Synthesis and Crystal Structure of [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)Cl$],† a Compound having a Cyclopentadienyl Proton with a Chemical Shift of δ 1.91 p.p.m.

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The room-temperature ^1H n.m.r. spectrum of [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)Cl$] (**1**) in [$^2H_8$]toluene contains a cyclopentadienyl resonance at δ 2.29; upon cooling to −60 °C this moves to δ 1.91. This high-field chemical shift is ascribed to the shielding effect of the aromatic ring current of a phenyl ring of the PPh_3 ligand. The *X*-ray crystal structure of (**1**) is reported; the crystals are orthorhombic, space group $Pc2_1n$ with a = 10.161(2), b = 15.735(3), c = 19.256(5) Å, and Z = 4. The structure was solved *via* the heavy-atom method and refined to R = 0.028 using 2137 independent reflections. Reaction of compound (**1**) with trimethyl phosphite gives [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)\{P(OMe)_3\}Cl$] (**2**) and with $AgBF_4$ and (+)-PhCH(Me)NH_2 yields the diastereoisomers of [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)\{(+)-NH_2CH(Me)Ph\}$]$BF_4$ (**3**).

Cyclopentadienes with a ligating donor-atom substituent are an interesting class of mixed-donor ligands which offer considerable potential for the synthesis of novel organometallic compounds.[1] This is reflected in the range of such functionalised cyclopentadienes synthesised in recent years.[2] We wish to use such ligands as part of a programme to investigate complexes containing various types of chiral ruthenium atoms[3,4] and set out to synthesise [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)Cl$].

This compound has been prepared previously but no experimental details or spectroscopic data were given.[5] The reported synthesis involved a prolonged two-stage reaction between [$Ru(PPh_3)_3Cl_2$] and $C_5H_5CH_2CH_2PPh_2$ first in ethanol and then in benzene. We found that a more direct approach, simply refluxing the two reagents together in 1,2-dichloroethane, quickly gave a yellow-orange solid in high yield. Elemental analysis was consistent with this solid being the desire compound [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)Cl$] as was the ^{31}P n.m.r. spectrum which showed the presence of two inequivalent phosphorus atoms bound to ruthenium. Moreover, the ^{13}C n.m.r. chemical shifts of the five-membered ring are broadly in the range previously observed for a substituted cyclopentadienyl ring η^5-bonded to a chiral ruthenium atom,[6] although one signal at δ 64.2 is at higher field than expected. The ^1H n.m.r. spectrum, however, was hard to rationalize with the anticipated structure in that η^5-cyclopentadienyl protons normally appear in the region of δ 5 ± 1[7,8] and only three such proton signals were observed. There was an additional signal (intensity 1 H) at δ 2.29 as well as the multiplets of the $-CH_2CH_2-$ side chain centred at δ 2.63 and 1.51. Upon cooling to −60 °C the signal previously observed at δ 2.29 moved upfield to 1.91. By carrying out nuclear Overhauser effect (n.O.e.) experiments it was possible to show that the high-field cyclopentadienyl signal arose from a proton adjacent to the ring substituent [*i.e.* H(2) or H(5), attached to C(2) and C(5) respectively, Figure 1]; thus, H(2) and H(5) each showed a n.O.e. on only one cyclopentadienyl signal whereas the inner protons H(3) and H(4) each showed a n.O.e. on two cyclopentadienyl signals.

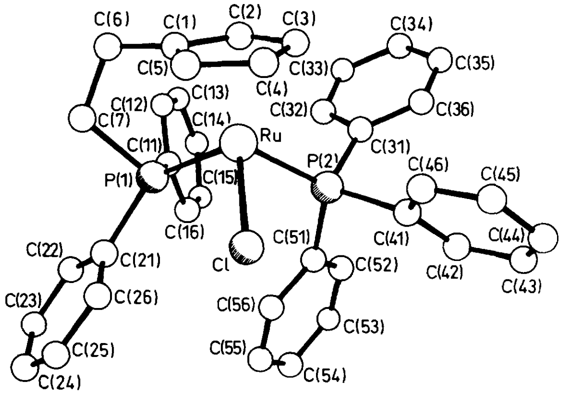

Figure 1. The structure of [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)Cl$] (**1**)

There is no reason to expect complexes of (2-diphenylphosphinoethyl)cyclopentadienyl to exhibit anomalous chemical shifts and indeed in the ^1H n.m.r. spectrum of [$Mn(\eta^5-C_5H_4CH_2CH_2PPh_2)(CO)_2$] the cyclopentadienyl protons appear at δ 3.9 and 4.2.[9] Further, since the ^1H n.m.r. spectrum of [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)\{P(OMe)_3\}Cl$] (**2**) does not contain a similar high-field signal (see below) it would appear that the triphenylphosphine ligand is responsible for the unusual chemical shifts.

To rationalize these unusual features in the ^1H n.m.r. spectrum and to characterise unambiguously the product an *X*-ray crystal structure determination was carried out. The structure of [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)Cl$] is illustrated in Figure 1 together with the atom labelling used in the Tables. Selected geometric parameters with estimated standard deviations are given in Table 1. In common with the analogous molecule [$Ru(\eta^5-C_5H_5)(PPh_3)_2Cl$], compound (**1**) contains a

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† Chloro[η^5-(2-diphenylphosphinoethyl)cyclopentadienyl-*P*]-(triphenylphosphine)ruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations, and shortest intramolecular contacts (Å) for [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)Cl$]

Ru–Cl	2.455(1)	Ru–C(1)	2.201(5)
Ru–C(2)	2.158(5)	Ru–C(3)	2.208(5)
Ru–C(4)	2.198(6)	Ru–C(5)	2.207(6)
Ru–P(1)	2.311(1)	Ru–P(2)	2.307(2)
C(1)–C(2)	1.403(7)	C(1)–C(5)	1.411(8)
C(1)–C(6)	1.492(8)	C(2)–C(3)	1.433(7)
C(3)–C(4)	1.391(9)	C(4)–C(5)	1.423(9)
C(6)–C(7)	1.532(8)	C(7)–P(1)	1.853(6)
P(1)–C(11)	1.835(5)	P(2)–C(31)	1.835(5)
C(32) ··· H(2)	3.10	C(36) ··· H(3)	3.24
C(31) ··· H(2)	3.30	C(31) ··· H(3)	3.21
C(11) ··· H(2)	3.67		
P(1)–Ru–Cl	100.7	P(2)–Ru–Cl	88.4(1)
P(1)–Ru–P(2)	99.9	C(2)–C(1)–C(5)	108.3(5)
C(2)–C(1)–C(6)	126.1(5)	C(5)–C(1)–C(6)	125.3(5)
C(1)–C(2)–C(3)	108.1(5)	C(2)–C(3)–C(4)	107.2(5)
C(3)–C(4)–C(5)	109.0(5)	C(1)–C(5)–C(4)	107.2(5)
C(1)–C(6)–C(7)	112.8(5)	C(6)–C(7)–P(1)	112.0(4)
Ru–P(1)–C(7)	102.2(2)	Ru–P(1)–C(11)	116.8(2)
C(7)–P(1)–C(11)	104.4(3)	Ru–P(1)–C(21)	128.6(2)
C(7)–P(1)–C(21)	97.8(2)	C(11)–P(1)–C(21)	102.9(2)
Ru–P(2)–C(31)	113.5(2)	Ru–P(2)–C(41)	115.8(2)
C(31)–P(2)–C(41)	100.6(2)	Ru–P(2)–C(51)	119.3(1)
C(31)–P(2)–C(51)	104.2(2)	C(41)–P(2)–C(51)	101.0(2)

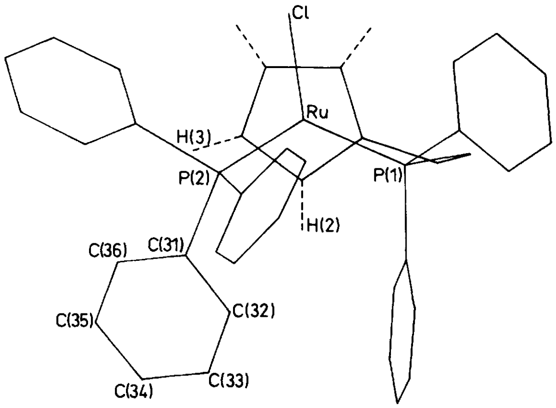

Figure 2. A diagrammatic view of complex (**1**) viewed normal to the C(31)—C(36) plane showing the idealised C–H bonds on the cyclopentadienyl ring

rather long Ru–Cl bond and exhibits significant variations in the P–Ph bonds.[10]

The anomalous ^1H n.m.r. spectrum of complex (**1**) could arise from a loss of aromaticity in the cyclopentadienyl ring, but it can be seen from the individual C–C bond lengths (Table 1) that, although there is some localisation of the bonding, the variations in the C–C bond lengths is not significantly different to that observed in other cyclopentadienyl compounds.[3,6,10] The average C–C ring bond length of 1.412 ± 0.021 Å compares with a corresponding figure of 1.421 ± 0.02 Å for the complex [$Ru(\eta^5-C_5H_5)(PPh_3)_2Cl$].[10]

The origin of the high-field ^1H and ^{13}C cyclopentadienyl signals is not immediately clear from the structure shown in Figure 1; however, inspection of Figure 2 suggests that the phenyl ring C(31)—C(36) on the triphenylphosphine ligand may be responsible for the observed shielding effect. Although the cyclopentadienyl protons were not refined, based on idealised geometries the intramolecular distances between the C(31)—C(36) phenyl ring and C(2)–H and C(3)–H are approximately 3 Å. In such an orientation (Figure 2) one might have expected both of these protons to exhibit high-field chemical shifts whereas only one high-field proton is observed. It must be appreciated, however, that the rotamer existing in the solid state may arise from crystal packing forces, *etc.* and is not necessarily the one that predominates in solution. The temperature dependence of the ^1H n.m.r. spectrum supports the fact that several rotamers exist in solution at room temperature. A rotation about the P(2)–C(31) bond would place the phenyl group C(31)—C(36) approximately 3 Å above C(2)H or C(3)H. Over such a distance, shielding by the phenyl ring could well produce a ^1H n.m.r. chemical shift change in the cyclopentadienyl proton of 1.27,[11] which is the difference observed at room temperature between the highest-field ^1H cyclopentadienyl signal in [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)LCl$](**1**; L = PPh_3) compared to that for [**2**; L = $P(OMe)_3$]. The increase in the chemical shift to δ 1.91 on cooling to −60 °C presumably reflects the reduction in molecular motion at lower temperature which makes the localisation of the shielding effect more pronounced. Related compounds such as [$Ru(\eta^5-C_5H_5)(PPh_3)_2Cl$] presumably fail to show high-field shifts because of the rapid rotation about the Ru–C_5H_5 bond; such rotation is of course not possible in compound (**1**).

One additional feature of the ^1H n.m.r. spectrum of compound (**1**) that merits a comment is that the signals due to the methylene protons broaden considerably as the temperature is lowered. This is possibly due to the slowing down of the inversion of the Ru–P–CH_2–CH_2–C_5H_4 ring. If this is the case then it is a very low energy process as the coalescence temperature is well below 213 K; this can be compared with 209K, the reported[12] coalescence temperature for the ring inversion of cyclohexane.

The triphenylphosphine ligand in (**1**) proves to be substitution labile and upon refluxing with a slight excess of trimethyl phosphite the compound [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)\{P(OMe)_3\}Cl$] (**2**) was formed in quantitative yield. The ^1H n.m.r. spectrum of (**2**) contains a cyclopentadienyl signal at δ 3.72 and although this is at relatively high field for such a proton it is at significantly lower field than the corresponding proton of (**1**).

Complex (**1**) contains a chiral ruthenium centre and an attempt was made to resolve this *via* its diastereomeric derivative [$Ru(\eta^5-C_5H_4CH_2CH_2PPh_2)(PPh_3)\{(+)-NH_2CH(Me)Ph\}$]$BF_4$ (**3**). However, although (**3**) was readily synthesised by abstracting the chloride ligand from (**1**) with $AgBF_4$ and then adding (*R*)(+)-PhCH(Me)NH_2, it proved too unstable in solution for the slow fractional recrystallisation necessary to separate the diastereomers. The presence of diastereoisomers is clearly evident in the ^1H, ^{13}C, and ^{31}P n.m.r. spectra (Experimental section). One might have expected this complex to exhibit a high-field cyclopentadienyl proton signal analogous to that of (**1**) due to a similar shielding effect of the triphenylphosphine ligand. Opposing this, however, is the effect of charge; a cyclopentadienyl ligand complexed to a monocation normally experiences ⩾ 1 p.p.m. shift downfield compared to similar neutral complexes.[7] Thus, although the cyclopentadienyl signals of compound (**3**) at δ 3.99 are at relatively high field they are significantly lower than the corresponding signal of (**1**).

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Laboratory. Proton and ^{13}C spectra were normally recorded on a Bruker AM-250 Fourier-transform spectrometer although where stated some ^1H spectra were recorded on a Perkin-Elmer R-34 220-MHz spectrometer. The chemical shifts for the ^{31}P n.m.r. spectra were measured from 85% H_3PO_4 (downfield positive) using a Bruker UP-80SY Fourier-transform spectrometer. Mass spectra were recorded on a Kratos MS80 spectrometer. Dichloromethane and 1,2-dichloroethane were dried by distillation from calcium hydride, toluene was dried by distillation from sodium, and dioxane was dried over sodium benzophenone; all solvents were freshly distilled before use. Reactions were carried out under an atmosphere of nitrogen although the compounds were subsequently found not to be particularly air-sensitive.

Published procedures were used to prepare $[Ru(PPh_3)_3Cl_2]$[13] and spiro[4.2]hepta-1,3-diene[14] [δ_H ($CDCl_3$, reference $SiMe_4$, 220 MHz), 1.69 (4 H, m, methylene), 6.18 and 6.54 (4 H, AA′BB′, olefinic)].

(2-Diphenylphosphinoethyl)cyclopentadiene.—A solution containing the diphenylphosphide anion was prepared by treating triphenylphosphine (5.2 g, 80 mmol) with K/Na alloy (1.6 g K, 0.4 g Na) in dioxane (20 cm^3) under argon at 80 °C for 17 h. The hot solution was filtered through Hiflo and degassed spiro[4.2]hepta-1,3-diene (1.8 g, 20 mmol) was then added dropwise to the hot stirred solution; stirring was continued for a further 30 min at 80 °C. After cooling the mixture was filtered and water (2 cm^3) carefully added to destroy any unreacted phosphide. The solvent was removed *in vacuo* to leave a dark brown oil which was chromatographed [Kieselgel 60; 90% light petroleum (b.p. 60—80 °C)–10% $CHCl_3$] to give an approximately equal mixture of 1- and 2-(2′-diphenylphosphinoethyl)-cyclopenta-1,3-diene as a colourless oil (2 g, 40%). Attempts to separate the two isomers by h.p.l.c. were unsuccessful. N.m.r. spectra: ^1H ($CDCl_3$, reference $SiMe_4$, 220 MHz), 2.20—2.58 (4 H, m, methylene), 2.80—2.95 (2 H, m, cyclopentadiene methylene), 5.98—6.47 (3 H, m, olefinic), and 7.21—7.52 (10 H, m, aromatic); ^{13}C ($CDCl_3$, 63 MHz), 28.1—26.0, 41.2, and 43.1 [CH_2 (methylene)], 125.8—134.3 (CH), 138.5 [C(olefinic)], and 147.0—149.4 [C(aromatic)]; ^{31}P (C_6D_6, 32.4 MHz), −15.5 and −15.7. Electron-impact mass spectrum: M^+ 278 (calc. for $C_{19}H_{19}P$: 278).

Chloro[η^5-(*2-diphenylphosphinoethyl*)*cyclopentadienyl-P*]-(*triphenylphosphine*)*ruthenium*. (**1**).—(*i*) (2-Diphenylphosphinoethyl)cyclopentadiene (220 mg, 0.8 mmol) and dichlorotris-(triphenylphosphine)ruthenium (780 mg, 0.8 mmol) were refluxed in 1,2-dichloroethane (10 cm^3) for 40 min and the mixture then evaporated to dryness *in vacuo*. The residue was extracted into diethyl ether and chromatographed [alumina, Et_2O–CH_2Cl_2 (1:1)] to yield the product as a yellow-orange solid (220 mg, 41% yield), m.p. 186—189 °C. N.m.r.: ^1H ($C_6D_5CD_3$, reference $SiMe_4$, 220 MHz), 1.51, 2.63 (4 H, m, methylene), 2.29, 4.43, 4.80, 5.02 (4 H, m, cyclopentadienyl), 6.55—8.25 (25 H, m, aromatic); ($CDCl_3$, 250 MHz), 1.93 (m) and 2.04 (m) (CH_2P), 2.95 (m) and 3.12 (m) ($CH_2C_5H_4$), 2.45(m) and 5.03(m) [H(2) and H(5)], 4.55(m) and 5.12(m) [H(3) and H(4)], and 6.86—8.03 (25 H, m, aromatic); ^{13}C ($CDCl_3$, 63 MHz), 21.5 [$CH_2C_5H_4$, J_{CP} 4.0 Hz], 50.3 [CH_2P, J_{CP} 31.0 Hz], 64.2, 75.5, 83.2, 86.2, and 115.0 (cyclopentadienyl), 127.5—134.8 [CH (aromatic)], 137.1—138.5 [C (aromatic)]; ^{31}P (C_6D_6, 32 MHz), 43.2 and 52.0 (J_{PP} 38 Hz). Fast atom bombardment (f.a.b.) mass spectrum (positive ion, argon): M^+ 676 (Found: C, 65.2, H, 5.2. Calc. for $C_{37}H_{33}ClP_2Ru$: C, 65.7, H, 4.9%, *M*, 676).

(*ii*) Dichlorotris(triphenylphosphine)ruthenium (470 mg, 0.5 mmol) and (2-diphenylphosphinoethyl)cyclopentadiene (150 mg, 0.5 mmol) were refluxed in ethanol (15 cm^3) for 17 h. The ethanol was removed *in vacuo* and benzene (15 cm^3) added. The solution was refluxed for 24 h, the benzene was removed *in vacuo*, and the solid extracted into ether. Chromatography (alumina, 30% CH_2Cl_2–ether 70%) gave a yellow solid (80 mg, 25%). The ^1H and ^{31}P n.m.r. spectra of this compound were identical to those reported in (*i*).

Chloro[η^5-(*2-diphenylphosphinoethyl*)*cyclopentadienyl*-P]-(*trimethyl phosphite*)*ruthenium* (**2**).—Compound (**1**) (150 mg, 0.22 mmol) was refluxed with freshly distilled trimethyl phosphite (0.11 g, 0.9 mmol) for 1.5 h in dry toluene (25 cm^3) under nitrogen. The mixture was allowed to cool to room temperature and the toluene evaporated *in vacuo*. Chromatography of the residue (alumina, diethyl ether–dichloromethane) and removal of the solvent *in vacuo* gave the desired compound (**2**) as a yellow solid (0.11 g, 92%), m.p. 158—160 °C. N.m.r.: ^1H ($CDCl_3$, reference $SiMe_4$, 220 MHz), 1.70—2.05 (2 H, m, methylene), 2.78—3.42 (2 H, m, methylene), 3.48 (9 H, d, J_{PH} 11 Hz, methoxy), 3.72, 4.92, 5.08, and 5.16 (4 H, s, cyclopentadienyl), 7.23—7.56 (8 H, m, aromatic), and 7.91—8.08 (2 H, m, aromatic); ^{13}C ($CDCl_3$, 63 MHz), 52.0 (CH_3), 21.3 and 50.0 [CH_2 (methylene)], 63.2 (2 signals), 79.8, 91.3, and 113.6 (cyclopentadienyl), 127.4—134.1 (8 signals) [CH (aromatic)], 138.5 and 138.9 [C(aromatic)]; ^{31}P ($CDCl_3$, 32 MHz), 60.4 (P, aromatic) and 156.2 (P, methoxy) (J_{PP} 68 Hz). F.a.b. mass spectrum (positive ion, argon): M^+ 538 (Found: C, 48.8, H, 5.1; Cl, 6.4. Calc. for $C_{22}H_{27}ClO_3P_2Ru$: C, 49.1; H, 5.1; Cl, 6.6%; *M*, 538).

[η^5-(*2-Diphenylphosphinoethyl*)*cyclopentadienyl*-P][(R)(+)-*α-methylbenzylamine*](*triphenylphosphine*)*ruthenium Tetrafluoroborate* (**3**).—A solution of compound (**1**) (190 mg, 0.28 mmol) in dry dichloromethane (10 cm^3) was stirred under nitrogen in the dark. Silver(I) tetrafluoroborate (60 mg, 0.3 mmol) was added and the mixture stirred at room temperature for 45 min. The solution was filtered, through filter-paper, into (+)-α-methylbenzylamine (50 mg, 0.45 mmol). The dichloromethane was evaporated *in vacuo* to give a dark yellow oil. Addition of diethyl ether gave a yellow solid which was washed with ether (4 × 8 cm^3), dissolved in dichloromethane, and evaporated to give (**3**) as a yellow lustrous solid (200 mg, 84%), m.p. 107—112 °C. N.m.r.: ^1H ($CDCl_3$, reference $SiMe_4$, 250 MHz), 0.70(d), 0.88(d) (3 H, *J* 7 Hz, Me), 1.69 (2 H, s, br, NH_2), 1.80—3.15 (2 H, m, methylene), 3.31 (m), 3.45 (m) (1 H, CH), 3.66—3.86 (2 H, m, methylene), 3.99 (1 H), 4.52 (0.5 H), 4.63 (1 H), 4.68 (0.5 H), 4.78 (0.5 H), 5.62 (0.5 H) (all s, br, cyclopentadienyl), and 6.60—8.10 (30 H, m, aromatics); ^{13}C ($CDCl_3$, 63 MHz), 24.9 and 27.3 (CH_3), 22.1 and 50.1—51.1 (CH_2), 60.7 and 61.3 ($CHNH_2$) 61.9, 62.9, 78.2, 78.3, 78.5, 78.6, 83.6, and 85.0 (CH, cyclopentadienyl), 125.2—133.2 [CH (aromatic)], 118.2 [m, C(cyclopentadienyl)], 134.0—135.8 [C(aromatic)]; ^{31}P ($CDCl_3$ 32 MHz), 51.7, 53.2, 59.6, and 62.2 (J_{PP} 66 Hz). F.a.b. mass spectrum (positive ion, argon): M^+ 762 (5%) and M^+ − $NH_2CH(Me)Ph$, 641 (100%) (Found: C, 63.8; H, 5.6; N, 1.6. Calc. for $C_{44}H_{46}NP_2Ru$: C, 63.7; H, 5.2; N, 1.7%; *M*, 762).

Crystallography.—*Crystal data*. $C_{37}H_{33}ClP_2Ru$, $M = 676.1$, crystallises from dichloromethane–pentane as dark red orthorhombic blocks. A single crystal of dimensions *ca.* 0.40 × 0.37 × 0.37 mm was selected. Orthorhombic, $a = 10.161(2)$, $b = 15.735(3)$, $c = 19.256(5)$ Å, $U = 3\,079$ Å^3, space group $Pc2_1n$, $Z = 4$, $D_c = 1.46$ g cm^{-3}, Cu radiation, $\lambda = 1.541\,78$ Å, $\mu(Cu\text{-}K_\alpha) = 62$ cm^{-1}, $F(000) = 1\,384$.

Data collection and processing. Data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω scans. Refined unit-cell parameters were obtained by centring 18 reflections. 2 165 Independent reflections were measured ($2\theta \leqslant 116°$), of which 2 137 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. No

Table 2. Atom co-ordinates (× 10^4)

Atom	*x*	*z*	*z*
Ru	361(1)	−832(1)	6 894(1)
Cl	−1 977(1)	−501(1)	7 070(1)
C(1)	1 366(5)	−2 058(3)	6 747(3)
C(2)	2 011(5)	−1 415(3)	6 374(3)
C(3)	1 133(6)	−1 113(4)	5 847(3)
C(4)	−57(7)	−1 539(4)	5 934(3)
C(5)	71(6)	−2 131(4)	6 488(3)
C(6)	1 900(7)	−2 526(4)	7 359(3)
C(7)	1 350(6)	−2 199(4)	8 050(3)
P(1)	1 031(1)	−1 040(1)	8 028(1)
C(11)	2 604(5)	−559(3)	8 284(2)
C(12)	3 779(5)	−933(5)	8 074(3)
C(13)	4 971(6)	−510(6)	8 221(3)
C(14)	5 015(7)	230(5)	8 581(4)
C(15)	3 865(6)	585(4)	8 798(3)
C(16)	2 660(5)	200(3)	8 657(3)
C(21)	45(5)	−969(3)	8 833(2)
C(22)	636(5)	−919(4)	9 484(3)
C(23)	−121(6)	−895(4)	10 078(3)
C(24)	−1 465(6)	−949(4)	10 041(3)
C(25)	−2 038(5)	−1 015(5)	9 405(3)
C(26)	−1 278(5)	−1 013(4)	8 798(3)
P(2)	756(1)	605(1)	6 787(1)
C(31)	2 385(5)	852(3)	6 428(3)
C(32)	3 492(5)	664(4)	6 810(3)
C(33)	4 729(5)	783(5)	6 546(4)
C(34)	4 898(7)	1 117(5)	5 904(4)
C(35)	3 785(7)	1 301(6)	5 500(4)
C(36)	2 566(6)	1 172(5)	5 767(3)
C(41)	−311(4)	1 181(3)	6 169(3)
C(42)	−304(5)	2 052(4)	6 125(3)
C(43)	−1 006(6)	2 461(4)	5 605(3)
C(44)	−1 717(6)	2 011(4)	5 129(3)
C(45)	−1 706(5)	1 144(4)	5 161(3)
C(46)	−1 039(5)	726(4)	5 682(3)
C(51)	627(4)	1 289(3)	7 557(2)
C(52)	1 394(5)	1 999(3)	7 675(3)
C(53)	1 202(6)	2 487(4)	8 264(3)
C(54)	242(6)	2 269(4)	8 745(3)
C(55)	−499(5)	1 558(4)	8 633(3)
C(56)	−338(5)	1 072(4)	8 044(3)

significant variation was observed in two standard reflections which were monitored every 50 reflections during the data collection. The data were corrected for Lorentz and polarisation factors; an empirical absorption correction based on 350 azimuthal measurements was applied (maximum and minimum transmission factors 0.13 and 0.05).

Structure analysis and refinement. The heavy atom was located by Patterson techniques, and the non-hydrogen atoms were found in successive difference Fourier syntheses. These atoms were refined anisotropically. The positions of the hydrogen atoms were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$, and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block-cascade, full-matrix least squares to $R = 0.028$, $R' = 0.029$, where $w^{-1} = \sigma^2(F) + 0.001\ 14F^2$. The polarity was determined by refinement of a free variable η which multiplies all f''. The maximum and minimum residual electron densities in the final ΔF map were 0.64 and −0.27 e Å^{-3} respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[15] Final atomic co-ordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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