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cis-[7,8-Bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborato-*P*,*P*′]dichlorogold(III) Chloroform Solvate

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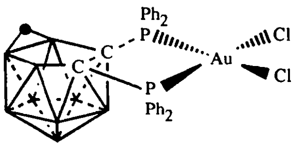
Abstract

The title compound, $[AuCl_2\{C_2B_9H_{10}(Ph_2P)_2\}].CHCl_3$, contains the expected *cis* square-planar gold(III) units, with Au—P 2.306 and 2.296 (2), and Au—Cl 2.335 and 2.326 (2) Å. The dicarbaundecaborate anion acts as a *P*,*P*′-bidentate ligand. The open B_2C_3 face contains one bridging (B—H—B) H atom.

Comment

We have recently started a systematic investigation of metal complexes of the partially degraded 1,2-dicarba-*closo*-dodecaborane derivative, the 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate anion $\{[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$, henceforth PP} (Crespo, Gimeno, Jones & Laguna, 1996, and references therein). The anion usually acts as a *P*,*P*′-bidentate ligand. We present here the structure of the neutral gold(III) complex $[AuCl_2(PP)]$, (I), which crystallizes as a chloroform solvate. The scheme shows BH groups as vertices, with the bridging H atom as a black dot. The preparation of the title compound and the structure of the analogous bis(diisopropylphosphino) complex have been reported by Teixidor, Viñas, Abad, Kivekäs & Sillanpää (1996).



(I)

As expected for Au^{III}, the metal atom displays a square-planar coordination; it lies only 0.068 (1) Å out of the plane of the four donor atoms (mean deviation 0.01 Å). An additional weak axial contact to a solvent Cl atom is observed [Au···Cl4 3.863 (3) Å]. The configuration is necessarily *cis* because of the restricted bite of the PP ligand; P1···P2 3.183 (3) Å and P2—Au—P1 87.53 (7)°. The chelate ring displays an envelope conformation, with the Au atom 0.490 (5) Å out of the plane formed by the C7, C8, P1 and P2 atoms (mean deviation < 0.001 Å). The Au—P [2.306 and 2.296 (2) Å] and Au—Cl [2.335 and 2.326 (2) Å] bond lengths are broadly similar to those given by Teixidor *et al.* (1996); Au—P 2.313 and 2.327 (2) Å (which are, however, significantly longer than those in the title compound), and Au—Cl 2.331 and 2.344 (2) Å. A search of the Cambridge Structural Database (April 1996 version; Allen & Kennard, 1993) revealed, surprisingly, no other example of P_2Cl_2 coordination at Au^{III}, perhaps because most compounds of this type would be

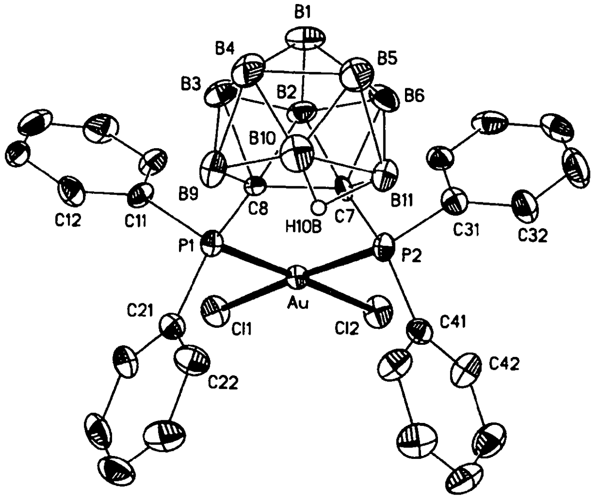


Fig. 1. The molecule of the title compound in the crystal (solvent omitted). Ellipsoids are drawn at the 50% probability level and all H atoms except the bridging open-face H atom have been omitted.

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cationic rather than neutral. Further comparable related bond lengths at Au^{III} are Au—P 2.335 (4) and Au—Cl (*trans* to P) 2.347 (4) Å in triclinic $[AuCl_3(Ph_3P)]$ (Bandoli, Clemente, Marangoni & Cattalini, 1973), and Au—P 2.329 (2) and Au—Cl (*trans* to P) 2.347 (2) Å in the monoclinic form (Staples, Grant, Fackler & Elduque, 1994).

There can be problems in locating H atoms in heavy-atom structures. In the current structure, most H atoms can be geometrically set, but the positions of the four carborane open-face H atoms cannot be assumed. We located these H atoms in difference syntheses and refined them using B—H distance restraints. One H atom, H10*B*, bridges B10 and B11, with B10—H10*B* 1.08 (3) and B11—H10*B* 1.37 (7) Å. Obviously, these values are imprecise, but they are consistent with our previous observations of this PP ligand [Crespo *et al.* (1996), and unpublished results of other heavy-atom derivatives]; we have in all cases but one (of seven to date) observed a bridging or semi-bridging fourth H atom on the open face. In view of the large e.s.d.'s, however, the differences between bridging, semi-bridging and terminal H atoms (the latter with B· · ·H *ca* 1.7 Å), are not completely unambiguous. In the structure of Teixidor *et al.* (1996), the B—H—B unit is described as 'bridging' in the chemical discussion, but not in the structural discussion, and the figure is not clear on this point. We hope to confirm the bridging nature of the fourth H atom by studies of derivatives without heavy atoms. The $NMe_4(PP)$ salt was studied by Teixidor *et al.* (1995), but not precisely enough to locate these H atoms. It should be noted here that a referee suggested that we are overstating the difficulties of locating H atoms in carbaborane metal complexes.

The carbaborane bond lengths involving C atoms are C7—C8 1.575 (9), open-face C—B 1.614 and 1.642 (11), and interior C—B 1.739–1.745 (10) Å. The bridged B—B bond length (B10—B11) is 1.878 (13) Å, at least 0.05 Å longer than all other B—B bonds (1.736–1.824, with e.s.d.'s 0.011–0.013 Å).

Experimental

To a refluxing solution of $[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$ (0.128 g, 0.25 mmol) was added $[AuCl_3(\text{tetrahydrothiophene})]$ (0.195 g, 0.5 mmol). The slurry was refluxed for 4 h, filtered off and washed with hot ethanol. A brown solid was obtained, which was recrystallized from dichloromethane/*n*-hexane (20 ml/5 ml) to give a yellow solid (60%). Analysis found: C 40.15, H 3.8%; calculated C 40.57, H 3.92%; IR: ν(B—H) 2598, 2587, ν(Au—Cl) 336 cm^{-1}; ^{1}H NMR: −2.1 (*s*, br, 1H), 7.1–8.2 (*m*, 20H, Ph) p.p.m; ^{31}P NMR: 96.3 (*s*) p.p.m. Single crystals were obtained from a chloroform/*n*-hexane solution.

Crystal data

$[AuCl_2(C_{26}H_{30}B_9P_2)].CHCl_3$
$M_r = 888.96$
Monoclinic
$P2_1/c$
$a = 11.872\ (2)$ Å
$b = 8.477\ (2)$ Å
$c = 34.557\ (5)$ Å
$\beta = 93.360\ (6)°$
$V = 3471.7\ (9)$ 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 62 reflections
$\theta = 2.5–11.5°$
$\mu = 4.735$ mm^{-1}
$T = 173\ (2)$ K
Tablet
0.40 × 0.20 × 0.06 mm
Yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{min} = 0.608$, $T_{max} = 0.753$
6164 measured reflections
6098 independent reflections
3852 reflections with $I > 2\sigma(I)$

$R_{int} = 0.0771$
$\theta_{max} = 25°$
$h = -14 \rightarrow 0$
$k = -10 \rightarrow 0$
$l = -40 \rightarrow 41$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0412$
$wR(F^2) = 0.0700$
$S = 0.820$
6097 reflections
413 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0171P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.839$ e Å^{-3}
$\Delta\rho_{min} = -1.107$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Au—P2	2.296 (2)	P2—C41	1.797 (8)
Au—P1	2.306 (2)	P2—C7	1.815 (7)
Au—Cl2	2.326 (2)	C7—C8	1.575 (9)
Au—Cl1	2.335 (2)	C7—B11	1.642 (11)
P1—C21	1.793 (7)	C8—B9	1.614 (11)
P1—C11	1.801 (7)	B9—B10	1.824 (12)
P1—C8	1.821 (7)	B10—B11	1.878 (13)
P2—C31	1.794 (7)		
P2—Au—P1	87.53 (7)	C21—P1—Au	106.4 (2)
P2—Au—Cl2	90.14 (7)	C11—P1—Au	114.4 (3)
P1—Au—Cl2	176.38 (8)	C8—P1—Au	108.4 (2)
P2—Au—Cl1	176.02 (7)	C31—P2—C41	108.0 (3)
P1—Au—Cl1	91.48 (7)	C31—P2—C7	109.8 (3)
Cl2—Au—Cl1	90.67 (7)	C41—P2—C7	111.3 (3)
C21—P1—C11	106.9 (3)	C31—P2—Au	112.8 (2)
C21—P1—C8	111.3 (3)	C41—P2—Au	106.8 (2)
C11—P1—C8	109.5 (3)	C7—P2—Au	108.1 (2)

Most H atoms were refined using a riding model; the H atoms of the carbaborane open face were located in difference syntheses and refined subject to the restraint of equal B(*n*)—H(*n*) distances. A total of 298 restraints were applied, involving displacement parameters of neighbouring atoms (*DELU*/*SIMU*) and local phenyl ring symmetry (*FLAT*/*SAME*) in addition to the B—H restraints. Details [instruction file in *SHELXL*93 (Sheldrick, 1993) format] are given in the CIF file.

Data collection: *XSCANS* (Siemens, 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. Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1231). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tricarbonyl(trifluoromethyl)(triphenylphosphine)cobalt

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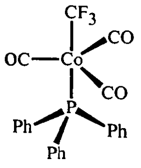
Abstract

The title compound, [$Co(CF_3)(C_{18}H_{15}P)(CO)_3$], has a trigonal bipyramidal geometry with the trifluoromethyl and triphenylphosphine ligands occupying the *trans*-axial positions. The three carbonyl ligands occupy the planar equatorial positions. Both the trifluoromethyl and triphenylphosphine ligands are in a staggered conformation relative to the carbonyl ligands in the equatorial plane. The structure of the title compound is similar to other alkylcobalt tricarbonyl triphenylphosphines. Important bond distances include Co—CF_3 1.953 (6), Co—P1 2.235 (1), mean Co—CO 1.752 and mean P1—C 1.822 Å.

Comment

The interconversion of alkyl and acyl functional groups through carbonylation/decarbonylation reactions of transition metal organometallic compounds plays an important role in many catalytic processes (Abel, Stone & Wilkinson, 1995). This interconversion can frequently be accelerated by oxidation (Fernandez, Prock & Giering, 1994) or reduction (Amatore, Bayachou, Verpeaux, Pospisil & Fiedler, 1995), and a project is currently underway examining the reductively induced decarbonylation of (CF_3CO)Co($CO)_3$(PPh_3). This reaction is known to occur thermally, giving the stable trifluoromethyl complex (CF_3)Co($CO)_3$(PPh_3) (Hieber, Beck & Lindner, 1961). The perfluorinated complexes are preferred for study due to their enhanced stability compared with the unsubstituted alkyl and aryl complexes. During the course of the current study, (CF_3CO)Co($CO)_3$(PPh_3) was thermally decarbonylated in tetrahydrofuran to yield the title complex, (I), which was subsequently isolated as colorless single crystals through slow evaporation of the solvent. As its structure had not previously been reported and in the interest of learning more about its properties, the X-ray crystal structure of the trifluoromethyl complex was determined.



(I)

The structures of three other alkylcobalt tricarbonyl triphenylphosphine complexes have been reported, namely, (HCF_2CF_2)Co($CO)_3$(PPh_3) (Wilford & Powel, 1967), ($PhCH_2OOCCH_2$)Co($CO)_3$(PPh_3) (Galamb, Palyi, Cser, Furmanova & Struchkov, 1981) and ($ClCH_2$)Co($CO)_3$(PPh_3) (Galamb, Palyi, Boese & Schmid, 1987). All three previously reported structures, as well as the present one, display the expected trigonal bipyramidal geometry with the alkyl and triphenylphosphine ligands occupying the *trans*-axial positions. The trigonal bipyramidal geometry is displayed in Fig. 1. Bond distances around the Co atom are quite normal when compared with those reported in BIDICS