METAL-ORGANIC COMPOUNDS

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1-[Chloro(diphenylphosphino)gold(I)-*P*]-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12)†

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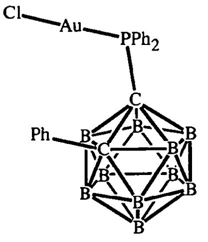
Abstract

The title compound, 1-[$(C_6H_5)_2PAuCl$]-2-(C_6H_5)-1,2-*closo*-$C_2B_{10}H_{10}$ or [$AuCl\{(C_6H_5)_2P(C_8H_{15}B_{10})\}$], is the first reported derivative of 1-[$(C_6H_5)_2P$]-2-(C_6H_5)-1,2-*closo*-$C_2B_{10}H_{10}$. The conformation of the cage phenyl group is comparable with the parent carbaborylphosphine, however, the $(C_6H_5)_2PAuCl$ substituent is less tilted from an idealized radial position on C1 due to a balance between two opposing sets of intramolecular forces. The P—Au—Cl fragment adopts the expected linear geometry.

Comment

The title compound, (I), arises from the coordination of 1-diphenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (McWhannell *et al.*, 1996) to an {AuCl} fragment, and results in the first reported derivative of the parent carbaborylphosphine.



(I)

The structural study of (I) (Fig. 1) reveals the expected near icosahedral geometry of the $\{C_2B_{10}\}$ cage. The conformation of the phenyl substituent is described by a θ value of 15.15° (θ is defined as the modulus of the average C_{Ph}—C_{Ph}—C_{cage}—C_{cage} torsion angle; Cowie *et al.*, 1994) compared with 1.15° in 1-diphenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (McWhannell *et al.*, 1996). The C1—C2 distance of 1.744 (13) Å and the P1—C1 distance of 1.902 (11) Å are comparable with those in the parent phosphine, 1.744 (8) and 1.876 (7) Å, respectively (McWhannell *et al.*, 1996).

The PPh_2AuCl substituent is distorted from an idealized radial position on C1, the B12···C1—P1 angle

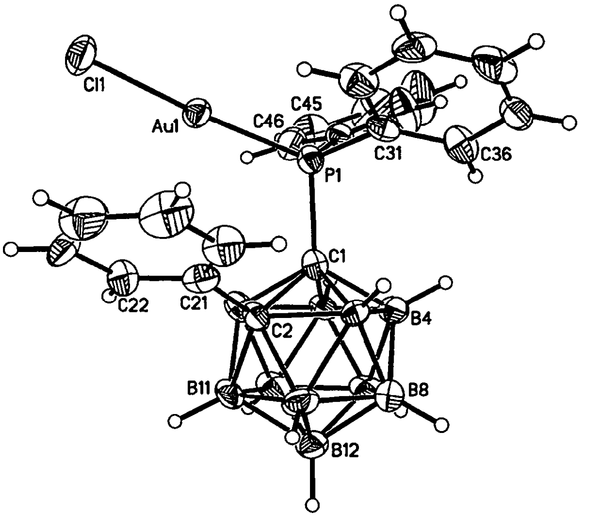


Fig. 1. The molecular structure of (I) shown with 40% probability displacement ellipsoids for non-H atoms. The cage-numbering scheme can be seen in this and Fig. 2. The phenyl-ring C atoms are numbered in sequence.

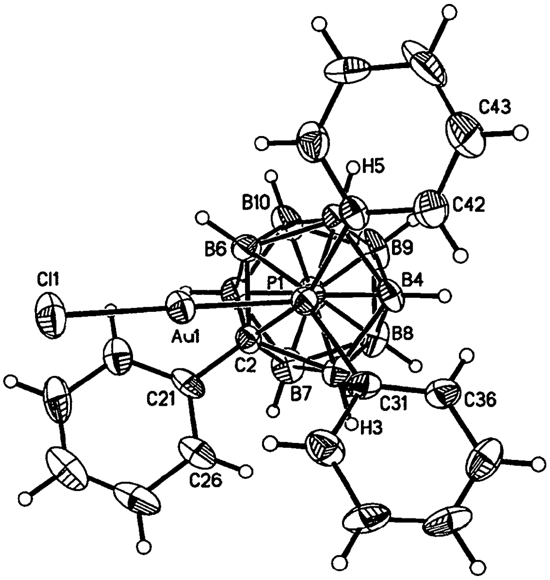


Fig. 2. A view down the C1···B12 vector showing the distortion of the phosphine away from the radial position at C1.

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† Alternative name: chloro{diphenyl[2-phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl(12)]phospine-*P*}gold(I).

having a value of 175.2 (5)°. However, this deformation is less pronounced than in the parent phosphine, where B12···C1—P1 is equal to 168.0 (3)°. Presumably a balance is struck between intramolecular crowding at the phosphorus-bound phenyl rings-H3,5 interface and further intramolecular crowding involving the {AuCl} fragment and the cage–phenyl substituent.

The P—Au—Cl fragment shows the linearity usually associated with bicoordinate gold(I) complexes. The {AuCl} fragment lies above the C2—B6 connectivity (shown in Fig. 2), reinforcing the prediction of the position of the phosphorus lone pair in the parent carbaborylphosphine.

Experimental

A solution (273 K) of 1-PPh$_2$2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$ (0.50 g, 1.24 mmol) (McWhannell *et al.*, 1996) in dichloromethane (10 ml) was added to a solution (273 K) of AuCl(SC_4H_8) (0.39 g, 1.24 mmol) (Uson *et al.*, 1989) in dichloromethane (20 ml). The resulting mixture was allowed to warm to room temperature with stirring over a period of 1 h. The solution was then reduced to *ca* 3 ml *in vacuo* and, on addition of petroleum ether (333–353 K, 10 ml), a white precipitate was formed. This solid was isolated by filtration and washed with petroleum ether (333–353 K) before being dried *in vacuo* (yield: 0.63 g, 80%). Crystals were grown by slow diffusion of a dichloromethane solution layered with petroleum ether (333–353 K) in a 1:3 ratio. Analysis calculated for $C_{20}H_{25}AuB_{10}ClP$: C 37.7, H 3.9%; found: C 37.4, H 4.2%. ^{1}H FT-NMR (400.1 MHz, TMS): δ (p.p.m.) 8.25–7.13 (*m*, Ar-H). ^{11}B-{^{1}H} FT-NMR (128.4 MHz, $BF_3.Et_2O$): δ (p.p.m.) 1.35 (1B), −2.16 (1B), −9.58 (8B). ^{31}P-{^{1}H} FT-NMR (162.0 MHz, H_3PO_4): δ (p.p.m.) 51.4 (*s*). NMR spectra were recorded from a $CDCl_3$ solution at 293 K on a Brüker DPX400 spectrometer.

Crystal data

[AuCl($C_{20}H_{25}B_{10}P$)]
$M_r = 636.89$
Monoclinic
$P2_1/n$
$a = 9.6749\ (8)$ Å
$b = 14.531\ (2)$ Å
$c = 18.053\ (2)$ Å
$\beta = 101.462\ (7)°$
$V = 2487.4\ (4)$ Å^3
$Z = 4$
$D_x = 1.701$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 4.89–12.35°$
$\mu = 6.095$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.62 × 0.44 × 0.15 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: by integration
$T_{min} = 0.147$, $T_{max} = 0.619$
5694 measured reflections
4366 independent reflections
2887 reflections with $I > 2\sigma(I)$

$R_{int} = 0.068$
$\theta_{max} = 25°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 17$
$l = -21 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: 5.77%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.116$
$S = 1.050$
4366 reflections
298 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.979$ e Å^{-3}
$\Delta\rho_{min} = -1.756$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Au1—P1	2.232 (3)	B4—B8	1.75 (2)
Au1—Cl1	2.279 (3)	B4—B5	1.75 (2)
P1—C41	1.816 (11)	B4—B9	1.77 (2)
P1—C31	1.822 (10)	B5—B9	1.74 (2)
P1—C1	1.902 (11)	B5—B10	1.77 (2)
C1—B4	1.670 (15)	B5—B6	1.77 (2)
C1—B5	1.707 (14)	B6—B10	1.76 (2)
C1—B6	1.724 (14)	B6—B11	1.80 (2)
C1—B3	1.734 (15)	B7—B12	1.76 (2)
C1—C2	1.744 (13)	B7—B11	1.78 (2)
C2—C21	1.506 (14)	B7—B8	1.79 (2)
C2—B11	1.71 (2)	B8—B9	1.76 (2)
C2—B7	1.72 (2)	B8—B12	1.78 (2)
C2—B6	1.74 (2)	B9—B10	1.76 (2)
C2—B3	1.76 (2)	B9—B12	1.76 (2)
B3—B4	1.78 (2)	B10—B11	1.73 (2)
B3—B8	1.78 (2)	B10—B12	1.76 (2)
B3—B7	1.82 (2)	B11—B12	1.78 (2)
P1—Au1—Cl1	175.84 (12)	C1—P1—Au1	113.9 (3)
C41—P1—C31	108.8 (5)	B4—C1—P1	122.5 (7)
C41—P1—C1	102.8 (5)	B5—C1—P1	122.5 (7)
C31—P1—C1	106.4 (5)	B6—C1—P1	116.6 (7)
C41—P1—Au1	111.9 (4)	B3—C1—P1	116.6 (7)
C31—P1—Au1	112.4 (4)	C2—C1—P1	117.4 (7)

The cage H atoms were constrained to idealized positions (B—H 1.10 Å). The isotropic displacement parameters of the cage H atoms were defined as $1.2U_{iso}$ of the bound cage atom. The U_{iso} parameters of the phenyl H atoms were defined as $1.2U_{iso}$ of the bound C atom. The largest remaining feature (−1.77 e Å^3) in the difference map is 1.09 Å from Au1.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1516). Services for accessing these data are described at the back of the journal.

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cis-Diamminechloro(2,5-dimethylbenzoxazole-N^1)platinum(II) Nitrate

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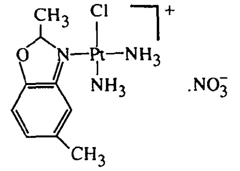
Abstract

In the title compound, $[PtCl(NH_3)_2(C_9H_9NO)]NO_3$, the complex cation features square-planar coordination around the Pt atom, with a mean deviation of 0.0007 (5) Å. The aromatic 2,5-dimethylbenzoxazole ring is planar with a mean deviation of 0.008 (8) Å. The dihedral angle between these two ring planes is 71.0 (2)°.

Comment

Triamino–Pt^{II} complexes of the form *cis*-$[PtCl(NH_3)_2L]$ with N-donor heterocyclic *L* ligands have been studied for their potential antitumor activities (Hollis, Amundsen & Stern, 1981). The ligands used for such complexes are often imidazoles, thiazoles and benzoxazoles (Gomez *et al.*, 1988). Modifications to these compounds may lead to a better understanding of the role that the ligand plays in improving the antitumor activity and water solubility of the complexes (Muir *et al.*, 1992). 2,5-Dimethylbenzoxazole (Me_2BO) is potentially an ambidentate ligand and has been reported to be coordinated through its O atom to Pt^{II} in the $[PtCl_2(Me_2BO)_2]$ complex based on IR spectroscopic data (Massacessi, Pinna & Ponticelli, 1981). We synthesized the title compound, (I), in order to clarify the coordination mode of the ligand.



(I)

The X-ray crystallographic analysis revealed that 2,5-dimethylbenzoxazole coordinates to the Pt^{II} center through the N-donor atom. The crystal lattice consists of NO_3^- anions and $[PtCl(NH_3)_2(Me_2BO)]^+$ cations linked by hydrogen bonds between the nitrate ion and coordinated ammonia molecules [N(3)···O(3) 2.917 (3) and N(2)···O(2) 3.081 (3) Å]. The $[PtCl(NH_3)_2(Me_2BO)]^+$ cation features square-planar coordination around the Pt atom, with a mean deviation of 0.0007 (5) Å (Fig. 1). Two ammonia ligands arrange themselves in a *cis* fashion. The Pt—N bond *trans* to the Cl atom exhibits a longer bond distance [2.042 (7) Å] than that *cis* to the Cl atom [2.007 (8) Å]. The aromatic Me_2BO ring is planar with a mean deviation of 0.008 (8) Å. The dihedral angle between these two planes is 71.0 (2)°. The other bond distances are in the normal range.

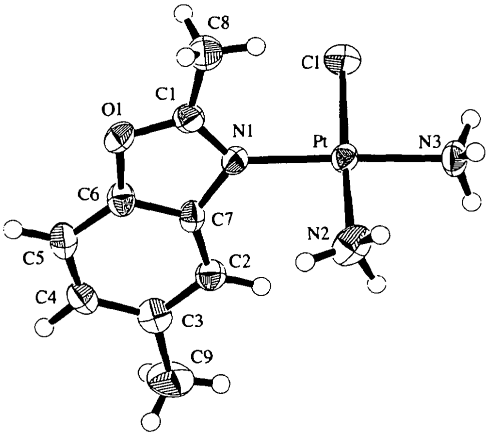


Fig. 1. An *ORTEP*II (Johnson, 1976) representation of the title compound showing 50% probability displacement ellipsoids.

Experimental

The detailed synthesis of the title compound will be published elsewhere. Slow evaporation of a dichloromethane solution of the compound at room temperature afforded pale-yellow single crystals of X-ray quality.

Crystal data

$[PtCl(NH_3)_2(C_9H_9NO)]NO_3$
$M_r = 473.78$
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å