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Regioselective Nucleophilic Additions on Indenyl−Ruthenium(II)−Allenylidene Complexes. X-ray Crystal Structure of the Alkynyl Complex $[Ru\{C{\equiv}CC(C{\equiv}CH)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[†]

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The diphenylallenylidene complexes $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)L_2][PF_6]$ ($L = PPh_3$; $L_2 =$ 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm)) (**1a**−**c**) react with NaOMe to yield the methoxyalkynyl derivatives $[Ru\{C{\equiv}CC(OMe)Ph_2\}(\eta^5\text{-}C_9H_7)\text{-}L_2]$ (**3a**−**c**). Protonation of these species gives back the starting allenylidene derivatives. Regioselective additions on the C_γ are also observed when **1a**,**b** are treated with LiR (R = Me, ^{n}Bu), giving the alkynyl complexes $[Ru\{C{\equiv}CC(R)Ph_2\}(\eta^5\text{-}C_9H_7)L_2]$ (**4a**,**b**, **5a**,**b**). Vinylidene derivatives $[Ru\{=C=C(H)C(R)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**6a**, **7a**) can be prepared by protonation of complexes **4a** and **5a** with HBF_4. The diphenylallenylidene compound **1c** reacts with Li^{t}Bu to yield the metallacycle complex $[Ru\{(\kappa^3(C,P,P)\text{-}C=C=CPh_2(Ph_2PCHPPh_2)\}\text{-}(\eta^5\text{-}C_9H_7)]$ (**8c**). The alkynyl complexes $[Ru\{C{\equiv}CC(C{\equiv}CR)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (R = Ph, ^{n}Pr, H) (**9a**−**11a**) have been obtained by reaction of **1a** with lithium or sodium acetylides. Protonation of these derivatives yields the vinylidene complexes $[Ru\{=C=C(H)C(C{\equiv}CR)\text{-}Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**12a**−**14a**). The crystal structure of $[Ru\{C{\equiv}CC(C{\equiv}CH)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**11a**) was determined by X-ray diffraction methods. In the structure the alkynyl chain is nearly linear (Ru−C(1)−C(2) = 175.0(2)°) with Ru−C(1) and C(1)−C(2) distances of 1.993(2) and 1.209(3) Å, respectively. The monosubstituted allenylidene complex $[Ru\{=C=C=C(H)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**2a**) reacts with PMe_3, PMe_2Ph, $PMePh_2$, and PPh_3 to yield the cationic alkynyl−phosphonio derivatives $[Ru\{C{\equiv}CC(PR_3)(H)Ph\}(\eta^5\text{-}C_9H_7)\text{-}(PPh_3)_2][PF_6]$ (**17a**−**20a**) in a regioselective way. Similarly, allenylidene complexes **1a**−**c** add PMe_3 to give the corresponding alkynyl−phosphonio derivatives **15a**−**c**. $[Ru\{C{\equiv}CC\text{-}(PMe_3)Ph_2\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**15c**) undergoes an isomerization process to yield the thermodynamically more stable allenyl−phosphonio complex $[Ru\{C(PMe_3)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**21c**). $[Ru\{C(PMe_2Ph)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**22c**) can be obtained directly by addition of PMe_2Ph to the C_α atom of **1c**. The behavior of the diphenylallenylidene complexes **1a**−**c** toward sodium 2-methylthiophenolate is also discussed.

Introduction

Metallacumulenes $[M]{=}(C{=})_nCR_2$ are a new class of unsaturated carbene complexes containing cumulative M=C and C=C double bonds. Metal−vinylidene ($n = 1$) and metal−allenylidene ($n = 2$) derivatives are the first members of this family.[1] Even though the first allenylidene complexes have been known since 1976,[2] their chemistry has not been so extensively studied compared with that of the vinylidene complexes.[3] However, during the last few years the study of metal−allenylidene complexes has notably increased, probably due to the discovery of a general synthetic method, based on the direct activation of propargyl alcohols.[4] The high degree of unsaturation of the organic chain, which contains three activated carbon atoms, has provided potential utility as reagents in organic synthesis analogous with the well-known chemistry of metal−carbene complexes.[5] Since the reactivity of the allenylidene chain still remains largely unexplored, the usefulness in chemical transformations has not been exploited yet. The involvement of allenylidene complexes in the cata-

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[†] Dedicated to Prof. Pascual Royo (Universidad de Alcalá de Henares) on the occasion of his 60th birthday.

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(1) Isolation of pentatetraenylidene complexes $[M]{=}(C{=})_4CR_2$ has been recently reported: (a) $[M] = trans\text{-}[RuCl(dppe)_2]^+$: Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157. (b) $[M] = [RuCl(\eta^6\text{-}C_6Me_6)(PMe_3)]^+$: Peron, D.; Romero, A.; Dixneuf, P. H. *Gazz. Chim. Ital.* **1994**, *124*, 497. (c) $[M] = trans\text{-}[IrCl(P^iPr_3)_2]$: Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.* **1996**, *2*, 19. (d) $[M] = Cr(CO)_5$ or $W(CO)_5$: Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 1139.

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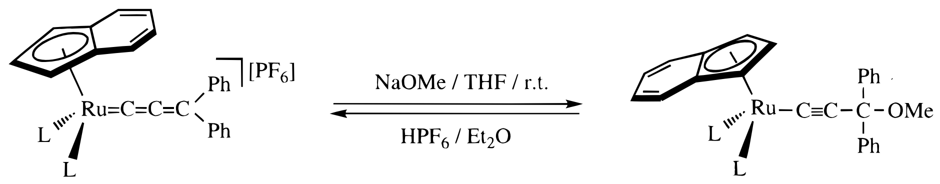
Scheme 1



L= PPh$_3$ (**1a**); L$_2$= dppe (**1b**), dppm (**1c**)

L= PPh$_3$ (**3a**); L$_2$= dppe (**3b**), dppm (**3c**)

lytic coupling of allylic alcohols and propargyl alcohols in the presence of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ has just been reported.[6]

Theoretical studies (MO) on the model $[Mn({=}C{=}C{=}CH_2)(\eta^5\text{-}C_5H_5)(CO)_2]$ showed[7] that C_α and C_γ atoms of the allenylidene chain are electrophilic centers and that C_β is nucleophilic. The nucleophilic character of C_β has been experimentally confirmed by Kolovoba and co-workers[8] on the neutral allenylidene complexes $[Mn({=}C{=}C{=}CR_2)(\eta^5\text{-}C_5H_5)(CO)_2]$ (R = Ph, ^{t}Bu) which undergo C_β protonation additions to give the cationic alkenyl–carbyne derivatives $[Mn\{{\equiv}CC(H){=}CR_2\}(\eta^5\text{-}C_5H_5)(CO)_2]^+$.[9] Although reactivity studies on neutral and cationic allenylidene complexes also confirm the electrophilic character of the C_α and C_γ atoms, the nucleophilic additions seem to be dependent on the metal fragment as well as on the C_γ substituents, as is shown in the regioselective additions of alcohols. Thus, alcohols can be added either at the C_α atom to give alkenyl–carbene derivatives[10] $[M]{=}C(OR)C(H){=}CR_2$ or at the C_γ to yield vinylidene complexes[10f,11] $[M]{=}C{=}C(H)C(OR)R_2$. In contrast, Dixneuf and co-workers and ourselves have demonstrated that the use of sterically hindered and/or electron rich metal fragments, such as *trans*-[RuCl(dppm)$_2$],[12] $[Ru\{N(CH_2CH_2PPh_2)_3\}_3]$,[13] or $[Ru(\eta^5\text{-}C_9H_7)L_2]$ (L$_2$ = 2PPh$_3$, dppe, dppm),[10f,14] prevents the nucleophilic addition of alcohols on the allenylidene chain.[15]

As part of our continuing interest in investigating the reactivity patterns of vinylidene– and allenylidene–ruthenium(II) complexes here we report a general study of the reactivity of the complexes $[Ru({=}C{=}C{=}CRR')(\eta^5\text{-}C_9H_7)L_2]^+$ with a variety of nucleophiles. In particular we were interested in finding out to what extent the electronic density and the steric properties of these metal fragments affect the reactivity of the cumulene system. Recent theoretical calculations (EHMO) carried out on the model $[Ru({=}C{=}C{=}CH_2)(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$ show that the LUMO of the molecule is centered on C_α (25%) and C_γ (33%) of the unsaturated chain.[16a] Part of this work has been previously communicated.[17]

Results and Discussion

Reaction of Allenylidene Complexes with Sodium Methoxide. The diphenylallenylidene complexes $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_9H_7)L_2][PF_6]$ (L$_2$ = 2PPh$_3$, dppe, dppm) (**1a**–**c**) react with NaOMe in tetrahydrofuran, at room temperature, to give selectively the yellow methoxyalkynyl derivatives **3a**–**c** (90–96%) (Scheme 1). Under similar reaction conditions the monosubstituted allenylidene complex $[Ru\{{=}C{=}C{=}C(H)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**2a**) also reacts with NaOMe to yield a mixture of products containing mainly the previously reported methoxyalkynyl complex $[Ru\{C{\equiv}CC(OMe)(H)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$.[10f]

The novel alkynyl complexes are air stable in the solid state. They have been characterized by microanalysis, mass spectra (FAB), infrared spectrometry, and NMR (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}) spectroscopy (details are given in the Experimental Section and Tables 1 and 2). The formation of the alkynyl chain is clearly confirmed by the appearance in the IR spectra (KBr) of a ν(C≡C) absorption in the range 2058–2086 cm^{-1}. The NMR data of **3a**–**c** can be compared with those reported for similar indenyl–ruthenium–alkynyl complexes $[Ru(C{\equiv}CR)(\eta^5\text{-}C_9H_7)L_2]$.[18] Thus, the ^{31}P{^{1}H} NMR spectra show a single resonance consistent with the chemical

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[16] (a) The absence of reactivity of these allenylidene–indenyl–ruthenium(II) complexes toward alcohols seems to indicate an effective steric protection of the electrophilic sites in the allenylidene chain by the indenyl and the ancillary phosphine ligands: Pérez-Carreño, E. Ph.D. Thesis, University of Oviedo, 1996. (b) The *trans* conformation on the model $[Ru(C{\equiv}CCH_3)(\eta^5\text{-}C_9H_7)(PH_3)_2]$ is 5.48 kcal/mol more stable than the *cis*: Pérez-Carreño, E. Ph.D. Thesis, University of Oviedo, 1996.

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

		^1H				
		η^5-C_9H_7[c]				
complex	$^{31}P\{^1H\}$	H-1,3	H-2	J_{HH}	H-4,7, H-5,6	others
$[Ru\{C{\equiv}CC(OMe)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**3a**)	53.55 s	4.59 d	5.29 t	2.4	6.61 m, *b*	6.83−8.00 m (PPh_3 and Ph)
$[Ru\{C{\equiv}CC(OMe)Ph_2\}(\eta^5\text{-}C_9H_7)(dppe)]$ (**3b**)	87.93 s	4.89 d	5.12 t	2.5	*b*, *b*	1.75 m, 2.15 m ($P(CH_2)_2P$); 3.05 s (OCH_3); 6.69−7.68 m (PPh_2 and Ph)
$[Ru\{C{\equiv}CC(OMe)Ph_2\}(\eta^5\text{-}C_9H_7)(dppm)]$ (**3c**)	20.05 s	5.48 d	5.42 t	2.6	*b*, *b*	3.34 s (OCH_3); 3.98 m, 4.23 m (PCH_aH_bP); 7.15−7.81 m (PPh_2 and Ph)
$[Ru\{C{\equiv}CC(Me)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**4a**)	54.28 s	4.86 d	5.53 t	2.2	6.87 m, *b*	2.30 s (CH_3); 7.00−8.07 m (PPh_3 and Ph)
$[Ru\{C{\equiv}CC(^nBu)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**5a**)	53.34 s	4.34 d	5.09 t	2.2	6.27 m, *b*	0.57 t (CH_3, J_{HH} = 3.3); 1.03 m, 1.22 m, 2.09 m (CH_2); 6.53−7.45 m (PPh_3 and Ph)
$[Ru\{C{\equiv}CC(Me)Ph_2\}(\eta^5\text{-}C_9H_7)(dppe)]$ (**4b**)	88.77 s	4.95 d	5.08 t	2.3	*b*, *b*	1.52 s (CH_3); 1.82 m, 2.16 m ($P(CH_2)_2P$); 6.99−7.67 m (PPh_2 and Ph)
$[Ru\{C{\equiv}CC(^nBu)Ph_2\}(\eta^5\text{-}C_9H_7)(dppe)]$ (**5b**)	88.35 s	4.96 d	5.12 t	2.4	*b*, *b*	0.87 t (CH_3, J_{HH} = 5.7); 1.24 m, 1.82 m, 2.14 m ($3CH_2$ and $P(CH_2)_2P$); 7.00−7.39 m (PPh_2 and Ph)
$[Ru\{C{\equiv}CC(C{\equiv}CPh)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**9a**)	53.33 s	4.64 d	5.38 t	2.2	6.58 m, *b*	6.86−7.75 m (PPh_3 and Ph)
$[Ru\{C{\equiv}CC(C{\equiv}C^nPr)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**10a**)	53.90 s	4.34 d	5.10 t	2.4	6.50 m, 6.82 m	1.03 t (CH_3, J_{HH} = 7.3); 1.60 m (CH_2); 2.34 t (CH_2, J_{HH} = 7.1); 6.92−7.68 m (PPh_3 and Ph)
$[Ru\{C{\equiv}CC(C{\equiv}CH)Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**11a**)	54.52 s	4.57 d	5.29 t	2.4	*b*, *b*	2.45 s (≡CH); 6.65−8.03 m (PPh_3 and Ph)
$[Ru\{C{\equiv}CC[S(o\text{-}C_6H_4Me)]Ph_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**23a**)	52.13 s	4.65 d	5.29 t	2.4	6.39 m, *b*	2.39 s (CH_3); 6.77−7.89 m (PPh_3 and Ph)

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

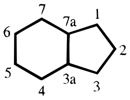


Table 2. $^{13}C\{^1H\}$ NMR Data for the Neutral Alkynyl Complexes[a]

	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	RuC_α	$^2J_{CP}$	C_β	C_γ	others
3a	74.86	95.68	110.83	−19.87	124.56, 126.88	105.78 t	24.3	112.29	83.16	52.43 s (OCH_3); 127.17−148.92 m (PPh_3 and Ph)
3b	70.76	92.29	109.11	−21.59	124.65, 125.40	109.20 t	24.0	108.72	82.62	28.34 m ($P(CH_2)_2P$); 51.70 s (OCH_3); 126.84−148.48 m (PPh_2 and Ph)
3c	68.64	89.20	*c*	*c*	124.16, *d*	*c*	*c*	*c*	82.61	49.54 t (PCH_2P, J_{CP} = 19.5); 51.79 s (OCH_3); 126.03−148.61 m (PPh_2 and Ph)
4a	73.09	93.13	108.21	−22.49	122.27, *d*	94.43 t	26.2	115.35	46.24	30.97 s (CH_3); 124.20−137.57 m (PPh_3 and Ph)
5a	72.66	93.92	108.78	−21.92	122.55, 124.08	92.48 t	24.1	114.10	50.78	13.20 s (CH_3); 22.54 s, 27.10 s, 41.91 s (CH_2); 124.50−149.21 m (PPh_3 and Ph)
4b	69.94	91.88	108.84	−21.86	*d*, *d*	97.18 t	25.1	114.83	47.01	28.24 m ($P(CH_2)_2P$); 31.74 s (CH_3); 123.80−150.80 m (PPh_2 and Ph)
5b	69.90	91.66	108.53	−22.17	*d*, *d*	97.28 t	24.5	112.32	51.64	14.79 s (CH_3); 23.78 s, 28.25 s, 42.52 s (CH_2); 27.75 m ($P(CH_2)_2P$); 123.85−149.87 m (PPh_2 and Ph)
9a	74.68	95.20	110.54	−20.16	124.45, *d*	101.06 t	25.0	109.55	49.36	84.58 s, 95.49 s (C≡C); 126.87−148.73 m (PPh_3 and Ph)
10a	74.70	95.29	110.54	−20.16	124.41, *d*	99.12 t	23.9	110.54	48.85	14.70 s (CH_3); 22.37 s, 23.72 s (CH_2); 83.92 s, 85.82 s (C≡C); 126.77−149.31 m (PPh_3 and Ph)
11a	73.92	94.10	109.47	−21.23	123.43, *d*	100.34 t	23.4	108.57	47.71	71.33 s (≡CH); 88.17 s (≡C); 125.87−147.24 m (PPh_3 and Ph)
23a	74.58	96.90	110.97	−19.73	*d*, *d*	103.78 t	21.9	112.93	62.73	22.64 s (CH_3); 124.50−146.77 m (PPh_3 and Ph)

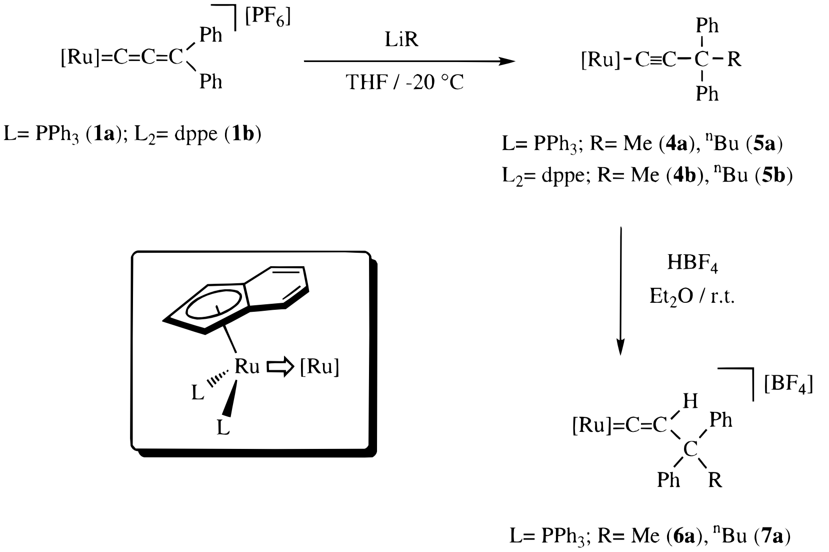
[a] Spectra recorded in C_6D_6; δ in ppm and J in Hz. Abbreviations: s, singlet; t, triplet; m, multiplet. [b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] 108.37−110.30 ppm (m, C-3a,7a, RuC_α, C_β). [d] Overlapped by PPh_3, PPh_2, or Ph carbons.

equivalence of the two phosphorus atoms (Table 1). ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit resonances for aromatic, indenyl, and methylene ($(CH_2)_2P_2$ or CH_2P) groups, in accordance with the proposed structures (Tables 1 and 2). The methoxy group appears as a single resonance in both ^1H and $^{13}C\{^1H\}$ NMR spectra at δ 3.05−3.50 and 51.70−52.43 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectra the C_α resonance appears as a triplet due to coupling with the two equivalent phosphorus atoms (δ 105.78−110.20 ppm, $^2J_{CP}$ *ca.* 24.0 Hz). The C_β and $C\gamma$ nuclei resonate as two singlets in the ranges δ 108.37−112.29 and 82.61−83.16 ppm, respectively.

Indenyl carbon resonances (Table 2) have been also assigned and are in accordance with the proposed η^5-coordination with values of $\Delta\delta$(C-3a,7a),[19] indicative of a slightly distorted η^5-indenyl coordination.[20]

It is well-known that alkynyl derivatives react with electrophiles at the β position to afford vinylidene complexes.[3] However, the treatment of **3a**−**c** with strong acids (HBF_4 or HPF_6) in diethyl ether or THF, even at −20 °C, gives back the precursor allenylidene

Scheme 2



complexes **1a**−**c** in almost quantitative yields (see Scheme 1). The elimination of methanol also occurs in the reactions of the methoxyalkynyl−ruthenium complex *trans*-[Ru{C≡CC(OMe)Ph$_2$}Cl(dppm)$_2$] with acids.[12]

Reaction of Allenylidene Complexes with LiR (R = Me, ^{n}Bu, ^{t}Bu). Allenylidene complexes [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)L$_2$][PF$_6$] (L$_2$ = 2PPh$_3$, dppe) (**1a**,**b**) add selectively alkyl groups (Me, ^{n}Bu) at the C$_\gamma$ atom to afford the neutral alkynyl derivatives [Ru{C≡CC(Me)Ph$_2$}(η^5-C$_9$H$_7$)L$_2$] (**4a**,**b**) and [Ru{C≡CC(^{n}Bu)Ph$_2$}(η^5-C$_9$H$_7$)L$_2$] (**5a**,**b**) (Scheme 2). However, no reaction occurs with Li^{t}Bu. The spectroscopic properties of **4a**,**b** and **5a**,**b** are similar to those of the methoxyalkynyl complexes **3a**,**b** (see Experimental Section and Tables 1 and 2).

In contrast to the behavior of the methoxyalkynyl complexes **3a**−**c**, protonation of alkynyl complexes **4a** and **5a** with HBF$_4$ in diethyl ether at room temperature yields the corresponding monosubstituted vinylidene derivatives **6a** (83%) and **7a** (79%) (Scheme 2). They have been isolated as air stable tetrafluoroborate salts and have been analytically and spectroscopically characterized (see Experimental Section). The most remarkable features of the NMR spectra are (i) (^{1}H NMR) the singlet resonance at δ 4.49 (**6a**) and 4.45 (**7a**) ppm of the *Ru*=C=C*H* proton and (ii) (^{13}C NMR) the typical low-field resonance of the carbenic C$_\alpha$, which appears as a triplet at δ 346.99 ($^2J_{CP}$ = 16.7 Hz, **6a**) and 344.64 ($^2J_{CP}$ = 17.3 Hz, **7a**) ppm, as well as the expected C$_\beta$ singlet resonance (δ 123.48 (**6a**) and 119.16 (**7a**) ppm). The $\Delta\delta$(C-3a,7a) values −14.32 (**6a**) and −13.12 (**7a**) are higher than that of the alkynyl complexes **4a** and **5a** (see Table 2), indicating a moderate distortion on the η^5-coordination of the indenyl ligand.

The reactions of LiMe and Li^{n}Bu with the allenylidene complex [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)(dppm)][PF$_6$] (**1c**) follow, however, a different pathway, resulting in a mixture of complexes. ^{31}P{^{1}H} NMR spectra of these solutions show two singlet resonances which reveal the formation of the expected alkynyl species [Ru{C≡CC(R)Ph$_2$}(η^5-C$_9$H$_7$)(dppm)] (R = Me, ^{n}Bu) along with an additional species. The latter can be selectively obtained by treatment of a THF solution of **1c** with Li^{t}Bu at −20 °C and isolated (80% yield) as a yellow solid (Scheme 3). Complex **8c** is identified on the basis of analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) as an allenyl metallacycle. Thus, the IR spectrum (KBr) shows a typical ν(C=C=C) absorption band at 1903 cm^{-1}. In the ^{31}P{^{1}H} NMR spectrum appears a single signal at δ 4.78 ppm which indicates the chemical equivalence of the two phosphorus atoms. The most remarkable feature of the ^{1}H NMR spectrum is the presence of a triplet signal at δ 5.57 ($^2J_{HP}$ = 2.3 Hz) ppm assigned to the (Ph$_2$P)$_2$C*H* proton. The ^{13}C{^{1}H} NMR spectrum exhibits triplet signals at δ 66.76 (J_{CP} = 21.1 Hz), 83.15 ($^2J_{CP}$ = 50.3 Hz), 105.48 ($^4J_{CP}$ = 7.2 Hz), and 209.39 ($^3J_{CP}$ = 15.2 Hz) ppm corresponding to the (Ph$_2$P)$_2$CH, C$_\alpha$, C$_\gamma$, and C$_\beta$ carbon resonances, respectively. These chemical shifts and coupling constants can be compared to those observed for the analogous indenyl−ruthenium complex [Ru{κ^2(*C*,*P*)-C=C=CPh$_2$)CH(PPh$_2$)C(=O)^{t}Bu}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$].[21]

The formation of metallacycle **8c** is probably the result of the competitive dppm deprotonation *vs* nucleophilic addition to the C$_\gamma$ atom. It is apparent that the initial deprotonation of one of the methylenic protons on the coordinated dppm ligand is taking place followed by a favorable intramolecular addition of the resulting methanide carbon atom at the α position of the allenylidene group.[22] It is possible that the more sterically demanding *tert*-butyl group compared to the methyl or *n*-butyl may prevent nucleophilic addition at the C$_\gamma$

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(19) 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: (a) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839. (b) Kohler, F. G. *Chem. Ber.* **1974**, *107*, 570.

(20) (a) Zhou, Z.; Jablonski, C.; Bridson, J. *J. Organomet. Chem.* **1993**, *461*, 215 and references therein. (b) Ceccon, A.; Elsevier, C. J.; Ernsting, J. M.; Gambaro, A.; Santi, S.; Venzo, A. *Inorg. Chim. Acta* **1993**, *204*, 15.

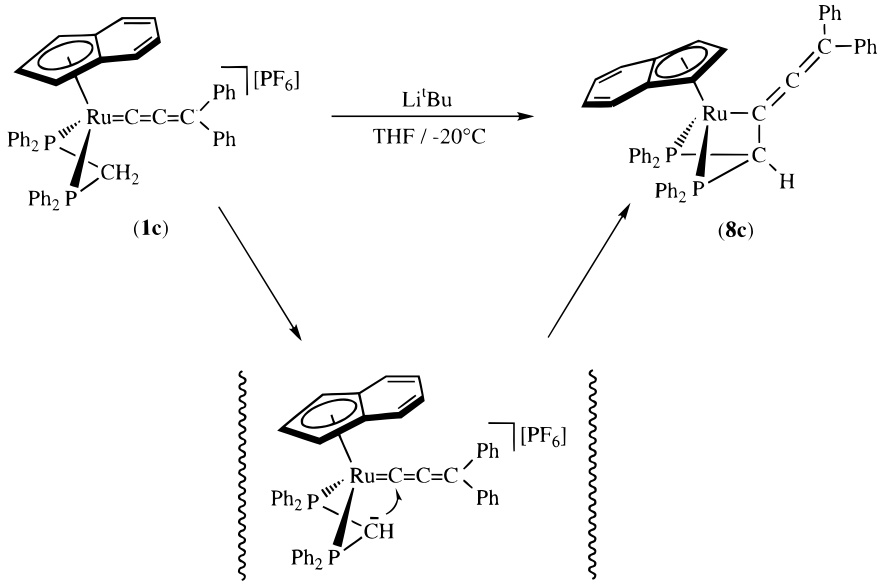
(21) Crochet, P.; Demerseman, B.; Vallejo-Roales, M. I.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics*, in press.

(22) We have reported similar intramolecular C−C coupling processes on cationic vinylidene−iron(II)−dppm complexes. Gamasa, M. P.; Gimeno, J.; Lastra, E.; Martín, B. M.; Aguirre, A.; García-Granda, S.; Pertierra, P. *J. Organomet. Chem.* **1992**, *429*, C19.

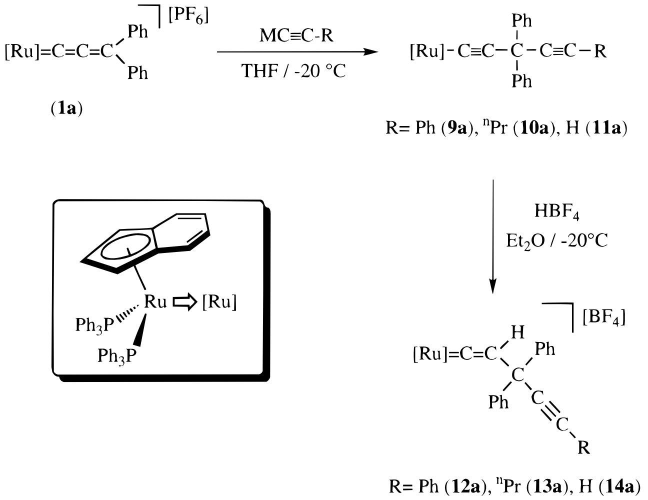
(23) Borge, J.; García-Granda, S. Unpublished results.

(24) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics*, in press.

Scheme 3



Scheme 4



position of the unsaturated chain. In accordance with this the allenylidene complexes **1a**,**b** do not react with Li^{t}Bu.

The behavior of the monosubstituted allenylidene complex [Ru{=C=C=C(H)Ph}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**2a**) toward LiR (R = Me, ^{n}Bu, ^{t}Bu) under different reaction conditions also has been examined; however, the reactions led to complex mixtures of compounds, which were not identified.

Reaction of Allenylidene Complexes with Acetylides. Regioselective additions to the C_γ of the allenylidene chain of the complex [Ru(=C=C=CPh$_2$)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1a**) also take place when acetylides are used as nucleophiles. Thus, complex **1a** reacts in THF with an equimolar amount of LiC≡CR (R = Ph, ^{n}Pr) at −20 °C or with a large excess of NaC≡CH at room temperature to furnish yellow solutions, from which the alkynyl complexes **9a**−**11a** are isolated (67−96% yield) (Scheme 4).

The analytical and spectroscopic data for **9a**−**11a** are fully consistent with these formulations (see Experimental Section and Tables 1 and 2). Moreover, the structure of complex **11a** has been confirmed by an X-ray diffraction study. A drawing of the molecular structure is shown in Figure 1. Selected bond distances and angles are listed in Table 3. 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 (Table 3). The alkynyl ligand, which is nearly linear (Ru−C(1)−C(2) angle of 175.0(2)°), is bound to ruthenium, showing bond lengths of Ru−C(1) of 1.993(2) Å and of C(1)−C(2) of 1.209(3) Å. These bonding parameters can be compared to those of the analogous alkynyl complex [Ru(C≡CC{CH$_2$C(OMe)=W(CO)$_5$}Ph$_2$)(η^5-C_9H_7)(PPh_3)$_2$].[18b] The C(4)−C(5) bond length (1.170(4) Å) shows a typical value of a C≡C bond.

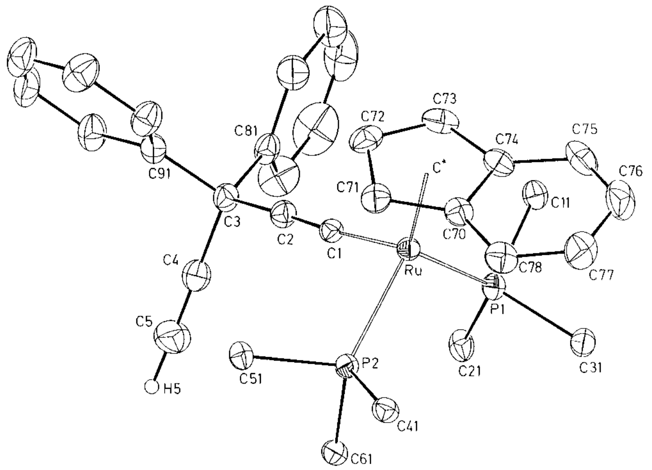


Figure 1. ORTEP view of the structure of the alkynyl complex [Ru{C≡CC(C≡CH)Ph$_2$}(η^5-C_9H_7)(PPh_3)$_2$] (**11a**). For clarity, aryl groups of the triphenylphosphine ligands are omitted (C* = centroid of the indenyl ring).

Although the indenyl group is η^5-bonded to the metal atom, the structure shows a slight distortion of the five-carbon ring from planarity with a hinge angle (HA) of 6.0(2)° and a fold angle (FA) of 11.8(2)° (Table 3). The characteristic slippage of the indenyl ring is also observed with a slip-fold (Δ) value of 0.168(2) Å, which is significantly lower than those shown by the analogous vinylidene derivatives (Table 4). The slight distortions toward an η^3 binding mode in the solid state appear to

Table 3. 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 11a

Distances			
Ru−C*	1.942(2)	P(2)−C(41)	1.844(2)
Ru−P(1)	2.3145(9)	P(2)−C(51)	1.849(2)
Ru−P(2)	2.292(1)	P(2)−C(61)	1.840(2)
Ru−C(70)	2.376(2)	Ru−C(1)	1.993(2)
Ru−C(71)	2.207(2)	C(1)−C(2)	1.209(3)
Ru−C(72)	2.196(2)	C(2)−C(3)	1.484(3)
Ru−C(73)	2.250(2)	C(3)−C(81)	1.549(3)
Ru−C(74)	2.416(2)	C(3)−C(91)	1.550(3)
P(1)−C(11)	1.842(2)	C(3)−C(4)	1.489(3)
P(1)−C(21)	1.833(2)	C(4)−C(5)	1.170(4)
P(1)−C(31)	1.836(2)	C(5)−H(5)	0.94(3)
Δ	0.168(2)		
Angles			
C*−Ru−C(1)	120.5(1)	C(2)−C(3)−C(81)	108.9(2)
C*−Ru−P(1)	125.6(1)	C(2)−C(3)−C(91)	113.4(2)
C*−Ru−P(2)	121.6(2)	C(2)−C(3)−C(4)	108.2(2)
C(1)−Ru−P(1)	85.44(7)	C(81)−C(3)−C(4)	111.1(2)
C(1)−Ru−P(2)	89.73(6)	C(91)−C(3)−C(4)	107.6(2)
P(1)−Ru−P(2)	103.55(4)	C(3)−C(4)−C(5)	178.1(3)
Ru−C(1)−C(2)	175.0(2)	C(4)−C(5)−H(5)	178.(2)
C(1)−C(2)−C(3)	176.7(2)		
FA	11.8(2)	HA	6.0(2)
DA	177.0(2)	CA	161.9(1)

[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).

be maintained in solution, according to the value of Δδ(C-3a,7a) = −21.23 ppm obtained from the $^{13}C\{^1H\}$ NMR spectra.

We have previously reported that the orientation of the benzo ring of the indenyl ligand in vinylidene− and allenylidene−indenyl−ruthenium(II) complexes is clearly dependent on the nature of the unsaturated chain.[10f,18a] Thus, while the preferred conformation of the indenyl ligand in vinylidene complexes is such that the benzo ring is oriented *trans* to the vinylidene group (CA ≈ 180°), the preferred conformation is *cis* (CA ≈ 0°) in allenylidene complexes (Table 4). The conformational angle (CA) in complex **11a** of 161.9(1)° (*trans* orientation) is in accordance with theoretical calculations (EHMO) carried out on the model [Ru(C≡CCH$_3$)(η^5-C$_9$H$_7$)(PH$_3$)$_2$] showing that the *trans* orientation is energetically more favored than the *cis*.[16b]

As described above for complexes **4a** and **5a** the ruthenium−alkynyl complexes **9a**−**11a** can be also protonated with HBF$_4$ in diethyl ether to yield the vinylidene derivatives **12a**−**14a** (77−82% yield) (Scheme 4). Spectroscopic data of **12a**−**14a** are in accordance with the proposed structures (see Experimental Section).

Reaction of Allenylidene Complexes with Phosphines. Phosphines are added regioselectively to the allenylidene group, the position of the addition (C$_\alpha$ or C$_\gamma$) being controlled by the ancillary ligands on the ruthenium atom. Thus, PMe$_3$ and PMe$_2$Ph react with complex **1a**, in THF at room temperature, to yield the air stable cationic alkynyl−phosphonio complexes **15a** (86%) and **16a** (65%) (Scheme 5). Similarly, alkynyl−phosphonio complexes **17a**−**20a** are obtained from the addition of PMe$_3$, PMe$_2$Ph, PMePh$_2$, and PPh$_3$ to the monosubstituted allenylidene complex [Ru{=C=C=C(H)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**2a**) in 52−98% yields (Scheme 5). However, the diphenylallenylidene complex **1a** does not react with PMePh$_2$ or PPh$_3$ even under refluxing THF, probably due to the steric requirements of the two bulky phenyl substituents on the C$_\gamma$ atom.

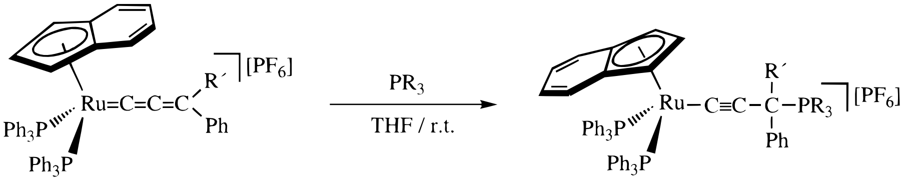
Complexes **15a**−**20a** have been analytically and spectroscopically (IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR) characterized (see Experimental Section and Tables 5 and 6 for details). The $^{31}P\{^1H\}$ NMR spectra of **15a**−**16a** and **17a** exhibit the expected resonances of an A$_2$M and an ABM spin system, respectively (Table 5). The unequivalency of the PPh$_3$ ligands in complex

Table 4. Slip Parameter Δ and Dihedral Angles FA, HA, and CA for Indenyl Ruthenium(II) Complexes[a]

complex	Ru−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)	18a
[{Ru}(=C=C(H)Ph)]$^+$	1.964(6)	0.175(6)	11.9(5)	6.6(5)	164.6(3)	23
[{Ru}(=C=C(Me)(C$_6$H$_9$))]$^+$	1.970(9)	0.1974(1)	12.2(4)	7.5(4)	160.0(3)	24
[{Ru}(=C=C=C(C$_{13}$H$_{20}$))]$^+$	1.942(5)	0.0820(4)	5.1(5)	5.3(5)	12.2(6)	14
[{Ru}(=C=C=CPh$_2$)]$^+$	1.951(5)	0.121(5)	8.1(3)	6.2(4)	9.6(3)	10f
(*E*)-[{Ru}(C(H)=C(PPh$_3$)(C$_6$H$_9$))]$^+$	1.981(5)	0.217(5)	14.8(4)	8.4(4)	160.5(2)	24
[{Ru}(C≡CC{CH$_2$C(OMe)=W(CO)$_5$}Ph$_2$)]	1.942(8)	0.1320	7.7(7)	4.4(7)	120.7(6)	18b
[{Ru}(C≡CC(C≡CH)Ph$_2$)]	1.942(2)	0.168(2)	11.8(2)	6.0(2)	161.9(1)	*b*

[a] Δ = *d*[Ru−C(74),C(70)] − *d*[Ru−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*, Ru/C*, Ru, C(1); {Ru} = Ru(η^5-C$_9$H$_7$)(PPh$_3$)$_2$. [b] This work.

Scheme 5



R´= Ph (**1a**), H (**2a**)

PR$_3$= PMe$_3$; R´= Ph (**15a**), H (**17a**)
PR$_3$= PMe$_2$Ph; R´= Ph (**16a**), H (**18a**)
PR$_3$= PMePh$_2$; R´= H (**19a**)
PR$_3$= PPh$_3$; R´= H (**20a**)

Table 5. $^{31}P\{^1H\}$ and ^1H NMR Data for the Alkynyl−Phosphonio Complexes[a]

				^1H				
				η^5-C_9H_7				
complex	$^{31}P\{^1H\}$	$^2J_{PP}$	$^5J_{PP}$	H-1,3	H-2	J_{HH}	H-4,7, H-5,6	others
[Ru{C≡CC(PMe_3)Ph_2}-(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**15a**)[b]	30.25 t (PMe_3) 52.57 d (PPh_3)		4.1	4.55 d	5.02 t	2.1	6.56 m, *d*	1.76 d (CH_3, $^2J_{HP}$ = 12.6); 6.94−7.38 m (PPh_3 and Ph)
[Ru{C≡CC(PMe_2Ph)Ph_2}-(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**16a**)[c]	28.78 t (PMe_2Ph) 53.74 d (PPh_3)		3.2	4.84 d	5.37 t	2.1	6.81 m, *d*	2.64 d (CH_3, $^2J_{HP}$ = 12.8); 7.24−7.95 m (PPh_3, PPh, and Ph)
[Ru{C≡CC(PMe_3)(H)Ph}-(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**17a**)[c]	29.23 m (PMe_3) 52.80 dd (PPh_3) 53.64 dd (PPh_3)	29.1	3.6	4.68 bs 4.71 bs	4.92 bs		6.64 m, *d*	1.79 d (CH_3, $^2J_{HP}$ = 13.5); 5.01 d (CH, $^2J_{HP}$ = 18.5); 7.08−7.60 m (PPh_3 and Ph)
[Ru{C≡CC(PMe_2Ph)(H)Ph}-(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**18a**)[c]	27.09 s (PMe_2Ph) 52.87 d (PPh_3) 53.33 d (PPh_3)	29.2		4.54 bs 4.72 bs	5.23 bs		6.33 m, 6.92 m	2.38 m (CH_3); 5.38 d (CH, $^2J_{HP}$ = 18.6); 6.95−7.98 m (PPh_3, PPh, and Ph)
[Ru{C≡CC($PMePh_2$)(H)Ph}-(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**19a**)[c]	23.08 s ($PMePh_2$) 51.36 d (PPh_3) 52.61 d (PPh_3)	30.6		4.36 bs 4.57 bs	5.16 bs		*d*, *e*	2.68 d (CH_3, $^2J_{HP}$ = 13.1); 6.64−8.42 m (PPh_3, PPh and Ph)
[Ru{C≡CC(PPh_3)(H)Ph}-(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**20a**)[c]	19.20 s ($CPPh_3$) 50.76 d ($RuPPh_3$) 51.16 d ($RuPPh_3$)	30.9		4.47 bs 4.59 bs	5.19 bs		6.00 m, *d*	6.05 d (CH, $^2J_{HP}$ = 9.8); 6.80−7.97 m (PPh_3 and Ph)
[Ru{C≡CC(PMe_3)Ph_2}-(η^5-C_9H_7)(dppe)][PF_6] (**15b**)[c]	32.14 t (PMe_3) 88.51 d (dppe)		3.9	5.64 bs	5.20 bs		*d*, *d*	1.57 d (CH_3, $^2J_{HP}$ = 13.1); 2.52 m (P(CH_2)$_2$P); 7.12−7.41 m (PPh_2 and Ph)
[Ru{C≡CC(PMe_3)Ph_2}-(η^5-C_9H_7)(dppm)][PF_6] (**15c**)[c]	18.45 d (dppm) 32.05 t (PMe_3)		2.8	5.78 bs	5.67 bs		*d*, *d*	1.68 d (CH_3, $^2J_{HP}$ = 13.0); 4.11 m, 5.03 m (P(CH_aH_b)P); 6.97−7.86 m (PPh_2 and Ph)

[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 $(CD_3)_2CO$. [d] Overlapped by PPh_3, PPh_2, PPh, or Ph protons. [e] 5.93−6.06 ppm (m, CH, H-4,7 or H-5,6).

Table 6. $^{13}C\{^1H\}$ NMR Data for the Alkynyl−Phosphonio Complexes[a]

	η^5-C_9H_7										
complex	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3a,7a)[d]	C-4,7, C-5,6	Ru−C_α	C_β	$^2J_{CP}$	C_γ	J_{CP}	others
15a[b]	72.66	94.99	109.86	−20.84	*e*, *e*	117.82 m	103.27 d	12.3	53.24 d	54.0	7.97 d (J_{CP} = 53.8, CH_3); 123.91−139.27 m (PPh_3 and Ph)
15b[c]	73.45	96.31	111.21	−19.49	125.07, 127.55	120.68 m	104.98 d	9.3	56.67 d	47.6	8.24 d (J_{CP} = 58.6, CH_3); 128.27−139.37 m (PPh_3, PPh, and Ph)
17a[c]	75.44	92.94	108.62 109.00	−21.89	123.85, 124.20 126.67, 126.99	114.75 m	96.53 d	10.9	39.55 d	50.3	6.51 d (J_{CP} = 54.4, CH_3); 127.74−138.51 m (PPh_3 and Ph)
18a[c]	73.68 74.81	93.32	108.56 109.47	−21.68	123.48, 124.03 126.48, 126.93	115.97 m	96.47 d	9.9	41.63 d	48.0	5.53 m (CH_3); 119.24−138.07 m (PPh_3, PPh, and Ph)
19a[c]	74.11 74.50	94.82	110.74	−19.96	119.79, 120.46 121.47, 122.01	114.82 m	98.32 d	9.8	40.09 d	47.1	4.25 d (J_{CP} = 59.0, CH_3); 123.20−138.79 m (PPh_3, PPh_2, and Ph)
20a[c]	74.47 74.97	94.59	111.86	−18.84	*e*, *e*, *e*, *e*	117.92 m	99.10 d	8.6	42.57 d	45.8	120.36−139.30 m (PPh_3 and Ph)
15b[c]	69.39	91.95	108.49	−22.21	*e*, *e*	121.45 m	99.45 d	10.7	52.48 d	54.0	7.24 d (J_{CP} = 54.3, CH_3); 27.15 m (P(CH_2)$_2$P); 124.10−133.43 m (PPh_2 and Ph)

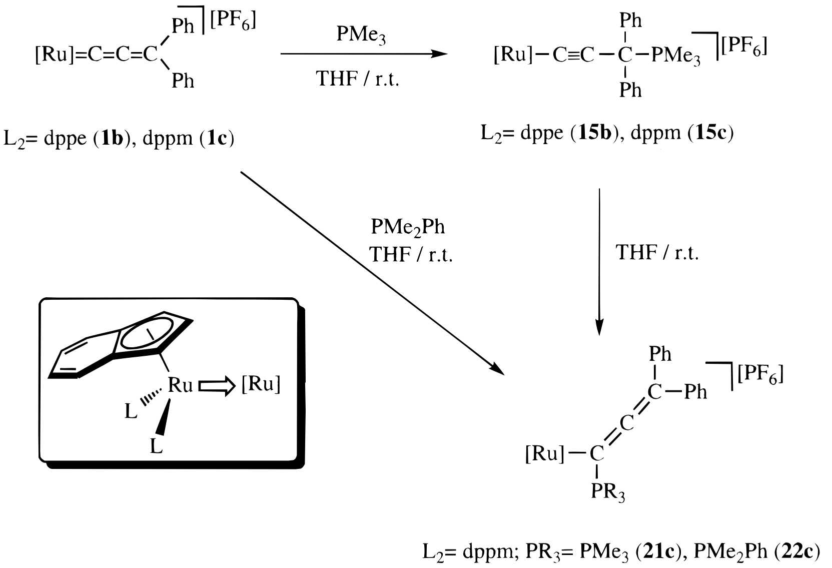
[a] δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; m, multiplet. [b] Spectra recorded in CD_2Cl_2. [c] Spectra recorded in $(CD_3)_2CO$. [d] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [e] Overlapped by PPh_3, PPh_2, PPh, or Ph carbons.

17a is due to the presence of the chiral C_γ atom in the alkynyl group. The $^{31}P\{^1H\}$ NMR spectra for complexes **18a**−**20a** are similar to that of **17a**, but in these cases the $^5J_{PP}$ could not be determined. ^1H and $^{13}C\{^1H\}$ NMR spectra (Tables 5 and 6) are in accordance with the proposed structures. In particular: (i) the CH proton resonance of the alkynyl group in complexes **17a**−**20a** appears as a doublet at δ 5.01−6.06 ($^2J_{HP}$ = 9.8−18.6 Hz) ppm due to the coupling with the phosphorus atom of the phosphine linked to the alkynyl group, and (ii) the C_α atom resonance for all the alkynyl−phosphonio complexes appears as a multiplet at δ 114.75−121.45 ppm, showing an effective coupling to the two phosphorus atoms of triphenylphosphine bonded to the metal and also to that of the phosphonio group. C_β and C_γ resonances appear as doublets at δ 96.53−103.27 ($^2J_{CP}$ = 8.6−12.3 Hz) and δ 39.55−53.24 (J_{CP} = 45.8−54.0 Hz) ppm, respectively.

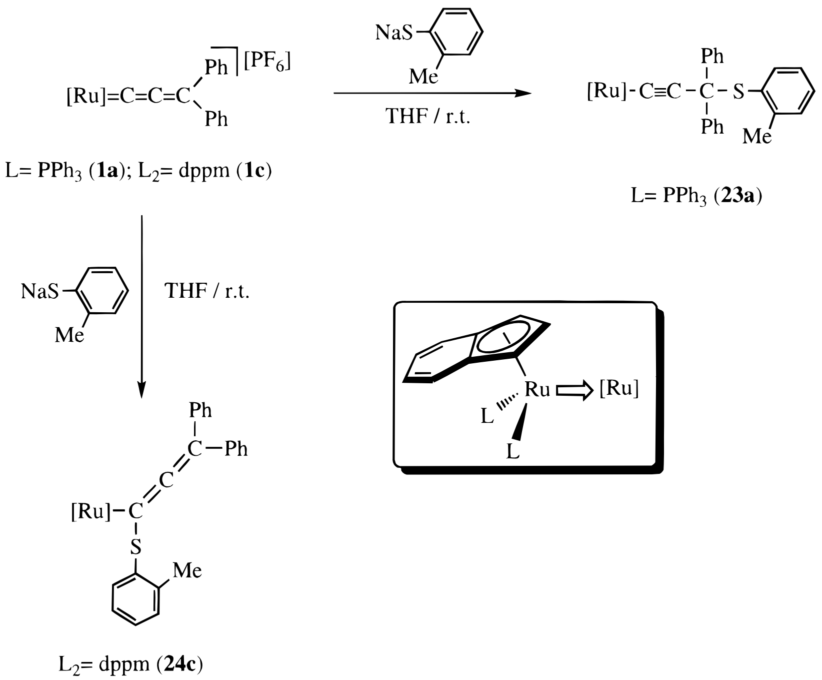
Allenylidene complexes **1b** and **1c** also react with PMe_3 to yield the alkynyl−phosphonio complexes **15b** (75%) and **15c** (90%), respectively (Scheme 6). Although complex **15b** is stable in solution, **15c** slowly rearranges in THF solution (14 h room temperature) to give the thermodynamically more stable allenyl−phosphonio complex [Ru{C(PMe_3)=C=CPh_2}(η^5-C_9H_7)(dppm)][PF_6] (**21c**) (70%), probably promoted by the steric requirements of the two bulky phenyl groups at the C_γ position (Scheme 6).

The IR spectrum (KBr) of **21c** shows a typical ν(C=C=C) absorption band at 1865 cm^{-1}. ^1H and $^{13}C\{^1H\}$ NMR spectra are also in accordance with the proposed structure. In particular, the carbon reso-

Scheme 6



Scheme 7



nances of the allenyl moiety appear in the $^{13}C\{^{1}H\}$ NMR spectrum at δ 83.46 (m, C_α), 210.81 (s, C_β) and 100.58 (d, $^{3}J_{CP} = 29.2$ Hz, C_γ) ppm. These resonances have been assigned accordingly to the data reported for the analogous allenyl−phosphonio complex $[Cr\{C(PMe_3)=C=CPh_2\}(CO)_5]$.[25] The $^{31}P\{^{1}H\}$ NMR spectrum of **21c** exhibits the expected resonances of an A_2M system at δ 11.79 ($^{3}J_{PP} = 6.8$ Hz, dppm) and δ 26.38 ($^{3}J_{PP} = 6.8$ Hz, PMe_3) ppm. The higher values of the coupling constants compared to that of **15c** ($^{5}J_{PP} = 2.8$ Hz) (see Table 5) are consistent with the position of PMe_3 in the C_α atom of the allenyl chain.

Complex **1c** also reacts with the bulkier phosphine PMe_2Ph leading to the direct formation of the allenyl−phosphonio complex **22c** (Scheme 6) identified on the basis of the NMR data by comparison with those of the analogous **21c** (see Experimental Section). In contrast, the reaction of diphenylallenylidene complex **1b** yields a mixture of the corresponding alkynyl−phosphonio and allenyl−phosphonio complexes. All attempts to form these complexes regioselectively were unsuccessful.

Reaction of Allenylidene Complexes with Sodium 2-Methylthiophenolate. The reaction of diphenylallenylidene ruthenium(II) complexes **1a**−**c** toward sodium 2-methylthiophenolate is similar to their reaction toward PMe_2Ph. Thus, starting from **1a** the alkynyl complex **23a** can be obtained in 45% yield, while using **1c** the allenyl derivative **24c** was formed in 56% yield (Scheme 7). Similarly, when complex **1b** was used a mixture of the corresponding alkynyl and allenyl complexes was obtained.

Analytical and spectroscopic data (IR and $^{31}P\{^{1}H\}$, ^{1}H, and $^{13}C\{^{1}H\}$ NMR) of **23a** and **24c** are in accordance with the proposed structures (see Experimental Section and Tables 1 and 2).

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[25] (a) Fischer, H.; Reindl, D.; Troll, C.; Leroux, F. *J. Organomet. Chem.* **1995**, *490*, 221. (b) For comparison with other mononuclear allenyl−ruthenium complexes, see ref 21.

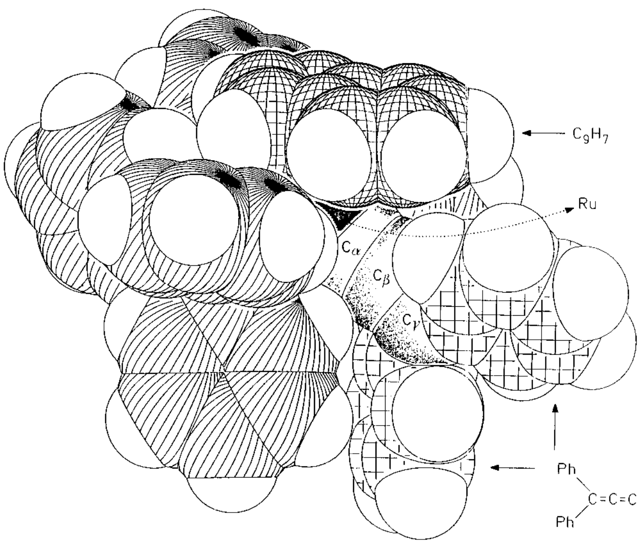

Figure 2. Space-filling representation of the allenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (**1a**).

Concluding Remarks

In this work a systematic study of nucleophilic additions to indenyl−ruthenium(II)−allenylidene complexes is reported. Although theoretical calculations (EHMO) only show small differences in the electrophilicity of C_α and C_γ atoms (LUMO is centered on C_α 25% and C_γ 33%),[16] the preferred *cis* orientation of the benzo ring of the indenyl ligand and the presence of bulky ancillary phosphine ligands on the ruthenium atom protect the electrophilic C_α atom of the unsaturated chain sterically. In contrast, the C_γ atom is more accessible and nucleophiles may be added to this position (Figure 2). Thus complexes $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)L_2]^+$ (L_2 = 2PPh_3 (**1a**), dppe (**1b**)) undergo regioselective additions to the C_γ atom with typical nucleophiles such as methoxide, alkyl, acetylide, and phosphines to give functionalized alkynyl derivatives $[Ru\{C{\equiv}CC(Nu)Ph_2\}(\eta^5\text{-}C_9H_7)L_2]^{n+}$ (n = 0 (**3a**,**b**−**5a**,**b**, **9a**−**11a**) and n = 1 (**15a**,**b**, **16a**, **19a**−**20a**)) in good yields.

The substitution of dppe or the two triphenylphosphine ligands by the small-bite chelating dppm decreases the steric protection of the electrophilic C_α atom. This allows the formation of the allenyl complexes $[Ru\{C(PR_3)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(dppm)]^+$ (**21c**, **22c**) which are obtained by the reaction of the complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(dppm)]^+$ (**1c**) with PMe_3 and PMe_2Ph. It is also apparent that the generation of the allenyl complex **21c** appears to be thermodynamically controlled since the alkynyl−phosphonio complex $[Ru\{C{\equiv}CC(PMe_3)Ph_2\}(\eta^5\text{-}C_9H_7)(dppm)]^+$ (**15c**) is formed initially. The steric influence of the two bulky phenyl groups in the C_γ position of the unsaturated chain *vs* dppm seems to determine the regioselective formation of the allenyl complex **22c** through the addition of the bulkier phosphine PMe_2Ph to the C_α atom (the putative alkynyl intermediate has not been detected). The subtle competence in the steric control between the ancillary ligands and the substituents in the C_γ atom is confirmed in the nucleophilic addition of PMe_2Ph to the complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ which takes place on the C_γ atom of the allenylidene chain to give the phosphonio-alkynyl complex **16a**.

A similar behavior is also observed in the nucleophilic addition of sodium 2-methylthiophenolate to complex **1a** or **1c** yielding the alkynyl complex **23a** or the allenyl complex **24c**, respectively.

In summary, it is shown that the regioselectivity of the nucleophilic additions to the allenylidene group is accomplished by the appropriate selection both of the substituents on the hydrocarbon unsaturated chain and of the ancillary ligands on the ruthenium atom. This strategy provides a good synthetic methodology for the generation of a wide series of derivatives showing the ability of the allenylidene complexes as precursors of novel hydrocarbon functionalities.

Experimental Section

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The allenylidene complexes $[Ru\{=C=C=C(R)Ph\}(\eta^5\text{-}C_9H_7)L_2][PF_6]$ (**1a**−**c**, **2a**) were prepared as previously reported.[10f] All reagents were purchased from commercial suppliers and used as received.

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 conductimeter. The C and H analyses were carried out with a Perkin-Elmer 240-B microanalyzer (uncompleted combustion was observed for complex **3c**). NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic data for the alkynyl complexes are collected in Tables 1, 2, 4 and 5.

Synthesis of $[Ru\{C{\equiv}CC(R)Ph_2\}(\eta^5\text{-}C_9H_7)L_2]$ (L = PPh_3, R = OMe (3a), Me (4a), ^{n}Bu (5a), C≡CPh (9a), C≡C^{n}Pr (10a), C≡CH (11a); L_2 = dppe, R = OMe (3b), Me (4b), ^{n}Bu (5b); L_2 = dppm, R = OMe (3c)). To a solution of the corresponding allenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)L_2][PF_6]$ (**1a**−**c**) (1 mmol) in 50 mL of THF was added, at −20 °C, NaOMe (0.08 g, 1.5 mmol), or the corresponding LiR (in hexane solution, 2 mmol), or a THF solution of the corresponding LiC≡CR (R = Ph, ^{n}Pr) (1 mmol), or a large excess (*ca.* 1:10) of NaC≡CH (suspension in xylene). The mixture was allowed to warm to room temperature, and the solvent was then removed *in vacuo*. The solid residue was extracted with hexane (for complexes **4a**,**b**, 5**a**,**b**) or diethyl ether (for complexes **3a**−**c** and **9a**−**11a**) and filtered. Evaporation of the solvent gave the alkynyl complexes **3a**−**c**, **4a**,**b**, **5a**,**b** and **9a**−**10a** as yellow-orange solids. Complex **11a** was purified by column chromatography (silica gel) collecting the orange band eluted with a mixture of hexane/diethyl ether (4/1). Yield (%) IR data (KBr, ν(C≡C), cm^{-1}), analytical data, and mass spectral data (FAB, m/e) are as follows. **3a**: 90; 2058. Anal. Calcd for $RuC_{61}H_{50}P_2O$: C, 76.15; H, 5.24. Found: C, 75.60; H, 5.12. $[M^+ + 1] = 963$, $[M^+ - R + 1] = 932$, $[M^+ - R - PPh_3] = 669$, $[M^+ - R - C_9H_7 - PPh_3] = 553$. (R = OCH_3). **3b**: 94; 2086. Anal. Calcd for $RuC_{51}H_{44}P_2O$: C, 73.27; H, 5.30. Found: C, 72.78; H, 5.35. $[M^+] = 835$, $[M^+ - R] = 805$. (R = OCH_3). **3c**: 96; 2081. Anal. Calcd for $RuC_{50}H_{42}P_2O$: C, 73.04; H, 5.15. Found: C, 72.03; H, 5.13. $[M^+ - R] = 791$. (R = OCH_3). **4a**: 75; 2086. Anal. Calcd for $RuC_{61}H_{50}P_2$: C, 77.36; H, 5.43. Found: C, 77.03; H, 5.50. **4b**: 62; 2089. Anal. Calcd for $RuC_{51}H_{44}P_2$: C, 74.70; H, 5.41. Found: C, 74.27; H, 5.48. **5a**: 71; 2077. Anal. Calcd for $RuC_{64}H_{56}P_2$: C, 77.79; H, 5.71. Found: C, 78.09; H, 6.19. **5b**: 75; 2088. Anal. Calcd for $RuC_{54}H_{50}P_2$: C, 75.24; H, 5.85. Found: C, 75.15; H, 5.94. **9a**: 67; 1953, 2074. Anal. Calcd for $RuC_{68}H_{52}P_2$: C, 79.12; H, 5.07. Found: C, 77.73; H, 5.43. $[M^+ + 1] = 1033$, $[M^+ - R] = 741$. (R = $C{\equiv}CCPh_2C{\equiv}CPh$). **10a**: 70; 1943, 2078. Anal. Calcd for $RuC_{65}H_{54}P_2$: C, 78.21; H, 5.45. Found: C, 77.84; H, 5.65. $[M^+ + 1] = 999$, $[M^+ - R]$

= 741. (R = C≡CCPh$_2$C≡C^{n}Pr). **11a**: 96; 1962, 2077. Anal. Calcd for $RuC_{62}H_{48}P_2$: C, 77.87; H, 5.06. Found: C, 76.87; H, 5.68.

Synthesis of [Ru{=C=C(H)C(R)Ph$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (R = Me (6a), ^{n}Bu (7a), C≡CPh (12a), C≡C^{n}Pr (13a), C≡CH (14a)). A solution of the corresponding alkynyl complex [Ru{C≡CC(R)Ph$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (**4a**, **5a**, or **9a**−**11a**) (1 mmol) in 100 mL of diethyl ether, at −20 °C, was treated dropwise with strong stirring with a dilute solution of HBF$_4$·Et$_2$O in diethyl ether. Immediately, an insoluble solid precipitated, but the addition was continued until no further solid was formed. The solution was then decanted and the brown solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield (%), IR data (KBr, ν(BF$_4^-$), cm^{-1}), analytical data, conductivity data (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), and NMR spectroscopic data are as follows. **6a**: 83; 1058. Anal. Calcd for $RuC_{61}H_{51}F_4P_2B$: C, 70.86; H, 4.97. Found: C, 70.08; H, 5.01. 121. NMR: $^{31}P\{^1H\}$ (CDCl$_3$) δ 38.04 (s) ppm; ^1H (CDCl$_3$) δ 1.54 (s, 3H, CH$_3$), 4.49 (s, 1H, Ru=C=CH), 5.37 (d, 2H, J_{HH} = 2.3 Hz, H-1,3), 5.70 (t, 1H, J_{HH} = 2.3 Hz, H-2), 5.75 (m, 2H, H-4,7 or H-5,6), 6.69−7.50 (m, 42H, Ph, H-4,7 or H-5,6) ppm; $^{13}C\{^1H\}$ (CDCl$_3$) δ 30.51 (s, CH$_3$), 47.62 (s, C$_\gamma$), 82.62 (s, C-1,3), 98.70 (s, C-2), 116.38 (s, C-3a,7a), 123.48 (s, C$_\beta$), 123.82 and 127.23 (s, C-4,7 and C-5,6), 127.50−149.06 (m, Ph), 346.99 (t, $^2J_{CP}$ = 16.7 Hz, Ru=C$_\alpha$) ppm. Δδ(C-3a,7a) = −14.32. **7a**: 79; 1061. Anal. Calcd for $RuC_{64}H_{57}F_4P_2B$: C, 71.44; H, 5.34. Found: C, 71.96; H, 5.16. 115. NMR: $^{31}P\{^1H\}$ (CDCl$_3$) δ 36.78 (s) ppm; ^1H (CDCl$_3$) δ 0.77 (t, 3H, J_{HH} = 7.1 Hz, CH$_3$), 1.14 (m, 2H, CH$_2$), 1.61 (m, 2H, CH$_2$), 1.70 (m, 2H, CH$_2$), 4.45 (s, 1H, Ru=C=CH), 5.21 (d, 2H, J_{HH} = 2.1 Hz, H-1,3), 5.32 (m, 2H, H-4,7 or H-5,6), 5.92 (t, 1H, J_{HH} = 2.1 Hz, H-2), 6.57−7.54 (m, 42H, Ph, H-4,7 or H-5,6) ppm; $^{13}C\{^1H\}$ (CDCl$_3$) δ 14.87 (s, CH$_3$), 23.40 (s, CH$_2$), 27.56 (s, CH$_2$), 41.73 (s, CH$_2$), 51.62 (s, C$_\gamma$), 80.96 (s, C-1,3), 98.86 (s, C-2), 117.58 (s, C-3a,7a), 119.16 (s, C$_\beta$), 123.92 and 127.22 (s, C-4,7 and C-5,6), 127.83−147.87 (m, Ph), 344.64 (t, $^2J_{CP}$ = 17.3 Hz, Ru=C$_\alpha$) ppm. Δδ(C-3a,7a) = −13.12. **12a**: 82; 1058, 1967: Anal. Calcd for $RuC_{68}H_{53}F_4P_2B$: C, 72.92; H, 4.77. Found: C, 73.25; H, 4.90. 125. NMR: $^{31}P\{^1H\}$ (CDCl$_3$) δ 38.46 (s) ppm; ^1H (CDCl$_3$) δ 4.42 (s, 1H, Ru=C=CH), 5.47 (d, 2H, J_{HH} = 2.5 Hz, H-1,3), 5.83 (m, 3H, H-2 and H-4,7 or H-5,6), 6.73−7.44 (m, 47H, Ph, H-4,7 or H-5,6) ppm; $^{13}C\{^1H\}$ (CDCl$_3$) δ 46.84 (s, C$_\gamma$), 82.31 (s, C-1,3), 86.77 and 93.03 (s, C≡C), 98.47 (s, C-2), 116.00 (s, C-3a,7a), 120.82 (s, C$_\beta$), 122.57−145.50 (m, Ph, C-4,7, C-5,6), 345.41 (t, $^2J_{CP}$ = 16.2 Hz, Ru=C$_\alpha$) ppm. Δδ(C-3a,7a) = −14.70. **13a**: 77; 1059, 1967: Anal. Calcd for $RuC_{65}H_{55}F_4P_2B$: C, 71.89; H, 5.10. Found: C, 71.22; H, 5.13. 119. NMR: $^{31}P\{^1H\}$ (CDCl$_3$) δ 38.51 (s) ppm; ^1H (CDCl$_3$) δ 0.95 (t, 3H, J_{HH} = 7.3 Hz, CH$_3$), 1.55 (m, 2H, CH$_2$), 2.19 (t, 2H, J_{HH} = 7.0 Hz, CH$_2$), 4.40 (s, 1H, Ru=C=CH), 5.37 (d, 2H, J_{HH} = 2.0 Hz, H-1,3), 5.81 (m, 3H, H-2 and H-4,7 or H-5,6), 6.73−7.47 (m, 42H, Ph, H-4,7 or H-5,6) ppm; $^{13}C\{^1H\}$ (CDCl$_3$) δ 13.66 (s, CH$_3$), 21.39 (s, CH$_2$), 22.21 (s, CH$_2$), 46.55 (s, C$_\gamma$), 81.72 (s, C-1,3), 84.11 and 87.37 (s, C≡C), 98.61 (s, C-2), 116.18 (s, C-3a,7a), 121.23 (s, C$_\beta$), 123.21 and 130.40 (s, C-4,7 and C-5,6), 127.09−146.09 (m, Ph), 347.62 (t, $^2J_{CP}$ = 16.4 Hz, Ru=C$_\alpha$) ppm. Δδ(C-3a,7a) = −14.52. **14a**: 79; 1059, 1966. Anal. Calcd for $RuC_{62}H_{49}F_4P_2B$: C, 71.33; H, 4.73. Found: C, 71.02; H, 4.68. 103. NMR: $^{31}P\{^1H\}$ (CDCl$_3$) δ 40.22 (s) ppm; ^1H (CDCl$_3$) δ 3.63 (s, 1H, ≡CH), 4.65 (s, 1H, Ru=C=CH), 5.70 (d, 2H, J_{HH} = 2.6 Hz, H-1,3), 5.95 (t, 1H, J_{HH} = 2.6 Hz, H-2), 6.17 (m, 2H, H-4,7 or H-5,6), 6.89−7.53 (m, 42H, Ph, H-4,7 or H-5,6) ppm; $^{13}C\{^1H\}$ (CDCl$_3$) δ 47.16 (s, C$_\gamma$), 78.09 (s, ≡CH), 84.60 (s, C-1,3), 88.32 (s, ≡C), 99.97 (s, C-2), 116.87 (s, C-3a,7a), 122.30 (s, C$_\beta$), 124.55 (s, C-4,7 or C-5,6), 128.31−146.52 (m, Ph, C-4,7 or C-5,6), 347.74 (t, $^2J_{CP}$ = 16.7 Hz, Ru=C$_\alpha$) ppm. Δδ(C-3a,7a) = −13.83.

Synthesis of [Ru{(κ^3(*C,P,P*)-$\overline{\text{C=C=CPh}_2\text{(Ph}_2\text{P}}$CHPPh$_2$)}(η^5-C$_9H_7$)] (8c). To a solution of [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)(dppm)][PF$_6$] (**1c**) (0.936 g, 1 mmol) in 50 mL of THF was added, at −20 °C, Li^{t}Bu (0.6 mL of a solution 1.6 M in hexane, 1 mmol). The mixture was allowed to warm to room temperature, and the solvent was then removed *in vacuo*. The solid residue was extracted with diethyl ether and filtered. Evaporation of the diethyl ether gave complex **8c** as a yellow solid. Yield (%), IR data (KBr, ν(C=C=C), cm^{-1}), analytical data, NMR spectroscopic data, and mass spectral data (FAB, *m/e*) are as follows: 80; 1903. Anal. Calcd for $RuC_{49}H_{38}P_2$: C, 74.51; H, 4.85. Found: C, 73.85; H, 4.88. NMR: $^{31}P\{^1H\}$ (C$_6$D$_6$) δ 4.78 (s) ppm; ^1H (C$_6$D$_6$) δ 5.57 (t, 1H, $^2J_{HP}$ = 2.3 Hz, (Ph$_2$P)$_2$C*H*), 5.66 (d, 2H, J_{HH} = 3.0 Hz, H-1,3), 6.17 (t, 1H, J_{HH} = 3.0 Hz, H-2), 6.80−8.00 (m, 34H, Ph, H-4,7, H-5,6) ppm; $^{13}C\{^1H\}$ (C$_6$D$_6$) δ 66.08 (s, C-1,3), 66.76 (t, J_{CP} = 21.1 Hz, (Ph$_2$P)$_2$*C*H), 83.15 (t, $^2J_{CP}$ = 50.3 Hz, Ru−C$_\alpha$), 87.17 (s, C-2), 102.22 (s, C-3a,7a), 105.48 (t, $^4J_{CP}$ = 7.2 Hz, C$_\gamma$), 122.47 (s, C-4,7 or C-5,6), 123.47−150.26 (m, Ph, C-4,7 or C-5,6), 209.39 (t, $^3J_{CP}$ = 15.2 Hz, C$_\beta$) ppm. Δδ(C-3a,7a) = −28.48. [M$^+$ + 1] = 791, [M$^+$ − C$_9$H$_7$] = 675.

Synthesis of [Ru{C≡CC(PR$_3$)(R′)Ph}(η^5-C$_9$H$_7$)L$_2$][PF$_6$] (L = PPh$_3$, R′ = Ph, PR$_3$ = PMe$_3$ (15a), PMe$_2$Ph (16a); L = PPh$_3$, R′ = H, PR$_3$ = PMe$_3$ (17a), PMe$_2$Ph (18a), PMePh$_2$ (19a), PPh$_3$ (20a); L$_2$ = dppe, R′ = Ph, PR$_3$ = PMe$_3$ (15b); L$_2$ = dppm, R′ = Ph, PR$_3$ = PMe$_3$ (15c)). To a solution of the corresponding allenylidene complex **1a**−**c** or **2a**−**c** (1 mmol) in 50 mL of THF was added, at room temperature, the corresponding PR$_3$ (1.5 mmol), and the resulting solution was stirred for 15 min. The solvent was then removed *in vacuo*, and the yellow-brown solid residue was washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield (%), IR data (KBr, ν(PF$_6^-$), ν(C≡C), cm^{-1}), analytical data, and mass spectral data (FAB, *m/e*) are as follows. **15a**: 86; 840, 2041. Anal. Calcd for $RuC_{63}H_{56}F_6P_4Ru$: C, 65.68; H, 4.90. Found: C, 64.91; H, 5.01. [M$^+$] = 1007, [M$^+$ − R] = 931, [M$^+$ − R − C$_9$H$_7$ − PPh$_3$] = 553. (R = PMe$_3$). **16a**: 65; 839, 2035: Anal. Calcd for $RuC_{68}H_{58}F_6P_4Ru$: C, 67.27; H, 4.81. Found: C, 66.79; H, 5.15. **17a**: 82; 840, 2082. Anal. Calcd for $RuC_{57}H_{52}F_6P_4Ru$: C, 63.62; H, 4.87. Found: C, 63.21; H, 4.96. [M$^+$] = 931, [M$^+$ − R] = 855, [M$^+$ − R − PPh$_3$] = 593. (R = PMe$_3$). **18a**: 52; 840, 2080. Anal. Calcd for $RuC_{62}H_{54}F_6P_4Ru$: C, 65.43; H, 4.78. Found: C, 64.24; H, 4.73. **19a**: 98; 838, 2076. Anal. Calcd for $RuC_{67}H_{56}F_6P_4Ru$: C, 70.46; H, 4.94. Found: C, 69.79; H, 4.98. **20a**: 98; 839, 2070. Anal. Calcd for $RuC_{72}H_{58}F_6P_4Ru$: C, 68.51; H, 4.63. Found: C, 68.68; H, 4.66. **15b**: 75; 838, 2051. Anal. Calcd for $RuC_{53}H_{50}F_6P_4Ru$: C, 61.98; H, 4.91. Found: C, 61.03; H, 5.04. [M$^+$] = 881, [M$^+$ − R] = 805. (R = PMe$_3$). **15c**: 90; 838, 2054: Anal. Calcd for $RuC_{52}H_{48}F_6P_4Ru$: C, 61.65; H, 4.78. Found: C, 60.95; H, 4.79.

Synthesis of [Ru{C(PMe$_3$)=C=CPh$_2$}(η^5-C$_9$H$_7$)(dppm)][PF$_6$] (21c). A solution of [Ru{C≡CC(PMe$_3$)Ph$_2$}(η^5-C$_9$H$_7$)(dppm)][PF$_6$] (**15c**) (1.012 g, 1 mmol) in 50 mL of THF was stirred, at room temperature, for 14 h. The solvent was then removed *in vacuo*, and the yellow-brown solid residue was washed with diethyl ether (2 × 20 mL) and vacuum-dried. Yield (%), IR data (KBr, ν(PF$_6^-$), ν(C=C=C) cm^{-1}), analytical data, NMR spectroscopic data, and mass spectral data (FAB, *m/e*) are as follows: 70; 839, 1865. Anal. Calcd for $RuC_{52}H_{48}F_6P_4Ru$: C, 61.65; H, 4.78. Found: C, 60.95; H, 4.79. NMR: $^{31}P\{^1H\}$ ((CD$_3$)$_2$CO) δ 11.79 (d, $^3J_{PP}$ = 6.8 Hz, dppm), 26.38 (t, $^3J_{PP}$ = 6.8 Hz, PMe$_3$) ppm; ^1H ((CD$_3$)$_2$CO) δ 1.54 (d, 9H, $^2J_{HP}$ = 12.7 Hz, CH$_3$), 4.18 (m, 2H, PCH$_a$H$_b$P), 5.16 (d, 2H, J_{HH} = 2.5 Hz, H-1,3), 6.10 (t, 1H, J_{HH} = 2.5 Hz, H-2), 6.84−7.63 (m, 34H, Ph, H-4,7, H-5,6) ppm; $^{13}C\{^1H\}$ ((CD$_3$)$_2$CO) δ 14.34 (d, J_{CP} = 55.2 Hz, CH$_3$), 50.31 (t, J_{CP} = 21.7 Hz, PCH$_2$P), 67.77 (s, C-1,3), 83.46 (m, RuC$_\alpha$), 88.45 (s, C-2), 100.58 (d, $^3J_{CP}$ = 29.2 Hz, C$_\gamma$), 109.34 (s, C-3a,7a), 124.69−138.41 (m, Ph, C-4,7, C-5,6), 210.81 (s, C$_\beta$) ppm. Δδ(C-3a,7a) = −21.36. [M$^+$] = 867, [M$^+$ − R] = 791. (R = PMe$_3$).

Synthesis of [Ru{C(PMe$_2$Ph)=C=CPh$_2$}(η^5-C$_9$H$_7$)(dppm)][PF$_6$] (22c). This compound was prepared from **1c** (0.936 g, 1 mmol) and PMe$_2$Ph (0.143 mL, 1 mmol) in a reaction analogous to that used for the preparation of **15a**−**20a**. Yield (%), IR data (KBr, ν(PF$_6^-$), ν(C=C=C) cm^{-1}), analytical data, and NMR spectroscopic data are as follows: 67; 838, 1858. Anal. Calcd for $RuC_{57}H_{50}F_6P_4Ru$; C, 63.74; H, 4.60. Found: C, 63.83; H, 4.62. NMR: $^{31}P\{^1H\}$ ((CD$_3$)$_2$CO) δ 8.85 (d, $^3J_{PP}$ = 5.1 Hz, dppm), 22.16 (t, $^3J_{PP}$ = 5.1 Hz, PMe$_2$Ph) ppm; ^1H

($(CD_3)_2CO$) δ 1.82 (d, 6H, $^2J_{HP}$ = 12.5 Hz, CH_3), 4.27 (m, 1H, PCH_aH_bP), 5.19 (d, 2H, J_{HH} = 2.4 Hz, H-1,3), 5.25 (m, 1H, PCH_aH_bP), 6.32 (t, 1H, J_{HH} = 2.4 Hz, H-2), 6.79−7.96 (m, 39H, Ph, H-4,7, H-5,6) ppm; $^{13}C\{^1H\}$ ($(CD_3)_2CO$) δ 13.06 (d, J_{CP} = 58.1 Hz, CH_3), 49.85 (t, J_{CP} = 22.4 Hz, PCH_2P), 67.62 (s, C-1,3), 81.82 (m, RuC_α), 87.76 (s, C-2), 99.94 (d, $^3J_{CP}$ = 24.3 Hz, C_γ), 108.61 (s, C-3a,7a), 124.61 and 125.78 (s, C-4,7 and C-5,6), 126.21−138.53 (m, Ph), 212.50 (s, C_β) ppm. $\Delta\delta$(C-3a,7a) = −22.09.

Synthesis of [Ru{C≡CC[S(*o*-C_6H_4Me)]Ph_2}(η^5-C_9H_7)(PPh_3)$_2$] (23a). To a solution of [Ru(=C=C=CPh_2)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1a**) (1.075 g, 1 mmol) in 50 mL of THF was added, at room temperature, NaS(*o*-C_6H_4Me) (0.146 g, 1 mmol), and the resulting solution was stirred for 15 min. The solvent was then removed *in vacuo*. The solid residue was extracted with hexane and filtered. Evaporation of the hexane gave complex **23a** as a yellow solid. Yield (%), IR data (KBr, ν-(C≡C) cm^{-1}), and analytical data are as follows. 45; 2050. Anal. Calcd for $RuC_{67}H_{54}P_2SRu$: C, 76.30; H, 5.17. Found: C, 76.94; H, 5.01.

Synthesis of [Ru{C[S(*o*-C_6H_4Me)]=C=CPh_2}(η^5-C_9H_7)(dppm)] (24c). This compound was prepared from **1c** (0.936 g, 1 mmol) and NaS(*o*-C_6H_4Me) (0.146 g, 1 mmol) in a reaction analogous to that used for the preparation of **23a**. Yield (%), IR data (KBr, ν(C=C=C) cm^{-1}), analytical data, and NMR spectroscopic data are as follows. 56; 1875. Anal. Calcd for $RuC_{56}H_{46}P_2SRu$: C, 73.58; H, 5.07. Found: C, 73.22; H, 4.98. NMR: $^{31}P\{^1H\}$ (C_6D_6) δ 16.92 (s) ppm; ^1H (C_6D_6) δ 2.11 (s, 3H, CH_3), 3.57 (m, 2H, PCH_aH_bP), 5.26 (d, 2H, J_{HH} = 2.2 Hz, H-1,3), 5.57 (t, 1H, J_{HH} = 2.2 Hz, H-2), 6.58−7.16 (m, 38H, Ph, H-4,7, H-5,6) ppm; $^{13}C\{^1H\}$ (C_6D_6) δ 22.01 (s, CH_3), 46.23 (t, J_{CP} = 21.6 Hz, PCH_2P), 69.47 (s, C-1,3), 89.06 (s, C-2), 100.41 (t, $^2J_{CP}$ = 12.8 Hz, RuC_α), 104.14 and 109.65 (s, C-3a,7a and C_γ), 124.96−142.35 (m, Ph, C-4,7, C-5,6), 199.25 (s, C_β) ppm.

X-ray Diffraction Study. Data collection, crystal, and refinement parameters are collected in Table 7. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 15° and 20°). 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 1.00 and 1.11. On all reflections, a profile analysis[26,27] was performed. Lorentz and polarization corrections were applied, and the data were reduced to $|F_o|$ values.

The structure was solved by DIRDIF[28] (Patterson methods and phase expansion). Isotropic full-matrix least-squares refinement on $|F_o|^2$ using SHELXL93[29] converged to R = 0.08. At this stage an empirical absorption correction was applied using XABS2.[30] Maximum and minimum transmission factors were 1.00 and 0.73, respectively.

Finally, all hydrogen atoms (except H(5)) 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 with a common thermal parameter, riding on their parent atoms. Coordinates for H(5) were also refined. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics.

Table 7. Crystallographic Data for Complex 11a

formula	$C_{62}H_{48}P_2Ru$
a, Å	11.568(3)
b, Å	14.157(6)
c, Å	14.950(3)
α, deg	96.46(3)
β, deg	104.59(2)
γ, deg	90.91(6)
mol wt	956.01
Z	2
V, Å^3	2352.0(1)
D_{calcd}, g cm^{-3}	1.35
F(000)	988
wavelength, Å	0.71073
temp, K	293
radiation	Mo Kα
monochromator	graphite cryst
space group	$P\bar{1}$
cryst syst	triclinic
cryst size, mm	0.40, 0.30, 0.26
μ, mm^{-1}	0.44
range of abs	0.73−1.00
diffraction geom	$\omega-2\theta$
θ range, deg	1.42−24.97
index ranges for data collecn	$-13 \le h \le 13$ $-16 \le k \le 16$ $0 \le l \le 17$
no. of rflns measd	9003
no. of indep rflns	8245
no. of variables	590
agreement between equiv rflns[a]	0.015
final R factors ($I > 2\sigma(I)$)	R_1 = 0.026, wR_2 = 0.071
final R factors (all data)	R_1 = 0.037, wR_2 = 0.072

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

The maximum shift to esd ratio in the last full-matrix least-squares cycle was −0.002. The final difference Fourier map showed no peaks higher than 0.27 e Å^{-3} nor deeper than −0.35 e Å^{-3}. Atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974).[31] Geometrical calculations were made with PARST.[32] The crystallographic plots were made with EUCLID.[33] All calculations were made at the University of Oviedo on the Scientific Computer Center and X-Ray Group DEC-ALPHA computers.

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Supporting Information Available: Crystal structure data for **11a**, including tables of atomic parameters, anisotropic thermal parameters, bond distances, and bond angles (19 pages). Ordering information is given on any current masthead page.

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