

Acta Cryst. (1996). **C52**, 2223–2225**1-Diisopropylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12)**REIJO SILLANPÄÄ,^{a*} RAIKKO KIVEKÄS,^{b†} FRANCESC TEIXIDOR,^c CLARA VIÑAS^c AND ROSARIO NUÑEZ^c^a*Department of Chemistry, University of Turku, FIN-20500 Turku, Finland,* ^b*Inorganic Chemistry Laboratory, PO Box 55, FIN-00014 University of Helsinki, Finland,* and ^c*Institut de Ciència dels Materials (CSIC), Campus de Bellaterra, 08193 Bellaterra, Barcelona, Spain*

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Abstract

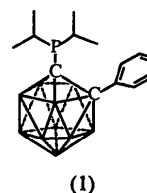
In the title compound, C₁₄H₂₉B₁₀P, the diisopropylphosphine and phenyl groups are bonded to the C atoms of the 1,2-dicarbadodecaborane cage. Bond lengths are P—C_{cage} 1.879 (3), P—C_{Pr} 1.866 (4) and 1.881 (4), and C_{cage}—C_{cage} 1.769 (4) Å. The elongation of the C_{cage}—C_{cage} bond is discussed.

Comment

C_{cage}—C_{cage} distances [C(1)—C(2) or C_c—C_c] in 1,2-dicarba-*closo*-dodecaboranes vary considerably depending on the cluster carbon substituents. Some general trends affecting the length of the cluster C_c—C_c distance have been observed: (i) the distance increases with increasing number of substituents on the cluster C atoms; (ii) in compounds substituted with sulfur, the distance is longer than in unsubstituted compounds or in compounds substituted with carbon or silicon; (iii) the distance seems to be longer in aryl than in non-aryl substituted compounds (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994; Lewis & Welch, 1993). Thus, in compounds containing two S substituents, long C(1)—C(2) distances of 1.858 (5), 1.826 (5) (Teixidor, Viñas, Rius, Miravittles & Casabó, 1990) and 1.816 (6) Å (Teixidor, Romerosa, Rius, Miravittles, Casabó, Viñas & Sanchez, 1990) are reported, whereas in the 1,2-unsubstituted compound 9,12-isopropylidenedithio-1,2-dicarba-*closo*-dodecaborane(12), the distance is only 1.634 (3) Å (Šubrtová, Líněk & Hašek, 1980).

In a recent series of papers, we have explained the elongation of the C_c—C_c bond and suggested an empirically derived equation to calculate this distance (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994; Kivekäs, Sillanpää, Teixidor, Viñas, Nuñez & Abad, 1995). We have also reported the crystal structures of several 1,2-dicarba-*closo*-dodecaborane compounds containing different substituents connected to the cluster

C atoms, namely, 1-diisopropylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane(12), (2), 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane(12), (3) (Kivekäs, Sillanpää, Teixidor, Viñas, Nuñez & Abad, 1995), 1-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane(12), (4) (Kivekäs, Teixidor, Viñas & Nuñez, 1995), and 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane(12), (5) (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994). To obtain further insight into the effect of the substituents on the lengthening of the C_c—C_c bond, we now report the preparation and crystal structure determination of the title compound, 1-diisopropylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12), (1).



In compound (1), the diisopropylphosphine and phenyl groups are connected to the cluster C atoms. These substituents are oriented so that they avoid mutual close contacts, as can be seen in Fig. 1 and from the torsion angle values in Table 2. The P atom is bonded in a pyramidal arrangement to two C atoms of two isopropyl groups and to the C(1) atom of the carborane moiety. The P—C bond lengths in (1) are equal within experimental error and the P—C distance is in reasonable agreement with those of compounds (2)–(5). In (1), the P—C(1)—X angles vary considerably and indicate a trend similar to that observed for compounds (2)–(5),

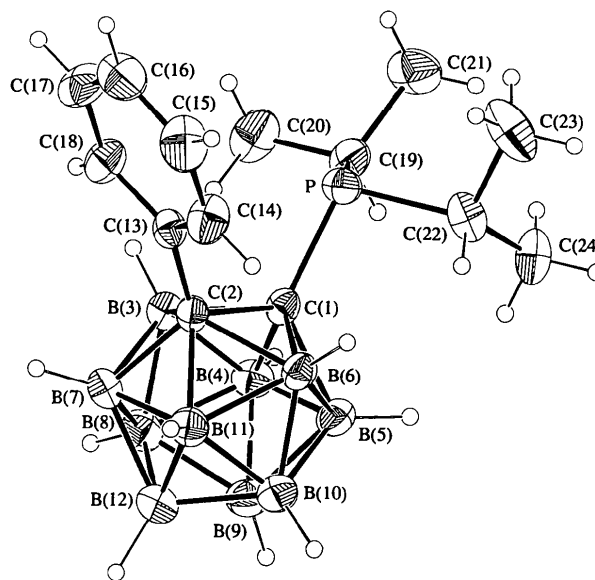


Fig. 1. ORTEPII (Johnson, 1976) plot of compound (1). Displacement ellipsoids are drawn at the 30% probability level.

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i.e. the P—C(1)—C(2) angle is relatively closed and the P—C(1)—B(4) and P—C(1)—B(5) angles are relatively open. The X—C(2)—C(13) angles, on the other hand, vary only slightly, as is also the case in compound (2). The P···C(13) distance is 3.310(4) Å, which is only *ca* 0.2 Å shorter than the sum of the corresponding van der Waals radii (Bondi, 1964; Allinger, Hirsch, Miller, Tyminski & van Catledge, 1968). The P···C(13) distance, the angles around the cluster C atoms and the low P—C(1)—C(2)—C(13) torsion angle value indicate the absence of a noteworthy repulsion between the C(13) and P atoms. The geometric parameters of the P—C(1)—C(2)—C(13) moiety in (1) are very similar to those of compound (2).

Because the C_c—C_c distances in aryl-substituted compounds are longer than those in non-aryl substituted compounds, we could predict that in (1), with P and C_{aryl} substituents, the distance should be longer than in (2) with P and C_{alkyl} substituents. The crystal structure of (1) confirms this. Thus, in compounds (1)–(5), the elongation of the C_c—C_c distances agrees with the general trends mentioned above, with the distance being shortest in monosubstituted compound (4) [1.666(9) Å]; the distances in compounds (2), (3) and (5) are longer than that in (4), with compound (1) having the longest bond. The C_c—C_c distances in (2), (3) and (5) do not differ significantly, although the substituents on one of the C_c atoms are very different, *i.e.* CH₃ in (2) and (5), and P[CH(CH₃)₂]₂ in (3). The distances are similar to the average distance of 1.727(6) Å found in 1,2-diphenyl-1,2-dicarba-*closo*-dodecaborane(12), (6) (Lewis & Welch, 1993). It was suggested that some degree of intramolecular crowding exists in (6), but no opening of the C_c—C_c—C_{aryl} angles was observed. As the e.s.d.'s of the C_c—C_c bonds in the comparison compounds are not all low, it has not been possible to account for the differences due to the following pairs of substituents: two P, P and one non-aryl, and two aryl. The C_c—C_c distance in compound (1) may be accounted for by the additive formula

$$d = d_o + \Sigma(a_i + S_i)$$

where $d_o = 1.634(3)$ Å and a_i and S_i are the electronic and steric contributions, respectively (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1995). Applying this equation to compound (6) gives $a_i + S_i = 0.04$ Å per C₆H₅ group. Earlier data have indicated $a_i = 0$ and $S_i = 0.04$ for the P[CH(CH₃)₂]₂ group, resulting in a calculated value of $d = 1.71$ Å, which is 0.06 Å shorter than that found experimentally. Further work is needed to understand the conversion between the *closo*, *nido* and *arachno* structures experienced in these clusters.

Experimental

The synthesis of (1) was carried out as for compounds (2)–(5) (Kivekäs, Sillanpää, Teixidor, Viñas, Nuñez & Abad, 1995; Kivekäs, Teixidor, Viñas & Nuñez, 1995; Kivekäs,

Sillanpää, Teixidor, Viñas & Nuñez, 1994) starting from 1-Ph-1,2-C₂B₁₀H₁₁ and ClP[CH(CH₃)₂]₂ (yield 85%). Analysis: calculated for C₁₄H₂₉B₁₀P: C 49.98, H 8.69%; found: C 49.98, H 8.58%. FT-IR (KBr): ν (cm⁻¹) 2952, 2924, 2868 (C—H), 2614, 2579 (B—H). ¹H FT-NMR [250 MHz, (CD₃)₂CO, 298 K, TMS]: δ 1.11 (*m*, 12H, CH₃), 2.10 (*m*, 2H, CH), 7.66–7.43 (*m*, 5H, C₆H₅). ¹¹B FT-NMR [128 MHz, (CD₃)₂CO, 298 K, BF₃·Et₂O]: δ -0.03 [*d*, ¹J(B,H) = 143.1 Hz, 1B], -3.56 [*d*, ¹J(B,H) = 147.1 Hz, 1B], -9.06 [*d*, ¹J(B,H) = 139.4 Hz, 4B], -10.05 [*d*, ¹J(B,H) = 157.2 Hz, 2B], -11.62 [*d*, ¹J(B,H) = 187.6 Hz, 2B]. ³¹P{¹H} FT-NMR [101 MHz, (CD₃)₂CO, 298 K, H₃PO₄]: δ 38.50 [*s*, P(Pr)₂]. ¹³C{¹H} NMR [75 MHz, (CD₃)₂CO, 298 K, TMS]: δ 18.65 [*d*, ²J(C,P) = 7.6 Hz], 22.15 [*d*, ²J(C,P) = 22.6 Hz], 26.35 [*d*, ¹J(C,P) = 26.35 Hz], 86.99 [*d*, J(C,P) = 86.05 Hz], 88.25 [*d*, J(C,P) = 18.87 Hz], 128.50 (*s*), 130.72 (*s*), 131.00 (*s*), 131.81 (*s*).

Crystal data

C₁₄H₂₉B₁₀P

$M_r = 336.46$

Monoclinic

$P2_1/n$

$a = 9.673(1)$ Å

$b = 20.021(2)$ Å

$c = 10.571(2)$ Å

$\beta = 90.89(1)^\circ$

$V = 2047.0(5)$ Å³

$Z = 4$

$D_x = 1.092$ Mg m⁻³

D_m not measured

Mo K α radiation

$\lambda = 0.71073$ Å

Cell parameters from 25

reflections

$\theta = 10.1$ – 15.9°

$\mu = 0.124$ mm⁻¹

$T = 295$ K

Plate

$0.35 \times 0.30 \times 0.15$ mm

Colourless

Data collection

Rigaku AFC-5S diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scans (North, Phillips & Mathews, 1968)

$T_{\min} = 0.935$, $T_{\max} = 1.000$

3966 measured reflections

3737 independent reflections

2141 observed reflections

[$F > 4\sigma(F)$]

$R_{\text{int}} = 0.031$

$\theta_{\max} = 25^\circ$

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 23$

$l = 0 \rightarrow 12$

3 standard reflections

monitored every 150

reflections

intensity decay: 0.5%

Refinement

Refinement on F

$R = 0.057$

$wR = 0.058$

$S = 1.626$

2141 reflections

256 parameters

H atoms: see below

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.2$ e Å⁻³

$\Delta\rho_{\min} = -0.3$ 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 (Å²)

	$U_{\text{eq}} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
P	0.1080 (1)	0.07041 (5)	0.20574 (9)	0.0503 (3)
C(1)	0.2075 (3)	0.1416 (2)	0.2787 (3)	0.042 (1)
C(2)	0.3296 (3)	0.1775 (2)	0.1759 (3)	0.041 (1)
B(3)	0.3833 (4)	0.1295 (2)	0.3017 (4)	0.047 (1)

B(4)	0.2716 (5)	0.1468 (2)	0.4300 (4)	0.053 (2)
B(5)	0.1455 (5)	0.2039 (2)	0.3737 (4)	0.056 (2)
B(6)	0.1798 (4)	0.2197 (2)	0.2125 (4)	0.048 (2)
B(7)	0.4699 (5)	0.2043 (2)	0.2613 (4)	0.051 (2)
B(8)	0.4347 (5)	0.1857 (2)	0.4214 (4)	0.059 (2)
B(9)	0.2873 (5)	0.2328 (2)	0.4648 (5)	0.063 (2)
B(10)	0.2298 (5)	0.2779 (2)	0.3309 (5)	0.060 (2)
B(11)	0.3424 (5)	0.2609 (2)	0.2058 (4)	0.053 (2)
B(12)	0.4092 (5)	0.2680 (2)	0.3620 (4)	0.061 (2)
C(13)	0.3453 (3)	0.1515 (2)	0.0437 (3)	0.046 (1)
C(14)	0.2772 (4)	0.1812 (2)	-0.0567 (4)	0.069 (2)
C(15)	0.2961 (5)	0.1589 (3)	-0.1780 (4)	0.087 (2)
C(16)	0.3820 (6)	0.1069 (3)	-0.2026 (4)	0.085 (2)
C(17)	0.4512 (5)	0.0774 (2)	-0.1044 (4)	0.080 (2)
C(18)	0.4339 (4)	0.0996 (2)	0.0187 (4)	0.062 (2)
C(19)	0.1088 (4)	0.0046 (2)	0.3308 (3)	0.058 (1)
C(20)	0.2495 (5)	-0.0277 (2)	0.3505 (4)	0.085 (2)
C(21)	0.0054 (5)	-0.0494 (2)	0.2870 (4)	0.087 (2)
C(22)	-0.0737 (4)	0.1039 (2)	0.2065 (4)	0.065 (2)
C(23)	-0.1547 (5)	0.0741 (3)	0.0929 (4)	0.103 (2)
C(24)	-0.1560 (4)	0.0988 (2)	0.3277 (4)	0.090 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

P—C(1)	1.879 (3)	C(1)—B(6)	1.731 (5)
P—C(19)	1.866 (4)	C(2)—C(13)	1.501 (5)
P—C(22)	1.881 (4)	C(19)—C(20)	1.519 (6)
C(1)—C(2)	1.769 (4)	C(19)—C(21)	1.540 (6)
C(1)—B(3)	1.730 (5)	C(22)—C(23)	1.544 (6)
C(1)—B(4)	1.710 (5)	C(22)—C(24)	1.522 (6)
C(1)—P—C(19)	104.4 (2)	B(6)—C(2)—C(13)	118.4 (3)
C(1)—P—C(22)	101.5 (2)	B(7)—C(2)—C(13)	120.7 (3)
C(19)—P—C(22)	104.0 (2)	B(11)—C(2)—C(13)	120.4 (3)
P—C(1)—C(2)	113.5 (2)	C(2)—C(13)—C(14)	120.9 (3)
P—C(1)—B(3)	116.6 (2)	C(2)—C(13)—C(18)	120.9 (3)
P—C(1)—B(4)	127.3 (2)	P—C(19)—C(20)	113.1 (3)
P—C(1)—B(5)	127.6 (2)	P—C(19)—C(21)	106.7 (3)
P—C(1)—B(6)	116.3 (2)	P—C(22)—C(23)	108.8 (3)
C(1)—C(2)—C(13)	120.5 (3)	P—C(22)—C(24)	118.7 (3)
B(3)—C(2)—C(13)	119.5 (3)		
C(19)—P—C(1)—C(2)	134.9 (2)		
C(22)—P—C(1)—C(2)	-117.2 (2)		
P—C(1)—C(2)—C(13)	0.7 (4)		
C(1)—C(2)—C(13)—C(14)	95.6 (4)		
C(1)—C(2)—C(13)—C(18)	-88.0 (4)		

The non-H atoms were refined with anisotropic displacement parameters and H(B) atoms with fixed isotropic displacement parameters. H(C) atoms were placed at fixed positions (C—H = 0.95 \AA) and not refined.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1989a). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYLSQ* in *Xtal3.0* (Hall & Stewart, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976) in *Xtal3.0*. Software used to prepare material for publication: *ATABLE* and *BONDLA* in *Xtal3.0*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and contact distances, have been deposited with the IUCr (Reference: AB1350). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-2-*sec*-Butyl-4-{4-[4-(4-{[2-(2,4-dichlorophenyl)-2-(1*H*-1,2,4-triazol-1-ylmethyl)-1,3-dioxolan-4-yl]methoxy}phenyl)-1-piperazinyl]phenyl}-2,4-dihydro-3*H*-1,2,4-triazol-3-one (Itraconazole†)

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Abstract

The molecular structure of itraconazole, $\text{C}_{35}\text{H}_{38}\text{Cl}_2\text{N}_8\text{O}_4$, has been determined from single-crystal X-ray diffraction data. The two molecules in the asymmetric unit differ mainly in the conformation of the methoxy-

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