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exo-2,7,11-μ_3-[Dihydro(triphenylphosphine)cuprio-2*Cu*,7*H*,11*H*]-2-triphenylphosphine-*closo*-1,2-selenacupradodecaborane(8)

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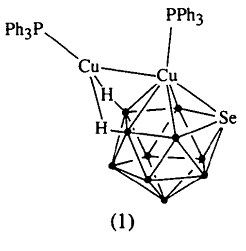
Abstract

The title compound, $\{exo\text{-}2,7,11\text{-}\mu_3\text{-}[(\mu\text{-}H)_2Cu(PPh_3)]\text{-}2\text{-}(PPh_3)\text{-}closo\text{-}2,1\text{-}CuSeB_{10}H_8\}$, $[Cu_2(C_{18}H_{15}P)(C_{18}H_{25}B_{10}PSe)]$, has an icosahedral *closo*-$CuSeB_{10}$ cage with Cu and Se atoms adjacent [Se1—Cu2 2.3939 (6) Å]. An *exo*-cage $[Cu(PPh_3)]$-unit is bonded to one triangular CuB_2 face *via* a Cu—Cu bond [Cu2—Cu3 2.6470 (7) Å] and two B—H—Cu3 interactions [Cu3—H7 1.97 (3), Cu3—H11 1.86 (2), Cu3···B7 2.234 (3), Cu3···B11 2.158 (3) Å].

Comment

The overall cluster structure of the title compound, (1), Fig. 1, may be viewed as a triangulated icosahedron, distorted from ideal, of $CuSeB_{10}$ atoms that is fused to a tetrahedron of CuB_2 atoms, with a common CuB_2 triangular face. It is analogous to both the cupratelluraborane $\{exo\text{-}2,7,11\text{-}\mu_3\text{-}[(\mu\text{-}H)_2Cu(PPh_3)]\text{-}2\text{-}(PPh_3)\text{-}closo\text{-}2,1\text{-}CuTeB_{10}H_8\}$, (2) (Thornton-Pett, Kennedy, Faridoon & Spalding, 1995), and the cupradicarbaborane $\{exo\text{-}3,4,8\text{-}\mu_3\text{-}[(\mu\text{-}H)_2Cu(PPh_3)]\text{-}3\text{-}(PPh_3)\text{-}closo\text{-}3,1,2\text{-}CuTeB_{10}H_8\}$, (3) (Do, Kang, Knobler & Hawthorne, 1987).



(1)

In the title compound, the *exo*-cage Cu atom is asymmetrically bound to the $CuSeB_{10}$ cluster *via* Cu—H—B bonds to B7 and B11 and a direct Cu—Cu linkage. The distances from the *exo* Cu atom (Cu3) to B7 and B11 are 2.234 (3) and 2.158 (3) Å, respectively; a difference of over 0.07 Å. Analogous bonding situations presumably exist in (2) and (3) but the differences are less marked in these than in the title compound. The relevant values are 2.207 (4), 2.161 (5) and 0.046 Å in (2) (Thornton-Pett *et al.*, 1995), and 2.210 (4), 2.173 (5) and 0.037 Å in (3) (Do *et al.*, 1987).

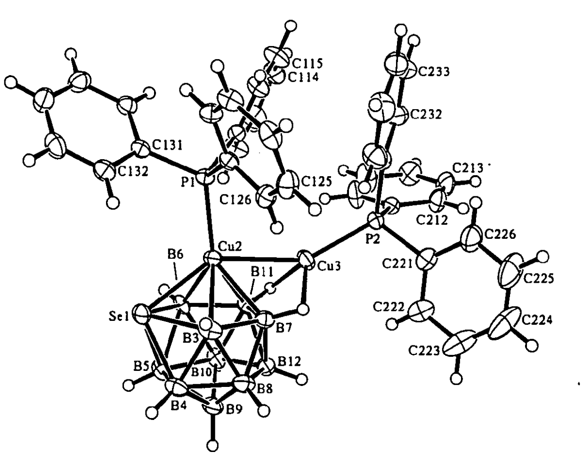


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as small circles of arbitrary radius; phenyl ring C atoms are labelled sequentially C*hk*1–C*hk*6, where *h* = 1 or 2 and *k* = 1, 2, 3.

Two of the Cu2—B distances are 'long', *i.e.* Cu2—B3 and Cu2—B6 are 2.267 (3) and 2.293 (2) Å, respectively, and two are 'short', *i.e.* Cu2—B7 and Cu2—B11 are 2.136 (3) and 2.145 (3) Å, respectively. This is typical of the bonding in metallaheteroboranes containing adjacent metal and hetero atoms. The *M*—B (and *E*—B, where *E* is the hetero atom) linkages involving B atoms that are attached to both *M* and *E* are generally longer than those with only one heteroatom interaction (see, *e.g.*, McGrath, Spalding, Fontaine, Kennedy & Thornton-Pett, 1991). The 'long' Se—B distances in the title compound are Se—B3 and Se—B6 of 2.182 (3) and 2.159 (3) Å, respectively, and the 'short' distances are Se—B4 and Se—B5 of 2.145 (3) and 2.135 (3) Å, respectively.

The Cu2—Cu3 distance is 2.6470 (7) Å in the title compound, close to distance of 2.6915 (8) Å observed in the tellurium analogue (2). Both of these values are notably longer than the value of 2.576 (1) Å reported for the dicarba compound (3).

The Cu2—Se distance of 2.3939 (6) Å appears to be remarkably short, although data for comparison are scarce. The Cu^{II}/Cu^{I} complex $[Cu(H_2O)(C_2H_8N_2)_2][Cu_2(CN)_2(SeCN)_2]$ contains two copper(I) centres doubly bridged by selenacyanato ligands with two Cu—Se distances of 2.613 (3) and 2.649 (3) Å, (Vrabel, Garaz & Kutschabsky, 1979).

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Experimental

Equimolar amounts of $[NEt_4]^+[nido\text{-}7\text{-}SeB_{10}H_{11}]^-$ and $[Cu(NO_3)(PPh_3)_2]$ were allowed to react together in ethanol at room temperature. The compound was isolated in 10% yield after preparative chromatography on silica (eluant: 3:2 CH_2Cl_2–cyclohexane).

Crystal data

$[Cu_2(C_{18}H_{15}P)(C_{18}H_{25}B_{10}PSe)]$
$M_r = 848.76$
Triclinic
$P\bar{1}$
$a = 12.0905\,(15)$ Å
$b = 12.0619\,(13)$ Å
$c = 13.970\,(2)$ Å
$\alpha = 89.416\,(8)°$
$\beta = 81.601\,(8)°$
$\gamma = 75.202\,(8)°$
$V = 1947.8\,(4)$ Å^3
$Z = 2$
$D_x = 1.447$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 32 reflections
$\theta = 12.5–15°$
$\mu = 2.135$ mm^{-1}
$T = 200.0\,(10)$ K
Prism
0.6 × 0.5 × 0.2 mm
Pale brown

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: ψ scans (8 reflections)
$T_{min} = 0.335$, $T_{max} = 0.486$
6076 measured reflections
6076 independent reflections
5379 observed reflections $[I > 2\sigma(I)]$

$\theta_{max} = 24.99°$
$h = -14 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0246$
$wR(F^2) = 0.0670$
$S = 1.115$
6076 reflections
501 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 1.3887P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.255$ e Å^{-3}
$\Delta\rho_{min} = -0.668$ 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}
Se1	0.09685 (2)	0.01501 (2)	0.08437 (2)	0.0298 (2)
Cu2	0.20589 (2)	0.13230 (2)	0.14398 (2)	0.0233 (2)
Cu3	0.25974 (3)	0.19226 (2)	0.30948 (2)	0.0300 (2)
P1	0.29354 (5)	0.23162 (5)	0.04130 (4)	0.0202 (3)
P2	0.33700 (5)	0.30664 (5)	0.38421 (4)	0.0237 (4)
B3	0.0119 (2)	0.1605 (2)	0.1833 (2)	0.028 (2)
B4	−0.0430 (3)	0.0285 (2)	0.2011 (2)	0.031 (2)
B5	0.0861 (3)	−0.1043 (2)	0.1971 (2)	0.030 (2)
B6	0.2270 (2)	−0.0587 (2)	0.1737 (2)	0.021 (2)
B7	0.0926 (2)	0.1638 (2)	0.2788 (2)	0.0241 (15)
B8	−0.0349 (3)	0.1138 (2)	0.2991 (2)	0.030 (2)
B9	0.0049 (3)	−0.0389 (2)	0.3055 (2)	0.030 (2)
B10	0.1587 (3)	−0.0852 (2)	0.2921 (2)	0.028 (2)
B11	0.2166 (2)	0.0363 (2)	0.2738 (2)	0.022 (2)
B12	0.0859 (3)	0.0456 (2)	0.3557 (2)	0.028 (2)
C111	0.4358 (2)	0.2347 (2)	0.06729 (15)	0.0212 (13)
C112	0.5019 (2)	0.1361 (2)	0.1042 (2)	0.033 (2)
C113	0.6139 (2)	0.1292 (2)	0.1185 (2)	0.038 (2)
C114	0.6614 (2)	0.2206 (2)	0.0978 (2)	0.0351 (15)
C115	0.5959 (2)	0.3192 (2)	0.0620 (2)	0.038 (2)
C116	0.4839 (2)	0.3269 (2)	0.0476 (2)	0.029 (2)
C121	0.2127 (2)	0.3811 (2)	0.03352 (15)	0.0219 (13)
C122	0.2325 (2)	0.4447 (2)	−0.0482 (2)	0.0266 (13)
C123	0.1689 (2)	0.5572 (2)	−0.0531 (2)	0.0299 (15)
C124	0.0864 (2)	0.6077 (2)	0.0236 (2)	0.032 (2)
C125	0.0651 (2)	0.5455 (2)	0.1044 (2)	0.035 (2)
C126	0.1273 (2)	0.4319 (2)	0.1092 (2)	0.0287 (15)
C131	0.3205 (2)	0.1884 (2)	−0.0867 (2)	0.0215 (14)
C132	0.2256 (2)	0.1909 (2)	−0.1333 (2)	0.030 (2)
C133	0.2393 (3)	0.1742 (2)	−0.2324 (2)	0.035 (2)
C134	0.3486 (2)	0.1533 (2)	−0.2860 (2)	0.040 (2)
C135	0.4436 (2)	0.1455 (2)	−0.2407 (2)	0.036 (2)
C136	0.4303 (2)	0.1633 (2)	−0.1410 (2)	0.0267 (14)
C211	0.4669 (2)	0.2387 (2)	0.43514 (15)	0.0254 (14)
C212	0.4983 (2)	0.2862 (2)	0.5143 (2)	0.035 (2)
C213	0.6044 (2)	0.2399 (2)	0.5430 (2)	0.041 (2)
C214	0.6812 (3)	0.1461 (2)	0.4939 (2)	0.042 (2)
C215	0.6509 (3)	0.0989 (3)	0.4155 (2)	0.052 (2)
C216	0.5441 (2)	0.1437 (2)	0.3870 (2)	0.042 (2)
C221	0.2320 (2)	0.3822 (2)	0.4844 (2)	0.0311 (15)
C222	0.1495 (2)	0.3287 (2)	0.5288 (2)	0.042 (2)
C223	0.0665 (3)	0.3845 (3)	0.6039 (2)	0.061 (2)
C224	0.0654 (3)	0.4924 (3)	0.6339 (2)	0.071 (3)
C225	0.1466 (3)	0.5458 (3)	0.5914 (2)	0.069 (3)
C226	0.2301 (3)	0.4916 (2)	0.5163 (2)	0.048 (2)
C231	0.3783 (2)	0.4221 (2)	0.3141 (2)	0.027 (2)
C232	0.4871 (2)	0.4417 (2)	0.3065 (2)	0.038 (2)
C233	0.5108 (3)	0.5337 (3)	0.2539 (2)	0.049 (2)
C234	0.4278 (3)	0.6041 (2)	0.2083 (2)	0.050 (3)
C235	0.3200 (3)	0.5849 (2)	0.2148 (2)	0.050 (2)
C236	0.2951 (3)	0.4944 (2)	0.2674 (2)	0.041 (2)

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

Se1—Cu2	2.3939 (6)	B3—B7	1.771 (4)
Se1—B3	2.182 (3)	B4—B5	1.924 (4)
Se1—B4	2.145 (3)	B4—B9	1.763 (4)
Se1—B5	2.135 (3)	B5—B6	1.903 (4)
Se1—B6	2.159 (3)	B5—B9	1.754 (4)
Cu2—Cu3	2.6470 (7)	B5—B10	1.743 (4)
Cu2—P1	2.1875 (8)	B6—B10	1.801 (4)
Cu2—B3	2.267 (3)	B6—B11	1.787 (4)
Cu2—B6	2.293 (2)	B7—B8	1.779 (4)
Cu2—B7	2.136 (3)	B7—B11	1.847 (4)
Cu2—B11	2.145 (3)	B7—B12	1.788 (4)
Cu3—P2	2.1997 (8)	B8—B9	1.785 (4)
Cu3—B7	2.234 (3)	B8—B12	1.773 (4)
Cu3—H7	1.97 (3)	B9—B10	1.782 (4)
Cu3—H11	1.86 (2)	B9—B12	1.793 (4)
Cu3—B11	2.158 (3)	B10—B11	1.779 (4)
B3—B4	1.877 (4)	B10—B12	1.774 (4)
B3—B8	1.770 (4)	B11—B12	1.789 (4)
B7—Cu2—Se1	91.81 (8)	Se1—Cu2—Cu3	139.94 (2)
B11—Cu2—Se1	90.89 (7)	Cu3—H7—B7	88.6 (15)
P1—Cu2—Se1	118.84 (2)	Cu3—H11—B11	88.9 (14)
P1—Cu2—Cu3	101.21 (2)		

Data were collected using an on-line profile fitting method (Clegg, 1981).

Geometrical restraints were applied to phenyl rings so that they were flat with overall $C2/v$ symmetry. Whereas phenyl H atoms were constrained to calculated positions, borane cage atoms were located on a difference synthesis and were freely refined.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990).

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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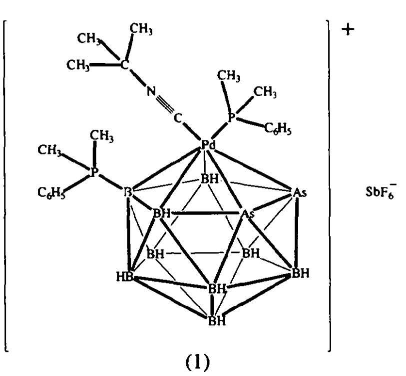
Abstract

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