Crystal data

$[V(C_5H_{10}NS_2)_3]$
$M_r = 495.75$
Monoclinic
$P2_1/c$
$a = 13.731\,(1)$ Å
$b = 10.294\,(1)$ Å
$c = 17.230\,(1)$ Å
$\beta = 103.06\,(1)°$
$V = 2372.35\,(1)$ Å^3
$Z = 4$
$D_x = 1.39$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 12–13°$
$\mu = 0.92$ mm^{-1}
$T = 293$ K
Prism
0.25 × 0.17 × 0.15 mm
Yellow–brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.841$, $T_{max} = 0.870$
4432 measured reflections
4267 independent reflections

2417 reflections with $I > 3\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 0.6%

Refinement

Refinement on F
$R = 0.0393$
$wR = 0.0456$
$S = 1.27$
2417 reflections
226 parameters
H atoms not refined
$w = 1/[\sigma^2(F)]$

$(\Delta/\sigma)_{max} = 0.0007$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

V—S1	2.434 (1)	S3—C20	1.716 (4)
V—S2	2.434 (1)	S4—C20	1.723 (4)
V—S3	2.423 (1)	S5—C30	1.721 (4)
V—S4	2.436 (1)	S6—C30	1.721 (4)
V—S5	2.445 (1)	N1—C10	1.321 (6)
V—S6	2.433 (1)	N2—C20	1.324 (6)
S1—C10	1.719 (4)	N3—C30	1.327 (6)
S2—C10	1.722 (4)		
S1—V—S2	72.69 (4)	V—S1—C10	86.6 (2)
S1—V—S3	91.44 (5)	V—S2—C10	86.5 (1)
S1—V—S4	153.65 (5)	V—S3—C20	86.6 (1)
S1—V—S5	96.16 (5)	V—S4—C20	86.0 (2)
S1—V—S6	104.54 (5)	V—S5—C30	86.4 (1)
S2—V—S3	107.75 (5)	V—S6—C30	86.8 (1)
S2—V—S4	91.55 (5)	S1—C10—S2	113.9 (2)
S2—V—S5	156.89 (5)	S1—C10—N1	122.8 (3)
S2—V—S6	90.30 (4)	S2—C10—N1	123.3 (3)
S3—V—S4	73.01 (4)	S3—C20—S4	114.4 (2)
S3—V—S5	92.39 (4)	S3—C20—N2	122.5 (3)
S3—V—S6	158.94 (5)	S4—C20—N2	123.1 (3)
S4—V—S5	105.43 (5)	S5—C30—S6	114.1 (2)
S4—V—S6	96.33 (5)	S5—C30—N3	122.6 (3)
S5—V—S6	72.61 (4)	S6—C30—N3	123.3 (3)

The title structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares methods. H atoms were located and added to the structure-factor calculations, but their positions were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Cycloboronated Nickelaundecaborane: $[(\mathrm{PhC}\overline{\mathrm{OS})_2\mathrm{NiB}}_{10}\mathrm{H}_8(\mathrm{PPh}_3)]$

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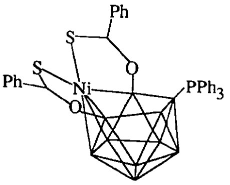
Abstract

The title compound 7,8:7,11-di(μ-thiobenzoato-*S*:*O*)-10-(triphenylphosphine-*P*)-8:9-μH-7-nickela-*nido*-undecaborane, $C_{32}H_{33}B_{10}NiO_2PS_2$, has been synthesized and characterized by X-ray diffraction analysis. The cluster is a *nido* eleven-vertex $\{NiB_{10}\}$ cage with the Ni atom in the open NiB_4 face. Cyclizations resulting in two five-membered rings, Ni7—S1—C1—O1—B8 and Ni7—S2—C2—O2—B11, have occurred.

Comment

Some metals of the third transition series can take part in *ortho*-cycloboronation in metallaborane clusters, for example, iridium (Crook, Greenwood, Kennedy & McDonald, 1981, 1982; Bould, Greenwood, Kennedy & McDonald, 1982; Bould, Crook, Greenwood, Kennedy & McDonald, 1983), platinum (Beckett, Greenwood, Kennedy & Thornton-Pett, 1985) and osmium (Elrington, Greenwood, Kennedy & Thornton-Pett, 1986). It has also been reported that reaction of $[RuCl_2(PPh_3)_3]$ and *closo*-$B_{10}H_{10}^{2-}$ with MeCOOH (Fontaine, Greenwood, Kennedy, Thornton-Pett & Zheng, 1987) or PhCOOH (Yao *et al.*, 1995) results in five-membered Ru—O—C—O—B rings by *ortho*-cycloboronation. So far, a cycloboronated metal cluster of the first transition series has not been reported. The preparation and structure of the title cycloboronated nickelaborane cluster compound, (I), are reported here.



(I)

The Ni atom is coordinated to two S atoms and four B atoms. The distances Ni7—B2 of 2.159 (4) Å and Ni7—B3 of 2.121 (3) Å are within the range of these distances found in reported nickelaborane compounds (Guggenberger, 1972). However, the Ni7—B8 and Ni7—B11 distances of 2.080 (4) and 2.085 (3) Å, respectively, are significantly shorter than the corresponding Ni—B distances in non-cycloboronated clusters (Guggenberger, 1972). This shows that the *ortho*-cycloboronation strengthens the Ni—B bonding. The PPh_3 ligand is bonded to B10 and the P1—B10 distance of 1.910 (3) Å is within the range of distances found in other metallaboranes (Crook *et al.*, 1985; Greenwood, Kennedy, Thornton-Pett & Woollins, 1985; Cheek, Kennedy & Thornton-Pett, 1985). The distances B10—B11 of 1.684 (4) Å and B10—B9 of 1.865 (4) Å are shorter than the corresponding B—B bond distances in Guggenberger (1972); this is due to the phosphine ligand acting as a two-electron donor, equivalent to a H^- ligand, thus eliminating the need for the bridging H atom, which thereby increases the two-centre contribution to the B10—B11 bonding vector (Bould, Crook, Greenwood, Kennedy & Thornton-Pett, 1990). There is a bridging H atom between the B8 and B9 atoms [B8—H89 1.24 (13) and B9—H89 1.29 (3) Å]. In the cluster, the two five-membered rings, Ni7—S1—C1—O1—B8 and Ni7—S2—C2—O2—B11, are planar. The dihedral angle between them is 26.57 (8)°. The two five-membered rings are on either side of a pseudo-mirror plane containing the Ni7, B5 and B1 atoms.

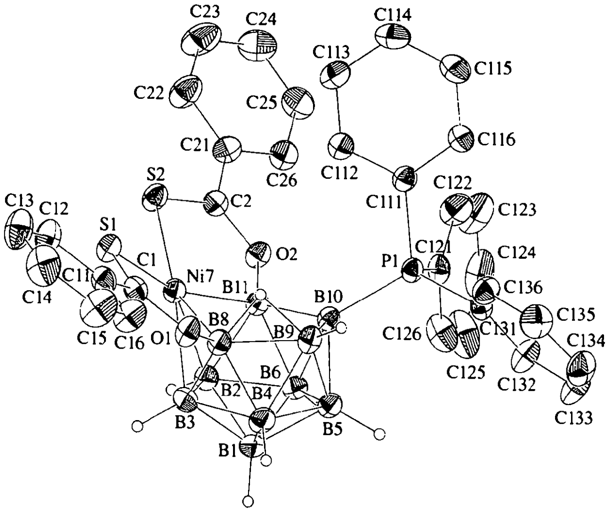


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. Some H atoms on C atoms have been omitted for clarity.

Experimental

The synthesis of the title compound was carried out by reaction of $[NiCl_2(PPh_3)_2]$ (0.6 mmol) and $[Et_4N]_2B_{10}H_{10}$ (0.6 mmol) with PhCOSH (1.2 mmol) in refluxing dichloromethane for 63 h under an atmosphere of dry nitrogen. The resulting solution was reduced in volume and chromatographed using dichloromethane/light petroleum (4:1) as the eluting medium to give a black title compound at R_f = 0.65. The product was recrystallized from an *n*-hexane/dichloromethane solution.

Crystal data

$C_{32}H_{33}B_{10}NiO_2PS_2$
M_r = 711.48
Monoclinic
$P2_1/c$
a = 11.959 (3) Å
b = 14.696 (4) Å
c = 20.203 (4) Å
β = 91.54 (2)°
V = 3549.3 (16) Å^3
Z = 4
D_x = 1.331 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.1–14.3°
μ = 0.740 mm^{-1}
T = 294 (2) K
Prism
0.40 × 0.30 × 0.20 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.761, T_{max} = 0.862
5997 measured reflections
5562 independent reflections

3932 reflections with $I > 2\sigma(I)$
R_{int} = 0.0135
θ_{max} = 24°
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 0$
$l = -23 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 0.3%

Refinement

Refinement on F^2
$R(F) = 0.0321$
$wR(F^2) = 0.1060$
$S = 1.065$
5562 reflections
441 parameters
H atoms were isotropically refined as riding atoms

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 1.6054P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.361$ e Å^{-3}
$\Delta\rho_{\min} = -0.305$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni7—B8	2.080 (4)	S1—C1	1.675 (3)
Ni7—B11	2.085 (3)	S2—C2	1.683 (3)
Ni7—B3	2.121 (3)	P1—B10	1.910 (3)
Ni7—B2	2.159 (4)	B8—O1	1.473 (4)
Ni7—S1	2.2056 (10)	B11—O2	1.483 (4)
Ni7—S2	2.2135 (10)		
B8—Ni7—B11	95.50 (13)	B8—Ni7—S1	81.76 (10)
B8—Ni7—B3	48.73 (14)	B3—Ni7—S1	105.09 (10)
B11—Ni7—B3	86.72 (13)	B11—Ni7—S2	82.78 (9)
B8—Ni7—B2	88.47 (14)	B2—Ni7—S2	109.25 (10)
B11—Ni7—B2	48.19 (13)	S1—Ni7—S2	91.08 (4)
B3—Ni7—B2	49.63 (14)		

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1444). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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ortho-Cycloboronation of a Thiobenzoate Cluster: $[(\mathrm{PPh_3})(\mathrm{PhC}\overline{\mathrm{OS})_2\mathrm{NiB}}_{10}\mathrm{H}_{10}]$.-$0.5\mathrm{C_6H_{14}}$

Chun-Hua Hu,[a] Jian-Min Dou,[a] Hai-Jun Yao,[b] Wen Li,[a] Ruo-Shui Jin[b] and Pei-Ju Zheng[a]

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(*Received 19 November 1996; accepted 4 February 1997*)

Abstract

The title compound, 2,7:3,7-di(μ-thiobenzoato-*S*:*O*)-7-(triphenylphosphine-*P*)-8,9:10,11-di-μ*H*-7-nickela-*nido*-undecaborane–hexane (1/0.5), $C_{32}H_{35}B_{10}NiO_2PS_2.0.5C_6H_{14}$, has been synthesized and characterized by X-ray diffraction analysis. The Ni atom is bound to one PPh_3 ligand, two S atoms and four B atoms of the $\{NiB_{10}\}$ cage. The *ortho*-cycloboronation of thiobenzoates produces two five-membered Ni—S—C—O—B rings.

Comment

In some metallaboranes, there is *ortho*-cycloboronation of a metal ligand to the cluster. The groups of cyclization include the phosphine–phenyl ligand (Crook, Greenwood, Kennedy & McDonald, 1982; Bould, Greenwood, Kennedy & McDonald, 1982; Bould, Crook, Greenwood, Kennedy & Thornton-

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