planar arrangement with Cu—N and Cu—O bond lengths of 1.981 (2) Å. The methanol oxygen atoms of the 2-pyridylmethanols with two much longer out-of-plane Cu—O bonds [2.331 (1) Å] complete the distorted octahedral coordination of the metal atom. The observed values of the Cu—O(2) and Cu—N bond lengths are somewhat different from the literature values (Davey & Stephens, 1971; Greenaway, Pezeshk, Cordes, Noble & Sorenson, 1984). In the structures of $Cu(sal)_2(C_6H_{12}N_2)$ (Muhonen & Hämäläinen, 1978), $Cu(sal)_2.2H_2O$ (Jagner, Grønbæk & Larsen, 1976) and $[Cu(sal)_2(H_2O)_2].2H_2O$ (Rissanen, Valkonen, Kokkonen & Leskelä, 1987) salicylate anions are bonded as chelates to the copper(II) atom by both carboxyl oxygen atoms and create a four-membered intrachelate ring with a very small O—Cu—O angle (nearly 45°), one short Cu—O bond (nearly 2.0 Å) and another longer one (ranging from 2.50 to 3.00 Å).

The dihedral angle between the least-squares planes through the pyridine and benzene rings of both ligands is 73.05 (9)°. The intrachelate five-membered metallocycles in the compound studied are not planar and the atom O(3) is displaced from the least-squares plane by 0.224 (2) Å. The dihedral angle between this plane and the least-squares plane of the pyridine ring is 9.61 (6)°. The carboxyl oxygen atoms O(1), O(2) and the copper atom are displaced from the least-squares plane of the salicylate ring by 0.096 (1), 0.152 (1) and 0.5335 (2) Å, respectively. O(1) and the monodentate atoms show similar thermal motion perpendicular to the salicylate least-squares plane. Details of least-squares planes and benzene rings have been deposited. The mean values of the C—C bond lengths and C—C—C bond angles in the benzene rings of the salicylates (Table 2) are close to the values of 1.38 (2) Å and 120.0 (4)° found in $[Cu(sal)_2(H_2O)_2].2H_2O$ (Rissanen, Valkonen, Kokkonen & Leskelä, 1987) and with values of 1.388 Å found in the salicylate ring of $Cu(sal)_2(C_6H_{12}N_2)$ (Muhonen & Hämäläinen, 1978). The mean values of the C—N and C—C bond lengths, and of the N—C—C, C—N—C and C—C—C bond angles in the 2-pycar pyridine ring (Table 2) agree well with the values of 1.390 and 1.400 Å found in the pyridine molecule (Bak, Hansen & Rastrup-Andersen, 1954).

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(1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane-*P*,*P*′,*P*″,*P*‴)hydridoplatinum(II) Tetraphenylborate

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Abstract. $[PtH\{(C_6H_5)_2PC_2H_4P(C_6H_5)CH_2\}_2][(C_6H_5)_4B]$, $M_r = 1186.06$, triclinic, $P\bar{1}$, $a = 12.126$ (3), $b = 16.343$ (4), $c = 16.390$ (6) Å, $\alpha = 74.31$ (3), $\beta = 76.02$ (2), $\gamma = 67.38$ (2)°, $V = 2851.72$ Å^3, $Z = 2$, $D_m = 1.40$, $D_x = 1.381$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.485$ mm^{-1}, $F(000) = 1204$, $T = 294$ K, final $R = 0.066$ for 4485 observed reflections. The X-ray structure analysis shows a

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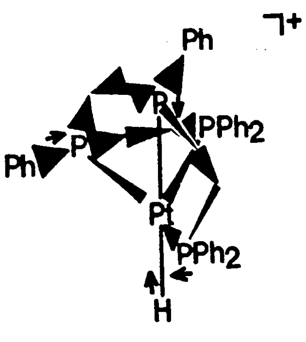
distorted trigonal-bipyramidal structure and corresponds to the chiral form of the two possible diastereomers of the title compound. The hydride ligand is assumed to occupy one axial position. The distortions of the trigonal bipyramid are mainly a consequence of the steric requirements of non-planar tetracoordinate forms of chiral 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (P_4), the hydride ligand being responsible for the deviation from a planar P_4 arrangement resulting in a fluxional solution structure belonging to a Berry-type mechanism. Two of the Pt—P bonds are shortened (mean value: 2.263 Å) compared with the other two [mean value: 2.344 (4) Å] and the P—Pt—P angles, where the phosphorus atoms are not connected by ethylene groups, are markedly opened.

Introduction. 1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane (P_4) is flexible enough to allow different coordination geometries (Bacci, Ghilardi & Orlandini, 1984; Brown & Canning, 1984; Brüggeller, 1989*a*,*b*). In the case of five-coordinate species of platinum(II) containing P_4 as a tetradentate ligand the coordination type of P_4 depends on the kind of fifth ligand present (Brüggeller, 1989*a*,*b*). Thus the reduction of chiral $[Pt(P_4)](BPh_4)_2$ with $NaBH_4$ leads to the title compound, chiral $[PtH(P_4)](BPh_4)$ (1), which shows an intermediate P_4 coordination along the square-planar to tetrahedral reaction coordinate in solution. Depending on the solvent and the counterion these five-coordinate platinum(II) hydrides of type (1) also show the presence of a Berry-type rearrangement process (Berry, 1960) (ligand movement indicated by arrows in the scheme below) leading to a trigonal bipyramid with the hydride ligand in an axial position as the energetically favoured coordination. In order to determine the kind of static limit structure of (1) within the square-planar to tetrahedral movement and the possible occurrence of a Berry mechanism an X-ray structure analysis was performed.



Experimental. The title compound (1) (Brüggeller, 1989*a*,*b*) was crystallized from CH_2Cl_2 and a crystal with dimensions 0.45 × 0.30 × 0.17 mm was sealed into a capillary. Data collection was with an Enraf–Nonius CAD-4 diffractometer in $\omega/2\theta$ scan mode. Cell parameters were obtained from the orientation matrix of 23 centred reflections in the range $1.6 \leq \theta \leq 12.0°$. Three monitor reflections ($0\bar{5}\bar{2}$, $\bar{3}\bar{3}\bar{8}$, $\bar{6}\bar{5}\bar{3}$) showed no significant intensity variations. Intensity data were collected in the range $0.0 \leq \theta \leq 22.5°$, $-13 \leq h \leq 13$, $-17 \leq k \leq 17$, $-17 \leq l \leq 17$ ($R_{\text{int}} = 0.054$) leading to 6306 unique reflections, 1768 of which were unobserved [$I \leq 2\sigma(I)$]. The data were corrected for Lorentz and polarization effects and for absorption. The empirical absorption correction was based on ψ scans of nine reflections (North, Phillips & Mathews, 1968). Min. and max. transmission factors were 0.81 and 0.99. The structure was solved by Patterson methods and completed by successive Fourier syntheses. The crystallographic computations were mainly performed using *SHELX76* and *SHELXS86* [Sheldrick (1976) and Sheldrick (1985) respectively]. The structure refinement was performed by using least-squares procedures on the basis of *F*. Some H atoms emerged from the difference Fourier syntheses; however, inclusion of these H atoms in the refinement led to no further H positions. With 4485 observed reflections (53 reflections with $|\Delta F| > 5$ omitted) convergence occurred at $R = 0.066$, $wR = 0.061$, $w = k/[\sigma^2(|F_o|) + 0.0005|F_o|^2]$, 602 parameters (neglecting the H atoms) refined. $(\Delta/\sigma)_{\max} = 0.15$ (neglecting the rigid group), min. and max. heights in final difference Fourier synthesis were −1.49 and 1.51 e Å^{-3}, $S = 1.5040$.

Discussion. Fractional atomic coordinates and equivalent isotropic thermal parameters are summarized in Table 1,* selected bond distances and bond angles in Table 2. The structure of the cation of (1) is shown in Fig. 1.

The crystal structure consists of discrete $[PtH(P_4)]^+$ cations and $(BPh_4)^-$ anions. The cation shows a strongly distorted trigonal-bipyramidal coordination geometry, which confirms the presence of the Berry mechanism in solutions of (1) (Brüggeller, 1989*a*,*b*) corresponding to the static limit structure of this rearrangement process (Meakin, Muetterties & Jesson, 1972; Tulip, Yamagata, Yoshida, Wilson, Ibers & Otsuka, 1979), and is the chiral form of the two possible diastereomers. The hydride ligand occupies an axial position which is the energetically favoured coordination type (Meakin,

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* Lists of structure factors, positional and temperature parameters, bond distances, bond angles and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54622 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and thermal parameters of non-*H *atoms*

The equivalent isotropic thermal parameters result from $\frac{1}{3}$ of the trace of the anisotropic B_{ij} tensor. The e.s.d.'s in the least significant figures are given in parentheses

	x	*y*	*z*	B_{eq}(Å^2)
Pt(1)	0.1125 (1)	0.2518 (5)	0.3600 (5)	2.8 (2)
P(1)	0.0339 (4)	0.2524 (3)	0.4984 (3)	4.2 (2)
P(2)	0.2894 (4)	0.2323 (3)	0.2586 (3)	3.5 (2)
P(3)	0.0173 (4)	0.2730 (3)	0.2437 (3)	3.9 (2)
P(4)	0.0374 (4)	0.4062 (3)	0.3379 (3)	3.6 (2)
C(1)	0.2349 (14)	0.3056 (12)	0.1581 (10)	4.8 (9)
C(2)	0.1287 (16)	0.2845 (12)	0.1458 (10)	5.4 (10)
C(3)	−0.1021 (14)	0.3857 (10)	0.2365 (11)	4.5 (9)
C(4)	−0.0514 (15)	0.4538 (10)	0.2464 (11)	4.4 (9)
C(5)	−0.0721 (15)	0.4361 (10)	0.4333 (11)	4.1 (9)
C(6)	−0.0195 (15)	0.3690 (11)	0.5131 (11)	4.8 (10)
C(11)	−0.0968 (16)	0.2149 (13)	0.5344 (10)	4.7 (10)
C(12)	−0.0754 (20)	0.1237 (14)	0.5429 (14)	7.5 (13)
C(13)	−0.1778 (25)	0.0938 (18)	0.5640 (17)	10.2 (18)
C(14)	−0.2943 (25)	0.1560 (26)	0.5780 (17)	9.9 (19)
C(15)	−0.3116 (22)	0.2430 (18)	0.5699 (17)	7.8 (16)
C(16)	−0.2141 (19)	0.2759 (15)	0.5484 (12)	6.5 (12)
C(21)	0.1283 (17)	0.1899 (11)	0.5785 (12)	6.5 (5)
C(22)	0.0813 (17)	0.1962 (11)	0.6640 (12)	10.3 (7)
C(23)	0.1568 (17)	0.1557 (11)	0.7265 (12)	16.6 (12)
C(24)	0.2793 (17)	0.1089 (11)	0.7035 (12)	15.8 (11)
C(25)	0.3263 (17)	0.1026 (11)	0.6180 (12)	22.4 (17)
C(26)	0.2508 (17)	0.1431 (11)	0.5555 (12)	13.5 (10)
C(31)	0.4109 (15)	0.2658 (12)	0.2681 (14)	4.8 (10)
C(32)	0.4602 (18)	0.3215 (14)	0.2098 (15)	7.2 (13)
C(33)	0.5614 (24)	0.3373 (20)	0.2257 (19)	9.0 (18)
C(34)	0.6045 (27)	0.2996 (24)	0.3007 (28)	12.3 (26)
C(35)	0.5567 (26)	0.2394 (22)	0.3576 (21)	12.1 (23)
C(36)	0.4574 (19)	0.2219 (15)	0.3461 (17)	7.8 (15)
C(41)	0.3619 (15)	0.1232 (11)	0.2271 (11)	4.0 (9)
C(42)	0.4771 (16)	0.1077 (13)	0.1729 (11)	5.1 (10)
C(43)	0.5295 (17)	0.0235 (13)	0.1406 (13)	5.4 (11)
C(44)	0.4749 (21)	−0.0368 (13)	0.1659 (14)	5.8 (12)
C(45)	0.3633 (20)	−0.0202 (12)	0.2215 (14)	6.8 (12)
C(46)	0.3084 (18)	0.0586 (13)	0.2538 (13)	6.4 (12)
C(51)	−0.0525 (16)	0.2009 (12)	0.2314 (13)	5.2 (10)
C(52)	−0.0916 (19)	0.2171 (17)	0.1499 (15)	8.5 (15)
C(53)	−0.1378 (27)	0.1564 (25)	0.1339 (23)	13.1 (25)
C(54)	−0.1614 (29)	0.0927 (21)	0.1998 (25)	11.6 (23)
C(55)	−0.1248 (29)	0.0756 (17)	0.2800 (25)	15.0 (25)
C(56)	−0.0747 (20)	0.1349 (14)	0.2999 (17)	8.9 (15)
C(61)	0.1349 (15)	0.4721 (11)	0.3186 (11)	3.8 (9)
C(62)	0.1125 (16)	0.5560 (12)	0.2623 (11)	5.2 (10)
C(63)	0.1927 (21)	0.6047 (13)	0.2465 (13)	6.3 (12)
C(64)	0.2915 (20)	0.5704 (15)	0.2898 (15)	6.6 (13)
C(65)	0.3125 (17)	0.4892 (15)	0.3478 (14)	6.7 (12)
C(66)	0.2343 (18)	0.4383 (12)	0.3629 (12)	5.4 (11)
B(1)	0.3675 (19)	0.3327 (15)	0.8701 (12)	4.6 (11)
C*A*(1)	0.2847 (16)	0.2656 (12)	0.9103 (11)	4.2 (10)
C*B*(1)	0.3239 (17)	0.1832 (12)	0.9645 (12)	5.0 (10)
C*C*(1)	0.2507 (25)	0.1262 (14)	0.9977 (12)	6.4 (13)
C*D*(1)	0.1418 (23)	0.1505 (17)	0.9711 (16)	6.9 (14)
C*E*(1)	0.0960 (18)	0.2327 (15)	0.9209 (17)	7.9 (14)
C*F*(1)	0.1702 (15)	0.2925 (13)	0.8853 (12)	5.3 (10)
C*A*(2)	0.3642 (13)	0.3716 (13)	0.7665 (12)	4.5 (10)
C*B*(2)	0.3460 (18)	0.3231 (15)	0.7152 (14)	6.7 (13)
C*C*(2)	0.3549 (20)	0.3521 (18)	0.6277 (16)	7.0 (15)
C*D*(2)	0.3745 (19)	0.4305 (20)	0.5869 (15)	7.0 (15)
C*E*(2)	0.3917 (15)	0.4822 (15)	0.6374 (16)	6.2 (13)
C*F*(2)	0.3849 (13)	0.4531 (12)	0.7270 (12)	4.3 (10)
C*A*(3)	0.5109 (16)	0.2738 (11)	0.8800 (13)	4.7 (10)
C*B*(3)	0.5954 (16)	0.2451 (10)	0.8142 (11)	4.1 (9)
C*C*(3)	0.7178 (21)	0.1939 (15)	0.8237 (19)	7.9 (16)
C*D*(3)	0.7548 (24)	0.1732 (18)	0.9047 (24)	10.0 (19)
C*E*(3)	0.6689 (28)	0.1976 (19)	0.9760 (19)	10.2 (8)
C*F*(3)	0.5427 (20)	0.2552 (18)	0.9615 (16)	8.6 (16)
C*A*(4)	0.3181 (16)	0.4131 (12)	0.9230 (11)	4.6 (10)
C*B*(4)	0.3887 (19)	0.4616 (14)	0.9335 (15)	7.7 (13)
C*C*(4)	0.3480 (23)	0.5299 (18)	0.9776 (17)	9.3 (17)
C*D*(4)	0.2259 (25)	0.5606 (15)	1.0120 (15)	7.5 (15)
C*E*(4)	0.1530 (18)	0.5203 (15)	1.0019 (12)	5.2 (11)
C*F*(4)	0.1974 (18)	0.4464 (12)	0.9596 (11)	5.0 (10)

Table 2. *Selected bond distances* (Å) *and angles* (°) *in* (1)

Pt(1)—P(1)	2.239 (5)	P(3)—C(2)	1.849 (16)
Pt(1)—P(2)	2.346 (4)	P(3)—C(3)	1.848 (14)
Pt(1)—P(3)	2.342 (6)	P(3)—C(51)	1.767 (25)
Pt(1)—P(4)	2.286 (4)	P(4)—C(4)	1.876 (19)
P(1)—C(6)	1.825 (19)	P(4)—C(5)	1.832 (16)
P(1)—C(11)	1.826 (22)	P(4)—C(61)	1.809 (22)
P(1)—C(21)	1.783 (20)	C(1)—C(2)	1.524 (31)
P(2)—C(1)	1.853 (16)	C(3)—C(4)	1.522 (29)
P(2)—C(31)	1.809 (24)	C(5)—C(6)	1.552 (22)
P(2)—C(41)	1.814 (18)		

P(1)—Pt(1)—P(2)	145.6 (2)	Pt(1)—P(3)—C(2)	106.6 (7)
P(1)—Pt(1)—P(3)	129.5 (2)	Pt(1)—P(3)—C(3)	107.0 (7)
P(1)—Pt(1)—P(4)	86.9 (2)	Pt(1)—P(3)—C(51)	125.4 (6)
P(2)—Pt(1)—P(3)	84.9 (2)	C(2)—P(3)—C(3)	104.4 (7)
P(2)—Pt(1)—P(4)	99.5 (2)	C(2)—P(3)—C(51)	106.9 (10)
P(3)—Pt(1)—P(4)	84.0 (2)	C(3)—P(3)—C(51)	104.8 (9)
Pt(1)—P(1)—C(6)	107.7 (5)	Pt(1)—P(4)—C(4)	110.4 (6)
Pt(1)—P(1)—C(11)	114.3 (7)	Pt(1)—P(4)—C(5)	106.8 (5)
Pt(1)—P(1)—C(21)	119.4 (6)	Pt(1)—P(4)—C(61)	121.7 (5)
C(6)—P(1)—C(11)	106.2 (8)	C(4)—P(4)—C(5)	105.7 (8)
C(6)—P(1)—C(21)	104.4 (9)	C(4)—P(4)—C(61)	105.4 (8)
C(11)—P(1)—C(21)	103.9 (8)	C(5)—P(4)—C(61)	105.8 (9)
Pt(1)—P(2)—C(1)	103.6 (5)	P(2)—C(1)—C(2)	108.5 (11)
Pt(1)—P(2)—C(31)	121.7 (7)	P(3)—C(2)—C(1)	114.8 (13)
Pt(1)—P(2)—C(41)	117.4 (6)	P(3)—C(3)—C(4)	109.3 (11)
C(1)—P(2)—C(31)	104.5 (9)	P(4)—C(4)—C(3)	110.5 (10)
C(1)—P(2)—C(41)	101.1 (8)	P(4)—C(5)—C(6)	107.9 (10)
C(31)—P(2)—C(41)	105.7 (9)	P(1)—C(6)—C(5)	110.9 (14)

Muetterties & Jesson, 1972; Ebsworth, Edward, Reed & Whitelock, 1978). The platinum atom is shifted out of the equatorial plane by 0.015 Å towards the hydride ligand. A larger shift of the platinum atom in the same direction (0.179 Å) has been observed for another trigonal-bipyramidal isomer of (1) $[\mathrm{PtH}(PP_3)](\mathrm{BPh_4})$ (2), where PP_3 is tris[(2-diphenylphosphino)ethyl]phosphine (Gieren, Brüggeller, Hofer, Hübner & Ruiz-Pérez, 1989). This phenomenon has been shown to be typical for trigonal-bipyramidal complexes containing PP_3 and related ligands (Brüggeller, Hübner & Gieren, 1989), the large shifts out of the equatorial planes being typical for tripodal ligands in contrast to the small shifts in (1) and also in trigonal-bipyramidal $[\mathrm{FeBr}(P_4)](\mathrm{BPh_4})$ (3) (0.07 Å) (Bacci & Ghilardi, 1974; Bacci, Ghilardi & Orlandini, 1984). Two equatorial Pt—P bonds are lengthened [Pt(1)—P(2) 2.346 (4), Pt(1)—P(3) 2.342 (6) Å] compared with the third [Pt(1)—P(1) 2.239 (5) Å] and the apical Pt—P bond [Pt(1)—P(4) 2.286 (4) Å], where each pair of different bond lengths consists of a Pt—$\mathrm{PPh_2}$ group and a Pt—PPh group, respectively. Also in (3) the bond lengths of one pair of Pt—$\mathrm{PPh_2}$ and Pt—PPh groups (mean value: 2.274 Å) deviate from the other pair (mean value: 2.198 Å). This is in contrast to complexes containing planar arrangements of P_4 where the pairs of Pt—$\mathrm{PPh_2}$ groups show different bond lengths compared with the pairs of Pt—PPh groups [Brüggeller & Hübner (1990), (4); Brüggeller & Nar, unpublished results]. In (2) the apical Pt—P bond (2.27 Å) is significantly shorter than the equatorial ones (2.33 Å) and the equatorial Pt—P bonds only differ slightly in length ($\Delta_{\max} = 0.03$ Å). The mean values of the Pt—P bonds in (1) (2.303 Å), (2) (2.314 Å), and (4) (2.293 Å) are very similar. The P—Pt—P angles, where the phosphorus atoms are connected by ethylene chains, are smaller than 90° as a consequence of the steric requirements of chiral P_4 consisting of a chain of P and C atoms with tetrahedral coordination and forming three fused five-membered rings [P(1)—Pt(1)—P(4) 86.9 (2), P(2)—Pt(1)—P(3) 84.9 (2), P(3)—Pt(1)—P(4) 84.0 (2)°]. This phenomenon has been observed for other complexes containing P_4 as well and has been reported previously. The mean value in (1) (85.3°, $\Delta_{\max} = 2.9°$) is larger than the corresponding values in $[Pt(P_4)](BPh_4)_2$ (4) (84.3°, $\Delta_{\max} = 1.8°$), (3) (82.8°, $\Delta_{\max} = 3.4°$), $[FeH(N_2)(P_4)]Br$ (5) (84.6°, $\Delta_{\max} = 3.5°$; Ghilardi, Midollini, Sacconi & Stoppioni, 1981), and $[RuCl_2(P_4)]$ (6) (83.2°, $\Delta_{\max} = 2.4°$; Rivera, De Gil & Fontal, 1985). This indicates a strained P_4 coordination in (1). The P(1)—Pt(1)—P(4) angle between the shortened Pt(1)—P(1) and Pt(1)—P(4) bonds is opened compared with the P(2)—Pt(1)—P(3) angle between the lengthened Pt(1)—P(2) and Pt(1)—P(3) bonds. The PhP—Pt—PPh angles between an axial and an equatorial PPh position in (1) [84.0 (2)°] and (3) [83.7 (2)°] are not significantly different. The $PhP—Pt—PPh_2$ angle connecting an axial and an equatorial position is larger in (1) [86.9 (2)°] than the two corresponding values in (3) [80.7 (2) and 84.1 (2)°]. The P—Pt—P angles, where the phosphorus atoms are not connected by ethylene groups, are markedly opened [P(2)—Pt(1)—P(4) 99.5 (2), P(3)—Pt(1)—P(1) 129.5 (2), P(1)—Pt(1)—P(2) 145.6 (2)°]. The value of 99.5 (2)° for the angle between an equatorial and an axial phosphorus atom is only slightly larger than the corresponding value of 97.2 (2)° in (3). Due to the connection of two equatorial phosphorus atoms by an ethylene group in (1) leading to the small P(2)—Pt(1)—P(3) angle of 84.9 (2)° and the opening of the other two equatorial P—Pt—P angles [129.5 (2) and 145.6 (2)°] the deviations from the theoretical value of 120° are larger in (1) than in (3) [105.0 (2), 130.5 (2), and 124.2 (2)°]. Since the chelate terminal arms of chiral P_4 are constrained to move towards different apical positions if both PPh groups occupy two equatorial positions of a trigonal bipyramid (Hale, Jewiss & Levason, 1985), the apical coordination of the hydride ligand in (1) leads to a PPh group in the second apical position. As a consequence of this different movement of the PPh_2 groups in (1) one equatorial angle is very markedly opened [P(1)—Pt(1)—P(2) 145.6 (2)°]. The strong deviations of the P—Pt—P angles not connected by ethylene groups in (1) from ideal trigonal-bipyramidal values may also reflect the participation of (1) in the Berry-type rearrangement process mentioned above (Brüggeller, 1989*a*,*b*). A movement of (1) along this reaction coordinate is possibly 'frozen-in'. This is explained by the structure correlation hypothesis of Auf der Heyde & Bürgi (1989), which has been shown to be relevant for a large number of five-coordinate d^8 complexes. In most of these examples distortions due to the Berry process occur, the angular deviations being more important than changes in bond lengths. Nevertheless both the deviations of the Pt—P bond lengths as well as of the P—Pt—P angles in (1) are mainly a consequence of the energetic competition between the electronic forces to form an ideal trigonal bipyramid and the steric requirements of chiral P_4. This is confirmed by the fact that the cation of (2) shows only a slight deviation from ideal threefold C_3 (3) symmetry mainly due to a packing effect. In (3) *meso*-P_4 occupies both axial positions of the trigonal bipyramid which shows significant but smaller distortions than (1). This accounts for the difficulty of chiral P_4 to form non-planar tetracoordinate forms in contrast to *meso*-P_4 which more comfortably adopts this coordination configuration (Brown & Canning, 1984). Differences in coordination properties between chiral and *meso*-P_4 are also observed for planar MP_4 arrangements and have been attributed to the distinct angular requirements of the two diastereomers (Brüggeller & Hübner, 1990). However, in the case of the above non-planar

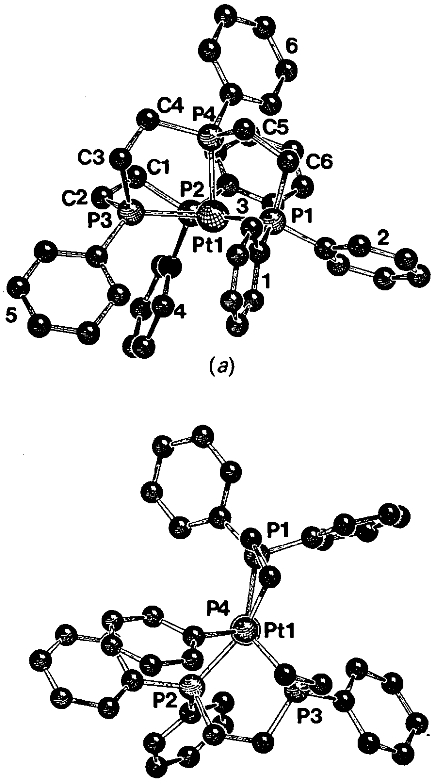

Fig. 1. Structure of the cation of (1). (*a*) Pt(1)—P(4) bond in the projection plane. (*b*) Projection along the P(4)—Pt(1) bond.

arrangements steric effects, including the phenyl groups, also become important (Brown & Canning, 1984). Thus distorted trigonal-bipyramidal structures are typically involved if large groups are present (Rappoli, Churchill, Janik, Rees & Atwood, 1987). All intermolecular distances of the crystal structure of (1) are larger than the corresponding van der Waals radii and no packing effects are observed.

As has been stated earlier (Brüggeller & Hübner, 1990) the square-planar arrangement of (4) is destabilized by the angular requirements of chiral P_4. A similar steric destabilization of square-planar platinum(II) complexes by repulsive ligand interactions leads to the favoured addition of fifth ligands and the formation of trigonal-bipyramidal species in the case of several platinum(II) complexes containing N—N bidentate ligands (De Felice, Ganis, Vitagliano & Valle, 1988; Albano, Braga, De Felice, Panunzi & Vitagliano, 1987). It has been shown that the electronic properties of the fifth ligands also play an important role in the stabilization of these five-coordinate platinum(II) complexes. In (1) the high electron-releasing ability of the hydride acting as a fifth ligand together with the destabilized coordination in (4) leads to a fluxional solution behavior with non-planar coordinated P_4 and a distorted trigonal-bipyramidal structure in the solid state. A similar complete destabilization of planar P_4 arrangements in five-coordinate platinum(II) species occurs upon addition of other fifth ligands with strong σ-donor abilities (Brüggeller, unpublished results).

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Structure of Triaqua(*N*,*N*-dimethylformamide)trinitratoneodymium(III) Monohydrate

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Abstract. $[Nd(C_3H_7NO)(NO_3)_3(H_2O)_3].H_2O$, $M_r = 475.5$, triclinic, $P\bar{1}$, $a = 7.255\,(3)$, $b = 9.100\,(5)$, $c = 12.456\,(4)$ Å, $\alpha = 74.32\,(3)$, $\beta = 73.65\,(3)$, $\gamma = 84.81\,(3)°$, $V = 759.6$ Å^3, $Z = 2$, $D_m = 2.10$, $D_x = 2.08$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 3.574$ mm^{-1}, $F(000) = 466$, $T = 291$ K, final $R =$

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