H^{5b}), 2.19–1.92 (m, 9H, H^{6b} , H^{7a} , H^1 + $P(CH_2CH_3)_3$), 1.86 (d, 1H, $^2J_{HH}$ = 3.6 Hz, H^{4b}), 1.82 (m, 1H, H^{5a}), 1.75, 1.66, 1.61, and 1.56 (all s, 3H each, $C_5(CH_3)_4$), 1.47 (d, 1H, $^2J_{HH}$ = 3.6 Hz, H^{4a}), 1.34 (m, 1H, H^{6a}), 1.20 (dt, 9H, $^3J_{HP}$ = 17.7 Hz, $^3J_{HH}$ = 7.9 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (δ , acetone- d_6 , 25 $^\circ$ C): 102.0 (d, $^2J_{CP}$ = 5.2 Hz, C^2), 106.3, 104.0, 99.9, 99.7, and 98.1 (s, $C_5(CH_3)_4$), 95.5 (s, C^3), 51.8 (d, $^3J_{CP}$ = 3.1 Hz, CH_2), 34.4 and 33.9 (both s, C^5 and C^7), 32.3 (s, C^4), 22.3 (s, C^6), 20.5 (d, $^1J_{CP}$ = 64.1 Hz, C^1), 17.3 and 17.8 (s, $P(CH_2CH_3)_3$), 10.0, 9.7, 8.4, and 8.2 (s, $C_5(CH_3)_4$), 6.5 (d, $^3J_{HP}$ = 5.2 Hz, $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (δ , acetone- d_6 , 25 $^\circ$ C): 43.6 (PEt $_3$). IR (Nujol, cm^{-1}): 1709 and 1579 (m, $\nu_{C=C}$).

X-ray Structure Determination for 3, 4a, 5, 6a, and 9b.

Crystals of **3**, **4a**, **5**, **6a**, and **9b** were obtained by diffusion of Et $_2$ O into CH $_2$ Cl $_2$ solutions. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite monochromated Mo K α radiation, α = 0.71073 \AA , 0.3 $^\circ$ ω scan frames covering complete spheres of the reciprocal space. Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. The structures of **3**, **4a**, **5**, and **6a** were solved by direct methods, while the structure of **9a** was solved with the Patterson method using in all cases the program SHELXS97.¹⁴ Structure refinement on F^2 was carried out with the program SHELXL97.¹⁵ All non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded; allyl or diene bound hydrogen atoms were freely refined in x , y , and z .

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, bond lengths and angles, and least-squares planes for **3**, **4a**, **5**, **6a**, and **9b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Sheldrick, G. M. *SHELXL97*: Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997.