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Structure of Dichloro(pentabenzylcyclopentadienyl)phosphine

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Abstract. $C_{40}H_{35}Cl_2P$, $M_r = 617.60$, monoclinic, $P2_1/n$, $a = 11.463$ (3), $b = 18.641$ (6), $c = 15.762$ (5) Å, $\beta = 103.42$ (2)°, $V = 3276$ (2) Å^3, $Z = 4$, $D_x = 1.25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.23$ mm^{-1}, $F(000) = 1296$, room temperature, $R = 0.039$ for 2856 unique reflections with $|F_o| > 4\sigma(|F_o|)$. The crystal-structure analysis of the first air-stable organodichlorophosphine shows that the P atom is σ-bonded to the cyclopentadienyl system. Two of the five benzyl groups are oriented towards the open coordination sphere of the PCl_2 unit. The shielding by the organic ligands protects the P—Cl bond from attack by air or water.

Introduction. Substitution of the cyclopentadienyl ligand in organoelement compounds with the bulky pentabenzylcyclopentadienyl system $[C_5(CH_2Ph)_5]$ leads to drastic changes in the chemical properties (stability) and the structural appearance (monomerization, geometry). The first monomeric air-stable cyclopentadienyl derivatives of indium(I) and thallium(I) have been synthesized using the $[C_5(CH_2Ph)_5]$ ligand (Schumann, Janiak, Pickardt & Börner, 1987; Schumann, Janiak, Khan & Zuckerman, 1988; Schumann, Janiak, Görlitz, Loebel & Dietrich, 1989). Fairly air-stable $C_5(CH_2Ph)_5$ derivatives of normally sensitive cyclopentadienyl metal compounds have also been reported for tin, germanium, lead (Schumann, Janiak, Hahn, Kolax, Loebel, Rausch & Zuckerman, 1986), gold (Schumann, Görlitz & Dietrich, 1989), iron, lutetium (Schumann, Janiak, Köhn, Loebel & Dietrich, 1989), cobalt (Chambers, Baskar, Bott, Atwood & Rausch, 1986), manganese (Rausch, Tsai & Chambers, 1989) and potassium (Lorberth, Shin, Wocadlo & Massa, 1989). The air stability could be explained by the orientation of one, two or three benzyl groups towards the coordinatively unsaturated metal. The attempt to obtain an air- and water-stable phosphine using the $[C_5(CH_2Ph)_5]^-$ ligand led to the preparation and crystallographic elucidation of the title compound.

Experimental. The title compound was synthesized by reaction of pentabenzylcyclopentadienyllithium and phosphorus(III) chloride at room temperature in THF. White air-stable parallelepipeds were grown in Et_2O at room temperature. A crystal of dimensions 0.63 × 0.38 × 0.24 mm was used on an Enraf–Nonius CAD-4 diffractometer. Intensities were measured at room temperature with ω–2θ scan technique, with variable scan width of $\Delta\omega = (0.85 + 0.35\tan\theta)°$; the maximum scan time was 60 s. Unit-cell dimensions were determined from least-squares fit of 25 reflections with $19.96 \leq 2\theta \leq 27.71°$. A total of 5540 reflections in the range $2 \leq 2\theta \leq 53°$ and $0 \leq h \leq 14$, $0 \leq k \leq 27$, $-19 \leq l \leq 19$ were measured and averaged to 4101 unique data with $R_{\rm int} = 0.029$. 2856 reflections with $F_o > 4\sigma F_o$ were used in the refinement. Three intensity-control monitor reflections, measured every 7200 s, showed −4.2% decay. No corrections for decay or absorption were applied ($\mu = 0.23$ mm^{-1}). The structure was solved using direct methods (*SHELXS*86; Sheldrick, 1986). H atoms were located in a difference Fourier map and were added at calculated positions (C—H = 0.95 Å and $U_{\rm iso} = 0.05$ Å^2) to the structure model. Blocked least-squares refinement with 527 variables, minimizing the function $\sum w(\Delta F)^2$, led to $R = 0.0388$ and $wR = 0.0447$ for $w = 1/\sigma^2[(F_o) + 0.000548(F_o)^2]$; $\Delta/\sigma \leq 0.003$ for non-H-atom parameters; $(\Delta\rho)_{\rm max} = 0.20$, $(\Delta\rho)_{\rm min} = -0.18$ e Å^{-3}. Scattering factors for P, C and H atoms were as given in *SHELX*76 (Sheldrick, 1976).

Discussion. Final fractional coordinates are given in Table 1.* Important bond lengths and angles are compiled in Table 2. The title compound consists of monomeric molecules. The molecular structure, along with the numbering scheme, is shown in Fig. 1. The P atom has three σ bonds to both of the Cl atoms and to the C1 atom of the cyclopentadienyl ring. The bond distances and angles involving the P

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55680 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1004]

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

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
P	0.06006 (8)	0.07906 (4)	0.83968 (5)	4.75
Cl1	0.14609 (9)	−0.00874 (4)	0.90841 (6)	7.77
Cl2	−0.1111 (1)	0.05284 (4)	0.8535 (1)	6.01
C1	0.1069 (2)	0.1537 (1)	0.9191 (2)	3.73
C2	0.0302 (2)	0.2122 (1)	0.8668 (2)	3.40
C3	0.0979 (2)	0.2478 (1)	0.8205 (2)	3.77
C4	0.2212 (2)	0.2230 (1)	0.8461 (2)	3.85
C5	0.2303 (2)	0.1681 (1)	0.9026 (2)	3.72
C11	0.0980 (3)	0.1399 (2)	1.0138 (2)	4.75
C12	0.1106 (3)	0.2064 (1)	1.0695 (2)	4.26
C13	0.2129 (3)	0.2485 (2)	1.0846 (2)	5.20
C14	0.2213 (3)	0.3107 (2)	1.1329 (2)	5.09
C15	0.1287 (4)	0.3315 (2)	1.1684 (2)	6.05
C16	0.0279 (4)	0.2901 (2)	1.1559 (2)	6.82
C17	0.0197 (3)	0.2280 (2)	1.1074 (2)	5.41
C21	−0.0985 (3)	0.2267 (2)	0.8689 (2)	4.00
C22	−0.1319 (3)	0.3047 (1)	0.8719 (2)	4.89
C23	−0.0692 (4)	0.3500 (2)	0.9336 (2)	5.85
C24	−0.1066 (6)	0.4212 (2)	0.9368 (3)	8.68
C25	−0.2043 (5)	0.4453 (2)	0.8764 (4)	11.96
C26	−0.2664 (4)	0.4011 (2)	0.8144 (4)	10.42
C27	−0.2314 (3)	0.3308 (2)	0.8132 (2)	6.84
C31	0.0565 (3)	0.3032 (2)	0.7504 (2)	4.90
C32	0.0876 (2)	0.2836 (2)	0.6650 (2)	4.51
C33	0.0610 (3)	0.2175 (2)	0.6277 (2)	5.87
C34	0.0914 (4)	0.2005 (2)	0.5499 (2)	6.85
C35	0.1495 (4)	0.2492 (3)	0.5103 (3)	8.82
C36	0.1760 (3)	0.3155 (3)	0.5460 (2)	7.62
C37	0.1448 (3)	0.3328 (2)	0.6227 (2)	5.49
C41	0.3244 (3)	0.2594 (2)	0.8197 (2)	5.18
C42	0.3439 (2)	0.3360 (1)	0.8500 (2)	4.42
C43	0.2980 (3)	0.3629 (2)	0.9171 (2)	6.33
C44	0.3186 (4)	0.4329 (2)	0.9451 (3)	7.40
C45	0.3882 (4)	0.4761 (2)	0.9061 (3)	6.55
C46	0.4341 (4)	0.4499 (2)	0.8412 (3)	8.26
C47	0.4126 (3)	0.3810 (2)	0.8124 (2)	6.51
C51	0.3435 (3)	0.1275 (2)	0.9418 (2)	5.01
C52	0.4013 (3)	0.0855 (1)	0.8799 (2)	4.65
C53	0.3519 (3)	0.0765 (2)	0.7925 (2)	5.95
C54	0.4074 (4)	0.0354 (2)	0.7400 (3)	6.52
C55	0.5149 (4)	0.0038 (2)	0.7754 (4)	8.93
C56	0.5668 (4)	0.0131 (2)	0.8609 (3)	9.50
C57	0.5105 (3)	0.0528 (2)	0.9135 (2)	6.50

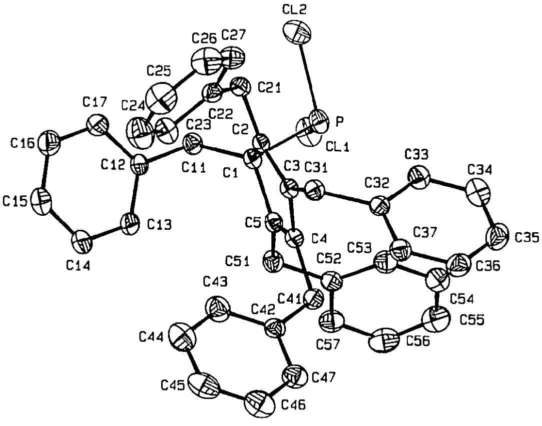

Fig. 1. Molecular structure of the title compound along with the atom-numbering scheme. H atoms are omitted. Thermal ellipsoids (*ORTEP*II; Johnson, 1976) are drawn at the 50% probability level.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

P—Cl1	2.081 (1)	C1—C11	1.542 (4)
P—Cl2	2.081 (1)	C2—C21	1.507 (4)
P—C1	1.866 (2)	C3—C31	1.508 (4)
C1—C2	1.518 (3)	C4—C41	1.503 (5)
C1—C5	1.518 (4)	C5—C51	1.506 (4)
C2—C3	1.354 (4)	C(CH$_2$)—C(Ph)	1.506 (4)–1.517 (5)
C3—C4	1.453 (4)	C(Ph)—C(Ph)	1.346 (8)–1.398 (6)
C4—C5	1.345 (4)		

Cl1—P—Cl2	96.03 (5)	C21—C22—C27	119.7 (3)
Cl1—P—C1	102.1 (1)	C2—C3—C31	127.4 (3)
Cl2—P—C1	103.7 (1)	C4—C3—C31	122.9 (3)
C11—C1—P	116.8 (2)	C3—C31—C32	112.7 (3)
C2—C1—P	97.5 (1)	C31—C32—C33	121.7 (3)
C5—C1—P	98.8 (2)	C31—C32—C37	120.1 (3)
C2—C1—C5	103.1 (2)	C3—C4—C41	123.8 (2)
C1—C2—C3	108.1 (2)	C5—C4—C41	125.6 (2)
C2—C3—C4	109.6 (2)	C4—C41—C42	114.1 (3)
C3—C4—C5	110.3 (2)	C41—C42—C43	122.2 (3)
C4—C5—C1	108.3 (2)	C41—C42—C47	120.0 (3)
C2—C1—C11	119.1 (2)	C1—C5—C51	126.2 (2)
C1—C11—C12	114.0 (2)	C4—C5—C51	125.6 (3)
C11—C12—C13	122.0 (3)	C5—C51—C52	117.2 (2)
C11—C12—C17	120.8 (3)	C51—C52—C53	124.6 (3)
C1—C2—C21	124.4 (2)	C51—C52—C57	118.1 (3)
C3—C2—C21	127.5 (2)	C5—C1—C11	117.8 (2)
C2—C21—C22	115.6 (2)	C(Ph)—C(Ph)—C(Ph)	117.2 (3)–121.8 (3)
C21—C22—C23	121.6 (3)		

atom are in good agreement with those found in PCl_3 [P—C 2.043 (3) Å; Cl—P—Cl 100.1 (3)° (Mitchell & Cross, 1958)] and $P(CH_3)_3$ [P—C 1.841 (3) Å; C—P—C 99.1 (2)° (Mitchell, Sommerfield & Cross, 1965)]. The C=C double bonds in the cyclopentadienyl ring are located between C2 and C3 as well as between C4 and C5. The internal bond parameters of the $C_5(CH_2Ph)_5$ system exhibit no unusual magnitudes.

The unexpected air stability of the title compound in the solid state can be explained by the orientation of two of the five benzyl groups (C31 through C37 and C51 through C57) to the open coordination sphere of the P atom; the benzyl groups shield the reactive centre of the molecule (PCl_2) from attack from moisture and oxygen. There are no close C···P contacts; therefore, arenic interactions of the phenyl system with the free electron pair of trivalent P atom have to be excluded.

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Structure of 4-Carboxy-2-nitrobenzeneboronic Acid

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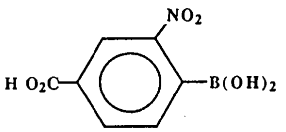
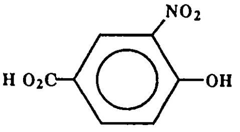
Abstract. 4-(Dihydroxyboryl)-3-nitrobenzoic acid, $C_7H_6BNO_6$, $M_r = 210.94$, monoclinic, $P2_1/n$, $a = 10.542\ (2)$, $b = 6.411\ (1)$, $c = 13.105\ (4)$ Å, $\beta = 106.47\ (2)°$, $V = 849.3\ (4)$ Å^3, $Z = 4$, $D_m = 1.65$ (flotation in CCl_4/1,2-dibromoethane), $D_x = 1.649$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.135$ mm^{-1}, $F(000) = 432$, $T = 293$ K, $R = 0.0530$ for 1328 observed reflections with $F > 2\sigma(F)$. The molecule is flat [the carboxy and nitro groups are rotated 5.8 (4) and 1.9 (4)°, respectively, out of the plane] with the boronic acid group almost normal to the plane of the benzene ring, 92.4 (3)°. The B atom and one O atom of the nitro group are separated by only 2.457 (4) Å implying an interaction that is consistent with observed chemical behavior.

Introduction. Benzeneboronic acids form stable complexes with *cis*-diols (Ferrier, 1978). The efficiency of boronate–diol complex formation and the utilization of this property in affinity chromatography for the isolation of biomolecules depend on the ionization constant of the benzeneboronic acid (Maestas, Prieto, Kuehn & Hageman, 1980; Hageman & Kuehn, 1992). Ionization constants and boronate–diol complex formation constants of several potentially useful benzeneboronic acids were determined by a sensitive spectral difference method (Soundararajan, Badawi, Kohlrust & Hageman, 1989). Among the benzeneboronic acids studied, the values obtained for 4-carboxy-2-nitrobenzeneboronic acid (I) by the spectral method were quite different from those obtained by a potentiometric method. In addition, aqueous solutions (pH = 9.0) of (I) were observed (Soundararajan, 1984) to undergo ultraviolet and visible spectral changes with time, which suggested the formation of (II).

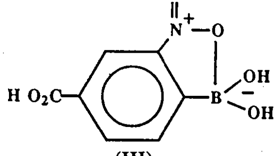
Furthermore, after several hours at pH 9.0, solutions of (I) could be resolved into four different species by thin-layer chromatography, which led to the suggestion that the *ortho*-nitro group might form the cyclized product (III) through intramolecular bonding at boron. These observations have prompted us to undertake the X-ray crystal structure analysis of (I) to determine the atomic arrangement in the solid state, a consideration of potential importance in the synthetic design of other boronic acids.



(I)



(II)



(III)

Experimental. Crude samples of (I) were obtained by nitration of 4-carboxybenzeneboronic acid (Torssell, 1957; Soundararajan *et al.*, 1989) and recrystallized

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