Articles

Intramolecular [2 + 2] Cycloaddition of Allyl C=C and Allenylidene C_α=C_β Bonds: Formation and Deprotonation of Cyclobutylidene Rings†

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The mixed-phosphine complex [Ru(η^5-C_5H_5)Cl{κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)] (**1**) has been prepared by a phosphine exchange reaction between [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$] and Ph_2PCH_2-$CH{=}CH_2$ (ADPP) (1:1 molar ratio) in refluxing THF. The treatment of complex **1** with $NaPF_6$ in refluxing ethanol affords diastereoselectively the cationic complex [Ru(η^5-C_5H_5){κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)][PF_6] (**2b**). The reaction of complexes [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)][PF_6] (**2a**) and **2b** with propargyl alcohols HC≡CC(OH)R_1R_2 (R_1, R_2 = $C_{12}H_8$; R_1 = Ph, R_2 = Ph, H, Me) in refluxing THF yields regio- and diastereoselectively the cyclobutylidene complexes [Ru(η^5-C_nH_m){κ^2(*P,C*)-{=CCH(CH_2PPh_2)CH_2C=CR_1R_2}}(PPh_3)]-[PF_6] (C_nH_m = C_9H_7, R_1, R_2 = $C_{12}H_8$ (**3a**), R_1 = Ph, R_2 = Ph (**3b**), H (**3c**), Me (**3d**); C_nH_m = C_5H_5, R_1, R_2 = $C_{12}H_8$ (**4a**), R_1 = Ph, R_2 = Ph (**4b**), H (**4c**)). The formation of complexes **3a**−**d** and **4a**−**c** proceeds through an intramolecular cycloaddition of the C=C allyl and C_α=C_β bonds in the intermediate allenylidene complexes [Ru(η^5-C_nH_m)(=C=C=CR_1R_2){κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)][PF_6]. The allenylidene complex [Ru(η^5-C_9H_7)(=C=C=CPh_2){κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)][PF_6] (**5**) has been isolated from the reaction of **2a** with 1,1-diphenyl-2-propyn-1-ol in CH_2Cl_2. The deprotonation of complexes **3a**−**d** and **4a** with potassium *tert*-butoxide gives rise to the neutral complexes [Ru(η^5-C_nH_m){κ^2(*P,C*)-{C=C-(CH_2PPh_2)CH_2C=CR_1R_2}}(PPh_3)] (C_nH_m = C_9H_7, R_1, R_2 = $C_{12}H_8$ (**6a**), R_1 = Ph, R_2 = Ph (**6b**), H (**6c**), Me (**6d**); C_nH_m = C_5H_5, R_1 = Ph, R_2 = H (**7c**)). The structures of derivatives **3a** and **6d** have been determined by single-crystal X-ray diffraction analysis.

Introduction

During the past decade, the chemistry of transition-metal allenylidene complexes has received special attention due to their usefulness in stoichiometric and catalytic processes.[1] In particular, ruthenium(II) allenylidene complexes display a versatile chemistry, nucleophilic attacks[2] and insertion reactions[3] being their most representative reactivity. These complexes have also been proposed as catalyst precursors or intermediate species in several catalytic processes,[4] including alkene metathesis[5] and propargylic substitution reactions.[6]

Recently Hidai, Uemura, and co-workers have described a new type of catalytic cycloaddition process involving propargylic alcohols and a series of alkenes,[7] 2-naphthol and phenol.[8] These reactions proceed through

† This work is dedicated to the memory of Dr. J. C. del Amo, victim of the terrorist attack in Madrid on March 11, 2004.

(1) For general reviews on the synthesis and reactivity of allenylidene complexes see: (a) Bruce, M. I. *Chem. Rev*. **1991**, *91,* 197. (b) Werner, H. *Chem. Commun*. **1997**, 903. (c) Bruce, M. I. *Chem. Rev*. **1998**, *98,* 2797. (d) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev*. **1998**, *178*−*180*, 409. (e) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res*. **1999**, *32*, 311. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem*. **2001**, 571. (g) Werner, H.; Ilg, K.; Lass, R.; Wolf, J. *J. Organomet. Chem*. **2002**, *661*, 137.

(2) For recent examples in addition of neutral and anionic nucleophiles: (a) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *Organometallics* **2002**, *21*, 3837. (b) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Falvello, L. R.; Llusar, R. M. *Organometallics* **2002**, *21*, 3716. (c) Bustelo, E.; Jimenez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21,* 1903. (d) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22,* 5274. (e) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22,* 162. (f) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *Dalton* **2003**, 3060. (g) Cadierno, V.; Conejero, S.; Díez, J.; Gamasa, M. P.; Gimeno, J.; García-Granda, S. *Chem. Commun*. **2003**, 840.

(3) For recent examples of insertion reactions in [M]=C=C=CR_2 see the following. [M] = Cr, W: (a) Gerhard, R.; Reindl, D.; Gockel, M.; Troll, C.; Fischer, H. *Organometallics* **1998**, *17*, 1393. [M] = Os: (b) Crochet, P.; Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479. [M] = Ru: (c) Conejero, S.; Díez, J.; Gamasa, M. P.; Gimeno, J.; Garcia-Granda, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3439. (d) Conejero, S.; Díez, J.; Gamasa, M. P.; Gimeno, J. *Organometallics* **2004**, *23*, 6299.

(4) *Topics in Organometallic Chemistry*; Springer-Verlag: Heidelberg, Germany, 2004; Vol. 11, p 125.

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the selective coupling of the unsaturated substrates and the allenylidene chain in the catalytic active species.

Despite the fact that stoichiometric cycloadditions of allenylidene transition-metal complexes are well-known processes,[9] only a few examples have been described for ruthenium. Esteruelas and co-workers have shown that the allenylidene complex $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)][BF_4]$ is able to undergo cycloaddition reactions with unsaturated hydrocarbon substrates, including dicyclohexylcarbodiimide[10] CyN=C=NCy and dienes such as butadiene and cyclopentadiene.[11] 1,2,3-Diheterocyclization reactions with pyrazole and 2-aminopyridine have been also reported.[12] We have also proposed the formation of a [2 + 2] cycloadduct intermediate through the cycloaddition of ynamines $R'C{\equiv}CNEt_2$ and the allenylidene $C_\beta{=}C_\gamma$ bond of the complexes $[Ru(\eta^5\text{-}C_9H_7)(=C=C=C(R)Ph)(PPh_3)_2][PF_6]$ (R = Ph, H). The subsequent cyclobutene ring opening gives the aminoallenylidene complexes $[Ru(\eta^5\text{-}C_9H_7)\{=C=C=C(NEt_2)\{C(R')=C(R)Ph\}\}(PPh_3)_2][PF_6]$, which formally result from the insertion reaction of the ynamine into the $C_\beta{=}C_\gamma$ bond of the starting allenylidene chain.[3c,d]

All of these examples prove the synthetic utility of the allenylidene moiety, which is able to promote selective cycloaddition processes between the cumulene function and C=N, C=C, or C≡C substrates.

We have recently reported that vinylidene ruthenium(II) complexes undergo an unusual diastereoselective [2 + 2] intramolecular cycloaddition of allyl and vinylidene C=C bonds to give a cyclobutylidene ring under mild thermal reaction conditions[13] (Scheme 1).

Scheme 1

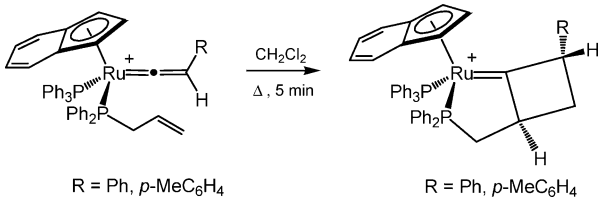
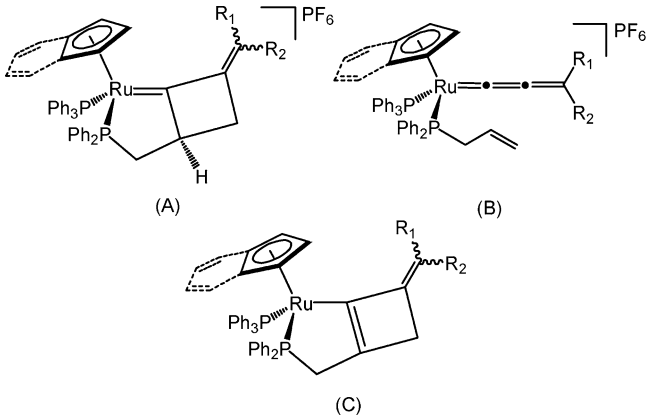


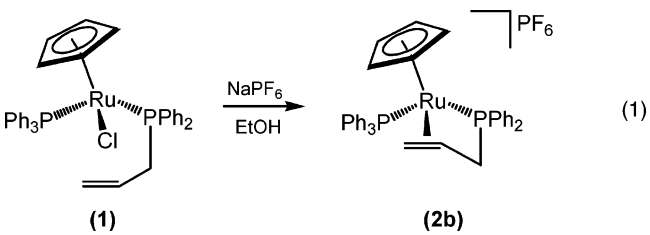
Chart 1



To explore the scope of these unusual processes, we have investigated the ability of analogous ruthenium(II) allenylidene derivatives to undergo this type of cycloaddition reaction. We now report a synthetic route to alkylidene complexes of the type A (Chart 1), consisting of the intramolecular [2 + 2] cycloaddition reaction between the allyl C=C and the allenylidene $C_\alpha{=}C_\beta$ bonds of complexes of the type B (Chart 1). To the best of our knowledge, this is the first example of a [2 + 2] intramolecular cycloaddition of a carbon−carbon double bond to an allenylidene moiety. The acidic nature of the methine hydrogen of the alkylidene moiety allows its ready deprotonation to give the bicyclic alkenyl complexes $[Ru(\eta^5\text{-}C_nH_m)\{\kappa^2(P,C)\text{-}\{\overline{C{=}C(CH_2PPh_2)\text{-}CH_2C{=}CR_1R_2}\}\}(PPh_3)][PF_6]$ of the type C (Chart 1).

Results and Discussion

Synthesis of Complexes $[Ru(\eta^5\text{-}C_5H_5)Cl\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)]$ (1) and $[Ru(\eta^5\text{-}C_5H_5)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)][PF_6]$ (2b). The reaction of $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ with allyldiphenylphosphine in refluxing THF for 30 min affords the complex $[Ru(\eta^5\text{-}C_5H_5)Cl\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)]$ (**1**; 81% yield) via phosphine exchange. The treatment of **1** with $NaPF_6$ in refluxing ethanol leads quantitatively (99% yield) to the cationic complex $[Ru(\eta^5\text{-}C_5H_5)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)][PF_6]$ (**2b**) through the chloride abstraction and concomitant π-coordination of the pendant allylic group to the ruthenium (eq 1).



(1)

Complexes **1** and **2b** have been isolated as orange and yellow air-stable solids, respectively. They have been

(5) (a) The first evidence was reported in 1998: Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun*. **1998**, 1315. (b) Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun*. **1998**, 2249. (c) Castarlenas, R.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *J. Mol. Catal. A: Chem*. **2004**, *213*, 31 and references therein.

(6) (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc*. **2000**, *122*, 11019. (b) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc*. **2001**, *123*, 3393. (c) Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc*. **2002**, *124*, 15172. (d) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc*. **2002**, *124*, 11846. (e) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 26. (f) Cadierno, V.; Díez, J.; García-Garrido, S. E.; Gimeno, J. *Chem. Commun*. **2004**, 2716.

(7) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc*. **2003**, *125*, 6060.

(8) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc*. **2002**, *124*, 7900.

(9) Several cycloaddition reactions have also been reported for other allenylidene transition metals. For a [2 + 2] reaction with the C−C triple bond of alkynes or acetylide complexes see the following. To the [M]−C_α double bond, [M] = Rh: (a) Werner, H.; Wiedemann, R.; Laubender, M.; Windmuller, B.; Steinert, P.; Gevert, O.; Wolf, J. *J. Am. Chem. Soc*. **2002**, *124*, 6966. To the C_α−C_β double bond, [M] = Cr or W: (b) Fischer, H.; Leroux, F.; Stumpf, R.; Roth, G. *Chem. Ber*. **1996**, *129*, 1475. [M] = Os: (c) See ref 3b. For a [2 + 2] reaction with the C−C triple bond of ynamines $R'C{\equiv}CNEt_2$ or imines $^iPrN{=}CHPh$, see the following. Ynamines, [M] = Cr, W: (d) See ref 3a. Imines, [M] = W: (e) Fischer, H.; Roth, G.; Reindl, D.; Troll, C. *J. Organomet. Chem*. **1993**, *454*, 133. For [3 + 2] dipolar cycloaddition with pyrazoles, see the following [M] = Re, W: (f) Bertolasi, V.; Mantovani, N.; Marvelli, L.; Rossi, R.; Bianchini, C.; De los Ríos, I.; Peruzzini, M.; Akbayeva, D. *Inorg. Chim. Acta* **2003**, *344*, 207.

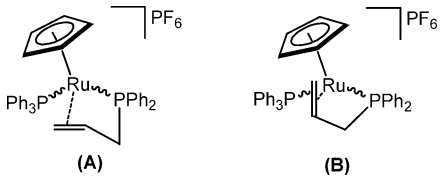
(10) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606.

(11) Baya, M.; Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E.; Rodríguez, J. R. *Organometallics* **2002**, *21*, 1841.

(12) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 3567.

(13) Álvarez, P.; Lastra, E.; Gimeno, J.; Bassetti, M.; Falvello, L. R. *J. Am. Chem. Soc*. **2003**, *125*, 2386.

Chart 2



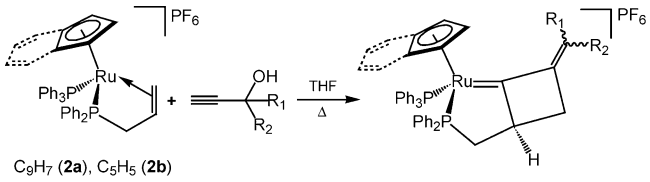
analytically and spectroscopically characterized (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR; see Experimental Section for details). ^{31}P{^{1}H} NMR spectra of these complexes show two doublet resonances at 36.6 and 44.1 ppm for **1** and at −69.8 and 52.5 ppm for **2b**, as expected for an AB system arising from the presence of the nonequivalent phosphines. The upfield shifting of the allyl phosphine resonance of **2b** with respect to that of **1** in the ^{31}P{^{1}H} NMR spectrum, along with the corresponding ^{1}H and ^{13}C{^{1}H} NMR resonances, confirm the coordination of the allyl group (see Experimental Section). All of these data can be compared to those reported for [Ru(η^5-C_5Me_5){κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}{κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}][PF_6][14] and for the analogous complexes [Ru(η^5-C_9H_7)Cl{κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)] and [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)][PF_6] (**2a**).[15]

The formation of complex **2b** is diastereoselective, as only one of the two diastereotopic faces of the κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$ ligand coordinates to the metal. Variable-temperature ^{31}P{^{1}H} NMR experiments reveal that there is no equilibrium between the two diastereoisomers within a wide temperature range (from −55 to 25 °C). The relatively large difference in geminal CH_2 chemical shifts in the ^{1}H NMR spectrum of **2b** (δ 2.86, 3.46 ppm) is consistent with a parallel orientation of the olefin with respect to the cyclopentadienyl ring[16] (**A** in Chart 2) and is in accordance with the orientation found in the X-ray structure of the analogous indenyl complex [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)][PF_6] (**2a**).[15]

Synthesis of [Ru(η^5-C_nH_m){κ^2(*P,C*)-{=C(CH(CH$_2$PPh$_2$)CH$_2$C=CR$_1$R$_2$}}(PPh$_3$)][PF$_6$] (C_nH_m = C_9H_7, R$_1$, R$_2$ = $C_{12}H_8$ (3a), R$_1$ = Ph, R$_2$ = Ph (3b), H (3c), Me (3d); C_nH_m = C_5H_5, R$_1$, R$_2$ = $C_{12}H_8$ (4a), R$_1$ = Ph, R$_2$ = Ph (4b), H (4c)). The treatment of complexes **2a**,**b** with a 10-fold excess of the corresponding propargyl alcohol in refluxing THF leads to the formation of the 2-ruthena-3-phosphabicyclo[3.2.0]hept-1(2)-ene complexes [Ru(η^5-C_nH_m){κ^2(*P,C*)-{=C(CH(CH$_2$-PPh$_2$)CH$_2$C=CR$_1$R$_2$}}(PPh_3)][PF_6] (C_nH_m = C_9H_7, R$_1$, R$_2$ = $C_{12}H_8$ (**3a**), R$_1$ = Ph, R$_2$ = Ph (**3b**), H (**3c**), Me (**3d**); C_nH_m = C_5H_5, R$_1$, R$_2$ = $C_{12}H_8$ (**4a**), R$_1$ = Ph, R$_2$ = Ph (**4b**), H (**4c**)) (Scheme 2).

Complexes **3a**−**d** and **4a**−**c** have been isolated as air-stable hexafluorophosphate salts (69−88%) which are soluble in THF and dichloromethane and insoluble in hexane. Elemental analyses and spectroscopic data (IR and the ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR; see Experimental Section) are in accordance with the proposed formulation. The most relevant features in the NMR spectra are (i) (^{31}P{^{1}H} NMR) two doublet resonances at δ 42.8−50.2 and 71.7−90.3 ppm due to the presence of the PPh_3 and allylphosphine phosphorus nuclei, respectively, (ii) (^{13}C{^{1}H} NMR) a doublet centered at δ 318.6−333.1 ppm (J_{CP} = 9.1−11.4 Hz) assigned to the carbene carbon, and (iii) the bridging sp^3 carbon resonance at δ 66.1−69.0 (J_{CP} = 15.3−20.3 Hz). The structure of complex **3a** has been confirmed by X-ray diffraction (see below).

Scheme 2



η^5-ring \ R$_1$, R$_2$	$C_{12}H_8$	Ph, Ph	Ph, H	Ph, Me
C_9H_7	**3a**	**3b**	**3c**	**3d**
C_5H_5	**4a**	**4b**	**4c**	

The stereochemistry of the exocyclic double bond has been determined through NOESY experiments performed on the complex [Ru(η^5-C_9H_7){κ^2(*P,C*)-{=CCH(CH$_2$PPh$_2$)CH$_2$C=C(Ph)Me}}(PPh_3)][PF_6] (**3d**). The cross-peak between the exocyclic methyl and the methylene protons indicates the spatial proximity of both groups, thus corroborating their cis disposition. The stereochemistry of the double bond in the case of derivatives **3c** and **4c** could not be established on the basis of NOESY experiments.

Complexes **3a**−**d** and **4a**−**c** are generated from a formal cycloaddition of the allylic C=C bond to the C_α=C_β bond of the metal allenylidene moiety, which is generated from complexes **2a**,**b** and the corresponding propargyl alcohol. The formation of an allenylidene intermediate complex is assessed by ^{31}P{^{1}H} NMR and IR spectroscopy, monitoring the reactions of **2a** with propargyl alcohols in CH_2Cl_2. The ^{31}P{^{1}H} NMR spectra of the reactions of **2a** with 9-ethynyl-9-fluorenol, 1-phenyl-2-propyn-1-ol, and 2-phenyl-3-butyn-2-ol recorded after 30 min show, in addition to the resonances of the starting material, two new doublet signals at δ 40.8, 51.0 (J_{PP} = 25.2 Hz), δ 32.6, 44.9 (J_{PP} = 24.4 Hz), and δ 40.7, 50.8 ppm (J_{PP} = 24.4 Hz), respectively. Similarly, an analogous resonance pattern (δ 36.9 and 44.9 ppm (J_{PP} = 28.5 Hz) and δ 38.9 and 49.3 ppm (J_{PP} = 28.5 Hz)) is observed after 2 h for the reaction of complex **2b** with 9-ethynyl-9-fluorenol and 1-phenyl-2-propyn-1-ol. The strong ν(C=C=C) absorption at 1900−1930 cm^{-1} in the IR spectra in CH_2Cl_2 confirm the transient formation of an allenylidene species. However, the attempts to isolate these allenylidene derivatives from the reaction mixture were unsuccessful, except for the reaction of **2a** with 1,1-diphenyl-2-propyn-1-ol (see below).

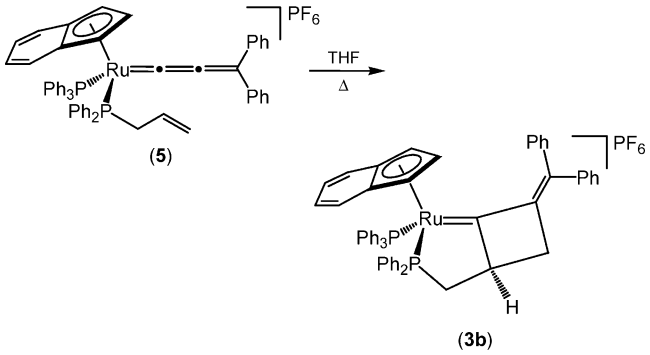
Synthesis of the Allenylidene [Ru(η^5-C_9H_7)(=C=C=CPh$_2$){κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)][PF_6] (5). The isolation of the allenylidene complex [Ru(η^5-C_9H_7)(=C=C=CPh$_2$){κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}-

(14) Barthel-Rosa, L. P.; Maitra, K.; Nelson, J. H. *Inorg. Chem.* **1998**, *37*, 633.
(15) Álvarez, P.; Lastra, E.; Gimeno, J.; Braña, P.; Sordo, J. A.; Gómez, J.; Falvello, L. R.; Bassetti, M. *Organometallics* **2004**, *23*, 2956.
(16) (a) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1989**, *122*, 1645. (b) Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *88*, 101. (c) Miguel-García, J. A.; Adams, H.; Maitlis, P. M. J. *J. Organomet. Chem.* **1991**, *413*, 427.

$(PPh_3)][PF_6]$ (**5**) has been achieved by reaction of **2a** with 1,1-diphenyl-2-propyn-1-ol in refluxing dichloromethane for 8 h.

Complex **5** has been isolated (83%) as a violet solid and characterized by elemental analysis and IR and NMR (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) spectroscopy. The following spectroscopic data are in accordance with the presence of the allenylidene chain. (i) The IR spectrum (CH_2Cl_2) shows the typical ν(=C=C=C) absorption at 1922 cm^{-1}. (ii) The $^{13}C\{^1H\}$ NMR spectrum[17] shows three low-field signals for the allenylidene carbon nuclei at δ 291.7 (C_α, J_{CP} = 18.3 Hz), 206.6 (C_β), and 155.6 ppm (C_γ). (iii) The $^{31}P\{^1H\}$ NMR spectrum shows two doublet resonances at δ 40.2 and 50.4 ppm (J_{PP} = 26.0 Hz) for the PPh_3 and the allylphosphine ligands, respectively. This is in accordance with the spectra shown by the transient formation of the allenylidene species (see above).

As expected, heating a solution of the allenylidene **5** in THF at reflux for 3.5 h leads to complex **3b** (eq 2). This fact confirms that the reaction of complexes **2a**,**b** with propargyl alcohols probably proceeds through the ring opening of the κ^3(*P,C,C*) allylphosphine chelate ring and formation of a cationic allenylidene intermediate. Further intramolecular regio- and diastereoselective [2 + 2] cycloaddition of the olefin double bond of the allylphosphine and the C_α=C_β double bond of the allenylidene chain gives rise to the final products **3a**−**d** and **4a**−**c**.



Deprotonation Reactions: Synthesis of [Ru(η^5-C_nH_m){κ^2(*P,C*)-{C=C(CH$_2$PPh$_2$)CH$_2$C=CR$_1$R$_2$}}-(PPh$_3$)] (C_nH_m = C$_9$H$_7$, R$_1$, R$_2$ = C$_{12}$H$_8$ (6a), R$_1$ = Ph, R$_2$ = Ph (6b), H (6c), Me (6d); C_nH_m = C$_5$H$_5$, R$_1$ = Ph, R$_2$ = H (7c)). The acidity of α-hydrocarbyl substituents of the carbene group has been widely studied and is a well-known property of electrophilic carbene complexes.[18] In this regard we have studied whether the C−H bridgehead group in complexes **3a**−**d** and **4c** could be deprotonated without affecting the entity of the carbocyclic ring. Thus, the treatment of complexes **3a**−**d** and **4c** with 1 equiv of NaO^{t}Bu in THF at room temperature gives the desired neutral complexes. The new 2-ruthena-3-phosphabicyclo-[3.2.0]hept-1(5)-ene complexes [Ru(η^5-C_nH_m){κ^2(*P,C*)-{C=C(CH$_2$PPh$_2$)CH$_2$C=CR$_1$R$_2$}}(PPh$_3$)] (C_nH_m = C$_9$H$_7$, R$_1$, R$_2$ = C$_{12}$H$_8$ (**6a**), R$_1$ = Ph, R$_2$ = Ph (**6b**), H (**6c**), Me (**6d**); C_nH_m = C$_5$H$_5$, R$_1$ = Ph, R$_2$ = H (**7c**)) result from the deprotonation of the CH group in the starting bicyclic alkylidene complexes (Scheme 3).

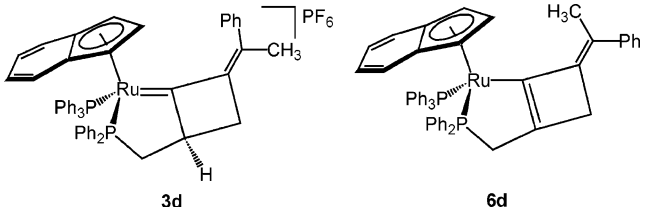
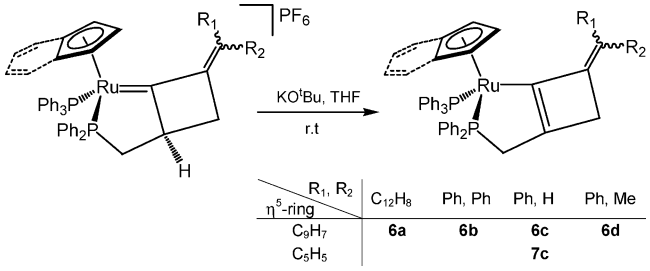


Figure 1.

Scheme 3



Complexes **6a**−**d** and **7c** are isolated (48−61%) as air-stable yellow solids. They are soluble in THF, CH_2Cl_2, and Et_2O and slightly soluble in hexane and pentane. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra are in accordance with the proposed structure. The most remarkable features of the spectroscopic data are as follows. (i) The $^{31}P\{^1H\}$ NMR spectra indicate the presence of the two phosphine ligands which appear as two doublet resonances in the ranges of δ 71.3−79.1 ppm (ADPP) and δ 56.4−59.3 ppm (PPh_3) for complexes **6a**−**d** and at δ 88.3 (ADPP) and 64.0 ppm (PPh_3) for the complex **7c**. (ii) The ^1H NMR spectra indicate the presence of the two CH_2 groups of the bicyclic ring and the absence of the CH proton. (iii) The absence of CH in the four-membered ring has been confirmed in the $^{13}C\{^1H\}$ NMR by DEPT experiments. The sp^2-C_α (δ 167.7−169.8 ppm for **6a**−**d** and δ 175.3 ppm for **7c**) was identified on the basis of HSQC and HMBC experiments.

To ascertain the stereochemistry of the exocyclic double bond,[19] an X-ray diffraction study (see below) has been performed on complex **6d**, which shows a trans arrangement of the methyl group (R_2 = Me) and the methylene group of the four-membered ring. This result is in sharp contrast with the cis arrangement observed for its precursor complex **3d** (Figure 1).

The change of the stereochemistry from **3d** to **6d** can be explained by assuming that complex **3d** is deprotonated not only at C2 (C_β-H) but also at allylic CH (either CH_2 or CH_3), allowing the isomerization to take place and thus leading to the thermodynamically more stable stereoisomer **6d**.

The acidic character of the hydrocarbyl groups in position α to an alkylidene group has been also shown in the alkynylalkylidene complex [Ru(η^5-C$_9$H$_7$){=C-(C≡CPh)CH$_2$Ph}(dppm)][BF$_4$], allowing its ready depro-

(17) Due to product decompositions during the experiment, the CH_2P could not be assigned, since a number of signals in the range 20−40 ppm appear over time.

(18) (a) Dotz, K. H.; Pfeiffer, J. *Transition Met. Org. Synth.* **1998**, *1*, 335. (b) Weyershausen, B.; Dotz, K. H. *Eur. J. Inorg. Chem.* **1999**, *17*, 1057.

(19) gNOESY experiments carried out for the derivative **6d** cannot determine the stereochemistry of the exocyclic double bond, since irradiation of the methyl group did not result in an enhancement of the signals of the CH_2 group of the cyclobutene.

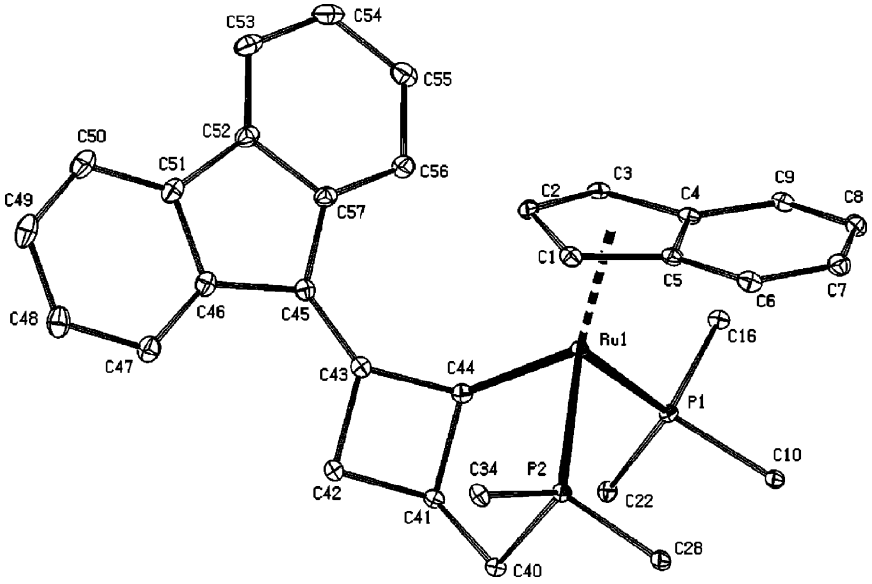


Figure 2. ORTEP type view of the molecular structure of the cation of the complex [Ru(η^5-C_9H_7){κ^2(*P,C*)-{=CCH-(CH_2PPh_2)CH_2C=$CC_{12}H_8$}}(PPh_3)][{3,5-(CF_3)$_2$$C_6H_3$}B] (**3a′**) drawn at the 10% probability level. Phenyl groups have been omitted for clarity. Only the C(ipso) atoms of the aryl groups are depicted.

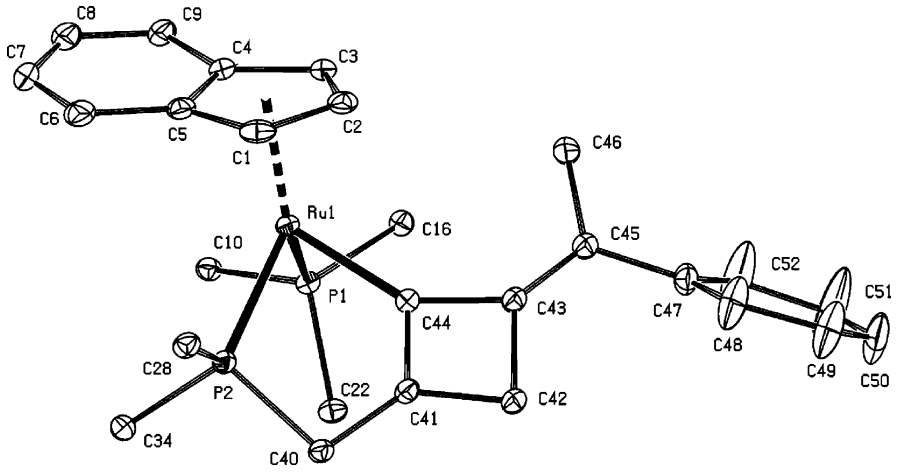


Figure 3. ORTEP type view of the molecular structure of the complex [Ru(η^5-C_9H_7){κ^2(*P,C*)-{C=C(CH_2PPh_2)CH_2C=C(Me)-Ph}}(PPh_3)]·OEt_2 (**6d**·OEt_2) drawn at the 10% probability level. Et_2O molecule and phenyl groups have been omitted for clarity. Only the C(ipso) atoms of the aryl groups are depicted.

tonation to form the alkenyl derivative [Ru{(*E*)-η^1-C-(C≡CPh)=CHPh}(η^5-C_9H_7)(dppm)].[20]

Crystal Structure of the Complexes [Ru(η^5-C_9H_7)-{κ^2(*P,C*)-{=CCH(CH_2PPh_2)CH_2C=$CC_{12}H_8$}}(PPh_3)]-[{3,5-(CF_3)$_2$$C_6H_3$}B] (3a′) and [Ru($\eta^5$-$C_9H_7$){$\kappa^2$(*P,C*)-{C=C($CH_2PPh_2$)$CH_2$C=C(Me)Ph}}($PPh_3$)] (6d). Slow diffusion of diethyl ether into a solution of **3a′** (obtained from **3a** via exchange of the hexafluorophosphate anion by the anion of Brookhart's salt[21]) in pentane allowed us to collect suitable crystals for X-ray diffraction studies. Crystals suitable for the X-ray study of **6d** were obtained from a diethyl ether/toluene solution of the complex. ORTEP type representations of the cation (**3a′**) and the molecule (**6d**) are shown in Figures 2 and 3, respectively, and selected bonding data are collected in Table 1.

Figure 2 illustrates the S_{Ru},S_C configuration of the cation of complex **3a′**, although both enantiomers are present in equal proportions in the crystal, which belongs to the centrosymmetric space group $P2_1/n$.

Both structures exhibit a three-legged piano-stool geometry, with the η^5-indenyl ligand displaying the usual allylene coordination mode. The benzo ring of the indenyl ligand is oriented trans to the metallacycle, slightly deviating over the triphenylphosphine ligand for **3a′**, as shown by the dihedral angle between the planes C*−C**−Ru and C*−Ru−P(1) of 47.59(2)° (**3a′**) and 67.14(2)° (**6d**).

The most remarkable feature in both cases is the presence of a metallaphosphabicycloheptene. For **3a′**, the bicycle contains a five-membered ruthenaphos-

(20) Bassetti, M.; Marini, S.; Díez, J.; Gamasa, M. P.; Gimeno, J.; Rodríguez-Álvarez, Y.; García-Granda, S. *Organometallics* **2002**, *21*, 4815.

(21) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 3a′ and 6d·OEt$_2$[a]

3a′		**6d**·OEt$_2$	
Bond Distances			
Ru(1)−C(44)	1.914(3)	Ru(1)−C(44)	2.049(3)
Ru(1)−C*	1.9720(2)	Ru(1)−C*	1.2036(57)
Ru(1)−P(1)	2.3639(6)	Ru(1)−P(1)	2.2974(9)
Ru(1)−P(2)	2.3191(6)	Ru(1)−P(2)	2.2998(9)
P(2)−C(40)	1.837(3)	P(2)−C(40)	1.859(3)
C(40)−C(41)	1.528(3)	C(40)−C(41)	1.479(5)
C(41)−C(44)	1.5468(3)	C(41)−C(44)	1.359(5)
C(41)−C(42)	1.555(3)	C(41)−C(42)	1.510(5)
C(43)−C(45)	1.354(4)	C(43)−C(45)	1.339(5)
C(43)−C(44)	1.482(3)	C(43)−C(44)	1.499(5)
Bond Angles			
C(44)−Ru(1)−P(2)	78.19(7)	C(44)−Ru(1)−P(2)	78.13(10)
P(2)−Ru(1)−P(1)	94.62(2)	P(2)−Ru(1)−P(1)	96.87(3)
P(1)−Ru(1)−C*	121.65(2)	P(1)−Ru(1)−C*	130.59(2)
P(2)−Ru(1)−C*	126.78(2)	P(2)−Ru(1)−C*	125.89(2)
C(44)−Ru(1)−C*	130.13(8)	C(44)−Ru(1)−C*	122.31(9)
C(41)−C(40)−P(2)	105.23(16)	C(41)−C(40)−P(2)	102.0(2)
C(40)−C(41)−C(42)	113.9(2)	C(40)−C(41)−C(42)	138.7(3)
C(44)−C(41)−C(42)	87.28(18)	C(44)−C(41)−C(42)	96.4(3)
C(43)−C(42)−C(41)	87.98(18)	C(43)−C(42)−C(41)	83.5(3)
C(44)−C(43)−C(42)	90.65(19)	C(44)−C(43)−C(42)	89.2(3)
C(43)−C(44)−C(41)	89.95(19)	C(43)−C(44)−C(41)	90.9(3)
C(41)−C(44)−Ru(1)	125.27(17)	C(41)−C(44)−Ru(1)	124.4(3)
C(40)−C(41)−C(42)	120.9(2)	C(40)−C(41)−C(42)	138.7(3)
C(45)−C(43)−C(44)	139.7(2)	C(45)−C(43)−C(44)	138.9(3)
C(45)−C(43)−C(42)	129.6(2)	C(45)−C(43)−C(42)	131.4(3)

[a] C* = centroid of C(1), C(2), C(3), C(4), C(5); C** = centroid of C(4), C(5), C(6), C(7), C(8), C(9).

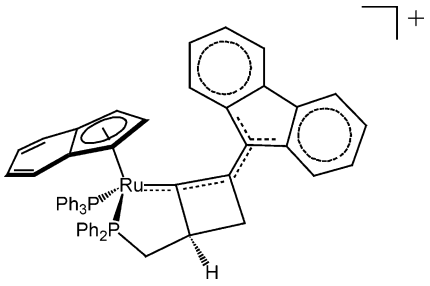


Figure 4.

phacycle fused to a four-membered ring with a dihedral angle of 117.68(8)°. In contrast, the two rings in complex **6d** are nearly coplanar with C(40) deviating 6.2° from planarity.

The bond length Ru−C(44) (1.914(3) Å) of the alkylidene **3a′** is longer than that found in typical ruthenium carbenes, such as the analogous alkylidene complex [Ru(η^5-C_9H_7){κ^2(*P,C*)-{=CC(Ph)HCH$_2$CHCH$_2$PPh$_2$}}(PPh$_3$)][BF$_4$][13] (1.864(5) Å), the vinylidene complex [Ru(η^5-C_9H_7)(=C=CMe$_2$)(PPh$_3$)$_2$][PF$_6$][22] (1.839(7) Å), and the allenylidene complex [Ru(η^5-C_9H_7)(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$][23] (1.878(5) Å). Moreover, the lengths of the single C(sp^2)−C(sp^2) bonds C(43)−C(44) (1.482(3) Å), C(45)−C(46) (1.482(4) Å), and C(45)−C(57) (1.475(4) Å) are shorter than that expected for a single C−C bond, while the C=C bond length C(43)−C(45) (1.354(4) Å) is rather longer than expected. These facts indicate an electronic delocalization along the metallapentadiene framework (Figure 4).

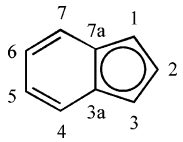
The Ru−C(44) bond length (2.049(3) Å) in complex **6d** is typical of a ruthenium−carbon single bond. Although the C(41)−C(44) (1.359(5) Å) and C(44)−C(43) (1.499(5) Å) bond lengths are longer and shorter, respectively, than those expected for C=C and C−C bonds, that of C(43)−C(45) (1.339(5) Å) is the length expected for a C=C double bond, indicating no electronic delocalization through the exocyclic double bond.

Conclusions

In summary, these reactions are, along with those of vinylidene complexes reported by us, the only examples that demonstrate the ability of cumulenylidene derivatives to undergo C−C coupling through [2 + 2] intramolecular cycloadditions with tethered C=C double bonds. The bicyclic systems thus obtained are stable, and no ring-opening reaction is observed. These cyclobutylidene complexes can be easily deprotonated, leading to very rare cyclobutenyl derivatives.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds [Ru(η^5-C_5H_5)Cl(PPh$_3$)$_2$],[24] [Ru(η^5-C_9H_7)Cl(PPh$_3$)$_2$],[25] [Ru(η^5-C_9H_7)Cl{κ^1(*P*)-Ph$_2$PCH$_2$CHCH$_2$}(PPh$_3$)],[26] [Ru(η^5-C_9H_7)Cl{κ^3(*P,C,C*)-Ph$_2$PCH$_2$CHCH$_2$}][PF$_6$)],[15] and Ph$_2$PCH$_2$CH=CH$_2$[27] were prepared by previously reported methods. Infrared spectra were recorded an a Perkin-Elmer 1720-XFT or a Perkin-Elmer 599 IR spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker AC200 instrument at 200 MHz (^{1}H), 81.0 MHz (^{31}P), or 50.3 MHz (^{13}C) and on Bruker AC300 and 300DPX instruments at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using SiMe$_4$ or 85% H_3PO_4 as standards. DEPT experiments were carried out for all the compounds. Coupling constants *J* are given in hertz. Abbreviations used: Ar, aromatic; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br, broad. The following atom labels have been used for the ^{1}H and ^{13}C{^{1}H} spectroscopic data:



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(24) Bruce, M. I.;. Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.

(25) Oro, L. A.; Ciriano, M. A.; Campo, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem*. **1989**, *289*, 177.

(26) The synthesis of [Ru(η^5-C_9H_7)Cl(κ^1(*P*)-Ph$_2$PCH$_2$CH=CH$_2$)(PPh$_3$)] is improved over the previously reported synthesis.[15] A solution of [Ru(η^5-C_9H_7)Cl(PPh$_3$)$_2$] (0.40 g, 0.52 mmol) and allyldiphenylphosphine (0.62 mmol, 1.2 equiv) in THF (35 mL) was refluxed for 10 min. The solution was concentrated to approximately 5 mL, and CuI (1.5 equiv) was added. After 25 min at room temperature the solution was evaporated to dryness and the residue was extracted with diethyl ether (2 × 20 mL). The product was precipitated with a mixture of Et$_2$O and hexane and vacuum-dried to afford a red solid. Yield: 0.327 g, 85%.

(27) Clark, P.; Curtis, J. L. S.; Garrou, P. E.; Hartewell, G. E. *Can. J. Chem*. **1974**, *52*, 1714.

Synthesis of [Ru(η^5-C_5H_5)Cl{κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}-(PPh_3)] (1). A solution of [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$] (0.73 g, 1 mmol) and allyldiphenylphosphine (1.5 mmol) in THF (40 mL) was refluxed for 30 min. The solution was evaporated to dryness to afford an orange solid, which was washed with hexane (2 × 20 mL) and vacuum-dried. Yield: 0.559 g, 81%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.76 (m, 1H, P−CH_2), 3.15 (m, 1H, P−CH_2), 4.13 (s, 5H, C_5H_5), 4.42 (d, J_{HH} = 17.1 Hz, 1H, =CH_2), 4.57 (d, J_{HH} = 10.0 Hz, 1H, =CH_2), 5.13 (m, 1H, =CH), 7.06−7.88 (m, 25H, Ar). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 36.6 (d, J_{PP} = 27.0 Hz), 44.1 (d, J_{PP} = 27.0 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 27.8 (d, J_{CP} = 18.1 Hz, P−CH_2), 80.7 (s, C_5H_5), 117.4 (s, =CH_2), 127.4−139.8 (m, Ar). Anal. Calcd for $C_{38}H_{35}ClP_2Ru$: C, 66.13; H, 5.11. Found: C, 65.01; H, 4.91.

Synthesis of [Ru(η^5-C_5H_5){κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}][PF_6)] (2b). To a solution of [Ru(η^5-C_5H_5)Cl{κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}(PPh_3)] (**1**; 0.69 g, 1 mmol) in EtOH (60 mL) was added $NaPF_6$ (0.24 g, 1.2 mmol). The resulting mixture was refluxed for 5 min and then was evaporated to dryness. The resulting solid was washed with diethyl ether and vacuum-dried to give **2b** as a pale yellow solid. Yield: 0.792 g, 99%. IR (KBr, ν(PF_6), cm^{-1}): 840. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 114. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.41 (m, 1H, P−CH_2), 2.86 (m, 1H, =CH_2), 3.46 (m, 1H, =CH_2), 4.38 (m, 1H, P−CH_2), 4.68 (br, 5H, C_5H_5), 4.79 (m, 1H, =CH), 7.00−7.81 (m, 25H, Ar). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ −69.8 (d, J_{PP} = 39.0 Hz, ADPP), 52.5 (d, J_{PP} = 39.0 Hz, PPh_3). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 30.7 (d, J_{CP} = 35.5 Hz, P−CH_2), 42.9 (d, J_{CP} = 22.1 Hz, =CH), 48.6 (s, =CH_2), 85.8 (s, C_5H_5), 127.8−137.3 (m, Ar). Anal. Calcd for $C_{38}H_{35}P_3F_6Ru{\cdot}CH_2Cl_2$: C, 52.95; H, 4.22. Found: C, 51.52; H, 4.12.

Synthesis of [Ru(η^5-C_nH_m){κ^2(*P,C*)-{=C$\overline{CH(CH_2PPh_2)-CH_2}$C=$CR_1R_2$}}($PPh_3$)][$PF_6$] ($C_nH_m$ = C_9H_7, R_1, R_2 = $C_{12}H_8$ (3a), R_1 = Ph, R_2 = Ph (3b), H (3c), Me (3d); C_nH_m = C_5H_5, R_1, R_2 = $C_{12}H_8$ (4a), R_1 = Ph, R_2 = Ph (4b), H (4c)). A solution of [Ru(η^5-C_nH_m){κ^3(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}][PF_6] (**2a**,**b**; 0.5 mmol) and the corresponding propargyl alcohol (5 mmol) in THF (85 mL) was refluxed until complete disappearance of the starting complex and the allenylidene intermediate (checked by ^{31}P{^{1}H} NMR). The solution was then evaporated to dryness and extracted with dicloromethane (2 × 20 mL). The residue was precipitated with a mixture of CH_2Cl_2/Et_2O, washed with diethyl ether, and vacuum-dried to afford **3a**−**d** and **4a**−**c** as brown solids.

C_nH_m = C_9H_7, R_1, R_2 = $C_{12}H_8$ (3a). Time: 4 h. Yield: 0.363 g, 70%. IR (KBr, ν(PF_6), cm^{-1}): 840. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 110. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (m, 1H, P−CH_2), 2.10 (m, 1H, P−CH_2), 2.60 (m, 1H, CH), 3.53 (m, 2H, CH_2), 4.81, 5.19, 6.15 (3 × s, H-1,2,3), 6.75−7.42 (m, 37H, Ar, H-4,5,6,7). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 42.8 (d, J_{PP} = 32.6 Hz, PPh_3), 72.4 (d, J_{PP} = 32.6 Hz, ADPP). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 31.7 (s, CH_2), 32.5 (d, J_{CP} = 30.7 Hz, P−CH_2), 69.0 (d, J_{CP} = 17.4 Hz, CH), 79.0 (d, J_{CP} = 7.2 Hz, C-1 or C-3), 86.6 (d, J_{CP} = 10.2 Hz, C-1 or C-3), 103.8 (s, C-2), 113.2 (s, C-3a, C-7a), 120.2−146.6 (m, Ar, C=C, C-4,5,6,7), 160.5 (s, C=C), 318.6 (d, J_{CP} = 10.2 Hz, Ru=C_α). Anal. Calcd for $C_{57}H_{45}P_3F_6Ru{\cdot}{}^1/_2CH_2Cl_2$: C, 63.92; H, 4.29. Found: C, 64.26; H, 3.38.

C_nH_m = C_9H_7, R_1 = R_2 = Ph (3b). Time: 6 h. Yield: 0.353 g, 68%; IR (KBr, ν(PF_6), cm^{-1}): 839. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 111. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.67 (m, 2H, P−CH_2), 2.43 (m, 1H, CH), 2.69 (m, 1H, CH_2), 2.81 (m, 1H, CH_2), 4.31, 5.22 (2 × s, H-1 or H-2 and/or H-3), 5.42 (d, 1H, J_{HH} = 8.25 Hz, H-4,5,6,7), 5.81 (s, 1H, H-1 or H-2 or H-3), 6.73−7.81 (m, 38H, Ar, H-4,5,6,7). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 44.8 (d, J_{PP} = 34.2 Hz, PPh_3), 71.7 (d, J_{PP} = 34.2 Hz, ADPP). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 33.5 (s, CH_2), 34.0 (d, J_{CP} = 31.5 Hz, P−CH_2), 67.0 (d, J_{CP} = 15.3 Hz, CH), 82.7 (d, J_{CP} = 7.1 Hz, C-1 or C-3), 83.1 (d, J_{CP} = 8.1 Hz, C-1 or C-3), 103.3 (s, C-2), 111.5 (s, C-3a, C-7a), 119.4−145.1 (m, Ar, C-4,5,6,7); 161.9, 162.6 (s, C=C), 325.2 (d, J_{CP} = 9.1 Hz, Ru=C_α). MS (FAB+): *m/z* 895 (M^+).

C_nH_m = C_9H_7, R_1 = Ph, R_2 = H (3c). Time: 1.5 h. Yield: 0.371 g, 77%. IR (KBr, ν(PF_6), cm^{-1}): 838. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 132. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.92 (m, 1H, CH), 2.16 (m, 1H, P−CH_2), 2.52 (m, 1H, P−CH_2), 3.55 (m, 1H, CH_2), 3.73 (m, 1H, CH_2), 4.52, 5.15 (2 × s, H-1 or H-2 and/or H-3), 5.36 (s, 1H, =CH), 6.36 (s, 1H, H-2), 6.52 (d, 1H, J_{HH} = 8.2 Hz, H-4,5,6,7), 6.85−7.85 (m, 33H, Ar, H-4,5,6,7). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 42.8 (d, J_{PP} = 32.6 Hz, PPh_3), 81.9 (d, J_{PP} = 32.6 Hz, ADPP). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 34.1 (d, J_{CP} = 32.5 Hz, P−CH_2), 34.9 (d, J_{CP} = 4.0 Hz, CH_2), 67.5 (d, J_{CP} = 20.3 Hz, CH), 81.4 (d, J_{CP} = 6.8 Hz, C-1 or C-3), 83.2 (d, J_{CP} = 8.1 Hz, C-1 or C-3), 100.2 (s, C-2), 112.1, 117.2 (s, C-3a, C-7a), 122.3−142.0 (m, =CH, Ar, C-4,5,6,7), 159.5 (s, *C*=CH), 327.2 (d, J_{CP} = 10.8 Hz, Ru=C_α). Anal. Calcd for $C_{51}H_{43}P_3F_6Ru$: C, 63.55; H, 4.50. Found: C, 63.13; H, 5.05.

C_nH_m = C_9H_7, R_1 = Ph, R_2 = Me (3d). Time: 2.5 h. Yield: 0.332 g, 68%. IR (KBr, ν(PF_6), cm^{-1}): 839. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 131. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.93 (m, 3H, P−CH_2, CH), 2.64 (s, 3H, CH_3), 3.20 (m, 2H, CH_2), 4.61, 4.89, 6.12 (3 × s, H-1,2,3), 6.70−7.84 (m, 34H, Ar, H-4,5,6,7). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 46.1 (d, J_{PP} = 32.1 Hz, PPh_3), 73.7 (d, J_{PP} = 32.1 Hz, ADPP). ^{13}C{^{1}H} NMR (200 MHz, CD_2Cl_2): δ 20.5 (s, CH_3), 33.8 (d, J_{CP} = 30.5 Hz, P−CH_2), 35.3 (s, CH_2), 68.1 (d, J_{CP} = 17.8 Hz, CH), 81.2 (d, J_{CP} = 7.6 Hz, C-1 or C-3), 84.8 (d, J_{CP} = 10.2 Hz, C-1 or C-3), 103.8 (s, C-2), 112.2 (s, C-3a, C-7a), 122.2−147.3 (m, Ar, C=C, C-4,5,6,7), 160.4 (s, C=C), 326.4 (d, J_{CP} = 11.4 Hz, Ru=C_α). MS (FAB+): *m/z* 833 (M^+). Anal. Calcd for $C_{52}H_{45}P_3F_6Ru{\cdot}1/2CH_2Cl_2$: C, 61.80; H, 4.54. Found: C, 62.62; H, 4.46.

C_nH_m = C_5H_5, R_1, R_2 = $C_{12}H_8$ (4a). Time: 2.5 h. Yield: 0.341 g, 69%. IR (KBr, ν(PF_6), cm^{-1}): 841. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 115. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71 (m, 1H, CH), 1.92 (m, 1H, P−CH_2), 2.04 (m, 1H, P−CH_2), 3.27 (m, 1H, CH_2), 3.56 (m, 1H, CH_2), 5.25 (s, 5H, C_5H_5), 6.60−7.88 (m, 33H, Ar). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 50.1 (d, J_{PP} = 32.6 Hz, PPh_3), 82.5 (d, J_{PP} = 32.6 Hz, ADPP). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 30.9 (s, CH_2), 32.5 (d, J_{CP} = 33.1 Hz, P−CH_2), 67.0 (d, J_{CP} = 16.5 Hz, CH), 94.4 (s, C_5H_5), 120.0−142.6 (m, Ar, C=C), 162.2 (s, C=C), 320.6 (d, J_{CP} = 10.2 Hz, Ru=C_α). MS (FAB+): *m/z* 843 (M^+).

C_nH_m = C_5H_5, R_1 = R_2 = Ph (4b). Time: 6 h. Yield: 0.336 g, 68%. IR (KBr, ν(PF_6), cm^{-1}): 839. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 125. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09 (m, 1H, CH), 2.36−2.92 (m, 4H, P−CH_2, CH_2), 4.75 (s, 5H, C_5H_5), 6.91−7.84 (m, 35H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 47.3 (d, J_{PP} = 33.3 Hz, PPh_3), 81.26 (d, J_{PP} = 33.3 Hz, ADPP). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ 34.1 (d, J_{CP} = 33.0 Hz, P−CH_2), 33.9 (s, CH_2), 66.4 (d, J_{CP} = 14.0 Hz, CH), 90.9 (s, C_5H_5), 126.3−145.2 (m, Ar, C=C), 162.3 (s, C=C), 328.1 (d, J_{CP} = 10.2 Hz, Ru=C_α).

C_nH_m = C_5H_5, R_1 = Ph, R_2 = H (4c). Time: 1.5 h. Yield: 0.311 g, 68%. IR (KBr, ν(PF_6), cm^{-1}): 839. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 114. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.83 (m, 1H, CH), 2.22 (m, 1H, P−CH_2), 2.66 (m, 1H, P−CH_2), 3.53 (m, 1H, CH_2), 3.83 (m, 1H, CH_2), 5.12 (s, 6H, C_5H_5, =CH), 6.61−7.83 (m, 30H, Ar). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 50.2 (d, J_{PP} = 32.6 Hz, PPh_3), 90.3 (d, J_{PP} = 32.6 Hz, ADPP). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 34.5 (d, J_{CP} = 5.1 Hz, CH_2), 35.6 (d, J_{CP} = 32.3 Hz, P−CH_2), 66.1 (d, J_{CP} = 17.9 Hz, CH), 91.83 (s, C_5H_5), 126.1−143.1 (m, =CH, Ar), 159.9 (s, *C*=CH), 333.1 (d, J_{CP} = 10.2 Hz, Ru=C_α). MS (FAB+): *m/z* 769 (M^+).

Synthesis of [Ru(η^5-C_9H_7)(=C=C=CPh_2)(PPh_3){κ^1(*P*)-$Ph_2PCH_2CH{=}CH_2$}][PF_6] (5). A solution of the complex [Ru(η^5-C_9H_7)Cl{κ^3-(*P,C,C*)-$Ph_2PCH_2CH{=}CH_2$}][PF_6] (**2a**; 0.5 g,

0.5 mmol) and 1,1-diphenyl-2-propyn-1-ol (1.04 g, 5 mmol) in CH_2Cl_2 (40 mL) was refluxed for 8 h and then was evaporated to dryness. The resulting solid was washed with diethyl ether and vacumm-dried to give **5** as a violet solid. Yield: 0.431 g, 83%. IR (KBr, ν(Ru=C=C=C), $\nu(PF_6)$, cm^{-1}): 1922, 840. Conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 123. ^1H NMR (300 MHz, CD_2Cl_2): δ 2.02 (m, 1H, P−CH_2), 2.70 (m, 1H, P−CH_2), 4.35 (d, 1H, J_{HH} = 15.2 Hz, =CH_2), 4.67 (d, 1H, J_{HH} = 10.1 Hz, =CH_2), 4.82 (m, 1H, =CH), 4.92 (m, 1H, H-2), 5.21, 5.72 (2 × s, H-1,3), 6.86−7.75 (m, 39H, Ar, H-4,5,6,7). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 40.2 (d, J_{PP} = 26.0 Hz), 50.4 (d, J_{PP} = 26.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 86.5, 87.6 (s, C-1, C-3), 96.5 (s, C-2), 109.7 (d, J_{CP} = 3.1 Hz, C-3a or C-7a), 112.9 (d, J_{CP} = 4.1 Hz, C-3a or C-7a), 120.3 (d, J_{CP} = 10.2 Hz, =CH_2), 123.3−145.7 (m, Ar, C-4,5,6,7), 155.6 (s, C_γ), 206.6 (s, C_β), 291.7 (t, J_{CP} = 18.3 Hz, Ru=C_α). MS (FAB+): *m/z* 895 (M^+). Anal. Calcd for $C_{57}H_{47}P_3F_6Ru\cdot{}^1/_2CH_2Cl_2$: C, 63.80; H, 4.47. Found: C, 64.27; H, 4.28.

Synthesis of [Ru(η^5-C_9H_7){κ^2(*P,C*)-{=C$\overline{CH(CH_2PPh_2)\text{-}CH_2}$C=$CPh_2$}}(PPh$_3$)][$PF_6$] (3b) from [Ru($\eta^5$-$C_9H_7$)(=C=C=$CPh_2$)(PPh$_3$){$\kappa^1$(*P*)-$Ph_2PCH_2CH$=$CH_2$}][$PF_6$] (5). A solution of [Ru(η^5-C_9H_7)(=C=C=CPh_2)(PPh$_3$){κ^1(*P*)-Ph_2PCH_2-CH=CH_2}][PF_6] (**5**; 0.208 g. 0.2 mmol) in THF (35 mL) was refluxed for 3.5 h and then was evaporated to dryness. The residue was washed with diethyl ether and vacuum-dried to afford **3b** as a brown solid. Yield: 0,133 g, 64%.

Synthesis of [Ru(η^5-C_nH_m){κ^2(*P,C*)-{C=C$\overline{(CH_2PPh_2)\text{-}CH_2}$C=$CR_1R_2$}}(PPh$_3$)] ($C_nH_m$ = C_9H_7, R_1 , R_2 = $C_{12}H_8$ (6a), R_1 = Ph, R_2 = Ph (6b), H (6c), Me (6d); C_nH_m = C_5H_5, R_1 = Ph, R_2 = H (7c)). To a solution of the complexes **3a**−**d** and **4c** (0.5 mmol) in THF (85 mL) was added KO^{t}Bu (0.561 g, 0.5 mmol). The mixture was stirred for 1 h at room temperature and then was evaporated to dryness. The residue was extracted with diethyl ether, precipitated with a mixture of CH_2Cl_2/hexane, washed with hexane (2 × 20 mL) and vacuum-dried to afford complexes **6a**−**d** and **7c** as yellow solids.

C_nH_m = C_9H_7, R_1, R_2 = $C_{12}H_8$ (6a). Yield: 0.259 g, 58%. ^1H NMR (300 MHz, CD_2Cl_2): δ 0.92 (m, 1H, P−CH_2), 2.17 (m, 1H, P−CH_2), 3.76 (s, 1H, H-1 or H-2 or H-3), 3.93 (m, 1H, CH_2), 4.42 (m, 1H, CH_2), 5.20, 5.57 (2 × s, H-1 or H-2 and/or H-3), 6.61−7.99 (m, 37H, Ar, H-4,5,6,7). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 56.4 (d, J_{PP} = 25.2 Hz, PPh_3), 71.3 (d, J_{PP} = 25.2 Hz, ADPP). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 31.7 (d, J_{CP} = 24.4 Hz, P−CH_2), 41.6 (d, J_{CP} = 18.3 Hz, CH_2), 70.3 (d, J_{CP} = 10.8 Hz, C-1 or C-3), 76.1 (d, J_{CP} = 11.2 Hz, C-1 or C-3), 94.9 (s, C-2), 106.6, 108.3 (s, C-3a, C-7a), 117.7−146.1 (m, Ar, C=C, C-4,5,6,7), 157.2 (s, C=C), 168.1 (d, J_{CP} = 14.2 Hz, Ru−*C*=C), 169.1 (d, J_{CP} = 25.4 Hz, Ru−C=*C*). Anal. Calcd for $C_{57}H_{45}P_2Ru\cdot{}^1/_2CH_2Cl_2$: C, 73.83; H, 4.96. Found: C, 73.85; H, 4.18.

C_nH_m = C_9H_7, R_1 = R_2 = Ph (6b). Yield: 0.273 g, 61%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.75 (d, 1H, J_{HH} = 17.1 Hz, P−CH_2), 2.01 (m, 1H, P−CH_2), 3.14 (m, 1H, CH_2), 3.63 (s, 1H, H-1 or H-2 or H-3), 3.73 (m, 1H, CH_2), 4.09, 4.75 (2 × s, H-1 or H-2 and/or H-3), 6.78−7.64 (m, 39H, Ar, H-4,5,6,7). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 58.4 (d, J_{PP} = 27.9 Hz, PPh_3), 73.7 (d, J_{PP} = 27.9 Hz, ADPP). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 32.6 (d, J_{CP} = 27.5 Hz, P−CH_2), 42.2 (d, J_{CP} = 17.1 Hz, CH_2), 72.9 (d, J_{CP} = 9.5 Hz, C-1 or C-3), 73.7 (d, J_{CP} = 10.4 Hz, C-1 or C-3), 95.6 (s, C-2), 107.3, 110.2 (s, C-3a, C-7a), 123.2−145.6 (m, Ar, C=C, C-4,5,6,7), 164.6 (d, J_{CP} = 23.7 Hz, Ru−C=*C*), 167.7 (d, J_{CP} = 15.2 Hz, Ru-*C*=C). Anal. Calcd. for $C_{57}H_{47}P_2Ru$: C, 76.49; H, 5.29. Found: C, 75.96; H, 6.20.

C_nH_m = C_9H_7, R_1 = Ph, R_2 = H (6c). Yield: 0.221 g, 54%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (d, J_{HH} = 17.1 Hz, 1H, P−CH_2), 2.24 (m, 1H, P−CH_2), 3.51 (m, 1H, CH_2), 3.75 (br, 1H, H-1 or H-3), 3.95 (m, 1H, CH_2), 4.73 (s, 1H, H-1 or H-3), 5.96 (s, 1H, H-2), 6.25 (s, 1H, =CH), 6.49 (d, 1H, J_{HH} = 8.3 Hz, H-4,5,6,7), 6.86−7.73 (m, 33H, Ar, H-4,5,6,7). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 59.3 (d, J_{PP} = 30.3 Hz, PPh_3), 79.1 (d, J_{PP} = 30.3 Hz, ADPP). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 32.1 (d, J_{CP} = 29.5 Hz, P−CH_2), 40.6 (d, J_{CP} = 16.3 Hz, CH_2), 69.9 (d, J_{CP} = 10.2 Hz, C-1 or C-3), 73.4 (d, J_{CP} = 10.2 Hz, C-1 or C-3), 89.8 (s, C-2), 105.6, 107.4 (s, C-3a, C-7a), 110.4 (s, =CH), 121.1−153.6 (m, Ar, *C*=CH, C-4,5,6,7), 160.3 (dd, J_{CP} = 32.5 Hz, J_{CP} = 3.2 Hz, Ru−C=*C*), 169.8 (dd, J_{CP} = 16.3 Hz, J_{CP} = 3.1 Hz, Ru−*C*=C). MS (FAB+): *m/z* 819 (M^+).

C_nH_m = C_9H_7, R_1 = Ph, R_2 = Me (6d). Yield: 0.200 g, 48%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.97 (m, 1H, P−CH_2), 1.92 (s, 3H, CH_3), 2.27 (m, 1H, P−CH_2), 3.33 (d, 1H, J_{HH} = 12.2 Hz, CH_2), 3.61 (s, 1H, H-1 or H-3), 3.81 (m, 1H, CH_2), 4.81 (s, 1H, H-1 or H-3), 5.65 (s, 1H, H-2), 6.83−7.75 (m, 34H, Ar, H-4,5,6,7). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 58.1 (d, J_{PP} = 26.7 Hz, PPh_3), 73.4 (d, J_{PP} = 26.7 Hz, ADPP). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 16.1 (s, CH_3), 32.2 (d, J_{CP} = 27.5 Hz, P−CH_2), 41.3 (d, J_{CP} = 17.3 Hz, CH_2), 73.12 (d, J_{CP} = 12.0 Hz, C-1 or C-3), 74.7 (d, J_{CP} = 11.2 Hz, C-1 or C-3), 96.1 (s, C-2), 111.8, 116.3 (s, C-3a, C-7a), 122.1−138.8 (m, Ar, C=C, C-4,5,6,7), 161.0 (dd, J_{CP} = 26.5 Hz, J_{CP} = 3.1 Hz, Ru−C=*C*), 168.2 (d, J_{CP} = 17.3 Hz, Ru−*C*=C). MS (FAB+): *m/z* 832 (M^+).

C_nH_m = C_5H_5, R_1 = Ph, R_2 = H (7c). Yield: 0.230 g, 60%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.42 (m, 1H, P−CH_2), 2.34 (m, 1H, P−CH_2), 3.60 (m, 1H, CH_2), 3.94 (m, 1H, CH_2), 4.61 (s, 5H, C_5H_5), 6.17 (1H, =CH), 6.98−7.73 (m, 30H, Ar). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 64.0 (d, J_{PP} = 39.6 Hz, PPh_3), 88.3 (d, J_{PP} = 39.6 Hz, ADPP). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 35.0 (d, J_{CP} = 29.5 Hz, P−CH_2), 42.0 (d, J_{CP} = 17.3 Hz, CH_2), 81.7 (s, C_5H_5), 111.3 (s, =CH), 125.0−147.7 (m, Ar), 155.6 (s, *C*=CH), 162.1 (dd, J_{CP} = 27.5 Hz, J_{CP} = 3.0 Hz, Ru−C=*C*), 175.3 (dd, J_{CP} = 17.3 Hz, J_{CP} = 5.1 Hz, Ru−*C*=C). MS (FAB+): *m/z* 779 (M^+ + 1).

Synthesis of [Ru(η^5-C_9H_7){κ^2(*P,C*)-{=C$\overline{CH(CH_2PPh_2)\text{-}CH_2}$C=C($C_{12}H_8$)}}(PPh$_3$)][{3,5-$(CF_3)_2C_6H_3$}$_4$B] (3a′). To a solution of **3a** (0.104 g, 0.1 mmol) in THF (10 mL) was added $[Na]^+[[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ (0.443 g, 0.5 mmol). The mixture was stirred for 2 h at room temperature and then was evaporated to dryness. The residue was extracted with dichloromethane and vacuum-dried.

X-ray Diffraction Study of 3a′ and 6d·OEt$_2$. The crystals were obtained by slow diffusion of diethyl ether into a saturated solution of **3a′** in pentane and from a saturated solution of **6d** in a mixture of diethyl ether and toluene (1:2). Crystallographic details are reported in Table 2.

Single crystals of **3a′** and **6d**·OEt_2 of appropriate dimensions with prismatic shapes were mounted on a glass fiber and transferred to a Bruker SMART 6K CCD[28] area-detector three-circle diffractometer with a MAC Science Co., Ltd. rotating anode (Cu Kα radiation, λ = 1.541 78 Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data were collected at 100 and 296 K, respectively, with a combination of six runs at different φ and 2θ angles. The data were collected using 0.3° wide ω scans (3 s/frame at 2θ = 40° and 10 s/frame at 2θ = 100°) and a crystal-to-detector distance of 40 mm for **3a′** and 0.3° wide ω scans (30 s/frame at 2θ = 40° and 90 s/frame at 2θ = 100°) and a crystal-to-detector distance of 40 mm for **6d**.

The substantial redundancy in data allows empirical absorption corrections[29] to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission: 0.688 027 for **3a′** and for **6d**). The unit cell parameters were obtained by full-matrix least-squares refinements of 7510 and 9668 reflections, respectively. The raw intensity data frames were integrated with

(28) SMART v. 5.625, Area-Detector Software Package; Bruker AXS, Madison, WI, 1997−2001.

(29) Sheldrick, G. M. SADABS, Version 2.03, a Program for Empirical Absorption Correction; Universität Göttingen, Göttingen, Germany, 1997−2001.

Table 2. Crystal Data and Structure Refinement Details for 3a′ and 6d·OEt$_2$

	3a′	**6d**·OEt$_2$
chem formula	$C_{94}H_{69}BF_{24}P_2Ru$	$C_{56}H_{54}OP_2Ru$
fw	1828.31	906.00
T (K)	100(2)	296(2)
wavelength (Å)	1.541 84	1.541 84
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	13.28880(10)	11.4352(3)
b (Å)	24.3673(2)	13.0419(4)
c (Å)	25.4806(2)	17.6182(5)
α (deg)	90	68.8050(10)
β (deg)	99.0630(10)	89.9420(10)
γ (deg)	90	71.1490(10)
V (Å^3)	8147.92(11)	2298.33(11)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.490	1.309
μ (mm^{-1})	2.835	3.710
F(000)	3712	944
cryst size (mm)	0.30 × 0.13 × 0.13	0.16 × 0.10 × 0.08
θ range (deg)	2.52−70.62	2.71−62.52
index ranges	$-13 \le h \le 15$ $-29 \le k \le 27$ $-27 \le l \le 30$	$-11 \le h \le 13$ $-14 \le k \le 14$ $-19 \le l \le 19$
no. of rflns collected	51 860	11 803
no. of unique rflns	14 685 (R(int) = 0.0293)	6211 (R(int) = 0.0324)
completeness to θ_{max}, %	94.0	84.8
no. of params/restraints	1329/0	544/0
goodness of fit on F^2	1.036	1.018
weight function (a, b)	0.0546, 13.5440	0.0694, 0.1691
R1[a] ($I > 2\sigma(I)$)	0.0410	0.0372
wR2[a] ($I > 2\sigma(I)$)	0.1064	0.1000
R1 (all data)	0.0423	0.0421
wR2 (all data)	0.1074	0.1040
largest diff peak and hole (e Å^{-3})	1.973 and −0.812	0.617 and −0.362

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

the SAINT program,[30] which also applied corrections for Lorentz and polarization effects.

The software package WINGX[31] was used for space group determination, structure solution, and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods[32] for **3a′** and by Patterson interpretation and phase expansion using DIRDIF[33] for **6d**, completed with difference Fourier syntheses, and refined with full-matrix least squares using[34] SHELXL-97 minimizing $w(F_o^2 - F_c^2)^2$. The functions minimized are shown in Table 2. Weighted R factors (R_w) and all goodness-of-fit values S are based on F^2, and conventional R factors (R) are based on F.

Atomic scattering factors were taken from ref 35. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by difference maps and refined isotropically for **3a′**. The coordinates of hydrogen atoms were geometrically located and refined riding with common isotropic thermal parameters for **6d**.

The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ($a = 0.0546$ and $b = 13.5440$ for **3a′**; $a = 0.0694$ and $b = 0.1691$ for **6d**) with $\sigma(F_o^2)$ from counting statistics and $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

Geometrical calculations were made with PARST.[36] The crystallographic plots were made with PLATON.[37]

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Supporting Information Available: Tables giving crystallographic data for **3a′** and **6d**·OEt$_2$; data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 263190 (**3a′**) and 263191 (**6d**·OEt$_2$). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (internat.) (+44)1223/336-033; e-mail deposit@ccdc.cam.ac.uk).

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