C(34)	1.2787 (18)	0.0900 (6)	0.5332 (11)	0.053 (3)
C(35)	1.1118 (17)	0.0914 (6)	0.4155 (10)	0.052 (3)
C(36)	1.4325 (19)	0.1723 (6)	0.5681 (11)	0.061 (3)
C(37)	1.4245 (21)	0.2320 (7)	0.4700 (13)	0.091 (3)
C(38)	1.2552 (21)	0.2192 (7)	0.5546 (13)	0.088 (3)
C(39)	0.7690 (17)	0.1750 (5)	0.2591 (10)	0.049 (3)
C(40)	0.7667 (19)	0.1656 (6)	0.1889 (10)	0.064 (3)
C(41)	0.6546 (21)	0.1681 (7)	0.1467 (12)	0.084 (3)
C(42)	0.5535 (22)	0.1810 (7)	0.1724 (14)	0.090 (3)
C(43)	0.5538 (22)	0.1909 (7)	0.2415 (14)	0.106 (3)
C(44)	0.6633 (18)	0.1880 (6)	0.2880 (11)	0.067 (3)
C(45)	0.4345 (19)	0.1844 (7)	0.1216 (11)	0.117 (3)
C(46)	1.5152 (16)	0.1076 (5)	0.4489 (9)	0.041 (3)
C(47)	1.5137 (17)	0.0649 (6)	0.4447 (10)	0.055 (3)
C(48)	1.6139 (16)	0.0412 (6)	0.4587 (9)	0.045 (3)
C(49)	1.7291 (18)	0.0608 (7)	0.4771 (10)	0.060 (3)
C(50)	1.7294 (19)	0.1028 (7)	0.4861 (11)	0.072 (3)
C(51)	1.6233 (17)	0.1268 (6)	0.4699 (10)	0.056 (3)
C(52)	1.8445 (17)	0.0338 (6)	0.4933 (11)	0.081 (3)

Table 2. *Selected geometric parameters (Å, °)*

Se(1)—Fe(1)	2.353 (3)	Se(1)—Fe(2)	2.353 (3)
Se(1)—Fe(3)	2.347 (3)	Se(1)—Fe(4)	2.358 (3)
Se(2)—Fe(1)	2.392 (3)	Se(2)—Fe(2)	2.390 (4)
Se(2)—C(13)	1.93 (2)	Se(3)—Fe(3)	2.386 (3)
Se(3)—Fe(4)	2.400 (4)	Se(3)—C(20)	1.92 (2)
Fe(1)—Fe(2)	2.601 (4)	Fe(3)—Fe(4)	2.575 (4)
Fe(1)—Se(1)—Fe(2)	67.1 (1)	Fe(1)—Se(1)—Fe(3)	140.4 (1)
Fe(2)—Se(1)—Fe(3)	133.4 (1)	Fe(1)—Se(1)—Fe(4)	135.4 (1)
Fe(2)—Se(1)—Fe(4)	126.4 (1)	Fe(3)—Se(1)—Fe(4)	66.4 (1)
Fe(1)—Se(2)—Fe(2)	65.9 (1)	Fe(3)—Se(3)—Fe(4)	65.1 (1)
Se(1)—Fe(1)—Se(2)	78.9 (1)	Se(1)—Fe(2)—Se(2)	78.9 (1)
Se(1)—Fe(3)—Se(3)	78.4 (1)	Se(1)—Fe(4)—Se(3)	77.9 (1)

The structure was solved by Patterson superposition and successive difference Fourier syntheses. The non-H atoms were subjected to anisotropic refinement. All H atoms were generated geometrically (C—H = 0.96 Å), allowed to ride on their respective parent C atom, assigned the same isotropic displacement parameters ($U = 0.08$ Å^2) and included in the structure-factor calculations. Computations were performed using a PC 486 computer.

Data collection: Seimens software. Cell refinement: Seimens software. Data reduction: Seimens software. Program(s) used to solve structure: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *XLS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1209). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis{[3-(diphenylphosphino)propyl]trimethylphosphonium-*P*}[(2,3,5,6-*η*)norbornadiene]rhodium(I) Tris(tetrafluoroborate)

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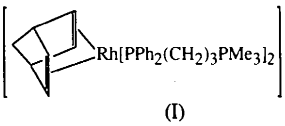
Abstract

The title complex, $[Rh(C_{18}H_{25}P_2)_2(C_7H_8)](BF_4)_3$, is representative of a family of excellent biphasic olefin hydrogenation catalysts. The cation exhibits essentially square-planar geometry around the Rh^I ion, with the two PPh_2 groups and the two norbornadiene C═C double bonds forming the inner coordination sphere; Rh—P 2.3082 (11) and 2.3332 (12), and Rh—C 2.180 (5)–2.204 (5) Å.

Comment

The chemistry and catalytic activity of rhodium(I) complexes containing two coordinated [3-(diphenylphosphino)propyl]trimethylphosphonium (henceforth III-phophos) ions and higher homologues have been of particular interest because of the ease with which the catalysts can be heterogenized. Thus, bis(phophos)-rhodium(I) complexes are active for the hydrogenation of olefins both in aqueous solution and when supported, *via* the phosphonium ion end groups, on a cationic exchange resin (Renaud, Russell, Fortier, Brown & Baird, 1991; Renaud & Baird, 1992, 1993). We have reported the crystal and molecular structure of the mono(II-phophos) cationic complex $[(NBD)RhCl(II\text{-}phophos)]PF_6$ {where NBD is norbornadiene and II-phophos is [2-(diphenylphosphino)ethyl]trimethylphosphonium} (Renaud, Russell, Fortier, Brown & Baird, 1991) and now report the crystal and molecular structure of the analogous bis(III-phophos) complex $[(NBD)Rh(III\text{-}phophos)_2](BF_4)_3$, (I), which is of interest both because it is the direct precursor of the III-phophos catalyst system and because no X-ray crystallographic information seems to be available for complexes of the type $[(NBD)Rh(monodentate\ phosphine)_2]^{n+}$.



(I)

The crystal structure consists of discrete $[cis\text{-}(NBD)Rh(III\text{-}phophos)_2]^{3+}$ cations and BF_4 anions, with no short anion–cation contacts. A perspective view of the cation is given in Fig. 1. The Rh atom assumes the expected four-coordinate square-planar structure, with the two diphenylphosphino groups and the two NBD C=C double bonds forming the inner coordination sphere. Thus, the sum of the angles P1—Rh—P3, *MP*1—Rh—*MP*2 (where *MP*1 is the midpoint of C37=C38 and *MP*2 is the midpoint of C40=C41), P1—Rh—*MP*2 and P3—Rh—*MP*1 is 360.8°.

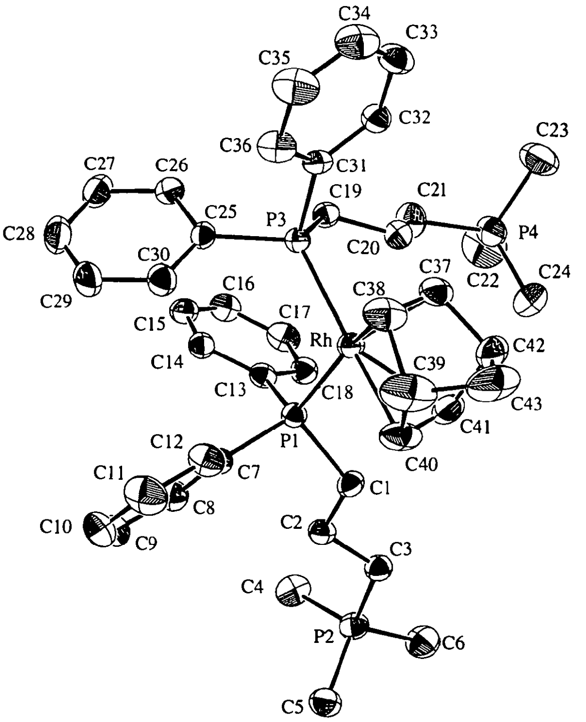


Fig. 1. The molecular structure of the title cation with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

The bite angle of the NBD ligand (*MP*1—Rh—*MP*2) is 69.7 (3)°, somewhat less than observed previously either for a four-coordinate NBD–rhodium(I) complex of a bidentate ligand (Cullen, Einstein, Huang, Willis & Yeh, 1980) or for two five-coordinate NBD complexes of tridentate ligands (Bachechi, Ott & Venanzi, 1989*a*,*b*). In addition, the P1—Rh—P3 bond angle of 96.96 (4)° is, as anticipated, considerably greater than has been observed for a number of similar complexes of rhodium(I) containing bidentate diphosphines (Ball & Payne, 1977).

The Rh—P distances of 2.3082 (11) and 2.3332 (12) Å are significantly larger than the Rh—P distance in $[(NBD)RhCl(III\text{-}phophos)]PF_6$ [2.293 (2) Å; Renaud *et al.*, 1991], possibly reflecting greater steric strain in the more crowded bis(phophos) complex. The difference between the Rh—P1 and Rh—P3 bonds is likely due to the different orientations of the coordinated III-phophos ligands relative to the NDB ligand. On the other hand, the Rh—NBD distances [2.195 (5), 2.180 (5), 2.204 (5) and 2.192 (6) Å] are all comparable to the Rh—NBD distances of the olefinic bond *trans* to the phophos ligand in $[(NBD)RhCl(II\text{-}phophos)]PF_6$ [2.220 (6) and 2.206 (7) Å; Renaud *et al.*, 1991]. The Rh—NBD distances of the olefinic bond *cis* to the phophos ligand in $[(NBD)RhCl(II\text{-}phophos)]PF_6$ are much shorter, [2.095 (6) and 2.089 (6) Å], presumably reflecting the position of the Cl atom relative to the phosphorus donors in the *trans*-influence series (Appleton, Clark & Manzer, 1973).

The intramolecular bond distances and angles of the coordinated NBD are much as anticipated. The C37=C38 [1.336 (10) Å] and C40=C41 [1.316 (11) Å] distances are normal for coordinated olefins and all other C—C bonds exhibit normal C—C single-bond distances (1.524–1.565 Å). The intramolecular bond distances and angles of the coordinated III-phophos ligands are also largely as anticipated, although it was noted that the two Me_3P—C—C [115.6 (3) and 117.0 (4)°] and the two Ph_2P—C—C [118.3 (3) and 114.8 (3)°] bond angles were all significantly greater than the CH_2—CH_2—CH_2 bond angles [109.5 (4) and 110.9 (4)°], again possibly reflecting the apparently differing degrees of steric congestion.

Experimental

Crystals of the title compound were obtained from acetone/ethanol solution.

Crystal data

$[Rh(C_{18}H_{25}P_2)_2(C_7H_8)]\text{-}(BF_4)_3$
$M_r = 1062.11$
Triclinic
$P\bar{1}$
$a = 14.021\ (2)$ Å
$b = 15.613\ (2)$ Å
$c = 15.430\ (2)$ Å
$\alpha = 116.34\ (1)°$
$\beta = 124.84\ (1)°$
$\gamma = 75.36\ (1)°$
$V = 2484.5\ (6)$ Å^3
$Z = 2$
$D_x = 1.420$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 13.2\text{–}14.6°$
$\mu = 0.547$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.55 × 0.40 × 0.09 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
11 273 measured reflections
10 824 independent reflections
6255 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0223$
$\theta_{\rm max} = 26.97°$
$h = 0 \rightarrow 17$
$k = -19 \rightarrow 19$
$l = -19 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0495$
$wR(F^2) = 0.1228$
$S = 1.155$
10 824 reflections
724 parameters
H atoms riding (C—H 0.93–0.98 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.012$
$\Delta\rho_{\rm max} = 0.809$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.374$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	$U_{\rm eq}$
Rh	1.00	0.19806 (3)	0.18089 (2)	0.05859 (3)	0.04471 (13)
P1	1.00	0.30075 (10)	0.22174 (8)	0.25527 (9)	0.0424 (3)
P2	1.00	0.31944 (12)	0.11163 (10)	0.57106 (11)	0.0554 (3)
P3	1.00	0.18036 (10)	0.33368 (8)	0.06321 (9)	0.0409 (3)
P4	1.00	−0.21014 (13)	0.36739 (12)	0.09491 (14)	0.0689 (4)
C1	1.00	0.2611 (4)	0.1432 (3)	0.2906 (4)	0.0499 (11)
C2	1.00	0.3228 (4)	0.1581 (3)	0.4167 (4)	0.0514 (11)
C3	1.00	0.2559 (4)	0.1065 (3)	0.4297 (4)	0.0531 (11)
C4	1.00	0.3673 (6)	0.2299 (4)	0.6701 (5)	0.075 (2)
C5	1.00	0.4393 (5)	0.0312 (4)	0.6065 (5)	0.0696 (15)
C6	1.00	0.2096 (6)	0.0762 (5)	0.5736 (6)	0.088 (2)
C7	1.00	0.4567 (4)	0.2043 (3)	0.3128 (4)	0.0488 (10)
C8	1.00	0.5367 (4)	0.2357 (4)	0.4285 (4)	0.0584 (12)
C9	1.00	0.6546 (5)	0.2216 (4)	0.4691 (5)	0.074 (2)
C10	1.00	0.6911 (5)	0.1782 (5)	0.3937 (7)	0.086 (2)
C11	1.00	0.6118 (6)	0.1461 (5)	0.2795 (7)	0.091 (2)
C12	1.00	0.4955 (5)	0.1591 (4)	0.2385 (5)	0.0653 (14)
C13	1.00	0.2868 (4)	0.3420 (3)	0.3471 (3)	0.0455 (10)
C14	1.00	0.3549 (4)	0.4163 (3)	0.3843 (4)	0.0493 (10)
C15	1.00	0.3334 (4)	0.5095 (3)	0.4424 (4)	0.0568 (12)
C16	1.00	0.2479 (5)	0.5291 (4)	0.4659 (4)	0.0618 (13)
C17	1.00	0.1814 (5)	0.4560 (4)	0.4307 (4)	0.0652 (14)
C18	1.00	0.1997 (4)	0.3623 (3)	0.3707 (4)	0.0539 (11)
C19	1.00	0.0832 (4)	0.4071 (3)	0.1122 (4)	0.0452 (10)
C20	1.00	−0.0156 (4)	0.3523 (3)	0.0801 (4)	0.0536 (11)
C21	1.00	−0.0821 (5)	0.4161 (4)	0.1349 (5)	0.0697 (15)
C22	1.00	−0.2346 (8)	0.4291 (7)	0.2086 (8)	0.130 (3)
C23	1.00	−0.3301 (6)	0.3817 (6)	−0.0320 (7)	0.114 (3)
C24	1.00	−0.1917 (6)	0.2434 (5)	0.0698 (7)	0.103 (2)
C25	1.00	0.3104 (4)	0.4061 (3)	0.1496 (3)	0.0461 (10)
C26	1.00	0.3084 (4)	0.5052 (3)	0.1956 (4)	0.0553 (12)
C27	1.00	0.4110 (5)	0.5571 (4)	0.2642 (4)	0.0693 (15)
C28	1.00	0.5138 (5)	0.5100 (5)	0.2849 (5)	0.077 (2)
C29	1.00	0.5172 (5)	0.4127 (5)	0.2385 (5)	0.070 (2)
C30	1.00	0.4162 (4)	0.3601 (4)	0.1704 (4)	0.0567 (12)
C31	1.00	0.1184 (4)	0.3377 (3)	−0.0762 (4)	0.0463 (10)
C32	1.00	−0.0005 (4)	0.3445 (3)	−0.1480 (4)	0.0556 (12)
C33	1.00	−0.0472 (5)	0.3401 (4)	−0.2570 (4)	0.071 (2)
C34	1.00	0.0231 (6)	0.3281 (4)	−0.2958 (5)	0.078 (2)
C35	1.00	0.1414 (6)	0.3214 (5)	−0.2254 (5)	0.081 (2)
C36	1.00	0.1892 (5)	0.3262 (4)	−0.1165 (5)	0.0645 (14)
C37	1.00	0.0674 (6)	0.1213 (4)	−0.1245 (4)	0.074 (2)
C38	1.00	0.1727 (7)	0.1030 (4)	−0.1104 (5)	0.078 (2)
C39	1.00	0.2079 (8)	0.0053 (5)	−0.1007 (6)	0.115 (3)
C40	1.00	0.2219 (8)	0.0254 (4)	0.0149 (5)	0.088 (2)
C41	1.00	0.1182 (7)	0.0470 (5)	0.0008 (5)	0.085 (2)
C42	1.00	0.0318 (7)	0.0369 (4)	−0.1232 (5)	0.099 (3)
C43	1.00	0.0889 (9)	−0.0431 (5)	−0.1812 (6)	0.150 (5)
B1	1.00	0.2748 (5)	−0.1747 (4)	0.2732 (5)	0.079 (2)
F11	1.00	0.3886 (3)	−0.1807 (3)	0.3493 (4)	0.1142 (14)
F12	1.00	0.2259 (4)	−0.2592 (3)	0.2038 (4)	0.151 (2)
F13	1.00	0.2617 (5)	−0.1190 (4)	0.2194 (5)	0.152 (2)
F14	1.00	0.2200 (4)	−0.1252 (3)	0.3347 (4)	0.1116 (13)
B2	1.00	0.4920 (5)	0.1719 (5)	−0.0559 (5)	0.102 (2)
F21	1.00	0.5469 (5)	0.1206 (4)	−0.1116 (5)	0.166 (2)
F22*A*	0.454 (14)	0.4934 (17)	0.1473 (11)	0.0150 (11)	0.152 (5)
F23*A*	0.454 (14)	0.5040 (18)	0.2681 (6)	−0.0182 (18)	0.139 (6)
F24*A*	0.454 (14)	0.3790 (8)	0.1495 (13)	−0.1542 (9)	0.136 (5)
F22*B*	0.440 (15)	0.3930 (10)	0.1466 (11)	−0.0856 (19)	0.188 (7)
F23*B*	0.440 (15)	0.5744 (12)	0.1831 (12)	0.0550 (7)	0.148 (6)
F24*B*	0.440 (15)	0.4789 (18)	0.2635 (7)	−0.0579 (16)	0.135 (6)
F22*C*	0.107 (12)	0.394 (2)	0.214 (3)	−0.107 (2)	0.166 (19)
F23*C*	0.107 (12)	0.571 (2)	0.235 (2)	0.0475 (14)	0.106 (8)
F24*C*	0.107 (12)	0.470 (4)	0.1032 (15)	−0.034 (3)	0.130 (6)
B3	1.00	−0.0005 (5)	0.2935 (4)	0.4332 (5)	0.088 (2)
F31	1.00	0.0019 (4)	0.2682 (4)	0.3388 (3)	0.123 (2)
F32*A*	0.34 (2)	−0.063 (2)	0.3666 (14)	0.456 (2)	0.105 (5)
F33*A*	0.34 (2)	−0.026 (2)	0.2143 (11)	0.4329 (18)	0.105 (4)
F34*A*	0.34 (2)	0.1173 (10)	0.313 (2)	0.5204 (14)	0.140 (10)
F32*B*	0.29 (2)	−0.0997 (13)	0.326 (3)	0.4248 (19)	0.133 (9)
F33*B*	0.29 (2)	0.090 (2)	0.353 (2)	0.5264 (11)	0.120 (7)
F34*B*	0.29 (2)	0.020 (4)	0.2051 (10)	0.445 (2)	0.179 (11)
F32*C*	0.16 (2)	0.059 (4)	0.241 (3)	0.494 (3)	0.124 (13)
F33*C*	0.16 (2)	0.022 (4)	0.3887 (10)	0.497 (3)	0.123 (11)
F34*C*	0.16 (2)	−0.1190 (13)	0.282 (3)	0.386 (2)	0.125 (11)
F32*D*	0.21 (2)	−0.076 (3)	0.251 (2)	0.425 (2)	0.097 (4)
F33*D*	0.21 (2)	0.1098 (12)	0.291 (3)	0.5222 (15)	0.106 (7)
F34*D*	0.21 (2)	−0.032 (3)	0.3903 (10)	0.454 (3)	0.142 (10)

Table 2. *Selected geometric parameters (Å, °)*

Rh—P1	2.3332 (12)	P3—C31	1.828 (4)
Rh—P3	2.3082 (11)	P4—C21	1.786 (5)
Rh—*MP*1 †	2.083 (5)	P4—C22	1.774 (8)
Rh—*MP*2 †	2.097 (5)	P4—C23	1.775 (7)
Rh—C37	2.195 (5)	P4—C24	1.777 (7)
Rh—C38	2.180 (5)	C1—C2	1.538 (6)
Rh—C40	2.204 (5)	C2—C3	1.520 (6)
Rh—C41	2.192 (6)	C19—C20	1.529 (6)
P1—C1	1.842 (4)	C20—C21	1.504 (7)
P1—C7	1.827 (5)	C37—C38	1.336 (10)
P1—C13	1.828 (4)	C37—C42	1.534 (8)
P2—C3	1.794 (5)	C38—C39	1.526 (9)
P2—C4	1.774 (6)	C39—C40	1.565 (10)
P2—C5	1.787 (5)	C39—C43	1.527 (12)
P2—C6	1.788 (6)	C40—C41	1.316 (11)
P3—C19	1.833 (4)	C41—C42	1.526 (8)
P3—C25	1.819 (4)	C42—C43	1.524 (12)
P1—Rh—P3	96.96 (4)	C21—P4—C22	107.7 (4)
P1—Rh—*MP*1	166.5 (2)	C21—P4—C23	109.9 (3)
P1—Rh—*MP*2	98.0 (2)	C21—P4—C24	110.4 (3)
P3—Rh—*MP*1	96.1 (2)	C22—P4—C23	110.6 (4)
P3—Rh—*MP*2	163.3 (2)	C22—P4—C24	109.8 (4)
*MP*1—Rh—*MP*2	69.7 (3)	C23—P4—C24	108.5 (4)
Rh—P1—C1	111.11 (15)	P1—C1—C2	118.3 (3)
Rh—P1—C7	110.8 (2)	C1—C2—C3	109.5 (4)
Rh—P1—C13	119.69 (14)	C2—C3—P2	115.6 (3)
C1—P1—C7	105.3 (2)	P3—C19—C20	114.8 (3)
C1—P1—C13	103.7 (2)	C19—C20—C21	110.9 (4)
C7—P1—C13	105.1 (2)	C20—C21—P4	117.0 (4)
C3—P2—C4	109.3 (2)	C38—C37—C42	108.1 (6)
C3—P2—C5	111.3 (3)	C37—C38—C39	106.2 (7)
C3—P2—C6	107.2 (3)	C38—C39—C40	102.5 (5)
C4—P2—C5	109.5 (3)	C38—C39—C43	99.8 (6)
C4—P2—C6	111.0 (3)	C40—C39—C43	98.2 (8)
C5—P2—C6	108.6 (3)	C39—C40—C41	107.0 (7)
Rh—P3—C19	111.63 (14)	C40—C41—C42	107.7 (7)
Rh—P3—C25	119.0 (2)	C37—C42—C41	101.1 (4)
Rh—P3—C31	113.59 (14)	C37—C42—C43	98.4 (7)

C19—P3—C25	104.7 (2)	C41—C42—C43	100.5 (6)
C19—P3—C31	105.1 (2)	C39—C43—C42	94.4 (5)
C25—P3—C31	101.4 (2)		

† *MP*1 and *MP*2 are the midpoints of the C37=C38 and C40=C41 double bonds, respectively.

Of the three tetrafluoroborate ions, one (that containing the B1 atom) was found to be well ordered, while the other two (those containing the B2 and B3 atoms) were found to be disordered in several orientations of three of the F atoms around the B—F bond to the fourth F atom. Ion 'B2' was modelled in three different orientations, *A*, *B* and *C* (with the sum of the occupation factors of these three being fixed as 100%), and ion 'B3' in four orientations, *A*, *B*, *C* and *D* (again with the sum of the occupation factors of these four being fixed as 100%). The refinement of these two ions was restrained to keep the geometry of the four F atoms around the B atom similar to the geometry of the ordered 'B1' ion. All the tetrafluoroborate atoms were refined with anisotropic displacement parameters; for disordered F atoms they were restrained by the commands *DELU* and *SIMU* of *SHELXL*93 (Sheldrick, 1993).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Monoclinic Form of Tetrakis(1-methylimidazole-N^3)platinum(II) Diperchlorate

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Abstract

The monoclinic polymorph of the title compound, $[Pt(C_4H_6N_2)_4](ClO_4)_2$, is reported. The two main differences between this form and the triclinic form reported previously lie in the conformation of the $[Pt(C_4H_6N_2)_4]^{2+}$ cation and in the crystal packing. In both forms, the cation lies on an inversion center, but the orientations of the 1-methylimidazole (MeIm) ligands are different. In the present study, two *trans*-MeIm ligands are oriented perpendicular to the Pt coordination plane, while the other two are approximately coplanar with this plane. This is the first reported instance of coplanarity in an *N*-alkylimidazole–platinum(II) complex. The packing of the molecular cations in the monoclinic form involves no π-stacking, in contrast to the packing observed in the triclinic form.

Comment

The anticancer properties of some platinum(II) complexes are well known (*e.g.* Pasini & Zunino, 1987, and references therein). We have begun a study of the synthesis and characterization of a number of Pt^{II}–amine complexes (Clement, 1995; Buncel & Clement, 1995; Roszak, Clement & Buncel, 1996; Clement, Roszak & Buncel, 1996*a*,*b*) in continuation of our study of metal ion–biomolecule interactions (Buncel, Joly & Jones, 1986; Buncel, Joly & Yee, 1989; Buncel, Clement, Fan, Joly, Jones & Onyido, 1991; Buncel, Clement & Onyido, 1994; Buncel, Fan, Moir & Onyido, 1995). In this regard, we have recently described the triclinic form of the title compound, tetrakis(1-methylimidazole)platinum(II) diperchlorate, $[Pt(MeIm)_4](ClO_4)_2$, (I), where MeIm is the 1-methylimidazole ligand (Clement, Roszak & Buncel, 1996*a*). The complex was isolated as small colorless prisms from a methanolic solution of *cis*-$[Pt(DMSO)_2Cl_2]$ and excess 1-methylimidazole, following the modified procedure of Reedijk and co-workers (Graves, Hodgson, van Kralingen & Reedijk, 1978). In the present study, a monoclinic form of (I) is described. In this work, the complex isolated from methanol was redissolved in water and allowed to crystallize slowly at

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