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.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(*tert*-Butyl isocyanide)-3,8-bis(dimethylphenylphosphine)octahydro-1,2-diarsa-3-pallada-*closo*-dodecaboron(1+) Hexafluoroantimonate

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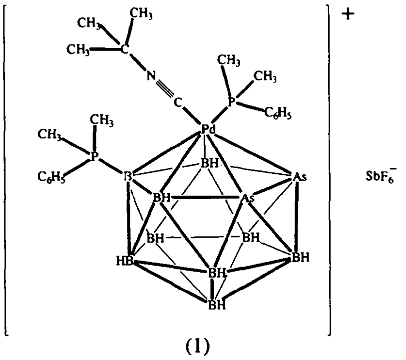
Abstract

The title compound, [$Pd(C_5H_9N)(C_8H_{11}P)\{B_9H_8As_2(C_8H_{11}P)\}$][$SbF_6$], contains a twelve-vertex ($PdAs_2B_9$) cage with the metal η^5-bonded to an As_2B_3 ring. The *exo*-cage ligands dimethylphenylphosphine and *tert*-butyl isocyanide are attached to Pd and a second PMe_2Ph ligand is attached to a cage B atom at position 8. The Pd—As interactions are notably asymmetric at 2.6434 (8) and 2.5296 (7) Å. Other principal dimensions are Pd—B 2.291 (6)–2.301, Pd—P 2.330 (2), Pd—C 2.011 (6) and As—As 2.492 (1) Å.

Comment

As part of our study of cationic metallaheteroborane clusters (Sheehan, Spalding, Ferguson, Gallagher, Kaitner & Kennedy, 1993; Ferguson, Gallagher, Sheehan, Spalding, Kennedy & Maciás, 1993), we have synthesized the title compound, (1), and determined its structure. This is the first cationic metallaarsenaborane to have been structurally characterized by X-ray diffraction techniques.



(1)

A view of the *closo*-[3-(^{t}BuNC)-3,8-($PMe_2Ph)_2$-3,1,2-$PdAs_2B_9H_8$]$^+$ cation in (1) is shown in Fig. 1, with our numbering scheme. Fractional atomic coordinates are given in Table 1 and principal dimensions are listed in Table 2. The *exo*-cage Pd3—P1 distance of 2.330 (2) Å is typical of such bonds. Previously reported Pd—P distances in palladaheteroborane cages are 2.311 (3) and 2.327 (3) Å in *closo*-[3,3-($PMe_2Ph)_2$-3,2,1-$PdAs_2B_9H_9$], (2) (Jasper, Roach, Stipp, Huffman & Todd, 1993), 2.344 (3) Å in *closo*-[3-Cl-3,8-($PPh_3)_2$-3,1,2-$PdAs_2B_9H_8$], (3) (McGrath, Spalding, Fontaine, Kennedy & Thornton-Pett, 1991), 2.3640 (13) and 2.3285 (13) Å in the cation *closo*-[2,2-($PMe_3)_2$-2,1-$PdTeB_{10}H_9(PPh_3)$]$^+$ (Ferguson, Gallagher, Sheehan, Spalding, Kennedy & Maciás, 1993) and 2.3301 (7) and 2.3354 (8) Å in the neutral species *closo*-[2,2-($PMe_2Ph)_2$-2,1-$PdTeB_{10}H_{10}$] (Ferguson, Gallagher, McGrath, Sheehan, Spalding & Kennedy, 1993).

The isocyanide Pd3—C3 distance of 2.011 (6) Å is similar to the equivalent distance of 1.992 (11) Å in the B-bonded carbene complex *closo*-[2-I-2-(^{t}BuNC)-6-(^{t}BuNHCH)-2,1-$PdTeB_{10}H_9$], (4) (Sheehan, 1992). In *closo*-[1,1-(^{t}BuNC)$_2$-2-(NMe_3)-1,2-$PdCB_{10}H_{10}$] (5) (Carroll, Green, Stone & Welch, 1975) the Pd—C distances

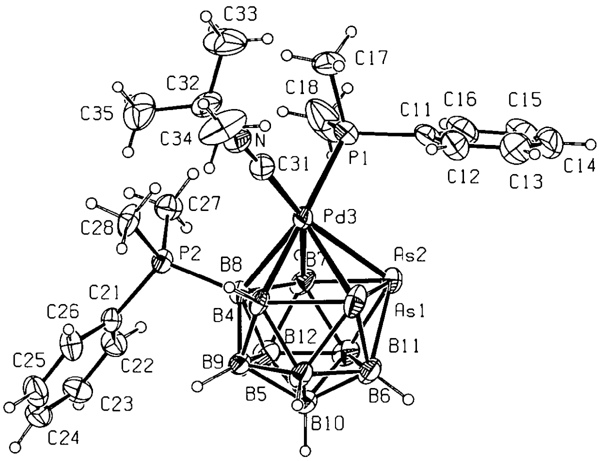


Fig. 1. A view of the cation in (1) with the numbering scheme indicated. The non-H atoms are shown as displacement ellipsoids drawn at the 30% probability level. For clarity, H atoms are drawn as small spheres of arbitrary radii and the minor component of the disordered *tert*-butyl group is not shown.

were found to be 2.022 (7) and 2.027 (6) Å. The Pd—C—N geometries in (1), (4) and (5) are close to being linear with angles of 177.6 (6) in (1), 178.9 (9) in (4), and 173.6 (6) and 175.7 (6)° in (5).

The Pd—As interactions in (1) are remarkably asymmetric [Pd3—As1 2.6434 (8) and Pd3—As2 2.5296 (7) Å]. This situation was also observed in the $(PMe_2Ph)_2Pd$ complex (2) (Jasper, Roach, Stipp, Huffman & Todd, 1993), with Pd—As distances of 2.6835 (18) and 2.5304 (13) Å, but not in (3) (McGrath, Spalding, Fontaine, Kennedy & Thornton-Pett, 1991), which has a much more symmetrically bonded $PdAs_2$ unit with distances of 2.563 (4) and 2.539 (4) Å. The As—As distance in (1) is 2.492 (1) Å, similar to 2.4885 (15) Å in (2) and 2.477 (3) Å in (3).

The Pd—B distances in (1) [mean 2.974 (4) Å] are notably similar to the related distances in (2) [mean 2.297 (11) Å] and in (3) [mean 2.28 (5) Å]. The range of As—B distances in (1) is 2.105 (7)–2.230 (7) Å. A similar range was reported for (2) [2.119 (12)–2.259 (12) Å], but that in (3) is slightly larger [2.101 (9)–2.281 (8) Å]. The B—B distances in (1) range from 1.732 (9) Å for B9—B12 to 1.879 (8) Å for B4—B5. The ranges in (2) and (3) are very similar [1.740 (16)–1.881 (17) Å in (2), 1.739 (12)–1.896 (10) Å in (3)].

The B—P distances to the *exo*-phosphine ligands on the cages of (1) and (3) are 1.919 (5) and 1.948 (8) Å, respectively. The remaining distances in the cation are within the normal range, as anticipated. The $[SbF_6]^-$ anion has the expected octahedral geometry with a mean Sb—F bond length of 1.81 (4) Å.

Experimental

Compound (1) was obtained by the reaction in CH_2Cl_2 solution of *closo*-$[3\text{-}Cl\text{-}3,8\text{-}(PPh_3)_2\text{-}3,1,2\text{-}PdAs_2B_9H_9]$ (McGrath, Spalding, Fontaine, Kennedy & Thornton-Pett, 1991) with $Ag[SbF_6]$, followed by the addition of a slight excess of ^{t}BuNC in CH_2Cl_2. Pink crystals of *closo*-$[3\text{-}(^t BuNC)\text{-}3,8\text{-}(PPh_3)_2\text{-}3,1,2\text{-}PdAs_2B_9H_8][SbF_6]$, (1), were obtained from a CH_2Cl_2 solution layered with heptane.

Crystal data

$[Pd(C_5H_9N)(C_8H_{11}P)\{B_9H_8\text{-}As_2(C_8H_{11}P)\}][SbF_6]$
$M_r = 956.75$
Triclinic
$P\overline{1}$
$a = 9.9342\ (8)$ Å
$b = 13.0495\ (13)$ Å
$c = 15.3141\ (14)$ Å
$\alpha = 96.6120\ (9)°$
$\beta = 102.2910\ (10)°$
$\gamma = 105.039\ (8)°$
$V = 1842.5\ (3)$ Å^3
$Z = 2$
$D_x = 1.725$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 14.50–21.00°$
$\mu = 3.136$ mm^{-1}
$T = 291\ (1)$ K
Block
0.31 × 0.19 × 0.12 mm
Pink

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: nine ψ scans at 4° steps
$T_{\min} = 0.570$, $T_{\max} = 0.703$
7201 measured reflections
7201 independent reflections

4403 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 25.90°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: no decay, variation 1.0%

Refinement

Refinement on F^2
$R(F) = 0.0430$
$wR(F^2) = 0.1071$
$S = 1.216$
7201 reflections
401 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.003$

$\Delta\rho_{\max} = 0.728$ e Å^{-3}
$\Delta\rho_{\min} = -1.101$ e Å^{-3} (0.95 Å from As2)
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 isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for C33*A*–C35*A*; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\rm eq}$
Pd3	0.21639 (4)	0.80885 (3)	0.18640 (3)	0.05057 (14)
Sb	0.76973 (6)	0.72643 (4)	0.42038 (3)	0.0866 (2)
As1	0.38647 (6)	0.76139 (6)	0.08680 (5)	0.0681 (2)
As2	0.35995 (8)	0.94647 (5)	0.11186 (4)	0.0685 (2)
P1	0.2783 (2)	0.9402 (2)	0.31649 (12)	0.0875 (7)
P2	−0.15502 (14)	0.70551 (11)	0.08108 (9)	0.0420 (3)
N	0.1883 (6)	0.6222 (4)	0.2993 (3)	0.075 (2)
B4	0.1526 (6)	0.6791 (4)	0.0586 (4)	0.0418 (13)
B5	0.2322 (7)	0.7094 (5)	−0.0397 (5)	0.055 (2)
B6	0.3352 (8)	0.8502 (5)	−0.0237 (5)	0.059 (2)
B7	0.1206 (8)	0.9005 (5)	0.0817 (4)	0.054 (2)
B8	0.0298 (6)	0.7607 (4)	0.0572 (4)	0.0372 (12)
B9	0.0506 (7)	0.7024 (5)	−0.0448 (4)	0.0481 (15)

B10	0.1594 (8)	0.8042 (5)	−0.0904 (4)	0.058 (2)
B11	0.2084 (8)	0.9259 (5)	−0.0128 (5)	0.059 (2)
B12	0.0348 (8)	0.8320 (5)	−0.0329 (4)	0.055 (2)
F1	0.6337 (7)	0.7240 (5)	0.3154 (4)	0.155 (2)
F2	0.8999 (7)	0.7211 (6)	0.5223 (4)	0.184 (3)
F3	0.7192 (11)	0.5817 (5)	0.3916 (6)	0.255 (5)
F4	0.9111 (9)	0.7339 (8)	0.3577 (5)	0.202 (3)
F5	0.8297 (13)	0.8681 (6)	0.4437 (8)	0.294 (6)
F6	0.6434 (10)	0.7276 (13)	0.4858 (6)	0.319 (7)
C11	0.4567 (8)	1.0329 (6)	0.3326 (4)	0.074 (2)
C12	0.5709 (9)	0.9920 (7)	0.3326 (5)	0.090 (2)
C13	0.7067 (10)	1.0599 (11)	0.3432 (6)	0.124 (4)
C14	0.7266 (14)	1.1677 (12)	0.3524 (7)	0.145 (6)
C15	0.6176 (15)	1.2100 (9)	0.3511 (6)	0.133 (5)
C16	0.4807 (10)	1.1430 (6)	0.3421 (4)	0.097 (3)
C17	0.2895 (13)	0.8893 (8)	0.4217 (5)	0.179 (6)
C18	0.1534 (10)	1.0189 (9)	0.3189 (8)	0.175 (6)
C21	−0.2980 (5)	0.6588 (4)	−0.0216 (3)	0.0432 (12)
C22	−0.3564 (6)	0.7317 (5)	−0.0642 (4)	0.0585 (15)
C23	−0.4609 (7)	0.6980 (5)	−0.1452 (4)	0.065 (2)
C24	−0.5051 (7)	0.5896 (6)	−0.1859 (4)	0.072 (2)
C25	−0.4488 (7)	0.5180 (5)	−0.1437 (5)	0.072 (2)
C26	−0.3470 (6)	0.5506 (5)	−0.0628 (4)	0.062 (2)
C27	−0.1972 (6)	0.8075 (5)	0.1518 (4)	0.062 (2)
C28	−0.1579 (6)	0.5955 (5)	0.1402 (4)	0.068 (2)
C31	0.2014 (7)	0.6902 (6)	0.2600 (4)	0.072 (2)
C32	0.1760 (7)	0.5337 (5)	0.3518 (4)	0.076 (2)
C33†	0.2160 (12)	0.5844 (7)	0.4481 (5)	0.123 (5)
C34†	0.2688 (11)	0.4678 (9)	0.3294 (7)	0.134 (6)
C35†	0.0179 (8)	0.4657 (7)	0.3228 (6)	0.103 (4)
C33*A*‡	0.090 (3)	0.551 (3)	0.4175 (18)	0.107 (11)
C34*A*‡	0.3324 (15)	0.554 (3)	0.402 (2)	0.107 (11)
C35*A*‡	0.118 (3)	0.4232 (17)	0.296 (2)	0.107 (11)

† Occupancy = 0.795 (13).
‡ Occupancy = 0.205 (13).

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

Pd3—As1	2.6434 (8)	As2—B7	2.226 (7)
Pd3—As2	2.5296 (7)	As2—B11	2.105 (7)
Pd3—P1	2.330 (2)	P1—C11	1.816 (7)
Pd3—C31	2.011 (6)	P1—C17	1.805 (8)
Pd3—B4	2.291 (6)	P1—C18	1.808 (10)
Pd3—B7	2.300 (7)	P2—C21	1.800 (5)
Pd3—B8	2.301 (5)	P2—C27	1.808 (6)
As1—As2	2.4919 (10)	P2—C28	1.780 (5)
As1—B4	2.215 (6)	P2—B8	1.919 (5)
As1—B5	2.111 (7)	N—C31	1.124 (7)
As1—B6	2.204 (7)	N—C32	1.475 (7)
As2—B6	2.230 (7)		
C31—Pd3—B4	88.1 (2)	B5—As1—B4	51.4 (2)
C31—Pd3—B7	152.9 (2)	B6—As1—B4	87.8 (2)
B4—Pd3—B7	80.9 (2)	B5—As1—As2	95.2 (2)
C31—Pd3—B8	110.7 (2)	B6—As1—As2	56.3 (2)
B4—Pd3—B8	46.6 (2)	B4—As1—As2	94.49 (14)
B7—Pd3—B8	45.2 (2)	B5—As1—Pd3	98.0 (2)
C31—Pd3—P1	91.7 (2)	B6—As1—Pd3	99.3 (2)
B4—Pd3—P1	179.28 (14)	B4—As1—Pd3	55.4 (2)
B7—Pd3—P1	99.0 (2)	As2—As1—Pd3	58.93 (2)
B8—Pd3—P1	133.0 (2)	B11—As2—B7	50.8 (2)
C31—Pd3—As2	151.1 (2)	B11—As2—B6	49.4 (3)
B4—Pd3—As2	91.64 (14)	B7—As2—B6	87.7 (2)
B7—Pd3—As2	54.6 (2)	B11—As2—As1	95.5 (2)
B8—Pd3—As2	89.42 (13)	B7—As2—As1	98.0 (2)
P1—Pd3—As2	88.86 (5)	B6—As2—As1	55.3 (2)
C31—Pd3—As1	100.8 (2)	B11—As2—Pd3	100.0 (2)
B4—Pd3—As1	52.76 (13)	B7—As2—Pd3	57.4 (2)
B7—Pd3—As1	92.0 (2)	B6—As2—Pd3	102.0 (2)
B8—Pd3—As1	88.96 (14)	As1—As2—Pd3	63.52 (2)
P1—Pd3—As1	127.95 (5)	C31—N—C32	178.2 (6)
As2—Pd3—As1	57.54 (2)	N—C31—Pd3	177.6 (6)
B5—As1—B6	49.7 (2)		

Molecule (1) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. The methyl groups of the *tert*-butyl moiety were disordered over two sites [occupancies 0.795 (13)/0.205 (13) from refinement]. The C atoms of the minor site were constrained to isotropic refinement; all other non-H atoms were refined anisotropically. H atoms were refined using a riding model (*SHELXL*93; Sheldrick, 1993). Examination of the structure with *PLATON* (Spek, 1994*a*) showed that there were no solvent accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1992). Cell refinement: Enraf–Nonius (1992) *SET*4 and *CELDIM*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX*94; *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94; *PLATON* (Spek, 1994*a*); *PLUTON* (Spek 1994*b*); *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX*94; *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1248). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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