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Twisted [(R_3P)PdX] groups above dicarbaborane ligands: 4-dimethylsulfido-3-iodo-3-triphenylphosphine-*closo*-3-pallada-1,2-dicarbadodecaborane and 3-dimethylphenylphosphine-3-chloro-4-dimethylsulfido-*closo*-3-pallada-1,2-dicarbadodecaborane

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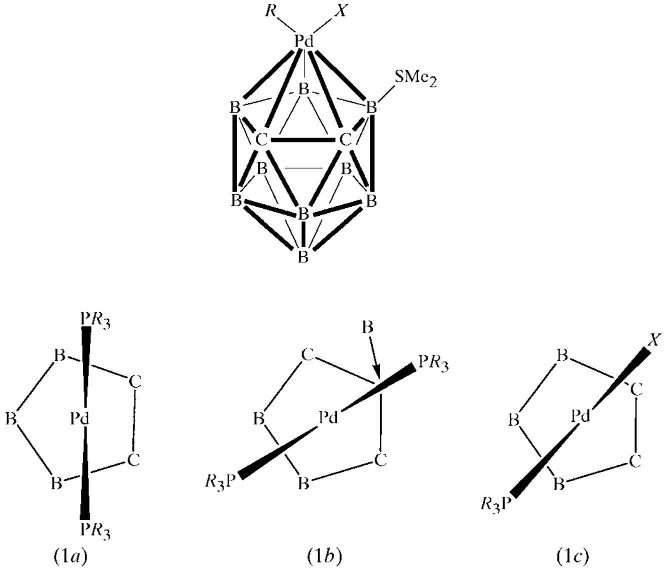
The structural analyses of [3-(PPh_3)-3-I-4-(SMe_2)-*closo*-3,1,2-$PdC_2B_9H_{10}$] or [Pd($C_4H_{16}B_9S$)I($C_{18}H_{15}P$)], (I), and [3-($PPhMe_2$)-3-Cl-4-(SMe_2)-*closo*-3,1,2-$PdC_2B_9H_{10}$] or [Pd($C_4H_{16}B_9S$)Cl($C_8H_{11}P$)], (II), show that in comparison with [3-(PR_3)$_2$-*closo*-3,1,2-$PdC_2B_9H_{11}$] the presence of the 4-SMe_2 group causes the [PdX(PR_3)] unit (X = halogen) to twist about an axis passing through the Pd atom and the directly opposite B atom of the carbaborane ligand. The halogen atoms are located almost directly above a C atom in the C_2B_3 face, and the conformations of the [PdX(PR_3)] units above the C_2B_3 faces are not those predicted from molecular orbital calculations of the *closo*-3,1,2-PdC_2B_9 system. The fact that the variation from the predicted conformation is greater in the case of (I) than in (II) may be ascribed to the greater steric interactions induced by the I atom in (I) compared with the Cl atom in (II).

Comment

The factors affecting the conformation of $L-M-X$ units (L and X may be phosphines or other ligands) above the faces of 11-atom heteroborane ligands in metalloheteroborane clusters, such as [3,3-(PR_3)$_2$-*closo*-3,1,2-$MC_2B_9H_{11}$], (III) (M = Pd or Pt), have been subject to both experimental (O'Connell *et al.*, 1995, 1996) and theoretical (Mingos *et al.*, 1978) studies. We have now continued these studies to obtain information about the effect that a substituent on a B atom in the C_2B_3 face adjacent to the Pd atom would have on the structure of the metalloheteroborane. We synthesized two palladium complexes with the [9-SMe_2-*nido*-7,8-$C_2B_9H_{10}$] dicarbaborane fragment as a ligand, namely [3-(PPh_3)-3-I-4-(SMe_2)-*closo*-3,1,2-$PdC_2B_9H_{10}$], (I), and [3-($PPhMe_2$)-3-Cl-4-(SMe_2)-*closo*-3,1,2-$PdC_2B_9H_{10}$], (II), which are isoelectronic in cluster terms (Wade, 1976) with [3-(PR_3)$_2$-*closo*-3,1,2-$PdC_2B_9H_{11}$], (III). In complex (III), which is a [*closo*-3,1,2-$MC_2B_9H_{11}$] species that contains 'C atoms adjacent' [*nido*-7,8-$C_2B_9H_{11}$] ligand fragments and no replacements of boron-bound *exo* H atoms by bulkier groups, the conformation of the P—Pd—P plane is aligned approximately parallel to the C—C vector in the C_2B_3 face to which the Pd atom is attached, as shown in the scheme (diagram 1*a*). This alignment is expected on the basis of the results of molecular orbital calculations (Mingos *et al.*, 1978). The alternative 'perpendicular' conformation is expected for [*closo*-2,1,7-$MC_2B_9H_{11}$] species that have 'C atoms apart' [*nido*-7,9-$C_2B_9H_{11}$] fragments as ligands (see diagram 1*b*) (Mingos *et al.*, 1978).



(I) R=PPh$_3$, X=I
(II) R=PMe$_2$Ph, X=Cl

Compounds (I) and (II) have *closo* 12-vertex PdC_2B_9 geometries based on distorted icosahedra with the Pd and C atoms adjacent, as shown in Figs. 1 and 2. Selected interatomic distances and angles are given in Table 1. In both (I) and (II), the substitution of a $BSMe_2$ group for a BH(*exo*) unit causes marked twisting of the [PdX(PR_3)] group (X = I or Cl) above the C_2B_3 face (see diagram 1*c*). The orientations of the [PdI(PPh_3)] and [PdCl($PPhMe_2$)] units above the C_2B_3 faces are clearly shown in Figs. 3 and 4. The conformations of the Pd—X and Pd—P vectors above the C_2B_3 faces have become more like the 'perpendicular' conformation that is expected for [*closo*-2,1,7-$MC_2B_9H_{11}$] species. It is noticeable that the twisting of the X—Pd—PR_3 unit away from the SMe_2 ligand is somewhat greater in (I) than in (II), as can be seen in the angles between the X—Pd and B4—S1 vectors when they are projected onto the plane of the C_2B_3 face; these are 71.7 (2)°

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in (I) and 53.7 (2)° in (II). This difference is also seen in the comparison between the S1—B4—Pd3—*X* twist angle, which is larger in (I), at −48.5 (3)°, with a smaller corresponding angle in (II) of −29.16 (9)°. All these values would be expected to be close to zero in the absence of substitution at B4. The difference in these pairs of angles is probably due to the steric interactions in the *X*—Pd3—C1—B4—S1(Me$_2$) region and, in particular, the difference in the effective radii of I and Cl, although the differential bulk of the PPh$_3$ *versus* the PPhMe$_2$ ligands will also affect the conformations, as will the locations of the methyl groups of the SMe$_2$ ligand attached at atom B4.

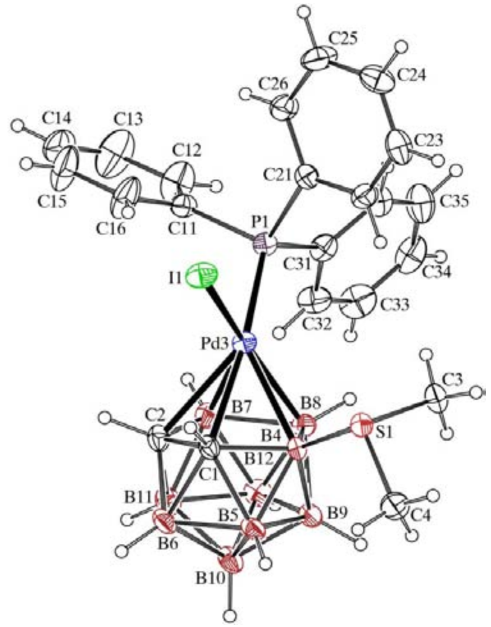

Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

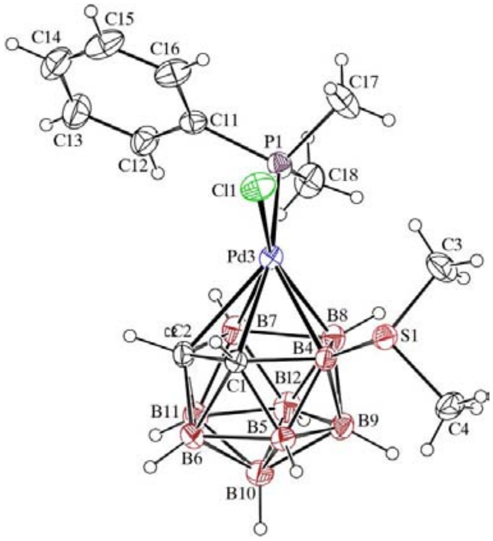

Figure 2
A view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The Pd—C distances of 2.274 (6) and 2.467 (6) Å in (I) are significantly different, with the Pd—C1 bond considerably shorter than the Pd—C2 bond. Atom C1 is adjacent to the SMe$_2$-substituted B4 atom, and the shorter Pd—C distance may be an artefact of this configuration if extra electron density due to the presence of the S atom is available in the Pd—B4—C1 region compared with the Pd—B7—C2 region. The Pd—C distances in (II), at 2.304 (2) and 2.478 (2) Å, are similar to those in (I). The Pd—C distances in (I) and (II) span those observed in the cation of [3-(η^2,η^2-C$_8$H$_{12}$)-4-SMe$_2$-*closo*-3,1,2-PdC$_2$B$_9$H$_{10}$]BF$_4$ [2.371 (4) and 2.434 (4) Å; Douek & Welch, 1993]. A search of the May 2005 release of the Cambridge Structural Database (CSD; Allen, 2002) for palladacarbaboranes resulted in 11 unique hits that yielded Pd—C distances in a wide range from 2.187 (5) Å in the 13-vertex bis(diphenylphosphino)ethane derivative [4-(dppe)-*closo*-4,1,6-PdC$_2$B$_{10}$H$_{12}$] (Alcock *et al.*, 1987; CSD refcode FODFOT) to 2.634 (7) Å in [1-(5-MeC$_4$H$_2$S)-3,3-(PMe$_2$Ph)$_2$-*closo*-3,1,2-PdC$_2$B$_9$H$_{10}$] (Michaelidou *et al.*, 1997; CSD refcode RUSWIL). It is noteworthy that, in the latter compound, which has a 5-methylthiophenyl substituent on atom C1, the conformation of the plane containing the P—Pd—P unit and the C—C vector is near to the ‘parallel’ type; the angle between the C—C vector and the plane containing the P—Pd—P unit projected onto the B$_3$C$_2$ plane is 26° rather than 0°.

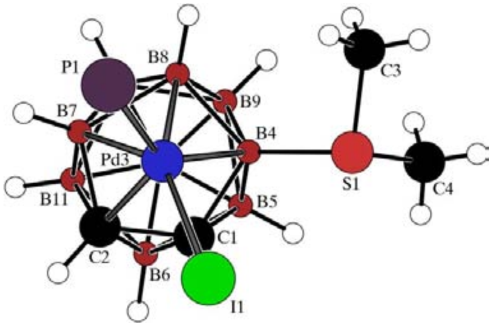

Figure 3
A view of the P—Pd—I unit above the C$_2$B$_3$ face with the SMe$_2$ ligand at B4 in (I).

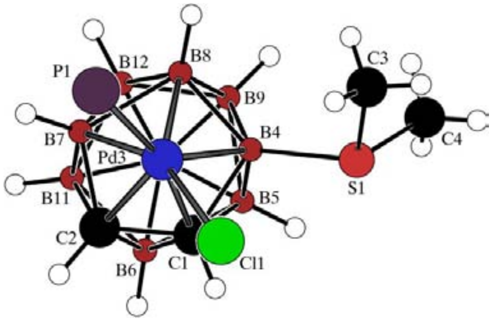

Figure 4
A view of the P—Pd—Cl unit above the C$_2$B$_3$ face with the SMe$_2$ ligand at B4 in (II).

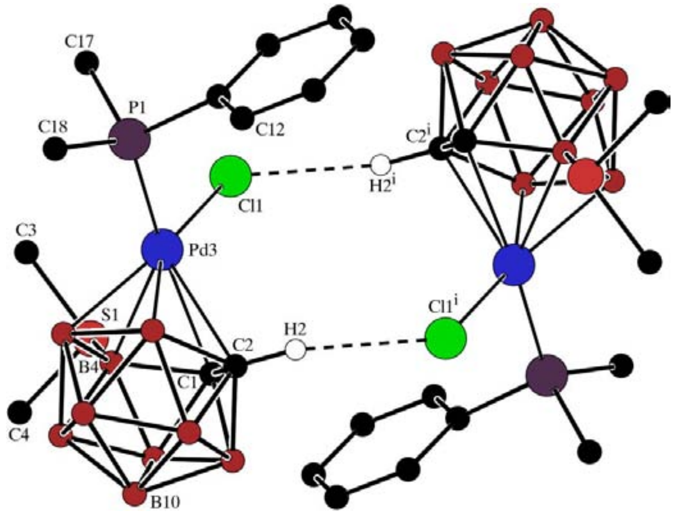

Figure 5
A view of a pair of molecules of (II), linked by weak C—H$\cdots$Cl interactions. [Symmetry code: (i) $1 - x$, $1 - y$, $-z$.]

The SMe_2 group has slightly different orientations in (I) and (II), quantified by the values of the Pd3—B4—S1—C3 torsion angles [−85.0 (4)° in (I) and −54.19 (13)° in (II)]. Presumably, this difference arises from packing effects. Examination of the intermolecular distances shows that there are no π–π or C—H$\cdots\pi$ interactions in the crystal structures of (I) and (II). In (I), there is a weak intramolecular C16—H16$\cdots$I1 interaction (see Table 2). In (II), there are no significant intramolecular interactions; the inversion-related shortest intermolecular interactions are shown in Fig. 5 with pairs of C—H$\cdots$Cl interactions leading to a weakly linked dimer (see Table 2). Such attractive interactions are consistent with the well known greater polarity and H-atom acidic character of carbaborane cluster CH(*exo*) units.

Experimental

Reactions were carried out under an inert atmosphere, and products were isolated and manipulated in air. The reagents Tl[9-SMe_2-7,8-*nido*-$C_2B_9H_{10}$] (Hamilton & Welch, 1991), [$Pd(PPhMe_2)_2Cl_2$] (Jenkins & Shaw, 1966) and [$Pd(PPh_3)_2I_2$] (Bailey & Mason, 1968) were prepared according to literature methods. For the synthesis of (I), a solution of [$Pd(PPh_3)_2I_2$] (0.044 g, 0.05 mmol) in CH_2Cl_2 (10 ml) was added to a solution of Tl[9-SMe_2-7,8-*nido*-$C_2B_9H_{10}$] (0.02 g, 0.05 mmol) in CH_2Cl_2 (10 ml). The mixture was heated at reflux temperature for 2.5 h. The dark-green solution was concentrated under reduced pressure (rotatory film evaporator, 298 K) and subjected to preparative thin-layer chromatography (TLC; CH_2Cl_2–hexane, 3:2). The major band was extracted into CH_2Cl_2 and recrystallized from CH_2Cl_2–hexane (3:2) as dark-green block-shaped crystals of (I) (0.028 g, 81.3%). Analysis found: C 38.4, H 5.0, I 18.1%; $C_{22}H_{31}B_9IPPdS$ requires: C 38.35, H 4.5, I 18.4%. For the synthesis of (II), a solution of [$Pd(PPhMe_2)_2Cl_2$] (0.1365 g, 0.301 mmol) in toluene (20 ml) was added to a solution of Tl[9-SMe_2-7,8-*nido*-$C_2B_9H_{10}$] (0.121 g, 0.304 mmol) in toluene (30 ml). The mixture was stirred at room temperature for 20 h. The purple solution was concentrated under reduced pressure (rotatory film evaporator, 308 K) and subjected to preparative TLC (CH_2Cl_2–hexane, 4:1). The major band was extracted into CH_2Cl_2 and recrystallized from CH_2Cl_2–hexane (1:1), affording purple crystals of (II) (0.143 g, 75.9%). Analysis found: C 30.7, H 5.9, S 6.85%; $C_{12}H_{27}B_9ClPPdS$ requires: C 30.4, H 5.8, S 6.8%. For details of the IR and NMR spectra for (I) and (II), see the archived CIF.

Compound (I)

Crystal data

[$Pd(C_4H_{16}B_9S)I(C_{18}H_{15}P)$]
$M_r = 689.12$
Orthorhombic, *Pbca*
$a = 10.9576$ (5) Å
$b = 16.8316$ (10) Å
$c = 30.2015$ (17) Å
$V = 5570.2$ (5) Å^3
$Z = 8$
$D_x = 1.643$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 9.9$–16.0°
$\mu = 1.92$ mm^{-1}
$T = 294$ (1) K
Block, dark green
0.20 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*ABSCOR* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.708$, $T_{max} = 0.751$
6057 measured reflections
6057 independent reflections

3546 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0$
$\theta_{max} = 27.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 38$
3 standard reflections every 250 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.162$
$S = 1.00$
6057 reflections
318 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1025P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.29$ e Å^{-3}
$\Delta\rho_{min} = -1.93$ e Å^{-3}

Compound (II)

Crystal data

[$Pd(C_4H_{16}B_9S)Cl(C_8H_{11}P)$]
$M_r = 473.54$
Monoclinic, $P2_1/n$
$a = 12.8117$ (8) Å
$b = 9.2670$ (7) Å
$c = 18.2948$ (10) Å
$\beta = 96.567$ (5)°
$V = 2157.8$ (2) Å^3
$Z = 4$

$D_x = 1.458$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 10.0$–16.5°
$\mu = 1.15$ mm^{-1}
$T = 294$ (1) K
Block, purple
0.33 × 0.25 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*ABSCOR* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.684$, $T_{max} = 0.760$
6506 measured reflections
6265 independent reflections

5023 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 30.0°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 13$
$l = -25 \rightarrow 25$
3 standard reflections every 250 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.064$
$S = 1.03$
6265 reflections
231 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.6303P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00185 (18)

Table 1
Selected bond distances (Å) and angles (°) for compounds (I) and (II).

X = I1 in (I) and Cl1 in (II).

	(I)	(II)
Pd3—X	2.6739 (7)	2.3751 (5)
Pd3—P1	2.2507 (17)	2.2275 (5)
Pd3—C1	2.274 (6)	2.304 (2)
Pd3—C2	2.467 (6)	2.478 (2)
Pd3—B4	2.315 (7)	2.278 (2)
Pd3—B7	2.269 (8)	2.212 (2)
Pd3—B8	2.254 (7)	2.229 (2)
S1—B4	1.899 (7)	1.896 (2)
C1—C2	1.584 (9)	1.561 (2)
C1—B4	1.693 (8)	1.697 (3)
C2—B7	1.644 (10)	1.686 (3)
B4—B8	1.766 (10)	1.764 (3)
X—Pd3—P1	95.06 (5)	92.00 (2)
X—Pd3—C1	90.64 (16)	97.52 (5)
X—Pd3—C2	106.07 (16)	116.77 (5)
X—Pd3—B4	110.47 (16)	108.25 (5)
X—Pd3—B7	143.2 (2)	148.67 (6)
X—Pd3—B8	155.09 (19)	148.67 (6)
P1—Pd3—C1	169.28 (16)	163.51 (5)
P1—Pd3—C2	130.57 (16)	125.64 (4)
P1—Pd3—B4	140.80 (16)	144.32 (5)
P1—Pd3—B7	100.3 (2)	95.72 (6)
P1—Pd3—B8	102.97 (19)	103.23 (6)
Pd3—B4—S1	104.2 (3)	106.64 (9)

Table 2
Hydrogen bond parameters (Å, °) for compounds (I) and (II).

	D—H···A	D—H	H···A	D···A	D—H···A
(I)	C16—H16···I1	0.86	2.98	3.831 (9)	153
(II)	C2—H2···Cl1^{i}	0.86	2.60	3.540 (2)	142

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

Molecule (I) crystallized in the orthorhombic system; space group *Pbca* was assigned from the systematic absences. Molecule (II) crystallized in the monoclinic system; space group $P2_1/n$ was assigned from the systematic absences. In both compounds, H atoms were treated as riding atoms, with C—H distances of 0.93, 0.96 and 1.10 Å, and B—H distances of 1.10 Å, and with $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$(C,B) or $1.5U_{\rm eq}$(methyl C). The maxima and minima in the final difference maps for (I) were adjacent to the I atom.

For both compounds, data collection: *DIFRAC* (Gabe & White, 1993) with profile analysis; cell refinement: *DIFRAC*; data reduction: *DATRD2* in *NRCVAX94* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX* (Version 1.70.01; Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1861). Services for accessing these data are described at the back of the journal.

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