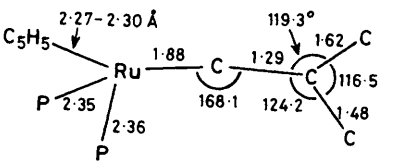
Cyclopentadienyl-Ruthenium and -Osmium Chemistry. Part 20.† Synthesis and *X*-Ray Structure of a Cationic Ruthenium–Vinylidene Complex, $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ ‡

Michael I. Bruce * and Fook Sin Wong
Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001
Brian W. Skelton and Allan H. White *
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

The complexes $[Ru(C{\equiv}CR)(PMe_3)L(\eta\text{-}C_5H_5)]$ (R = Me or Ph, L = PMe_3: R = Ph, L = PPh_3) were obtained from reactions between $[Ru(C{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)]$ and PMe_3, while $[Ru(C{=}CHR)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (R = H, Me, or Ph) were formed from $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$, $HC{\equiv}CR$, and NH_4PF_6. Alkylation of $[Ru(C{\equiv}CPh)(PMe_3)_2(\eta\text{-}C_5H_5)]$ with OMe_3PF_6 gave $[Ru(C{=}CMePh)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$. The molecular structure of $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ is described. It has the distorted 'piano-stool' configuration, with the plane of the vinylidene ligand bisecting the molecular symmetry plane. For the vinylidene ligand, Ru–C 1.845(7), C–C 1.313(10) Å, Ru–C=C 180(2) and C–C–Me 125.1(6)°.

Recent papers from this laboratory have described high-yield syntheses of cationic vinylidene complexes of ruthenium and osmium,[1,2] and related derivatives containing iron [3,4] and ruthenium [5,6] have also been made by other workers. The chemistry associated with the vinylidene ligand is now becoming established, and extensive studies of the addition of water or alcohols to give alkyl, acyl, or alkoxycarbene complexes have been reported.[7] These have given substance to the earlier rationalisations of reactions of cationic platinum complexes with 1-alkynes and alcohols in the presence of silver(I) ion as proceeding *via* 'metal-stabilised carbonium ions,' or vinylidenes, as intermediates.[8] Other reactions of these complexes of the iron triad include reversible deprotonation at the β-carbon atom,[1,4] complexing of the unsaturated system with an iron carbonyl group,[9] and intramolecular cyclisations, either within a hydroxyalkylvinylidene,[10] or with an adjacent ligand.[11]

While extensive studies of ^{13}C n.m.r. spectra have pointed to the extremely electron-deficient nature of the α-carbon (which resonates at *ca.* 360 p.p.m. in the ruthenium complexes, for example), no structural studies of the $M{-}C{=}CR_2$ group have been made; as noted below, several *X*-ray structures of neutral complexes have been reported. Data obtained from crystals of $[Ru(C{=}CMe_2)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ were refined only to the point of indicating the presence of an almost linear Ru–C–C moiety (A), and no accurate bond parameters were obtained.[12] In this paper we report the syntheses of some vinylidene and acetylide complexes containing the $Ru(PMe_3)_2(\eta\text{-}C_5H_5)$ moiety, and the crystal and molecular structure of $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$.



(A)

Experimental

General experimental details have been described previously.[13] The complex $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ was prepared by the literature method.[13]

Reactions between $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ *and 1-Alkynes.*—(*a*) *Acetylene.* A reaction between $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (59.3 mg, 0.17 mmol), NH_4PF_6 (28.7 mg, 0.2 mmol), and acetylene (*ca.* 2.0 mmol) in methanol at room temperature for 4 h afforded yellow crystals with a yellow supernatant. The mixture was evaporated, extracted with dichloromethane, and filtered; slow evaporation of the filtrate gave yellow *crystals* of $[Ru(C{=}CH_2)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (1) (66 mg, 79%), decomp. >100 °C (Found: C, 31.9; H, 5.1. $C_{13}H_{25}F_6P_3Ru$ requires C, 32.1; H, 5.1%). Infrared (Nujol): ν(CC) 1 749m, 1 632w; ν(PF) 830vs(br) cm^{-1}. N.m.r. $[(CD_3)_2CO]$: ^1H, δ 1.65 (apparent t, '*J*' 9.8 Hz, 18 H, PMe_3), 5.23 (s, 5 H, C_5H_5), and 5.35 [t, 2 H, *J*(HP) 7.2 Hz, $=CH_2$]; ^{13}C, δ 21.0 [t, *J*(CP) 16.0 Hz, PMe_3], 87.69 (s, C_5H_5), 127.35 (s, $=CH_2$), RuC not located.

(*b*) *Propyne.* Similarly, propyne (*ca.* 1.5 mmol) gave directly orange *crystals* of $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (2) (83 mg, 83%), m.p. 155 °C (decomp.) (Found: C, 33.5; H, 5.4. $C_{14}H_{27}F_6P_3Ru$ requires C, 33.4; H, 5.4%). Infrared (Nujol): ν(CC) 1 686w, 1 650m; ν(PF) 836vs(br) cm^{-1}. ^1H N.m.r.: δ $[(CD_3)_2CO]$ 4.37 (s, 5 H, C_5H_5), 6.30 (s, 3 H, Me), and 8.30 [t, *J*(HP) 10.0 Hz, 18 H, PMe_3].

(*c*) *Phenylacetylene.* A mixture of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (118 mg, 0.33 mmol), phenylacetylene (51 mg, 0.5 mmol), and NH_4PF_6 (57 mg, 0.35 mmol) in methanol was heated at *ca.* 40 °C for 2 h. Work-up afforded pink $[Ru(C{=}CHPh)(PMe_3)_2$-

† Part 19, M. I. Bruce, T. W. Hambley, J. R. Rodgers, M. R. Snow, and F. S. Wong, *Aust. J. Chem.*, 1982, **35**, 1323.

‡ (1—5-η-Cyclopentadienyl)propenylidenebis(trimethylphosphine)-ruthenium hexafluorophosphate.

Supplementary data available (No. SUP 23350, 14 pp.): H-atom coordinates, thermal parameters, anion geometry, structure-factor amplitudes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

$(\eta\text{-}C_5H_5)]PF_6$ (3) (119 mg, 63%), m.p. 185—190 °C (decomp.) (lit.,[6] 236—238 °C) (Found: C, 40.7; H, 4.4. $C_{19}H_{29}F_6P_3Ru$ requires C, 40.4; H, 5.1%). Infrared (Nujol): ν(CC) 1 650m cm^{-1}. N.m.r. (CD_2Cl_2): ^1H, δ 1.62 (apparent t, 'J' 10.25 Hz, 18 H, PMe_3), 5.40 [t, J(HP) 2.2 Hz, =CH], 5.55 (s, 5 H, C_5H_5), and 7.25 (m, 5 H, Ph); ^{13}C, δ 22.9 (t, PMe_3), 92.1 (s, C_5H_5), 114.7 (s, =*C*HPh), and 126.2—132.5 (m, Ph).

The same complex was obtained by addition of HPF_6 (89 mg, 0.37 mmol) to a solution of $[Ru(C{\equiv}CPh)(PMe_3)_2(\eta\text{-}C_5H_5)]$ (147 mg, 0.35 mmol) in dichloromethane. Addition of the mixture dropwise to excess of diethyl ether afforded an orange-red flocculent precipitate of the product (164 mg, 84%), which was filtered off, washed with ether, and dried.

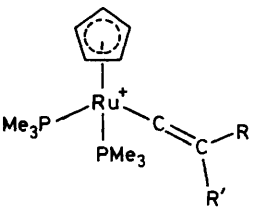
Preparations.—$[Ru(C{\equiv}CMe)(PMe_3)_2(\eta\text{-}C_5H_5)]$. Trimethylphosphine (207 mg, 2.72 mmol) was condensed onto a suspension of $[Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (945 mg, 1.3 mmol) in light petroleum (b.p. 100—120 °C, 5 cm^3), and the mixture was heated at 160 °C for 36 h (Carius tube). On cooling, crystals of PPh_3 separated; after removal of these, the product also crystallised with some difficulty as yellow *crystals* of $[Ru(C{\equiv}CMe)(PMe_3)_2(\eta\text{-}C_5H_5)]$ (4) (339 mg, 73%), m.p. 112 °C (Found: C, 47.7; H, 7.7. $C_{14}H_{26}P_2Ru$ requires C, 47.1; H, 7.3%). Infrared (Nujol): ν(C≡C) 2 098w; ν(PC) 952w, 936s cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 1.46 (apparent t, 'J' 9.0 Hz, 18 H, PMe_3), 1.98 [t, J(HP) 2.6 Hz, Me], and 4.62 (s, 5 H, C_5H_5); ^{13}C, δ 7.0 (s, Me), 23.3 [t, J(CP) 15 Hz, PMe_3], 80.2 (s, C_5H_5), 98.7 (s, ≡*C*Me), RuC not located.

$[Ru(C{\equiv}CPh)(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)]$. A similar ligand-exchange reaction carried out using only 1 mol equivalent of trimethylphosphine gave a yellow *solid* identified as $[Ru(C{\equiv}CPh)(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)]$ (5), m.p. 170 °C (Found: C, 67.6; H, 5.6%; M, 606. $C_{34}H_{34}P_2Ru$ requires C, 67.4; H, 5.6%; M, 606). Infrared (Nujol): ν(CC) 2 070 cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 1.19 [d, J(HP) 9.03 Hz, 9 H, PMe_3], 4.52 (s, 5 H, C_5H_5), 7.05, 7.32, and 7.68 (all m, 20 H, Ph); ^{13}C, δ 22.09 [d, J(CP) 29.6 Hz, PMe_3], 83.02 [t, J(CP) 1.9 Hz, C_5H_5], 123.0 (s, Ru*C*≡*C*), and 127.4—134.7 (m, Ph).

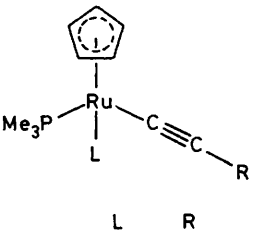
$[Ru(C{\equiv}CPh)(PMe_3)_2(\eta\text{-}C_5H_5)]$. This complex was obtained by heating a mixture of $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (317 mg, 0.4 mmol) and trimethylphosphine (76 mg, 1.0 mmol) in light petroleum (20 cm^3), contained in a Carius tube, for 15 h at 160 °C. On cooling, crystals separated. These were washed with light petroleum to give very pale yellow *crystals* of $[Ru(C{\equiv}CPh)(PMe_3)_2(\eta\text{-}C_5H_5)]$ (6) (389 mg, 97%), m.p. 135 °C (Found: C, 54.9; H, 6.9%; M, 420. $C_{19}H_{28}P_2Ru$ requires C, 54.4; H, 6.7%; M, 420). Infrared (Nujol): ν(C≡C) 2 105 cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 1.51 (apparent t, 'J' 9.03 Hz, 18 H, P*Me*$_3$), 4.71 (s, 5 H, C_5H_5), and 7.18 (m, 5 H, Ph); ^{13}C, δ 23.32 [t, J(CP) 15.3 Hz], 81.02 (s, C_5H_5), 123.0 (s, Ru*C*≡*C*), 123.0 (C_m), 127.9 (C_o), 131.0 (C_p), and 134.2 (C^1).

$[Ru(C{=}CMePh)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$. Addition of OMe_3PF_6 (41 mg, 0.2 mmol) to a solution of $[Ru(C{\equiv}CPh)(PMe_3)_2(\eta\text{-}C_5H_5)]$ (67 mg, 0.16 mmol) in dichloromethane resulted in an immediate colour change to pink. Filtration directly into dry diethyl ether gave a flocculent precipitate, which was filtered off, washed, and dried to give $[Ru(C{=}CMePh)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (7) as a pink solid, m.p. 195 °C (decomp.) (52 mg, 56%) (Found: C, 41.1; H, 4.8. $C_{20}H_{31}F_6P_3Ru$ requires C, 41.45; H, 5.35%). Infrared (Nujol): ν(C=C) 1 650 cm^{-1}. N.m.r. [$(CD_3)_2SO$]: ^1H, δ 1.37 (t, 3 H, Me), 1.62 (apparent t, 'J' 10.7 Hz, 18 H, PMe_3), 5.73 (s, 5 H, C_5H_5), and 7.3 (m, 5 H, Ph); ^{13}C, [$(CD_3)_2CO$] δ 5.35 (m, Me), 19.7—23.6 (m, PMe_3), 91.7 (s, C_5H_5), and 125.2—129.7 (m, Ph).

Crystallography.—*Crystal data.* $C_{14}H_{27}F_6P_3Ru$, M = 503.4, Monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), a = 33.43(1), b = 10.084(7), c = 12.989(7) Å, β = 109.75(4)°, U = 4 121(4) Å^3, D_c = 1.62 g cm^{-3}, Z = 8, $F(000)$ = 2 032, monochromatic Mo-K_α radiation, λ = 0.71069 Å, μ = 10.3 cm^{-1}, 295 K.



	R	R′
(1)	H	H
(2)	H	Me
(3)	H	Ph
(7)	Me	Ph



	L	R
(4)	PMe_3	Me
(5)	PPh_3	Ph
(6)	PMe_3	Ph

Structure determination. A unique data set was measured in the range $2\theta < 50°$ using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ sum mode, yielding 3 652 independent reflections, 2 761 of these with $I > 3\sigma(I)$ being considered ' observed ' and used in the least-squares refinement after solution of the structure and absorption correction. Full-matrix least-squares refinement was used, anisotropic thermal parameters being employed for the non-hydrogen atoms; for the hydrogen atoms, (x,y,z) were set at trigonal/tetrahedral positions and constrained, U_H being held at $1.25\bar{U}_{il}$ (parent C). Final residuals (R,R') were 0.046, 0.059. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[14] Computation used the *X*-RAY 76 program system [15] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Atom numbering is given in Figure 1 for the non-hydrogen atoms. The hydrogen-atom numbering follows that of the parent carbon, suffixed A,B,C where needed for distinguishing purposes. Atomic co-ordinates, the ruthenium environment, and ligand geometry are given in Tables 1—3.

Results and Discussion

As expected, the chloro-complex $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ reacts immediately with acetylene and propyne in the presence of NH_4PF_6 to give the yellow or orange vinylidene complexes $[Ru(C{=}CHR)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (1, R = H; 2, R = Me). We have also confirmed the preparation of a further example with R = Ph (3), which had been described earlier.[6] The first two complexes differ from vinylidene-ruthenium complexes obtained previously in their colour; other examples have been pink to reddish purple. Their characterisation as vinylidene derivatives, rather than as η^2-alkyne complexes, finally rests on the structural study reported below. In the i.r. spectrum, bands assigned to ν(CC) occur at 1 749 and 1 632 cm^{-1} for (1), and at 1 686 and 1 650 cm^{-1} for (2). The ^1H n.m.r. spectrum of (1) contains a triplet at δ 5.35, assigned to the methylene protons; in (2), the corresponding CH resonance probably lies under the C_5H_5 resonance at δ 4.37.

Deprotonation of (2) affords $[Ru(C{\equiv}CMe)(PMe_3)_2(\eta\text{-}C_5H_5)]$ (4) as a bright yellow solid; the complex is more conveniently prepared by tertiary phosphine exchange in $[Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)]$. Complex (4) was readily identified from the characteristic ν(CC) at 2 098 cm^{-1} and from its mass spectrum, which showed a molecular ion centred on m/e 358 (^{102}Ru). Similar tertiary phosphine exchange reactions with $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$ afforded the complexes $[Ru(C{\equiv}CPh)(PMe_3)_n(PPh_3)_{2-n}(\eta\text{-}C_5H_5)]$ [n = 1 (5) or 2 (6)], the former being obtained when 1 mol equivalent of PMe_3 was

Table 1. Non-hydrogen atom co-ordinates for $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$

Atom	*x*	*y*	*z*
Ru	0.104 41(1)	0.271 16(5)	0.468 00(4)
Vinylidene ligand			
C(A)	0.151 8(2)	0.295 4(5)	0.427 7(4)
C(B)	0.185 5(2)	0.312 8(6)	0.399 1(5)
C(C)	0.206 9(2)	0.207 4(8)	0.356 7(7)
Phosphine ligand 1			
P(1)	0.133 38(5)	0.414 1(2)	0.612 5(1)
C(11)	0.189 9(2)	0.441 8(8)	0.664 3(6)
C(12)	0.120 9(3)	0.382 3(10)	0.734 9(7)
C(13)	0.114 3(4)	0.582 1(9)	0.580 0(10)
Phosphine ligand 2			
P(2)	0.135 40(5)	0.086 5(2)	0.565 5(1)
C(21)	0.191 3(2)	0.088 1(8)	0.646 7(6)
C(22)	0.109 4(3)	0.020 2(10)	0.656 2(9)
C(23)	0.133 1(3)	−0.052 8(7)	0.477 4(7)
Cyclopentadienyl			
C(1)	0.049 4(2)	0.386 5(9)	0.356 2(10)
C(2)	0.036 6(2)	0.337 9(14)	0.440 1(8)
C(3)	0.036 1(2)	0.204 0(13)	0.434 9(10)
C(4)	0.048 6(3)	0.167 8(9)	0.347 4(10)
C(5)	0.055 6(2)	0.281 0(13)	0.300 8(6)
C(0)	0.045 2(−)	0.275 4(−)	0.375 9(−)
Anion 1			
P	0.500 0(−)	0.274 1(3)	0.250 0(−)
F(1)	0.487 4(2)	0.162 6(5)	0.319 1(5)
F(2)	0.486 8(3)	0.383 1(6)	0.315 9(7)
F(3)	0.454 5(2)	0.269 9(9)	0.169 3(8)
Anion 2			
P	0.250 0(−)	0.250 0(−)	0.000 0(−)
F(1)	0.231 3(3)	0.237 9(7)	0.094 1(6)
F(2)	0.275 1(4)	0.360 7(13)	0.062 4(10)
F(3)	0.284 8(5)	0.164 0(16)	0.052 6(9)

Table 2. Ruthenium atom environment. The entries in the first column are the ruthenium–ligand distances (Å); the other entries are the angles (°) subtended by the appropriate atoms at the head of the respective rows and columns

	r(Ru–X)	C(A)	P(1)	P(2)
C(1)	2.246(9)	110.1(3)	103.3(3)	153.7(2)
C(2)	2.275(9)	145.2(4)	93.8(3)	124.6(3)
C(3)	2.281(9)	152.6(4)	117.2(3)	95.7(3)
C(4)	2.246(9)	117.0(4)	151.6(3)	97.0(2)
C(5)	2.236(7)	97.7(3)	137.0(3)	128.2(4)
P(1)	2.305(2)	89.0(2)		
P(2)	2.293(2)	89.6(2)	94.08(8)	
C(A)	1.845(7)			
C(0)	1.936(−)	128.2(−)	123.36(−)	122.41(−)

Table 3. Ligand non-hydrogen geometries for $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$

Distances/Å

C(A)–C(B)	1.313(10)	P(1)–C(11)	1.802(7)
C(B)–C(C)	1.485(11)	P(1)–C(12)	1.803(10)
C(1)–C(2)	1.39(2)	P(1)–C(13)	1.809(10)
C(2)–C(3)	1.35(2)	P(2)–C(21)	1.809(7)
C(3)–C(4)	1.39(2)	P(2)–C(22)	1.812(13)
C(4)–C(5)	1.35(2)	P(2)–C(23)	1.797(9)
C(5)–C(1)	1.34(2)		

Angles/°

Ru–C(A)–C(B)	180(2)	C(11)–P(1)–C(12)	103.0(4)
C(A)–C(B)–C(C)	125.1(6)	C(11)–P(1)–C(13)	100.7(4)
C(5)–C(1)–C(2)	107(1)	C(12)–P(1)–C(13)	101.8(6)
C(1)–C(2)–C(3)	108(1)	Ru–P(2)–C(21)	120.0(3)
C(2)–C(3)–C(4)	108(1)	Ru–P(2)–C(22)	115.6(3)
C(3)–C(4)–C(5)	107(1)	Ru–P(2)–C(23)	111.7(3)
C(4)–C(5)–C(1)	110(1)	C(21)–P(2)–C(32)	104.6(4)
Ru–P(1)–C(11)	120.0(3)	C(21)–P(2)–C(23)	101.0(4)
Ru–P(1)–C(12)	116.6(3)	C(22)–P(2)–C(23)	101.5(5)
Ru–P(1)–C(13)	112.2(3)		

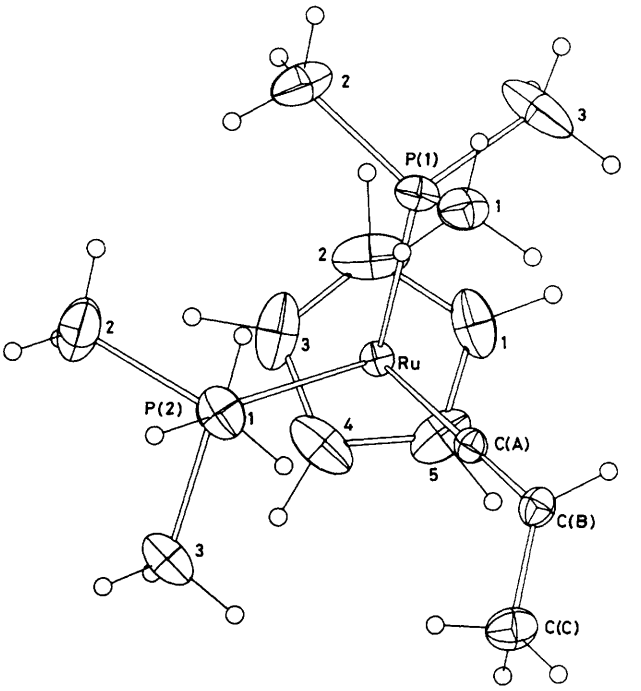


Figure. Molecular projection down the C(0)–Ru bond. Non-hydrogen-atom numbering and 20% thermal ellipsoids are shown

added to the reaction mixture. These complexes were again identified on the basis of their spectroscopic properties, showing ν(CC) bands at 2 070 and 2 105 cm^{-1}, and molecular ion clusters centred on *m/e* 606 and 420, respectively. The ^1H n.m.r. spectrum of (5) contained a doublet at δ 1.19, and a multiplet between δ 7.05 and 7.68, of relative intensities consistent with the presence of one PMe_3 and one PPh_3 ligand, together with the acetylide phenyl group. For (6), the doublet PMe_3 resonance is replaced by the usual multiplet found for complexes containing two PMe_3 ligands in other than a mutually *trans* arrangement; the signal consists of a sharp doublet, with a central broad hump, and is the $X_9X'_9$ part of an $X_9AA'X'_9$ spin system. The separation of the sharp doublets ('*J*' in the Experimental section) is a measure of $|J(AX) + J(A'X)|$.

Alkylation of (6) with trimethyloxonium hexafluorophosphate afforded the disubstituted vinylidene complex $[Ru(C{=}CMePh)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (7). This compound was

Table 4. Comparative ruthenium environments. Comparative geometries about the ruthenium are given for the present complex (2), $[RuCl(PMe_3)_2(C_5H_5)]$ (8) (two molecules), and $[RuCl(PPh_3)_2(C_5H_5)]$ (9); C(0) is the ' atom ' at the centre of the C_5H_5 ring

	(2)	(8)	(9)
Distances/Å			
Ru–C(0)	1.936(–)	1.850(–), 1.849(–)	1.847(4)
Ru–P(1)	2.305(2)	2.273(5), 2.280(6)	2.337(1)
Ru–P(2)	2.293(2)	2.275(6), 2.273(6)	2.335(1)
Ru–X	1.845(7)	2.451(6), 2.440(5)	2.453(2)
Angles/°			
C(0)–Ru–P(1)	123.36(–)	122.7(–), 123.8(–)	121.5(–)
C(0)–Ru–P(2)	122.41(–)	126.3(–), 124.7(–)	121.4(–)
C(0)–Ru–X	128.2(–)	123.3(–), 124.0(–)	122.5(–)
P(1)–Ru–P(2)	94.08(8)	94.7(2), 95.0(2)	103.99(4)
P(1)–Ru–X	89.0(2)	89.7(2), 90.6(2)	89.05(3)
P(2)–Ru–X	89.6(2)	90.1(2), 88.9(2)	90.41(4)

characterised by elemental microanalysis, and had i.r., ^1H, and ^{13}C n.m.r. spectra entirely consistent with this formation.

One reason for studying the PMe_3 complexes was in the expectation that their ^{13}C n.m.r. spectra would allow unequivocal assignment of the resonances of the Ru–C≡C unit. In this area we were only partially successful, the β-carbon being found at δ 127.4 in (1) and at δ 114.7 in (3); in neither case were we able to locate the α-carbon resonance below δ 400. For the methylacetylide complexes (4) and $[Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)]$, the β-carbon resonates at δ 98.7 and 104.3, respectively, while for (5), (6), and $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$, it occurs at δ 123.0, 123.0, and 123.5, indicating that the chemical shift is dependent more on the acetylide substituent than on any possible differences in degree of back bonding from the metal into the acetylide moiety as a result of changes in tertiary phosphine, and hence electron density on the metal. Other features of the ^{13}C n.m.r. spectra are in accord with the structures of these complexes; the C_5H_5 resonance was a singlet in all cases except (5), where a small $J(CP)$ coupling (1.9 Hz) was observed. The chemical shifts of the C_5H_5 carbons fall in the range δ 80—83 for the neutral complexes, and δ 87—92 for cationic derivatives, as found previously.[16]

The structure determination of (2) confirms the stoicheiometry and molecular formula of the complex to be $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$; the asymmetric unit of the structure is a single molecule of the complex. The compound represents a further example of a structure determination in the series $[RuX(PR_3)_2(\eta\text{-}C_5H_5)]$ for which previous studies have been reported for $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (8), and $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (9), and it is of interest to compare the present geometry with those already established for those two complexes, particularly (8). This is done with the aid of Table 4. Initially we note that the two most significant differences in geometry for (8) and (9) are found to be in respect of Ru–P distances, which diminish by *ca.* 0.06 Å on passing from (9) to (8), and the P–Ru–P, C(0), angles the first of which is diminished by *ca.* 9° on passing from (9) to (8). The latter angular change is attributed to steric effects, but it is likely that the change in Ru–P bond length is electronic in origin. It is notable that the angles subtended at the Ru by the non-cyclopentadienyl ligand are very close to 90° and it is not unreasonable to think of the structure as pseudo-octahedral with one face of the octahedron occupied by the C_5H_5 group.

In many respects (2) and (8) are very similar. The most notable change in the angular geometry is the C(0)–Ru–X angle which is enlarged by some 5° in the present complex relative to the halides (8) and (9). Nevertheless, the non-cyclopentadienyl angles remain close to 90° and the octahedral analogy remains useful. The most pronounced changes are found in regard to bond lengths. Relative to (8), Ru–P are increased by *ca.* 0.02 Å, a relatively minor change; most notable is the increase in distance of the cyclopentadienyl ring from the Ru atom, Ru–C(0) increasing from *ca.* 1.85 to 1.93_6 Å; Ru–C(*n*) range between 2.236(7) and 2.281(9) Å indicative of a slight tilt of the Ru–C(0) ' bond ' relative to the C_5 ring plane.

The Ru–C–C system is linear [180(2)°], with bond lengths C(A)–C(B) 1.313(10) Å and C(B)–C(C) 1.485(11) Å; the Ru–C(A) bond is 1.845(7) Å. The latter is closely comparable to common Ru–C (carbonyl) distances and is significantly shorter than found for either Ru–C(sp^2) (2.05 Å in $[Ru\{C(CF_3){=}C(CF_3)C(CF_3){=}CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)]$ [17]) or Ru–C(*sp*) bonds [2.106(9) Å in $[Ru\{C{\equiv}CPh(CuCl)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ [18]], and implies a bond order close to two. Similarly, the short C(A)–C(B) bond is also consistent with the presence of a C–C multiple bond. A formal representation of this system is Ru=C=CHMe, with the methylvinylidene ligand being an efficient π acceptor of metal electron density. The ^{13}C n.m.r. chemical shift of the α-carbon (*ca.* 350 p.p.m.) is also an indication of the extreme electron deficiency of this carbon. As found for $[Mn(C{=}CHPh)(CO)_2(\eta\text{-}C_5H_5)_2]$,[19] $[(C_5H_5)(CO)_2Re(C{=}CPhCPh{=}CH_2)Re(CO)_2(\eta\text{-}C_5H_5)]$,[20] and $[MoCl\{C{=}C(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$,[21] the plane of the vinylidene ligand bisects the molecular symmetry plane. This feature is predicted by a theoretical analysis,[22] and is a result of optimal overlap between the *p* prbital of the α-carbon and the *a''* molecular orbital of the $ML_2(\eta\text{-}C_5H_5)^+$ fragment.

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