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## (1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetrlyphosphadecane-*P,P',P'',P'''*)platinum(II) Bis(tetraphenylborate)

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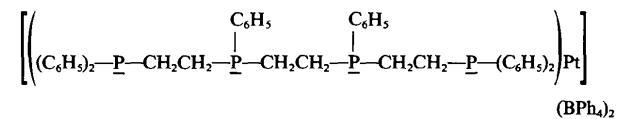
(Received 3 April 1989; accepted 2 June 1989)

**Abstract.** [Pt(C<sub>42</sub>H<sub>42</sub>P<sub>4</sub>)][B(C<sub>24</sub>H<sub>20</sub>)<sub>2</sub>],  $M_r = 1504.24$ , monoclinic,  $P2_1/c$ ,  $a = 23.187$  (4),  $b = 13.543$  (2),  $c = 28.211$  (3) Å,  $\beta = 113.29$  (1)°,  $V = 8137.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (by flotation) = 1.23,  $D_x = 1.22$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } \text{K}\alpha) = 0.71069$  Å,  $\mu = 1.76$  mm<sup>-1</sup>,  $F(000) = 3080$ ,  $T = 294$  K, final  $R = 0.079$  for 6004 observed reflections. The X-ray structure analysis shows a distorted square-planar structure and the chiral form of the two possible diastereomers of the title compound. The two pairs of P atoms, *trans* to each other, lie above (PPh 0.254, PPh<sub>2</sub> 0.199 Å) and below (PPh 0.273, PPh<sub>2</sub> 0.220 Å) the best plane through the Pt and the P atoms. The Pt atom is shifted out of this plane by 0.039 Å. The Pt—PPh bonds [2.258 (4) Å] are significantly shorter than the Pt—PPh<sub>2</sub> bonds [2.327 (4) Å]. The PhP—Pt—PPh<sub>2</sub> angles and the PhP—Pt—PPh angle are of similar size (mean value 84.3°,  $\Delta_{\max} = 1.8$ °), whereas the Ph<sub>2</sub>P—Pt—PPh<sub>2</sub> angle is wide open [109.5 (2)°].

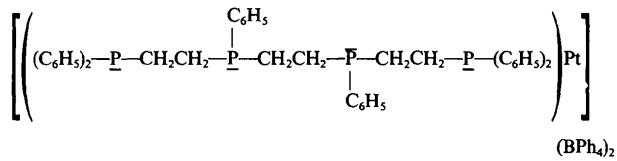
**Introduction.** The tetradeятate ligand 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetrlyphosphadecane ( $P_4$ ) has two diastereomeric forms: the chiral *R,R* and *S,S* diastereomer and the *meso-(R,S* and *S,R*) form (King, Heckley & Cloyd, 1974). Early attempts to separate the two diastereomers of  $P_4$  via reaction of

the ligand mixture with [Mn(CO)<sub>5</sub>X] ( $X = \text{Br}, \text{I}$ ) failed (Butler & Coville, 1974). Brown & Canning (1984) obtained both diastereomers of  $P_4$  in pure form by fractional crystallization of the ligand mixture. Only recently could the two forms of  $P_4$  be separated by reaction of commercial  $P_4$  with [PtCl<sub>4</sub>]<sup>2-</sup> (Brüggeller, 1989). This reaction led to both diastereomers of [Pt( $P_4$ )](BPh<sub>4</sub>)<sub>2</sub>. In order to distinguish the two complexes, an X-ray structure analysis was performed with one diastereomeric form (1).

*meso*-(1):



*chiral* (1):



**Experimental.** (1) (Brüggeller, 1989) was recrystallized from CH<sub>3</sub>NO<sub>2</sub> and a crystal with dimensions 0.35 × 0.25 × 0.16 mm was sealed into a capillary. Data collection was with an Enraf–Nonius CAD-4

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diffractometer in  $\omega/2\theta$  scan mode. Cell parameters were obtained from the orientation matrix of 25 centered reflections in the range  $4.5 \leq \theta \leq 16.8^\circ$ . Three monitor reflections ( $10.2, \bar{1}, \bar{7}53, \bar{1}, 1, 10$ ) showed no significant intensity variation. 14 837 intensity data were collected in the range  $0.0 \leq \theta \leq 23.5^\circ$ ,  $-26 \leq h \leq 26$ ,  $-15 \leq k \leq 15$ ,  $0 \leq l \leq 31$  ( $R_{\text{int}} = 0.035$ ) leading to 8849 unique reflections, 2793 of which were unobserved [ $I \leq 2\sigma(I)$ ]. The data were corrected for Lorentz and polarization effects and for those of absorption. The empirical absorption correction was based on  $\psi$ -scans of nine reflections (North, Phillips & Mathews, 1968). Min. and max. transmission factors were 0.94 and 1.00. The structure was solved by Patterson methods and completed by successive Fourier syntheses. The crystallographic computations were mainly performed using *SHELX76/SHELXS86* (Sheldrick, 1976, 1985). 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, including these H atoms in the refinement led to no further H-atom positions. With 6004 observed reflections (52 reflections with  $|\Delta F| > 3$  omitted) convergence occurred at  $R = 0.079$ ,  $wR = 0.071$ , 914 parameters refined,  $w = k/[\sigma^2(|F_o|) + 0.0005|F_o|^2]$ . ( $\Delta/\sigma$ )<sub>max</sub> = 0.40, min. and max. heights in final difference Fourier synthesis were -1.35 and 1.63 e Å<sup>-3</sup>. Scattering factors used were those internal to *SHELX*.\*

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

The crystal structure consists of discrete  $[\text{Pt}(P_4)]^{2+}$  cations and  $(\text{BPh}_4)^-$  anions. The cation shows a distorted square-planar coordination geometry and is the chiral form of the two possible diastereomers. All known X-ray structures of complexes containing  $P_4$  are *meso*-forms (Bacci & Ghilardi, 1974; Bacci, Ghilardi & Orlandini, 1984; Ghilardi, Midollini, Sacconi & Stoppioni, 1981; Rivera, De Gil & Fontal, 1985). Two P atoms of (1), *trans* to each other, lie above [P(2) 0.199, P(4) 0.254 Å] and below [P(1) 0.220, P(3) 0.273 Å] the best plane through the Pt atom and the P atoms. The Pt atom is shifted out of this plane by 0.039 Å.  $P_4$  is flexible enough to permit different coordination geometries. Distortions are

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters of nonhydrogen atoms*

$B_{\text{eq}}$  is defined as 1/3 of the trace of the anisotropic  $B_{ij}$  tensor. E.s.d.'s in the least significant figure are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
Pt(1)	0.3090 (04)	0.1869 (1)	0.0562 (03)	3.0 (01)
P(1)	0.2742 (2)	0.3308 (4)	0.0805 (2)	3.4 (2)
P(2)	0.2525 (3)	0.0525 (4)	0.0677 (2)	3.9 (3)
P(3)	0.3391 (3)	0.0774 (3)	0.0104 (2)	3.6 (3)
P(4)	0.3852 (2)	0.2847 (3)	0.0504 (2)	3.7 (3)
C(1)	0.2715 (11)	-0.0562 (14)	0.0371 (8)	6.7 (13)
C(2)	0.3371 (11)	-0.0474 (13)	0.0358 (8)	5.8 (12)
C(3)	0.4154 (10)	0.1183 (12)	0.0121 (8)	4.5 (11)
C(4)	0.4128 (9)	0.2313 (14)	0.0023 (7)	4.4 (10)
C(5)	0.3519 (10)	0.4081 (13)	0.0348 (7)	4.7 (11)
C(6)	0.3282 (9)	0.4331 (15)	0.0793 (6)	3.9 (10)
C(11)	0.2715 (10)	0.3402 (11)	0.1445 (7)	3.9 (10)
C(12)	0.3291 (10)	0.3547 (14)	0.1865 (8)	4.2 (11)
C(13)	0.3243 (15)	0.3492 (17)	0.2351 (11)	6.6 (16)
C(14)	0.2704 (16)	0.3298 (22)	0.2428 (10)	7.7 (16)
C(15)	0.2195 (11)	0.3171 (22)	0.2004 (11)	7.7 (15)
C(16)	0.2169 (9)	0.3229 (18)	0.1508 (7)	5.0 (11)
C(21)	0.1981 (9)	0.3641 (15)	0.0332 (7)	4.3 (10)
C(22)	0.1705 (12)	0.4522 (17)	0.0352 (9)	6.2 (14)
C(23)	0.1098 (15)	0.4745 (18)	-0.0057 (13)	8.8 (19)
C(24)	0.0826 (13)	0.4103 (22)	-0.0450 (12)	8.1 (18)
C(25)	0.1081 (12)	0.3228 (24)	-0.0451 (9)	7.6 (15)
C(26)	0.1700 (10)	0.2931 (15)	-0.0061 (8)	5.3 (13)
C(31)	0.2770 (10)	0.0155 (16)	0.1359 (7)	4.6 (11)
C(32)	0.3140 (10)	0.0826 (16)	0.1729 (8)	4.8 (12)
C(33)	0.3278 (11)	0.0532 (19)	0.2265 (10)	6.1 (14)
C(34)	0.3070 (12)	-0.0325 (19)	0.2378 (10)	6.6 (15)
C(35)	0.2701 (12)	-0.0952 (18)	0.1974 (10)	7.1 (15)
C(36)	0.2539 (11)	-0.0726 (15)	0.1466 (9)	6.7 (14)
C(41)	0.1691 (11)	0.0591 (15)	0.0414 (9)	4.9 (13)
C(42)	0.1391 (12)	0.0926 (17)	0.0727 (11)	7.3 (16)
C(43)	0.0708 (18)	0.1121 (28)	0.0475 (19)	11.7 (28)
C(44)	0.0434 (24)	0.0989 (32)	-0.0042 (25)	12.3 (36)
C(45)	0.0682 (24)	0.0588 (24)	-0.0333 (15)	9.6 (27)
C(46)	0.1353 (16)	0.0487 (20)	-0.0124 (12)	8.6 (20)
C(51)	0.2847 (9)	0.0815 (14)	-0.0565 (7)	4.3 (11)
C(52)	0.2547 (10)	0.1667 (14)	-0.0766 (8)	5.1 (12)
C(53)	0.2116 (13)	0.1737 (19)	-0.1293 (9)	7.8 (16)
C(54)	0.2001 (11)	0.0913 (20)	-0.1601 (9)	6.2 (14)
C(55)	0.2294 (13)	0.0013 (21)	-0.1395 (9)	7.5 (17)
C(56)	0.2732 (9)	-0.0030 (15)	-0.0878 (8)	5.0 (12)
C(61)	0.4537 (8)	0.2906 (11)	0.1108 (7)	3.5 (10)
C(62)	0.5059 (11)	0.3413 (13)	0.1103 (8)	5.2 (12)
C(63)	0.5592 (10)	0.3514 (14)	0.1565 (10)	5.3 (13)
C(64)	0.5585 (12)	0.3127 (17)	0.2025 (9)	6.3 (13)
C(65)	0.5033 (10)	0.2651 (14)	0.2019 (8)	4.4 (11)
C(66)	0.4500 (10)	0.2544 (13)	0.1548 (8)	4.5 (11)
B(1)	0.4856 (10)	0.7244 (13)	0.1039 (8)	3.2 (10)
C <sub>A</sub> (1)	0.4931 (8)	0.3407 (11)	0.3773 (7)	3.3 (9)
C <sub>B</sub> (1)	0.5197 (9)	0.4020 (13)	0.3497 (7)	3.9 (10)
C <sub>C</sub> (1)	0.5017 (10)	0.4968 (15)	0.3385 (8)	4.9 (12)
C <sub>D</sub> (1)	0.4584 (11)	0.5424 (18)	0.3542 (9)	5.8 (14)
C <sub>E</sub> (1)	0.4269 (10)	0.4835 (14)	0.3809 (8)	4.8 (12)
C <sub>F</sub> (1)	0.4451 (10)	0.3871 (14)	0.3912 (7)	4.8 (11)
C <sub>A</sub> (2)	0.4565 (8)	0.1592 (12)	0.3984 (7)	3.2 (10)
C <sub>B</sub> (2)	0.3945 (10)	0.1714 (14)	0.3614 (7)	4.6 (11)
C <sub>C</sub> (2)	0.3424 (10)	0.1135 (15)	0.3613 (8)	5.2 (12)
C <sub>D</sub> (2)	0.3507 (12)	0.0442 (15)	0.3984 (9)	6.1 (13)
C <sub>E</sub> (2)	0.4146 (11)	0.0290 (13)	0.4364 (8)	5.2 (12)
C <sub>F</sub> (2)	0.4666 (10)	0.0866 (12)	0.4364 (7)	4.5 (10)
C <sub>A</sub> (3)	0.4587 (9)	0.6738 (13)	0.1433 (7)	3.5 (9)
C <sub>B</sub> (3)	0.4848 (9)	0.5903 (14)	0.1739 (8)	4.1 (10)
C <sub>C</sub> (3)	0.4615 (12)	0.5433 (15)	0.2075 (8)	6.2 (13)
C <sub>D</sub> (3)	0.4102 (11)	0.5773 (14)	0.2122 (8)	5.2 (12)
C <sub>E</sub> (3)	0.3770 (10)	0.6606 (15)	0.1803 (8)	5.4 (13)
C <sub>F</sub> (3)	0.4015 (10)	0.7070 (15)	0.1476 (7)	4.6 (11)
C <sub>A</sub> (4)	0.4320 (9)	0.7703 (12)	0.5460 (7)	3.5 (9)
C <sub>B</sub> (4)	0.4389 (9)	0.7145 (13)	0.5062 (7)	4.5 (11)
C <sub>C</sub> (4)	0.3945 (12)	0.7149 (16)	0.4562 (8)	5.8 (13)
C <sub>D</sub> (4)	0.3390 (12)	0.7683 (17)	0.4408 (8)	5.8 (13)
C <sub>E</sub> (4)	0.3307 (10)	0.8213 (17)	0.4797 (9)	6.3 (13)
C <sub>F</sub> (4)	0.3758 (11)	0.6735 (14)	0.0315 (7)	4.7 (11)
B(2)	0.1201 (12)	0.6641 (19)	0.1639 (10)	5.4 (15)
C <sub>A</sub> (5)	0.1849 (10)	0.6692 (17)	0.2184 (9)	5.6 (13)
C <sub>B</sub> (5)	0.2318 (11)	0.5937 (15)	0.2311 (9)	5.6 (13)
C <sub>C</sub> (5)	0.2882 (10)	0.6072 (19)	0.2729 (9)	5.2 (13)
C <sub>D</sub> (5)	0.2984 (11)	0.6841 (22)	0.3043 (8)	6.2 (13)
C <sub>E</sub> (5)	0.2520 (13)	0.7564 (18)	0.2972 (8)	6.1 (14)
C <sub>F</sub> (5)	0.1935 (11)	0.7498 (16)	0.2544 (9)	5.8 (13)
C <sub>A</sub> (6)	0.0650 (15)	0.7379 (18)	0.1662 (9)	6.7 (16)

\* Lists of structure factors, positional and temperature parameters, bond distances, bond angles, and selected torsion angles have been deposited at the British Library Document Supply Centre as Supplementary Publication No. SUP 52296 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
CB(6)	0.0123 (13)	0.7068 (35)	0.1774 (12)	11.4 (23)
CC(6)	-0.0274 (17)	0.7803 (32)	0.1818 (17)	13.1 (29)
CD(6)	-0.0130 (19)	0.8884 (37)	0.1769 (15)	11.4 (28)
CE(6)	0.0383 (20)	0.9191 (32)	0.1675 (14)	12.6 (28)
CF(6)	0.0731 (12)	0.8425 (19)	0.1599 (10)	7.0 (17)
CA(7)	0.1388 (12)	0.6935 (17)	0.1150 (9)	6.2 (13)
CB(7)	0.0898 (15)	0.7208 (22)	0.0678 (11)	8.5 (19)
CC(7)	0.1034 (16)	0.7479 (23)	0.0268 (14)	9.6 (22)
CD(7)	0.1656 (19)	0.7336 (19)	0.0277 (12)	9.1 (19)
CE(7)	0.2146 (12)	0.6997 (17)	0.0741 (10)	6.2 (13)
CF(7)	0.2014 (11)	0.6780 (17)	0.1156 (9)	7.1 (14)
CA(8)	0.0927 (10)	0.5453 (17)	0.1556 (10)	5.4 (13)
CB(8)	0.0839 (13)	0.4985 (19)	0.1977 (12)	9.0 (19)
CC(8)	0.0551 (19)	0.4030 (28)	0.1867 (18)	12.3 (28)
CD(8)	0.0379 (17)	0.3506 (28)	0.1419 (18)	10.8 (28)
CE(8)	0.0480 (15)	0.3995 (23)	0.1021 (15)	9.2 (21)
CF(8)	0.0725 (12)	0.4923 (21)	0.1092 (10)	6.5 (15)

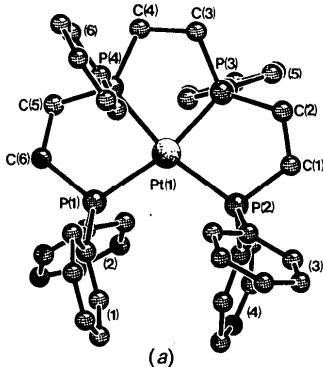
Table 2. Selected bond distances (Å) and angles (°) in (1)

Pt(1)—P(1)	2.314 (6)	P(3)—C(2)	1.844 (20)
Pt(1)—P(2)	2.339 (6)	P(3)—C(3)	1.836 (25)
Pt(1)—P(3)	2.251 (6)	P(3)—C(51)	1.809 (17)
Pt(1)—P(4)	2.265 (5)	P(4)—C(4)	1.860 (24)
Pt(1)—C(6)	1.877 (22)	P(4)—C(5)	1.820 (18)
Pt(1)—C(11)	1.836 (23)	P(4)—C(61)	1.814 (16)
Pt(1)—C(21)	1.799 (17)	C(1)—C(2)	1.541 (38)
Pt(2)—C(1)	1.846 (23)	C(3)—C(4)	1.552 (25)
Pt(2)—C(31)	1.847 (20)	C(5)—C(6)	1.593 (32)
Pt(2)—C(41)	1.779 (24)		
Pt(1)—Pt(1)—P(2)	109.5 (2)	Pt(1)—P(3)—C(2)	108.6 (9)
Pt(1)—Pt(1)—P(3)	161.5 (2)	Pt(1)—P(3)—C(3)	107.5 (7)
Pt(1)—Pt(1)—P(4)	84.4 (2)	Pt(1)—P(3)—C(51)	109.4 (7)
Pt(2)—Pt(1)—P(3)	83.4 (2)	C(2)—P(3)—C(3)	116.0 (10)
Pt(2)—Pt(1)—P(4)	163.9 (2)	C(2)—P(3)—C(51)	108.6 (9)
Pt(3)—Pt(1)—P(4)	85.2 (2)	C(3)—P(3)—C(51)	106.6 (10)
Pt(1)—P(1)—C(6)	107.6 (7)	Pt(1)—P(4)—C(4)	109.2 (6)
Pt(1)—P(1)—C(11)	120.1 (5)	Pt(1)—P(4)—C(5)	106.6 (8)
Pt(1)—P(1)—C(21)	110.2 (7)	Pt(1)—P(4)—C(61)	112.1 (7)
C(6)—P(1)—C(11)	104.4 (8)	C(4)—P(4)—C(5)	114.6 (10)
C(6)—P(1)—C(21)	105.5 (9)	C(4)—P(4)—C(61)	106.0 (9)
C(11)—P(1)—C(21)	107.9 (10)	C(5)—P(4)—C(61)	108.5 (7)
Pt(1)—P(2)—C(1)	107.8 (9)	P(2)—C(1)—C(2)	111.7 (13)
Pt(1)—P(2)—C(31)	113.4 (7)	P(3)—C(2)—C(1)	104.9 (13)
Pt(1)—P(2)—C(41)	118.6 (7)	P(3)—C(3)—C(4)	108.9 (14)
C(1)—P(2)—C(31)	103.8 (10)	P(4)—C(4)—C(3)	104.7 (16)
C(1)—P(2)—C(41)	105.4 (10)	P(4)—C(5)—C(6)	104.5 (13)
C(31)—P(2)—C(41)	106.5 (12)	P(1)—C(6)—C(5)	107.3 (12)

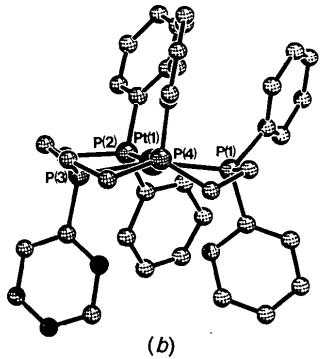
mainly a consequence of the steric requirements produced by three connected five-membered rings. Thus the PhP—Pt—PPh<sub>2</sub> angles and the PhP—Pt—PPh angle cannot reach 90° due to the chain of P and C atoms with tetrahedral geometry: P(1)—Pt—P(4) = 84.4 (2), P(2)—Pt—P(3) = 83.4 (2), P(3)—Pt—P(4) = 85.2 (2)° (mean value: 84.3°). This is also observed in the compounds [FeBr(P<sub>4</sub>)](BPh<sub>4</sub>) (2) (Bacci & Ghilardi, 1974; Bacci, Ghilardi & Orlandini, 1984), [FeH(N<sub>2</sub>)(P<sub>4</sub>)]Br (3) (Ghilardi, Midollini, Sacconi & Stoppioni, 1981) and [RuCl<sub>2</sub>(P<sub>4</sub>)] (4) (Rivera, De Gil & Fontal, 1985). (2) shows a trigonal-bipyramidal structure, (3) and (4) have octahedral coordination. In (3) and (4) P<sub>4</sub> occupies the equatorial positions, where in both cases the four P atoms are within a plane. The Fe atom in (3) is shifted out of the equatorial plane towards the N<sub>2</sub> ligand by 0.34 Å. The fact that the Ru atom in (4) is also shifted out of the equatorial plane by 0.12 Å, although both axial

ligands are equal, shows that the angular requirements of P<sub>4</sub> produce these shifts of the central atoms out of the equatorial planes. Apart from the axial ligands in (3) and (4) they are comparable with (1). As a result it is shown that meso-P<sub>4</sub> and chiral P<sub>4</sub> lead to completely different deviations from a planar MP<sub>4</sub> configuration. This is a consequence of the different angular requirements of meso-P<sub>4</sub> and chiral P<sub>4</sub> in occupying four approximately planar positions.

The Pt—PPh bond distances in (1) [mean value 2.258 (4) Å] are significantly shorter than the Pt—PPh<sub>2</sub> bond distances [mean value 2.327 (4) Å]. The same is true for the compounds (3) [Fe—PPh bonds 2.207 (4), Fe—PPh<sub>2</sub> bonds 2.239 (4) Å] and (4) [Ru—PPh bonds 2.295 (3), Ru—PPh<sub>2</sub> bonds 2.392 (3) Å]. In (2) the shortening of the equatorial Fe—P bond distances is believed to be a consequence of the coplanarity of these bonds with adjacent phenyl rings and the formation of a partially conjugated system. A corresponding coplanarity is not observed in the compounds (1), (3) and (4). The similarity of the differences in the bond distances between each pair of M—PPh and M—PPh<sub>2</sub> groups, respectively, in (1), (3) and (4) indicates that this effect is also a consequence of the angular



(a)



(b)

Fig. 1. Structure of the cation of (1). (a) The best plane through the Pt atom and the P atoms in the projection plane. (b) Projection along the best plane through the Pt atom and the P atoms.

requirements of  $P_4$  occupying four approximately planar positions.

The  $\text{Ph}_2\text{P}—\text{Pt}—\text{PPh}_2$  angle in (1) [109.5 (2) $^\circ$ ] is wide open compared with the  $\text{PhP}—\text{Pt}—\text{PPh}_2$  angles and the  $\text{PhP}—\text{Pt}—\text{PPh}$  angle (mean value 84.3,  $\Delta_{\max} = 1.8^\circ$ ). The mean values of the  $\text{PhP}—M—\text{PPh}_2$  angles and the  $\text{PhP}—M—\text{PPh}$  angle in (2) [82.8,  $\Delta_{\max} = 3.4^\circ$ ], (3) (84.6,  $\Delta_{\max} = 3.5^\circ$ ), and (4) (83.2,  $\Delta_{\max} = 2.4^\circ$ ) is comparable with the corresponding value in (1). The  $\text{Ph}_2\text{P}—M—\text{PPh}_2$  angles in (2), (3) and (4) are also wide open: they are 97.2 (2), 101.4 (2) and 109.8 (2) $^\circ$ , respectively. Obviously, replacing a 3d [in (2) and (3)] by a 4d central atom [in (4)] leads to a larger opening of the  $\text{Ph}_2\text{P}—M—\text{PPh}_2$  angles, whereas the replacement by a 5d central atom in (1) results in no further opening of this angle. All intermolecular distances of the crystal structure of (1) are larger than the corresponding van der Waals radii and no packing effects are observed.

The cation of (1) is destabilized by the deviations from an idealized square-planar structure, which is electronically favoured in the case of  $d^8$  complexes. The occurrence of sterically favoured tetrahedral complexes, which are common for some  $d^8$  metals (Rappoli, Churchill, Janik, Rees & Atwood, 1987), is not possible for  $\text{Pt}^{II}$ , where this coordination is completely electronically destabilized (Atwood, 1985).

However, in the synthesis of (1) a five-coordinate intermediate occurs, which shows the tetrahedral arrangement of  $P_4$  (Brüggeller, 1989).

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## Structure of Iodo-1 $\kappa$ I- $\mu$ -(*O*-isopropyl dithiocarbonato-1 $\kappa^2$ S,S':2 $\kappa$ S')-bis[ (*O*-isopropyl dithiocarbonato)cadmium] Cd<sub>2</sub>I(S<sub>2</sub>CO<sup>i</sup>Pr)<sub>3</sub>

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**Abstract.** [Cd<sub>2</sub>I(C<sub>4</sub>H<sub>7</sub>OS<sub>2</sub>)<sub>3</sub>],  $M_r = 757.4$ , monoclinic,  $P2_1/c$ ,  $a = 12.028$  (2),  $b = 19.261$  (4),  $c = 10.864$  (2) Å,  $\beta = 102.60$  (2) $^\circ$ ,  $V = 2456$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.05$ ,  $D_x = 2.048$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 3.440$  mm<sup>-1</sup>,  $F(000) = 1448$ ,  $T = 295$  (2) K,  $R = 0.028$  for 3511 observed reflections. The structure is polymeric with Cd atoms linked by xanthate (ROCS<sub>2</sub><sup>-</sup>) bridges forming infinite chains in the  $c$  direction. The chains are interlinked by a series of (S<sub>2</sub>CO<sup>i</sup>Pr)<sub>2</sub>CdI<sub>2</sub>Cd(S<sub>2</sub>CO<sup>i</sup>Pr)<sub>2</sub> bridging units.

**Introduction.** Structural studies of metal halo xanthate complexes have shown a range of novel structures which are often a consequence of the halo atoms' ability to bridge metal centres (Gable, Hos-

kins, Steen & Winter, 1982; Gable, Hoskins, Steen, Tiekkink & Winter, 1983). Further interest in these complexes has emerged from their usefulness in the preparation of mixed-ligand complexes (Hoskins, Tiekkink & Winter, 1985). Recently we have reported (Abrahams, Corbett, Dakternieks, Gable, Hoskins, Tiekkink & Winter, 1986) on the reaction of cadmium and mercury isopropyl xanthates [ $M(\text{ipxan})_2$ ] with the corresponding metal halides. Significant shifts in the characteristic IR absorptions of the xanthate ligands in the C—O and C—S region are consistent with the formation of metal halo xanthate complexes (Abrahams *et al.*, 1986). The poor solubility of the products, suggesting a polymeric structure, prevented examination by NMR spectroscopy. However, the