*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.187$
$S = 1.175$
4764 reflections
264 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1279P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.924$ e Å$^{-3}$
$\Delta\rho_{min} = -1.865$ e Å$^{-3}$
Extinction correction:
   SHELXL97
Extinction coefficient:
   0.0054 (13)
Scattering factors from
   *International Tables for*
   *Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Rh—P | 2.1690 (11) | O1—C1 | 1.270 (5) |
| Rh—O1 | 2.031 (3) | O2—C9 | 1.281 (6) |
| Rh—O2 | 2.059 (3) | O3—C16 | 1.139 (6) |
| Rh—C16 | 1.803 (5) | C1—C2 | 1.496 (6) |
| P—O4 | 1.587 (4) | C9—C10 | 1.492 (6) |
| P—O5 | 1.588 (3) | C20—C21 | 1.544 (6) |
| P—O6 | 1.582 (3) | | |
| O1—Rh—P | 91.57 (10) | C16—Rh—O2 | 92.78 (19) |
| O2—Rh—P | 176.07 (11) | O4—P—Rh | 114.78 (14) |
| O1—Rh—O2 | 88.06 (14) | O5—P—Rh | 118.03 (13) |
| C16—Rh—P | 87.75 (17) | O6—P—Rh | 114.36 (13) |
| C16—Rh—O1 | 177.4 (2) | O3—C16—Rh | 179.4 (5) |

H atoms were allowed for as riding atoms with C—H = 0.93–0.97 Å. The H atoms on the methyl C21 atom were allowed to rotate but not tip around the C20—C21 bond. The largest positive maximum (0.924 e Å$^{-3}$) in the final difference map was at 1.42 Å from the Rh atom and the largest negative minimum (−1.865 e Å$^{-3}$) was at 0.73 Å from the Rh atom.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1995). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1997). Software used to prepare material for publication: *TEXSAN* and *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1391). Services for accessing these data are described at the back of the journal.

References

Fan, H.-F. (1991). *SAPI91. Structure Analysis Program with Intelligent Control.* Rigaku Corporation, Tokyo, Japan.
Heitsch, C. W. & Verkade, J. G. (1962). *Inorg. Chem.* **1**, 392–398.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lamprecht, D., Lamprecht, G. J., Botha, J. M., Umakoshi, K. & Sasaki, Y. (1997). *Acta Cryst.* C53, 1403–1405.
Lamprecht, G. J., Leipoldt, J. G. & van Biljon, C. P. (1984). *Inorg. Chim. Acta,* **88**, 55–58.
Leipoldt, J. G., Basson, S. S., Bok, L. D. C. & Gerber, T. I. A. (1978). *Inorg. Chim. Acta,* **26**, L35–L37.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software.* Version 1.7. 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.
Rigaku Corporation (1995). *Rigaku/AFC Diffractometer Control Software.* Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1997). *PLATON. Molecular Geometry and Plotting Program.* Version of November 1997. University of Utrecht, The Netherlands.
Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.

# Iodo(1,10-phenanthroline-*N*,*N'*)(triphenylphosphine)copper(I)

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## Abstract

In the title complex, [CuI(C$_{12}$H$_8$N$_2$)(C$_{18}$H$_{15}$P)], phenanthroline acts as a bidentate ligand coordinating *via* two N atoms to copper. The coordination polyhedron around the Cu atom is a distorted tetrahedron, with a Cu—P distance of 2.1977 (9) Å, Cu—N distances of 2.111 (3) and 2.071 (3) Å, and a Cu—I distance of 2.6157 (6) Å.

## Comment

In the course of our work on the synthesis of Mo(W)–Cu–S clusters containing large N-donor ligands, the title complex, (I), was prepared and used as one of the reactants.
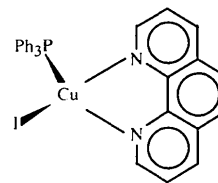


(I)

The [Cu(phen)(PPh$_3$)]$^+$ cation of the title complex (where phen is 1,10-phenanthroline) can be regarded as being analogous to the [Cu(phen)(PPh$_3$)$_2$]$^{2+}$ cation of [Cu(phen)(PPh$_3$)$_2$]NO$_3$.1.5EtOH, (II) (Kirchhoff *et*

*al.*, 1985), and to the [Cu(phen)₂]⁺ cations of [{Cu-(phen)₂}{Cu(OAc)₂}(OAc)₂H], (III) (Darensbourg *et al.*, 1992), [Cu(phen)₂]ClO₄, (IV), and [Cu(phen)₂-(CuBr₂)], (V) (Healy *et al.*, 1985). Complex (I) can also be regarded as being analogous to the pentacoordinated complex α-[Cu(phen)(PPh₃)(BH₄)], (VI) (Green *et al.*, 1984), with its bidentate $BH_4^-$ ligand replaced by a monodentate iodine ligand. The X-ray structure analysis of (I) reveals a distorted tetrahedral coordination of the Cu atom, with the four vertices occupied by two N atoms from phen, one P atom from PPh₃ and one I atom. Here phen acts as a bidentate ligand coordinating *via* two N atoms to the Cu atom. The N—Cu—N bond angle in complex (I) [79.93 (10)°] is more acute than those in complexes (II)–(VI). The two N—Cu—P bond angles of (I) are 110.68 (7) and 130.43 (8)°, similar to the corresponding angles in (II) and (VI). The Cu—P bond length [2.1977 (9) Å] and the Cu—N distances [2.071 (3) and 2.111 (3) Å] in (I) are comparable to those in complexes (II)–(VI). The Cu—I bond length is 2.6157 (6) Å.

The phen ligands are packed in a parallel fashion with alternate interlayer separations of 3.56 and 6.85 Å. Pairs of phen ligands are related by crystallographic inversion centres.
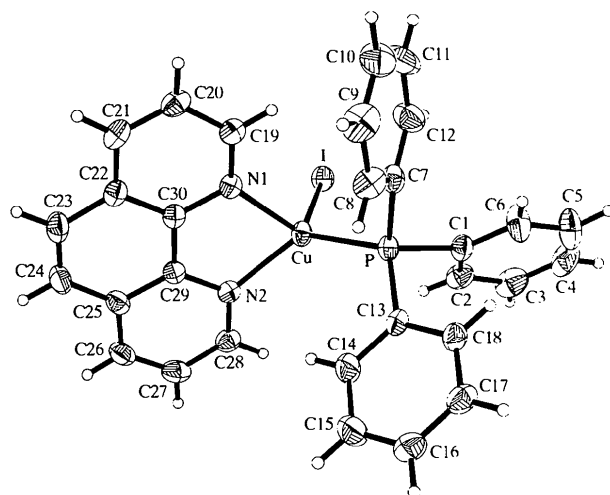


Fig. 1. View of the title complex. Displacement ellipsoids are shown at the 30% probability level. H atoms are of arbitrary size.

## Experimental

The title complex was prepared by reaction of CuI, PPh₃ and phen (molar ratio 1:2:2) in CH₂Cl₂ solution at room temperature. ⁱPrOH was added on the superficial layer of the filtrate. Orange columnar prismatic crystals were obtained by slow evaporation of the solvent.

### Crystal data

| | |
|---|---|
| [CuI(C₁₂H₈N₂)(C₁₈H₁₅P)] | Mo *K*α radiation |
| $M_r$ = 632.91 | $\lambda$ = 0.71073 Å |
| Triclinic | Cell parameters from 30 |
| $P\bar{1}$ | reflections |
| $a$ = 10.128 (2) Å | $\theta$ = 5.48–14.80° |
| $b$ = 10.599 (2) Å | $\mu$ = 2.042 mm⁻¹ |
| $c$ = 12.784 (4) Å | $T$ = 293 (2) K |
| $\alpha$ = 86.75 (2)° | Column |
| $\beta$ = 86.35 (2)° | 0.60 × 0.55 × 0.30 mm |
| $\gamma$ = 79.079 (9)° | Orange |
| $V$ = 1343.3 (5) Å³ | |
| $Z$ = 2 | |
| $D_x$ = 1.565 Mg m⁻³ | |
| $D_m$ not measured | |

### Data collection

| | |
|---|---|
| Siemens *P*4 diffractometer | $R_{int}$ = 0.012 |
| 2θ/ω scans | $\theta_{max}$ = 26.01° |
| Absorption correction: | $h$ = −1 → 11 |
| ψ scan (*XEMP*; Siemens, 1991) | $k$ = −13 → 12 |
| | $l$ = −15 → 15 |
| $T_{min}$ = 0.267, $T_{max}$ = 0.542 | 3 standard reflections |
| 5601 measured reflections | every 97 reflections |
| 4718 independent reflections | intensity decay: none |
| 4119 reflections with | |
| $I > 2\sigma(I)$ | |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $\Delta\rho_{max}$ = 0.88 e Å⁻³ |
| $R[F^2 > 2\sigma(F^2)]$ = 0.031 | $\Delta\rho_{min}$ = −0.75 e Å⁻³ |
| $wR(F^2)$ = 0.084 | Extinction correction: |
| $S$ = 1.117 | *SHELXL*93 (Sheldrick, |
| 4718 reflections | 1993) |
| 318 parameters | Extinction coefficient: |
| H atoms: see below | 0.0371 (14) |
| $w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.193P]$ | Scattering factors from *International Tables for Crystallography* (Vol. C) |
| where $P = (F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{max}$ = −0.001 | |

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

| | | | |
|---|---|---|---|
| I—Cu | 2.6157 (6) | Cu—N1 | 2.111 (3) |
| Cu—N2 | 2.071 (3) | Cu—P | 2.1977 (9) |
| N2—Cu—N1 | 79.93 (10) | N2—Cu—I | 107.06 (7) |
| N2—Cu—P | 130.43 (8) | N1—Cu—I | 110.97 (7) |
| N1—Cu—P | 110.68 (7) | P—Cu—I | 112.70 (3) |

All non-H atoms were refined anisotropically. H atoms were placed at calculated positions, with C—H distances of 0.93 Å, and were refined with a common isotropic displacement parameter [0.08 (3) Å²].

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

## References

Darensbourg, D. J., Longridde, E. M., Atnip, E. V. & Reibenspies, J. H. (1992). *Inorg. Chem.* **31**, 3951–3955.

Fait, J. (1991). *XSCANS Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Green, B. E., Kennard, C. H. L., Smith, G., Elcombe, M. M., Moore, F. H., James, B. D. & White, A. H. (1984). *Inorg. Chim. Acta*, **83**, 177–189.

Healy, P. C., Engelhardt, L. M., Patrick, V. A. & White, A. H. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2541–2545.

Kirchhoff, J. R., McMillin, D. R., Robinson, W. R., Powell, D. R., McKenzie, A. T. & Chen, S. (1985). *Inorg. Chem.* **24**, 3928–3933.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1991). *XEMP. Empirical Absorption Correction Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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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-($\mu$-thiobenzoato-$S$:$O$)-7-(triphenylphosphine-$P$)-8,9:10,11-di-$\mu H$-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)
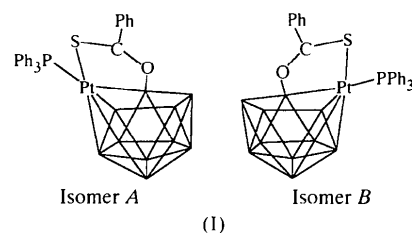
The asymmetric unit includes two approximate geometric isomers, $A$ and $B$, and one $CH_2Cl_2$ solvent molecule (Fig. 1). Molecules $A$ and $B$ differ in the position of the thiobenzoate linkage, which bridges atoms Pt7$A$ and B11$A$, or alternatively atoms Pt7$B$ and B8$B$, respectively. Each molecule has an 11-vertex *nido*-{PtB$_{10}$} cage, with the Pt atom as part of the open PtB$_4$ face. Each Pt atom is bound to four B atoms, one PPh$_3$ 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-(PMe$_2$Ph)$_2$-7-PtB$_{10}$H$_{12}$], 2.231 (10)–2.325 (11) Å in [4-(2'-B$_{10}$H$_{13}$)-7,7-(PMe$_2$Ph)$_2$-7-PtB$_{10}$H$_{11}$] (Boocock *et al.*, 1981) and 2.206 (12)–2.342 (13) Å in [8-Cl-7,7-(PMe$_2$Ph)$_2$-7-PtB$_{10}$H$_{11}$] (Crook *et al.*, 1984). The five-membered Pt7$A$—S1$A$—C1$A$—O1$A$—B11$A$ ring of molecule $A$ is more planar than the Pt7$B$—S1$B$—C1$B$—O1$B$—B8$B$