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Phosphonioalkynyl indenylruthenium(II) complexes $[Ru\{C{\equiv}CC(R)H(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = Ph, $PR_3 = PMe_3$; R = H, $PR_3 = PPh_3$): suitable precursors of highly unsaturated σ-alkynyl and vinylidene derivatives

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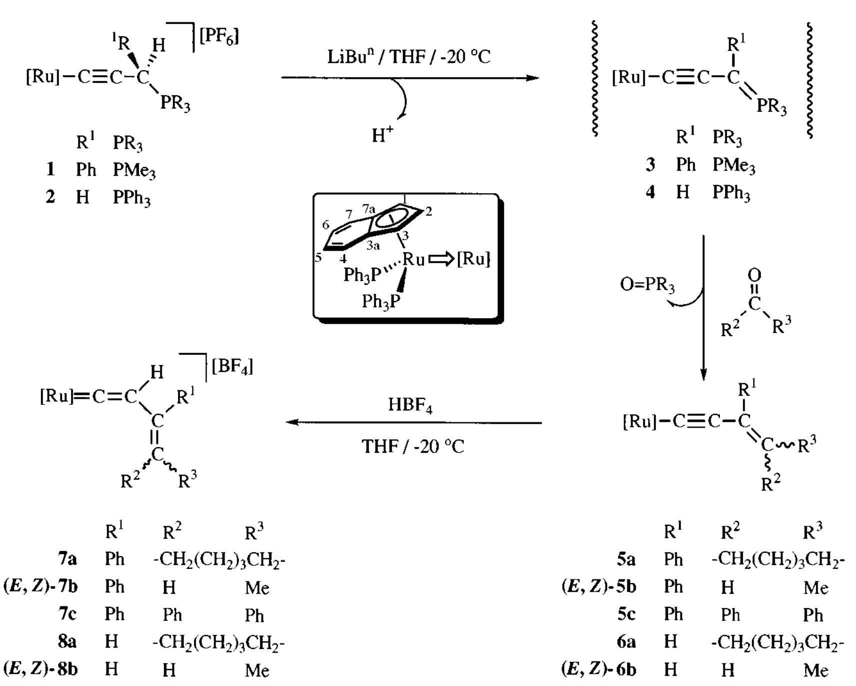
Deprotonation of the phosphonioalkynyl ruthenium(II) complexes $[Ru\{C{\equiv}CC(R^1)H(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R^1 = Ph$, $PR_3 = PMe_3$ **1**; $R^1 = H$, $PR_3 = PPh_3$ **2**) with $LiBu^n$ in THF at −20 °C gave the ylide alkynyl derivatives $[Ru\{C{\equiv}CC(R^1){=}PR_3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ ($R^1 = Ph$, $PR_3 = PMe_3$ **3**; $R^1 = H$, $PR_3 = PPh_3$ **4**), which react *in situ* with aldehydes or ketones *via* a Wittig process to afford the neutral σ-enynyl complexes $[Ru\{C{\equiv}CC(R^1){=}CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ [$R^2R^3 = CH_2(CH_2)_3CH_2$, $R^1 = Ph$ **5a** or H **6a**; $R^2 = H$, $R^3 = Me$, $R^1 = Ph$ **5b** or H **6b**; $R^2 = R^3 = R^1 = Ph$ **5c**]. Compounds **5b** and **6b** have been obtained as mixtures of the corresponding *E* and *Z* stereoisomers. Protonation of **5** and **6** with $HBF_4{\cdot}Et_2O$ in THF at −20 °C takes place selectively on the C_β of the enynyl chain to yield the cationic vinylvinylidene derivatives $[Ru\{{=}C{=}C(H)C(R^1){=}CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ [$R^2R^3 = CH_2(CH_2)_3CH_2$, $R^1 = Ph$ **7a** or H **8a**; $R^2 = H$, $R^3 = Me$, $R^1 = Ph$ **7b** or H **8b**; $R^2 = R^3 = R^1 = Ph$ **7c**]. The σ-polyenynyl complexes $[Ru\{C{\equiv}CC(R^1){=}CH(CH{=}CH)_nR^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ ($n = 1$, $R^2 = Ph$, $R^1 = Ph$ **9a** or H **10a**; $R^2 = Pr^n$, $R^1 = Ph$ **9b** or H **10b**; $n = 2$, $R^2 = Me$, $R^1 = Ph$ **11** or H **12**) have been obtained in high yields, as mixtures of the *E* and *Z* stereoisomers, by reaction of **3** and **4** with unsaturated aldehydes. Protonation of these derivatives yielded the highly unsaturated vinylidene complexes $[Ru\{{=}C{=}C(H)C(R^1){=}CH(CH{=}CH)_nR^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ ($n = 1$, $R^2 = Ph$, $R^1 = Ph$ **13a** or H **14a**; $R^2 = Pr^n$, $R^1 = Ph$ **13b** or H **14b**; $n = 2$, $R^2 = Me$, $R^1 = Ph$ **15** or H **16**). The σ-ynenynyl and σ-keteniminyl complexes $[Ru\{C{\equiv}CC(Ph){=}CH(C{\equiv}CPh)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and $[Ru\{C{\equiv}CC(Ph){=}C{=}NPh\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ have also been prepared by reaction of **3** with $PhC{\equiv}CCHO$ and phenyl isocyanate, respectively. The ^1H, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR data for all the novel complexes are reported.

The chemistry of ruthenium(II) complexes containing σ-alkynyl ligands $[Ru]{-}C{\equiv}CR$ has received increased interest in recent years.[1] Their versatile chemical and physical properties provide a variety of applications which have given rise to wide utility as materials in electronics, catalysis and synthesis. Thus, these complexes have been found to promote selective carbon–carbon coupling reactions[2] and catalytic transformations involving terminal alkynes.[3] They have been also used as valuable synthons to generate bi- and poly-metallic species containing hydrocarbon bridges,[4] metal containing polymers[5] and metallacumulenes.[6] The π system of the C≡C bond provides the $[Ru]{-}C{\equiv}C$ moiety with a suitable pathway for the electronic communication between the metal and functional groups attached at the end of the hydrocarbon chain. In particular, this type of ruthenium(II) complex incorporating appropriate electron acceptor groups exhibits non-linear optical properties.[7] Analogous σ-alkynyl derivatives containing conjugated carbon–carbon double bonds, namely polyenynyl complexes $[Ru]{-}C{\equiv}CCR{=}CR(CR{=}CR)_nR$, should show even more attractive properties since the introduction of these C=C bonds into the hydrocarbon chain provides not only a longer π system for charge delocalization (with a potential enhancement of the NLO properties) but also additional reaction centers. However, to date only ruthenium(II) σ-vinylalkynyl derivatives $[Ru]{-}C{\equiv}CC(R^1){=}CR^2R^3$ are known: $[Ru] = [Ru(\eta^5\text{-}C_5H_5)L(L')]$ ($L = L' = PPh_3$ or PMe_3; L = CO, $L' = PPr^i{}_3$),[6b,d,8a,b,9] $[Ru(\eta^5\text{-}C_5Me_5)(dippe)]$ [dippe = 1,2-bis(diisopropylphosphino)ethane],[10c] $[Ru(\eta^5\text{-}C_9H_7)L_2]$ [$L_2 = 2PPh_3$, 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm)],[8c,d] *trans*-$[RuCl(P{-}P)_2]$ (P–P = dppm or dippe),[6c,e,8e,10a] and [Ru(Tp)(dippe)] [Tp = hydrotris(pyrazolyl)borate].[10b] The most general synthetic approach employs terminal alkynes as a source of the enynyl group which is formed: (*i*) by deprotonation of cumulene complexes either vinylvinylidene[8] $[Ru]^+{=}C{=}C(H)C(R^1){=}CR^2R^3$ or methyl-substituted allenylidene $[Ru]^+{=}C{=}C{=}C(Me)R$ derivatives[8d,10] which are both obtained from 1-alkyn-3-ols $HC{\equiv}C{-}CR^1(OH)C(H)R^2R^3$, and (*ii*) by regioselective addition of nucleophiles on the C_γ atom of butatrienylidene complexes[6b–e] $[Ru]^+{=}C{=}C{=}C{=}C(H)R$ which are synthesized from terminal 1,3-diynes $HC{\equiv}CC{\equiv}CR$. Classical halide exchange by enynyl anions in the complex $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ to yield σ-enynyl derivatives $[Ru\{C{\equiv}CC(R^1){=}CR^2R^3\}(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ has also been reported.[9]

In the course of our investigations aimed at understanding the reactivity patterns of cationic indenylruthenium(II) allenylidene complexes $[Ru({=}C{=}C{=}CR^1R^2)(\eta^5\text{-}C_9H_7)L_2]^+$,[8c,d,11] we have recently shown that these derivatives add phosphines regioselectively at the C_γ of the allenylidene chain to afford a large variety of phosphonioalkynyl derivatives $[Ru\{C{\equiv}CC(R^1)R^2(PR_3)\}(\eta^5\text{-}C_9H_7)L_2]^+$.[8c,11a] Since we are especially interested in exploiting the synthetic utility of these derivatives we wondered about the possibility of using the monosubstituted derivatives $[Ru\{C{\equiv}CC(R^1)H(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R^1 = Ph$, $PR_3 = PMe_3$ **1**; $R^1 = H$, $PR_3 = PPh_3$ **2**) as suitable substrates for Wittig type processes.[12] Thus, we report here: (*i*) the synthesis of σ-enynyl and the first examples of σ-polyenynyl ruthenium(II) complexes $[Ru\{C{\equiv}CC(R^1){=}CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and $[Ru\{C{\equiv}CC(R^1){=}CH(CH{=}CH)_nR^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (n = 1 or 2), respectively obtained *via* Wittig reactions starting from the phosphonioalkynyl derivatives **1** and **2** by treatment with $LiBu^n$, to form probably a phosphorus ylide species $[Ru\{C{\equiv}CC(R^1){=}PR_3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$, followed by



Scheme 1 Synthesis of σ-enynyl and vinylvinylidene ruthenium(II) complexes.

the addition of an aldehyde or ketone, and (*ii*) the regioselective synthesis of vinylvinylidene and polyenylvinylidene complexes $[Ru\{=C=C(H)C(R^1)=CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ and $[Ru\{=C=C(H)C(R^1)=CH(CH=CH)_nR^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$-$[BF_4]$ ($n = 1$ or 2), respectively, formed by protonation of the corresponding σ-enynyl and σ-polyenynyl derivatives. Using this methodology highly functionalized σ-alkynyl derivatives can be also obtained as is shown in the synthesis of the σ-ynenynyl $[Ru\{C{\equiv}CC(Ph){=}CH(C{\equiv}CPh)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and σ-keteniminyl $[Ru\{C{\equiv}CC(Ph){=}C{=}NPh\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ complexes from PhC≡CCHO and phenyl isocyanate, respectively. Part of this work has been preliminarily communicated.[13]

Results and discussion

Synthesis of σ-enynyl and vinylvinylidene ruthenium(II) complexes

As expected, the phosphonioalkynyl complexes **1** and **2** containing an acidic hydrogen atom at C_γ are excellent substrates for Wittig reactions leading to the formation of new double carbon–carbon bonds. Thus, the treatment of yellow THF solutions of **1** or **2** with 1 equivalent of $LiBu^n$ at −20 °C gave rise to an immediate change to dark green (**1**) or violet (**2**) solutions probably containing the highly unstable ylide alkynyl derivatives $[Ru\{C{\equiv}CC(R^1){=}PR_3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (R^1 = Ph, PR_3 = PMe_3 **3**; R^1 = H, PR_3 = PPh_3 **4**). These species were not isolated but instead, when treated *in situ* with an excess (*ca.* 3:1) of cyclohexanone, acetaldehyde or benzophenone, afford the neutral σ-enynyl complexes $[Ru\{C{\equiv}CC(R^1){=}CR^2R^3\}(\eta^5\text{-}C_9H_7)$-$(PPh_3)_2]$ [R^2R^3 = $CH_2(CH_2)_3CH_2$, R^1 = Ph **5a** or H **6a**; R^2 = H, R^3 = Me, R^1 = Ph **5b** or H **6b**; $R^2 = R^3 = R^1$ = Ph **5c**] (Scheme 1). They have been isolated after column chromatography as air stable yellow-orange solids (64–86% yield). Complexes **5b** and **6b** were obtained as non-separable mixtures of the corresponding *E* and *Z* stereoisomers in *ca.* 3:1 and 10:11 ratios, respectively.

The novel σ-enynyl complexes have been characterized by microanalysis, mass spectra (FAB), 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). The formation of the enynyl chain is confirmed by the appearance in the IR spectra (KBr) of a $\nu(C{\equiv}C)$ absorption in the range 2041–2062 cm^{-1}. The NMR data can be compared with those reported for similar indenylruthenium(II) σ-alkynyl complexes $[Ru(C{\equiv}CR)$-$(\eta^5\text{-}C_9H_7)(PPh_3)_2]$.[4a,8c,d,11,13,14] Thus, the room-temperature ^{31}P-$\{^1H\}$ NMR spectra exhibit a single resonance (δ 50.78–52.77) consistent with the chemical equivalence of both phosphorus atoms (Table 1). The ^1H NMR spectra show signals for aromatic, indenyl and olefinic substituent groups, in accordance with the proposed structures (Table 1). It is worth mentioning that the assignment of the resonances of **5b** was carried out on the basis of NOE experiments. Thus, irradiation of the methyl resonance at δ 1.60 [d, J(HH) = 7.2 Hz] gave an increase of the intensity of the aromatic and olefinic protons at δ 7.53 [d, J(HH) = 6.3 Hz] and 5.81 (m), respectively. From this, we can conclude that these resonances correspond to the *Z* stereoisomer. In a further NOE experiment it was shown that saturation of the methyl resonance at δ 2.00 [d, J(HH) = 6.8 Hz] increased only the intensity of the olefinic proton resonance at δ 5.81 (m), as expected for an *E* configuration. The rest of the proton resonances were assigned by taking into account their relative integration values. Both olefinic protons for **6b** appear as doublets of quatriplets in the range δ 5.57–7.47, showing a mutual coupling constant of J(HH) = 15.1 (*E* stereoisomer) or 11.6 Hz (*Z* stereoisomer).

The ^{13}C-$\{^1H\}$ NMR spectra display characteristic triplet resonances at δ 105.37–123.56 [^2J(CP) = 21.9–25.9 Hz] for the RuC≡ carbon nucleus, while the C_β resonance appears as a singlet in the range δ 111.12–120.05 (Table 2). Singlet signals of the olefinic carbons have been assigned using DEPT experiments, being partially overlapped by the aromatic carbon resonances. Indenyl carbon resonances (Table 2) have been also assigned, and they are in accordance with the proposed η^5 co-ordination.[15] As has been shown previously, the parameter $\Delta\delta(C^{3a,7a}) = \delta[C^{3a,7a}(\text{indenyl complex})] - \delta[C^{3a,7a}$-(indenylsodium)] can be used as an indication of the indenyl distortion.[16] The calculated values for the σ-enynyl complexes **5** and **6**, which are in the range *ca.* −19 to −23 ppm, can be compared to those reported for other indenylruthenium(II) σ-alkynyl complexes[4a,8c,d,11,13,14] and are indicative of a non-distorted η^5-indenyl co-ordination.

Protonation of neutral σ-alkynyl ruthenium(II) complexes is a well known route to the corresponding cationic vinylidene derivatives.[6a] In the case of σ-enynyl complexes this protonation can generate both vinylvinylidene (**A**, electrophilic addition on the C_β position)[8a,c,9] or allenylidene (**B**, electrophilic addition on the C_δ position)[9,10] derivatives (see Chart 1).

Table 1 The ^{31}P-{^{1}H} and ^{1}H NMR data for the neutral σ-alkynyl complexes[a]

		^{1}H				
		η^5-C$_9$H$_7$				
Complex	^{31}P-{^{1}H}	H^{1,3}	H^2	*J*(HH)	H^{4,7}, H^{5,6}	Others
5a	52.77 (s)	4.37 (d)	5.17 (t)	2.5	6.17 (m), 6.44 (m)	1.04, 1.28, 1.50, 2.09, 2.76 (m, CH$_2$); 6.53–7.19 (m, PPh$_3$ and Ph)
(*E*)-**5b**	52.47 (s)	4.45 (d)	5.31 (t)	2.2	6.09 (m), 6.39 (m)	2.00 [d, *J*(HH) = 6.8, CH$_3$]; 5.81 (m, =CH); 6.57–7.14 (m, PPh$_3$ and Ph); 7.33 (d, *J*(HH) = 7.0, Ph)
(*Z*)-**5b**	52.47 (s)	4.39 (d)	5.23 (t)	2.2	6.09 (m), 6.39 (m)	1.60 [d, *J*(HH) = 7.2, CH$_3$]; 5.81 (m, =CH); 6.57–7.14 (m, PPh$_3$ and Ph); 7.53 [d, *J*(HH) = 6.3, Ph]
5c	50.78 (s)	4.74 (d)	5.23 (t)	2.3	5.98 (m), 6.73 (m)	6.85–8.24 (m, PPh$_3$ and Ph)
6a	52.01 (s)	4.71 (d)	5.60 (t)	2.2	6.36 (m), 6.70 (m)	1.57 (m, 2CH$_2$); 1.65, 2.29, 2.81 (m, CH$_2$); 5.94 (s, =CH); 6.92–7.52 (m, PPh$_3$)
(*E*)-**6b**	52.01 (s)	4.72 (d)	5.66 (t)	2.2	6.32 (m), 6.68 (m)	2.19 [dd, *J*(HH) = 6.6, 1.3, CH$_3$]; 5.86 [dq, *J*(HH) = 15.1, 6.6, =CH]; 6.88–7.47 (m, PPh$_3$ and =CH)
(*Z*)-**6b**	52.07 (s)	4.71 (d)	5.62 (t)	2.2	6.32 (m), 6.68 (m)	1.81 [dd, *J*(HH) = 6.5, 1.3, CH$_3$]; 5.57 [dq, *J*(HH) = 11.6, 6.5, =CH]; 6.21 [dq, *J*(HH) = 11.6, 1.3, =CH]; 6.88–7.47 (m, PPh$_3$)
(*E*)-**9a**	51.75 (s)	4.72 (d)	5.52 (t)	1.9	6.34 (m), [b]	6.64–8.16 (m, PPh$_3$, Ph and 3=CH)
(*Z*)-**9a**	52.36 (s)	4.78 (d)	5.53 (t)	1.9	6.48 (m), [b]	6.64–8.16 (m, PPh$_3$, Ph and 3=CH)
(*E*)-**9b**	52.51 (s)	4.77 (d)	5.56 (t)	2.0	6.45 (m), [b]	0.91 [t, *J*(HH) = 7.3, CH$_3$]; 1.41, 2.08 (m, CH$_2$); 5.84 (m, =CH); 6.67–7.45 (m, PPh$_3$, Ph and 2=CH); 7.89 [d, *J*(HH) = 7.1, Ph]
(*Z*)-**9b**	52.16 (s)	4.70 (d)	5.53 (t)	2.0	6.35 (m), [b]	0.82 [t, *J*(HH) = 7.3, CH$_3$]; 1.31, 1.98 (m, CH$_2$); 5.77 (m, =CH); 6.67–7.45 (m, PPh$_3$, Ph and 2=CH); 7.72 [d, *J*(HH) = 7.1, Ph]
(*E*)-**10a**	51.68 (s)	4.73 (d)	5.69 (t)	2.3	[b], [b]	6.23–7.47 (m, PPh$_3$, Ph and 4=CH)
(*Z*)-**10a**	51.34 (s)	4.73 (d)	5.58 (t)	2.5	[b], [b]	6.23–7.47 (m, PPh$_3$, Ph and 3=CH); 8.00 [dd, *J*(HH) = 15.7, 9.7, =CH]
(*E*)-**10b**	51.79 (s)	4.72 (br)	5.67 (br)		6.23 (m),[c] 6.69 (m)	0.87 [t, *J*(HH) = 7.3, CH$_3$]; 1.40, 2.05 (m, CH$_2$); 5.63 (m, =CH); 6.57 [dd, *J*(HH) = 14.8, 10.9, =CH]; 6.94–7.46 (m, PPh$_3$)
(*Z*)-**10b**	52.13 (s)	4.72 (br)	5.58 (br)		6.23 (m),[c] 6.69 (m)	0.90 [t, *J*(HH) = 7.3, CH$_3$]; 1.40, 2.12 (m, CH$_2$); 5.73 (m, =CH); 7.26 [dd, *J*(HH) = 15.3, 10.3, =CH]; 6.94–7.46 (m, PPh$_3$)
(*E*)-**11**	52.07 (s)	4.70 (d)	5.50 (m)[d]	2.3	6.34 (m), 6.72 (m)	1.59 [d, *J*(HH) = 6.6, CH$_3$]; 5.96 [dd, *J*(HH) = 14.8, 10.9, =CH]; 6.80–7.54 (m, PPh$_3$, Ph and 3=CH); 7.70 [d, *J*(HH) = 7.9, Ph]
(*Z*)-**11**	52.54 (s)	4.77 (d)	5.55 (t)	2.1	6.45 (m), 6.72 (m)	1.65 [d, *J*(HH) = 6.6, CH$_3$]; 5.60 [dq, *J*(HH) = 14.2, 6.8, =CH]; 6.15 [dd, *J*(HH) = 14.2, 10.9, =CH]; 6.80–7.54 (m, PPh$_3$, Ph and 3=CH); 7.89 [d, *J*(HH) = 7.1, Ph]
(*E*)-**12**	52.03 (s)	4.72 (d)	5.56 (m)[d]	2.6	[b], [b]	1.64 [d, *J*(HH) = 6.9, CH$_3$]; 6.13–7.45 (m, PPh$_3$ and 5=CH)
(*Z*)-**12**	51.69 (s)	4.71 (d)	5.66 (t)	2.6	[b], [b]	1.66 [d, *J*(HH) = 7.0, CH$_3$]; 5.56 (m, =CH); 6.13–7.45 (m, PPh$_3$ and 5=CH)
(*E*)-**17**	52.51 (s)	4.68 (d)	5.41 (t)	2.0	6.38 (m), 6.71 (m)	6.34 (s, =CH); 6.84–7.45 (m, PPh$_3$ and Ph); 8.42 [d, *J*(HH) = 7.6, Ph]
(*Z*)-**17**	51.22 (s)	4.90 (d)	6.26 (m)[e]	1.3	6.26 (m),[e] 6.63 (m)	6.43 (s, =CH); 6.84–7.45 (m, PPh$_3$ and Ph); 7.58 [d, *J*(HH) = 6.5, Ph]; 7.73 [d, *J*(HH) = 7.6, Ph]
19	52.92 (s)	4.40 (d)	5.12 (t)	1.6	6.20 (m), 6.44 (m)	6.58–7.57 (m, PPh$_3$ and Ph)

[a] Spectra recorded in C$_6$D$_6$; δ in ppm and *J* in Hz. Abbreviations: s, singlet; br, broad; d, doublet; dd, doublet of doublets; t, triplet; dq, doublet of quadruplets; m, multiplet. [b] Overlapped by PPh$_3$ or Ph protons. [c] H^{4,7} or H^{5,6} and 2=CH. [d] H^2 and =CH. [e] H^2 and H^{4,7} or H^{5,6}.

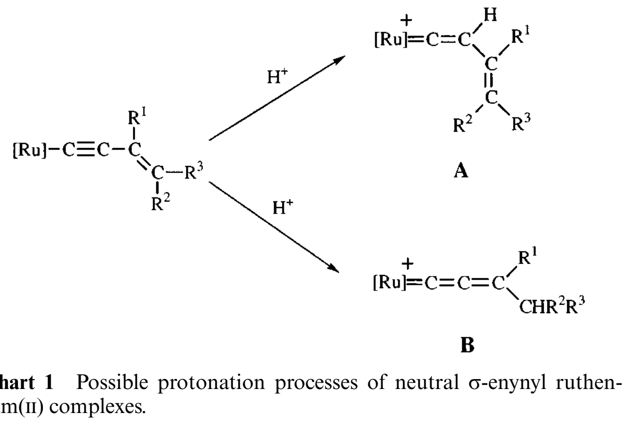


Chart 1 Possible protonation processes of neutral σ-enynyl ruthenium(II) complexes.

We have, therefore, examined the protonation of the σ-enynyl complexes **5** and **6**. Thus, the addition of HBF$_4$·Et$_2$O to solutions of **5** and **6**, in THF at −20 °C, regioselectively affords the cationic vinylvinylidene derivatives [Ru{=C=C(H)C(R^1)=CR^{2}R^3}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] [R^{2}R^3 = CH$_2$(CH$_2$)$_3$CH$_2$, R^1 = Ph **7a** or H **8a**; R^2 = H, R^3 = Me, R^1 = Ph **7b** or H **8b**; R^2 = R^3 = R^1 = Ph **7c**], isolated as air stable brown solids (64–87% yield) (Scheme 1). No isomeric allenylidene species were detected by NMR spectroscopy. Complexes **7b** and **8** have been obtained as mixtures of the corresponding *E* and *Z* stereoisomers (*ca.* 3:1 and 10:11 ratios, respectively) in accordance with the isomeric mixtures of the precursor derivatives **5b** and **6b**.

Analytical and spectroscopic data are in agreement with the proposed formulations (see Experimental section and Tables 3 and 4). In particular, the presence of the vinylidene moiety was identified, as usual, on the basis of: (*i*) (^{1}H NMR) the singlet (**7a**–**7c**), doublet (**8a**) or doublet of triplets (**8b**) signal of the Ru=C=CH proton (δ 5.08–6.37), and (*ii*) (^{13}C-{^{1}H} NMR) the typical low-field resonance of the carbenic Ru=C$_\alpha$, which appears as a triplet at δ 339.12–354.92 [^2J(CP) = 16.1–16.9 Hz], as well as the expected C$_\beta$ singlet resonance (δ 111.16–122.39). Indenyl carbon resonances (Table 4) indicate a moderate distortion of the η^5-indenyl co-ordination,[16] in accordance with the data previously reported for similar indenylruthenium(II) vinylidene complexes.[4a,8c,d,11,13,14]

Synthesis of σ-polyenynyl and polyenylvinylidene ruthenium(II) complexes

The easy access to the σ-vinylalkynyl complexes **5** and **6** prompted us to study the reactions of the phosphonioalkynyl derivatives **1** and **2** with aldehydes containing conjugated

Table 2 ^{13}C-{^{1}H} NMR data for the neutral σ-alkynyl complexes[a]

	η^5-C$_9$H$_7$								
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$_\beta$	Others
5a	73.16 (s)	93.88 (s)	108.23 (s)	−22.47	121.99 (s) 124.16 (s)	110.08 (t)	24.6	113.44 (s)	26.11, 27.68, 27.71, 30.07, 32.36 (s, CH$_2$); 121.06 (s, =C); 123.06–142.47 (m, PPh$_3$, Ph and =C)
(*E*)-**5b**	73.20 (s)	94.37 (s)	108.42 (s)	−22.28	122.05 (s) 124.69 (s)	114.73 (t)	25.9	111.12 (s)	15.77 (s, CH$_3$); 122.73 (s, =CH); 124.75–142.36 (m, PPh$_3$, Ph and =C)
(*Z*)-**5b**	73.38 (s)	93.97 (s)	107.95 (s)	−22.75	121.78 (s) 124.50 (s)	105.37 (t)	24.9	115.11 (s)	14.21 (s, CH$_3$); 122.32 (s, =CH); 124.75–140.74 (m, PPh$_3$, Ph and =C)
5c	79.04 (s)	98.04 (s)	110.93 (s)	−19.77	124.51 (s) 126.58 (s)	123.56 (t)	21.9	120.05 (s)	126.36–146.63 (m, PPh$_3$, Ph and 2=C)
6a	75.44 (t)[c]	96.19 (s)	110.14 (s)	−20.56	123.89 (s) 126.47 (s)	109.34 (t)	24.9	113.01 (s)	28.11, 29.31, 29.91, 32.35, 36.64 (s, CH$_2$); 109.55 (s, =CH); 127.89–143.78 (m, PPh$_3$ and =C)
(*E*)-**6b**	74.86 (s)	95.58 (s)	109.42 (s)	−21.28	123.13 (s) 125.85 (s)	106.83 (t)	25.1	113.38 (s)	16.01 (s, CH$_3$); 117.97 (s, =CH); 126.81–139.21 (m, PPh$_3$ and =CH)
(*Z*)-**6b**	74.86 (s)	95.58 (s)	109.49 (s)	−21.21	123.32 (s) 125.90 (s)	114.66 (t)	24.7	112.11 (s)	18.39 (s, CH$_3$); 116.81 (s, =CH); 126.81–139.21 (m, PPh$_3$ and =CH)
(*E*)-**9a**	75.45 (s)	95.54 (s)	109.93 (s)	−20.77	123.66 (s) [d]	122.56 (t)	24.2	120.23 (s)	126.57–143.34 (m, PPh$_3$, Ph, =C and 3=CH)
(*Z*)-**9a**	75.07 (s)	96.00 (s)	110.35 (s)	−20.35	123.92 (s) [d]	126.27 (t)	23.5	114.94 (s)	126.57–143.34 (m, PPh$_3$, Ph, =C and 3=CH)
(*E*)-**9b**	74.94 (s)	95.48 (s)	109.48 (s)	−21.22	123.21 (s) 126.02 (s)	115.17 (t)	24.6	118.42 (s)	13.97 (s, CH$_3$); 23.37, 35.55 (s, CH$_2$); 132.40 (s, =CH); 126.47–143.36 (m, PPh$_3$, Ph, =C and 2=CH)
(*Z*)-**9b**	74.69 (s)	95.68 (s)	109.84 (s)	−20.86	123.49 (s) 126.21 (s)	120.18 (t)	24.1	113.61 (s)	14.16 (s, CH$_3$); 23.59, 35.75 (s, CH$_2$); 132.59 (s, =CH); 126.47–143.36 (m, PPh$_3$, Ph, =C and 2=CH)
(*E*)-**10a**	75.10 (s)	95.61 (s)	109.65 (s)	−21.05	123.16 (s) [d]	125.35 (t)	24.0	120.41 (s)	116.73, 131.65, 131.97, 133.56 (s, =CH); 126.10–139.05 (m, PPh$_3$ and Ph)
(*Z*)-**10a**	74.85 (s)	95.61 (s)	109.69 (s)	−21.01	123.31 (s) [d]	123.30 (t)	25.1	117.84 (s)	114.88, 129.31, 129.47 (s, =CH); 126.10–139.05 (m, PPh$_3$, Ph and =CH)
(*E*)-**10b**	74.88 (s)	95.58 (s)	109.53 (s)	−21.17	123.13 (s) [d]	116.55 (t)	24.6	115.22 (s)	14.00 (s, CH$_3$); 23.30, 35.42 (s, CH$_2$); 117.41, 129.99, 132.89, 133.39 (s, =CH); 125.97–139.05 (m, PPh$_3$)
(*Z*)-**10b**	74.88 (s)	95.45 (s)	109.53 (s)	−21.17	123.27 (s) [d]	119.42 (t)	24.7	113.72 (s)	14.13 (s, CH$_3$); 23.50, 35.53 (s, CH$_2$); 114.99, 130.93, 131.32, 131.86 (s, =CH); 125.97–139.05 (m, PPh$_3$)
(*E*)-**11**	75.03 (s)	95.42 (s)	109.50 (s)	−21.20	123.22 (s) 126.09 (s)	[d]	[d]	119.61 (s)	18.50 (s, CH$_3$); 126.66–143.14 (m, PPh$_3$, Ph, =C and 5=CH)
(*Z*)-**11**	74.74 (s)	95.58 (s)	109.87 (s)	−20.83	123.51 (s) 126.30 (s)	123.96 (t)	23.7	114.36 (s)	18.63 (s, CH$_3$); 126.66–143.14 (m, PPh$_3$, Ph, =C and 5=CH)
(*E*)-**12**	75.04 (s)	95.56 (s)	109.57 (s)	−21.13	123.14 (s) [d]	123.89 (t)	25.1	116.44 (s)	18.53 (s, CH$_3$); 119.05, 128.36, 130.46, 131.90, 133.17 (s, =CH); 126.08–138.97 (m, PPh$_3$ and =CH)
(*Z*)-**12**	74.99 (s)	95.46 (s)	109.57 (s)	−21.13	123.28 (s) [d]	121.02 (t)	25.1	114.59 (s)	18.63 (s, CH$_3$); 116.60, 126.93, 129.33, 131.08, 133.32 (s, =CH); 126.08–138.97 (m, PPh$_3$ and =CH)
(*E*)-**17**	75.83 (s)	95.65 (s)	110.19 (s)	−20.51	123.97 (s) 126.92 (s)	[d]	[d]	119.30 (s)	93.09, 96.38 (s, ≡C); 106.75 (s, =CH); 128.22–142.46 (m, PPh$_3$, Ph and =C)
(*Z*)-**17**	75.83 (s)	98.41 (s)	110.96 (s)	−19.74	126.20 (s) 127.60 (s)	[d]	[d]	116.48 (s)	94.27, 94.80 (s, ≡C); 106.95 (s, =CH); 128.22–142.46 (m, PPh$_3$, Ph and =C)
19	73.22 (s)	94.71 (s)	108.94 (s)	−21.76	[d] [d]	[d]	[d]	[e]	117.64–137.91 (m, PPh$_3$ and Ph); 153.15 (s, =C=N)

[a] Spectra recorded in C$_6$D$_6$; δ in ppm and J in Hz. [b] $\Delta\delta$(C^{3a,7a}) = δ[C^{3a,7a}(η-indenyl complex)] − δ[C^{3a,7a}(indenyl sodium)], δ(C^{3a,7a}) for indenyl sodium 130.70. [c] ^2J(CP) = 3.6. [d] Overlapped by PPh$_3$ or Ph carbons. [e] δ 111.47 and 113.06 (s, C$_\beta$ and =C).

carbon–carbon double bonds in order to prepare the first examples of σ-polyenynyl ruthenium(II) complexes. Thus, compounds **1** and **2** react with LiBu^n and unsaturated aldehydes, in THF at −20 °C, to afford the σ-polyenynyl derivatives [Ru{C≡CC(R^1)=CH(CH=CH)$_n$R^2}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] [n = 1, R^2 = Ph, R^1 = Ph **9a** or H **10a**; R^2 = Pr^n, R^1 = Ph **9b** or H **10b**;

Table 3 The $^{31}P-\{^{1}H\}$ and ^{1}H and NMR data for the cationic vinylidene complexes[a]

		^{1}H					
		$\eta^{5}-C_9H_7$					
Complex	$^{31}P-\{^{1}H\}$	$H^{1,3}$	H^{2}	J(HH)	$H^{4,7}$, $H^{5,6}$	Ru=C=CH	Others
7a	35.13 (s)	5.25 (d)	5.36 (m)[b]	2.5	5.36 (m)[b] 7.10 (m)	6.26 (s)	0.86, 1.43, 1.59, 1.95, 2.06 (m, CH_2); 6.54–7.51 (m, PPh_3 and Ph)
(*E*)-**7b**	34.70 (s)	5.32 (m)[c]	5.32 (m)[c]		5.32 (m)[c] [d]	5.17 (s)	1.22 [d, J(HH) = 7.0, CH_3]; 4.83 [q, J(HH) = 7.0, =CH]; 6.46–7.49 (m, PPh_3 and Ph)
(*Z*)-**7b**	34.80 (s)	5.32 (m)[e]	5.32 (m)[e]		5.32 (m)[e] [d]	5.08 (s)	1.20 [d, J(HH) = 7.1, CH_3]; 6.46–7.49 (m, PPh_3 and Ph)
7c	34.86 (s)	5.40 (d)	5.05 (t)	2.1	5.28 (m) 6.82 (m)	6.37 (s)	6.53–7.47 (m, PPh_3 and Ph)
8a	39.72 (s)	5.45 (d)	5.92 (m)[b]	2.5	5.92 (m)[b] 7.23 (m)	[f]	1.50, 1.96 (m, $2CH_2$); 1.80 (m, CH_2); 6.83–7.52 (m, PPh_3)
(*E*)-**8b**	39.92 (s)	5.79 (d)	5.97 (t)	2.6	6.19 (m) [d]	5.47 (dt)[g]	1.65 [dd, J(HH) = 6.6, 1.3, CH_3]; 5.23 [dq, J(HH) = 14.8, 6.6, =CH]; 5.66 (m, =CH); 6.96–7.58 (m, PPh_3)
(*Z*)-**8b**	40.08 (s)	5.78 (d)	6.04 (t)	2.6	6.19 (m) [d]	5.60 (dt)[h]	1.55 [dd, J(HH) = 7.1, 1.6, CH_3]; 4.82 [dq, J(HH) = 10.0, 7.1, =CH]; 5.75 (m, =CH); 6.96–7.58 (m, PPh_3)
(*E*)-**13a**	35.27 (s)	5.39 (m)[i]	5.39 (m)[i]		5.45 (m) [d]	6.41 (s)	5.68 [d, J(HH) = 7.1, =CH]; 6.49–7.55 (m, PPh_3, Ph and 2=CH)
(*Z*)-**13a**	34.68 (s)	5.37 (m)[j]	5.14 (t)	1.7	5.37 (m)[j] [d]	6.47 (s)	5.94 [d, J(HH) = 10.8, =CH]; 6.49–7.55 (m, PPh_3, Ph 2=CH)
(*E*)-**13b**	34.70 (s)	5.35 (m)[j]	5.29 (br)		5.35 (m)[j] [d]	6.44 (s)	0.95 [t, J(HH) = 7.3, CH_3]; 1.45, 2.17 (m, CH_2); 5.77 (m, 2=CH); 6.66–7.49 (m, PPh_3, Ph and =CH)
(*Z*)-**13b**	34.87 (s)	5.42 (m)[j]	5.06 (br)		5.42 (m)[j] [d]	6.25 (s)	0.84 [t, J(HH) = 7.3, CH_3]; 1.35, 2.02 (m, CH_2); 5.77 (m, 2=CH); 6.66–7.49 (m, PPh_3, Ph and =CH)
(*E*)-**14a**	39.77 (s)	5.51 (br)	5.75 (m)[k]		6.06 (m) [d]	5.31 (dt)[l]	6.33 [d, J(HH) = 15.5, =CH]; 6.50 [dd, J(HH) = 15.5, 10.4]; 6.83–7.50 (m, PPh_3 and Ph)
(*Z*)-**14a**	39.55 (s)	5.50 (br)	5.75 (m)[m]		6.01 (m) [d]	5.75 (m)[m]	6.41 [d, J(HH) = 15.4, =CH]; 6.66 [dd, J(HH) = 15.4, 10.8]; 6.83–7.50 (m, PPh_3 and Ph)
(*E*)-**14b**	40.09 (s)	5.49 (br)	5.72 (m)[n]		5.72 (m)[n] [d]	5.18 (dt)[o]	0.91 [t, J(HH) = 7.3, CH_3]; 1.41, 2.12 (m, CH_2); 6.83–7.52 (m, PPh_3)
(*Z*)-**14b**	39.86 (s)	5.51 (br)	5.72 (m)[p]		5.72 (m)[p] [d]	5.72 (m)[p]	0.95 [t, J(HH) = 7.4, CH_3]; 1.43, 2.12 (m, CH_2); 6.83–7.52 (m, PPh_3)
(*E*)-**15**	34.68 (s)	5.37 (br)	5.08 (br)		5.43 (m) [d]	6.01 (m)[q]	1.78 [d, J(HH) = 6.5, CH_3]; 6.54–7.48 (m, PPh_3 and Ph)
(*Z*)-**15**	34.81 (s)	5.37 (br)	5.27 (br)		5.43 (m) [d]	6.46 (s)	1.88 [d, J(HH) = 6.8, CH_3]; 5.51 [d, J(HH) = 11.0, =CH]; 6.01 (m, 4=CH); 6.54–7.48 (m, PPh_3 and Ph)
(*E*)-**16**	39.76 (s)	5.68 (m)[r]	5.68 (m)[r]		5.68 (m)[r] [d]	5.68 (m)[r]	1.84 [d, J(HH) = 7.2, CH_3]; 6.82–7.49 (m, PPh_3 and =CH)
(*Z*)-**16**	39.71 (s)	5.68 (m)[r]	5.68 (m)[r]		5.68 (m)[r] [d]	5.68 (m)[r]	1.82 [d, J(HH) = 7.6, CH_3]; 6.82–7.49 (m, PPh_3 and =CH)
(*E*)-**18**	34.37 (s)	5.40 (m)[j]	5.14 (t)	1.7	5.40 (m)[j] [d]	5.29 (s)	6.39–7.57 (m, PPh_3, Ph and =CH)
(*Z*)-**18**	33.00 (s)	5.40 (m)[j]	5.90 (t)	2.0	5.40 (m)[j] [d]	4.80 (s)	6.39–7.57 (m, PPh_3, Ph and =CH)

[a] Spectra recorded in $CDCl_3$; δ in ppm and J in Hz. [b] H^{2} and $H^{4,7}$ or $H^{5,6}$. [c] $H^{1,3}$, H^{2} and $H^{4,7}$ or $H^{5,6}$. [d] Overlapped by PPh_3 or Ph protons. [e] $H^{1,3}$, H^{2}, =CH and $H^{4,7}$ or $H^{5,6}$. [f] δ 5.19 and 5.27 [d, J(HH) = 9.9 Hz, Ru=C=CH and =CH]. [g] J(HH) = 9.5, ^{4}J(HP) = 2.0 Hz. [h] J(HH) = 10.0, ^{4}J(HP) = 1.7 Hz. [i] $H^{1,3}$ and H^{2}. [j] $H^{1,3}$ and $H^{4,7}$ or $H^{5,6}$. [k] H^{2} and 2=CH. [l] J(HH) = 10.3, ^{4}J(HP) = 1.3 Hz. [m] H^{2}, 2=CH and Ru=C=CH. [n] H^{2}, 4=CH and $H^{4,7}$ or $H^{5,6}$. [o] J(HH) = 9.9, ^{4}J(HP) = 1.8 Hz. [p] H^{2}, 4=CH, Ru=C=CH and $H^{4,7}$ or $H^{5,6}$. [q] 5=CH and Ru=C=CH. [r] $H^{1,3}$, H^{2}, 5=CH, Ru=C=CH and $H^{4,7}$ or $H^{5,6}$.

$n = 2$, R^2 = Me, R^1 = Ph **11** or H **12**] (Scheme 2), isolated after column chromatography as air stable yellow-orange solids (62–75% yield). Similarly to the σ-enynyl complexes **5b** and **6b**, compounds **9**–**12** were obtained as non-separable mixtures of the *E* and *Z* stereoisomers in *ca.* 10 : 15 **9a**, 16 : 10 **9b**, 11 : 10 **10a**, 10 : 12 **10b**, 1 : 7 **11** and 1 : 2 **12** ratios. All attempts to form these compounds stereoselectively by changing the reaction conditions or the base used [NaOMe or $KN(SiMe_3)_2$ instead of $LiBu^n$] were unsuccessful. The spectroscopic properties (see Tables 1 and 2 and the Experimental section) of all these complexes are consistent with the proposed formulations. Significant features are: (*i*) the ν(C≡C) IR absorption band (2041–2059 cm^{-1}), (*ii*) the olefinic proton resonances, in the ^{1}H NMR spectra, which appear at *ca.* δ 5.5–7.5 (see Table 1), (*iii*) the typical triplet resonance in the $^{13}C-\{^{1}H\}$ NMR spectra for the RuC≡ carbon nucleus at δ 115.17–126.27 [^{2}J(CP) = 23.5–25.1 Hz], and (*iv*) singlet signals of C_β and the olefinic carbons in the range *ca.* δ 110–140 (assigned using DEPT experiments). It is worth noting that for complexes **10a** and **10b** and **12** containing an hydrogen atom on the C_γ position the resonance of this carbon shifts to high field (δ 114.88–119.05) compared with those of the rest of the olefinic carbons of the polyenynyl chain (*ca.* δ >126.00) (see Table 2). In order to confirm the stereochemical assignation, ^{13}C NMR experiments were carried out. Thus, we have found that for complexes **9a**, **9b** and **11** the C_β resonance appears as a doublet due to the coupling with the proton located at the C_δ atom, while for **10a**, **10b** and **12** a doublet of broad singlets was observed, showing an effective coupling with the protons located at the C_δ and C_γ positions. The coupling constants observed clearly indicate an *E* [^{3}J(CH) = 3.1–6.3] or *Z* [^{3}J(CH) = 10.0–11.9 Hz] configuration.

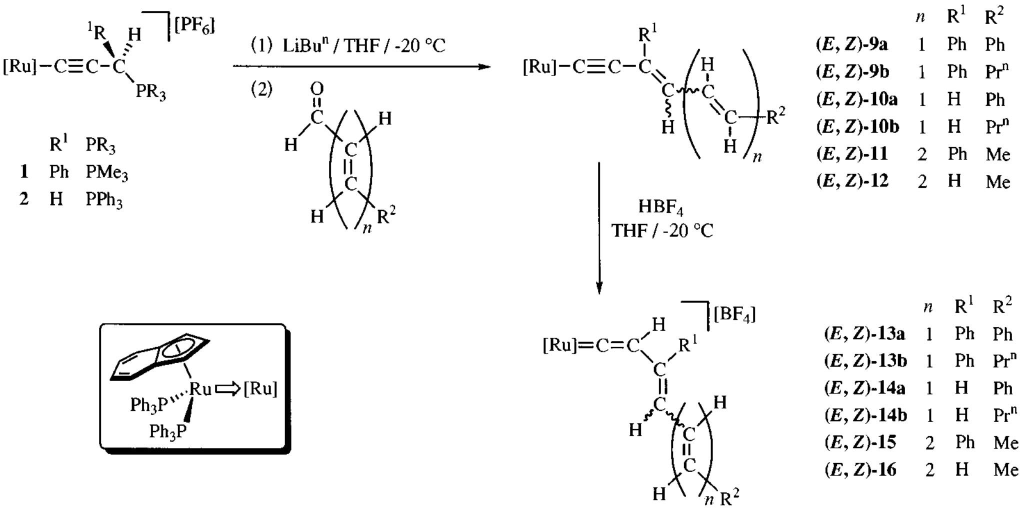
The corresponding vinylidene derivatives containing polyenyl chains have been synthesized through the regioselective protonation in THF of the σ-polyenynyl complexes **9**–**12** with tetrafluoroboric acid at −20 °C. The treatment leads to the formation of the desired tetrafluoroborate complexes **13**–**16** isolated as air stable brown solids (67–86% yield) (Scheme 2). The *E* : *Z* stereoisomer ratio for these derivatives is the same as that found in the parent σ-polyenynyl compounds **9**–**12**. The ^{1}H and $^{13}C-\{^{1}H\}$ NMR data are consistent with the presence of

Table 4 $^{13}C\text{-}\{^1H\}$ NMR data for the cationic vinylidene complexes[a]

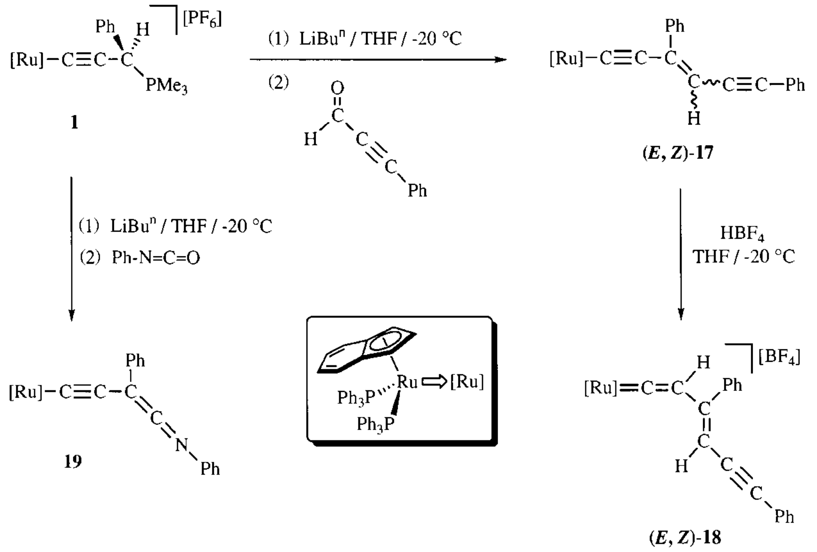
	$\eta^5\text{-}C_9H_7$								
Complex	$C^{1,3}$	C^2	$C^{3a,7a}$	$\Delta\delta(C^{3a,7a})$	$C^{4,7}$, $C^{5,6}$	Ru=C_α	^2J(CP)	C_β	Others
7a	80.39 (s)	99.61 (s)	117.43 (s)	−13.27	129.93 (s) [b]	354.92 (t)	16.6	116.76 (s)	26.36, 28.17, 28.53, 31.01, 32.12, (s, CH_2); 117.58 (s, =C); 128.00–141.75 (m, PPh_3, Ph and =C)
(*E*)-**7b**	81.15 (s)	99.23 (s)	117.35 (s)	−13.35	123.15 (s) [b]	350.73 (t)	16.8	120.71 (s)	15.24 (s, CH_3); 113.72 (s, =CH); 127.27–135.35 (m, PPh_3 and Ph); 143.09 (s, =C)
(*Z*)-**7b**	80.62 (s)	99.61 (s)	117.35 (s)	−13.35	123.15 (s) [b]	353.06 (t)	16.8	[c]	14.13 (s, CH_3); 127.27–135.35 (m, PPh_3 and Ph); 139.03 (s, =C)
7c	80.53 (s)	100.19 (s)	117.94 (s)	−12.76	123.28 (s) [b]	353.73 (t)	16.4	120.17 (s)	126.17–142.51 (m, PPh_3, Ph and 2=C)
8a	83.00 (t)	98.69 (s)	115.37 (s)	−15.33	122.92 (s) 129.96 (s)	339.12 (t)	16.9	112.47 (s)	26.40, 27.82, 28.76, 29.29, 37.04 (s, CH_2); 101.31 (s, =CH); 128.41–133.83 (m, PPh_3 and =C)
(*E*)-**8b**	83.56 (s)	98.78 (s)	115.17 (s)	−15.53	122.90 (s) [b]	342.37 (t)	16.1	117.24 (s)	17.86 (s, CH_3); 112.29, 123.45 (s, =CH); 127.83–133.46 (m, PPh_3)
(*Z*)-**8b**	83.56 (s)	98.78 (s)	115.17 (s)	−15.53	122.90 (s) [b]	342.37 (t)	16.1	[d]	13.41 (s, CH_3); 123.04 (s, =CH); 127.83–133.46 (m, PPh_3)
(*E*)-**13a**	81.25 (s)	99.61 (s)	117.58 (s)	−13.12	123.34 (s) 126.34 (s)		17.4	122.09 (s)	124.51, 125.04, 127.46 (s, =CH); 128.33–142.43 (m, PPh_3, Ph and =C)
(*Z*)-**13a**	81.84 (s)	99.30 (s)	117.58 (s)	−13.12	123.40 (s) 126.25 (s)	349.56 (t)	16.9	114.03 (s)	125.07, 125.98, 127.97 (s, =CH); 128.33–142.43 (m, PPh_3, Ph and =C)
(*E*)-**13b**	81.49 (s)	99.14 (s)	117.42 (s)	−13.28	[b] [b]	350.15 (t)	16.8	114.08 (s)	13.71 (s, CH_3); 22.41, 35.15 (s, CH_2); 125.26, 126.27, 137.24 (s, =CH); 123.22–142.71 (m, PPh_3, Ph and =C)
(*Z*)-**13b**	80.89 (s)	99.53 (s)	117.42 (s)	−13.28	[b] [b]	355.91 (t)	16.9	121.94 (s)	13.58 (s, CH_3); 22.54, 34.76 (s, CH_2); 124.76, 126.34, 137.04 (s, =CH); 123.22–142.71 (m, PPh_3, Ph and =C)
(*E*)-**14a**	84.28 (s)	98.95 (s)	115.22 (s)	−15.48	123.01 (s) 126.25 (s)	360.10 (t)	17.0	114.90 (s)	111.71, 123.20, 126.79 (s, =CH); 128.21–136.99 (m, PPh_3, Ph and =CH)
(*Z*)-**14a**	83.90 (s)	98.95 (s)	115.46 (s)	−15.24	126.50 (s) 127.37 (s)	358.39 (t)	16.4	118.16 (s)	113.33, 125.75, 127.77 (s, =CH); 128.21–136.99 (m, PPh_3, Ph and =CH)
(*E*)-**14b**	83.92 (s)	98.77 (s)	113.16 (s)	−15.45	122.96 (s) 130.26 (s)	360.22 (t)	16.5	113.16 (s)	13.66 (s, CH_3); 22.59, 34.56 (s, CH_2); 108.48, 124.93, 126.22, 135.01 (s, =CH); 128.56–133.43 (m, PPh_3)
(*Z*)-**14b**	84.23 (s)	98.77 (s)	115.04 (s)	−15.66	122.96 (s) 130.26 (s)	358.58 (t)	16.4		13.74 (s, CH_3); 22.59, 34.95 (s, CH_2); 111.48, 127.14, 129.56, 136.73 (s, =CH); 128.56–133.43 (m, PPh_3)
(*E*)-**15**	81.12 (s)	99.56 (s)	117.58 (s)	−13.12	123.35 (s) [b]	356.89 (t)	17.4	114.06 (s)	18.32 (s, CH_3); 122.23, 124.75, 134.65 (s, =CH); 126.51–142.62 (m, PPh_3, Ph, =C and 2=CH)
(*Z*)-**15**	81.66 (s)	99.11 (s)	117.58 (s)	−13.12	123.35 (s) [b]	350.51 (t)	16.6	114.19 (s)	18.53 (s, CH_3); 126.44, 126.58, 134.98 (s, =CH); 126.51–142.62 (m, PPh_3, Ph, =C and 2=CH)
(*E*)-**16**	84.20 (s)	98.82 (s)	115.21 (s)	−15.49	122.95 (s) 130.29 (s)	359.22 (t)	16.7	[e]	18.32 (s, CH_3); 126.01, 126.93, 129.47 (s, =CH); 128.53–133.41 (m, PPh_3 and 2=CH)
(*Z*)-**16**	84.05 (s)	98.79 (s)	115.14 (s)	−15.56	122.95 (s) 130.29 (s)	361.11 (t)	16.7	118.22 (s)	18.36 (s, CH_3); 109.94, 124.56, 130.12, 131.51, 134.20 (s, =CH); 128.53–133.41 (m, PPh_3 and =CH)
(*E*)-**18**	81.77 (s)	99.36 (s)	117.60 (s)	−13.10	[b] [b]	351.02 (t)	16.7	120.32 (s)	88.54, 92.19 (s, ≡C); 102.14 (s, =CH); 122.86–141.26 (m, PPh_3, Ph and =C)
(*Z*)-**18**	81.34 (s)	99.36 (s)	117.75 (s)	−12.95	[b] [b]	348.78 (t)	16.9	116.77 (s)	88.35, 97.64 (s, ≡C); 102.14 (s, =CH); 122.86–141.26 (m, PPh_3, Ph and =C)

[a] Spectra recorded in $CDCl_3$; δ in ppm and *J* in Hz. [b] Overlapped by PPh_3 or Ph carbons. [c] δ 121.62 and 122.39 (s, C_β and =CH). [d] δ 111.16 and 112.17 (s, C_β and =CH). [e] δ 113.02 and 113.38 (s, C_β and =CH).

polyenylvinylidene moieties (see Tables 3 and 4). Thus, the $^{13}C\text{-}\{^1H\}$ NMR spectra show in all cases a low-field triplet signal for the carbenic C_α atom at δ 349.56–361.11 [^2J(CP) = 16.4–17.4 Hz], while the C_β atom appears as a singlet in the range δ 113.02–122.09. Similarly to their σ-polyenynyl precursors, the olefinic carbon [Ru]=C=C(H)*C*H= in complexes **14** and **16** resonates at higher field (δ 108.48–113.38) compared to the rest of olefinic carbons of the polyenylvinylidene skeleton (δ > 120). As expected, the calculated $\Delta\delta(C^{3a,7a})$ values (Table 4) for **13**–**16** are similar to those found for the analogous vinylvinylidene complexes **7** and **8**, and higher than that of the σ-polyenynyl derivatives **9**–**12** (Table 2).



Scheme 2 Synthesis of σ-polyenynyl and polyenylvinylidene ruthenium(II) complexes.



Scheme 3 Wittig reactions of phosphonioalkynyl complex **1** with PhC≡CCHO and phenyl isocyanate.

Synthesis of σ-ynenynyl and σ-keteniminyl ruthenium(II) complexes

In order to demonstrate the generality of this synthetic methodology we have explored the reactivity of the phosphonioalkynyl complex **1** towards other carbonyl compounds such as PhC≡CCHO or phenyl isocyanate. Thus, under analogous conditions, **1** reacts with $LiBu^n$ and PhC≡CCHO to give the σ-ynenynyl derivative $[Ru\{C{\equiv}CC(Ph){=}CH(C{\equiv}CPh)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **17** (72% yield) (Scheme 3), which was obtained as a mixture of the *E* and *Z* stereoisomers in *ca.* 8 : 1 ratio. Protonation of **17** with $HBF_4{\cdot}Et_2O$ takes place also on the C_β of the alkynyl group, leading to the selective formation of the cationic ynenylvinylidene complex $[Ru\{{=}C{=}C(H)\text{-}C(Ph){=}CH(C{\equiv}CPh)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ **18** (83% yield; *E*:*Z ca.* 8 : 1). Analytical and spectroscopic data (IR and ^1H, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{^1H\}$ NMR) are in accordance with the proposed formulations (see the Experimental section and Tables).

Similarly, the reaction of complex **1** with $LiBu^n$ and phenyl isocyanate yields $[Ru\{C{\equiv}CC(Ph){=}C{=}NPh\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **19**, a rare example of a functionalized σ-alkynyl derivative containing a keteniminyl moiety (57% yield; Scheme 3). The IR and $^{13}C\text{-}\{^1H\}$ NMR spectroscopic data show the expected signals for the alkynylheterocumulene moiety, *i.e.* ν(C=C=N) 1991, ν(C≡C) 2070 cm^{-1}; δ_C (=C=N) 153.15.

Conclusion

The present study reports a general synthetic route for preparing highly unsaturated σ-alkynyl ruthenium(II) complexes based on the reaction of phosphonioalkynyl derivatives $[Ru\{C{\equiv}CC(R^1)H(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ **1** and **2** with carbonyl compounds *via* a Wittig process. Thus, a wide series of σ-enynyl **5** and **6** and the first examples of σ-polyenynyl **9**–**12** complexes have been prepared in excellent yields. It should be noted that recent studies carried out in our laboratory indicate that similar σ-alkynyl derivatives containing strong electron-acceptor groups at the end of the hydrocarbon chain exhibit large second-order non-linear optical (NLO) properties.[14b,17] These results clearly indicate that the polyenynyl skeleton is an excellent pathway for electronic delocalization between the metal and terminal functional groups.

Furthermore, it is also shown that the protonation of these σ-enynyl and σ-polyenynyl ruthenium(II) derivatives proceeds regioselectively at the C_β atom of the alkynyl group. It is apparent that the electrophilic attack at this position is favored over electrophilic addition on the olefinic moieties which would lead to cumulenylidene derivatives. These processes disclose a ready entry to the high yield synthesis of alkenylvinylidene complexes **7** and **8** and polyenylvinylidene derivatives **13**–**16**, a type of organometallic species of potential interest for synthesis, provided there is high unsaturation in the hydrocarbon chain. We have recently reported the utility of some of these derivatives as excellent synthons of organometallic cyclopentenones obtained *via* intermolecular Pauson–Khand reactions.[14c]

Experimental

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $[Ru\{C\equiv CC(R^1)H(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = Ph, $PR_3 = PMe_3$;[11a] R^1 = H, $PR_3 = PPh_3$[17]) were prepared by following the literature methods. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Mass spectra (FAB) were recorded using a VG Autospec spectrometer, operating in the positive ion mode; 3-nitrobenzyl alcohol was used as the matrix. The NMR spectra were recorded on a Bruker AC300 instrument at 300 (^{1}H), 121.5 (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT Experiments have been carried out for all the complexes.

Synthesis

$[Ru\{C\equiv CC(R^1)=CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ [$R^2R^3 = CH_2(CH_2)_3CH_2$, R^1 = Ph 5a or H 6a; R^2 = H, R^3 = Me, R^1 = Ph (*E*,*Z*)-5b or H (*E*,*Z*)-6b; $R^2 = R^3 = R^1$ = Ph 5c]. *General procedure.* A solution of $LiBu^n$ (1.6 M in hexane, 0.625 cm^3, 1 mmol) was added, at −20 °C to a solution of $[Ru\{C\equiv CC(R^1)H(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ **1** or **2** (1 mmol) in THF (25 cm^3). After the addition was complete the original yellow solution changed to dark green (**1**) or violet (**2**). The reaction mixture was then stirred for 15 min, the corresponding aldehyde or ketone (3 mmol) added, warmed to room temperature and stirred for 30 min. The solvent was then removed *in vacuo* and the solid residue transferred to an Alox I chromatography column. Elution with hexane–diethyl ether (1 : 1) gave complexes **5** and **6** as yellow-orange solids.

Complex **5a**: yield 65% (Found: C, 76.25; H, 5.43. $C_{60}H_{42}P_2Ru$ requires C, 76.98; H, 5.59%); ν_{max}/cm^{-1} (KBr) 2058m (C≡C); *m*/*z* 936 (M^+), 741 [M^+ − C≡CC(Ph)=C(CH$_2$)$_5$] and 673 (M^+ − PPh$_3$). Complex **5b**: yield 64% (Found: C, 74.01; H, 5.31. $C_{56}H_{46}P_2Ru$ requires C, 74.89; H, 5.25%); ν_{max}/cm^{-1} (KBr) 2054m (C≡C, *E* isomer), 2025w (C≡C, *Z* isomer); *m*/*z* 882 (M^+), 741 [M^+ − C≡CC(Ph)=CHMe], 620 (M^+ − PPh$_3$) and 358 (M^+ − 2PPh$_3$). Complex **5c**: yield 72% (Found: C, 78.58; H, 5.17. $C_{67}H_{52}P_2Ru$ requires C, 78.88; H, 5.13%); ν_{max}/cm^{-1} (KBr) 2041m (C≡C); *m*/*z* 1020 (M^+), 741 [M^+ − C≡CC(Ph)=CPh$_2$] and 495 (M^+ − 2PPh$_3$). Complex **6a**: yield 86% (Found: C, 75.82; H, 4.44. $C_{54}H_{38}P_2Ru$ requires C, 76.31; H, 4.51%); ν_{max}/cm^{-1} (KBr) 2056m (C≡C). Complex **6b**: yield 77% (Found: C, 74.21; H, 5.17. $C_{50}H_{42}P_2Ru$ requires C, 74.52; H, 5.25%); ν_{max}/cm^{-1} (KBr) 2062s (C≡C, *E* and *Z* isomers).

$[Ru\{=C=C(H)C(R^1)=CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ [$R^2R^3 = CH_2(CH_2)_3CH_2$, R^1 = Ph 7a or H 8a; R^2 = H, R^3 = Me, R^1 = Ph (*E*,*Z*)-7b or H (*E*,*Z*)-8b; $R^2 = R^3 = R^1$ = Ph 7c]. *General procedure.* A solution of $HBF_4{\cdot}Et_2O$ (1.9 cm^3, 1.5 mmol) in diethyl ether (10 cm^3) was added dropwise, at −20 °C, to a solution of the corresponding σ-enynyl complex **5** or **6** (1 mmol) in THF (30 cm^3). The reaction mixture was gradually warmed to room temperature and then concentrated (*ca.* 5 cm^3). Addition of diethyl ether (*ca.* 100 cm^3) gave complexes **7** and **8** as brown solids which were washed with diethyl ether (3 × 20 cm^3) and vacuum dried.

Complex **7a**: yield 64% (Found: C, 69.31; H, 4.89. $C_{60}H_{53}BF_4P_2Ru$ requires C, 70.38; H, 5.21%); conductivity (acetone, 20 °C) 104 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1060s (BF$_4^-$). Complex **7b**: yield 87% (Found: C, 68.97; H, 4.79. $C_{56}H_{47}BF_4P_2Ru$ requires C, 69.35; H, 4.88%); conductivity (acetone, 20 °C) 110 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1065s (BF$_4^-$, *E* and *Z* isomers). Complex **7c**: yield 79% (Found: C, 72.94; H, 5.01. $C_{67}H_{53}BF_4P_2Ru$ requires C, 72.63; H, 4.82%); conductivity (acetone, 20 °C) 115 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1060s (BF$_4^-$). Complex **8a**: yield 70% (Found: C, 67.66; H, 5.12. $C_{54}H_{49}BF_4P_2Ru$ requires C, 68.43; H, 5.21%); conductivity (acetone, 20 °C) 120 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1090s (BF$_4^-$). Complex **8b**: yield 77% (Found: C, 66.89; H, 4.57. $C_{50}H_{43}BF_4P_2Ru$ requires C, 67.19; H, 4.85%); conductivity (acetone, 20 °C) 106 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1058s (BF$_4^-$, *E* and *Z* isomers).

$[Ru\{C\equiv CC(R^1)=CH(CH=CH)_nR^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ [*n* = 1, R^2 = Ph, R^1 = Ph (*E*,*Z*)-9a or H (*E*,*Z*)-10a; $R^2 = Pr^n$, R^1 = Ph (*E*,*Z*)-9b or H (*E*,*Z*)-10b; *n* = 2, R^2 = Me, R^1 = Ph (*E*,*Z*)-11 or H (*E*,*Z*)-12]. These complexes were synthesized analogously to **5** and **6**. Complex **9a**: yield 64% (Found: C, 77.62; H, 5.04. $C_{63}H_{50}P_2Ru$ requires C, 78.00; H, 5.19%); ν_{max}/cm^{-1} (KBr) 2041s (C≡C, *E* and *Z* isomers). Complex **9b**: yield 75% (Found: C, 76.77; H, 5.87. $C_{60}H_{52}P_2Ru$ requires C, 76.98; H, 5.60%); ν_{max}/cm^{-1} (KBr) 2046m (C≡C, *E* and *Z* isomers); *m*/*z* 936 (M^+), 741 [M^+ − C≡CC(Ph)=CHCH=CHPr^n] and 674 (M^+ − PPh$_3$). Complex **10a**: yield 62% (Found: C, 76.17; H, 5.15. $C_{57}H_{46}P_2Ru$ requires C, 76.57; H, 5.18%); ν_{max}/cm^{-1} (KBr) 2056m (C≡C, *E* isomer) and 2059s (C≡C, *Z* isomer). Complex **10b**: yield 69% (Found: C, 74.95; H, 5.57. $C_{54}H_{48}P_2Ru$ requires C, 75.41; H, 5.64%); ν_{max}/cm^{-1} (KBr) 2050m (C≡C, *E* and *Z* isomers). Complex **11**: yield 63% (Found: C, 77.23; H, 5.22. $C_{60}H_{50}P_2Ru$ requires C, 77.15; H, 5.39%); ν_{max}/cm^{-1} (KBr) 2041s (C≡C, *E* and *Z* isomers). Complex **12**: yield 69% (Found: C, 75.52; H, 5.38. $C_{54}H_{46}P_2Ru$ requires C, 75.59; H, 5.40%); ν_{max}/cm^{-1} (KBr) 2044s (C≡C, *E* and *Z* isomers).

$[Ru\{=C=C(H)C(R^1)=CH(CH=CH)_nR^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ [*n* = 1, R^2 = Ph, R^1 = Ph (*E*,*Z*)-13a or H (*E*,*Z*)-14a; $R^2 = Pr^n$, R^1 = Ph (*E*,*Z*)-13b or H (*E*,*Z*)-14b; *n* = 2, R^2 = Me, R^1 = Ph (*E*,*Z*)-15 or H (*E*,*Z*)-16]. These complexes were synthesized analogously to **7** and **8** with **9**–**12** as starting materials. Complex **13a**: yield 79% (Found: C, 71.07; H, 4.83. $C_{63}H_{51}BF_4P_2Ru$ requires C, 71.53; H, 4.86%); conductivity (acetone, 20 °C) 118 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1061s (BF$_4^-$, *E* and *Z* isomers). Complex **13b**: yield 79% (Found: C, 69.97; H, 5.18. $C_{60}H_{53}BF_4P_2Ru$ requires C, 70.38; H, 5.22%); conductivity (acetone, 20 °C) 103 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1058s (BF$_4^-$, *E* and *Z* isomers). Complex **14a**: yield 86% (Found: C, 69.25; H, 4.70. $C_{57}H_{47}BF_4P_2Ru$ requires C, 69.73; H, 4.82%); conductivity (acetone, 20 °C) 104 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1057s (BF$_4^-$, *E* and *Z* isomers). Complex **14b**: yield 74% (Found: C, 67.83; H, 5.02. $C_{54}H_{49}BF_4P_2Ru$ requires C, 68.43; H, 5.21%); conductivity (acetone, 20 °C) 119 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1059s (BF$_4^-$, *E* and *Z* isomers). Complex **15**: yield 67% (Found: C, 70.81; H, 4.91. $C_{60}H_{51}BF_4P_2Ru$ requires C, 70.52; H, 5.03%); conductivity (acetone, 20 °C) 99 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1060s (BF$_4^-$, *E* and *Z* isomers). Complex **16**: yield 81% (Found: C, 67.91; H, 4.96. $C_{54}H_{47}BF_4P_2Ru$ requires C, 68.57; H, 5.01%); conductivity (acetone, 20 °C) 115 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 1057s (BF$_4^-$, *E* and *Z* isomers).

$[Ru\{C\equiv CC(Ph)=CH(C\equiv CPh)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (*E*,*Z*)-17. This complex was obtained as an orange solid analogously to **5** and **6** from PhC≡CCHO (0.367 cm^3, 3 mmol). Yield 72% (Found: C, 79.17; H, 5.15. $C_{63}H_{48}P_2Ru$ requires C, 78.16; H, 4.99%). ν_{max}/cm^{-1} (KBr) 2043s (RuC≡C, *E* and *Z* isomers) and 2178w (C≡CPh, *E* and *Z* isomers).

$[Ru\{=C=C(H)C(Ph)=CH(C\equiv CPh)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (*E*,*Z*)-18. This complex was obtained as a brown solid analogously to **7** and **8** with **17** as starting material. Yield 83% (Found: C, 70.34; H, 4.65. $C_{63}H_{49}BF_4P_2Ru$ requires C, 71.66; H, 4.68%); conductivity (acetone, 20 °C) 110 Ω^{-1} cm^2 mol^{-1}. ν_{max}/cm^{-1} (KBr) 1059s (BF_4^-, *E* and *Z* isomers) and 2181w (C≡C, *E* and *Z* isomers).

[Ru{C≡CC(Ph)=C=NPh}(η^5-C_9H_7)(PPh_3)$_2$] 19. A solution of LiBu^n (1.6 M in hexane, 0.625 cm^3, 1 mmol) was added, at −20 °C, to a solution of [Ru{C≡CC(Ph)H(PMe_3)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] **1** (1.076 g, 1 mmol) in THF (25 cm^3). After the addition was complete the original yellow solution changed to violet. The reaction mixture was then stirred for 15 min, phenyl isocyanate (0.108 cm^3, 1 mmol) added, warmed to room temperature and stirred for 30 min. The solvent was then removed *in vacuo* and the solid residue extracted with hexane and filtered. Evaporation of the solvent gave **19** as a yellow solid. Yield 57% (Found: C, 76.12; H, 4.81; N, 1.60. $C_{61}H_{47}NP_2Ru$ requires C, 76.55; H, 4.95; N, 1.46%). ν_{max}/cm^{-1} (KBr) 1991m (C=C=N) and 2070m (C≡C).

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