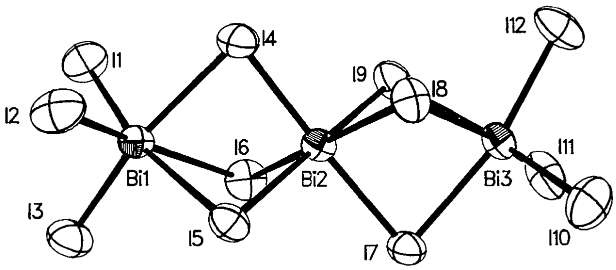

Fig. 1. The $\mathrm{Bi_3I_{12}^{3-}}$ anion in $[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]_3\mathrm{Bi_3I_{12}}$. The thermal ellipsoids are drawn at the 50% probability level.

tetrabutylammonium cation, as there are numerous examples in the literature. Otherwise, data would have been collected at cryogenic temperatures. Other factors contributing to the high R values (and residual difference density near the heavy atoms) include a low $(\sin\theta/\lambda)$ cut-off due to the extremely small plate thickness of the crystals available, resulting in Fourier series truncation problems.

Related literature. The title compound was prepared as an intermediate in the synthesis of the organic conductor (BEDT-TTF)$\mathrm{BiI_4}$ (Geiser, Wang, Budz, Lowry, Williams, Ren & Whangbo, 1990) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, $\mathrm{C_{10}H_8S_8}$] as part of an ongoing search for organic superconductors (Williams, Wang, Emge, Geiser, Beno, Leung, Carlson, Thorn, Schultz & Whangbo, 1987). The main interest of the current structure determination was the identification of the bismuth iodide anion species in this intermediate product. During the electrocrystallization of (BEDT-TTF)$\mathrm{BiI_4}$, the anion rearranges to form an infinite, edge-sharing chain of $[\mathrm{BiI_6}]$ octahedra (Geiser *et al.*, 1990). The $\mathrm{Bi_3I_{12}^{3-}}$ anion has not previously been observed in a crystal structure. However, a dimeric analogue, $\mathrm{Bi_2I_9^{3-}}$, exists in $\mathrm{Cs_3Bi_2I_9}$ (Lindqvist, 1968) and $[\mathrm{N(CH_3)_4}]_3\mathrm{Bi_2I_9}$ (Lazarini, 1980).

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References

Geiser, U., Wang, H. H., Budz, S. M., Lowry, M. J., Williams, J. M., Ren, J. & Whangbo, M.-H. (1990). *Inorg. Chem.* **29**, 1611–1614.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Lazarini, F. (1980). *Cryst. Struct. Commun.* **9**, 815–819.

Lindqvist, O. (1968). *Acta Chem. Scand.* **22**, 2943–2952.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Strouse, C. (1985). *UCLA Crystallographic Package*. Univ. of California, Los Angeles, USA.

Williams, J. M., Wang, H. H., Emge, T. J., Geiser, U., Beno, M. A., Leung, P. C. W., Carlson, K. D., Thorn, R. J., Schultz, A. J. & Whangbo, M.-H. (1987). *Prog. Inorg. Chem.* **35**, 51–218.

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{Bis[2-(diphenylphosphino)ethyl]phenylphosphine}chloropalladium(II) Chloride

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Abstract. $[\mathrm{Pd(C_{34}H_{33}P_3)Cl}]^+.\mathrm{Cl}^-$, $M_r = 711{\cdot}88$, monoclinic, $P2_1/n$, $a = 10{\cdot}248\ (2)$, $b = 20{\cdot}520\ (4)$, $c = 15{\cdot}833\ (3)$ Å, $\beta = 95{\cdot}81\ (1)^\circ$, $V = 3312\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}428$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 8{\cdot}73$ cm^{-1}, $F(000) = 1448$, $T = 296$ K, $R = 5{\cdot}17\%$ for 3561 unique reflections with $F_o \geq 5\sigma(F_o)$ and 311 parameters. The Pd atom has a distorted square-planar geometry formed by the three P atoms of the chelating triphosphine and a Cl atom, with the angles subtending Pd ranging from 83·8 (1) to

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Pd	2450·1 (6)	1337·1 (3)	6844·4 (4)	33·3 (2)
Cl(1)	3316 (2)	1536 (1)	5546 (1)	51·6 (8)
Cl(2)	197 (3)	−789 (1)	8732 (2)	49 (1)
Cl(2′)	1745 (8)	−241 (4)	10462 (4)	56 (3)
P(1)	4397 (2)	1032 (1)	7653 (1)	38 (1)
P(2)	1538 (2)	1112 (1)	8024 (1)	39 (1)
P(3)	324 (2)	1621 (1)	6313 (1)	36 (1)
C(1)	3961 (8)	751 (4)	8698 (5)	47 (3)
C(2)	2519 (8)	498 (4)	8635 (5)	48 (3)
C(3)	−158 (8)	870 (4)	7724 (5)	45 (3)
C(4)	−766 (7)	1414 (4)	7140 (5)	46 (3)
C(11)	4876 (5)	123 (3)	6414 (4)	54 (3)
C(12)	5598	−357	6044	74 (4)
C(13)	6766	−586	6471	60 (4)
C(14)	7212	−335	7267	52 (3)
C(15)	6489	144	7637	52 (3)
C(16)	5321	373	7210	40 (3)
C(21)	6460 (6)	1647 (3)	8644 (3)	56 (3)
C(22)	7371	2145	8827	74 (4)
C(23)	7381	2684	8291	75 (5)
C(24)	6480	2725	7572	69 (4)
C(25)	5569	2227	7388	52 (3)
C(26)	5559	1688	7924	41 (3)
C(31)	1825 (6)	2428 (3)	8467 (3)	65 (4)
C(32)	1641	2967	8978	74 (4)
C(33)	1069	2889	9735	80 (5)
C(34)	681	2271	9980	64 (4)
C(35)	865	1732	9469	55 (3)
C(36)	1437	1810	8712	44 (3)
C(41)	25 (5)	1423 (3)	4564 (4)	56 (3)
C(42)	−416	1092	3821	71 (4)
C(43)	−1222	547	3856	74 (4)
C(44)	−1587	333	4635	70 (4)
C(45)	−1146	665	5378	57 (3)
C(46)	−340	1210	5343	42 (3)
C(51)	−1093 (4)	2773 (3)	6061 (4)	59 (4)
C(52)	−1229	3448	5989	70 (4)
C(53)	−120	3841	5980	82 (5)
C(54)	1125	3560	6044	79 (5)
C(55)	1261	2885	6117	63 (4)
C(56)	152	2492	6125	43 (3)

98·5 (1)°. The Pd atom is 0·136 Å above the ClP_3 plane. The average Pd—P distance is 2·297 (2) Å and the Pd—Cl distance is 2·355 (2) Å.

Table 2. *Bond distances* (Å) *and angles* (°)

Pd—Cl(1)	2·355 (2)	Pd—P(1)	2·344 (2)
Pd—P(2)	2·220 (2)	Pd—P(3)	2·328 (2)
P(1)—C(1)	1·848 (9)	P(1)—C(16)	1·830 (6)
P(1)—C(26)	1·820 (6)	P(2)—C(2)	1·827 (8)
P(2)—C(3)	1·823 (8)	P(2)—C(36)	1·810 (6)
P(3)—C(4)	1·854 (9)	P(3)—C(46)	1·823 (6)
P(3)—C(56)	1·816 (6)	C(1)—C(2)	1·560 (12)
C(3)—C(4)	1·540 (11)		

Cl(1)—Pd—P(1)	98·5 (1)	Cl(1)—Pd—P(2)	176·4 (1)
P(1)—Pd—P(2)	83·8 (1)	Cl(1)—Pd—P(3)	93·6 (1)
P(1)—Pd—P(3)	167·8 (1)	P(2)—Pd—P(3)	84·1 (1)
Pd—P(1)—C(1)	107·6 (3)	Pd—P(1)—C(16)	115·6 (2)
C(1)—P(1)—C(16)	107·1 (3)	Pd—P(1)—C(26)	115·6 (2)
C(1)—P(1)—C(26)	103·4 (3)	C(16)—P(1)—C(26)	106·5 (3)
Pd—P(2)—C(2)	109·4 (3)	Pd—P(2)—C(3)	108·0 (3)
C(2)—P(2)—C(3)	114·1 (4)	Pd—P(2)—C(36)	113·4 (2)
C(2)—P(2)—C(36)	106·8 (3)	C(3)—P(2)—C(36)	105·1 (3)
Pd—P(3)—C(4)	107·2 (2)	Pd—P(3)—C(46)	116·4 (2)
C(4)—P(3)—C(46)	106·7 (3)	Pd—P(3)—C(56)	112·2 (2)
C(4)—P(3)—C(56)	106·6 (3)	C(46)—P(3)—C(56)	107·2 (3)
P(1)—C(1)—C(2)	111·1 (5)	P(2)—C(2)—C(1)	105·7 (6)
P(2)—C(3)—C(4)	106·0 (5)	P(3)—C(4)—C(3)	110·8 (5)
P(1)—C(16)—C(11)	118·9 (2)	P(1)—C(16)—C(15)	121·0 (2)
P(1)—C(26)—C(21)	120·8 (2)	P(1)—C(26)—C(25)	119·2 (2)
P(2)—C(36)—C(31)	121·1 (2)	P(2)—C(36)—C(35)	118·7 (2)
P(3)—C(46)—C(41)	119·3 (2)	P(3)—C(46)—C(45)	120·6 (2)
P(3)—C(56)—C(51)	119·5 (2)	P(3)—C(56)—C(55)	120·3 (2)

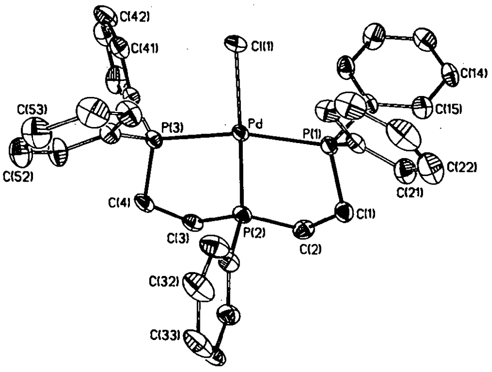

Fig. 1. Molecular structure and labeling scheme for $[Pd(C_{34}H_{33}ClP_3)]^+$. H atoms have been omitted for clarity.

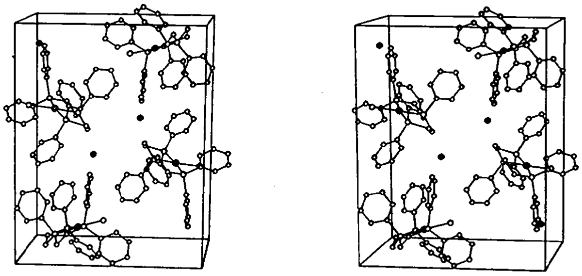

Fig. 2. Stereoview of the packing diagram of $[Pd(C_{34}H_{33}ClP_3)]^+.Cl^-$ viewed down the *a* axis (c horizontal). Majority Cl^- position only is shown.

Experimental. Colorless crystals (0·30 × 0·28 × 0·36 mm) obtained from the reaction of bis(2-diphenylphosphinoethyl)phenylphosphine in THF and $Na_2(PdCl_4)$ previously dissolved in ethanol. Nicolet *R*3*m*/*μ*, *ω* scans; lattice parameters from a least-squares fit of 25 reflections, $19 \leq 2\theta \leq 24°$; no absorption correction ($\mu = 8{\cdot}73\ \text{cm}^{-1}$, uniform crystal shape, $T_{max}/T_{min} = 1{\cdot}03$); $2\theta_{max} = 48°$ ($h = \pm 12$, $k = +24$, $l = +19$); standard reflections 1102, 208, $\bar{5}34$, variation < 1%; 5689 reflections collected, 5592 independent, $R_{int} = 0{\cdot}0205$, 3562 observed with $F_o \geq 5\sigma(F_o)$. Direct-methods (SOLV) structure solution; least-squares refinement on 311 parameters; all non-H atoms anisotropic, H atoms idealized (C—H = 0·96 Å, $U = 1{\cdot}2\ U$ of attached C); phenyl rings rigid planar hexagons (C—C = 1·395 Å). Cl ion disordered: Cl(2), 0·714 (3) occupancy; Cl(2′), 0·286 (3). $R_F = 5{\cdot}17$, $wR_F = 5{\cdot}48\%$, $S = 1{\cdot}511$, $w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0{\cdot}001$; $(\Delta/\sigma)_{max} = 0{\cdot}015$; $(\Delta\rho)_{max} = 1{\cdot}171$, $(\Delta\rho)_{min} = -0{\cdot}403\ \text{e Å}^{-3}$; $N_o/N_v = 11{\cdot}6$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs:

SHELXTL, Sheldrick (1984). Table 1* lists final atomic coordinates and Table 2 bond lengths and angles. Fig. 1 shows the molecular structure and Fig. 2 shows a packing diagram.

Related literature. Bertinsson (1983) has reported the structures of the chloronickel and iodonickel analogues of the cation as tetraphenylborate salts; these analogues and the title complex are structurally very similar.

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References

Bertinsson, G.-I. (1983). *Acta Cryst.* C**39**, 563–567.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers Dordrecht.)

Sheldrick, G. M. (1984). *SHELXTL User's Manual.* Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52867 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure at 173 K of a Chiral, Tricyclic Aminopyranone

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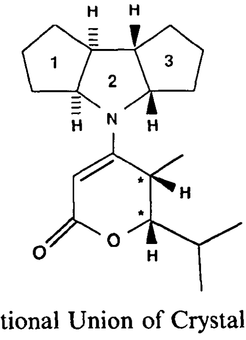
Abstract. *Chemical Abstracts* name {3a*S*-[3aα,4(5*R**,6*R**),4aβ,7aβ,7bα]}-4-(decahydro-1*H*-dicyclopenta[*b*,*d*]pyrrol-4-yl)-5,6-dihydro-5-methyl-6-(1-methylethyl)-2*H*-pyran-2-one, $C_{19}H_{29}NO_2$, $M_r = 303\cdot4$, orthorhombic, $P2_12_12_1$, $a = 13\cdot187\,(4)$, $b = 13\cdot144\,(4)$, $c = 9\cdot668\,(3)$ Å, $V = 1675\cdot8\,(9)$ Å^3, $Z = 4$, $D_x = 1\cdot203$ g cm^{-3}, $\mu = 0\cdot72$ cm^{-1}, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $F(000) = 664$, $T = 173$ K, $R = 0\cdot0418$ for 1617 reflections [$F_o \geq 6\sigma(F_o)$]. Crystal chirality was assigned to correspond to the known chirality of the parent amine. All five-membered rings in the title compound exhibit envelope conformations with atom C(4) occupying the flap position for ring 1 (E^4), and rings 2 (E^6) and 3 (E^6) sharing the same flap position [C(6)]. Ring 3 adopts a conformation different from the E^7 conformation of similar tricyclic amine compounds studied in this laboratory. The short N—C(11) and C(12)—C(13) bonds [1·350 (3) Å and 1·436 (3) Å, respectively] and the long C(11)—C(12) double bond [1·372 (3) Å] indicate an extended conjugation along all bonds between N and O(2). Such conjugation is also supported by the small torsion angles of C(1)—N—C(11)—C(12) [−1·1 (3)°] and C(10)—N—C(11)—C(15) [3·2 (3)°]. The N atom is slightly outside the plane of C(1), C(10) and C(11) [0·036 (5) Å]. The molecules pack in a head-to-tail arrangement along a 2_1 screw axis.

Experimental. Crystals of the title compound were obtained from a chloroform/ethyl acetate solution, and had m.p. 483–484 K and $[\alpha]_D^{25\,°C}$ + 134° (ethanol, $c = 0\cdot69$). The data crystal had dimensions $0\cdot12 \times 0\cdot17 \times 0\cdot22$ mm. A Nicolet *R3m/V* diffractometer equipped with a graphite monochromator and a Nicolet LT-2 low-temperature delivery system (173 K) was used to collect the data. The lattice parameters were obtained from the least-squares refinement of 50 reflections with $22\cdot01 < 2\theta < 28\cdot65°$. The data were collected using the ω-scan technique with a 2θ range 3·0–55·0° and a 1·0° ω scan at 3–6° min^{-1} ($h = 0\rightarrow16$, $k = -16\rightarrow16$, $l = -11\rightarrow0$). Of the 3728 reflections measured, 1888 were unique, with $R_{\rm int} = 0\cdot012$ from averaging symmetry-equivalent reflections. Four reflections (302, $\bar{1}2\bar{2}$, 032, $\bar{6}\bar{4}2$) were remeasured every 96 reflections to monitor instrument and crystal stability



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