Diffraction intensities from the crystals were generally weak and only 49% of the reflections were observed with $I > 2\sigma(I)$, as evidenced by the high R_{int} value. All H-atom positions (except for H1O and H2O) were calculated using a riding model and were considered with fixed isotropic displacement parameters in all refinements. The H1O and H2O atoms were found in the difference Fourier maps calculated at the end of the refinement process as small positive electron densities and were not refined.

Data collection: *Nonius Diffractometer Control Software* (Nonius, 1993). Cell refinement: *Nonius Diffractometer Control Software*. Data reduction: *REDU*4 (Stoe & Cie, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

References

Cimerman, Z., Galešić, N. & Bosner, B. (1992). *J. Mol. Struct.* **274**, 131–144.
Cohen, M. D., Schmidt, G. M. J. & Flavian, S. (1964). *J. Chem. Soc.* pp. 2041–2051.
Corden, J. P., Errington, W., Moore, P. & Wallbridge, M. G. H. (1996). *Acta Cryst.* **C52**, 125–127.
Elerman, Y., Elmali, A., Atakol, O. & Svoboda, I. (1995). *Acta Cryst.* **C51**, 2344–2346.
Elerman, Y., Elmali, A., Kabak, M., Aydin, M. & Peder, M. (1994). *J. Chem. Crystallogr.* **24**, 603–606.
Elerman, Y., Elmali, A., Kendi, E., Özbey, S. & Ertüzün, V. (1997). *Acta Cryst.* **C53**, 1158–1160.
Elerman, Y., Kabak, M., Elmali, A. & Svoboda, I. (1998). *Acta Cryst.* **C54**, 128–130.
Elerman, Y., Paulus, H., Svoboda, I. & Fuess, H. (1992). *Z. Kristallogr.* **198**, 135–136.
Elerman, Y., Svoboda, I. & Fuess, H. (1991). *Z. Kristallogr.* **196**, 309–311.
Elmali, A. & Elerman, Y. (1997). *Acta Cryst.* **C53**, 791–793.
Elmali, A. & Elerman, Y. (1998). *J. Mol. Struct.* **441**, 31–37.
Elmali, A., Elerman, Y. & Zeyrek, C. T. (1998). *J. Mol. Struct.* **443**, 123–130.
Elmali, A., Özbey, S., Kendi, E., Kabak, M. & Elerman, Y. (1995). *Acta Cryst.* **C51**, 1878–1880.
Garnovskii, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* **126**, 1–69.
Gavranić, M., Kaitner, B. & Meštrović, E. (1996). *J. Chem. Cryst.* **26**, 23–28, and references therein.
Hadjoudis, E., Vitterakis, M., Moustakali-Mavridis, I. (1987). *Tetrahedron*, **43**, 1345–1360.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nonius (1993). *Nonius Diffractometer Control Software.* Release 5.1. Nonius GmbH, Solingen, Germany.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Pahor, N. B., Calligaris, M., Delize, P., Dodic, G., Nardin, G. & Randaccio, L. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2478–2483.
Pahor, N. B., Calligaris, M., Nardin, G. & Randaccio, L. (1978). *Acta Cryst.* **B34**, 1360–1363.
Senn, R. & Nowacki, W. (1977). *Z. Kristallogr.* **145**, 16–27.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Stoe & Cie (1991). *REDU*4. *Data Reduction Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.
Subrahmanyam, C., Seshasayee, M. & Aravamudan, G. (1982). *Cryst. Struct. Commun.* **11**, 1719–1723.

2,4-Cl₂-6,9-*exo,endo*-(PMe₂Ph)₂-*arachno*-B₁₀H₁₀

Udo Dörfler, Thomas D. McGrath, Paul A. Cooke, John D. Kennedy and Mark Thornton-Pett

School of Chemistry, The University of Leeds, Leeds LS2 9JT, England. E-mail: marktp@chem.leeds.ac.uk

Abstract

The title compound, 2,4-dichloro-6-*exo*-9-*endo*-bis(dimethylphenylphosphino)-*arachno*-decaborane(10) [(PMe₂Ph)₂B₁₀H₁₀Cl₂ or C₁₆H₃₂B₁₀Cl₂P₂], has a typical *arachno* ten-vertex cluster geometry, with one of the phosphine ligands bound *exo*-polyhedrally and the other in an uncommon *endo* configuration.

Comment

Ten years ago, Fontaine & Kennedy (1987) reported the identification by NMR spectroscopy of the previously unknown *exo,endo*-isomer, (I), of [6,9-(PMe₂Ph)₂-*arachno*-B₁₀H₁₂], formed concomitantly with the corresponding conventional *exo,exo*-isomer, (II). We have recently (Dörfler *et al.*, 1997) confirmed the structures of (I) and (II) by single-crystal X-ray diffraction studies, and also confirmed the structure of (III), the 2-bromo-substituted analogue of (I). These structural studies suggested some differential perturbation of the cluster that arises from the presence of an *endo*-P *versus* *exo*-P substituent. However, in (III), there are some deviations in structure that may be due to the presence of the single boron-bound halogen and this substituent might equally contribute to apparent *exo versus endo* perturbation. To examine further for patterns of structure flexing which might be attributable to *exo/endo* substitution, and for any effect of a halogen substituent upon this, we have determined the structure of the symmetrically dichloro-substituted title compound, (IV).

$C_{16}H_{32}B_{10}Cl_2P_2$

(I)   (II)

(III)   (IV)
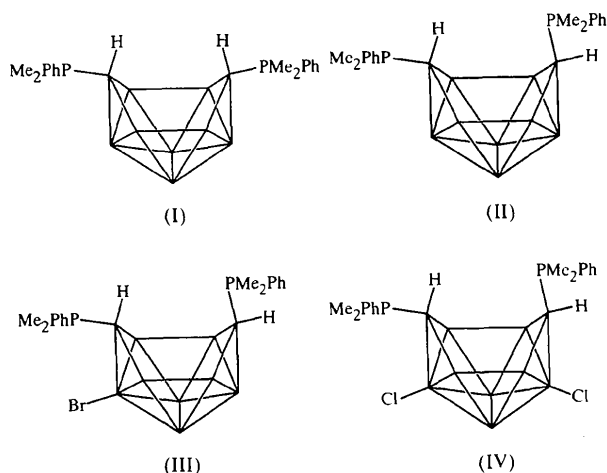
The molecule of (IV) has approximate C_s molecular symmetry (ignoring the dispositions of the P-bound organic groups). As expected, the cluster has typical *arachno*-decaboranyl character, exemplified by the presence of two H atoms symmetrically bridging the B5—B10 and B7—B8 connectivities; the lengths of these two vectors [1.879 (3) and 1.886 (3) Å, respectively] are further consistent with the *arachno* descriptor. [These distances are typically longer (*ca* 2.0 Å) in a *nido* ten-vertex cluster.] Atoms Cl2 and Cl4 are bound at 1.823 (2) and 1.827 (2) Å from B2 and B4, respectively, these distances being typical of *exo*-(B—Cl) separations in polyhedral boranes (Fletcher *et al.*, 1996). Interestingly, there is no significant shortening [compared with the parent (I)] of those B—B connectivities involving chloro-substituted B2 and B4, in contrast to the apparent effect of the single bromo substituent in (III).

However, the most significant feature of the geometry determined for (IV) is the structural confirmation of a further example of an *exo,endo*-6,9-disubstituted *arachno*-decaborane. The two P atoms, P1 and P2, are bound at distances of 1.922 (2) and 1.924 (2) Å from their respective parent B atoms, B6 and B9, which compare with a range of 1.912 (3)–1.928 (4) Å for *exo,exo*-(II) and *exo,endo*-(III). This contrasts with the situation in *exo,endo*-(I), where the *exo*-P atom is 1.9145 (14) Å from B6, but the *endo*-P atom is much further [1.941 (2) Å] from B9. In addition, the B2—B6—P1 and B4—B9—P2 angles in (IV) [117.38 (14) and 157.66 (15)°, respectively] are both slightly more obtuse than in (I), where they are 110.20 (8) and 155.86 (10)°, respectively. This may arise from the steric and/or electronic influence of the two chloro substituents, but may equally be due simply to a slightly different molecular-packing arrangement in the solid state.

There are, however, some small but potentially significant effects upon the structure of the decaboranyl cluster that may be attributable to the presence of an *endo*-P versus *exo*-P substituent. The three B—B connectivities involving B9 are slightly longer than the three

corresponding vectors involving B6. Similarly, there is some enlargement of the B5—B10—B9 and B7—B8—B9 angles [116.25 (14) and 115.68 (14)°, respectively] in (IV) compared with the equivalent angles to B6, namely, B6—B5—B10 and B6—B7—B8 [112.66 (14) and 113.42 (14)°, respectively]; and the B1—B4—B9 and B3—B4—B9 angles [118.20 (16) and 118.21 (16)°, respectively] are slightly larger than B1—B2—B6 and B3—B2—B6 [116.24 (15) and 115.40 (16)°, respectively]. The pattern of these perturbations mirrors that seen in (I), and has been attributed to the presence of *endo* versus *exo* substituents (Dörfler *et al.*, 1997). Perhaps surprisingly, it has been found that (IV) does not readily isomerize on heating to its *exo,exo* counterpart (Dörfler *et al.*, 1997), despite the significant weakening of the bonds to the *endo*-P-substituted vertex B9. Such lengthening in non-chlorinated (I) has been suggested (Dörfler *et al.*, 1997) to facilitate the thermal conversion of (I) to (II). The chloro substituents, therefore, appear to have either a steric and/or an electronic influence on the course of such a reaction. We are currently probing this phenomenon further.
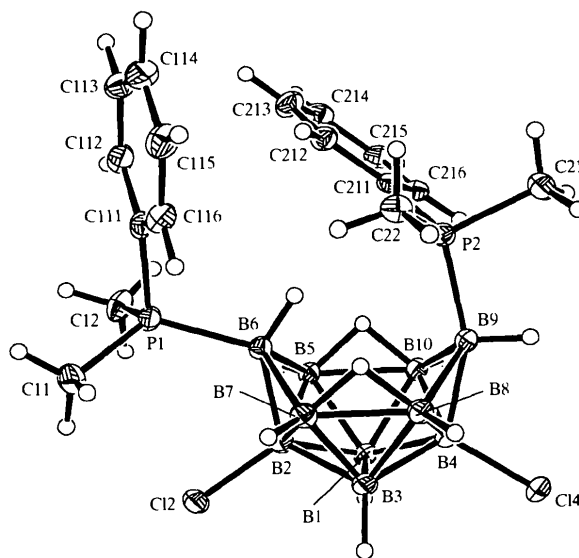

Fig. 1. Perspective view of a molecule of (IV) drawn with 40% probability ellipsoids and with H atoms shown as small circles of arbitrary radii for clarity.

Experimental

Compound (IV) was prepared as reported elsewhere (Dörfler *et al.*, 1997). Suitable single crystals were obtained by the slow mutual diffusion of hexane and a dichloromethane solution at 293 K.

Crystal data

$C_{16}H_{32}B_{10}Cl_2P_2$
$M_r = 465.36$

Cu $K\alpha$ radiation
$\lambda = 1.54186$ Å

Monoclinic
$P2_1/n$
$a = 9.7987\,(8)$ Å
$b = 19.1424\,(14)$ Å
$c = 13.3366\,(11)$ Å
$\beta = 98.816\,(7)°$
$V = 2472.0\,(3)$ Å^3
$Z = 4$
$D_x = 1.250$ Mg m^{-3}
D_m not measured

Cell parameters from 74
reflections
$\theta = 30.1-39.7°$
$\mu = 3.578$ mm^{-1}
$T = 160\,(2)$ K
Prism
$0.50 \times 0.29 \times 0.15$ mm
Colourless

Data collection

Stoe Stadi-4 four-circle
diffractometer
ω/θ scans
Absorption correction:
ψ scans (North *et al.*,
1968)
$T_{min} = 0.338$, $T_{max} = 0.585$
8127 measured reflections
4091 independent reflections

3693 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.0229$
$\theta_{max} = 64.39°$
$h = -11 \rightarrow 11$
$k = -22 \rightarrow 22$
$l = -14 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 3.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.054$
4091 reflections
315 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 1.2956P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.032$
$\Delta\rho_{max} = 0.513$ e Å^{-3}
$\Delta\rho_{min} = -0.377$ e Å^{-3}
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

B1—B2	1.757 (3)	B4—B9	1.758 (3)
B1—B4	1.760 (3)	B4—B8	1.761 (3)
B1—B5	1.775 (3)	B4—B10	1.764 (3)
B1—B10	1.785 (3)	B4—Cl4	1.827 (2)
B1—B3	1.838 (3)	B5—B6	1.878 (3)
B2—B6	1.742 (3)	B5—B10	1.879 (3)
B2—B3	1.758 (3)	B6—B7	1.846 (3)
B2—B5	1.764 (3)	B6—P1	1.922 (2)
B2—B7	1.767 (3)	B7—B8	1.886 (3)
B2—Cl2	1.823 (2)	B8—B9	1.887 (3)
B3—B4	1.750 (3)	B9—B10	1.888 (3)
B3—B7	1.779 (3)	B9—P2	1.924 (2)
B3—B8	1.785 (3)		
B6—B2—B1	116.24 (15)	B10—B4—Cl4	119.17 (14)
B6—B2—B3	115.40 (16)	B6—B5—B10	112.66 (14)
B6—B2—Cl2	115.57 (13)	B7—B6—B5	104.85 (14)
B1—B2—Cl2	118.38 (14)	B2—B6—P1	117.38 (14)
B3—B2—Cl2	118.05 (14)	B7—B6—P1	122.38 (13)
B5—B2—Cl2	119.64 (14)	B5—B6—P1	120.33 (13)
B7—B2—Cl2	118.87 (14)	B6—B7—B8	113.42 (14)
B3—B4—B9	118.21 (16)	B7—B8—B9	115.68 (14)
B9—B4—B1	118.20 (16)	B8—B9—B10	102.33 (14)
B3—B4—Cl4	118.63 (14)	B4—B9—P2	157.66 (15)
B9—B4—Cl4	112.19 (13)	B8—B9—P2	111.47 (13)
B1—B4—Cl4	118.45 (14)	B10—B9—P2	111.90 (13)
B8—B4—Cl4	118.98 (14)	B5—B10—B9	116.25 (14)

B—B—B acute angles are in the range 57.05 (12)–64.85 (13)°.

Phosphine H atoms were constrained to idealized positions with a riding model including free rotation of the methyl groups and with PPh units restrained to have C_{2v} symmetry.

Borane H atoms were located in difference Fourier maps and all associated parameters were refined freely.

Data collection: *STADI4* (Stoe & Cie, 1996*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEX5* (McArdle, 1995). Software used to prepare material for publication: *SHELXL97* and a local program.

References

Dörfler, U., McGrath, T. D., Cooke, P. A., Kennedy, J. D. & Thornton-Pett, M. (1997). *J. Chem. Soc. Dalton Trans.* pp. 4739–4746.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. J. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746.
Fontaine, X. L. R. & Kennedy, J. R. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1573–1575.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Stoe & Cie (1996*a*). *STADI4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1996*b*). *X-RED. Data Reduction Program.* Version 1.08. Stoe & Cie, Darmstadt, Germany.

(1R,7S,8aS)-1,7-Dihydroxyindolizidine Hydrate

LIDIA GAROFANO, ANNALISA GUERRI AND PIERLUIGI ORIOLI

Department of Chemistry, University of Florence, via G. Capponi 7, 50121 Florence, Italy. E-mail: orioli@risc1.lrm.fi.cnr.it

Abstract

The title compound [(1R,7S,8aS)-1,7-dihydroxyperhydro-indolizine hydrate, $C_8H_{15}NO_2.H_2O$] crystallizes with one water solvate molecule, which is involved in strong hydrogen bonds with the hydroxyl O atoms. Bond lengths and angles in the molecule are in agreement with literature values.