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## References

- Akselrud, L. G., Zavalij, P. Y., Grin, Yu. N., Pecharsky, V. K., Baumgartner, B. & Wolfel, E. (1993). *Mater. Sci. Forum*, **133–136**, 335–340.
- Chen, R., Zavalij, P. Y. & Whittingham, M. S. (1998). *J. Mater. Chem.* In the press.
- Chirayil, T., Zavalij, P. Y. & Whittingham, M. S. (1996). *Solid State Ion.* **84**, 163–168.
- Chirayil, T., Zavalij, P. Y. & Whittingham, M. S. (1997). *J. Mater. Chem.* **7**, 2193–2197.
- Janauer, G. G., Doble, A. D., Zavalij, P. Y. & Whittingham, M. S. (1997). *Chem. Mater.* **9**, 647–649.
- Sheldrick, G. M. (1996). *SADABS. Empirical Absorption Correction Program*. University of Göttingen, Germany.
- Siemens (1995). *SMART and SAINT. Data Collection and Processing Software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Zavalij, P. Y., Chirayil, T. & Whittingham, M. S. (1997a). *Acta Cryst.* **C53**, 879–881.
- Zavalij, P. Y., Chirayil, T. & Whittingham, M. S. (1997b). *Z. Kristallogr.* **212**, 321–322.
- Zavalij, P. Y., Whittingham, M. S., Boylan, E. A., Pecharsky, V. K. & Jacobson, R. A. (1996). *Z. Kristallogr.* **211**, 464–464.
- Zavalij, P. Y., Whittingham, M. S., Chirayil, T., Pecharsky, V. K. & Jacobson, R. A. (1997). *Acta Cryst.* **C53**, 170–171.

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## An Exopolyhedral Cyclized Platinaundecaborane: [(PPh<sub>3</sub>)(PhCOS)PtB<sub>10</sub>H<sub>9</sub>(PPh<sub>3</sub>)]·1.5CHCl<sub>3</sub>

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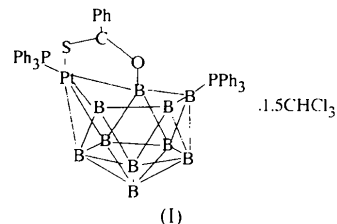
## Abstract

The title platinaundecaborane species, 7,11-( $\mu$ -thiobenzoato-*S*:*O*)-7,10-bis(triphenylphosphine-*P*)-8:9- $\mu$ H-7-platina-*nido*-undecaborane-chloroform (1/1.5), has a *nido*-type {PtB<sub>10</sub>} cage with a five-membered Pt—S—

C—O—B ring. Of the two PPh<sub>3</sub> ligands, one is bound to the Pt atom and the other to a B atom.

## Comment

We have developed an interest in exopolyhedral cyclization of metal ligands to clusters, especially sulfur-containing ligands. Beckett *et al.* (1985) reported an exopolyhedral heterocyclic platinaundecaborane [ $\mu$ -2,7-(SCSNET<sub>2</sub>)-7-(PMe<sub>2</sub>Ph)-*nido*-7-PtB<sub>10</sub>H<sub>11</sub>] via a ligand-exchange-type process from the reaction of [7,7-(PMe<sub>2</sub>Ph)<sub>2</sub>-*nido*-7-PtB<sub>10</sub>H<sub>12</sub>] with [AuBr<sub>2</sub>(SCSNET<sub>2</sub>)]. The reactions of CS<sub>2</sub> with metallated boron-containing cluster compounds result in a series of exopolyhedral cyclic compounds containing five-membered M—S—C—S—B rings; metals include Rh (Ferguson *et al.*, 1990), Re and Os (Coldicott, 1994), and Ir (Coldicott, 1994; Coldicott *et al.*, 1996). We have developed a further type of exopolyhedral cyclization process resulting in a five-membered M—S—C—O—B ring on the eleven-vertex metallaborane; this occurs via a direct process from the reaction of MCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (M = Ni, Pt) or MCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (M = Ru) and (NEt<sub>4</sub>)<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with PhCOSH in dichloromethane solution (Dou, Hu, Yao *et al.*, 1997; Dou, Hu, Sun *et al.*, 1997; Hu *et al.*, 1997, 1998; Yao *et al.*, 1998). We report here another example of thiobenzoate linkage, a platinaundecaborane, (1), [(PPh<sub>3</sub>)(PhCOS)PtB<sub>10</sub>H<sub>9</sub>(PPh<sub>3</sub>)]·1.5CHCl<sub>3</sub>.



The cluster has a *nido*-eleven-vertex {PtB<sub>10</sub>} polyhedral skeleton and has a five-membered Pt—S—C—O—B ring of exopolyhedral cyclization via one thiobenzoate. Its structure is shown in Fig. 1. The Pt atom is bound to the S atom of thiobenzoate, the P atom of the PPh<sub>3</sub> ligand and four B atoms of the {PtB<sub>10</sub>} cage. The Pt—P and Pt—S bond lengths are similar to those in previous reports (Beckett *et al.*, 1985; Hu *et al.*, 1998). The Pt—B bond lengths [2.187 (12)–2.256 (10) Å] are significantly shorter than the corresponding distances in non-cyclized platinaundecaboranes [2.214 (5)–2.301 (6) (Boocock *et al.*, 1981) and 2.206 (12)–2.342 (13) Å (Crook *et al.*, 1984)]. This could be due to the formation of the five-membered Pt—S—C—O—B ring. This ring is only approximately planar (r.m.s. deviation 0.0577 Å). Cyclization occurs on the B11 atom of the open PtB<sub>4</sub> face, which is similar to our previous report (Hu *et al.*, 1998), but on the B2 atom in the work of Beckett *et al.* (1985). In the cluster, a PPh<sub>3</sub> ligand connects with the

B10 atom of the cage [P1—B10 1.921 (12) Å]. The distances B10—B11 1.659 (15) and B10—B9 1.848 (15) Å are shorter than the corresponding B—B distances in the literature (Boocock *et al.*, 1981; Crook *et al.*, 1984; Beckett *et al.*, 1985; Hu *et al.*, 1998); this is due to the PPh<sub>3</sub> ligand acting as a two-electron donor, thus eliminating the need for the bridging H atom, which thereby increases the two-centre contribution to the B10—B11 bonding vector (Dou, Hu, Yao *et al.*, 1997; Dou, Hu, Sun *et al.*, 1997).

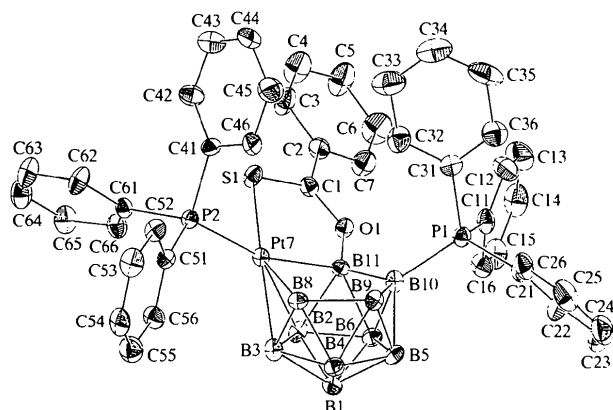


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms and the chloroform solvent have been omitted for clarity.

## Experimental

The synthesis of the title platinumundecaborane was carried out by reaction of [PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.316 g, 0.4 mmol) and (NEt<sub>4</sub>)<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (0.512 g, 0.4 mmol) with PhCOSH (0.112 g, 0.8 mmol) in refluxing dichloromethane (75 ml) for 112 h under an atmosphere of dry nitrogen. The initially colourless solution turned orange–yellow and a precipitate appeared. After filtration, the bright yellow solution was reduced in volume and chromatographed using dichloromethane/light petroleum (b.p. 333–363 K) (4:1) as the eluting medium to give the title compound at *R<sub>f</sub>* = 0.57. The product was recrystallized from *n*-pentane/chloroform (3:1) by liquid diffusion.

### Crystal data

C<sub>43</sub>H<sub>44</sub>B<sub>10</sub>OP<sub>2</sub>PtS.1.5CHCl<sub>3</sub>

*M<sub>r</sub>* = 1153.0

Monoclinic

*Cc*

*a* = 28.851 (5) Å

*b* = 11.615 (2) Å

*c* = 19.992 (4) Å

β = 127.42 (1)°

*V* = 5320.7 (17) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.439 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 21

reflections

θ = 9.1–10.7°

μ = 2.995 mm<sup>-1</sup>

*T* = 293 (2) K

Square prism

0.30 × 0.20 × 0.20 mm

Red

### Data collection

Rigaku AFC-7R diffractometer

ω scans

Absorption correction:

ψ scan (North *et al.*, 1968)

*T<sub>min</sub>* = 0.438, *T<sub>max</sub>* = 0.549

5203 measured reflections

5203 independent reflections

4606 reflections with

*I* > 2σ(*I*)

θ<sub>max</sub> = 27.49°

*h* = 0 → 34

*k* = 0 → 15

*l* = -24 → 20

3 standard reflections

every 200 reflections

intensity decay: 0.7%

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.037

*wR*(*F*<sup>2</sup>) = 0.104

*S* = 1.070

5203 reflections

583 parameters

H atoms: see below

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0745*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.028

Δρ<sub>max</sub> = 1.576 e Å<sup>-3</sup>  
(1 Å from Pt)

Δρ<sub>min</sub> = -0.923 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter =

-0.010 (9)

Table 1. Selected geometric parameters (Å, °)

Pt7—B3	2.187 (12)	Pt7—S1	2.359 (3)
Pt7—B11	2.204 (11)	P1—B10	1.921 (12)
Pt7—B8	2.208 (10)	S1—C1	1.699 (11)
Pt7—B2	2.256 (10)	O1—C1	1.267 (12)
Pt7—P2	2.328 (2)	O1—B11	1.504 (12)
B3—Pt7—B11	83.7 (4)	B8—Pt7—P2	89.5 (3)
B3—Pt7—B8	47.9 (4)	B2—Pt7—P2	150.1 (4)
B11—Pt7—B8	90.3 (4)	B3—Pt7—S1	155.1 (3)
B3—Pt7—B2	48.8 (5)	B11—Pt7—S1	81.2 (3)
B11—Pt7—B2	47.1 (4)	B8—Pt7—S1	151.2 (3)
B8—Pt7—B2	86.0 (4)	B2—Pt7—S1	107.1 (3)
B3—Pt7—P2	108.8 (3)	P2—Pt7—S1	90.66 (9)
B11—Pt7—P2	162.6 (3)		

A half occupancy of one CHCl<sub>3</sub> molecule gave the most satisfactory agreement factors and displacement parameters: these atoms were refined isotropically. H atoms were refined with a riding model, except for free refinement of those on B8 and B9. The bridging H atom between B8 and B9 was not located.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1994b). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1268). Services for accessing these data are described at the back of the journal.

## References

- Beckett, M. A., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1985). *Polyhedron*, **4**, 505–511.
- Boocock, S. K., Greenwood, N. N., Kennedy, J. D., McDonald, W. S. & Staves, J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2573–2584.
- Coldicott, R. S. (1994). *Current Topics in the Chemistry of Boron*, edited by G. W. Kabalka, pp. 297–300. Cambridge: Royal Society of Chemistry.
- Coldicott, R. S., Kennedy, J. D. & Thornton-Pett, M. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3819–3824.
- Crook, J. E., Greenwood, N. N., Kennedy, J. D. & McDonald, W. S. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2487–2495.
- Dou, J.-M., Hu, C.-H., Sun, J., Wei, J.-D. & Zheng, P.-J. (1997). *Polyhedron*, **16**, 3873–3875.
- Dou, J.-M., Hu, C.-H., Yao, H.-J., Li, W., Jin, R.-S. & Zheng, P.-J. (1997). *Acta Cryst.* **C53**, 693–695.
- Ferguson, G., Jennings, M. C., Lough, A. J., Coughlan, S., Spalding, T. R., Kennedy, J. D., Fontaine, X. L. R. & Stibr, B. (1990). *J. Chem. Soc. Chem. Commun.* pp. 891–894.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hu, C.-H., Dou, J.-M., Sun, J., Yao, H.-J., Wei, J.-D., Jin, R.-S. & Zheng, P.-J. (1998). *Acta Cryst.* **C54**, 1089–1091.
- Hu, C.-H., Dou, J.-M., Yao, H.-J., Li, W., Jin, R.-S. & Zheng, P.-J. (1997). *Acta Cryst.* **C53**, 695–697.
- Molecular Structure Corporation (1994a). *MSCI/AFSC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1994b). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Yao, H.-J., Hu, C.-H., Dou, J.-M., Jin, R.-S., Wei, J.-D., Li, W. & Zheng, P.-J. (1998). *Polyhedron*, **17**, 1877–1881.
- Zsolnai, L. & Huttner, G. (1994). *ZORTEP. Program for Molecular Graphics*. University of Heidelberg, Germany.

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### [*N*-(3-Aminopropyl)-*N*-methyl-1,3-propanediamine- $\kappa^3N$ ]dichlorocopper(II)

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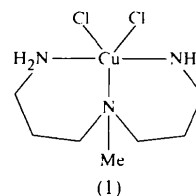
#### Abstract

The preparation and crystal structure of the title complex, [CuCl<sub>2</sub>(C<sub>7</sub>H<sub>19</sub>N<sub>3</sub>)], are described. The Cu<sup>II</sup> ion has distorted tetragonal pyramidal geometry, with Cl axial;

the axial Cu—Cl distance [2.505 (1) Å] is elongated compared with the basal Cu—Cl distance [2.400 (1) Å]. In the basal plane, Cu—N(tertiary) [2.138 (3) Å] is considerably longer than Cu—N(primary) [1.985 (4) Å mean], presumably reflecting the reduced basicity of the ligand atom.

#### Comment

The title compound, (1), was synthesized during our mechanistic studies of metal template reactions involving 2,6-diacetylpyridine and 3'-diamino-*N*-methylpropylamine. The experimental conditions normally used for the synthesis of metal complexes of 2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene, (2), and analogous macrocyclic ligands suggest that such reactions are true template reactions involving substrates that are both coordinated to the metal ion concerned. This is supported by the failure of such reactions when the metal ion is present as its hydroxide, *i.e.* it is not coordinated by the triamine (Prince *et al.*, 1974). The title compound, (1), was isolated at an early stage in the preparation of the copper complex of (2). This further indicates that complexation of the metal by the triamine is required prior to forming the Schiff base linkages that complete the macrocycle.



Typical template syntheses of complexes of the tetradentate macrocycle (2) involve refluxing a metal salt with stoichiometric equivalents of the dicarbonyl and triamine for several hours in mixtures of ethanol and water (Karn & Busch, 1966; Caira *et al.*, 1975; Nelson *et al.*, 1981). The title compound was formed as the initial product of this reaction and the structure was determined to confirm its identity. Most of the structures already examined that share the CuN<sub>3</sub>Cl<sub>2</sub> ligand set (from the Cambridge Structural Database; Allen & Kennard, 1993) are simple tris(monodentate ligand) complexes; all except one have trigonal bipyramidal geometry, with the bulkier Cl groups occupying the equatorial positions as expected [*e.g.* dichlorotris(1,2-dimethylimidazole)copper; Huq & Skapski, 1971]. One example only, dichlorotris(4-methylthiazole)copper (Cu<sub>4</sub>MT) (Marsh *et al.*, 1988), has tetragonal pyramidal geometry, a difference attributed to the bulk of the thiazole ligand.

This geometry is also shown by the title compound (Fig. 1); it is probably preferred because the rigidity