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9-Dicyclohexylphenylphosphino-*arachno*-6-thiadecaborane(11)

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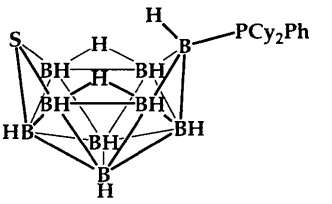
Abstract

The $\{SB_9\}$ cage residue in the title compound, $C_{18}H_{38}B_9PS$, has the expected *arachno* ten-vertex geometry and the PCy_2Ph substituent occupies an *exo* position on B9, with B9—P1 = 1.953 (6) Å.

Comment

There is current interest in bis(phosphine)rhodathiaboranes whose molecular structures appear to be at variance with those expected by electron-counting rules (Ferguson *et al.*, 1990; Murphy, Spalding, Ferguson & Gallagher, 1992) unless intramolecular agostic interactions are invoked (Adams, McGrath & Welch, 1995; Adams, McGrath, Thomas, Weller & Welch, 1996). As part of our studies in this area, we attempted the synthesis of 8,8-$(Cy_2PhP)_2$-8,7-*nido*-$RhSB_9H_{10}$ (Cy = cyclohexyl) by reaction between $[RhCl(PCy_2Ph)_2(C_2H_4)]$, generated *in situ* from $[RhCl(C_2H_4)_2]_2$ and PCy_2Ph, and $Cs[SB_9H_{12}]$ in Et_2O. However, the major tractable product afforded by work-up proved to be the title compound. Since there is current interest in 9-substituted *arachno*-6-SB_9H_{11} species (Stibr *et al.*, 1996) and since 9-PPh_3-*arachno*-6-SB_9H_{11} has been variously described (by the same workers) as *endo*-9- (Nestor, Fontaine, Greenwood, Kennedy & Thornton-Pett, 1991) and *exo*-9- (Stibr *et al.*, 1996), we undertook a crystallographic study of the title compound.



The compound crystallizes with no short intermolecular contacts. A perspective view of a single molecule is shown in Fig. 1.

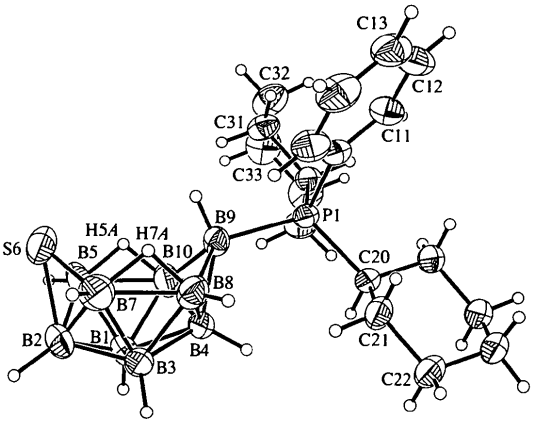


Fig. 1. Perspective view with 40% ellipsoids for non-H atoms. Ring C atoms are numbered in sequence.

This is the first crystallographic characterization of a 9-phosphino-6-SB_9H_{11} species. The $\{SB_9\}$ residue has the same basic *arachno* structure as that found in 9-NEt_3-*arachno*-6-SB_9H_{11} (Hilty & Rudolf, 1979), [*arachno*-6-$SB_9H_{12}]^-$ (Nestor *et al.*, 1991) and 9-MeCN-*arachno*-6-SB_9H_{11} (Stibr *et al.*, 1996). Similar to the situation in all these three analogous compounds, the B—B distances in the title compound appear to fall into three fairly distinct groups: *ca* 1.90 Å for B2—B5, B2—B7, B8—B9 and B9—B10; *ca* 1.85 Å for the hydrogen-bridged edges B5—B10 and B7—B8; *ca* 1.75–1.80 Å for all others. S—B distances in the title compound are comparable with those in the thiaboranes referenced above, but more spread than usual with S6—B2 being just significantly longer than S6—B5 and S6—B7.

Overall, the thiaborane cage has approximate C_s symmetry about the plane through S6, B2, B4 and B9, and the ^{11}B NMR spectrum is fully consistent with such symmetry in solution. However, it is clear from Fig. 1 that the PCy_2Ph substituent at B9 [which is clearly in an *exo* position, B9—P1 1.953 (6) Å] is not oriented so as to maintain overall C_s symmetry in the solid state. We assume that in solution at room temperature, the PCy_2Ph ligand is free to rotate about the B9—P1 bond.

Experimental

Under an atmosphere of dry nitrogen, a solution of $[RhCl(PCy_2Ph)_2(C_2H_4)]$ in Et_2O was prepared *in situ* by slow

addition of PCy_2Ph (0.25 g, 0.912 mmol) to $[RhCl(C_2H_4)_2]_2$ (0.09 g, 0.227 mmol) over 1 h. Subsequent addition of $Cs[SB_9H_{12}]$ (0.125 g, 0.454 mmol) and stirring for 4 h afforded a red solution. Solvent was removed *in vacuo* and the resultant solid extracted into CH_2Cl_2 and filtered through celite. Yellow crystals were grown by slow cooling of a light petroleum (60–80) solution. ^1H FTNMR (400.1 MHz, $CDCl_3$, 293 K, TMS): δ = 7.85–7.40 (*m*, 5H, Ar), 1.92–1.05 (*m*, 22H, Cy), −1.70 (*br*, 2H, μ-H) p.p.m. ^{11}B-{^1H} FTNMR (128.4 MHz, $CDCl_3$, 293 K, $BF_3.Et_2O$): δ = 9.0 (1B), −1.9 (*br*, 1B), −5.1 (2B), −23.3 [*d*, 1B, *J*(PB) 120 Hz], −27.5 (2B), −32.7 (2B) p.p.m. ^{31}P-{^1H} FTNMR (162.0 MHz, $CDCl_3$, 293 K, H_3PO_4): δ = 8.3 [*q*, *J*(PB) 120 Hz] p.p.m. Mass spectrum (FAB, Noba) parent ion 415. NMR spectra were recorded on a Brüker DPX400 spectrometer and mass spectrum on a VG/MS9 spectrometer.

Crystal data

$C_{18}H_{38}B_9PS$
M_r = 414.80
Monoclinic
$P2_1/n$
a = 10.432 (2) Å
b = 15.737 (3) Å
c = 15.406 (3) Å
β = 96.57 (2)°
V = 2512.8 (7) Å^3
Z = 4
D_x = 1.096 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 34 reflections
θ = 4.99–10.33°
μ = 0.196 mm^{-1}
T = 293 (2) K
Block
0.4 × 0.3 × 0.2 mm
Yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans, (*SHELXTL/PC*; Sheldrick, 1994)
T_{min} = 0.85, T_{max} = 0.96
5528 measured reflections
4369 independent reflections
1908 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0582
θ_{max} = 25.01°
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 18$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 97 reflections
intensity decay: 17.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0694
$wR(F^2)$ = 0.1880
S = 0.995
4367 reflections
295 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.238 e Å^{-3}
$\Delta\rho_{min}$ = −0.205 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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}
P1	0.14239 (13)	0.81160 (9)	0.52263 (9)	0.0378 (3)
B1	0.3259 (8)	0.8907 (5)	0.8008 (5)	0.068 (2)
B2	0.3894 (8)	0.9925 (6)	0.8102 (6)	0.074 (2)
B3	0.4488 (6)	0.9223 (5)	0.7365 (5)	0.058 (2)
B4	0.3237 (7)	0.8526 (4)	0.6924 (4)	0.050 (2)
B5	0.2084 (8)	0.9718 (6)	0.7987 (6)	0.079 (3)
S6	0.2701 (2)	1.07309 (13)	0.7486 (2)	0.0889 (7)
B7	0.4086 (8)	1.0249 (5)	0.6949 (6)	0.072 (2)
B8	0.3821 (6)	0.9290 (5)	0.6250 (5)	0.055 (2)
B9	0.2078 (6)	0.8924 (4)	0.6133 (4)	0.0423 (14)
B10	0.1770 (7)	0.8755 (5)	0.7310 (5)	0.059 (2)
C10	0.1363 (5)	0.8623 (3)	0.4159 (3)	0.0430 (13)
C11	0.0541 (6)	0.8317 (4)	0.3454 (3)	0.055 (2)
C12	0.0552 (6)	0.8670 (5)	0.2638 (4)	0.070 (2)
C13	0.1365 (7)	0.9334 (5)	0.2522 (4)	0.071 (2)
C14	0.2165 (7)	0.9640 (4)	0.3196 (5)	0.073 (2)
C15	0.2181 (6)	0.9282 (4)	0.4028 (4)	0.060 (2)
C20	0.2355 (5)	0.7134 (3)	0.5147 (3)	0.0422 (13)
C21	0.3717 (5)	0.7329 (4)	0.4928 (4)	0.059 (2)
C22	0.4501 (6)	0.6512 (4)	0.4904 (5)	0.075 (2)
C23	0.3852 (6)	0.5866 (4)	0.4282 (4)	0.072 (2)
C24	0.2513 (6)	0.5684 (4)	0.4489 (4)	0.066 (2)
C25	0.1704 (6)	0.6482 (4)	0.4514 (4)	0.055 (2)
C30	−0.0261 (5)	0.7812 (3)	0.5329 (3)	0.0431 (13)
C31	−0.1109 (5)	0.8586 (4)	0.5366 (4)	0.055 (2)
C32	−0.2507 (6)	0.8318 (4)	0.5403 (5)	0.074 (2)
C33	−0.2622 (6)	0.7726 (5)	0.6168 (5)	0.083 (2)
C34	−0.1778 (6)	0.6958 (5)	0.6117 (5)	0.072 (2)
C35	−0.0373 (5)	0.7205 (4)	0.6098 (4)	0.057 (2)

Table 2. *Selected geometric parameters (Å)*

P1—C10	1.822 (5)	B3—B7	1.771 (11)
P1—C20	1.837 (5)	B3—B4	1.778 (9)
P1—C30	1.846 (5)	B3—B8	1.781 (10)
P1—B9	1.953 (6)	B4—B9	1.732 (9)
B1—B2	1.732 (12)	B4—B10	1.742 (10)
B1—B5	1.767 (12)	B4—B8	1.743 (10)
B1—B4	1.773 (9)	B5—B10	1.848 (10)
B1—B3	1.778 (11)	B5—S6	1.914 (11)
B1—B10	1.802 (10)	S6—B7	1.902 (9)
B2—B3	1.748 (11)	B7—B8	1.856 (11)
B2—B7	1.881 (13)	B8—B9	1.896 (9)
B2—B5	1.904 (11)	B9—B10	1.897 (10)
B2—S6	1.947 (9)		

H atoms attached to B were located from ΔF maps and allowed positional refinement subject to a common refined B—H distance [1.10 (5) for terminal H atoms and 1.20 (5) Å for bridging H atoms at convergence] and fixed U_{iso} = 0.08 Å^2. C-bound H atoms were refined using a riding model [phenyl C—H = 0.93, cyclohexyl C—H = 0.97 Å, U(*H*) = 1.2 × U_{eq}(C)].

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Directly Linked *C*-Disaccharides: Structures of Two 3,4-Dihydro-2*H*-pyran Derivatives

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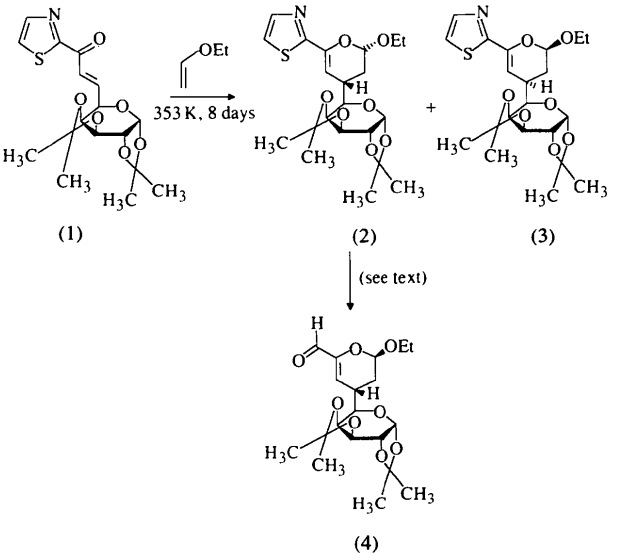
Abstract

Analysis of the crystal structures of the two diastereomeric *C*-disaccharides, (2*R*, 4*R*)-4-(1,2;3,4-di-*O*-isopropylidene-α-D-*galacto*-1,5-pyranose-5-yl)-2-ethoxy-6-(2-thiazolyl)-3,4-dihydro-2*H*-pyran, $C_{21}H_{29}NO_7S$, (3), and (2*R*,4*S*)-4-(1,2;3,4-di-*O*-isopropylidene-α-D-*galacto*-1,5-pyranose-5-yl)-2-ethoxy-6-formyl-3,4-dihydro-2*H*-pyran, $C_{19}H_{28}O_8$, (4), allows the definition of the absolute configurations of the products of the cycloaddition reaction between 1-oxa-1,3-butadiene and ethyl vinyl ether. The relevant conformational aspects of the two molecules are discussed. In the crystals of (3), a water molecule participates in hydrogen bonds to the thiazole N atom and an O atom of a dioxapentane ring of the sugar moiety within the same molecule.

Comment

Recent work by Dondoni and co-workers has been directed towards the synthesis of *C*-disaccharides wherein the two sugars are directly linked by a C—C bond (Dondoni, Kniezo & Martinkova, 1994, 1996). The interest in this hitherto scarcely explored class of sugar analogues (Danishefsky & Barbachyn, 1985; Lopez & Fraser-Reid, 1989; Armstrong & Teegarden, 1992) stems from their properties as re-engineered disaccharides with predictable restricted conformations, and as their potential use as glycosidase inhibitors. The synthetic method employed by Dondoni and co-workers involves the *de novo* construction of a second pyranose ring on an existing one by an asymmetric hetero-Diels–Alder (HDA) reaction (Boger & Weinreb, 1987; Waldmann, 1994). Thus, the cycloaddition reaction between the galactosyl-bearing 1-oxa-1,3-butadiene, (1), and ethyl vinyl ether led to a mixture of diastereomeric 3,4-dihydro-2*H*-pyran derivatives (2) and (3) in 4:1 ratio and 97% total yield. Suitable synthetic elaborations of the newly formed 3,4-dihydropyran ring of these compounds (*i.e.* conversion of the thiazole ring into the formyl group and hydroxylation of the double bond) afforded the target diastereomeric *C*-disaccharides.



(1) (2) (3)

(4)

The relative configuration at the newly formed stereocentres of (2) and (3) was obtained by analysis of the ^{1}H NMR spectra. The X-ray crystal structure determination of (3) and (4) defined their absolute stereochemistry while that of the major diastereomer (2), which did not give crystals suitable for an X-ray analysis, was deduced from that of (4) which was derived from (2) by thiazolyl-to-formyl conversion and epimerization at C2 of the dihydropyran ring.

As shown in the scheme and the figures, the configurations at C6 are opposite in (3) and (4) being *R* and *S*, respectively, while at the other chiral centres, the configurations are identical for the two compounds: *R* at C7, C11, C13 and *S* at C8, C10 of the *galacto*-pyranosyl