

Data collection

Stoe Siemens AED-2 diffractometer
 ω/θ scans
 Absorption correction: ψ scans (XEMP; Siemens 1990a)
 $T_{\min} = 0.142$, $T_{\max} = 0.275$
 8726 measured reflections
 8023 independent reflections

6280 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 25.01^\circ$
 $h = 0 \rightarrow 16$
 $k = -15 \rightarrow 1$
 $l = -29 \rightarrow 29$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.100$
 $S = 1.048$
 8021 reflections
 547 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 26.1665P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
 $\Delta\rho_{\max} = 2.322 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -2.049 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Au1—P1	2.264 (2)	S1—C2	1.756 (8)
Au1—S3	2.327 (2)	S2—C1	1.739 (9)
Au1...Au2	3.2217 (8)	S2—C3	1.754 (8)
Au2—P2	2.265 (2)	S3—C2	1.739 (9)
Au2—S4	2.331 (2)	S4—C3	1.750 (8)
S1—C1	1.722 (11)	S5—C1	1.649 (9)
P1—Au1—S3	160.14 (8)	C2—S3—Au1	107.2 (3)
P2—Au2—S4	174.89 (8)	C3—S4—Au2	102.6 (3)

The significant residual electron density is in the heavy-atom region; the distance of the maximum peak, $2.322 \text{ e } \text{\AA}^{-3}$, to the nearest atom (Au2) is 1.11 \AA . H atoms of the methyl groups were refined as rigid groups; others were included using a riding model.

Data collection: DIF4 (Stoe, 1987a). Cell refinement: DIF4. Data reduction: REDU4 (Stoe, 1987b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1990b). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1240). Services for accessing these data are described at the back of the journal.

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μ -[7,8-Bis(diphenylphosphino)-7,8-dicarbonyl-undecaborato-1 κ P,2 κ P']](pentafluorophenyl-1 κ C)(triphenylphosphine-2 κ P)-digold(I) Dichloromethane Solvate

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Abstract

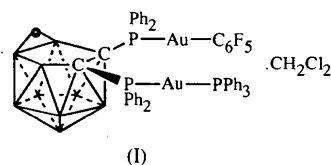
The title compound, $[\text{Au}_2(\text{C}_{26}\text{H}_{30}\text{B}_9\text{P}_2)(\text{C}_6\text{F}_5)(\text{C}_{18}\text{H}_{15}\text{P})_2]\cdot\text{CH}_2\text{Cl}_2$, has a dinuclear structure with the diphosphinocarbaborane moiety bridging the two Au atoms. There is a short intramolecular Au...Au contact of $2.9885(8) \text{ \AA}$. The linear coordination at the Au^I atoms is highly distorted: P—Au—C $166.6(2)$ and P—Au—P

164.69 (7)°. The open B₃C₂ face contains one bridging (B—H—B) H atom.

Comment

We are currently studying the coordination behaviour of the 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate anion (Crespo, Gimeno, Laguna & Jones, 1996). We have observed that the anionic diphosphine coordinates to gold(I) centres as a chelate, thus yielding three- and four-coordinated derivatives.

We report here the structure of the neutral title complex, (I), which crystallizes as a dichloromethane solvate. The 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate anion acts as a *P,P'*-bidentate bridging ligand, being bonded to two different Au—L groups. This represents the first example of a structure where the anionic diphosphine acts as a bridging ligand.



The molecule shows a distorted linear coordination at the Au^I atoms, with a P—Au—P angle of 164.69 (7)° and a P—Au—C angle of 166.6 (2)°, associated with a short Au··Au contact of 2.9885 (8) Å. This weak metal–metal interaction, termed ‘aurophilic attraction’, is interesting from a theoretical viewpoint, because the classical theory of chemical bonding does not provide a satisfactory explanation for it. Only when considered as a correlation effect, strengthened by relativistic effects, can this phenomenon be accounted for by theoretical studies (Kaltsoyannis, 1997; Pyykkö, 1997; Pyykkö, Runeberg & Mendizabal, 1997; Pyykkö & Mendizabal, 1997). These Au··Au contacts are comparable in strength to typical hydrogen bonds, associated with a bond energy of the order of 5–10 kcal mol⁻¹ (Schmidbaur *et al.*, 1988; Narayanaswamy *et al.*, 1993). Furthermore, Hawthorne and co-workers (Harwell *et al.*, 1996) calculated, by a variable-temperature NMR investigation, that the energy barrier separating the gold–gold bonded state and the non-bonded state in a digold-*closo*-carborane derivative is 11 ± 1 kcal mol⁻¹.

The Au^I atom is bonded to a P and a C atom (Fig. 1), with Au—P and Au—C bond distances of 2.300 (2) and 2.068 (8) Å, respectively; similar values were observed in related complexes such as [Au₂(dppm)(C₆F₅)₂] [dppm is bis(diphenylphosphino)methane] [Au—P = 2.288 (3) and 2.279 (3) Å, and Au—C = 2.063 (12) and 2.058 (12) Å; Jones & Thöne, 1992] or [Au(C₆F₅)(PPh₃)] [Au—P = 2.27 (1) Å and Au—C = 2.07 (2) Å; Baker *et al.*, 1972].

The Au^{II} atom is bonded to two P atoms, with Au—P bond distances of 2.326 (2) and 2.312 (2) Å; these values compare well with those found in

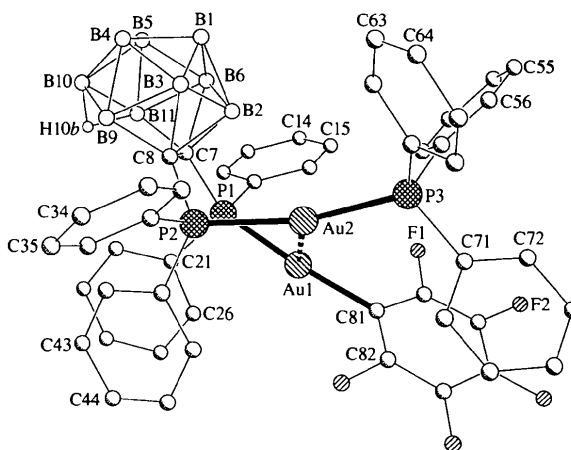


Fig. 1. The molecular structure of the title compound (solvent omitted). All H atoms, except the bridging open-face H atom, have been omitted.

other P—Au^I—P derivatives such as [Au(PPh₃)₂](BF₄) [2.321 (3), 2.322 (3) Å; Wang, 1996] or [Au₂(dppm)₂](BF₄)₂ [2.311 (3) and 2.310 (3) Å; Porter *et al.*, 1989].

The Au—P(diphosphine) bond distances differ slightly; the bond *trans* to the PPh₃ group is longer, 2.326 (2) Å, probably as a consequence of the major *trans* influence of the PPh₃ moiety.

Phenyl and closed-faced carborane H atoms were geometrically set with a riding model, but the four open-face carborane H atoms were located in difference syntheses and refined using B—H distance restraints. The extra H atom, H10*b*, in the pentagonal C₂B₃ open face is strongly bonded to the central B atom [B10—H10*b* 1.00 (4) Å], but it can be considered as semibridging B11 [B11—H10*b* 1.50 (8) Å]. This distance is, however, longer than in other derivatives such as [AuCl₂{(PPh₂)₂C₂B₉H₁₀}] [1.37 (7) Å; Jones, Villacampa *et al.*, 1997] or [Au{(PPh₂)₂C₂B₉H₁₀}]{(PPh₂)₂-C₂B₁₀H₁₀}]ClO₄ [1.35 Å; Crespo *et al.*, 1997]. As a consequence of the presence of heavy atoms, these values are imprecise, although we have observed a similar arrangement of H atoms in other complexes of the open-face carborane ligand (Crespo, Gimeno, Jones & Laguna, 1996). We have also determined the structure of the compound [C₂B₉H₁₀(SC₅H₄NH₂)(CF₃SO₃)], where the H atoms were freely refined, clearly showing the bridging nature of this H atom [B—H distances 1.12 (3) and 1.39 (3) Å; Jones, Crespo *et al.*, 1997].

Experimental

To a solution of [Au{(PPh₂)₂C₂B₉H₁₀}](PPh₃) (Crespo, Gimeno, Laguna & Jones, 1996) (0.096 g, 0.1 mmol) in dichloromethane, [Au(C₆F₅)(C₄H₈S)] (0.0452 g, 0.1 mmol) was added. The solution was stirred for 1 h. Concentration of the solution to *ca* 5 ml and addition of *n*-hexane afforded a yellow solid (yield 65%). Analysis calculated for C₅₀H₄₅Au₂B₉F₅P₃: C 43.05, H 3.25%; found: C 43.4, H 3.7%;

Λ_M 5 Ω^{-1} cm² mol⁻¹. NMR data: ¹H, δ = -2.0 (*br*, 1H, BHB), 7.3–8 (*m*, 20H, Ph) p.p.m.; ³¹P{¹H} (*ABX* system), δ_A = 40.1, δ_B = 54.2, δ_X = 50.3 p.p.m., $J(AB)$ = 306 Hz, $J(AX)$ = 56.2 Hz, $J(BX)$ = 0. ¹⁹F, δ = -114.0 (*m*, 2F, *o*-F), -158.2 [*t*, 1F, *p*-F, $J(FF)$ = 20.4 Hz], -161.3 (*m*, 2F, *m*-F). Mass spectrum (LSIMS+): m/z = 1326 ($[M]^+$, 35%), 961 ($[M - AuC_6F_5]^+$, 40%), 459 ($[AuPPh_3]^+$, 100%). Single crystals were obtained from an *n*-heptane–dichloromethane solution.

Crystal data

[Au₂(C₂₆H₃₀B₉P₂)(C₆F₅)₋
(C₁₈H₁₅P)].CH₂Cl₂

M_r = 1409.92

Monoclinic

$P2_1/c$

a = 12.360 (2) Å

b = 17.042 (3) Å

c = 25.080 (5) Å

β = 92.93 (3)°

V = 5275.9 (16) Å³

Z = 4

D_x = 1.775 Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

λ = 0.71073 Å

Cell parameters from 44 reflections

θ = 15–19°

μ = 5.801 mm⁻¹

T = 173 K

Tablet

0.61 × 0.57 × 0.22 mm

Colourless

Data collection

Siemens Stoe AED-2 diffractometer

ω/θ scans

Absorption correction:

ψ scans (*XEMP*; Siemens, 1990a)

T_{\min} = 0.458, T_{\max} = 0.961

8846 measured reflections

8287 independent reflections

6670 reflections with

$I > 2\sigma(I)$

R_{int} = 0.036

θ_{\max} = 24.04°

h = 0 → 14

k = -19 → 1

l = -28 → 28

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)]$ = 0.043

$wR(F^2)$ = 0.108

S = 1.040

8285 reflections

665 parameters

H atoms: H9, H10, H10b

and H11 refined with

distance restraints, others

riding

$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 7.0867P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001

$\Delta\rho_{\max}$ = 2.57 e Å⁻³

$\Delta\rho_{\min}$ = -1.83 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Au1—C81	2.068 (8)	P2—C8	1.841 (8)
Au1—P1	2.300 (2)	B9—C8	1.619 (12)
Au1—Au2	2.9885 (8)	B9—B10	1.817 (13)
Au2—P3	2.312 (2)	B10—B11	1.824 (14)
Au2—P2	2.326 (2)	B11—C7	1.623 (12)
P1—C7	1.836 (8)	C7—C8	1.611 (10)
C81—Au1—P1	166.6 (2)	C7—P1—Au1	119.3 (2)
P3—Au2—P2	164.69 (7)	C41—P2—C31	102.8 (4)
C11—P1—C21	103.3 (3)	C41—P2—C8	108.3 (3)
C11—P1—C7	105.3 (4)	C31—P2—C8	107.1 (4)
C21—P1—C7	110.3 (3)	C41—P2—Au2	119.1 (2)
C11—P1—Au1	106.2 (3)	C31—P2—Au2	107.8 (3)
C21—P1—Au1	111.0 (2)	C8—P2—Au2	110.9 (2)

The significant residual electron density is in the heavy-atom region; the distance of the maximum peak, 2.570 e Å⁻³, to

the nearest atom (Au2) is 0.89 Å. All non-H atoms were refined anisotropically. Most H atoms were refined using a riding model; those of the carborane open face were located in difference syntheses and refined with B—H distance restraints. A total of 82 restraints were applied, involving local phenyl and pentafluorophenyl ring symmetry (*FLAT/SAME* in *SHELXL93*; Sheldrick, 1993) in addition to the B—H restraints.

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *XP* (Siemens, 1990b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1248). Services for accessing these data are described at the back of the journal. A displacement ellipsoid plot of the title compound has also been deposited.

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