The interaction of [Cp*RuCl(dippe)] and [CpRuCl(dippe)] with alkynols: hydroxyvinylidene, allenylidene and related derivatives (dippe = 1,2-bis(diisopropylphosphino)ethane)

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Abstract

The reactions of [Cp*RuCl(dippe)] and [CpRuCl(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) with several alkynols $HC\equiv CC(OH)RR'$ (R = R' = H, Me; R = Me, R' = Ph) have been studied. These reactions leads to the formation of the corresponding allenylidene derivatives, although in some cases hydroxyvinylidene complexes were isolated as intermediates in such process. The X-ray crystal structure of [CpRu=C=C=CMePh(dippe)][BPh$_4$] was determined. In the course of the reaction of [CpRuCl(dippe)] with $HC\equiv CC(OH)Me_2$, there is evidence for the formation of a deep blue dimeric alkynyl-carbene (or alkenyl-allenylidene) complex [{CpRu(dippe)}$_2$(μ-C$_{10}$H$_{11}$)][BPh$_4$] resulting formally from the coupling of two allenylidene moieties followed by the loss of one proton. The reaction of [Cp*Ru=C=C=CMePh(dippe)][BPh$_4$] with KOBu' leads to the ene-yne derivative [Cp*Ru(C$\equiv$CC(Ph)=CH$_2$)(dippe)] as result of the deprotonation of the allenylidene ligand at the δ-position. This compound was structurally characterized by single crystal X-ray crystallography. In an attempt to obtain the primary allenylidene complex [Cp*Ru=C=C=CH$_2$(dippe)][BPh$_4$] by dehydration of the hydroxyvinylidene [Cp*Ru=C=CHCH$_2$OH(dippe)][BPh$_4$] using P$_2$O$_5$, the previously reported carbonyl complex [Cp*Ru(CO)(dippe)][BPh$_4$] was obtained and its crystal structure determined. This is also accessible by aerial oxidation of the hydroxy-vinylidene derivative. © 1997 Elsevier Science S.A.

Keywords: Alkynol; Allenylidene complex; Vinylidene complex; Ruthenium; Phosphine

1. Introduction

Since their discovery by Fischer et al. [1] and Berke [2], allenylidene complexes constitute after vinylidene complexes the simplest class of metallocumulenes, and its chemistry is only beginning to be studied in detail, in contrast to that of their vinylidene homologues [3]. The interest of these species arises not only from their material properties [4], but also from the fact that they contain a carbon-rich unsaturated chain with a M=C linkage, having potential as building blocks for the synthesis of unsaturated organic molecules, as well as for the access to metal-containing copolymers [5,6]. It is reasonably well established now that the reaction of propargyl alcohols $HC\equiv CC(OH)R_2$ with transition metal complexes represents a simple and convenient

route for the preparation of allenylidene complexes via dehydration of an intermediate hydroxyvinylidene complex [7,8]. A related procedure has been used recently for the preparation of novel types of organometallic cumulenes, such as pentatetraenylidene complexes [9]. When hydrogen atoms are present at the carbon atom adjacent to the one bearing the OH group, the dehydration may take two different reaction pathways, leading alternatively to allenylidene or vinyl-vinylidene derivatives [10]. In some instances coupled products have also been obtained [11,12]. We have recently reported the synthesis of half-sandwich complexes [Cp*RuCl(dippe)] and [CpRuCl(dippe)] (dippe = 1,2-bis(diisopropylphosphino)-ethane) [13], and their reactivity towards small molecules [14] and alkynes [15,16]. We have observed that the reaction of [CpRuCl(dippe)] with 1-alkynes in MeOH yields the corresponding vinylidene complexes [CpRu = C = CHR(dippe)]$^+$, whereas in case of [Cp*RuCl(dippe)] oxidative addition

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of the alkyne takes place furnishing Ru^{IV} hydrido–alkynyl derivatives $[Cp^*RuH(C\equiv CR)(dippe)]^+$, which rearrange to their vinylidene isomers both in solution and in the solid state [15,16]. In order to complete the study of the reactivity displayed by these half-sandwich ruthenium complexes towards alkynes, we have investigated their reactions with alkynols. This has led to the isolation of allenylidene derivatives and other related species. The results of this research are reported in this paper.

2. Results and discussion

$[Cp^*RuCl(dippe)]$ reacts with propargyl alcohol, $HC\equiv CCH_2OH$, in MeOH in the presence of $NaBPh_4$ yielding a light brown crystalline precipitate. The IR spectrum of this material displays strong bands at 3528 cm^{-1} and 1636 cm^{-1}, attributable to $\nu(OH)$ and $\nu(C=C)$ of a vinylidene ligand, respectively. These data, together with microanalysis, support the formation of the hydroxyvinylidene complex $[Cp^*Ru=C=CHCH_2OH(dippe)][BPh_4]$ (1). The ^1H NMR spectrum of this compound shows one doublet

and one triplet at 3.99 ppm and 4.06 ppm respectively, in the intensity ratio 2:1, corresponding to the CH_2 protons and to the proton attached to the β-carbon of the vinylidene coupled each other ($J_{HH} = 6.8$ Hz). No resolvable coupling with phosphorus is observed, although in some other instances it is resolved, i.e., for $[Cp^*Ru=C=CHCH_2OH(PMe_2Ph)_2][PF_6]$ [17], and the vinylidene proton appears as a triplet of triplets. No signal attributable to the OH proton is present, most probably due to rapid exchange. In some cases in which it has been observed, it appears as a broad resonance [17]. The $^{31}P\{^1H\}$ NMR spectrum of 1 consists of one sharp singlet, whereas its $^{13}C\{^1H\}$ NMR spectrum indicates the presence of the vinylidene carbon atom directly attached to Ru at low field (δ 339.5 ppm, $J_{CP} = 14.1$ Hz). The hydroxyvinylidene complex $[Cp^*Ru=C=CHC(OH)Me_2(dippe)][BPh_4]$ (2) was obtained in a similar fashion by reaction of $[Cp^*RuCl(dippe)]$ with $HC\equiv CC(OH)Me_2$ and $NaBPh_4$ in MeOH. The spectral properties of this compound are very similar to those of 1, including the presence of $\nu(OH)$ and $\nu(C=C)$ bands at 3545 cm^{-1} and 1639 cm^{-1} respectively in its IR spectrum. In contrast with 1, which is very stable towards dehydration, 2 loses H_2O easily in

Table 1
Summary of data for the crystal structure analysis of 5, 8 and 9

Compound	5	8	9
Formula	$C_{53}H_{65}BP_2Ru$	$C_{34}H_{54}P_2Ru$	$C_{49}H_{67}BOP_2Ru$
F.W.	875.92	625.82	845.90
Crystal size (mm)	$0.23 \times 0.08 \times 0.31$	$0.22 \times 0.24 \times 0.43$	$0.19 \times 0.18 \times 0.24$
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1 (No. 2)	P-1 (No. 2)	$P2_1/n$ (No. 14)
Cell parameters	$a = 12.672(2)$ Å	$a = 9.834(4)$ Å	$a = 17.233(4)$ Å
	$b = 16.364(3)$ Å	$b = 18.435(4)$ Å	$b = 14.942(2)$ Å
	$c = 12.535(2)$ Å	$c = 9.174(2)$ Å	$c = 17.623(4)$ Å
	$\alpha = 95.30(2)°$	$\alpha = 91.94(2)°$	
	$\beta = 96.24(2)°$	$\beta = 103.26(2)°$	$\beta = 106.53(2)°$
	$\gamma = 107.06(2)°$	$\gamma = 96.41(2)°$	
Volume	2338(1) Å^3	1641(1) Å^3	4416(1) Å^3
Z	2	2	4
ρ_{calc}	1.244 g cm^{-3}	1.266 g cm^{-3}	1.272 g cm^{-3}
λ	1.54178 Å (CuK$_\alpha$)	1.54178 Å (CuK$_\alpha$)	0.71069 Å (MoK$_\alpha$)
μ	36.64 cm^{-1} (CuK$_\alpha$)	50.19 cm^{-1} (CuK$_\alpha$)	4.52 cm^{-1} (MoK$_\alpha$)
F(000)	924	664	1792
Transmision factors	0.80–1.00	0.81–1.00	0.95–1.00
Scan speed (ω)	8° min^{-1}	8° min^{-1}	8° min^{-1}
2θ interval	$5° < 2\theta < 100°$	$5° < 2\theta < 100°$	$5° < 2\theta < 50°$
Measured reflections	5200	3631	6965
Unique reflections	5113	3374	6762
Observed reflections ($I > 3\sigma_I$)	4160	3023	4157
Number of parameters	514	370	487
Reflection/parameter ratio	8.09	8.17	8.54
R^a	0.034	0.049	0.042
R_w ($w = \sigma_F^{-2}$)^b	0.041	0.061	0.048
Maximum Δ/σ in Final Cycle	0.15	4.09	1.17
g.o.f.	1.53	2.81	1.36

$^a R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|;$ $^b R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}.$

Table 2

Fractional atomic coordinates and B_{eq} for [CpRu=C=C=CMePh-(dippe)][BPh$_4$]

Positional parameters and B_{eq}
for [CpRu = C = C = CMePh(dippe)][BPh$_4$]

Atom	x	y	z	B_{eq}
Ru	0.26498(3)	0.24874(2)	0.11981(3)	2.91(1)
P(1)	0.4582(1)	0.26064(8)	0.1449(1)	3.09(4)
P(2)	0.3205(1)	0.24828(8)	0.3114(1)	3.30(4)
C(1)	0.0776(5)	0.1653(4)	0.0653(4)	5.4(2)
C(2)	0.0857(4)	0.2311(4)	0.0018(5)	5.2(2)
C(3)	0.1535(5)	0.2212(4)	−0.0666(4)	5.0(2)
C(4)	0.1851(5)	0.1481(4)	−0.0448(5)	5.2(2)
C(5)	0.1378(5)	0.1125(4)	0.0349(5)	5.5(2)
C(6)	0.2973(4)	0.3699(3)	0.1546(4)	3.3(2)
C(7)	0.2999(4)	0.4476(3)	0.1652(4)	3.9(2)
C(8)	0.3003(4)	0.5296(3)	0.1685(4)	3.8(2)
C(9)	0.3820(5)	0.5989(4)	0.2705(5)	5.5(2)
C(10)	0.2231(4)	0.5530(3)	0.0747(4)	3.5(2)
C(11)	0.2127(5)	0.6357(3)	0.0809(4)	4.7(2)
C(12)	0.1418(5)	0.6568(4)	−0.0101(6)	5.8(3)
C(13)	0.0783(6)	0.5967(5)	−0.1065(6)	6.5(3)
C(14)	0.0874(6)	0.5148(4)	−0.1152(5)	6.2(3)
C(15)	0.1584(5)	0.4927(3)	0.0254(4)	4.9(2)
C(16)	0.5460(4)	0.3549(3)	0.1030(4)	4.2(2)
C(17)	0.4842(6)	0.3611(4)	0.0189(5)	6.5(3)
C(18)	0.5835(5)	0.4411(3)	0.1837(5)	5.6(2)
C(19)	0.4839(5)	0.1682(3)	0.0709(4)	4.1(2)
C(20)	0.4233(5)	0.0812(3)	0.0980(5)	5.2(2)
C(21)	0.6133(6)	0.1805(4)	0.0946(6)	6.9(3)
C(22)	0.2950(5)	0.1381(3)	0.3461(4)	4.9(2)
C(23)	0.1672(6)	0.0930(4)	0.3360(5)	6.2(3)
C(24)	0.3746(6)	0.1363(5)	0.4616(5)	7.3(3)
C(25)	0.2603(5)	0.3042(3)	0.4026(4)	4.3(2)
C(26)	0.1386(5)	0.3034(4)	0.3402(5)	5.5(2)
C(27)	0.3396(5)	0.3976(4)	0.4604(4)	5.6(2)
C(28)	0.5366(4)	0.2668(3)	0.2947(4)	3.9(2)
C(29)	0.4786(4)	0.3029(3)	0.3684(4)	4.2(2)
C(30)	1.0124(4)	0.2171(3)	0.5999(4)	3.3(2)
C(31)	1.0504(5)	0.1447(3)	0.6026(4)	4.4(2)
C(32)	1.1674(5)	0.1522(4)	0.6446(5)	5.1(2)
C(33)	1.2511(5)	0.2313(5)	0.6868(4)	5.1(2)
C(34)	1.2198(5)	0.3046(4)	0.6881(4)	4.7(2)
C(35)	1.1018(4)	0.2974(3)	0.6457(4)	3.8(2)
C(36)	0.8096(4)	0.1793(3)	0.6458(4)	3.6(2)
C(37)	0.8556(4)	0.1437(3)	0.7385(4)	4.1(2)
C(38)	0.7975(5)	0.1172(4)	0.8139(5)	5.2(2)
C(39)	0.6884(6)	0.1247(4)	0.8004(5)	5.4(2)
C(40)	0.6411(5)	0.1604(4)	0.7117(5)	5.6(2)
C(41)	0.7007(5)	1866(3)	0.6382(5)	4.5(2)
C(42)	0.8602(4)	0.2992(3)	0.5196(4)	3.3(2)
C(43)	0.8574(4)	0.3215(3)	0.4144(4)	3.7(2)
C(44)	0.8526(4)	0.4029(4)	0.3907(5)	4.6(2)
C(45)	0.8485(5)	0.4631(3)	0.4716(6)	4.9(2)
C(46)	0.8516(5)	0.4442(3)	0.5758(5)	4.9(2)
C(47)	0.8573(5)	0.3637(3)	0.5986(4)	4.4(2)
C(48)	0.8091(4)	0.1300(3)	0.4346(4)	3.6(2)
C(49)	0.6954(5)	0.0739(3)	0.4057(4)	4.5(2)
C(50)	0.6415(5)	0.0129(4)	0.3044(6)	5.7(2)
C(51)	0.6998(7)	0.0069(4)	0.2303(5)	6.4(2)
C(52)	0.8126(6)	0.0601(4)	0.2559(5)	6.1(2)
C(53)	0.8651(5)	0.1205(3)	0.3562(4)	4.7(2)
B	0.8730(5)	0.2061(3)	0.5518(5)	3.3(2)

solution affording the allenylidene complex [Cp * Ru=C=C=CMe$_2$(dippe)][BPh$_4$] (3). The reaction of [Cp * RuCl(dippe)] with HC≡CC(OH)MePh and NaBPh$_4$ EtOH yielded the corresponding allenylidene complex [Cp * Ru=C=C=CMePh(dippe)][BPh$_4$] (4) directly. In this case the intermediate hydroxyvinylidene complex was not isolated or detected. No isolable product could be obtained from the reaction of [CpRuCl(dippe)] with propargyl alcohol, whereas the reaction with HC≡CC(OH)MePh led also directly to the allenylidene [CpRu=C=C=CMePh(dippe)][BPh$_4$] (5). All these allenylidene complexes display one strong band in their IR spectra in the range 1900–1950 cm^{-1}, attributable to the stretching of the cumulated C=C=C bonds. The most relevant spectral feature for these compounds are the resonances of the carbon atoms of the unsaturated carbon chain in the ^{13}C{^{1}H} NMR spectra. These appear

Table 3

Selected bond distances (Å) and angles (deg) for [CpRu=C=C=CMeP2h–(dippe)][BPh$_4$]

Intramolecular distances[a]

Atom	Atom	Distance
Ru(1)	P(1)	2.324(1)
Ru(1)	P(2)	2.304(1)
Ru(1)	C(1)	2.230(5)
Ru(1)	C(2)	2.249(5)
Ru(1)	C(3)	2.283(5)
Ru(1)	C(4)	2.280(5)
Ru(1)	C(5)	2.275(5)
Ru(1)	C(6)	1.884(5)
C(6)	C(7)	1.257(6)
C(7)	C(8)	1.338(7)
C(8)	C(9)	1.510(7)
C(8)	C(10)	1.460(6)

Intramolecular bond angles[b]

Atom	Atom	Atom	Angle
P(1)	Ru(1)	P(2)	82.90(5)
P(1)	Ru(1)	C(1)	148.9(2)
P(1)	Ru(1)	C(2)	149.0(2)
P(1)	Ru(1)	C(3)	112.9(2)
P(1)	Ru(1)	C(4)	96.4(1)
P(1)	Ru(1)	C(5)	112.8(2)
P(1)	Ru(1)	C(6)	94.3(1)
P(2)	Ru(1)	C(1)	100.8(1)
P(2)	Ru(1)	C(2)	127.9(2)
P(2)	Ru(1)	C(3)	161.3(1)
P(2)	Ru(1)	C(4)	137.1(2)
P(2)	Ru(1)	C(5)	105.6(2)
P(2)	Ru(1)	C(6)	88.6(1)
Ru(1)	C(6)	C(7)	169.3(4)
C(6)	C(7)	C(8)	175.9(5)
C(7)	C(8)	C(9)	119.4(4)
C(7)	C(8)	C(10)	120.9(4)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.
[b] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

either as singlets (C_β, C_γ) or triplets (C_α) in the range expected for allenylidene complexes of ruthenium. The X-ray crystal structure of **5** was determined. General details about the X-ray structure analysis of this and of other compounds prepared in this work are listed in Table 1. Fractional atomic coordinates, and relevant bond distances and angles are listed in Tables 2 and 3 respectively. An ORTEP view of the complex cation is shown in Fig. 1 The complex has a three-legged piano-stool geometry, the allenylidene ligand being linearly assembled to ruthenium in a fashion very similar to that found in other half-sandwich allenylidene complexes structurally characterized, such as [CpRu=C=C=CPh$_2$(PMe$_3$)$_2$][PF$_6$] [7] and [(η^5-Indenyl)Ru=C=C=C(C$_{13}$H$_{20}$)(PPh$_3$)$_2$][PF$_6$][12]. The plane defined by the cyclopentadienyl ring lies 1.925 Å apart from the ruthenium atom. The Ru(1)–C(6) bond distance of 1.884(5) Å is shorter than a single Ru–C bond, as expected, comparing well with the values found in other Ru allenylidene, i.e., 1.884(5) Å in [CpRu=C=C=CPh$_2$(PMe$_3$)$_2$][PF$_6$] [7], and 1.889(5) Å in [(η^5-Indenyl)Ru=C=C=C(C$_{13}$H$_{20}$)(PPh$_3$)$_2$][PF$_6$] [12]. The C(6)–C(7) separation of 1.257(6) Å is only slightly longer than a C≡C triple bond, whereas the C(7)–C(8) bond distance of 1.338(7) Å is consistent with a double bond. This sequence of bond lengths

indicate, as pointed out for most cationic allenylidene complexes studied by X-ray diffraction [3,5–7,12], a substantial contribution from two different mesomeric forms. The methyl and phenyl substituents and the unsaturated carbon chain lie approximately in the same plane, which forms a dihedral angle with the plane defined by Ru(1), C(6) and the centroid of the Cp ring of 15.9°, an orientation which has been found to maximize the effectiveness of the metal–ligand π-overlap [18]. The dimensions of the Cp and phosphine ligands, as well as those of the [BPh$_4$]$^-$ counterion are in the expected range, being unexceptional.

The reaction of [CpRuCl(dippe)] with HC≡CC(OH)Me$_2$ in MeOH in the presence of NaBPh$_4$ also leads initially to the allenylidene derivative [CpRu=C=C=CMe$_2$(dippe)][BPh$_4$] (**6**), which precipitates from the reaction mixture as a brown microcrystalline solid. However, prolonged stirring at room temperature, as well as attempts made for recrystallizing **6**, yielded deep blue solutions from which a dark blue microcrystalline material was isolated. This blue solid displays one strong band at 1936 cm^{-1} in its IR spectrum, ascribed to ν(C=C=C) or ν(C≡C), being very similar to that shown in the IR spectra of allenylidene complexes. However, the ^{1}H NMR spectrum is rather complicated. Two separate C$_5$H$_5$ resonances are pre-
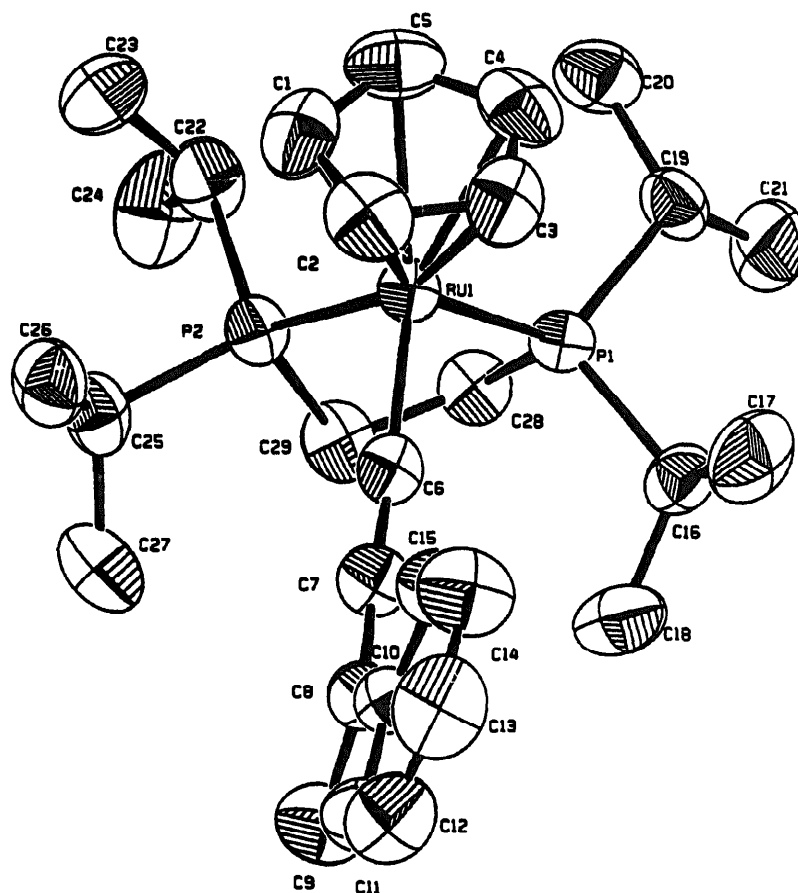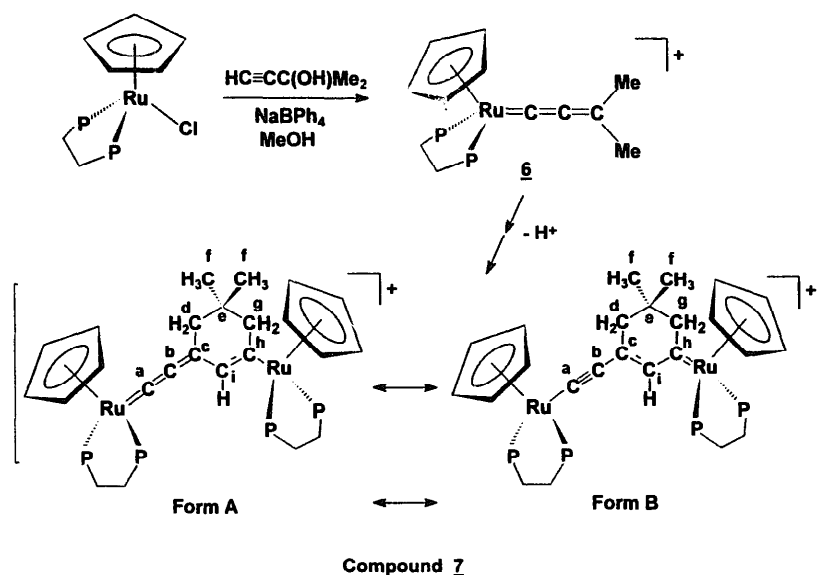

Fig. 1. ORTEP drawing of the cation [CpRu=C=C=CMePh(dippe)]$^+$ with 50% probability thermal ellipsoids. Hydrogen atoms, are omitted.

Scheme 1. Interaction of [CpRuCl(dippe)] with HC=CC(OH)Me$_2$, showing the structure of the coupled product **7**, and atom labelling.

sent, together with a series of singlets which were absent in the ^{1}H NMR spectrum of compound **6**. The ^{31}P{^{1}H} NMR spectrum consists of two singlets of the same intensity, a pattern which suggests the presence of two sets of non-equivalent phosphorus atoms. These spectral data match those reported for the binuclear alkynyl–carbene (or alkenyl–allenylidene) derivatives [{CpRu(PPh$_3$)$_2$}$_2$(μ-C$_{10}$H$_{11}$)][BF$_4$] [11] and [{TpRu(dippe)}$_2$(μ-C$_{10}$H$_{11}$)][BPh$_4$] (Tp = hydrotris(pyrazolyl) borate) [19], which result from the formal coupling of
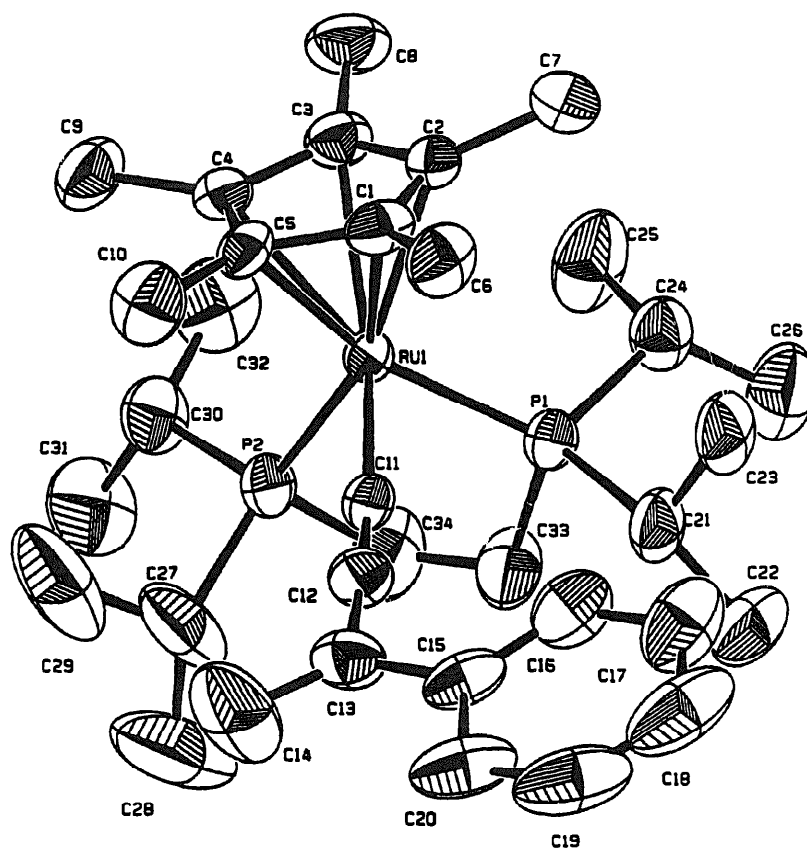

Fig. 2. ORTEP drawing (50% probability thermal ellipsoids) of one of the two independent, virtually identical molecules [Cp·Ru(C=CC(Ph)=CH$_2$(dippe)] in the crystal structure of **5**. Hydrogen atoms, are omitted.

two allenylidene units followed by the loss of one proton. It has been proposed that the coupling takes place between an allenylidene complex and a vinyl-vinylidene derivative, both generated in situ as dehydration products of the corresponding intermediate hydroxyvinylidene complex, not isolated [10,11]. For the $CpRu(PPh_3)_2$ system, this coupling leads to a binuclear vinylidene–carbene complex of formula $[\{CpRu(PPh_3)_2\}_2(\mu\text{-}C_{10}H_{12})][BF_4]_2$, which has been structurally characterized [11], this being reversibly deprotonated to yield the corresponding alkynyl–carbene. An alternative mechanism has been postulated, in which the coupling occurs between one allenylidene complex and an ene-yne derivative formed spontaneously on loss of a proton from the allenylidene [20]. Analytical data in our case support the formulation as $[\{CpRu(dippe)\}_2(\mu\text{-}C_{10}H_{11})][BPh_4]$ (7) for the blue material. Unfortunately, no single crystals of this compound suitable for X-ray crystal structure analysis were obtained, and hence the structure shown in Scheme 1 can only be tentatively assigned based upon spectral data and by analogy with the complex $[\{CpRu(PPh_3)_2\}_2(\mu\text{-}C_{10}H_{11})][BF_4]$ [11]. The $^{13}C\{^1H\}$ NMR resonances for all the non-quaternary carbon atoms of the bridging ligand were assigned by means of a DEPT experiment. The chemical shift of the resonances tentatively assigned to the carbon atoms C_a, C_b and C_c (see Scheme 1) appear in the range expected for allenylidene complexes, suggesting that the contribution of the mesomeric form A (Scheme 1) is more important, and therefore compound 7 can be better regarded as an alkenyl–allenylidene. Addition of one drop of HBF_4 to a blue solution of 7 in dichloromethane causes an immediate colour change to dark red, as it occurs with the related $CpRu(PPh_3)_2$ and $TpRu(dippe)$ systems, suggesting that protonation at the C_b takes place to yield the corresponding vinylidene–carbene complex. However, no pure product was isolated from this protonation reaction. Furthermore, when the protonation was carried out in situ inside a NMR tube, new broad resonances along with other sharper ones were observed in the $^{31}P\{^1H\}$ NMR spectrum. Clearly, the protonation of 7 is a complex process, which gives a mixture of substances, some of them possibly paramagnetic. In any case, no spectral evidence for the formation of vinylidene–carbene species has been obtained.

None of the allenylidene derivatives described here reacted with refluxing MeOH or EtOH to yield vinyl-carbene species, as it has been observed in other cases [21,22]. However, compound 4 reacted with KOBu' in THF to yield a yellow, crystalline material which showed to be the neutral ene-yne derivative $[Cp^*Ru(C\equiv CC(Ph)=CH_2)(dippe)]$ (8), resulting from the deprotonation of the allenylidene ligand at the δ-carbon. A similar process is known to occur spontaneously in the course of the reaction of other half-

sandwich Ru–phosphine complexes with cyclic propargyl alcohols [12,9]. In other cases, the reaction of allenylidenes with alkoxides yields neutral akynyl complexes resulting from the nucleophillic attack at the γ carbon atom of the allenylidene ligand [3]. The allenylidene complexes 3 and 5 also react with KOBu', but in these cases oily uncharacterized substances were obtained. Compound 8 displays one strong $\nu(C\equiv C)$ band at 2048 cm^{-1} in its IR spectrum. The ^1H NMR spectrum shows two doublets at 5.017 and 5.284 ppm attributable to the non-equivalent protons of the terminal $=CH_aH_b$ unit of the $C\equiv CC(Ph)=CH_2$ ligand, a pattern which has been previously observed for the related complex $[TpRu(C\equiv CC(Ph)=CH_2)(dippe)]$ [19]. The connectivity between the protons and their corresponding carbon resonances was determined by a 2D-HETCOR NMR experiment. The X-Ray crystal structure of 8 was determined and an ORTEP view of the molecule is shown in Fig. 2. Fractional atomic coordinates, and selected bond lengths and angles are listed in Tables 4 and 5 respectively. This compound displays a three-legged piano stool structure which results very similar to that adopted by the allenylidene derivative 5. The plane of the pentamethylcyclopentadienyl ring lies at 1.929 Å from the ruthenium atom. The ene-yne ligand appears linearly assembled to ruthenium, with all the atoms including those of the methylene and phenyl substituents situated approximately in the same plane, which in this case forms a dihedral angle of 93.4° with the plane defined by Ru(1), C(11) and the centroid of the Cp* ring. The Ru(1)–C(11) bond distance of 1.994(7) Å is longer than that found in compound 5, and corresponds to a single bond, comparing well with Ru–C separations found in the only other mononuclear ruthenium ene-yne derivatives structurally characterised, $[TpRu(C\equiv CC(Ph)=CH_2)(dippe)]$ (2.004(6) Å) [19], and $[CpRu-C\equiv CC(O_2CCF_3)=CMe_2(PPh_3)_2]$ (2.02(1) Å) [23]. The $C(11)–C(12)$ and $C(12)–C(13)$ bond lengths, 1.22(1) Å and 1.44(1) Å respectively, correspond to a triple and a single bond, whereas the $C(13)–C(14)$ separation of 1.32(1) Å is consistent with a double bond, as expected. As it occurs in the related ene-yne complexes $[TpRu(C\equiv CC(Ph)=CH_2)(dippe)]$ [19] and $[CpRu-C\equiv CC(O_2CCF_3)=CMe_2(PPh_3)_2]$ [23], the observed sequence of very distinct C–C bond distances in the ene-yne fragment is consistent with little electron delocalisation across this ligand.

We were interested in preparing the unsubstituted primary allenylidene complex $[Cp^*Ru=C=C=CH_2(dippe)][BPh_4]$ starting from the hydroxyvinylidene 1. So far, primary allenylidenes have proven to be elusive to isolation. In fact, even monosubstituted(secondary) allenylidene complexes are rare, and have been reported only recently [3,24]. Primary allenylidenes have been postulated as intermediates, being trapped as phosphonium salts in some instances [20]. Given the robust

nature of the hydroxyvinylidene complex **1**, we attempted to promote dehydration using a suitable reagent, such as P_2O_5. Thus, the reaction of **1** with an excess of P_2O_5 in THF yielded a purplish solution from which a microcrystalline material was isolated. This material displays one strong absorption band at 1926 cm^{-1}, which was thought initially to correspond to $\nu(C=C=C)$ of an allenylidene ligand. However, crystal structure analysis showed that this compound was the known carbonyl complex [Cp*Ru(CO)(dippe)][BPh$_4$] (**9**) [14]. An ORTEP view of the molecule is shown in Fig. 3. Fractional atomic coordinates, and selected bond lengths and angles are listed in Tables 6 and 7 respectively. The complex cation has the expected three-legged piano stool structure, having the pentamethylcyclopentadienyl ring 1.925 Å apart from the ruthenium atom. The Ru(1)–C(11) bond distance of 1.843(6) Å is similar to that found in [Cp*Ru=C=CHPh(PMe$_2$Ph)$_2$][Cp*Ru (CO)(PMe$_2$Ph)$_2$][PF$_6$]$_2$ (1.86(1) Å) [17], and slightly shorter than the value expected for a Ru–C single bond, suggesting an appreciable metal–ligand backbonding. Accordingly, the C(11)–O(1) bond length of 1.152(7) Å indicates a relaxation in the C≡O triple bond. All the dimensions of the ligands and counterion are in the expected range, being quite unexceptional. Thus, P_2O_5 acts as an oxidant of the hydroxyvinylidene **1**. Atmospheric oxygen may also perform this oxidation, but more slowly, being necessary several days for complete oxidation. There are several reports of the formation of

carbonyl complexes by aerial oxidation of vinylidene species [17,25]. This has been interpreted in terms of a cycloaddition reaction between molecular oxygen and the vinylidene ligand [20], which results in the oxidative cleavage of the C=C bond and affords the corresponding carbonyl complex and an organic acid. In our case, the fate of the organic fragment of the hydroxyvinylidene ligand resulting from the oxidative cleavage is unknown.

3. Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethylether and petroleum ether (boiling point range 40–60°C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane [26,27] was prepared according to reported procedures. [Cp*RuCl(dippe)] and [CpRuCl(dippe)] were obtained as reported in the literature [13], although a modified procedure has been developed for [Cp*RuCl(dippe)], which is outlined here. IR spectra were recorded in Nujol mulls on Perkin-Elmer 881 or Perkin-Elmer FTIR Spectrum 1000 spectrophotometers. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipments. Chemical shifts are given in ppm
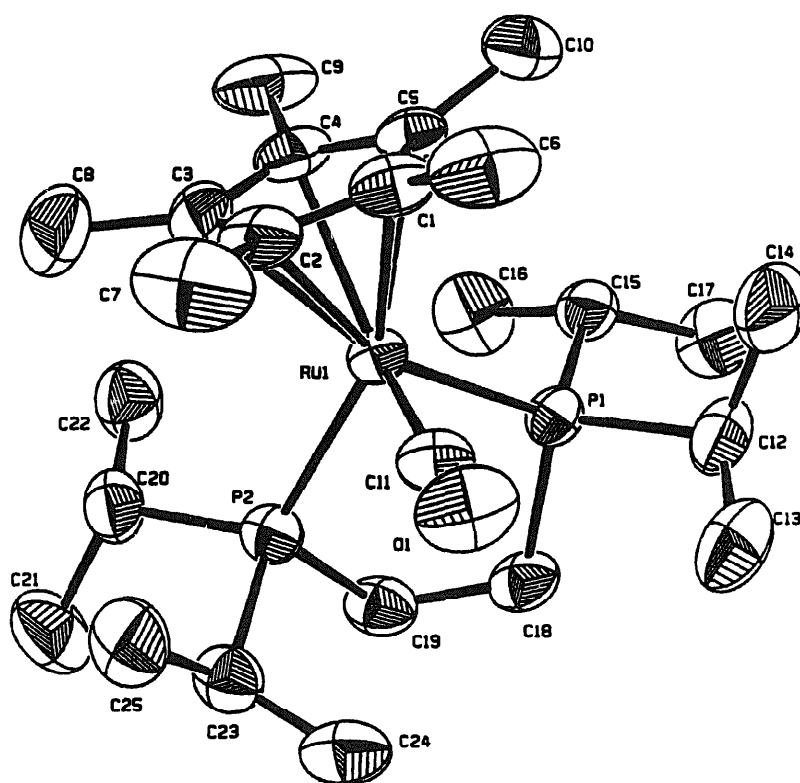

Fig. 3. ORTEP drawing of the cation [Cp*Ru(CO)(dippe)] with 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

Table 4
Fractional atomic coordinates and B_{eq} for [Cp*Ru(C≡CC(Ph)=CH₂)(dippe)]

Positional parameters and B_{eq}
for [CpRu-C≡C-C(Ph)=CH₂(dippe)]

Atom	x	y	z	B_{eq}
Ru	0.38671(5)	0.23529(3)	0.43611(5)	2.45(2)
P(1)	0.2897(2)	0.3315(1)	0.3310(2)	3.10(7)
P(2)	0.1938(2)	0.1675(1)	0.3159(2)	3.61(8)
C(1)	0.5954(7)	0.2538(4)	0.5640(7)	3.4(3)
C(2)	0.5076(7)	0.2888(4)	0.6450(7)	3.1(3)
C(3)	0.4082(7)	0.2361(4)	0.6905(7)	3.5(3)
C(4)	0.4348(7)	0.1671(4)	0.6357(7)	3.3(3)
C(5)	0.5508(7)	0.1765(4)	0.5559(7)	3.1(3)
C(6)	0.7263(8)	0.2876(4)	0.5057(9)	4.6(4)
C(7)	0.5328(9)	0.3681(4)	0.7001(9)	4.7(4)
C(8)	0.320(1)	0.2478(5)	0.8118(8)	5.2(4)
C(9)	0.3694(9)	0.0939(4)	0.6786(9)	4.8(4)
C(10)	0.6247(8)	0.1183(5)	0.493(1)	5.2(4)
C(11)	0.4810(7)	0.2247(3)	0.2561(7)	2.8(3)
C(12)	0.5554(7)	0.2153(4)	0.1610(7)	3.4(3)
C(13)	0.6507(8)	0.2027(4)	0.0563(8)	4.2(3)
C(14)	0.657(1)	0.1357(5)	0.005(1)	8.1(6)
C(15)	0.7399(7)	0.2677(5)	0.0120(8)	4.1(3)
C(16)	0.7430(8)	0.3339(5)	0.082(1)	5.1(4)
C(17)	0.8256(9)	0.3957(5)	0.044(1)	6.5(5)
C(18)	0.909(1)	0.3884(6)	-0.066(1)	7.9(5)
C(19)	0.9094(9)	0.3223(6)	-0.135(1)	7.2(5)
C(20)	0.8262(9)	0.2610(6)	-0.0994(9)	6.2(4)
C(21)	0.3974(8)	0.3854(4)	0.2086(9)	4.3(3)
C(22)	0.329(1)	0.4293(5)	0.089(1)	6.7(5)
C(23)	0.517(1)	0.4323(4)	0.297(1)	5.2(4)
C(24)	0.2275(8)	0.4011(4)	0.4512(9)	4.2(3)
C(25)	0.131(1)	0.3663(5)	0.554(1)	7.4(5)
C(26)	0.165(1)	0.4645(5)	0.378(1)	6.8(5)
C(27)	0.224(1)	0.1090(5)	0.158(1)	7.1(5)
C(28)	0.118(2)	0.0932(8)	0.027(1)	12.4(8)
C(29)	0.291(1)	0.0435(6)	0.214(1)	10.3(7)
C(30)	0.0792(8)	0.1083(4)	0.421(1)	4.7(4)
C(31)	-0.047(1)	0.0649(5)	0.334(1)	7.3(5)
C(32)	0.035(1)	0.1509(5)	0.549(1)	6.5(5)
C(33)	0.139(1)	0.2966(4)	0.202(1)	5.9(4)
C(34)	0.073(1)	0.2282(5)	0.238(1)	7.3(5)

from SiMe₄ (^{1}H and ^{13}C{^{1}H}) or 85% H₃PO₄ (^{31}P{^{1}H}). The phosphine protons for all compounds appeared in the corresponding ^{1}H NMR spectra as a series of overlapping multiplets in the range 0.5–3 ppm. and were not assigned. Microanalysis were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

3.1. Preparation of [Cp*RuCl(dippe)]

To a mixture of [{Cp*RuCl₂}₂] (0.61 g, 1 mmol) and dippe (0.7 ml, ca. 2.3 mmol) in tetrahydrofuran, zinc dust (2 g, excess) was added. The mixture was stirred at room temperature for ca. 2 h. Then, it was taken to dryness, and the residue extracted with several portions of diethylether. The resulting orange solution was filtered through celite. Addition of petroleum ether. con-

centration and cooling to −20°C afforded orange crystals, which were filtered off, washed with a small portion of cold petroleum ether and dried in vacuo. Yield: 0.85 g, 80%.

3.2. Preparation of hydroxyvinylidene complexes [Cp*Ru=C=CHCR₂OH(dippe)][BPh₄] (R = H ⅃, Me 2)

[Cp*RuCl(dippe)] (0.26 g, ca. 0.5 mmol) in MeOH (15 ml) was treated with an excess of the corresponding alkynol HC≡CCR₂(OH) (R = H or Me), and solid NaBPh₄ (0.3 g, excess). An orange–brown microcrystalline precipitate was immediately obtained in the case of R = Me, whereas for R = H the mixture was stirred at room temperature for several minutes, in order to complete the precipitation. The crystalline solids were

Table 5
Selected bond distances (Å) and angles (deg) for [Cp*Ru(C≡CC(Ph)=CH₂)-(dippe)]

Intramolecular distances[a]

Atom	Atom	Distance
Ru(1)	P(1)	2.297(2)
Ru(1)	P(2)	2.301(2)
Ru(1)	C(1)	2.235(6)
Ru(1)	C(2)	2.275(6)
Ru(1)	C(3)	2.320(7)
Ru(1)	C(4)	2.293(7)
Ru(1)	C(5)	2.252(7)
Ru(1)	C(11)	1.994(7)
C(11)	C(12)	1.22(1)
C(12)	C(13)	1.44(1)
C(13)	C(14)	1.32(1)
C(13)	C(15)	1.50(1)

Intramolecular bond angles[b]

Atom	Atom	Atom	Angle
P(1)	Ru(1)	P(2)	83.35(7)
P(1)	Ru(1)	C(1)	120.1(2)
P(1)	Ru(1)	C(2)	102.4(2)
P(1)	Ru(1)	C(3)	116.1(2)
P(1)	Ru(1)	C(4)	150.5(2)
P(1)	Ru(1)	C(5)	157.3(2)
P(1)	Ru(1)	C(11)	87.8(2)
P(2)	Ru(1)	C(1)	156.1(2)
P(2)	Ru(1)	C(2)	150.8(2)
P(2)	Ru(1)	C(3)	116.2(2)
P(2)	Ru(1)	C(4)	101.8(2)
P(2)	Ru(1)	C(5)	118.8(2)
P(2)	Ru(1)	C(11)	88.9(2)
Ru(1)	C(11)	C(12)	169.8(6)
C(11)	C(12)	C(13)	175.9(7)
C(12)	C(13)	C(14)	119.6(8)
C(12)	C(13)	C(15)	117.5(7)

[a]Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.
[b]Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

filtered off, washed with ethanol and petroleum ether and dried in vacuo. Compound **2** obtained in this fashion always appeared containing minor amounts of the

Table 6
Fractional atomic coordinates and B_{eq} for [Cp*Ru(CO)(dippe)][BPh$_4$]

Positional parameters and B_{eq} for [CpRu(CO)(dippe)][BPh$_4$]

Atom	x	y	z	B_{eq}
Ru(1)	0.09881(3)	0.23566(3)	0.18155(3)	2.60(2)
P(1)	0.01895(9)	0.1542(1)	0.24872(9)	2.80(6)
P(2)	0.11844(9)	0.3283(1)	0.29270(9)	2.99(7)
C(1)	0.1128(4)	0.1925(5)	0.0627(3)	4.2(3)
C(2)	0.1556(4)	0.2747(5)	0.832(3)	4.5(3)
C(3)	0.0988(5)	0.3415(5)	0.0869(4)	4.6(3)
C(4)	0.0218(4)	0.3023(4)	0.0713(3)	3.8(3)
C(5)	0.0318(4)	0.2095(4)	0.0556(3)	3.4(3)
C(6)	0.1482(5)	0.1069(6)	0.0398(4)	7.0(4)
C(7)	0.2425(5)	0.2894(7)	0.0867(5)	9.1(6)
C(8)	0.1166(6)	0.4397(5)	0.0908(5)	7.9(5)
C(9)	−0.0569(5)	0.3490(5)	0.0510(4)	6.1(4)
C(10)	−0.0341(4)	0.1476(5)	0.0193(3)	5.1(3)
C(11)	0.1874(4)	0.1673(4)	0.2230(3)	3.8(3)
O(1)	0.2447(3)	0.1248(4)	0.2360(3)	6.4(3)
C(12)	0.0307(4)	0.0314(4)	0.2589(4)	4.4(3)
C(13)	0.1118(5)	−0.0001(5)	0.3050(5)	6.2(4)
C(14)	0.0092(5)	−0.0142(5)	0.1801(5)	7.0(4)
C(15)	−0.0903(3)	0.1664(4)	0.2135(3)	3.3(3)
C(16)	−0.1167(3)	0.2612(5)	0.2238(4)	4.9(3)
C(17)	−0.1400(4)	0.1014(5)	0.2490(4)	5.2(3)
C(18)	0.0407(3)	0.1904(4)	0.3508(3)	3.6(3)
C(19)	0.0592(3)	0.2889(4)	0.3603(3)	3.6(3)
C(20)	0.0941(4)	0.4493(4)	0.2813(4)	4.0(3)
C(21)	0.1153(4)	0.5030(5)	0.3567(4)	5.7(4)
C(22)	0.0062(4)	0.4647(4)	0.2406(4)	4.6(3)
C(23)	0.2203(4)	0.3325(4)	0.3548(4)	4.0(3)
C(24)	0.2507(4)	0.2455(5)	0.3947(4)	5.2(3)
C(25)	0.2791(4)	0.3711(5)	0.3109(5)	5.9(4)
C(26)	0.1629(4)	0.1611(4)	0.6313(4)	3.9(3)
C(27)	0.1828(4)	0.1331(4)	0.5623(4)	4.5(3)
C(28)	0.2393(4)	0.0693(5)	0.5593(5)	5.8(4)
C(29)	0.2794(4)	0.0276(5)	0.6285(7)	6.8(4)
C(30)	0.2589(5)	0.0494(6)	0.6960(6)	6.6(4)
C(31)	0.2028(4)	0.1143(5)	0.6976(4)	5.0(3)
C(32)	0.1352(3)	0.3369(4)	0.6047(3)	3.2(3)
C(33)	0.2046(4)	0.3454(4)	0.5770(3)	3.6(3)
C(34)	0.2332(4)	0.4277(4)	0.5586(4)	4.2(3)
C(35)	0.1919(4)	0.5051(4)	0.5667(4)	4.7(3)
C(36)	0.1248(5)	0.4991(4)	0.5941(4)	5.3(4)
C(37)	0.0983(4)	0.4169(4)	0.6131(4)	4.7(3)
C(38)	0.0168(3)	0.2136(4)	0.5632(3)	3.2(3)
C(39)	−0.0348(4)	0.2737(4)	0.5175(3)	3.8(3)
C(40)	−0.1059(4)	0.2485(5)	0.4664(4)	4.4(3)
C(41)	−0.1268(4)	0.1598(5)	0.4609(4)	4.6(3)
C(42)	−0.0779(4)	0.0979(4)	0.5041(4)	4.6(3)
C(43)	−0.0076(4)	0.1253(4)	0.5542(4)	4.2(3)
C(44)	0.0747(4)	0.2575(4)	0.7127(3)	4.1(3)
C(45)	0.1327(5)	0.2822(5)	0.7788(4)	6.0(4)
C(46)	0.1171(6)	0.2973(6)	0.8511(4)	7.1(5)
C(47)	0.0407(7)	0.2915(5)	0.8598(4)	7.3(5)
C(48)	−0.0192(5)	0.2717(5)	0.7960(5)	6.2(4)
C(49)	−0.0025(4)	0.2538(4)	0.7238(4)	4.81(3)
B	0.0982(4)	0.2408(5)	0.6278(4)	3.4(3)

Table 7
Selected bond distances (Å) and angles (deg) for [Cp*Ru(CO)(dippe)][BPh$_4$]

Intramolecular distances[a]

Atom	Atom	Distance
Ru(1)	P(1)	2.350(2)
Ru(1)	P(2)	2.358(2)
Ru(1)	C(1)	2.257(6)
Ru(1)	C(2)	2.255(5)
Ru(1)	C(3)	2.299(6)
Ru(1)	C(4)	2.312(6)
Ru(1)	C(5)	2.289(6)
Ru(1)	C(11)	1.843(6)
C(11)	O(1)	1.152(7)

Intramolecular bond angles[b]

Atom	Atom	Atom	Angle
P(1)	Ru(1)	P(2)	82.79(5)
P(1)	Ru(1)	C(1)	121.3(2)
P(1)	Ru(1)	C(2)	158.3(2)
P(1)	Ru(1)	C(3)	145.0(2)
P(1)	Ru(1)	C(4)	110.9(2)
P(1)	Ru(1)	C(5)	100.2(1)
P(1)	Ru(1)	C(11)	92.3(2)
P(2)	Ru(1)	C(1)	155.9(2)
P(2)	Ru(1)	C(2)	118.8(2)
P(2)	Ru(1)	C(3)	100.1(2)
P(2)	Ru(1)	C(4)	113.0(2)
P(2)	Ru(1)	C(5)	148.2(2)
P(2)	Ru(1)	C(11)	92.7(2)
Ru(1)	C(11)	O(1)	168.2(5)

[a]Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.
[b]Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

allenylidene derivative [Cp*Ru=C=C=CMe$_2$(dippe)][BPh$_4$] (**3**), which is formed by spontaneous dehydration of **2** in solution. For this reason, satisfactory microanalysis could not be obtained for this compound. Yield: 75% in both cases. **1**: Anal: Calc. for C$_{51}$H$_{71}$BOP$_2$Ru C, 70.1; H, 8.19. Found C. 69.8; H, 8.08. IR (Nujol): ν(OH) 3528 cm^{-1}; ν(C=C) 1636 cm^{-1}; NMR (CDCl$_3$): ^{1}H δ 1.811 (s, C$_5$(CH$_3$)$_5$); 3.991 (d, J_{HH} = 19 Hz, Ru=C=CHCH$_2$OH); 4.062 (t, J_{HH} = 19 Hz, Ru=C=CHCH$_2$OH). ^{31}P{^{1}H} 86.8 s. ^{13}C{^{1}H} 10.98 (s, C$_5$(CH$_3$)$_5$); 18.42, 18.70, 19.46, 19.94 (s, P(CH(CH$_3$)$_2$)$_2$); 21.52 (t, J_{CP} = 19.8 Hz, PCH$_2$); 25.55 (t, J_{CP} = 20.0 Hz, P(CH(CH$_3$)$_2$)$_2$); 31.70 (t, J_{CP} = 16 Hz, P(CH(CH$_3$)$_2$)$_2$); 53.51 (s, CHCH$_2$O$_4$); 102.77 (s, C$_5$Me$_5$); 112.07 (s, Ru=C=CHCH$_2$OH); 339.51 (t, J_{CP} = 14.1 Hz, Ru=C=CHCH$_2$OH). **2**: IR (Nujol): ν(OH) 3545 cm^{-1}; ν(C=C) 1639 cm^{-1}; NMR (CDCl$_3$): ^{1}H δ 1.325 (s, C(CH$_3$)$_2$OH); 1.845 (s, C$_5$(CH$_3$)$_5$); 3.676 (s, Ru=C=CHCMe$_2$OH). ^{31}P{^{1}H} 83.5 s. ^{13}C{^{1}H} NMR spectrum not recorded due to transformation into the allenylidene complex **3**.

3.3. [Cp*Ru=C=C=CRR'(dippe)][BPh₄] (R = R' = Me 3; R = Me, R' = Ph 4)

To a solution of [Cp* RuCl(dippe)] (0.26 g, 0.5 mmol) in MeOH (15 ml), an excess of the corresponding alkynol (HC≡CCMe₂(OH) for 3, or HC≡CCMePh(OH) for 4) and NaBPh₄ (0.3 g, excess) was added. The mixture was heated using a water bath for 3 h, and then allowed to cool. The resulting brown microcrystalline precipitate was filtered off, washed with EtOH and petroleum ether and dried in vacuo. These products were recrystallized from acetone–EtOH. Yield: 80–85%. 3: Anal: Calc. for C₅₃H₇₃BP₂Ru C, 72.0; H, 8.32. Found C, 72.0; H, 8.27. IR (Nujol): ν(C=C=C) 1936 cm⁻¹. NMR (CDCl₃): ¹H 1.550 (s, Ru=C=C=C(CH₃)₂); 1.850 (s, C₅(CH₃)₅).³¹P{¹H} 87.8 s. ¹³C{¹H} 12.03 (s, C₅(CH₃)₅); 19.60, 19.77, 20.13, 20.28 (s, P(CH(CH₃)₂)₂); 21.77 (m, PCH₂); 25.86 (m, P(CH(CH₃)₂)₂); 28.68 (m, P(CH(CH₃)₂)₂); 54.66 (s, C=C=C(CH₃)₂); 91.46 (s, C₅Me₅); 153.52 (s, Ru=C=C=CMe₂); 199.0 (s, Ru=C=C=CMe₂); 288.34 (t, J_{CP} = 17.1 Hz, Ru=C=C=CMe₂). 4: Anal: Calc. for C₅₈H₇₅BP₂Ru C, 73.6; H, 7.99. Found C, 73.3; H, 7.85. IR (Nujol): ν(C=C=C) 1915 cm⁻¹; reinforced ν(C=C) in phenyl ring 1645 cm⁻¹. NMR (CDCl₃): ¹H δ 1.506 (s, Ru=C=C=C(CH₃)Ph); 1.901 (s, C₅(CH₃)₅); 7.339, 7.635, 7.870 (m, C₆H₅). ³¹P{¹H} 88.2 s. ¹³C{¹H} 11.38 (s, C₅(CH₃)₅); 18.18, 19.37, 19.85 (s, P(CH(CH₃)₂)₂); 21.58 (t, J_{CP} = 19 Hz, PCH₂); 25.97 (m, PCH(CH₃)₂); 30.59 (m, P(CH(CH₃)₂)₂); 52.37 (s, C=C=C(CH₃)Ph); 102.38 (s, C₅Me₅); 127.24, 129.56, 131.67 (s, C₆H₅); 147.90 (s, Ru=C=C=CMePh); 209.21 (s, Ru=C=C=CMePh); 271.04 (m br, Ru=C=C=CMePh).

3.4. [CpRu=C=C=CMePh(dippe)][BPh₄] (5)

This compound was obtained following an experimental procedure identical to that outlined for the Cp*Ru allenylidene derivatives 3–4. A solution of [CpRuCl(dippe)] (0.23 g, 0.5 mmol) in MeOH (15 ml) was treated with an excess of HC≡CCMePh(OH) and NaBPh₄ (0.3 g, excess). The mixture was heated in a water bath for ca. 3, and then allowed to cool. The crystalline precipitate was filtered, washed with EtOH and petroleum ether and dried in vacuo. Recrystallisation from acetone–EtOH afforded single crystals, suitable for X-Ray structure analysis. Yield: 0.35 g, 80%. Anal: Calc. for C₅₃H₆₅BP₂Ru C, 72.7; H, 7.48. Found C, 72.6; H, 7.55. IR (Nujol): ν(C=C=C) 1936 cm⁻¹. NMR (CDCl₃): ¹H δ 1.871 (s, Ru=C=C=C(CH₃)Ph); 5.450 (s, C₅H₅); 7.368, 7.648, 7.849 (m, C₆H₅).³¹P{¹H} 99.8 s. ¹³C{¹H} 18.69, 18.80, 18.99, 19.93 (s, P(CH(CH₃)₂)₂); 22.93 (t, J_{CP} = 19.3 Hz, PCH₂); 28.26

(m, PCH(CH₃)₂); 30.31 (m, P(CH(CH₃)₂)₂); 29.44 (s, C=C=C(CH₃)Ph); 88.75 (s, C₅H₅); 127.91, 129.53, 131.91 (s, C₆H₅); 141.92 (s, Ru=C=C=CMePh); 150.53 (s, Ru=C=C=C MePh); 285.24 (t, J_{CP} = 17.2 Hz, Ru=C=C=CMePh).

3.5. Reaction of [CpRuCl(dippe)] with HC≡CCMe₂(OH)

To a solution of [CpRuCl(dippe)] (0.23 g, ca. 0.5 mmol) in MeOH (15 ml), an excess of HC≡CCMe₂(OH) and solid NaBPh₄ was added. The mixture was stirred for 15 min, and a dark brown microcrystalline precipitate was obtained. It was filtered off, washed with ethanol and petroleum ether and dried in vacuo. This brown material contains mainly the allenylidene complex [CpRu=C=C=CMe₂(dippe)][BPh₄] (6), plus minor amounts of the binuclear derivative 7. Accurate microanalysis could not be obtained for this material, which does not precipitate, and therefore is not isolated, if diluted solutions are used. If the reaction mixture is heated up using a water bath for 30 min. and then stirred for 18 h at room temperature, a dark blue suspension was obtained. The dark blue solids were filtered off, washed with petroleum ether and dried in vacuo. Concentration and cooling of the mother liquor afforded another crop of blue microcrystals. Yield: 0.21 g, 63%. Anal: Calc. for C₇₂H₁₀₅BP₄Ru₂ C, 66.2; H, 8.04. Found C, 65.8; H, 8.16.

Selected spectral data for [CpRu=C=C=CMe₂(dippe)][BPh₄] (6): IR (Nujol): ν(C=C=C) 1946 cm⁻¹. NMR (CD₂Cl₂): ¹H 1.308 (s, Ru=C=C=C(CH₃)₂); 5.510 (s, C₅H₅).³¹P{¹H} 96.7 s. ¹³C{¹H} 19.36, 19.63, 19.89, 19.84 (s, P(CH(CH₃)₂)₂); 23.34 (t, J_{CP} = 19.8 Hz, PCH₂); 31.14 (t, J_{CP} = 9.7 Hz, P(CH(CH₃)₂)₂); 31.87 (t, J_{CP} = 16.4 Hz, P(CH(CH₃)₂)₂); 80.78 (s, C₅H₅); 29.31 (s, C=C=C(CH₃)₂); quaternary carbons: not observed, due to transformation into 7 during the overnight recording of the ¹³C{¹H} NMR spectrum.

Selected spectral data for [{CpRu(dippe)}₂(μ-C₁₀H₁₁)][BPh₄] (7): IR (Nujol): ν(C≡C) 1972 cm⁻¹. NMR (CD₂Cl₂, see Scheme 1 for atom proton and carbon labels): ¹H 0.858 (s, (CH¹₃)₂); 1.588, 2.893 (s, CH^d₂ and CH^g₂): 6.396 (s, CH^f); 5.080, 5.296 (s, C₅H₅).³¹P{¹H} 100.24, 110.04 s.¹³C{¹H} 19.17, 19.43, 19.49, 19.67, 20.27, 20.44, 20.66, 20.93 (s, P(CH(CH₃)₂)₂); 23.91 (t, J_{CP} = 18.8 Hz, PCH₂);); 24.78 (t, J_{CP} = 18.2 Hz, PCH₂); 28.05 (t, J_{CP} = 15.2 Hz, P(CH(CH₃)₂)₂); 29.62 (t, J_{CP} = 10.9 Hz, P(CH(CH₃)₂)₂); 30.25 (t, J_{CP} = 9.7 Hz, P(CH(CH₃)₂)₂); 33.20 (t, J_{CP} = 11.5 Hz, P(CH(CH₃)₂)₂); 83.47, 87.80 (s, C₅H₅); 28.47 (s, (C^aH3)₂); 44.33, 58.50 (s, C^dH₂ and C^gH₂); 113.07 (s, C^fH); 149.05 (s, Ru=C=C=C^c); 186.7 (s, Ru=C=C^b=C); 271.12 (t, J_{CP} = 11.1 Hz,

Ru=C^a=C=C); remaining quaternary carbons: not observed.

3.6. [Cp*Ru–C≡C–C(Ph)=CH$_2$(dippe)] (8)

To a solution of **4** (0.1 g, ca. 0.1 mmol) in THF, and excess of solid KOBu^t was added. An immediate color change from dark brown to yellow was observed. The mixture was stirred for 30 min at room temperature, and then taken to dryness. The residue was extracted with diethylether and centrifuged. Addition of petroleum ether, concentration and cooling to −20°C afforded well-formed yellow crystals of **8**, suitable for X-ray structure analysis. Yield: 0.036 g, 57%. Anal: Calc. for $C_{34}H_{54}P_2Ru$ C, 65.3; H, 8.70. Found C, 65.8; H, 8.63. IR (Nujol): ν(C≡C) 2048 cm^{-1}; NMR (C_6D_6): ^{1}H δ 1.846 (s, $C_5(CH_3)_5$); 5.017 (d, J_{HH} = 2.4 Hz, RuC≡CC(Ph)=CH_aH$_b$), 5.284 (d, J_{HH} = 2.4 Hz, RuC≡CC(Ph)=CH$_a$$H_b$); 7.173, 7.258, 7.758 (m, RuC≡CC(C_6H_5)=CH$_2$); ^{31}P{^{1}H} 88.3 s; ^{13}C{^{1}H} 11.27 (s, $C_5(CH_3)_5$); 18.75, 18.89, 19.02, 19.45 (s, P(CH(CH$_3$)$_2$)$_2$); 21.12 (t, J_{CP} = 9.8 Hz, PCH$_2$); 25.25 (t, J_{CP} = 4.0 Hz, P(CH(CH$_3$)$_2$)$_2$); 28.29 (t, J_{CP} = 7.3 Hz, P(CH(CH$_3$)$_2$)$_2$); 91.85 (s, C_5Me$_5$); 109.6 (s, RuC≡CC(Ph)=CH$_2$); 129.1 (s, RuC≡CC(Ph)=CH$_2$); 134.5 (t, J_{CP} = 21.1 Hz, RuC≡CC(Ph)=CH$_2$); 135.8 (s, RuC≡CC(Ph)=CH$_2$); 126.5, 126.7, 127.4 (s, RuC≡CC(C_6H_5)=CH$_2$).

3.7. [Cp*Ru(CO)(dippe)][BPh$_4$] (9) from 1

To a THF solution of **1**, an excess of solid P_2O_5 was added. The mixture turns purple upon stirring at room temperature for some minutes. It was allowed to react for 15 min. Then, the excess of P_2O_5 was removed by filtration. Addition of ethanol and concentration yielded lavender crystals, which were filtered off, washed with petroleum ether and dried in vacuo. Yield: essentially quantitative. Single crystals of compound **9** were obtained by slow recrystallization of **1** from acetone–ethanol in air. The spectral data for this complex were consistent with those already reported in the literature [14].

3.8. Experimental data for the X-ray crystal structure determinations

A summary of crystallographic data for compounds **5**, **8** and **9** is given in Table 1. X-ray measurements were made on crystals of the appropriate size, which were mounted onto a glass fiber, and transferred to an AFC6S-Rigaku automatic diffractometer, using CuK$_\alpha$ (for compounds **5** and **8**) or MoK$_\alpha$ (for compound **9**) graphite-monochromated radiation. Cell parameters were determined from the settings of 25 high-angle reflec-

tions. Data were collected by the ω–2θ scan method. Lorentz, polarization, and absorption (ψ-scan method) corrections were applied. A decay correction was also applied for each of the compounds, the correction based on the measure of three standards reflections after every 200 reflections (for compounds **5** and **8**) or 100 reflections (compound **9**) were −2.30% for **5**, −0.20% for **8**, and −4.20% for **9** during data collection. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN [28] software system and ORTEP [29] for plotting. All the structures were solved by the Patterson method, and refined by full-matrix least-squares. Reflections having I > 3σ(I) were used for structure refinement. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at geometrically calculated positions and were not refined. Maximum and minimum peaks in the final difference Fourier maps were +0.51 and −0.55 e Å^{-3} for **5**, +1.06 and −1.29 e Å^{-3} for **8**, and +0.61 and −0.42 e Å^{-3} for **9**. Atomic coordinates and B_{eq}, and selected bond lengths and angles for each compound are listed in Tables 2–7.

4. Supplementary material

Tables of X-ray crystallographic data, including atomic coordinates and anisotropic thermal parameters, interatomic distances and angles (48 pp.), and listings of calculated and observed structure factors (44 pp.). Ordering information is given on any current masthead page.

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