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1-Diphenylphosphino-1,2-dicarba-*closo*-dodecaborane(12) at 153 K

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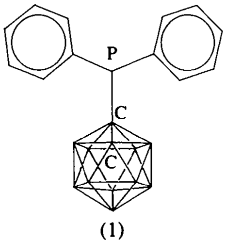
Abstract

The title molecule, $C_{14}H_{21}B_{10}P$, assumes *m* symmetry, with the P atom, the two cluster C atoms and the two B atoms forming the mirror plane. Bond lengths are P—C(cage) 1.871 (6), P—C(aryl) 1.828 (4) and C(cage)—C(cage) 1.666 (9) Å.

Comment

Considerable variation in the C1—C2 bond length has been observed for 1,2-*RR*′-1,2-dicarba-*closo*-dodecaborane derivatives, depending on substituents *R* and *R*′. A C1—C2 distance of 1.634 (3) Å is reported for 9,12-μ-[$(CH_3)_2CS_2$]-1,2-$C_2B_{10}H_{10}$, in which H atoms are attached to both cluster C atoms (Šubrtová, Línek & Hašek, 1980), and much longer distances of 1.858 (5) and 1.826 (5) Å are reported for 1,2-μ-S($CH_2CH_2OCH_2CH_2OCH_2$)S-$C_2B_{10}H_{10}$, in which S atoms are bonded to both cluster C atoms (Teixidor, Viñas, Rius, Miravitlles & Casabó, 1990). Recently, we suggested an explanation for the lengthening of the C1—C2 bond (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994) and proposed empirically derived equations for calculating the C1—C2 distances in *o*-carborane derivatives (Kivekäs, Sillanpää, Teixidor, Viñas, Nuñez & Abad, 1995). Computational studies of dithioether *o*-carborane compounds using semi-empirical quantum-mechanical calculations (CNDO and MNDO) suggest extremely long and unrealistic C1—C2 distances. To obtain more realistic C1—C2 distances in *o*-carborane derivatives using CNDO and MNDO methods, crystal structure analyses of numerous compounds incorporating various types of C substituents are required. To this end, we have synthesized the title compound, (1), and determined its crystal structure at 153 K.



(1)

In (1), the P atom is bonded in a pyramidal arrangement to a C atom of each of the phenyl groups, and C1 of the carborane moiety. The molecule assumes *m* symmetry, with the P atom, the two cluster C atoms and two B atoms (B7 and B8) occupying the mirror plane. The P—C(cage) bond is longer than the P—C(aryl) bonds and the bond lengths do not deviate significantly from those reported for 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane, (2) (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994). However, there are slight differences in the C—P—C angles between the two compounds.

The most notable difference between (1) and the 2-methyl substituted derivative (2) is in the molecular symmetry. Compound (2) assumes C_1 symmetry and the orientation of the phenyl groups with respect to the carborane cage is significantly different from that in (1), where the symmetry is *m*. In (2), the C(aryl)—P—C1—C2 torsion angles are 95.8 (3) and −154.9 (3)°, while in (1) the angle is 124.6 (1)°. This difference may be attributed to packing effects.

Although the orientations of the phenyl groups differ in the two compounds, the bond angles of the diphenylphosphine groups and those around C1 show similar trends. The P—C(aryl)—C(aryl) angles are significantly different and opening of the P—C9—C14 angle in (1) can also be assumed to result from the mutual repulsion between the two phenyl rings. In the borane polyhedron, the C1—B bond lengths are equal but the angles around C1 vary from 108.5 (4) to 129.7 (3)°. The considerable opening of the P—C1—B3 angle is probably due to the need to avoid repulsion between the phenyl groups and the carborane polyhedron.

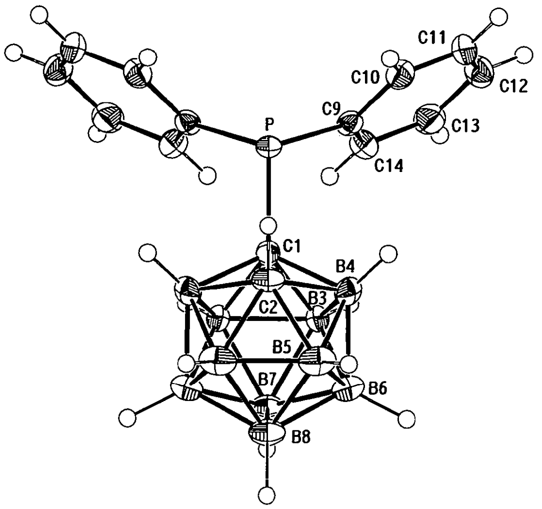


Fig. 1. View of the structure of (1) with displacement ellipsoids at 50% probability levels. H atoms are drawn as small circles or arbitrary radii.

The C1—C2 bond of 1.666 (9) Å in (1) is just significantly longer than the distance of 1.634 (3) Å reported for 9,12-μ-[$(CH_3)_2CS_2$]-1,2-$C_2B_{10}H_{10}$, which has non-substituted cluster C atoms (Šubrtová, Línek & Hašek, 1980). On the other hand, the C1—C2 distance in (1) is slightly shorter than in the 1,2-substituted compound (2). These differences in the C1—C2 bond lengths, nevertheless, are not great and can be considered to be as expected. The values support the generalization that an increasing number of cluster C-atom substituents increases the C—C bond length. However, the distance in the title compound does not differ significantly from the value 1.688 (5) Å reported for 1,1′;2,2′-bis-μ-dimethylsilyl-bis[dicarba-*closo*-dodecaborane(12)] (Kivekäs, Romerosa & Viñas, 1994). This is in agreement with our assumption that electronic factors do not affect the C—C distance when the substituent is silicon (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994).

Experimental

Before use, *o*-carborane (Dexsil Chemical Corporation) was sublimed under high vacuum. A 1.6 *M* solution of *n*-butyllithium in hexane from Fluka and chlorodiphenylphosphine from Aldrich were used as purchased. To a three-necked round bottom flask (250 ml) fitted with a dinitrogen inlet/outlet, containing deoxygenated dry toluene (50 ml), *o*-carborane (1.5 g, 10.4 mmol) was added. The mixture was cooled (ice–water) during the addition of *n*-butyllithium (6.5 ml, 10.4 mmol). After stirring for 30 min at the ice–water temperature, the mixture was stirred at room temperature for 30 min, and again cooled at 273 K before the addition of chlorodiphenylphosphine (2.30 g, 10.4 mmol) over a period of 30 min. The mixture was stirred for 1 h at this temperature and 1 h more at room temperature, and under reflux for 2 h. Once cooled, diethyl ether (15 ml) and water (20 ml) were added. Stirring was continued for 10 min before the two layers were separated. The toluene extract was dried and evaporated under vacuum. The evaporation of the solvent yielded a yellow oily material which was recrystallized by a 1:1 (*v*/*v*) proportion of petroleum ether and diethyl ether (1.8 g, 53%).

Analysis: calculated for $C_{14}H_{21}B_{10}P$, C 51.21, H 6.5%; found, C 52.22, H 6.6%. FTIR (KBr) ν (cm^{-1}): 3050 (BC—H); 2607, 2579, 2551 (B—H); 1433, 1068, 1018 (C—H); 744, 702, 498 (P—Ph). ^1H FTNMR (250 MHz, $CDCl_3$, 298 K, TMS) δ (p.p.m.): 3.43 (*s*, 1, C_c—H), 7.39–7.78 (*m*, 10, P—C_6H_5). ^{11}B FTNMR (128 MHz, $CDCl_3$, 298 K, $BF_3.Et_2O$) δ (p.p.m.): −1.68 [*d*, ^1J(B,H) = 146.9 Hz, 2B], −7.58 [*d*, ^1J(B,H) = 149.6 Hz, 2B], −10.64 [*d*, ^1J(B,H) = 148.5 Hz, 2B], −12.52 [*d*, ^1J(B,H) = 180.0 Hz, 4B]. ^{31}P FTNMR (161 MHz, $CDCl_3$, 298 K, H_3PO_4) δ (p.p.m.): 25.58 (*s*, PPh_2).

Elemental analyses were performed with a Perkin-Elmer 240-B microanalyser. The ^1H NMR, ^{11}B NMR and ^{31}P NMR spectra were obtained with a Bruker AM 400WB or AC 250 instrument, and IR spectra of KBr pellets were recorded with a Nicolet 710-FT spectrophotometer.

Crystal data

$C_{14}H_{21}B_{10}P$
$M_r = 328.39$
Orthorhombic
$Cmc2_1$
$a = 16.037\ (3)$ Å
$b = 8.769\ (4)$ Å
$c = 12.804\ (3)$ Å
$V = 1801\ (1)$ Å^3
$Z = 4$
$D_x = 1.211$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.2$–$15.1°$
$\mu = 0.14$ mm^{-1}
$T = 153$ K
Plate
0.41 × 0.32 × 0.10 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans
$T_{min} = 0.947$, $T_{max} = 1.000$
1119 measured reflections
1119 independent reflections

958 observed reflections [$F > 2\sigma(F)$]
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 150 reflections intensity decay: 0.2%

Refinement

Refinement on *F*
$R = 0.062$
$wR = 0.045$
$S = 1.253$
958 reflections
139 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.22$

$\Delta\rho_{max} = 0.5$ e Å^{-3}
$\Delta\rho_{min} = -0.4$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	*y*	*z*	U_{eq}
P	1/2	0.5177 (2)	0.30000†	0.0208 (4)
C1	1/2	0.7261 (7)	0.3314 (5)	0.021 (2)
C2	1/2	0.7464 (7)	0.4608 (5)	0.025 (2)

B3	0.4443 (3)	0.8737 (5)	0.2746 (4)	0.023 (2)
B4	0.4103 (3)	0.7869 (6)	0.3936 (4)	0.025 (2)
B5	0.4443 (4)	0.9014 (6)	0.5005 (5)	0.032 (2)
B6	0.4097 (3)	0.9873 (6)	0.3817 (4)	0.027 (2)
B7	1/2	1.0415 (7)	0.3107 (7)	0.022 (2)
B8	1/2	1.0593 (9)	0.4470 (6)	0.030 (3)
C9	0.4092 (3)	0.4908 (5)	0.2157 (3)	0.022 (1)
C10	0.3533 (3)	0.3806 (5)	0.2525 (4)	0.028 (1)
C11	0.2822 (3)	0.3428 (6)	0.1975 (4)	0.035 (2)
C12	0.2659 (3)	0.4129 (6)	0.1033 (4)	0.034 (2)
C13	0.3206 (3)	0.5208 (6)	0.0640 (4)	0.036 (2)
C14	0.3932 (3)	0.5586 (5)	0.1198 (4)	0.026 (1)

† Fixed to define origin.

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

P—C1	1.871 (6)	C1—B4	1.729 (6)
P—C9	1.828 (4)	C2—B4	1.714 (6)
C1—C2	1.666 (9)	C2—B5	1.705 (8)
C1—B3	1.732 (7)		
C1—P—C9	104.7 (2)	P—C1—B4	113.6 (3)
C9—P—C9^{i}	105.6 (2)	P—C9—C10	113.6 (3)
P—C1—C2	108.5 (4)	P—C9—C14	127.9 (3)
P—C1—B3	129.7 (3)		
C9—P—C1—C2	124.6 (1)	C9—P—C1—B4	59.4 (4)
C9—P—C1—B3	−13.3 (4)		

Symmetry code: (i) $1 - x, y, z$.

Non-H atoms were refined with anisotropic displacement parameters and H atoms of the carborane cage with fixed isotropic displacement parameters. H atoms of the phenyl ring were placed at calculated positions (C—H = 0.95 Å and U_H equal to U_{eq} of carrying atom) and not refined.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement: *Xtal*3.2 (Hall, Flack & Stewart, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976) in *Xtal*3.2. Preparation of material for publication: *ATABLE* and *BONDLA* in *Xtal*3.2.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1245). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-(Diethyldithiocarbamato)diiodo(phenyl)tellurium(IV), $PhTe(S_2CNEt_2)I_2$, and its Methoxy-Substituted Mixed Br/I Analogue *cis*-Bis(0.4-bromo/0.6-iodo)(diethyldithiocarbamato)(4-methoxyphenyl)tellurium(IV), *p*-$MeOC_6H_4Te(S_2CNEt_2)(Br_{0.4}I_{0.6})_2$

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Abstract

The Te^{IV} complexes $PhTe(S_2CNEt_2)I_2$, (1), and *p*-$MeOC_6H_4Te(S_2CNEt_2)(Br_{0.4}/I_{0.6})_2$, (2), have been synthesized by reacting $PhTeI_3$ with NaS_2CNEt_2, and *p*-$MeOC_6H_4Te(S_2CNEt_2)_2I$ with Br_2, respectively. In (2), both I atoms are partially replaced by Br atoms in a 3:2 ratio. The structures display distorted octahedral Te coordination with two symmetrically coordinated S atoms [Te—S 2.550 (2)–2.569 (2) Å in three independent molecules of (1) and 2.523 (1) and 2.535 (1) Å in (2)] and with two *cis*-disposed halogen atoms [Te—I 2.941 (1)–2.986 (1) Å in (1) and 3.003 (4) and 3.049 (3) Å in (2); Te—Br 2.962 (8) and 2.967 (8) Å in (2)] in equatorial positions. The aryl group is axial in both complexes [Te—C 2.137 (6)–2.146 (6) and 2.123 (5) Å in (1) and (2), respectively] and the second axial posi-

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