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Exopolyhedral Cyclized Platinaundecaboranes: [(PPh3)(PhCOS)PtB10H11].0.5CH2Cl2

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Abstract

The asymmetric unit of the title compound 7,11- or 7,8-(μ-thiobenzoato-S:O)-7-(triphenylphosphine-P)-8,9:10,11-di-μH-7-platina-*nido*-undecaborane–dichloromethane (1/0.5), $C_{25}H_{31}B_{10}OPPtS.0.5CH_2Cl_2$, contains two metallaborane molecules, which are approximate geometric isomers, and one molecule of dichloromethane solvent. Each isomer has an exopolyhedral

thiobenzoate ligand bridging one Pt and one B atom to give a five-membered Pt—S—C—O—B ring.

Comment

Metallaborane chemistry has expanded rapidly and several hundred polyhedral compounds have been synthesized and characterized. It is interesting that some clusters contain one or more five-membered ring(s) of exopolyhedral cyclization of metal ligand(s) to cluster. The best represented of these exopolyhedral cyclization processes is that of *ortho*-cycloboronation. This occurs with P-phenyl ligands on the metal centres and leads to five-membered M—P—C—C—B rings (Crook *et al.*, 1982; Bould *et al.*, 1982, 1983, 1989, 1992, 1993; Elrington *et al.*, 1986; Bould, Brint *et al.*, 1990; Bould, Crook *et al.*, 1990; Bould, Greenwood & Kennedy, 1990; Dou, Hu, Li *et al.*, 1997). Besides *ortho*-cycloboronation, it is possible to generate five-membered M—O—C—O—B rings using acetate (Fontaine *et al.*, 1987) or benzoate (Yao *et al.*, 1995), and M—S—C—S—B rings using dithiocarbamate ligands (Beckett *et al.*, 1985; Coldicott *et al.*, 1996). Previously, we have prepared and characterized some 11-vertex metallaboranes containing two or even three five-membered M—S—C—O—B rings (M = Ru, Ni) using thiobenzoate (Yao *et al.*, 1998; Dou, Hu, Yao *et al.*, 1997; Hu *et al.*, 1997; Dou, Hu, Sun *et al.*, 1997). We now report an 11-vertex platinaundecaborane, (I), containing one thiobenzoate linkage.

Isomer A   Isomer B

(I)
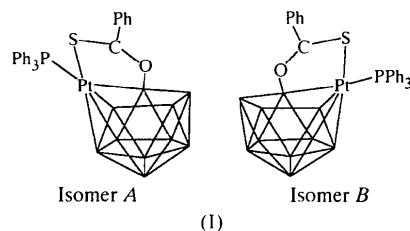
The asymmetric unit includes two approximate geometric isomers, A and B, and one CH_2Cl_2 solvent molecule (Fig. 1). Molecules A and B differ in the position of the thiobenzoate linkage, which bridges atoms Pt7A and B11A, or alternatively atoms Pt7B and B8B, respectively. Each molecule has an 11-vertex *nido*-{PtB10} cage, with the Pt atom as part of the open PtB4 face. Each Pt atom is bound to four B atoms, one PPh3 ligand and one S atom. The Pt—B bond lengths of 2.18 (3)–2.26 (3) Å are similar to the corresponding distances found in related compounds: 2.214 (5)–2.301 (6) Å in [7,7-(PMe2Ph)2-7-PtB10H12], 2.231 (10)–2.325 (11) Å in [4-(2'-B10H13)-7,7-(PMe2Ph)2-7-PtB10H11] (Boocock *et al.*, 1981) and 2.206 (12)–2.342 (13) Å in [8-Cl-7,7-(PMe2Ph)2-7-PtB10H11] (Crook *et al.*, 1984). The five-membered Pt7A—S1A—C1A—O1A—B11A ring of molecule A is more planar than the Pt7B—S1B—C1B—O1B—B8B
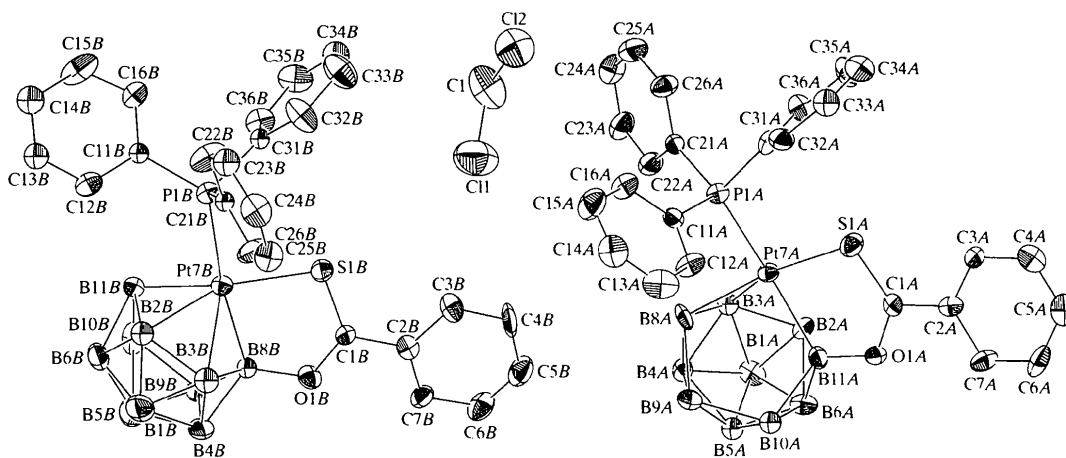
Fig. 1. A view of the asymmetric unit of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

ring of molecule B; the corresponding mean r.m.s. deviations are 0.021 (4) and 0.047 (8) Å.

Experimental

The synthesis of the title platinaundecaborane was carried out by reaction of [PtCl$_2$(PPh$_3$)$_2$] (0.316 g, 0.4 mmol) and (Et$_4$N)$_2$B$_{10}$H$_{10}$ (0.155 g, 0.4 mmol) with PhCOSH (0.122 g, 0.8 mmol) in refluxing dichloromethane for 112 h under an atmosphere of dry nitrogen. The initially colourless solution turned orange–yellow and the precipitate appeared. After filtration, the bright-yellow solution was reduced in volume and chromatographed using dichloromethane/light petroleum (b.p. 333–353 K) (4:1) as the eluting medium to give the title compound at R_f = 0.96. The product was recrystallized from n-pentane/dichloromethane (1:1) solution.

Crystal data

C$_{25}$H$_{31}$B$_{10}$OPPtS.0.5CH$_2$Cl$_2$
M_r = 756.18
Monoclinic
$P2_1/n$
a = 11.642 (2) Å
b = 33.225 (3) Å
c = 16.312 (4) Å
β = 93.21 (2)°
V = 6300 (2) Å^3
Z = 8
D_x = 1.595 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 7.1–10.7°
μ = 4.677 mm^{-1}
T = 293 (2) K
Square prism
0.30 × 0.20 × 0.20 mm
Orange–red

Data collection

Rigaku AFC-7R diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (North et al., 1968)
T_{min} = 0.289, T_{max} = 0.392
8918 measured reflections
8346 independent reflections

6157 reflections with
$I > 2\sigma(I)$
R_{int} = 0.181
θ_{max} = 25°
h = 0 → 12
k = 0 → 38
l = −19 → 19
3 standard reflections
every 200 reflections
intensity variation: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.258
S = 1.102
8346 reflections
660 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 599.5P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.034
$\Delta\rho_{max}$ = 2.76 e Å^{-3}
(1.16 Å from Pt7B)
$\Delta\rho_{min}$ = −2.37 e Å^{-3}
(1.38 Å from Pt7A)
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pt7A—B11A	2.22 (3)	Pt7B—B3B	2.19 (4)
Pt7A—B8A	2.24 (3)	Pt7B—B8B	2.21 (3)
Pt7A—B2A	2.25 (4)	Pt7B—B11B	2.22 (3)
Pt7A—B3A	2.26 (3)	Pt7B—S1B	2.340 (7)
Pt7A—S1A	2.330 (7)	Pt7B—P1B	2.346 (7)
Pt7A—P1A	2.352 (6)	O1B—B8B	1.47 (3)
Pt7B—B2B	2.18 (3)	O1A—B11A	1.44 (3)
B11A—Pt7A—S1A	79.8 (8)	B2B—Pt7B—S1B	156.7 (9)
B8A—Pt7A—S1A	158.5 (9)	B3B—Pt7B—S1B	108.5 (9)
B2A—Pt7A—S1A	103.5 (9)	B8B—Pt7B—S1B	80.4 (8)
B3A—Pt7A—S1A	148.8 (8)	B11B—Pt7B—S1B	151.5 (9)
B11A—Pt7A—P1A	155.6 (9)	B2B—Pt7B—P1B	103.4 (9)
B8A—Pt7A—P1A	89.2 (9)	B3B—Pt7B—P1B	138.8 (10)
B2A—Pt7A—P1A	157.1 (9)	B8B—Pt7B—P1B	172.2 (8)
B3A—Pt7A—P1A	113.8 (8)	B11B—Pt7B—P1B	93.9 (9)
S1A—Pt7A—P1A	89.1 (2)	S1B—Pt7B—P1B	92.2 (2)

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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1-Bromomercurio-2-(2,5,8,11,14-pentaoxapentadecyl)benzene

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Abstract

The crystal structure of the title compound, [HgBr(C_{16}-$H_{25}O_5$)], shows a nearly-linear geometry at the Hg atom [C1—Hg—Br = 177.52 (13)°], and only weak interactions between the Hg atom and the O atoms in the open-chain polyether ligand. The three shortest Hg···O distances [2.862 (4), 2.949 (4) and 3.010 (4) Å], of which only one is intramolecular, are distinctly longer than in comparable ketones and carboxylates.

Comment

In recent years, we have investigated the influence of coordination number on the reactivity of organomagnesium and organomercury compounds. The coordination number of the metals can be increased by coordination to crown ethers or open-chain polyethers. The title compound, (I), is an open-chain analogue of [2-(bromomercurio)-1,3-xylene]-18-crown-5 (Markies *et al.*, 1993).

(I)
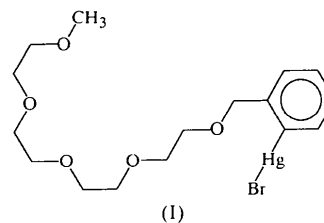
A view of the polyether complex, with our numbering scheme, is shown in Fig. 1. The distances Hg···O1 = 2.862 (4), Hg···O1^i = 2.949 (4) and Hg···O2^i = 3.010 (4) Å [symmetry code: (i) $x + \frac{1}{2}$, $1 - y$, z] in the open-chain compound are even longer than the Hg···O distances of 2.754 (6), 2.855 (6) and 3.060 (6) Å in the crown ether complex, the latter set being all intramolecular. These distances are much longer than for the corresponding carboxylate and keto compounds (Fig. 2). The Hg···O interactions can therefore be considered as extremely weak. Another indication of the