Preparation, and Crystal and Molecular Structure of π-Cyclopentadienyl-η-(tetraphenylborato)ruthenium(II)

By **Gert J. Kruger,*** National Physical Research Laboratory, C.S.I.R., Pretoria
A. Louis du Preez,* Department of Inorganic and Analytical Chemistry, University of Pretoria, Pretoria
Raymond J. Haines, Department of Chemistry, University of Cape Town, Cape Town, Republic of South Africa

The preparation of the title compound is reported. Crystals are monoclinic, a = 9·527(4), b = 15·381(6), c = 15·518(7) Å, β = 105·09(5)°, Z = 4, space group $P2_1/c$. The structure was determined by Patterson and Fourier methods from diffractometer data and refined by least-squares methods to a final R of 0·032 for 2048 reflections. The ruthenium atom is sandwiched between the cyclopentadienyl ring and one of the phenyl rings of the tetraphenylborate anion. The rings are planar, parallel, and 3·52 Å apart.

THE title compound has been identified as a zwitterionic sandwich species.[1] $(\pi\text{-}C_5H_5)Ru(BPh_4)$ is prepared by heating under reflux a solution of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ [2] and sodium tetraphenylborate in methanol for 14 h and was characterised [3] by means of elemental analysis, i.r. and p.m.r. spectroscopy, and a conductivity measurement in acetone.

With a view to synthesising similar arene-bonded 'sandwich' compounds by utilising $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ as starting compound, the reactions of benzene, tetramethyl-, hexamethyl-, and hexafluoro-benzene with $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ in methanol and in the presence of hexafluorophosphate ions, or with $\{(\pi\text{-}C_5H_5)Ru(PPh_3)_2(\text{solvent})\}SbF_6$ (solvent = acetone or methanol), in the appropriate solvent, were studied. No evidence was obtained for the formation of any arene-bonded species, however.† The reason why only those reactions involving tetraphenylborate ions afforded a derivative containing an arene ring π-bonded to the ruthenium atom is puzzling,‡ and led us to investigate fully the crystal and molecular structure of the title compound.

EXPERIMENTAL

Preparation.—A solution of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (0·50 g, 0·69 mmol) and $NaBPh_4$ (0·48 g, 1·4 mmol) in methanol (*ca.* 500 ml) was heated under reflux for 14 h under nitrogen. The filtered solution was concentrated to *ca.* 400 ml and set aside for 24 h, when brown crystals separated. The mother liquor was decanted and the crystals (20%), which are only slightly soluble in most common organic solvents, washed with methanol and light petroleum (Found: C, 71·9; H, 5·3; B, 2·0. $C_{29}H_{25}BRu$ requires C, 71·8; H, 5·2; B, 2·2%). Molar conductivity in acetone (10^{-4} M-solution) 1·2 ohm^{-1} cm^2 mol^{-1}. ^{1}H n.m.r. spectrum (τ values, p.p.m. *vs.* tetramethylsilane, $CDCl_3$ solution): 5·24 $(\pi\text{-}C_5H_5)$, 3·78 and 4·39 (bonded phenyl group resonances, centres of multiplets). I.r. spectrum (1500—1350 cm^{-1}, KBr disc): 1481m, 1442m, 1430m, 1415m, and 1393mw.

Crystals are well formed and approximately cube-shaped. Laue symmetry and space group were determined by use of oscillation and Weissenberg photographs. Cell parameters were obtained from least-squares refinement of 25 2θ values measured on a Philips diffractometer.

Crystal Data.—$C_{29}H_{25}BRu$, M = 484·9, Monoclinic, a = 9·527(4), b = 15·381(6), c = 15·518(7) Å, β = 105·09(5)°, D_m = 1·46(2) (by flotation), Z = 4, D_c = 1·466, $F(000)$ = 92. Space group $P2_1/c$ ($h0l$, $l = 2n$; $0k0$, $k = 2n$), Mo-K_α radiation, λ = 0·7107 Å, μ(Mo-K_α) = 7·1 cm^{-1}.

Intensity data were collected on a Philips PW 1100 four-circle automatic diffractometer, equipped with a graphite monochromator, from a crystal *ca.* 0·24 × 0·16 × 0·16 mm³. The ω—2θ scan mode was used at a scan rate of 0·04° s^{-1} in θ with a constant scan-width of 1·2° θ. The background on each side of the reflection was counted for half the total scanning time. A unique set of reflections in the θ range 3—20° was measured. Three reference reflections were measured at regular intervals and both their optimum positions and intensities stayed constant during data collection. Of the 2048 independent reflections, 320 had $I < 1{\cdot}65\,\sigma(I)$ and were classified as unobserved. $\sigma^2(I)$ Was calculated as $S + B + (0{\cdot}02S)^2$, where S is the scan count and B the total background count. Lorentz and polarisation corrections were applied and no corrections were made for absorption.

Structure Solution and Refinement.—All calculations were done on an IBM 360/65 computer using the '*X*-Ray '72' system of crystallographic programs.[5] Stereoscopic drawings were obtained by the thermal-ellipsoid plot program ORTEP.[6] The structure was solved by the application of the heavy-atom method. The position of the Ru atom was deduced from a three-dimensional Patterson map and successive Fourier syntheses revealed the positions of all the non-hydrogen atoms.

Refinement was by full-matrix least-squares methods minimising the quantity $\Sigma\omega(|F_o| - |F_c|)^2$. The R index was reduced to 0·090 on isotropic refinement and to 0·051 on anisotropic refinement. All the hydrogen positions were found from a difference electron-density synthesis at this stage. The isotropic temperature factors for the hydrogen atoms were kept constant at u 0·03, and the overall temperature factor for the crystal, as estimated from a Wilson plot, and the positional parameters were then refined together with all other atomic parameters. During refinement unit weights were used except in the last few cycles where those reflections with large F_o and/or small sin θ values were weighted according to the scheme $\omega = \left(\frac{\sin\theta}{0{\cdot}25} \times \frac{120}{F_o}\right)$ for reflections with $\sin\theta < 0{\cdot}25$ and/or $F_o >$

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† Unpublished data.

‡ The mixed-sandwich compound $[(\pi\text{-}C_5H_5)Ru(\pi\text{-}C_6H_6)]Cl$ has been reported.[4]

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[3] A. L. du Preez, Ph.D. Thesis, University of Pretoria, 1972.

[4] R. A. Zelonka and M. C. Baird, *J. Organometallic Chem.*, 1972, **44**, 383.

[5] J. M. Stewart, G. J. Kruger, H. Ammon, C. H. Dickinson, and S. R. Hall, University of Maryland Computer Sci. Tech. Report TR 192, College Park, Maryland, 1972.

[6] C. K. Johnson, program ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

120. This weighting scheme resulted in no observable trend in the values of $\omega(|F_o| - |F_c|)^2$ for subsets of reflections divided into ranges of sin θ and F_o. In the final cycle R was 0·032 and R' 0·036 for the observed reflections {where $R' = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{\frac{1}{2}}$}. The average shift-to-error for all parameters was 0·07, the maximum being 0·66. The standard deviation of an observation of unit weight was 1·26. The largest peak in a difference electron-density synthesis calculated after the final cycle of refinement was *ca.* 0·3 eÅ^{-3}. Scattering factors were taken from ref. 7 except for hydrogen, which was taken from ref. 8; that for Ru was corrected for the effects of anomalous dispersion, according to ref. 9.

TABLE 1

Final fractional atomic co-ordinates

	x	y	z
Ru	0·2559(1)	0·2371(1)	0·4177(1)
B	0·6457(7)	0·1979(4)	0·4840(4)
C(11)	0·6399(6)	0·1557(4)	0·3852(4)
C(12)	0·6750(7)	0·2013(4)	0·3173(4)
C(13)	0·6751(8)	0·1639(6)	0·2371(5)
C(14)	0·6386(8)	0·0789(6)	0·2199(5)
C(15)	0·6058(9)	0·0311(5)	0·2857(5)
C(16)	0·6077(8)	0·0692(4)	0·3652(5)
C(21)	0·7177(6)	0·2953(4)	0·4952(4)
C(22)	0·8475(7)	0·3169(4)	0·5567(4)
C(23)	0·9044(8)	0·4000(5)	0·5659(5)
C(24)	0·8327(8)	0·4668(5)	0·5150(5)
C(25)	0·7045(9)	0·4490(5)	0·4522(5)
C(26)	0·6492(7)	0·3651(4)	0·4425(5)
C(31)	0·7416(6)	0·1328(4)	0·5613(4)
C(32)	0·7059(7)	0·1109(4)	0·6402(4)
C(33)	0·7952(9)	0·0589(5)	0·7056(5)
C(34)	0·9237(8)	0·0276(5)	0·6947(5)
C(35)	0·9619(7)	0·0462(4)	0·6178(5)
C(36)	0·8734(7)	0·0973(4)	0·5532(4)
C(41)	0·4823(6)	0·2030(4)	0·5016(4)
C(42)	0·3870(7)	0·1305(4)	0·4893(4)
C(43)	0·2521(7)	0·1316(5)	0·5114(5)
C(44)	0·2057(8)	0·2065(5)	0·5456(5)
C(45)	0·2924(8)	0·2801(5)	0·5564(5)
C(46)	0·4280(7)	0·2785(5)	0·5356(4)
C(51)	0·1961(12)	0·1984(6)	0·2785(5)
C(52)	0·0699(11)	0·2167(8)	0·3042(7)
C(53)	0·0747(10)	0·3027(8)	0·3278(8)
C(54)	0·2019(11)	0·3407(6)	0·3190(7)
C(55)	0·2797(11)	0·2763(7)	0·2886(5)
H(12)	0·697(5)	0·257(3)	0·326(3)
H(13)	0·695(4)	0·195(4)	0·199(4)
H(14)	0·636(6)	0·053(4)	0·172(4)
H(15)	0·582(7)	−0·019(4)	0·280(4)
H(16)	0·582(7)	0·035(4)	0·395(4)
H(22)	0·896(7)	0·280(4)	0·587(4)
H(23)	0·981(7)	0·409(4)	0·599(4)
H(24)	0·875(6)	0·520(4)	0·522(4)
H(25)	0·656(6)	0·491(4)	0·417(4)
H(26)	0·553(6)	0·357(4)	0·395(4)
H(32)	0·615(7)	0·137(4)	0·641(4)
H(33)	0·767(6)	0·049(4)	0·758(4)
H(34)	0·983(7)	−0·005(4)	0·731(4)
H(35)	1·037(7)	0·028(4)	0·606(4)
H(36)	0·902(6)	0·110(4)	0·506(4)
H(42)	0·409(6)	0·083(4)	0·459(4)
H(43)	0·184(6)	0·085(4)	0·490(4)
H(44)	0·100(7)	0·206(4)	0·540(4)
H(45)	0·276(7)	0·325(4)	0·574(4)
H(46)	0·488(7)	0·322(4)	0·547(4)
H(51)	0·214(6)	0·146(4)	0·250(4)
H(52)	−0·002(7)	0·180(4)	0·294(4)
H(53)	0·007(7)	0·320(5)	0·338(4)
H(54)	0·241(7)	0·389(4)	0·333(4)
H(55)	0·366(7)	0·287(4)	0·283(4)

Atomic parameters from the final least-squares cycle are given in Tables 1 and 2. Interatomic distances and angles are listed in Table 3, and some appropriate least-squares planes in Table 4. Estimated standard deviations are given in brackets and refer to the least significant figures in the parameter values. Bond lengths are uncorrected for thermal motion. The atom numbering is shown in Figure 1, hydrogen atoms being numbered according to the carbon atoms to which they are bonded. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20952 (12 pp., 1 microfiche).*

TABLE 2

Anisotropic thermal parameters; * ($U_{ij} \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	252(3)	292(3)	443(4)	−19(2)	0(2)	46(3)
B	331(40)	242(41)	243(40)	−15(33)	79(32)	53(33)
C(11)	189(34)	279(36)	224(35)	33(28)	53(27)	54(30)
C(12)	390(40)	398(41)	206(35)	−20(33)	81(31)	−12(32)
C(13)	517(49)	559(62)	372(46)	−30(42)	233(38)	202(41)
C(14)	526(51)	614(65)	324(49)	92(42)	199(40)	−125(46)
C(15)	634(55)	366(45)	442(52)	−57(42)	167(41)	−100(48)
C(16)	535(49)	299(43)	305(47)	−29(35)	178(35)	19(34)
C(21)	236(37)	271(36)	219(34)	−45(29)	140(30)	34(29)
C(22)	218(41)	297(45)	318(42)	−39(32)	109(34)	29(32)
C(23)	321(43)	501(52)	438(48)	−203(41)	79(35)	−131(38)
C(24)	446(51)	315(44)	602(51)	−209(37)	235(43)	−102(38)
C(25)	524(55)	298(50)	638(56)	19(41)	270(47)	180(40)
C(26)	326(41)	310(45)	417(44)	−43(34)	78(35)	41(34)
C(31)	253(36)	152(33)	282(38)	−100(28)	76(29)	−31(28)
C(32)	314(41)	343(41)	283(41)	39(34)	83(35)	31(34)
C(33)	594(57)	402(46)	261(43)	−102(41)	125(41)	57(37)
C(34)	401(51)	328(44)	442(49)	−44(38)	−150(38)	47(36)
C(35)	243(39)	322(42)	555(49)	14(34)	96(38)	66(38)
C(36)	263(39)	325(40)	254(38)	−31(32)	52(33)	49(34)
C(41)	185(33)	209(37)	184(32)	10(30)	−7(26)	85(28)
C(42)	264(41)	219(39)	334(39)	−18(32)	97(31)	76(31)
C(43)	291(45)	276(44)	503(46)	−99(35)	89(36)	84(36)
C(44)	241(42)	474(54)	644(51)	−51(41)	227(38)	14(40)
C(45)	410(48)	383(50)	516(49)	22(43)	200(37)	−109(39)
C(46)	218(41)	333(45)	399(41)	−94(33)	63(32)	−49(35)
C(51)	916(82)	657(68)	266(47)	−131(64)	−178(47)	−41(42)
C(52)	404(66)	922(98)	885(73)	−237(60)	−258(55)	289(64)
C(53)	418(74)	880(93)	1093(86)	257(67)	−129(59)	534(72)
C(54)	632(73)	450(60)	898(73)	−96(58)	−167(55)	350(56)
C(55)	558(57)	964(83)	394(49)	−147(70)	−63(46)	247(51)

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

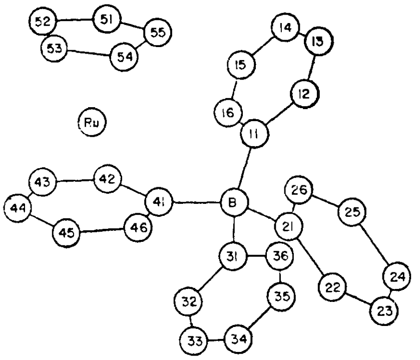

FIGURE 1 A diagram of the structure which shows the numbering system used for the carbon atoms. The rings are numbered according to the first digit of the carbon atom number

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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[8] R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, p. 216.

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Ru–C(51)	2·170(8)	C(21)–C(22)	1·391(8)
Ru–C(52)	2·172(9)	C(22)–C(23)	1·380(10)
Ru–C(53)	2·166(10)	C(23)–C(24)	1·366(10)
Ru–C(54)	2·179(10)	C(24)–C(25)	1·377(10)
Ru–C(55)	2·162(9)	C(25)–C(26)	1·387(10)
Ru–C(41)	2·271(5)	C(26)–C(21)	1·404(8)
Ru–C(42)	2·181(6)	C(31)–C(32)	1·396(10)
Ru–C(43)	2·185(7)	C(32)–C(33)	1·394(9)
Ru–C(44)	2·210(8)	C(33)–C(34)	1·367(12)
Ru–C(45)	2·191(8)	C(34)–C(35)	1·367(11)
Ru–C(46)	2·209(6)	C(35)–C(36)	1·367(9)
C(51)–C(52)	1·392(17)	C(36)–C(31)	1·405(9)
C(52)–C(53)	1·371(18)	C(41)–C(42)	1·419(8)
C(53)–C(54)	1·384(16)	C(42)–C(43)	1·415(10)
C(54)–C(55)	1·393(16)	C(43)–C(44)	1·387(11)
C(55)–C(51)	1·425(15)	C(44)–C(45)	1·385(11)
C(11)–C(12)	1·377(9)	C(45)–C(46)	1·411(11)
C(12)–C(13)	1·372(10)	C(46)–C(41)	1·428(9)
C(13)–C(14)	1·362(12)	B–C(11)	1·654(9)
C(14)–C(15)	1·359(12)	B–C(21)	1·638(9)
C(15)–C(16)	1·363(11)	B–C(31)	1·644(8)
C(16)–C(11)	1·382(9)	B–C(41)	1·651(10)
C(12)–H(12)	0·89(5)	C(22)–H(22)	0·80(6)
C(13)–H(13)	0·82(7)	C(23)–H(23)	0·79(6)
C(14)–H(14)	0·84(7)	C(24)–H(24)	0·90(6)
C(15)–H(15)	0·80(6)	C(25)–H(25)	0·89(6)
C(16)–H(16)	0·78(7)	C(26)–H(26)	1·03(5)
C(32)–H(32)	0·95(6)	C(42)–H(42)	0·91(6)
C(33)–H(33)	0·93(7)	C(43)–H(43)	0·97(6)
C(34)–H(34)	0·85(6)	C(44)–H(44)	0·99(6)
C(35)–H(35)	0·83(7)	C(45)–H(45)	0·78(7)
C(36)–H(36)	0·86(7)	C(46)–H(46)	0·87(6)
C(51)–H(51)	0·96(7)		
C(52)–H(52)	0·86(6)		
C(53)–H(53)	0·75(6)		
C(54)–H(54)	0·84(6)		
C(55)–H(55)	0·87(7)		

(*b*) Angles

C(11)–B–C(21)	111·6(5)		
C(11)–B–C(31)	108·4(5)	C(51)–C(52)–C(53)	107·5(10)
C(11)–B–C(41)	111·6(4)	C(52)–C(53)–C(54)	110·5(10)
C(21)–B–C(31)	110·0(4)	C(53)–C(54)–C(55)	106·9(10)
C(21)–B–C(41)	109·0(5)	C(54)–C(55)–C(51)	107·7(9)
C(31)–B–C(41)	106·1(5)	C(55)–C(51)–C(52)	107·4(9)
C(11)–C(12)–C(13)	122·6(6)	C(31)–C(32)–C(33)	122·4(7)
C(12)–C(13)–C(14)	121·3(8)	C(32)–C(33)–C(34)	120·5(7)
C(13)–C(14)–C(15)	118·0(8)	C(33)–C(34)–C(35)	119·1(6)
C(14)–C(15)–C(16)	119·8(8)	C(34)–C(35)–C(36)	120·2(7)
C(15)–C(16)–C(11)	124·6(7)	C(35)–C(36)–C(31)	123·3(7)
C(16)–C(11)–C(12)	113·7(6)	C(36)–C(31)–C(32)	114·4(5)
C(21)–C(22)–C(23)	123·2(6)	C(41)–C(42)–C(43)	123·2(6)
C(22)–C(23)–C(24)	120·9(6)	C(42)–C(43)–C(44)	120·2(6)
C(23)–C(24)–C(25)	118·5(7)	C(43)–C(44)–C(45)	119·0(7)
C(24)–C(25)–C(26)	120·2(7)	C(44)–C(45)–C(46)	120·8(7)
C(25)–C(26)–C(21)	123·0(6)	C(45)–C(46)–C(41)	122·7(6)
C(26)–C(21)–C(22)	114·3(5)	C(46)–C(41)–C(42)	114·1(6)

TABLE 4

Least-square planes. *x*, *y*, and *z* in the equations of the planes are fractional co-ordinates in the direct cell. σ is the standard deviation from the plane of the atoms defining the plane

Equations of planes defined by C atoms in respective rings:

Ring (1): $8{\cdot}582x - 3{\cdot}807y + 1{\cdot}703z = 5{\cdot}565$

Ring (2): $-6{\cdot}732x + 3{\cdot}021y + 13{\cdot}054z = 2{\cdot}517$

Ring (3): $3{\cdot}608x + 12{\cdot}558y + 4{\cdot}997z = 7{\cdot}141$

Ring (4): $2{\cdot}025x - 4{\cdot}558y + 13{\cdot}084z = 6{\cdot}598$

Ring (5): $2{\cdot}073x - 3{\cdot}826y + 13{\cdot}264z = 3{\cdot}347$

C(42)—(46) $2{\cdot}072x - 4{\cdot}589y + 13{\cdot}047z = 6{\cdot}590$

TABLE 4 (*Continued*)

Distances (Å) from planes

Atoms \ Planes	(1)	(2)	(3)	(4)	(5)	C(42)—(46)
Ru				−1·701	1·817	−1·698
B	0·047	0·052	0·092	0·135		0·155
C(1)	−0·010	0·008	0·007	0·010	−0·005	0·021
C(2)	0·002	0·001	−0·002	−0·011	0·004	−0·004
C(3)	0·008	−0·010	−0·006	0·001	−0·002	0·001
C(4)	−0·010	0·010	0·010	0·010	−0·001	0·006
C(5)	0·002	−0·001	−0·005	−0·010	0·004	−0·010
C(6)	0·008	−0·008	−0·004	0·000		0·007
H(1)					−0·15	
H(2)	−0·01	−0·04	0·00	−0·14	−0·14	−0·13
H(3)	0·00	−0·07	0·03	−0·20	−0·08	−0·21
H(4)	−0·02	−0·02	0·00	−0·27	0·08	−0·28
H(5)	−0·02	0·00	−0·02	−0·02	0·06	−0·02
H(6)	−0·03	0·00	0·02	0·07		0·07
σ	0·008	0·008	0·007	0·009	0·004	0·007

DISCUSSION

The molecular structure of the compound is illustrated by the stereopair in Figure 2. The ruthenium atom is sandwiched between, and directly bonded to, the cyclopentadienyl ring [ring (5)] and one of the phenyl rings [ring (4)] of the BPh_4 group. The distances between the ruthenium atom and the best planes through the five-membered ring and the phenyl ring (Table 4) are 1·817 and 1·701 Å. The inter-ring distance is 3·52 Å and the angle between the two planes is 2·95°. Both rings are planar in contrast to the distortion of the bonded phenyl ring observed in $Rh[P(OMe)_3]_2BPh_4$,[10] and in (C_6H_6)-$RuCl_2(PMePh_2)$ and (p-$MeC_6H_4CHMe_2$)$RuCl_2(PMePh_2)$.[11]

Electron-diffraction studies of gaseous bis(benzene)-chromium [12] and ferrocene [13] showed that the hydrogen atoms on the carbon rings are probably bent out of the planes of these rings towards the metal atom by *ca.* 5°. The hydrogen atoms in this study appear not to be placed accurately enough to allow any conclusions regarding this effect as some of them are bent out of the plane of the carbon atoms in the ring by as much as 16°, but not all in the direction of the ruthenium atom. The mean C–H bond distance found is 0·87 Å which is shorter than that normally found for inorganic structures.[14]

The distances between the ruthenium and the carbon atoms in the cyclopentadienyl ring are all within 1σ of the mean value [2·170(6) Å]. The Ru–C(41) distance (*i.e.* to the carbon atom attached to the boron atom) 2·721 Å differs significantly from the mean [2·195(12) Å] to the other five carbon atoms in ring (4). This could be a steric effect and is a result of a number of deviations from the symmetrical shape of the six-membered ring, which are not individually significant but taken together could give rise to this lengthening: C(41) lies 0·021 Å from the best plane through atoms C(42)—(46), *i.e.* the plane through C(41), C(42), and C(46) makes an angle of

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1·47° with the aforementioned plane; bond lengths C(41)–C(42) and C(41)–C(46) are slightly longer than the other four; the projection of the ruthenium atom on the plane through ring (4) is 0·029 Å away from the centre of the ring.

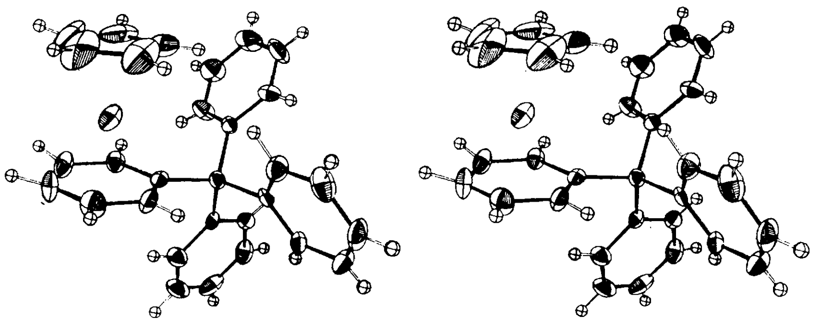

FIGURE 2 Stereoscopic drawing of the molecule showing the thermal ellipsoids at the 50% probability level

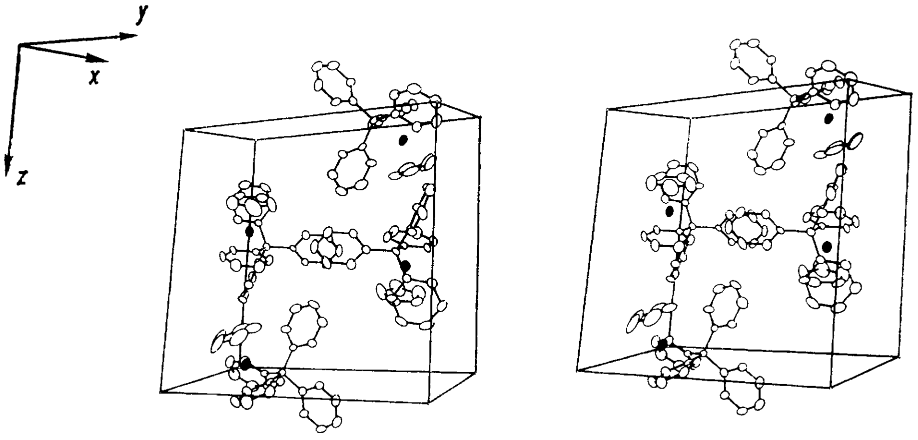

FIGURE 3 Stereoscopic view of the contents of the unit cell

The tetraphenylborate anion shows no appreciable distortion and the phenyl rings are bonded to the boron atom in a normal tetrahedral configuration with mean B–C 1·647(6) Å. Rings (1), (2), and (3) are planar, and the mean C–C distance for all three rings is 1·379(12) Å. The mean C–C distance in ring (4) [1·408(16) Å] compares well with that [1·410(4) Å] observed in the planar ring in bis(hexamethylbenzene)ruthenium(0).[15] The mean C–C distance in the five-membered ring is 1·394 (18) Å which is shorter than in ruthenocene [16] (1·43 Å), and in bis(dicarbonyl-π-cyclopentadienylruthenium) [17] (1·42 Å), but not significantly so.

The molecular packing is illustrated by the stereopair in Figure 3. Intermolecular contacts correspond to van der Waals interactions, the shortest being H · · · H 2·66, C · · · H 2·75, and C · · · C 3·53 Å.

The *X*-ray crystal structure determination of the title compound has revealed it to possess the structure originally suggested.[1] Although (π-C_5H_5)Ru(BPh_4) still represents the only example of a mixed-sandwich structure containing the tetraphenylborate anion directly bonded to the metal, its ready formation compared to the inability to obtain other mixed-sandwich complexes by a similar route still cannot be explained. A more detailed investigation of (π-C_5H_5)Ru(PPh_3)$_2$Cl may enable us to explain these anomalies.

[3/1908 *Received*, 17*th September*, 1973]

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