Cyclopentadienyl-ruthenium and -osmium Chemistry. Part 11.† Reactions and Structures of [RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)] ‡ and its Trimethylphosphine Analogue

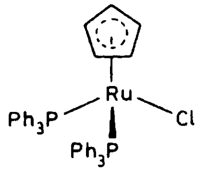
By **Michael I. Bruce** § and **Fook Sin Wong**, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia, 5001
Brian W. Skelton and **Allan H. White**,¶ Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009

The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction at 295 K and refined by least squares to a residual of 0.036 for 7 290 ' observed ' reflections. Crystals are triclinic, space group $P\bar{1}$, with a = 14.493(8), b = 11.315(4), c = 11.745(4) Å, α = 69.99(3), β = 84.67(4), γ = 62.27(3)°, and Z = 2. The ruthenium environment is pseudo-tetrahedral, Ru–Cl 2.453(2), Ru–P 2.337(1), 2.335(1), $\langle$Ru–C(n)$\rangle$ 2.20$_7$ Å. The phenyl ring environments are highly crowded and the nature of the steric interactions between them is examined. The structure of the trimethylphosphine analogue [RuCl(PMe$_3$)$_2$(C$_5$H$_5$)] has also been determined, 1 805 ' observed ' reflections being refined to a residual of 0.059. Crystals are orthorhombic, space group *Pbca*, with a = 29.251(8), b = 14.703(4), c = 14.649(7) Å, and Z = 16. The two ruthenium environments are similar to that of the triphenylphosphine analogue. The Ru–Cl distances are 2.451(6), 2.440(5), and Ru–P 2.273(5)—2.280(6) Å. The value of $\langle$Ru-C(n)$\rangle$ is 2.20 Å. The syntheses and properties of [RuCl(PMe$_3$)$_2$(η-C$_5$H$_5$)] and of the cationic derivatives [RuL(PMe$_3$)$_2$(η-C$_5$H$_5$)]$^+$ (L = MeCN, CO, CNBu^t, or PMe$_3$) are also described.

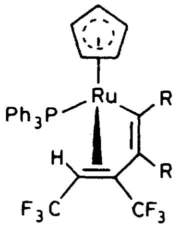
SINCE its discovery in 1969,[1] the complex [RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)], (1), has been the source of much unusual chemistry. The complex undergoes ready substitution of one of the PPh$_3$ ligands, *e.g.* by CO,[2] other tertiary phosphines,[2] phosphites,[3] or isocyanides,[4] while the halide atom is readily displaced by anionic reagents,[2] and also by neutral ligands with the formation of cations [RuL(PPh$_3$)$_2$(η-C$_5$H$_5$)]$^+$.[2,5] Indeed the equilibrium (shown below) lies largely on the right when the chloride is dissolved in methanol.[6]

$$[\mathrm{RuCl(PPh_3)_2(\eta\text{-}C_5H_5)}] + \mathrm{MeOH} \rightleftharpoons [\mathrm{Ru(HOMe)(PPh_3)_2(\eta\text{-}C_5H_5)}]^+ + \mathrm{Cl}^-$$

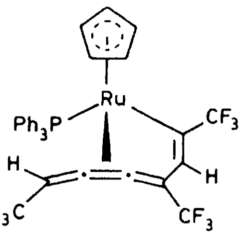
The ready loss of PPh$_3$ is a feature also of the reactions of hydrides and alkyls, particularly with alkynes, when a variety of chelating ligands are formed by oligomerisation of two or three molecules of alkyne, and stabilised by chelation *via* a C=C double bond and an Ru–C σ bond. Examples include the 3—4-η-buta-1,3-dien-1-yl, (2) and (3),[7,8] 4—5-η-penta-1,3,4-trien-1-yl,[9] and 4—5-η-hexa-1,3,4,5-tetraen-1-yl, (4),[9] ligands. This tendency is also manifest in the ready cyclometallation reactions which occur with appropriate tertiary phosphines, phosphites, and azobenzenes.[3] There is also some evidence for activation of the η-C$_5$H$_5$ group towards substitution, as



(1)



(2) R = CF$_3$
(3) R = CO$_2$Me



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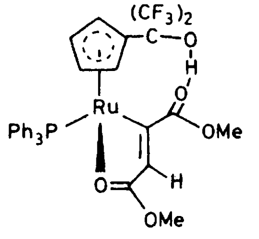

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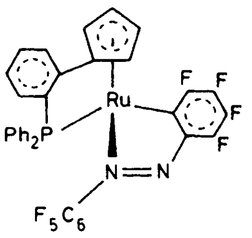

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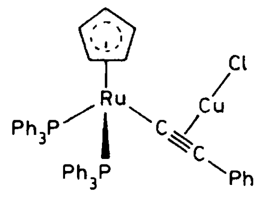

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† Part 10, M. I. Bruce and A. G. Swincer, *Aust. J. Chem.*, 1980, **33**, 1471.

‡ Chloro(η-cyclopentadienyl)bis(triphenylphosphine)ruthenium.

§ Author to whom correspondence regarding synthesis should be addressed.

¶ Author to whom correspondence regarding structure should be addressed.

found in the formation of complexes such as (5) and (6). A further feature resulting from the lability of one PPh_3 ligand is the high relative abundance of the ion $[Ru(PPh_3)(C_5H_5)]^+$ in the mass spectra of $[RuX(PPh_3)_2(\eta\text{-}C_5H_5)]$ complexes; this is often the most abundant metal-containing ion.[10]

Two factors have been suggested which may account for this behaviour: the high electron density on the metal atom resulting from the presence of the tertiary phosphine ligands, and the steric interactions between these bulky PPh_3 groups (cone angle [11] 145°). Although several structural studies of complexes containing the $[Ru(PPh_3)(\eta\text{-}C_5H_5)_7]$ moiety have been reported, only one, the CuCl adduct of $[Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$, (7),[12] contains two PPh_3 ligands. In this example, the geometry about ruthenium is significantly distorted (*e.g.* two Ru–P distances of 2.317, 2.348 Å), presumably by interactions with the highly asymmetric $CuCl(\eta^2\text{-}C{\equiv}CPh)$ unit.[13] The crystal and molecular structures of $[RuCl(PR_3)_2(\eta\text{-}C_5H_5)]$ [R = Me (8) and Ph] are reported in this paper, together with some initial studies of the chemistry of the PMe_3 complex, as part of an attempt to assess the relative importance of the various electronic and steric factors on the chemistry of these ruthenium complexes.

EXPERIMENTAL

General experimental conditions were the same as described in previous parts of this series. Trimethylphosphine was supplied by the Strem Chemical Company, Danvers, Massachussetts; the complex $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ was obtained as previously described.[11]

Preparation of Trimethylphosphine Complexes.—(*a*) $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$. Trimethylphosphine (420 mg, 5.52 mmol) was condensed onto $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1 820 mg, 2.5 mmol) in light petroleum (b.p. 100—120 °C) (10 cm³) in a Carius tube. After sealing, the tube and contents were heated (14 h at 200 °C). The resulting orange solution was cooled to give orange *needles* of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$, (8) (770 mg, 87%), m.p. 130 °C [Found: C, 37.7; H, 6.6; *M* (mass spectrometry), 354. $C_{11}H_{23}ClP_2Ru$ requires C, 37.3; H, 6.5%; *M*, 354]. ^1H N.m.r. ($CDCl_3$): δ 1.52 [t, *J*(HP) 8.8 Hz, 18 H, $P\mathit{Me}_3$], 4.44 (s, 5 H, $C_5\mathit{H}_5$). ^{13}C N.m.r. ($CDCl_3$): δ 21.5 [t, *J*(CP) 14.7, $P\mathit{Me}_3$], 77.3 [t, *J*(CP) 2.2 Hz, C_5H_5].

(*b*) $[RuCl(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)]$. A similar reaction to (*a*) above, between PMe_3 (130 mg, 1.7 mmol) and $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1 230 mg, 1.7 mmol), gave an orange solution, which was separated into two fractions by chromatography on Florisil. The major fraction, eluted by light petroleum–diethyl ether mixtures, afforded orange *crystals* of $[RuCl(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)]$, (9) (690 mg, 75%), m.p. 120 °C [Found: C, 57.8; H, 5.5; *M* (mass spectrometry), 540. $C_{26}H_{29}ClP_2Ru$ requires C, 57.8; H, 5.4%; *M*, 540]. ^1H N.m.r. ($CDCl_3$): δ 1.25 [d, *J*(HP) 7.5 Hz, 9 H, $P\mathit{Me}_3$], 4.30 (s, 5 H, $C_5\mathit{H}_5$), 7.17—7.83 (m, 15 H, Ph). ^{13}C N.m.r. ($CDCl_3$): δ 20.5 [d, *J*(CP) 26.1, $P\mathit{Me}_3$], 79.4 [t, *J*(CP) 2.4 Hz, C_5H_5], 127.9—139.9 (m, Ph). A second fraction, eluted with acetone, was shown to contain $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (n.m.r.), but decomposed rapidly to a presently unidentified dark green material.

(*c*) $[Ru(NCMe)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$. A mixture of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (120 mg, 0.33 mmol) and $[NH_4][PF_6]$ (60 mg, 0.35 mmol) was dissolved in acetonitrile, and warmed to 45 °C (1 h) to give a yellow solution. Evaporation, extraction of the residue with $CHCl_3$, and addition of light petroleum to the filtered solution gave yellow *crystals* of $[Ru(NCMe)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$, (10) (150 mg, 88%) (Found: C, 31.2; H, 4.4; N, 2.5. $C_{13}H_{26}F_6NP_3Ru$ requires C, 31.0; H, 5.2, N, 2.8%), ν(CN) (Nujol) 2 276 cm⁻¹. ^1H N.m.r. ($CDCl_3$): δ 1.52 [t, 18 H, $P\mathit{Me}_3$, *J*(HP) 9.0], 2.38 [t, 3 H, *Me*CN, *J*(HP) 1.6 Hz], 4.64 (s, 5 H, $C_5\mathit{H}_5$). ^{13}C N.m.r. ($CDCl_3$): δ 10.7 (s, *Me*CN), 21.4 [t, $P\mathit{Me}_3$, *J*(CP) 15.9], 79.2 [t, C_5H_5, *J*(CP) 1.1 Hz].

(*d*) $[Ru(CO)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$. Carbon monoxide was bubbled into a solution of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (60 mg, 0.17 mmol) and $[NH_4][PF_6]$ (30 mg, 0.2 mmol) in MeOH (20 cm³) at 60 °C for 4 h. The resulting pale yellow solution was evaporated and the residue was extracted with CH_2Cl_2 (4 cm³). The solution was filtered into Et_2O (100 cm³) to give a white *precipitate* of $[Ru(CO)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$, (11) (40 mg, 52%), decomp. >100 °C (Found: C, 29.1; H, 4.7. $C_{12}H_{23}F_6OP_3Ru$ requires C, 29.3; H, 4.7%), ν(CO) (Nujol) at 1 961vs cm⁻¹. ^1H N.m.r. [$(CD_3)_2CO$]: δ 1.77 [t, 18 H, $P\mathit{Me}_3$, *J*(HP) 10.0 Hz], 5.60 (s, 5 H, $C_5\mathit{H}_5$). ^{13}C N.m.r. [$(CD_3)_2SO$]: δ 21.5 [t, *J*(CP) 19.5 Hz, $P\mathit{Me}_3$], 87.7 (s, C_5H_5). The carbonyl resonance was not detected.

(*e*) $[Ru(CNBu^t)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$. Addition of Bu^tNC (170 mg, 0.2 mmol) to a mixture of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (60 mg, 0.17 mmol) and $[NH_4][PF_6]$ (0.03 g, 0.2 mmol) in MeOH (10 cm³) gave a pale yellow solution. After 30 min at room temperature, evaporation of the solution, extraction of the residue with CH_2Cl_2 (4 cm³), and filtration into Et_2O (100 cm³) gave a white *precipitate* of $[Ru(CNBu^t)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$, (12) (60 mg, 66%), decomp. >130 °C (Found: C, 35.1; H, 5.8; N, 2.6. $C_{16}H_{32}F_6NP_3Ru$ requires C, 35.2; H, 5.9; N, 2.6%). Infrared (Nujol): ν(CN) 2 118m, ν(PF) 843vs(br) cm⁻¹. ^1H N.m.r. [$(CD_3)_2CO$]: δ 1.57 (s, 9 H, Bu^tNC), 1.67 [t, 18 H, $P\mathit{Me}_3$, *J*(HP) 10.0 Hz], 5.20 (s, 5 H, $C_5\mathit{H}_5$). ^{13}C N.m.r. [$(CD_3)_2SO$]: δ 21.8 [t, *J*(CP) 17.1 Hz, $P\mathit{Me}_3$], 30.2 (s, $C\mathit{Me}_3$), 83.9 (s, C_5H_5), 153.4 (s, Ru*C*?). The *C*Me₃ carbon was not detected.

(*f*) $[Ru(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$. Trimethylphosphine (60 mg, 0.8 mmol) was condensed onto $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (120 mg, 0.33 mmol), $[NH_4][PF_6]$ (60 mg, 0.35 mmol), and MeCN (5 cm³) in a Carius tube. The tube was sealed, and the whole heated at 60 °C (2 h) and 110 °C (1 h) to give a colourless solution. This solution was filtered and evaporated, and the residue extracted with CH_2Cl_2 (4 cm³). Filtration of the extract into Et_2O (200 cm³) afforded a white *precipitate* of $[Ru(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$, (13) (140 mg, 78%), decomp. >100 °C (Found: C, 30.6; H, 5.5. $C_{14}H_{32}F_6P_4Ru$ requires C, 31.2; H, 6.0%). Infrared (Nujol): ν(PF) 836vs cm⁻¹. ^1H N.m.r. (CD_2Cl_2): δ 1.50 [t, *J*(HP) 9.0 Hz, 27 H, $P\mathit{Me}_3$], 4.82 (s, 5 H, $C_5\mathit{H}_5$). ^{13}C N.m.r. [$(CD_3)_2SO$]: δ 23.1 [q, *J*(CP) 9.8 Hz, $P\mathit{Me}_3$], 83.7 (s, C_5H_5).

Crystallography.—$[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$. Crystals suitable for the *X*-ray study were formed by slow cooling of a filtered methanol solution, obtained by the literature method.[11]

$[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$. The complex, prepared as above, was recrystallised from light petroleum (b.p. 100—120 °C).

Crystal data, (1). $C_{41}H_{35}ClP_2Ru$, $M = 726.2$, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 14.493(8)$, $b = 11.315(4)$, $c = 11.745(4)$ Å, $\alpha = 69.99(3)$, $\beta = 84.67(4)$, $\gamma = 67.27(3)°$, $U = 1\,668(1)$ Å³, $D_m = 1.44(1)$, $Z = 2$, $D_c = 1.45$ g cm⁻³,

TABLE 1

Non-hydrogen atomic fractional cell co-ordinates for complexes (1) and (2)

(*a*) Complex (1)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ru(1)	0.264 13(2)	0.143 30(2)	0.131 54(2)
P(1)	0.284 53(5)	−0.063 62(7)	0.283 57(6)
P(2)	0.207 29(5)	0.301 52(7)	0.233 29(6)
Cl(1)	0.438 25(5)	0.104 04(8)	0.173 21(7)
C(1)	0.245 0(3)	0.275 5(3)	−0.060 3(3)
C(2)	0.150 0(2)	0.285 6(3)	−0.013 1(3)
C(3)	0.143 2(3)	0.156 4(4)	0.022 8(3)
C(4)	0.236 2(3)	0.065 1(3)	−0.005 8(3)
C(5)	0.298 3(3)	0.138 3(4)	−0.055 4(3)
C(111)	0.382 7(2)	−0.212 3(3)	0.254 9(3)
C(112)	0.438 6(2)	−0.196 2(3)	0.152 0(3)
C(113)	0.514 5(2)	−0.307 0(3)	0.132 2(3)
C(114)	0.537 0(3)	−0.435 1(3)	0.217 0(3)
C(115)	0.482 9(3)	−0.453 3(3)	0.320 3(3)
C(116)	0.405 9(3)	−0.342 8(3)	0.338 8(3)
C(121)	0.320 0(2)	−0.109 1(3)	0.443 8(2)
C(122)	0.407 0(2)	−0.096 6(3)	0.468 5(3)
C(123)	0.440 9(3)	−0.133 7(3)	0.587 4(3)
C(124)	0.387 5(3)	−0.183 4(4)	0.682 8(3)
C(125)	0.301 8(3)	−0.198 6(4)	0.659 5(3)
C(126)	0.267 9(2)	−0.162 4(3)	0.541 1(3)
C(131)	0.169 2(2)	−0.097 6(3)	0.294 1(3)
C(132)	0.085 8(2)	−0.018 1(4)	0.339 1(3)
C(133)	−0.004 8(3)	−0.032 4(5)	0.344 6(4)
C(134)	−0.013 7(4)	−0.126 1(6)	0.302 7(5)
C(135)	0.065 6(4)	−0.203 7(6)	0.254 7(6)
C(136)	0.158 6(3)	−0.191 6(5)	0.251 0(4)
C(211)	0.221 9(2)	0.458 4(3)	0.131 7(3)
C(212)	0.318 9(3)	0.455 2(3)	0.105 9(3)
C(213)	0.333 7(3)	0.572 1(4)	0.031 9(3)
C(214)	0.252 8(4)	0.690 4(4)	−0.018 8(3)
C(215)	0.158 0(3)	0.693 3(4)	0.001 9(4)
C(216)	0.142 1(3)	0.578 1(4)	0.077 5(3)
C(221)	0.258 4(2)	0.281 5(3)	0.380 0(3)
C(222)	0.308 2(3)	0.358 5(4)	0.395 0(3)
C(223)	0.339 7(3)	0.341 5(5)	0.509 8(3)
C(224)	0.323 3(3)	0.246 6(4)	0.611 1(3)
C(225)	0.271 1(3)	0.172 7(4)	0.597 7(3)
C(226)	0.238 8(3)	0.189 7(3)	0.483 8(3)
C(231)	0.072 9(2)	0.364 7(3)	0.267 0(3)
C(232)	0.036 9(3)	0.453 2(4)	0.332 9(3)
C(233)	−0.063 0(3)	0.497 4(4)	0.361 9(4)
C(234)	−0.127 6(3)	0.452 8(4)	0.325 7(4)
C(235)	−0.093 1(3)	0.366 0(4)	0.260 5(4)
C(236)	0.006 5(2)	0.322 7(4)	0.230 4(3)

(*b*) Complex (2)

	Molecule 1			Molecule 2		
	x/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*
Ru	0.210 05(5)	0.116 1(1)	0.119 4(1)	0.459 72(5)	0.323 5(1)	0.393 3(1)
Cl	0.200 8(2)	0.271 8(4)	0.062 4(4)	0.441 5(2)	0.338 0(4)	0.555 2(3)
Cyclopentadienyl ligand						
C(1)	0.145 3(6)	0.036 2(13)	0.122 4(17)	0.400 7(7)	0.373 6(17)	0.310 3(14)
C(2)	0.182 1(8)	−0.020 6(14)	0.145 8(17)	0.435 0(8)	0.340 3(16)	0.254 3(12)
C(3)	0.213 4(7)	−0.021 4(13)	0.070 2(18)	0.476 1(8)	0.394 0(17)	0.264 6(14)
C(4)	0.192 2(7)	0.029 0(15)	−0.000 4(17)	0.464 3(7)	0.459 3(15)	0.332 8(14)
C(5)	0.154 6(8)	0.067 3(15)	0.033 6(17)	0.419 4(8)	0.445 8(15)	0.359 6(12)
C(0)	0.177 5(—)	0.018 1(—)	0.074 3(—)	0.439 1(—)	0.402 6(—)	0.304 3(—)
Phosphine ligand 1						
P	0.287 1(2)	0.129 2(3)	0.103 6(4)	0.535 0(2)	0.302 0(4)	0.427 4(4)
C(1)	0.306 7(7)	0.117 3(20)	−0.010 0(15)	0.570 4(9)	0.403 0(17)	0.422 9(21)
C(2)	0.316 0(7)	0.231 8(15)	0.137 7(16)	0.551 7(9)	0.258 4(26)	0.538 7(18)
C(3)	0.323 2(7)	0.042 2(16)	0.159 1(17)	0.566 6(9)	0.229 4(24)	0.356 8(24)
Phosphine ligand 2						
P	0.208 9(2)	0.168 6(4)	0.265 5(4)	0.441 0(2)	0.173 7(4)	0.401 6(4)
C(1)	0.158 3(9)	0.141 9(24)	0.326 9(19)	0.380 5(8)	0.152 7(17)	0.398 4(24)
C(2)	0.213 1(12)	0.287 3(17)	0.290 6(16)	0.454 4(11)	0.105 3(19)	0.496 6(19)
C(3)	0.248 8(11)	0.123 9(22)	0.347 4(17)	0.459 9(12)	0.098 8(16)	0.312 5(18)

$F(000) = 744$. Monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 6.3$ cm^{-1}. Specimen: prism, 0.37 × 0.36 × 0.15 mm.

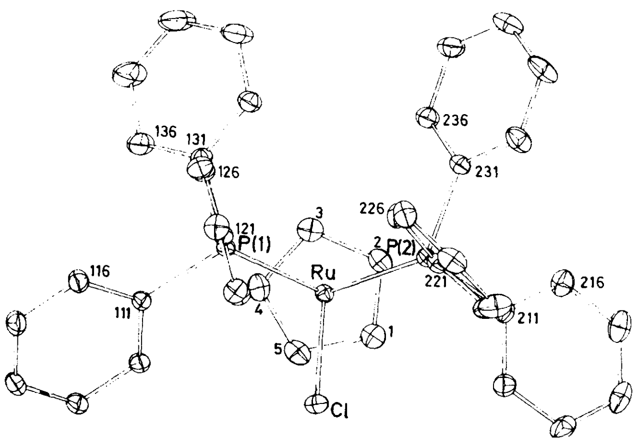

FIGURE 1 A single molecule of complex (1) in projection down Ru–' C(0) ' showing atom labelling; carbon atoms are designated by number only

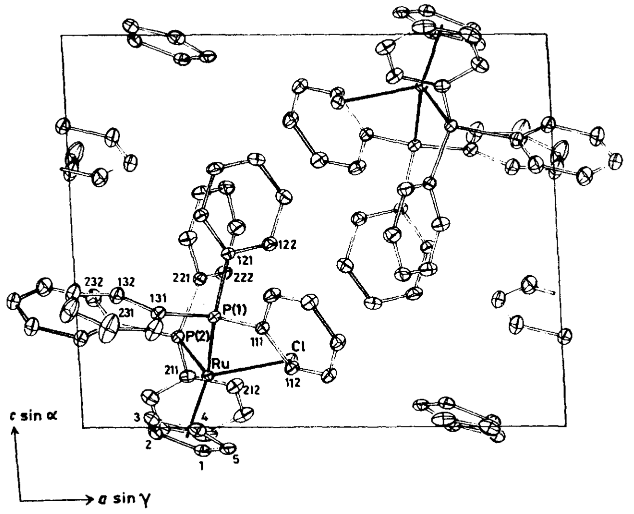

FIGURE 2 Unit-cell contents of complex (1) projected down *b*, showing non-hydrogen atoms with 20% thermal ellipsoids. Phenyl ring atom numbering is given

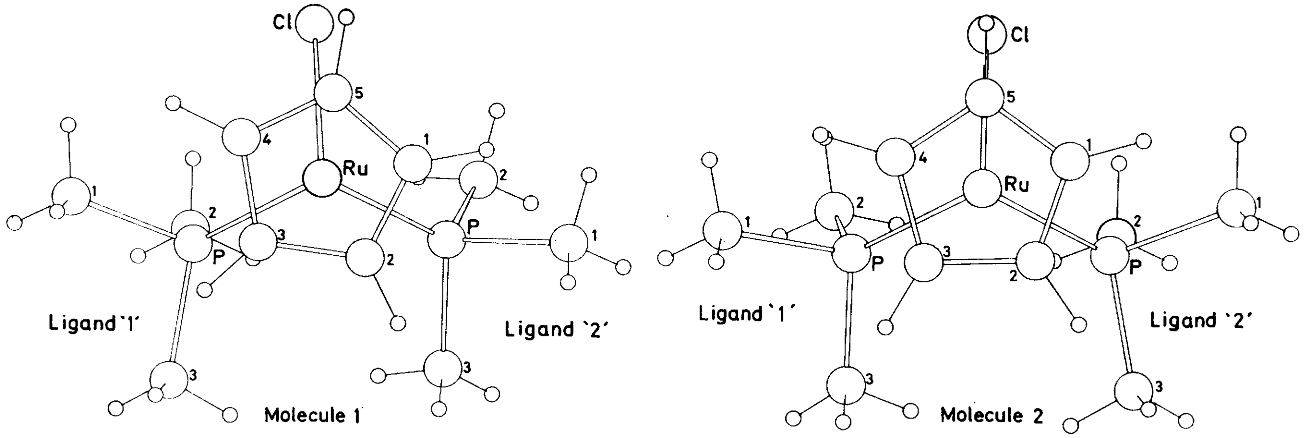

FIGURE 3 Projection of molecules 1 and 2 of complex (8) down the Ru–' C(0) ' bonds

(8). $C_{11}H_{23}ClP_2Ru$, $M = 355.8$, Orthorhombic, space group *Pbca* (D_{2h}^{15}, no. 61), $a = 29.251(8)$, $b = 14.703(4)$, $c = 14.649(7)$ Å, $U = 6\,300(4)$ Å^3, $Z = 16$, $D_c = 1.36$ g cm^{-3}, $F(000) = 2\,880$, $\mu_{Mo} = 11.4$ cm^{-1}. Specimen: needle, 0.05 × 0.45 × 0.10 mm.

Structure determinations. Unique data sets were measured within a $2\theta_{max.}$ limit of 50° using a Syntex $P2_1$ four-circle diffractometer in conventional θ—2θ scan mode. A total of 9 774 [for (1)], 5 545 [for (8)] independent reflections was measured; of these 7 290 [for (1)], 1 805 [for (8)] with $I > 3\sigma(I)$ were considered ' observed ' and used in the solution and refinement after absorption correction in each case. Refinement was by 9 × 9 block-diagonal least squares, non-hydrogen atom thermal parameters being set anisotropic. Hydrogen atoms were included as invariants at positions found from difference maps and ' improved ' to tetrahedral and trigonal estimates with U_H set at 1.5 $\bar{U}_{ii}$ (parent C) (methyl), 1.25 $\bar{U}_{ii}$ (parent

TABLE 2

Non-hydrogen molecular geometry for complexes (1) and (8)

(*a*) Complex (1)

(*i*) Distances (Å)

Ru–C(1)	2.210(3)	[Ru–C(0)]	[1.847(4)]
Ru–C(2)	2.192(3)	Ru–Cl	2.453(2)
Ru–C(3)	2.194(4)	Ru–P(1)	2.337(1)
Ru–C(4)	2.220(3)	Ru–P(2)	2.335(1)
Ru–C(5)	2.220(3)		

(*ii*) Angles (°) (selected)

(a) About the ruthenium

C(0)–Ru–Cl	122.5(1)	C(2)–Ru–P(2)	88.6(1)
C(0)–Ru–P(1)	121.5(1)	C(3)–Ru–Cl	153.8(1)
C(0)–Ru–P(2)	121.4(1)	C(3)–Ru–P(2)	111.7(1)
Cl–Ru–P(1)	89.05(3)	C(3)–Ru–P(1)	98.5(1)
Cl–Ru–P(2)	90.41(4)	C(4)–Ru–P(1)	90.2(1)
P(1)–Ru–P(2)	103.99(4)	C(4)–Ru–P(2)	149.1(1)
C(1)–Ru–Cl	99.6(1)	C(4)–Ru–Cl	117.5(1)
C(1)–Ru–P(1)	152.4(1)	C(5)–Ru–P(1)	116.9(1)
C(1)–Ru–P(2)	102.1(1)	C(5)–Ru–P(2)	139.1(1)
C(2)–Ru–Cl	135.2(1)	C(5)–Ru–Cl	91.1(1)
C(2)–Ru–P(1)	134.4(1)		

(b) About the phosphorus (ligands 1, 2)

Ru–P–C(11)	113.9(1), 107.1(1)
Ru–P–C(21)	125.7(1), 126.1(1)
Ru–P–C(31)	110.2(1), 118.6(1)
C(11)–P–C(21)	97.5(1), 102.2(2)
C(11)–P–C(31)	104.6(2), 102.2(1)
C(21)–P–C(31)	102.4(1), 97.4(1)

(*b*) Complex (8) *

(*i*) Distances (Å)

Ru–Cl	2.451(6), 2.440(5)	P(1)–C(12)	1.80(2), 1.82(3)
Ru–P(1)	2.273(5), 2.280(6)	P(1)–C(13)	1.85(2), 1.75(3)
Ru–P(2)	2.275(6), 2.273(6)	P(2)–C(21)	1.78(3), 1.80(3)
Ru–C(1)	2.17(2), 2.24(2)	P(2)–C(22)	1.79(3), 1.76(3)
Ru–C(2)	2.23(2), 2.17(2)	P(2)–C(23)	1.79(3), 1.79(3)
Ru–C(3)	2.15(2), 2.21(2)	C(1)–C(2)	1.41(3), 1.39(3)
Ru–C(4)	2.20(2), 2.19(2)	C(2)–C(3)	1.44(3), 1.45(3)
Ru–C(5)	2.23(2), 2.21(2)	C(3)–C(4)	1.42(3), 1.43(3)
Ru–C(0)	1.850(—), 1.849(—)	C(4)–C(5)	1.33(3), 1.39(3)
P(1)–C(11)	1.77(2), 1.81(3)	C(5)–C(1)	1.41(3), 1.40(3)

TABLE 2 (*continued*)

(*ii*) Angles (°) (selected)

C(0)–Ru–Cl	123.3(1), 124.0(2)
C(0)–Ru–P(1)	122.7(2), 123.8(2)
C(0)–Ru–P(2)	126.3(2), 124.7(2)
Cl–Ru–P(1)	89.7(2), 90.6(2)
Cl–Ru–P(2)	90.1(2), 88.9(2)
Cl–Ru–C(1)	113.9(5), 109.3(6)
Cl–Ru–C(2)	150.5(6), 145.9(6)
Cl–Ru–C(3)	140.3(7), 146.9(6)
Cl–Ru–C(4)	104.0(6), 109.1(6)
Cl–Ru–C(5)	91.7(6), 91.7(5)
P(1)–Ru–P(2)	94.7(2), 95.0(2)
P(1)–Ru–C(1)	152.7(5), 155.5(6)
P(1)–Ru–C(2)	117.6(6), 122.8(6)
P(1)–Ru–C(3)	90.0(5), 92.4(6)
P(1)–Ru–C(4)	101.5(5), 99.0(6)
P(1)–Ru–C(5)	135.1(7), 132.7(6)
P(2)–Ru–C(1)	98.5(6), 99.4(6)
P(2)–Ru–C(2)	98.0(7), 94.6(6)
P(2)–Ru–C(3)	129.4(7), 123.6(6)
P(2)–Ru–C(4)	158.4(6), 157.0(6)
P(2)–Ru–C(5)	130.2(7), 132.3(6)
Ru–P(1)–C(11)	114.1(8), 115.5(9)
Ru–P(1)–C(12)	120.6(7), 120.2(8)
Ru–P(1)–C(13)	117.6(7), 117.7(10)
Ru–P(2)–C(21)	114.4(10), 113.7(9)
Ru–P(2)–C(22)	121.5(8), 122.8(10)
Ru–P(2)–C(23)	119.6(10), 118.8(9)
C(11)–P(1)–C(12)	101.1(11), 99.7(14)
C(12)–P(1)–C(13)	100.9(11), 100.0(15)
C(13)–P(1)–C(11)	99.2(12), 100.2(14)
C(21)–P(2)–C(22)	99.7(15), 98.1(15)
C(22)–P(2)–C(23)	100.1(14), 100.3(14)
C(23)–P(2)–C(21)	97.1(13), 99.0(13)
C(5)–C(1)–C(2)	106(2), 107(2)
C(1)–C(2)–C(3)	108(2), 110(2)
C(2)–C(3)–C(4)	106(2), 104(2)
C(3)–C(4)–C(5)	108(2), 109(2)
C(4)–C(5)–C(1)	112(2), 109(2)

* The two values in each entry are for molecules 1 and 2, respectively.

C) (other). Residuals (*R*, *R′*) were 0.036, 0.050 [for (1)]; 0.059, 0.067 [for (8)], reflection weights being $[\sigma^2(F_o) + 0.000\,5\,(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (*f′*, *f″*).[14-16] Computation was carried out using the '*X*-RAY '76' program system [17] implemented by S. R. Hall on a Perkin-Elmer 8/32 computer. Material deposited in Supplementary Publication No. SUP 23023 (59 pp.) * comprises hydrogen-atom parameters, thermal parameters, structure-factor amplitudes, and least-squares planes.

TABLE 3

Aromatic ring non-hydrogen atom geometries for (1)

Ring	11	12	13	21	22	23	cp *
(*a*) Distances (Å)							
P–C(1)	1.848(3)	1.839(3)	1.838(4)	1.847(3)	1.846(4)	1.853(3)	
C(1)–C(2)	1.391(4)	1.388(5)	1.384(5)	1.399(5)	1.388(7)	1.388(6)	1.414(5)
C(2)–C(3)	1.385(4)	1.391(5)	1.378(6)	1.397(6)	1.391(6)	1.388(5)	1.417(6)
C(3)–C(4)	1.381(4)	1.384(5)	1.363(10)	1.376(5)	1.377(6)	1.378(8)	1.441(5)
C(4)–C(5)	1.380(5)	1.381(6)	1.360(8)	1.363(7)	1.377(7)	1.366(7)	1.410(6)
C(5)–C(6)	1.385(5)	1.387(5)	1.401(8)	1.394(6)	1.385(6)	1.388(5)	1.425(5)
C(6)–C(1)	1.395(4)	1.400(4)	1.386(7)	1.383(4)	1.394(4)	1.382(6)	
(*b*) Angles (°)							
P–C(1)–C(2)	120.8(2)	117.4(2)	118.4(3)	118.3(2)	124.4(3)	120.5(3)	
P–C(1)–C(6)	120.9(2)	123.9(3)	123.7(3)	123.6(3)	117.4(3)	121.3(3)	
C(2)–C(1)–C(6)	118.2(3)	118.6(3)	117.8(4)	118.1(3)	117.2(3)	118.2(3)	107.6(4)
C(1)–C(2)–C(3)	121.0(3)	120.9(3)	122.1(4)	120.4(3)	120.8(4)	120.8(5)	109.2(3)
C(2)–C(3)–C(4)	119.9(3)	119.9(4)	119.3(4)	120.0(4)	120.7(5)	120.0(5)	106.8(3)
C(3)–C(4)–C(5)	120.1(3)	119.8(4)	120.4(6)	120.1(4)	119.0(4)	119.7(4)	108.2(3)
C(4)–C(5)–C(6)	119.9(3)	120.5(3)	120.5(7)	120.4(3)	120.6(3)	120.4(5)	108.3(3)
C(5)–C(6)–C(1)	120.9(3)	120.3(4)	119.8(5)	120.9(4)	121.0(4)	120.9(4)	

* cp = Cyclopentadienyl.

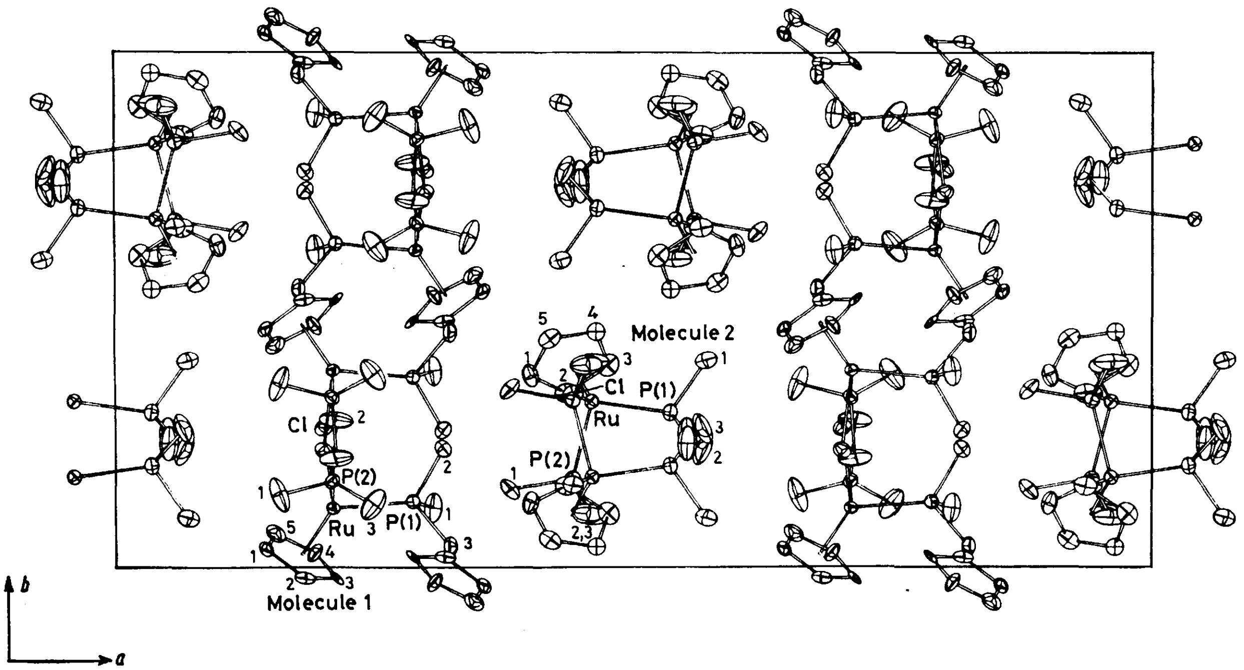

FIGURE 4 Unit-cell contents of complex (2) projected down *c*

Non-hydrogen atom numbering for each case is shown in the molecular projections. Hydrogen-atom numbering follows that of the parent carbon, suffixed A, B, C where distinction is necessary. A dummy central atom is defined [C(0)] for reference purposes at the centre of gravity of the cyclopentadienyl ring. Results are given in the Tables and depicted in the Figures.

RESULTS AND DISCUSSION

Trimethylphosphine Complexes.—Simple substitution of PPh_3 in $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ by PMe_3 occurs on heating the reactants at *ca*. 120 °C in light petroleum. On cooling, $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$, (8), crystallised. If a deficiency of PMe_3 was used, the mixed phosphine complex $[RuCl(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)]$, (9), was obtained. Both compounds were initially characterised on the basis of elemental analysis and spectroscopic properties.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 4

Intramolecular non-bonded hydrogen-adjacent ring interactions (see text) for (1)

Atoms	Distance (Å)	Atoms	Distance (Å)
C(2) · · · H(236)	2.7_5	H(126) · · · C(132)	2.5_9
H(2) · · · H(236)	2.4_6	H(222) · · · C(211)	2.6_4
C(3) · · · H(236)	2.6_7	H(222) · · · C(212)	2.4_8
H(3) · · · H(236)	2.2_9	H(222) · · · H(212)	2.4_4
C(4) · · · H(112)	2.7_4	H(116) · · · C(121)	2.7_6
H(4) · · · C(112)	2.8_9	H(116) · · · C(126)	2.9_5
H(4) · · · H(112)	2.4_6	H(232) · · · C(221)	2.6_5
C(5) · · · H(112)	2.7_3	C(232) · · · H(216)	2.9_1
H(5) · · · H(112)	2.4_5	H(132) · · · C(236)	2.7_9
H(226) · · · C(121)	2.7_9	C(132) · · · H(236)	2.9_2
H(226) · · · C(126)	2.9_8	H(136) · · · C(111)	2.7_0
H(122) · · · Cl	2.7_0	H(136) · · · C(116)	2.8_6
H(126) · · · C(131)	2.6_0	H(212) · · · Cl	2.6_9

Ready formation of cationic complexes $[RuL(PMe_3)_2(\eta-C_5H_5)][PF_6]$ [L = MeCN (10), CO (11), $CNBu^t$ (12), or PMe_3 (13)] occurs on heating (8) with the ligand L, in the presence of $[NH_4][PF_6]$. These compounds were obtained as white to pale yellow solids, stable in air, and their properties parallel those of the PPh_3 analogues described earlier.

Trimethylphosphine is a better σ donor, but poorer π acceptor than PPh_3. The effect of replacing PPh_3 by PMe_3 is to increase the electron density on the metal atom, and this is reflected in some of the spectroscopic properties. Thus, in their i.r. spectra, the ν(CO) absorptions of (11) and its PPh_3 analogue are found at 1 961 and 1 984 cm^{-1}, respectively. Similarly, the ν(CN) band shifts from 2 118 cm^{-1} in (12) to 2 136 cm^{-1} in the PPh_3 complex. Both PMe_3 complexes show a low-energy shift indicating increased back bonding to the carbonyl or isocyanide ligand as a result of the presence of the more basic PMe_3 ligand.

The ^1H n.m.r. spectra of the PMe_3 complexes contain the characteristic strong doublet, and associated central fine structure, expected for the XX′ part of an $X_9AA'X'_9$ spin system. The ^{13}C n.m.r. spectra contained triplets at *ca.* 21 p.p.m. for the PMe_3 carbons, and around 77—84 p.p.m. for the C_5H_5 carbons, except for (13), when the C_5H_5 resonance was a quartet. Coupling of the ^{31}P nuclei to both the protons and carbons of the C_5H_5 resonances is much stronger for the PMe_3 complexes; in the PPh_3 derivatives, such coupling is either not detected, or at the limits of resolution of our instrument.

The effect of increased electron density at the ruthenium atom is nicely illustrated by the cyclopentadienyl chemical shifts of typical complexes $[RuX(PR_3)_2(\eta-C_5H_5)]^n$ as shown below.

X	Cl		C_2Ph		CO		$CNBu^t$	
n	0		0		+1		+1	
R	Me	Ph	Me	Ph	Me	Ph	Me	Ph
$\delta(C_5\mathit{H}_5)$	4.44	4.10	4.71	4.32	5.60	4.97	5.20	4.68
$\delta(\mathit{C}_5H_5)$	77.3	81.5	81.0	85.4	87.7	91.0	83.9	87.8

These data provide further evidence for a change in electron density at the metal, the proton chemical shifts being consistent with the expected increase. Such a simple correlation is not possible with the carbon chemical shifts, although all examples studied so far have shown a shift of between 3 and 4 p.p.m. on replacement of PPh_3 by PMe_3.

The Structure of $[RuCl(PPh_3)_2(\eta-C_5H_5)]$, (1).—*Co-ordination about ruthenium.* The molecular structure and atom numbering are shown in Figure 1; the asymmetric unit of the structure comprises one molecule of the complex. The ruthenium atom is bonded to one chlorine, two triphenylphosphine ligands, and an η-cyclopentadienyl group. The geometry about the metal atom may be considered as distorted octahedral, if the $\eta-C_5H_5$ is assumed to occupy three co-ordination positions, or distorted tetrahedral, if the perpendicular axis of the C_5 ring is taken to be one position. We prefer the latter description, when the molecule may be considered to be a member of the $M(C_5H_5)L_3$ series, distorted by the differing steric requirements of the ligands.

The η-cyclopentadienyl ring. The average Ru–C distance of 2.207 Å is similar to those found for other structures containing ruthenium in association with phosphine and cyclopentadienyl ligands and falls within the range of the individual Ru–C distances (2.18—2.26 Å). In $[Ru(\eta-C_5H_5)(\eta-PhBPh_3)]$, a zwitterionic complex in which the metal atom has some positive charge, which would be expected to result in a shorter ring–metal distance, the average Ru–C distance is 2.170(6) Å. In ruthenocene itself, the Ru–C distance is 2.21(1) Å; the related compounds 1,1′-diacetylruthenocene (2.18 Å) [18] and $[RuI(\eta-C_5H_5)_2]I_3$ [2.197(12) Å] [19] also have similar parameters. In $[Ru\{C_2(CO_2Me)_2H\}(PPh_3)\{\eta-C_5H_4C(CF_3)_2OH\}]$, (5), the plane of the ring is tilted by 3.2° as a result of hydrogen bonding, leading to some short Ru–C bonds. In the present compound, some variation is found in Ru–C(*n*) bond length (Table 2), the range being 2.192(3)—2.220(3) Å. A least-squares plane was calculated through the five carbon atoms of the cyclopentadienyl ring (σ 0.006 Å) with the ruthenium deviation being 1.846 Å; the Ru–C(0) line makes an angle of 1.0° with the normal to this plane.

The Ru–Cl *bond.* The Ru–Cl distance of 2.453(2) Å is longer than found in $[RuCl_2(PPh_3)_3]$[2.387(7) Å],[20] $[RuCl_2(PMePh_2)(\eta\text{-arene})]$ (2.409—2.415 Å),[21] and $[RuHCl(PPh_3)_3]$ [2.421(4) *trans* to H],[22] but similar to those found in $[RuCl_2(dmppe)_2]$ (2.438 Å) (dmppe = $PhMePCH_2CH_2PMePh$),[23] and in $[Ru_2Cl_3(PEt_2Ph)_6][RuCl_3(PEt_2Ph)_3]$ [2.481(7) (cation), 2.444(7), 2.513(7) (*trans* to P) (anion)],[24] and is consistent with the tendency to lose chloride ion.

The Ru–P *bond.* The calculated value of the Ru–P single bond is 2.43 Å, and tabulated values for several tertiary phosphine complexes range over 2.206—2.426 Å.[25] The present values of 2.337(1), 2.335(1), 2.335(1) Å lie in the middle of this range, and indicate a considerable degree of d_π–d_π multiple bonding. By comparison with related complexes, there appears to be no pronounced lengthening of either bond or both bonds which might be ascribed to steric interaction. Angles about the phosphorus are likewise similar to those observed in ruthenium–triphenylphosphine derivatives.

Geometry about the ruthenium. In the majority of related ruthenium–phosphine derivatives studied there is only one PPh_3 ligand, and the constraints of associated chelating ligands have to a large part minimised other interactions; P–Ru–X angles of *ca.* 90° are found. In (7), P–Ru–P is 97.1(1)°, and the two P–Ru–C angles are 86.1 and 96.9(3)°. In the present case, P–Ru–Cl angles of 89.1, 90.4° are found, with P–Ru–P of 103.9°. It is evident from Figure 2 that the rings 22 and 12 have intermeshed to reduce interactions of the aromatic C–H atoms, both with each other, and with the Cl atom.

Intramolecular inter-ring interactions. Likely interactions between the ligands are given in Table 4; to allow for possible error in estimating hydrogen-atom positions, this table includes contacts at the sum of the van der Waals radii *plus* 0.1 Å, the van der Waals radii assumed being H, 1.2; C(aromatic ring), 1.7; P, 1.9; Cl, 1.8 Å.[26]

(*i*) *The cyclopentadienyl ring.* The projection of Figure 1 shows that the potential pseudo-*m* symmetry of the molecular core [*m* passing through C, Ru, C(0), C(3), midpoint of C(1,5)] is lost, by virtue of the cyclopentadienyl ring having rotated about the Ru–C(0) ' bond '. The reason for this appears to lie in the presence of a torque exerted on the ring and about this bond by virtue of its interaction with H(112) and H(236) because of the disposition of the phenyl rings. In consequence P(2) · · · C(2), 3.165(4) Å, is rather shorter than P(1) · · · C(4) [3.230(4) Å].

(*ii*) *The triphenylphosphine ligands.* The range of P–C(1) distances is 1.839(3)—1.853(3) Å. The angular variations about the phosphorus atoms are much more pronounced, however. In triphenylphosphine, the mean C–P–C angle is 103.0°;[27] the majority of the C–P–C angles in the parent compound lie about this value, but in each ligand one of the angles is considerably smaller (Table 3). Given a C–P–C angle of 103.0°, Ru–P–C should be $180 - \arcsin(\sin 51.5/\cos 30) = 116.4°$; considerable variations from this mean are found.

The molecule overall, as well as the ruthenium environment, may be seen from Figure 1 to have overall molecular symmetry which is pseudo-*m*; deviations from this presumably arise from the necessity for minimization of intermoiety contacts. Insofar as the cyclopentadienyl ring is concerned, this distortion is seen to be a rotation about Ru–C(0), consequent upon the unsymmetrical nature of its interactions with the neighbouring aromatic hydrogen atoms; the dominant contacts comprising this torque are those from H(112) and H(236) (Table 4).

In the projection down Ru–C(0) of Figure 1, it is seen that in each ligand one of the phenyl rings has its axis lying parallel to the direction of projection (rings 12,22), evidencing a considerably strained arrangement, and necessitating contacts of the *ortho*-hydrogen atoms H(126) and H(222) with the nearby carbon atoms of rings 13 and 21 respectively; these contacts are presumably responsible for the unsymmetrical nature of the exocyclic angles at C(121) and C(221). A similar asymmetry is observed also at C(131) and C(211) (Table 3). Although the interaction of rings 12 and 22 is a common element here, the larger of the exocyclic angles, P–C(1)–C(6), lies *away* from the approach of the 12 or 22 ring, and it may be relevant that in each case H(6) of rings 13 and 21 lies at a contact distance from H(116) and H(232) respectively. The angles C(121)–P(1)–C(111) and C(221)–P(2)–C(231) have already been noted as being remarkably small; this presumably, is a cumulative consequence of the above interactions, and, presumably, interactions H(236) · · · H(3) and H(111) · · · H(5) precluded any further rotation of these rings about P(1)–C(111) and P(2)–C(231) as well as being instrumental in reducing these angles at the phosphorus atoms.

The Structure of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (8).—This structure determination is less precise than that of (1), largely a consequence of smaller specimen size, and consequently does not merit as detailed a discussion. The asymmetric unit of the cell comprises two molecules in an array which displays a number of elements of added pseudo-symmetry, the most notable of which is the equivalence of *b* and *c*. The ruthenium atom environments closely resemble that of (1). The following additional features are noteworthy. (*a*) Whereas other bond lengths and angles about the ruthenium atoms are similar to those of (1), the ruthenium–phosphorus distances are notably shorter, being 2.273(5)—2.280(6) (mean 2.27_5 Å). If this effect were electronic in origin, it might reasonably be expected that the Ru–C, Cl distances might be sensitive to such a change; such does not appear to be the case, and, given the steric crowding found in (1), it seems more likely that these shorter distances are consequent upon a diminution in steric strain in the molecule. All of the angles C(0)–Ru–Cl, P(1,2) are increased at the expense of P(1)–Ru–P(2), in (8) relative to (1), constituting a better approximation to octahedral geometry.

(*b*) The nature of co-ordination of the phosphine moieties in (8) are preserved, relative to (1). In (1) Ru–P–C(21) was the larger of the Ru–P–C angles; in (8) Ru–P–C(2) are still appreciably larger than Ru–P–C(1,3) within each ligand. Hydrogen contacts are not recorded for (8) because of their relative uncertainty; nevertheless it seems likely that although interligand steric effects may be diminished, relative to (1), inter-ligand interactions are still sufficiently large to be a determinant of the overall molecular geometry.

We thank the Australian Research Grants Committee for grants in support of this work.

[0/1084 *Received, 9th July*, 1980]

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