Selective Synthesis of Indenylruthenium(II) Vinylvinylidene Complexes *via* Unstable Allenylidene Intermediates: Unexpected Formation of Alkenyl−Phosphonio Complexes (*E*)-[Ru{C(H)=C(PPh$_3$)R}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = 1-Cyclohexenyl, 1-Cycloheptenyl) through Nucleophilic Addition of Triphenylphosphine on Vinylvinylidene Derivatives

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The vinylvinylidene complexes [Ru{=C=C(H)C=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)L$_2$][PF$_6$] (L = PPh$_3$, L$_2$ = 1,2-bis(diphenylphosphino)ethane (dppe); n = 1 (**2a**,**b**), 2 (**3a**,**b**), 3 (**4a**,**b**)) have been prepared by reaction of [RuCl(η^5-C$_9$H$_7$)L$_2$] with 1-ethynyl-1-cycloalkanols and NaPF$_6$ in refluxing methanol. Deprotonation of the vinylidene derivatives with Al$_2$O$_3$ yields the neutral enynyl complexes [Ru{C≡CC=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)L$_2$] (**5a**,**b**, **6a**,**b**, and **7a**,**b**). The reaction of the enynyl complex [Ru(C≡CR)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (R = 1-cyclohexenyl; **6a**) with MeOSO$_2$CF$_3$ produces the disubstituted vinylvinylidene derivative [Ru{=C=C(Me)R}-(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][CF$_3$SO$_3$] (R = 1-cyclohexenyl; **8a**). The crystal structure of **8a** was determined by X-ray diffraction methods. In the structure the Ru=C=C chain is nearly linear (Ru−C(1)−C(2) = 176.2(4)°) with an Ru−C(1) distance of 1.838(5) Å. The indenyl ligand is η^5-bonded to the metal with the benzo ring orientated "*trans*" with respect to the vinylidene group. When the reaction of [RuCl(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] with 1-ethynylcyclohexanol or 1-ethynylcyclopentanol and NaPF$_6$ takes place in the presence of PPh$_3$, the alkynyl−phosphonio complexes [Ru{C≡CC(PPh$_3$)CH$_2$CH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (n = 1 (**11a**), 2 (**12a**)) were obtained *via* nucleophilic attack of the PPh$_3$ on C$_\gamma$ of the unstable allenylidene complexes [Ru{=C=C=CCH$_2$CH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (n = 1 (**9a**), 2 (**10a**)). The vinylvinylidene complexes **3a** (n = 2) and **4a** (n = 3) also react with PPh$_3$, giving the alkenyl−phosphonio complexes (*E*)-[Ru{C(H)=C(PPh$_3$)C=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (n = 2 (**13a**), 3 (**14a**)). The structure of **13a** was confirmed by X-ray diffraction methods. A possible mechanism for the formation of **13a** and **14a** is proposed.

Introduction

During the last decade, the chemistry of ruthenium(II) vinylidene complexes [Ru]$^+$=C=CR$_2$ has experienced important developments due to the discovery of general synthetic methodologies[1] and their involvement in selective catalytic transformations of terminal alkynes.[2] In contrast, the chemistry of allenylidene analogs [Ru]$^+$=C=C=CR$_2$ has been less developed[1] and the potential utility of such types of derivatives in chemical transformations has not yet been exploited.[3] So far, the most general route to ruthenium(II) allenylidene complexes was that reported for the first time by Selegue.[4] The process is based on the direct activation of propargyl alcohols with ruthenium(II) chloride complexes (Scheme 1), and involves the formation of hydroxyvinylidene **A**,[5] through an initial chloride elimination, followed by the

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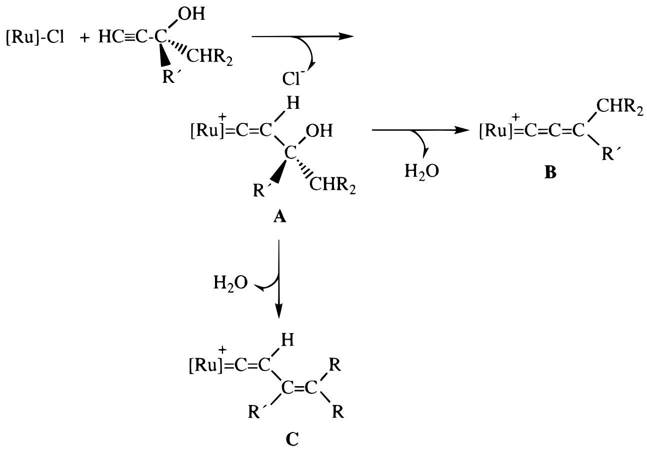
(2) (a) Trost, B. M. *Chem. Ber.* **1996**, *129*, 1313 and references cited therein. (b) Höfer, J.; Doucet, H.; Bruneau, C; Dixneuf, P. H. *Tetrahedron Lett.* **1991**, *32*, 7409. (c) Doucet, H.; Höfer, J.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 850. (d) Rappert, T.; Yamamoto, A. *Organometallics* **1994**, *13*, 4984. (e) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616. (f) Doucet, H.; Martín-Vaca, B. M.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247. (g) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968. (h) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.
(3) The first example of the involvement of ruthenium allenylidene species in catalysis have been reported for coupling of 2-propyn-1-ol derivatives with allylic alcohols in the presence of the [RuCl(η^5-C$_5$H$_5$)-(PPh$_3$)$_2$] catalyst: Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476.
(4) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

Scheme 1



spontaneous dehydration of the acidic vinylidene proton to give the allenylidene complexes **B**.

However, the dehydration of hydroxyvinylidene species **A**, containing hydrogen atoms adjacent to the hydroxy group, can occur in a different way to give vinylvinylidene derivatives **C**.[6a,b] The fate of the dehydration reaction clearly depends on the electronic properties of the metal auxiliary and the nature of the propargyl alcohol substituents. This alternative process shows the synthetic limitations of this well-established methodology.

We have recently reported the synthesis of novel ruthenium(II) allenylidene complexes *via* the activation of aromatic propargyl alcohols with the indenyl derivatives $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ ($L_2 = 2PPh_3$, 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm)).[5d] Furthermore, we have also reported that the allenylidene complexes $[Ru({=}C{=}C{=}CRR')(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = Ph, R′ = Ph, H; R = R′ = H) are excellent building blocks for the preparation of organometallic derivatives containing polyunsaturated chains.[7]

Continuing with these studies, we report herein the synthesis of stable indenylruthenium(II) vinylvinylidene complexes by activation of 1-ethynyl-1-cycloalkanols with $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ ($L_2 = 2PPh_3$, dppe). It is also shown that the formation of these vinylidene derivatives involves the initial formation of unstable allenylidene species which rapidly undergo a tautomerization to the most thermodynamically stable vinylvinylidene complexes. Part of this work has been previously communicated.[8]

(5) Ruthenium hydroxyvinylidene derivatives have been isolated: (a) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132. (b) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030. (c) Braun, T.; Steinert, P.; Werner, H. *J. Organomet. Chem.* **1995**, *488*, 169. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.

(6) (a) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972. (b) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. (c) We have recently reported similar results using indenylosmium and tricarbonyltungsten derivatives: Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1996**, 2547. Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R. J.; López-Ortiz, F.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1996**, *15*, 4274.

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Results and Discussion

Synthesis of Vinylvinylidene Complexes. The reaction of complexes $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ ($L_2 = 2PPh_3$ (**1a**), dppe (**1b**)) with 1-ethynyl-1-cycloalkanols in refluxing methanol and in the presence of $NaPF_6$ and $MgSO_4$ results in the formation of vinylvinylidene complexes **2a**,**b**, **3a**,**b**, and **4a**,**b**, which have been isolated as brown air-stable hexafluorophosphate salts (56−89% yield) (Scheme 2). No isomeric allenylidene species are detected even when the reactions are carried out at room temperature.[6c]

All the complexes **2**−**4** are soluble in chlorinated solvents and tetrahydrofuran. They have been characterized by microanalysis, conductance measurements, and IR and NMR (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) spectroscopy (details are given in the Experimental Section and Tables 1 and 2). Conductivity data (in acetone) show that the complexes are 1:1 electrolytes, and the IR spectra (KBr) exhibit the expected absorption for the hexafluorophosphate anion $[PF_6]^-$ (see Experimental Section). Absorption bands which appear in the range 1600−1700 cm^{-1} could be tentatively assigned to ν(C═C) of the vinylidene group, but they are in general overlapped by those of the phosphines, and consequently, the assignment is uncertain.

The $^{31}P\{^1H\}$ NMR spectra of all the vinylvinylidene complexes show, at room temperature, a single resonance (Table 1). The chemical equivalence of the phosphorus atoms is consistent with a rapid rotation of the vinylidene group around the Ru═C bond on the NMR time scale, which is in agreement with the data reported for other indenylruthenium(II) vinylidene complexes.[9] Proton and $^{13}C\{^1H\}$ NMR spectra exhibit resonances for aromatic, indenyl, methylene ($(CH_2)_2P_2$), and cyclopentenyl (**2a**,**b**), cyclohexenyl (**3a**,**b**), or cycloheptenyl (**4a**,**b**) moieties (Tables 1 and 2), in accordance with the proposed structures. The resonance of the vinylidene hydrogen appears as a singlet in the range δ 4.03−5.31 ppm. The $^{13}C\{^1H\}$ NMR spectra show a low-field triplet signal for the carbenic C_α atom, due to the coupling with the two equivalent phosphorus atoms (δ 337.88−358.33 ppm, $^2J_{CP}$ = 14.4−17.4 Hz). This typical low-field resonance has been explained as a consequence of a paramagnetic σ_P term rather than of an electron deficiency.[10] The C_β atom appears as a singlet at δ 112.81−123.63.

Indenyl carbon resonances (Table 2) have also been assigned, and they are in accordance with the proposed η^5 coordination.[11] As has been proven previously, the parameter $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)) can be used as an indication of the indenyl distortion.[12] The calculated values

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Scheme 2

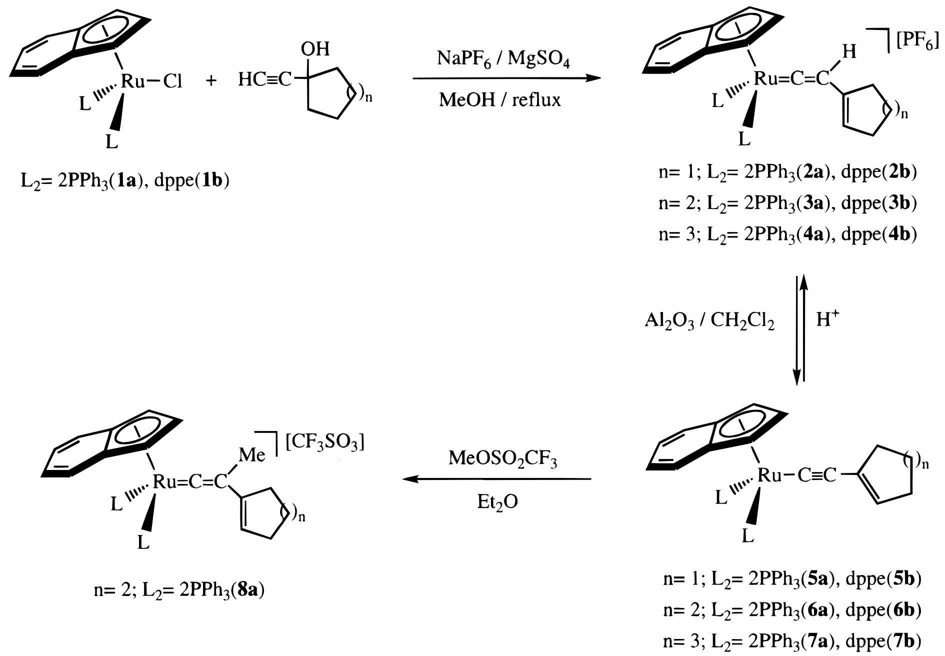
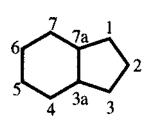


Table 1. $^{31}P\{^1H\}$ and ^1H NMR Data for the Vinylvinylidene Complexes[a]

		^1H							
		η^5-C_9H_7[f]							
complex	$^{31}P\{^1H\}$	H-1,3	H-2	J_{HH}	H-4,7, H-5,6	Ru=C=CH	=CH	J_{HH}	others
2a[b]	37.80 s	5.55 d	5.85 t	2.6	5.91 m[d]	5.31 s	5.08 bs		1.73 (m, CH_2); 1.94 (m, CH_2); 2.44 (m, CH_2); 6.86−7.49 (m, PPh_3)
3a[c]	37.55 s	5.50 d	5.79 t	2.7	5.85 m[d]	4.81 s	5.37 bs		1.41 (m, 2 CH_2); 1.64 (m, CH_2); 2.14 (m, CH_2); 6.78−7.52 (m, PPh_3)
4a[c]	37.67 s	5.53 d	5.74 t	2.6	5.99 m[d]	4.90 s	5.49 t	6.7	1.29 (m, CH_2); 1.42 (m, CH_2); 1.63 (m, CH_2); 1.93 (m, CH_2); 2.21 (m, CH_2); 6.81−7.50 (m, PPh_3)
2b[b]	73.53 s	5.83 d	5.94 t	2.7	*d*	4.42 s	4.97 bs		1.57 (m, CH_2); 1.91 (m, CH_2); 2.23 (m, CH_2); 2.33 and 2.73 (m, $P(CH_2)_2P$); 6.70−7.58 (m, PPh_2)
3b[c]	78.78 s	5.79 d	5.88 t	2.7	*d*	4.03 s	4.90 bs		0.81 (m, CH_2); 1.12 (m, CH_2); 1.25 (m, CH_2); 1.89 (m, CH_2); 2.32 and 2.69 (m, $P(CH_2)_2P$); 6.65−7.53 (m, PPh_2)
4b[c]	73.41 s	*e*	*e*	*e*	6.30 m[d]	4.10 s	5.01 t	5.9	0.99 (m, CH_2); 1.15 (m, CH_2); 1.28 (m, CH_2); 1.51 (m, CH_2); 1.90 (m, CH_2); 2.39 and 2.69 (m, $P(CH_2)_2P$); 6.73−7.53 (m, PPh_2)

[a] δ in ppm and J in Hz. Abbreviations: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet. [b] Spectra recorded in CD_2Cl_2. [c] Spectra recorded in $CDCl_3$. [d] Overlapped by PPh_3 or PPh_2 protons. [e] 5.84 ppm (m, H-1,3 and H-2). [f] Legend for indenyl skeleton:



for the vinylvinylidene complexes, which are in the range *ca.* −13 to −18 ppm, can be compared to that of $[Ru(=C=CR_2)(\eta^5\text{-}C_9H_7)L_2]^+$ [9] and are indicative of a moderate distortion of the η^5-indenyl coordination.

Synthesis of Enynyl Complexes. The efficient access to the cationic vinylvinylidene derivatives allowed the synthesis of enynylruthenium derivatives through deprotonation reactions to be explored. Thus, complexes **2**−**4** are readily deprotonated by treatment with an excess of Al_2O_3 in dichloromethane at room temperature, to give the orange enynyl complexes **5a**,**b**, **6a**,**b**, and **7a**,**b** (84−97% yield) (Scheme 2). These deprotonations are reversible, since the addition of 1 equiv of $HBF_4{\cdot}Et_2O$ in diethyl ether at room temperature to the enynyl complexes give selectively the parent vinylvinylidene derivatives. Complexes **5**−**7** were analytically and spectroscopically characterized (see Tables 3 and 4 and Experimental Section). In particular, IR spectra exhibit the expected ν(C≡C) absorption band in the range 2051−2069 cm^{-1} and $^{13}C\{^1H\}$ NMR spectra display characteristic triplet resonances at δ 104.47−113.98 ppm ($^2J_{CP}$ = 24.5−25.8 Hz) for the Ru−C≡ carbon nucleus. The C_β resonance appears as a singlet in the range δ 109.77−118.20 ppm. Indenyl carbon resonances (Table 4) have also been assigned, and the calculated values for the parameter $\Delta\delta$(C-3a,7a), which are in the range *ca.* −20 to −25 ppm, are indicative of a nondistorted η^5-indenyl coordination.[12]

Synthesis and Molecular Structure of the Complex $[Ru\{=C=C(Me)R\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][CF_3SO_3]$ (R = Cyclohexenyl; 8a). Alkynyl complexes can be used as suitable precursors of methyl-substituted vinylidene complexes through electrophilic additions of methyl groups.[1] Thus, the reaction of **6a** with $MeOSO_2CF_3$ in Et_2O leads to the formation of the disubstituted vinyl-

(16) Borge, J.; García-Granda, S. Unpublished results.

Table 2. $^{13}C\{^1H\}$ NMR Data for the Vinylvinylidene Complexes[a]

	η^5-C_9H_7										
complex	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3a,7a)[b]	C-4,7, C-5,6	Ru=C$_\alpha$	$^2J_{CP}$	C$_\beta$	=CH	=C	others
2a	83.26	99.28	116.33	−14.37	123.65, 130.52	355.65 t	16.4	115.28	126.67	127.90	24.27, 32.41, and 35.57 (s, CH_2); 128.80−134.37 (m, PPh_3)
3a	83.19	99.74	116.80	−13.90	124.01[c]	355.36 t	16.5	121.58	124.14	124.84	22.56, 23.39, 26.38, and 30.49 (s, CH_2); 129.15−134.45 (m, PPh_3)
4a	83.29	99.45	116.23	−14.47	123.74, 130.70	340.26 t	15.1	123.63	128.17	*c*	26.92, 27.75, 28.97, 32.52, and 34.59 (s, CH_2); 129.06−134.06 (m, PPh_3)
2b	78.76	98.61	113.40	−17.30	123.67, 125.89	358.33 t	16.5	112.81	*c*	*c*	23.70, 32.48, and 33.89 (s, CH_2); 26.33 (m, $P(CH_2)_2P$); 128.99−134.32 (m, PPh_2)
3b	78.59	98.46	113.25	−17.45	122.53[c]	358.21 t	14.4	119.07	121.81	123.33	21.90, 22.85, 25.77, and 28.09 (s, CH_2); 26.20 (m, $P(CH_2)_2P$); 127.20−134.75 (m, PPh_2)
4b	79.29	98.45	113.26	−17.44	123.77[c]	337.88 t	17.4	121.30	126.50	*c*	26.81, 27.51, 28.57, 32.41, and 32.53 (s, CH_2); 26.40 (m, $P(CH_2)_2P$); 129.53−134.21 (m, PPh_2)

[a] Spectra recorded in CD_2Cl_2; δ in ppm and J in Hz. Abbreviations: s, singlet; t, triplet; m, multiplet. [b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] Overlapped by PPh_3 or PPh_2 carbons.

Table 3. $^{31}P\{^1H\}$ and ^1H NMR Data for the Enynyl Complexes[a]

		^1H						
		η^5-C_9H_7						
complex	$^{31}P\{^1H\}$	H-1,3	H-2	J_{HH}	H-4,7, H-5,6	=CH	J_{HH}	others
5a	51.98 s	4.71 d	5.83 t	2.2	6.30 m, 6.66 m	5.64 t	2.5	1.92 (m, CH_2); 2.57 (m, 2 CH_2); 6.90−7.52 (m, PPh_3)
6a	52.35 s	4.95 d	5.83 t	2.1	6.58 m, 6.92 m	6.25 bs		1.90 (m, 2 CH_2); 2.49 (m, CH_2); 2.64 (m, CH_2); 7.18−7.74 (m, PPh_3)
7a	52.33 s	4.69 d	5.58 t	2.2	6.36 m, 6.66 m	6.20 t	6.8	1.60 (m, 2 CH_2); 1.75 (m, CH_2); 2.29 (m, CH_2); 2.54 (m, CH_2); 6.91−7.49 (m, PPh_3)
5b	87.67 s	5.27 d	5.42 t	2.5	7.10 m[b]	5.51 bs		1.92 (m, CH_2); 2.34 (m, CH_2); 2.54 (m, CH_2); 2.10 and 2.69 (m, $P(CH_2)_2P$); 7.25−7.89 (m, PPh_2)
6b	87.98 s	5.27 d	5.41 t	2.7	7.13 m[b]	5.65 t	1.7	1.67 (m, 2 CH_2); 2.08 (m, CH_2); 2.23 (m, CH_2); 2.70 (m, $P(CH_2)_2P$); 7.26−7.90 (m, PPh_2)
7b	87.60 s	5.28 d	5.42 t	2.5	7.11 m[b]	5.84 t	6.8	1.63 (m, 2 CH_2); 1.83 (m, CH_2); 2.27 (m, 2 CH_2); 2.09 and 2.70 (m, $P(CH_2)_2P$); 7.26−7.89 (m, PPh_2)

[a] Spectra recorded in C_6D_6; δ in ppm and J in Hz. Abbreviations: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet. [b] Overlapped by PPh_3 or PPh_2 protons.

Table 4. $^{13}C\{^1H\}$ NMR Data for the Enynyl Complexes[a]

	η^5-C_9H_7										
complex	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3a,7a)[b]	C-4,7, C-5,6	Ru−C$_\alpha$	$^2J_{CP}$	C$_\beta$	=CH	=C	others
5a	74.89[c]	95.70	109.37	−21.33	123.09, 125.87	110.41 t	24.9	111.63	125.36	131.33	24.00, 33.03, and 38.29 (s, CH_2); 127.29−139.18 (m, PPh_3)
6a	75.54	96.29	109.94	−20.76	123.41, 126.22	104.47 t	24.5	117.22	124.39	*d*	23.42, 23.68, 26.88, and 32.61 (s, CH_2); 126.87−139.55 (m, PPh_3)
7a	74.85	95.55	109.27	−21.43	123.09, 125.82	104.86 t	25.1	118.20	*d*	133.66	27.54, 28.55, 29.32, 33.55, and 36.69 (s, CH_2); 127.34−139.27 (m, PPh_3)
5b	70.75	93.27	108.62	−22.08	124.48, 124.95	113.98 t	25.0	109.77	125.83	131.91	24.41, 33.41, and 38.55 (s, CH_2); 28.85 (m, $P(CH_2)_2P$); 128.21−142.89 (m, PPh_2)
6b	68.64	91.17	106.59	−24.11	122.37, 122.93	105.25 t	25.8	112.82	122.14	125.05	21.38, 22.10, 24.55, and 30.05 (s, CH_2); 26.84 (m, $P(CH_2)_2P$); 126.87−139.55 (m, PPh_2)
7b	68.63	91.15	106.52	−24.18	122.34, 122.88	106.00 t	25.5	114.58	*d*	131.92	25.86, 26.69, 27.68, 31.88, and 34.91 (s, CH_2); 26.71 (m, $P(CH_2)_2P$); 126.31−140.76 (m, PPh_2)

[a] Spectra recorded in C_6D_6; δ in ppm and J in Hz. Abbreviations: s, singlet; t, triplet; m, multiplet. [b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] t, $^2J_{CP}$ = 3.4. [d] Overlapped by PPh_3 or PPh_2 carbons.

vinylidene complex **8a**, which has been isolated as an insoluble solid from the reaction mixture (Scheme 2).

The spectroscopic properties of **8a** are similar to those of the monosubstituted vinylvinylidene complex **3a**. Significantly, NMR spectra show the expected proton and carbon resonances of the methyl group at δ 1.50 (^1H NMR) and δ 10.38 ($^{13}C\{^1H\}$ NMR), respectively. The $^{13}C\{^1H\}$ NMR spectra also show the carbenic C$_\alpha$ resonance at δ 352.77 (t, $^2J_{CP}$ = 17.7 Hz). It is noteworthy that the C$_\beta$ resonance appears at a field lower than that of the monosubstituted species, a shift which is also observed in the spectra of similar derivatives.[9]

We have previously reported that the orientation of the benzo ring of the indenyl ligand in indenylruthe-

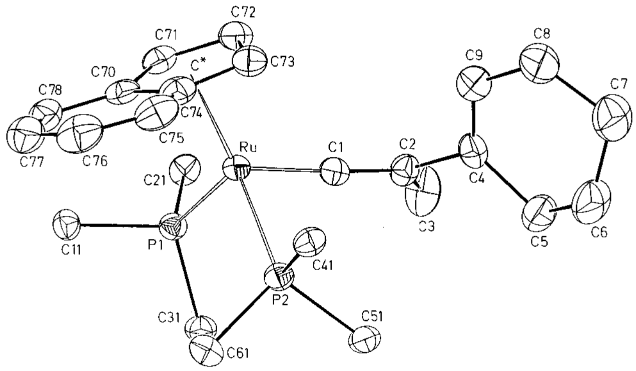


Figure 1. View of the structure of the vinylvinylidene complex [Ru{=C=C(Me)R}(η^5-C_9H_7)(PPh_3)$_2$]$^+$ (R = 1-cyclohexenyl; **8a**). For clarity, aryl groups of the triphenylphosphine ligands are omitted (C* = centroid of the indenyl ring).

Table 5. Selected Bond Distances and Slip Parameter Δ[a] (Å) and Bond Angles and Dihedral Angles FA,[b] HA,[c] DA,[d] and CA[e] (deg) for Complex 8a

Distances			
Ru−C*	1.970(9)	P(2)−C(61)	1.830(5)
Ru−P(1)	2.373(1)	Ru−C(1)	1.838(5)
Ru−P(2)	2.353(1)	C(1)−C(2)	1.299(6)
Ru−C(70)	2.423(5)	C(2)−C(3)	1.501(7)
Ru−C(71)	2.237(5)	C(2)−C(4)	1.513(7)
Ru−C(72)	2.216(5)	C(4)−C(5)	1.509(7)
Ru−C(73)	2.246(5)	C(4)−C(9)	1.316(7)
Ru−C(74)	2.456(5)	C(5)−C(6)	1.503(8)
P(1)−C(11)	1.834(5)	C(6)−C(7)	1.475(8)
P(1)−C(21)	1.834(5)	C(7)−C(8)	1.513(8)
P(1)−C(31)	1.849(5)	C(8)−C(9)	1.500(8)
P(2)−C(41)	1.839(5)	Δ	0.198(5)
P(2)−C(51)	1.839(5)		
Angles			
C*−Ru−C(1)	121.9(2)	C(2)−C(4)−C(9)	121.6(5)
C*−Ru−P(1)	117.1(2)	C(2)−C(4)−C(5)	115.9(4)
C*−Ru−P(2)	124.9(2)	C(4)−C(2)−C(3)	118.2(4)
C(1)−Ru−P(1)	94.5(2)	C(4)−C(9)−C(8)	123.1(5)
C(1)−Ru−P(2)	87.3(1)	C(9)−C(4)−C(5)	122.5(5)
P(1)−Ru−P(2)	103.9(1)	C(9)−C(8)−C(7)	122.9(5)
Ru−C(1)−C(2)	176.2(4)	C(8)−C(7)−C(6)	111.9(5)
C(1)−C(2)−C(3)	123.1(5)	C(7)−C(6)−C(5)	112.3(6)
C(1)−C(2)−C(4)	118.6(5)	C(6)−C(5)−C(4)	112.1(5)
FA	12.2(4)	HA	7.5(4)
DA	118.1(5)	CA	160.0(3)

[a] Δ = *d*(Ru−C(74),C(70)) − *d*(Ru−C(71),C(73)). [b] FA (fold angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(70), C(74), C(75), C(76), C(77), C(78). [c] HA (hinge angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(71), C(74), C(70), C(73). [d] DA (dihedral angle) = angle between normals to least-squares planes defined by C*, Ru, C(1) and C(1), C(2), C(3). [e] CA (conformational angle) = angle between normals to least-squares planes defined by C**, C*, Ru and C*, Ru, C(1). C* = centroid of C(70), C(71), C(72), C(73), C(74). C** = centroid of C(70), C(74), C(75), C(76), C(77), C(78).

nium(II) alkynyl, vinylidene and allenylidene complexes depends on the nature of the unsaturated chain.[5d,9] In order to find out this orientation in the vinylvinylidene complexes, the structure of complex **8a** has been determined by X-ray diffraction. The molecular structure is shown in Figure 1 and consists of [Ru{=C=C(Me)R}(η^5-C_9H_7)(PPh_3)$_2$]$^+$ (R = 1-cyclohexenyl) cations and triflate anions. Selected bond distances and angles are listed in Table 5. The molecule exhibits the usual allylene structure of the η^5-indenyl ligand in the pseudooctahedral three-legged piano-stool geometry. The interligand angles P(1)−Ru−P(2), C(1)−Ru−P(1), and C(1)−Ru−P(2) and those between the centroid C* and the legs show values typical of a pseudooctahedron. The vinylidene ligand is bound to Ru with an Ru−C(1) distance of 1.838(5) Å, a C(1)−C(2) distance of 1.299(6) Å, and a Ru−C(1)−C(2) angle of 176.2(4)°. These bonding parameters can be compared to those reported for other ruthenium vinylidene complexes (Table 6). The dihedral angle DA between the pseudo mirror plane of the metallic moiety (containing the Ru atom, the C(1) atom, and the centroid C* of the five-carbon ring of the indenyl ligand) and the mean vinylidene plane (containing the C(1), C(2), C(3), and C(4) atoms) is 118.1(5)°, showing a deviation from the orthogonal relationship calculated by theoretical studies.[17] Typical deviations of this relationship are also observed in other vinylidene complexes. The C(4)−C(9) bond length (1.316(7) Å) shows a value typical of a C=C bond.

Although the indenyl group is η^5-bonded to ruthenium, the structure shows moderate distortions of the five-carbon ring from planarity, which are similar to those shown by analogous vinylidene derivatives (see Tables 5 and 7). The moderate distortions toward an η^3 binding mode in the solid state appear to be maintained in solution, according to the value Δδ(C-3a,7a) = −13.75 obtained from the $^{13}C\{^1H\}$ NMR spectra. As has been also observed for the indenyl vinylidene complexes [Ru(=C=CMe$_2$)(η^5-C_9H_7)(PPh_3)$_2$]$^+$ [9] and [Ru{=C=C(H)Ph}(η^5-C_9H_7)(PPh_3)$_2$]$^+$,[16] the preferred conformation of the indenyl ligand is such that the benzo ring is oriented *trans* to the vinylidene group. However, their C(1) and C(2) atoms are not contained in the mirror plane of the indenyl ring (Figure 1), showing a conformational angle (CA) (Table 5) of 160.0(3)°. The preferred *trans* conformation for the vinylidene derivatives can be rationalized on the basis of theoretical calculations (EHMO), which predict that the *trans* orientation (CA = 180°) is energetically more favored than the *cis* (CA = 0°).[9] It is noteworthy that the *cis* orientation is preferred to the *trans* in indenylruthenium(II) allenylidene complexes (Table 7).[5d]

Synthesis of Alkynyl−Phosphonio Complexes. The complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$] reacts with the propargyl alcohols 1-ethynyl-1-cyclopentanol and 1-ethynyl-1-cyclohexanol to afford, in the presence of an excess of triphenylphosphine, the alkynyl−phosphonio derivatives **11a** (73%) and **12a** (61%) (Scheme 3). Analytical and spectroscopic data (IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR) are in accordance with the proposed formulations. The IR spectra show the typical ν(C≡C) and ν(PF_6^-) absorptions (see Experimental Section for details), and the $^{31}P\{^1H\}$ NMR spectra exhibit resonances consistent with an A_2M system (**11a**, δ 28.85 (t, $^5J_{PP}$ = 3.8 Hz, C−PPh$_3$), 49.34 (d, $^5J_{PP}$ = 3.8 Hz, Ru−PPh$_3$); **12a**, δ 25.42 (t, $^5J_{PP}$ = 3.9 Hz, C−PPh$_3$), 49.02 (d, $^5J_{PP}$ = 3.9 Hz, Ru−PPh$_3$)), also in accordance with the spectra shown by similar alkynyl−phosphonio complexes.[7] The presence of the alkynyl group is confirmed by the $^{13}C\{^1H\}$ NMR spectra, which show multiplet resonances at δ 112.15 (**11a**) and 113.19 (**12a**), assigned to the C_α nuclei. This seems to indicate an effective coupling of these nuclei with the two equivalent phosphorus atoms bonded to the metal and also with that of the alkynyl group. C_β and C_γ resonances appear as doublets at δ 103.84−107.12 ($^2J_{CP}$ = 3.5−6.8 Hz) and δ 44.22−44.96 (J_{CP} = 45.3−49.0 Hz), respectively.

(17) (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Kostic, N. M.; Fenske, R. J. *Organometallics* **1982**, *1*, 974.

Table 6. Comparative Structural Data for $[Ru]^{+}{=}C{=}CRR'$ Complexes

[Ru]	R	R'	Ru−C(1) (Å)	C(1)−C(2) (Å)	Ru−C(1)−C(2) (deg)	ref
$Ru(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2$	H	H	1.843(1)	1.287(1)	174.1(8)	13
$Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2$	H	C_6H_9[a]	1.843(7)	1.30(1)	178.2	6a
$Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2$	H	Me	1.845(7)	1.313(1)	180(2)	14
$Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2$	Me	Ph	1.86(1)	1.29(2)	173	15
$Ru(\eta^5\text{-}C_5Me_5)(PMe_2Ph)_2$	H	Ph	1.76(1)	1.34(2)	174(1)	5b
$Ru(\eta^5\text{-}C_5Me_5)(PMe_2Ph)_2$	H	CHMeOMe	1.854(8)	1.29(1)	174(6)	5b
$Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2$	Me	Me	1.839(7)	1.30(1)	173.7(6)	9
$Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2$	H	Ph	1.821(5)	1.270(7)	179.1(5)	16
$Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2$	Me	C_6H_9[a]	1.838(5)	1.299(6)	176.2(4)	*b*
$RuCl(dppm)_2$	H	H	1.882(8)	1.22(1)	178.3(8)	5a

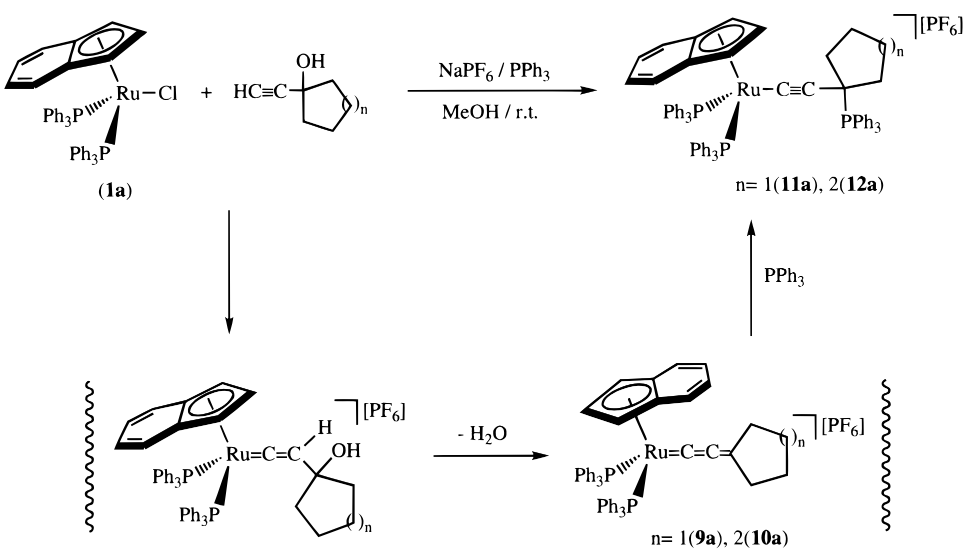
[a] C_6H_9= cyclohexenyl. [b] This work.

Table 7. Slip Parameter Δ and Dihedral Angles FA, HA, and CA for Indenyl Complexes[a]

complex	M−C* (Å)	Δ (Å)	FA (deg)	HA (deg)	CA (deg)	ref
$[\{Ru\}({=}C{=}CMe_2)]^+$	1.97(9)	0.197(7)	13.1(6)	8.1(6)	157.8(4)	9
$[\{Ru\}({=}C{=}C(H)Ph)]^+$	1.964(6)	0.175(6)	11.9(5)	6.6(5)	164.6(3)	16
$[\{Ru\}({=}C{=}C(Me)(C_6H_9))]^{+}$[b]	1.970(9)	0.1974(1)	12.2(4)	7.5(4)	160.0(3)	*c*
$[\{Ru\}({=}C{=}C{=}C(C_{13}H_{20}))]^+$	1.942(5)	0.0820(4)	5.1(5)	5.3(5)	12.2(6)	8
$[\{Ru\}({=}C{=}C{=}CPh_2)]^+$	1.951(5)	0.1211(4)	8.1(3)	6.2(4)	9.6(3)	5d
$[\{Os\}({=}C{=}C{=}CPh_2)]^+$	1.950(5)	0.095(4)	7.9(3)	5.3(3)	9.4(2)	5d
$(E)\text{-}[\{Ru\}(C(H){=}C(PPh_3)(C_6H_9))]^{+}$[b]	1.981(5)	0.217(5)	14.8(4)	8.4(4)	160.5(2)	*c*

[a] $\Delta = d[M-C(74),C(70)] - d[M-C(71),C(73)]$. FA = C(71),C(72),C(73)/C(70),C(74),C(75),C(76),C(77),C(78). HA = C(71),C(72),C(73)/C(71),C(74),C(70),C(73). CA = C**,C*,M/C*,M,C(1). {M} = $M(\eta^5\text{-}C_9H_7)(PPh_3)_2$ (M = Ru, Os). [b] C_6H_9 = cyclohexenyl. [c] This work.

Scheme 3



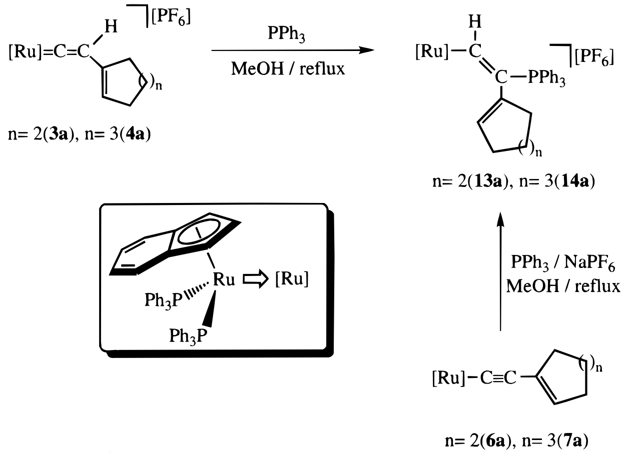
As has been mentioned above, the activation of 1-ethynyl-1-cycloalkanols to give either allenylidene or vinylvinylidene species (see Scheme 1) leads regioselectively to vinylvinylidene complexes. We have reported that alkynyl−phosphonio complexes can be readily prepared through the regioselective nucleophilic addition of phosphines to the C_γ atom of the allenylidene chain.[7] On the basis of this synthetic approach the formation of **11a** and **12a** may be understood assuming that allenylidene intermediates **9a** and **10a** are formed as transient species which undergo a rapid nucleophilic addition of triphenylphosphine to the electrophilic C_γ atom. This seems to indicate that the allenylidene species are kinetically controlled products, since in the absence of PPh_3 the more stable tautomeric vinylvinylidene complexes **2**−**4** are formed. It is noteworthy to mention that although the reaction has taken place in methanol as a solvent no addition of methanol or water to the C_α atom of the allenylidene chain has occurred.[18] This behavior is in accordance with the inertness of the similar indenylruthenium(II) allenylidene complexes $[Ru({=}C{=}C{=}CRR')(\eta^5\text{-}C_9H_7)L_2][PF_6]$ (R = R′ = Ph, L = PPh_3, L_2 = dppe, dppm; RR′ = $C_{13}H_{20}$, L = PPh_3), all of them exhibiting an efficient protection of the C_α atom due to the preferred *cis* orientation of the indenyl group with respect to the allenylidene chain.[5d,8]

Attempts to obtain the corresponding alkynyl-phosphonio complex with 1-ethynyl-1-cycloheptanol as the starting material have failed, giving instead the vinylvinylidene complex **7a**. The more sterically demanding cycloheptyl group compared to the cyclopentyl or cyclohexyl group seems to prevent the triphenylphosphine addition to the corresponding allenylidene intermediate.

Synthesis of Alkenyl−Phosphonio Complexes. Since cationic vinylvinylidene complexes **2**−**4** are suitable substrates to study the nature and positions of the electrophilic sites, we became interested in studying the reactivity of these complexes toward phosphines. In particular, we expected to obtain information on the regioselectivity of the nucleophilic additions in order to

(18) Ruthenium(II) cyclohexylallenylidene complexes have been trapped by addition of methanol or water to yield alkenyl−carbene derivatives: (a) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809. (b) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

Scheme 4



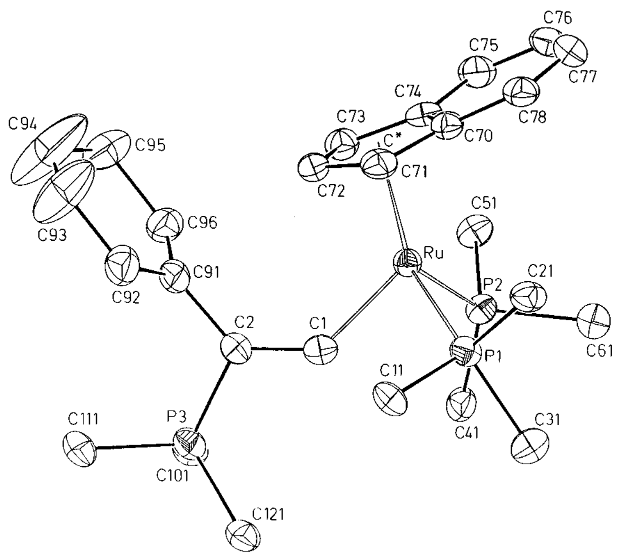


Figure 2. View of the structure of the alkenyl−phosphonio complex (*E*)-[Ru{C(H)=C(PPh$_3$)R}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ (R = 1-cyclohexenyl; **13a**). For clarity, aryl groups of the triphenylphosphine ligands are omitted (C* = centroid of the indenyl ring).

compare their reactivity to that of the tautomeric allenylidene moieties. However, the reactions follow a different path.

Thus, compounds **3a** and **4a** react with a large excess of triphenylphosphine, in refluxing methanol, to yield the alkenyl−phosphonio derivatives **13a** (72%) and **14a** (79%), respectively (Scheme 4). Since analytical and spectroscopic data did not allow the structure to be established unequivocally, an X-ray structural determination was carried out for complex **13a**.

Crystals of **13a** suitable for X-ray diffraction analysis were obtained from a CH$_2$Cl$_2$/Et$_2$O solution. The crystal structure consists of (*E*)-[Ru{C(H)=C(PPh$_3$)R}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ (R = 1-cyclohexenyl) cations, hexafluorophosphate anions, and CH$_2$Cl$_2$ and Et$_2$O molecules of crystallization (CH$_2$Cl$_2$/Et$_2$O/solvate). A view of the molecular structure is shown in Figure 2, and selected bond distances and bond angles are listed in Table 8. The geometry of the [Ru(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] moiety is similar to that found in the vinylvinylidene complex **8a**, showing also a *trans* orientation of the indenyl ligand with respect to the alkenyl moiety (CA = 160.5(2)°).

The most remarkable feature is the presence of a planar alkenyl−phosphonio fragment in which the phosphine is bonded to the C$_\beta$ atom of the alkenyl group

Table 8. Selected Bond Distances and Slip Parameter Δ[a] (Å) and Bond Angles and Dihedral Angles FA,[b] HA,[c] DA,[d] and CA[e] (deg) for Complex 13a

Distances			
Ru−C*	1.981(5)	Ru−C(1)	2.045(6)
Ru−P(1)	2.327(2)	C(1)−C(2)	1.371(7)
Ru−P(2)	2.349(2)	C(2)−C(91)	1.499(7)
Ru−C(70)	2.465(5)	C(91)−C(96)	1.356(8)
Ru−C(71)	2.239(5)	C(91)−C(92)	1.482(8)
Ru−C(72)	2.205(2)	C(92)−C(93)	1.483(9)
Ru−C(73)	2.240(5)	C(93)−C(94)	1.34(1)
Ru−C(74)	2.447(5)	C(94)−C(95)	1.44(1)
P(1)−C(11)	1.838(6)	C(95)−C(96)	1.497(8)
P(1)−C(21)	1.845(5)	C(2)−P(3)	1.790(6)
P(1)−C(31)	1.852(5)	P(3)−C(101)	1.808(5)
P(2)−C(41)	1.855(6)	P(3)−C(111)	1.819(6)
P(2)−C(51)	1.830(5)	P(3)−C(121)	1.799(6)
P(2)−C(61)	1.836(6)	Δ	0.217(5)
Angles			
C*−Ru−C(1)	124.3	C(2)−P(3)−C(101)	109.9(2)
C*−Ru−P(1)	121.8(2)	C(2)−P(3)−C(111)	113.1(3)
C*−Ru−P(2)	123.0(2)	C(2)−P(3)−C(121)	112.0(2)
C(1)−Ru−P(1)	89.6(2)	C(2)−C(91)−C(96)	120.6(5)
C(1)−Ru−P(2)	89.2(2)	C(2)−C(91)−C(92)	117.9(5)
P(1)−Ru−P(2)	100.23(6)	C(91)−C(92)−C(93)	115.2(6)
Ru−C(1)−C(2)	135.9(4)	C(92)−C(93)−C(94)	119.8(7)
C(1)−C(2)−C(91)	129.6(5)	C(93)−C(94)−C(95)	124.5(8)
C(1)−C(2)−P(3)	117.5(4)	C(94)−C(95)−C(96)	112.2(6)
C(91)−C(2)−P(3)	112.5(4)	C(95)−C(96)−C(91)	122.6(6)
FA	14.8(4)	HA	8.4(4)
DA	4.9(3)	CA	160.5(2)

[a] Δ = *d*(Ru−C(74),C(70)) − *d*(Ru−C(71),C(73)). [b] FA (fold angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(70), C(74), C(75), C(76), C(77), C(78). [c] HA (hinge angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(71), C(74), C(70), C(73). [d] DA (dihedral angle) = angle between normals to least-squares planes defined by C*, Ru, C(1) and Ru, C(1), C(2), C(3). [e] CA (conformational angle) = angle between normals to least-squares planes defined by C**, C*, Ru and C*, Ru, C(1). C* = centroid of C(70), C(71), C(72), C(73), C(74). C** = centroid of C(70), C(74), C(75), C (76), C(77), C(78).

with an *E* configuration (the ruthenium atom is *trans* to the triphenylphosphine group). Its orientation with respect to the mirror molecular plane deviates 4.9(3)° (dihedral angle (DA) between the planes Ru−C(1)−C* and Ru−C(1)−C(2)) from the expected 90° according to theoretical calculations.[17b] The Ru−C(1) bond length (2.045(6) Å) is similar to that shown by the analogous alkenylruthenium complexes (*E*)-[Ru{C(CO$_2$Me)=CH(CO$_2$Me)}(η^5-C$_5$H$_5$)(dppe)] (2.07(1) Å)[19] and (*Z*)-[Ru{C(CO$_2$Me)=CH(CO$_2$Me)}(η^5-C$_5$H$_5$)(CO)(PPh$_3$)] (2.080(8) Å).[19] The bond lengths C(1)−C(2) = 1.371(7) Å and C(91)−C(96) = 1.356(8) Å show the expected values for C=C bonds.

The indenyl group is η^5-bonded to the metal, but the structure shows important distortions of the five-carbon ring from planarity with hinge angle (HA) and fold angle (FA) values of 8.4(4) and 14.8(4)°, respectively (Table 5). The slippage of the indenyl ring is higher than that shown in vinylidene or allenylidene derivatives (Table 7). These distortion parameters toward an η^3 binding mode, which appear to be maintained in solution (Δδ-(C-3a,7a) = −16.56 ppm) (see Experimental Section), are the highest yet described for indenylruthenium(II) complexes.

Analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) are in accordance with the proposed formulations. The ^{31}P{^{1}H} NMR spectra show reso-

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nances which are consistent with an ABM system (**13a**, δ 11.92 (dd, $^4J_{PP}$ = 6.0 Hz, $^4J_{PP}$ = 3.8 Hz, C−PPh$_3$), 43.18 (dd, $^2J_{PP}$ = 29.6 Hz, $^4J_{PP}$ = 6.0 Hz, Ru−PPh$_3$), 46.24 (dd, $^2J_{PP}$ = 29.6 Hz, $^4J_{PP}$ = 3.8 Hz, Ru−PPh$_3$); **14a**, δ 12.33 (bs, C−PPh$_3$), 43.11 (dbs, $^2J_{PP}$ = 27.2 Hz, Ru−PPh$_3$), 46.41 (dbs, $^2J_{PP}$ = 27.2 Hz, Ru−PPh$_3$)). The two nonequivalent PPh$_3$ ligands are in accordance with the structure in the solid state and seem to indicate that the alkenyl group does not rotate around the Ru−C$_\alpha$ bond, due likely to the steric hindrance of the bulky phosphine ligands.

The ^{1}H and ^{13}C{^{1}H} NMR spectra also support the (*E*)-alkenyl configuration. We note in particular (i) the typical downfield resonance of the vinylic hydrogen, which appears in the ^{1}H NMR spectra as a doublet of virtual triplets, due to the coupling with the phosphonium phosphorus nucleus (**13a**, δ 10.25 ($^3J_{HP}$ = 35.0 Hz); **14a**, δ 10.20 ($^3J_{HP}$ = 34.9 Hz)) and with the two nonequivalent phosphorus nuclei bonded to ruthenium (**13a**, $^3J_{HP} = {}^3J_{HP'}$ = 10.3 Hz; **14a**, $^3J_{HP} = {}^3J_{HP'}$ = 10.1 Hz) and (ii) the typical low-field resonance for the Ru−C$_\alpha$ atom in alkenyl complexes in the ^{13}C{^{1}H} NMR spectra, which appears as a multiplet at δ 198.30 (**13a**) and 196.51 (**14a**).

Providing that a formal addition of PPh$_3$ to the C$_\beta$ atom of the vinylidene chain is found, we have examined the reactivity of the neutral enynyl complexes **6a** and **7a** toward triphenylphosphine. Similarly, the treatment of **6a** and **7a** with an excess of PPh$_3$ in refluxing methanol and in the presence of NaPF$_6$ also affords complexes **13a** and **14a** (Scheme 4). The formation of **13a** and **14a** is unusual, since typical nucleophilic additions to the C$_\alpha$ atom of the vinylidene group should be expected. The reactions were monitored by ^{31}P{^{1}H} NMR spectroscopy, but no further resonances besides those of the enynyl complexes **6a** and **7a** and the final products **13a** and **14a** were observed. Since the mechanism of these atypical reactions is still unknown, further work using nucleophilic attacks on a series of ruthenium(II) vinylidene complexes is in progress.[20]

Conclusions

We have recently reported that the activation of 2-propyn-1-ol derivatives containing aromatic substituents by indenylruthenium(II) complexes [RuCl(η^5-C$_9$H$_7$)L$_2$] (L = PPh$_3$; L$_2$ = dppe, dppm) selectively affords allenylidene complexes [Ru(=C=C=CR$_2$)(η^5-C$_9$H$_7$)L$_2$][PF$_6$].[5d] In this work it is shown that the activation of 1-ethynyl-1-cycloalkanols by indenylruthenium(II) complexes gives selectively the vinylvinylidene complexes [Ru{=C=C(H)C=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)L$_2$][PF$_6$] (L = PPh$_3$; L$_2$ = 1,2-bis(diphenylphosphino)ethane (dppe)). This behavior can be compared to that shown by the similar ruthenium(II) complex [RuCl(η^5-C$_5$H$_5$)(PPh$_3$)$_2$].[6a] In contrast, we have also reported that the activation of 1-ethynyl-1-cyclohexanol by [RuCl(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] gives an unprecedented allenylidene complex, namely [Ru(=C=C=C(C$_{13}$H$_{20}$))(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$], which contains the bicyclic [3.3.1]non-2-en-9-ylidene moiety C$_{13}$H$_{20}$. This spiro bicycle results from the formal addition of two molecules of the alkyn-1-ol *via* a metal-promoted double dehydration of 1-ethynyl-1-cyclohexanol.[8] This selective synthetic route to give either vinylvinylidene or allenylidene complexes demonstrates that the activation of substituted propargyl alcohols is clearly dependent on the nature of the substituents. Since both unsaturated carbene vinylvinylidene and allenylidene groups are tautomeric forms, this behavior raises the question of the driving force that governs the allenylidene *vs* vinylvinylidene formation in the activation of 1-ethynyl-1-cycloalkanols.

Studies carried out in our laboratory indicate that the stability of vinylidene and allenylidene moieties are also strongly influenced by the electrophilicity of the ruthenium substrate, *e.g.* [Ru(1,2,3-Me$_3$C$_9$H$_4$)(CO)L] (L = PPh$_3$, P^{i}Pr$_3$).[21] Further reactivity and theoretical (EHMO) studies on these unsaturated carbene complexes and related derivatives are in progress.

Experimental Section

The manipulations were performed under 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 complexes [RuCl(η^5-C$_9$H$_7$)L$_2$] (L = PPh$_3$,[22] L$_2$ = dppe[23]) were prepared by following the methods reported in the literature.

Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the possitive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. The conductivities were measured at room temperature, in *ca*. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductometer. The C and H analyses were carried out with a Perkin-Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using SiMe$_4$ or 85% H$_3$PO$_4$ as standard. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic data for the vinylvinylidene and enynyl complexes are collected in Tables 1−4.

Synthesis of [Ru{=C=C(H)C=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)L$_2$][PF$_6$] (*n* = 1, L = PPh$_3$ (2a), L$_2$ = dppe (2b); *n* = 2, L = PPh$_3$ (3a), L$_2$ = dppe (3b); *n* = 3, L = PPh$_3$ (4a), L$_2$ = dppe (4b)). General procedure. To a solution of [RuCl(η^5-C$_9$H$_7$)L$_2$] (**1a**,**b**; 1 mmol) in 50 mL of MeOH were added NaPF$_6$ (336 mg, 2 mmol), MgSO$_4$ (3 g, 25 mmol), and the corresponding propargylic alcohol (2 mmol). The reaction mixture was heated under reflux for 30 min. The solvent was then removed under vacuum, the crude product extracted with CH$_2$Cl$_2$, and the extract filtered. Concentration of the resulting solution to *ca*. 5 mL followed by the addition of 50 mL of diethyl ether precipitated a brown solid, which was washed with diethyl ether (2 × 20 mL) and dried in vacuo. Yield (%), IR (KBr, ν(PF$_6^-$), cm^{-1}), analytical data, conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), and mass spectral data (FAB, *m*/*e*) are as follows. **2a:** 68; 838. Anal. Calcd for RuC$_{52}$H$_{45}$F$_6$P$_3$: C, 63.86; H, 4.64. Found: C, 63.45; H, 4.58. 125. **2b:** 56; 838. Anal. Calcd for RuC$_{42}$H$_{39}$F$_6$P$_3$: C, 59.22; H, 4.61. Found: C, 59.67; H, 4.96. 115. **3a:** 66; 840. Anal. Calcd for RuC$_{53}$H$_{47}$F$_6$P$_3$: C, 64.17; H, 4.77. Found: C, 63.82; H, 4.98. 123. [M$^+$] = 847, [M$^+$ − C$_8$H$_{10}$] = 741. **3b:** 76; 837. Anal. Calcd for RuC$_{43}$H$_{41}$F$_6$P$_3$: C, 59.65; H, 4.77. Found: C, 59.01; H, 4.69. 122. **4a:** 80; 838. Anal. Calcd for RuC$_{54}$H$_{49}$F$_6$P$_3$: C, 64.47; H, 4.91. Found: C, 63.87; H, 5.11. 113. **4b:** 89; 837.

(20) A reviewer has brought to our attention that alkenyl−phosphonio complexes (**13a** and **14a**) could be formally generated from the nucleophilic attack of PPh$_3$ the π-alkyne complexes [Ru(η^2-HC≡CR)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = 1-cyclohexenyl, 1-cycloheptenyl). Theoretical and experimental studies focused on the potential equilibrium between these complexes and the corresponding vinylidene tautomers will be undertaken.

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Anal. Calcd for $RuC_{44}H_{43}F_6P_3$: C, 60.06; H, 4.90. Found: C, 59.79; H, 5.03. 120.

Synthesis of [Ru{C≡CC=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C_9H_7)-L$_2$] (n = 1, L = PPh$_3$, (5a), L$_2$ = dppe (5b); n = 2, L = PPh$_3$ (6a), L$_2$ = dppe (6b); n = 3, L = PPh$_3$ (7a), L$_2$ = dppe (7b)). General procedure. A mixture of the corresponding vinylvinylidene complex **2**−**4** (1 mmol) and Al_2O_3 (10 mL) in 50 mL of CH_2Cl_2 was stirred at room temperature for 2 h. The mixture was then evaporated under reduced pressure, the residue extracted with diethyl ether, and the extract filtered. Evaporation of the diethyl ether gave **5**−**7** as orange solids. Yield (%), IR (KBr, ν(C≡C), cm^{-1}), analytical data, and mass spectral data (FAB, *m/e*) are as follows. **5a:** 88; 2069. Anal. Calcd for $RuC_{52}H_{44}P_2$: C, 75.07; H, 5.33. Found: C, 75.27; H, 5.42. **5b:** 97; 2068. Anal. Calcd for $RuC_{42}H_{38}P_2$: C, 71.47; H, 5.42. Found: C, 70.89; H, 5.88. **6a:** 84; 2051. Anal. Calcd for $RuC_{53}H_{46}P_2$: C, 75.25; H, 5.48. Found: C, 74.71; H, 5.73. [M$^+$] = 846, [M$^+$ − C_8H_9] = 741, [M$^+$ − C_8H_9 − C_9H_7] = 625, [M$^+$ − PPh$_3$] = 583. **6b:** 91; 2062. Anal. Calcd for $RuC_{43}H_{40}P_2$: C, 71.75; H, 5.60. Found: C, 71.03; H, 5.81. **7a:** 94; 2066. Anal. Calcd for $RuC_{54}H_{48}P_2$: C, 75.42; H, 5.62. Found: C, 74.84; H, 5.68. **7b:** 92; 2058. Anal. Calcd for $RuC_{44}H_{42}P_2$: C, 72.01; H, 5.77. Found: C, 71.21; H, 6.01.

Synthesis of [Ru{=C=C(Me)C=CHCH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C_9H_7)(PPh$_3$)$_2$][CF$_3$SO$_3$] (8a). A stirred solution of **6a** (846 mg, 1 mmol) in diethyl ether (50 mL), at room temperature, was treated dropwise with a dilute solution of $MeOSO_2CF_3$ in diethyl ether. Inmediately, an insoluble solid precipitated but the addition was continued until no further solid was formed. The solution was decanted and the solid washed with diethyl ether (2 × 25 mL) and vacuum-dried. Slow crystallization in a CH_2Cl_2/hexane (1:4) mixture gave **8a** as orange-brown crystals. Yield (%), IR (KBr, ν(CF_3SO_3), cm^{-1}), analytical data, conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), and NMR spectroscopic data (ppm) are as follows. 63; 1270, 1225, 1156. Anal. Calcd for $RuC_{54}H_{45}F_3O_3P_2S$: C, 65.24; H, 4.56. Found: C, 64.52; H, 4.70. 104. ^{31}P{^{1}H} (CD_2Cl_2) δ 39.35 (s); ^{1}H (CD_2Cl_2) δ 0.85 (m, 2H, CH$_2$), 1.32 (m, 2H, CH$_2$), 1.47 (m, 2H, CH$_2$), 1.50 (s, 3H, CH$_3$), 2.24 (m, 2H, CH$_2$), 5.30 (bs, 2H, H-1,3), 5.54 and 7.11 (m, 2H each, H-4,7 and H-5,6), 5.68 (bs, 1H, H-2), 5.96 (bs, 1H, =CH), 6.69−7.45 (m, 30H, Ph); ^{13}C{^{1}H} (CD_2Cl_2) δ 10.38 (s, CH$_3$), 22.62 (s, CH$_2$), 23.50 (s, CH$_2$), 26.81 (s, CH$_2$), 26.84 (s, CH$_2$), 81.04 (s, C-1,3), 100.12 (s, C-2), 116.95 (s, C-3a,7a), 123.98−135.37 (m, Ph, C$_\beta$, =C, =CH, Ind$_6$), 352.77 (t, $^2J_{CP}$ = 17.7 Hz, Ru=C$_\alpha$); $\Delta\delta$(C-3a,7a) = −13.75.

Synthesis of [Ru{C≡CC(PPh$_3$)CH$_2$CH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C_9H_7)(PPh$_3$)$_2$][PF$_6$] (n = 1 (11a), 2 (12a)). General procedure. A mixture of [RuCl(η^5-C_9H_7)(PPh$_3$)$_2$] (776 mg, 1 mmol), $NaPF_6$ (336 mg, 2 mmol), PPh$_3$ (2.623 g, 10 mmol), and the corresponding propargylic alcohol (2 mmol) in 50 mL of MeOH was stirred at room temperature for 8 h. A yellow suspension was formed. The solvent was then decanted, the residue dissolved in CH_2Cl_2 (ca. 40 mL), and this solution filtered. The resulting solution was evaporated to dryness and the yellow solid obtained washed with diethyl ether (2 × 20 mL) and vacuum-dried. Yield (%), IR (KBr, ν(C≡C), ν(PF$_6^-$), cm^{-1}), analytical data, and NMR spectroscopic data (ppm) are as follows. **11a:** 73; 2054, 837. Anal. Calcd for $RuC_{70}H_{60}F_6P_4$: C, 67.79; H, 4.87. Found: C, 67.61; H, 4.80. ^{31}P{^{1}H} (CD_2Cl_2) δ 28.85 (t, $^5J_{PP}$ = 3.8 Hz, C−PPh$_3$), 49.34 (d, $^5J_{PP}$ = 3.8 Hz, Ru−PPh$_3$); ^{1}H (CD_2Cl_2) δ 1.37 (m, 2H, CH$_2$), 1.68 (m, 2H, CH$_2$), 2.08 (m, 2H, CH$_2$), 2.38 (m, 2H, CH$_2$), 4.30 (d, 2H, J_{HH} = 2.2 Hz, H-1,3), 4.47 (t, 1H, J_{HH} = 2.2 Hz, H-2), 5.66 and 6.73 (m, 2H each, H-4,7 and H-5,6), 6.83−7.94 (m, 45H, Ph); ^{13}C{^{1}H} (CD_2Cl_2) δ 25.56 (d, $^2J_{CP}$ = 9.9 Hz, 2 CH$_2$), 40.44 (s, 2 CH$_2$), 44.96 (d, J_{CP} = 49.0 Hz, C$_\gamma$), 73.94 (s, C-1,3), 95.17 (s, C-2), 107.12 (d, $^2J_{CP}$ = 3.5 Hz, C$_\beta$), 110.22 (s, C-3a,7a), 112.15 (m, Ru−C$_\alpha$), 119.61−138.72 (m, Ph, Ind$_6$); $\Delta\delta$(C-3a,7a) = −20.48. **12a:** 61; 2050, 840. Anal. Calcd for $RuC_{71}H_{62}F_6P_4$: C, 67.99; H, 4.98. Found: C, 67.42; H, 4.89. ^{31}P{^{1}H} (CD_2Cl_2) δ 25.42 (t, $^5J_{PP}$ = 3.9 Hz, C−PPh$_3$), 49.02 (d, $^5J_{PP}$ = 3.9 Hz, Ru−PPh$_3$); ^{1}H (CD_2Cl_2) δ 1.47 (m, 2H, CH$_2$), 1.56 (m, 2H, CH$_2$), 1.82 (m, 4H, 2 CH$_2$), 2.34 (m, 2H, CH$_2$), 4.48 (m, 3H, H-1,3 and H-2), 5.63 (m, 2H, Ind$_6$), 6.82−7.74 (m, 47H, Ph, Ind$_6$); ^{13}C{^{1}H} (CD_2Cl_2) δ 21.90 (d, $^2J_{CP}$ = 10.9 Hz, 2 CH$_2$), 21.18 (s, CH$_2$), 34.73 (s, 2 CH$_2$), 44.22 (d, J_{CP} = 45.3 Hz, C$_\gamma$), 73.39 (s, C-1,3), 95.29 (s, C-2), 103.84 (d, $^2J_{CP}$ = 6.8 Hz, C$_\beta$), 110.81 (s, C-3a,7a), 113.19 (m, Ru−C$_\alpha$), 119.07−138.99 (m, Ph, Ind$_6$); $\Delta\delta$(C-3a,7a) = −19.89.

Synthesis of (*E*)-[Ru{C(H)=C(PPh$_3$)C=CHCH$_2$-(CH$_2$)$_n$CH$_2$}(η^5-C_9H_7)(PPh$_3$)$_2$] [PF$_6$] (n = 2 (13a), 3 (14a)). General procedure. A mixture of the corresponding vinylvinylidene complex **3a** and **4a** (1 mmol) and PPh$_3$ (2.623 g, 10 mmol) in 50 mL of MeOH was heated under reflux for approximately 1 h. The solution was then evaporated to dryness, the solid residue was extracted with CH_2Cl_2 (ca. 20 mL), and the extracts were filtered into 100 mL of stirred diethyl ether, giving a yellow precipitate. The solution was decanted and the solid washed with diethyl ether (2 × 20 mL) and vacuum-dried. Yield (%), IR (KBr, ν(PF$_6^-$), cm^{-1}), analytical data, NMR spectroscopic data (ppm), and mass spectral data (FAB, *m/e*) are as follows. **13a:** 72; 841. Anal. Calcd for $RuC_{71}H_{62}F_6P_4$: C, 67.99; H, 4.98. Found: C, 67.59; H, 4.85. ^{31}P{^{1}H} ($CDCl_3$) δ 11.92 (dd, $^4J_{PP}$ = 6.0 Hz, $^4J_{PP}$ = 3.8 Hz, C−PPh$_3$), 43.18 (dd, $^2J_{PP}$ = 29.6 Hz, $^4J_{PP}$ = 6.0 Hz, Ru−PPh$_3$), 46.24 (dd, $^2J_{PP}$ = 29.6 Hz, $^4J_{PP}$ = 3.8 Hz, Ru-PPh$_3$); ^{1}H ($CDCl_3$) δ 1.23 (m, 4H, 2 CH$_2$), 1.60 (m, 4H, 2 CH$_2$), 4.92, 5.00, and 5.05 (bs, 1H each one, H-1, H-2 and H-3), 5.27 (d, 1H, $^4J_{HP}$ = 7.2 Hz, =CH), 6.16 (m, 2H, Ind$_6$), 6.55−7.67 (m, 47H, Ph, Ind$_6$), 10.25 (dvt, 1H, $^3J_{HP}$ = 35.0 Hz, $^3J_{HP}$ = $^3J_{HP'}$= 10.3 Hz, =CH); ^{13}C{^{1}H} ($CDCl_3$) δ 20.64 (s, CH$_2$), 22.04 (s, CH$_2$), 25.45 (s, CH$_2$), 31.34 (s, CH$_2$), 73.22 (d, $^2J_{CP}$ = 9.7 Hz, C-1 or C-3), 74.79 (d, $^2J_{CP}$ = 7.1 Hz, C-1 or C-3), 92.33 (s, C-2), 109.48 and 118.79 (s, C-3a and C-7a), 117.53−138.53 (m, Ph, Ind$_6$, =CH, =C), 198.30 (m, Ru−C$_\alpha$) ppm; $\Delta\delta$(C-3a,7a) = −16.56. [M$^+$] = 1109, [M$^+$ − PPh$_3$] = 847, [M$^+$ − 2PPh$_3$] = 585. **14a:** 79; 839. Anal. Calcd for $RuC_{71}H_{62}F_6P_4$: C, 68.19; H, 5.09. Found: C, 68.22; H, 4.98. ^{31}P{^{1}H} ($CDCl_3$) δ 12.33 (bs, C−PPh$_3$), 43.11 (dbs, $^2J_{PP}$ = 27.2 Hz, Ru−PPh$_3$), 46.41 (dbs, $^2J_{PP}$ = 27.2 Hz, Ru−PPh$_3$); ^{1}H ($CDCl_3$) δ 1.47 (m, 2H, CH$_2$), 1.69 (m, 4H, 2 CH$_2$), 2.23 (m, 2H, CH$_2$), 2.41 (m, 2H, CH$_2$), 4.91 (m, 2H, =CH and Ind$_5$), 5.10 and 5.27 (bs, 1H each, Ind$_5$), 6.24 (m, 2H, Ind$_6$), 6.52−7.62 (m, 47H, Ph, Ind$_6$), 10.20 (dvt, 1H, $^3J_{HP}$ = 34.9 Hz, $^3J_{HP}$ = $^3J_{HP'}$ = 10.1 Hz, =CH); ^{13}C{^{1}H} ($CDCl_3$) δ 24.96 (s, CH$_2$), 25.80 (s, CH$_2$), 28.92 (s, CH$_2$), 29.67 (s, CH$_2$), 37.42 (s, CH$_2$), 72.85 (d, $^2J_{CP}$ = 5.2 Hz, C-1 or C-3), 74.94 (s, C-1 or C-3), 92.61 (s, C-2), 109.16 and 118.19 (s, C-3a and C-7a), 120.91−142.42 (m, Ph, Ind$_6$, =CH, =C), 196.51 (m, Ru−C$_\alpha$); $\Delta\delta$(C-3a,7a) = −17.02.

X-ray Diffraction Studies. Complex 8a. Data collection, crystal, and refinement parameters are collected in Table 9. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 15 and 18°). Data were collected with the $\omega-2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The final drift correction factors were between 0.99 and 1.76. On all reflections, profile analysis[24,25] was performed. Lorentz and polarization corrections were applied, and the data were reduced to $|F_o|$ values.

The structure was solved by SHELXS86[26] (Patterson methods) and DIRDIF[27] (phase expansion). Isotropic least-squares refinement, using SHELX76,[28,29] converged to R = 0.083. At

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Table 9. Crystallographic data for Complexes 8a and 13a

	8a	**13a**
formula	$C_{55}H_{49}F_3O_3P_2RuS$	$C_{76}H_{74}Cl_2F_6OP_4Ru$
a, Å	37.29(1)	11.335(5)
b, Å	14.123(3)	29.62(5)
c, Å	17.912(9)	20.116(9)
β, deg	97.99(4)	93.03(4)
mol wt	1010.06	1413.20
V, Å^3	9342(7)	6745(12)
D_{calcd}, g cm^{-3}	1.43	1.392
F(000)	4160	2920
wavelength, Å	0.71073	0.71073
temp, K	200	200
radiation	Mo Kα	Mo Kα
monochromator	graphite cryst	graphite cryst
space group	*C*2/*c*	$P2_1/c$
cryst syst	monoclinic	monoclinic
cryst size, mm	0.39, 0.33, 0.19	0.52, 0.40, 0.33
μ, mm^{-1}	0.49	0.468
range of abs	0.60−1.00	0.78−1.00
diffraction geom	$\omega-2\theta$	$\omega-2\theta$
θ range, deg	1.00−25.00	1.22−22.99
index ranges for data collecn	$-44 \le h \le +43$ $0 \le k \le +16$ $0 \le l \le +21$	$-12 \le h \le +12$ $0 \le k \le +32$ $0 \le l \le +22$
no. of rflns measd	9253	9922
no. of indep rflns	8221	9367
no. of variables	587	782
agreement between equiv rflns[a]	0.027	0.026
final *R* factors $R(I > 3\sigma(I))$	$R = 0.040$ $R_w = 0.041$	
final *R* factors $R(I > 2\sigma(I))$		R1 = 0.053 *R*w2 = 0.146
final *R* factors *R*(all data)		R1 = 0.080 *R*w2 = 0.156

[a] $R_{int} = \sum(I - \langle I \rangle)/\sum I$.

this stage additional empirical absorption correction was applied using DIFABS,[30] resulting in a further decrease of *R* to 0.075. The maximum and minimum absorption correction factors were respectively 1.00 and 0.60. Hydrogen atoms were geometrically placed.

During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. The hydrogen atoms were isotropically refined with a common thermal parameter. The function minimized was $\sum w(F_o - F_c)^2$ ($w = 1/[\sigma^2(F_o) + (0.0004 F_o^2)]$, with $\sigma(F_o)$ from counting statistics). The maximum shift to esd ratio in the last full-matrix least-squares cycle was 0.008. The final difference Fourier map showed no peaks higher than 0.43 e Å^{-3} or deeper than −0.40 e Å^{-3}. Atomic scattering factors were taken from ref 31. Geometrical calculations were made with PARST.[32] The crystallographic plots were made with EUCLID.[33] All calculations were performed at the University of Oviedo on the Scientific Computer Center and X-ray group VAX computers.

Complex 13a. Data collection, crystal, and refinement parameters are collected in Table 9. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 10 and 12°). Data were collected with the $\omega-2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The final drift correction factors were between 0.97 and 1.14. On all reflections, profile analysis[24,25] was performed. Lorentz and polarization corrections were applied, and the data were reduced to $|F_o|^2$ values.

The structure was solved by DIRDIF[27] (Patterson methods and phase expansion). Isotropic full-matrix least-squares refinement on $|F_o|^2$ using SHELXL93[34] converged to $R = 0.127$. At this stage an empirical absorption correction was applied using XABS2.[35] Maximum and minimum transmission factors were 1.00 and 0.78, respectively.

Finally, all hydrogen atoms (except H(1)) were geometrically placed. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. The geometrically placed hydrogen atoms were isotropically refined, riding on their parent atoms, with two common thermal parameters; one for the hydrogen atoms bonded to aromatic rings and the other for the hydrogen atoms bonded to the cyclohexenyl ring. H(1) was independently (and also isotropically) refined. The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ ($w = 1/[\sigma^2(F_o^2) + (0.0777P)^2 + 19.62P]$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics).

The CH_2Cl_2 solvent molecule was affected by strong structural disorder. Its hydrogen atoms were omitted during the refinement. C and Cl atoms were anisotropically refined. Cl-(2) was found in two disordered positions (occupation factors 0.515(8) and 0.485(8)).

The Et_2O solvent molecule was also affected by very strong structural disorder and could not be located exactly; instead, it was omitted from the parameter set of the refined discrete-atom model. It was taken into account in the structure factor calculations by direct Fourier transformation of the electron density in the corresponding cavity, using the BYPASS[36] procedure.

The maximum shift to esd ratio in the last full-matrix least-squares cycle was 0.201. The final difference Fourier map showed no peaks higher than 1.01 e Å^{-3} (near the disordered CH_2Cl_2 solvent molecule) or deeper than −0.78 e Å^{-3}. Atomic scattering factors were taken from ref 31. Geometrical calculations were made with PARST.[32] The crystallographic plots were made with EUCLID.[33] All calculations were performed at the University of Oviedo on the Scientific Computer Center and X-ray group VAX computers.

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Supporting Information Available: Crystal structure data for **8a** and **13a**, including tables of atomic parameters, anisotropic thermal parameters, bond distances, and bond angles (33 pages). Ordering information is given on any current masthead page.

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