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Bis(tri-*n*-butylphosphino)gold(I) Tetraphenylborate

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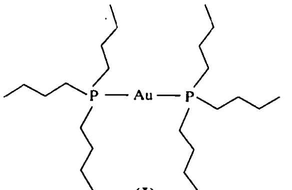
Abstract

The Au atom is linearly coordinated to two disordered tri-*n*-butylphosphine ligands with Au—P distances of 2.310 (3) and 2.305 (4) Å and a P—Au—P bond angle of 176.1 (1)°.

Comment

We have been structurally characterizing a number of bisphosphine complexes of gold(I) (Staples, King, Khan, Winpenny & Fackler, 1993). The cation bis(tri-*n*-butylphosphine)gold(I), (I), is shown in Fig. 1.



(I)

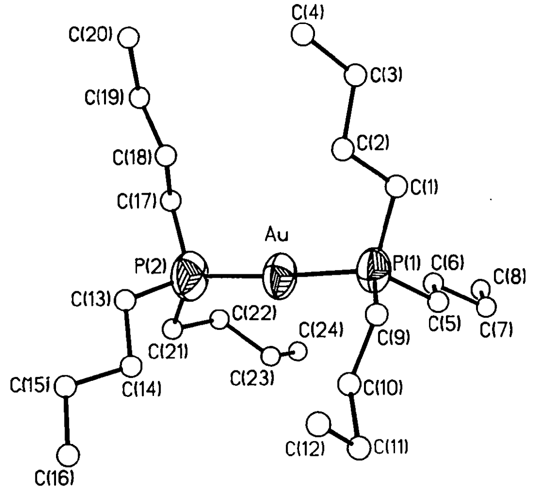


Fig. 1. A view of the disordered cation in bis(tri-*n*-butylphosphine)gold(I) tetraphenylborate, showing the numbering scheme. The C atoms are shown as spheres of arbitrary radii.

The Au—P bond lengths in the title complex are unexceptional at 2.310 (3) and 2.305 (4) Å, which compare with other bis(alkylphosphine) complexes reported: bis(tricyclohexylphosphine)gold chloride [2.32 Å (Muir, Muir, Pulgar, Jones & Sheldrick, 1985)], bis(tricyclohexylphosphine)gold thiocyanate [2.30 and 2.32 Å (Muir, Muir & Lorca, 1980)], bis(tricyclohexylphosphine)gold(I) hexafluorophosphate [2.32 and 2.32 Å (Cooper, Dennis, Henrick & McPartlin, 1980)], bis(dicyclohexylphenylphosphine)gold(I) chloride [2.30 and 2.32 Å (Muir, Cuadrado, Muir & Barnes, 1988)] and bis[tris(2-cyanoethyl)phosphine]gold(I) chloride [2.31 Å (Khan, King, Fackler & Winpenny, 1993)]. The P—Au—P angle is 176.1 (1)° and is also unexceptional compared with the linear bis(alkylphosphine) complexes with non-coordinating anions.

Experimental

Crystal data

$[Au(C_{12}H_{27}P)_2][B(C_6H_5)_4]$
$M_r = 920.8$
Monoclinic
$P2_1/n$
$a = 14.429\ (3)$ Å
$b = 20.995\ (10)$ Å
$c = 17.047\ (8)$ Å
$\beta = 107.75\ (3)°$
$V = 4918\ (4)$ Å^3
$Z = 4$
$D_x = 1.24$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$30°$
$\mu = 3.08$ mm^{-1}
$T = 293$ K
Irregular
0.5 × 0.2 × 0.1 mm
Colorless
Crystal source: CH_2Cl_2/Et_2O

Data collection

Nicolet *R*3*m*/*E* diffractometer
Wyckoff scans
Absorption correction: empirical (216 azimuthal reflections)
$T_{min} = 0.51$, $T_{max} = 0.98$
5023 measured reflections
4870 independent reflections
3464 observed reflections $[F_o^2 > 3\sigma(F_o)^2]$

$R_{int} = 0.024$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 21$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 97 reflections intensity variation: <1%

Refinement

Refinement on F
$R = 0.0543$
$wR = 0.0612$
$S = 1.31$
3464 reflections
451 parameters
$w = [\sigma^2(F_o) + 0.000963F_o^2]^{-1}$
$(\Delta/\sigma)_{max} = 0.24$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

Extinction correction: partial secondary, $F_c \times [1 + 0.002xF_c^2(\sin\theta)]^{-1/4}$
Extinction coefficient: $x = 0.000090$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Au	0.0060 (1)	0.6843 (1)	0.6810 (1)	0.082 (1)
P(1)	0.0501 (2)	0.7101 (2)	0.5655 (2)	0.078 (1)
C(1)	−0.0271 (6)	0.6702 (5)	0.4727 (5)	0.083 (6)
C(2)	−0.1351 (6)	0.6799 (7)	0.4641 (7)	0.107 (7)
C(3)	−0.1984 (8)	0.6350 (7)	0.3984 (8)	0.124 (8)
C(4)	−0.3065 (9)	0.6487 (10)	0.3842 (11)	0.169 (10)
C(5)	0.1751 (5)	0.6894 (5)	0.5690 (7)	0.089 (6)
C(6)	0.2068 (7)	0.6234 (5)	0.6060 (7)	0.087 (6)
C(7)	0.3097 (7)	0.6092 (7)	0.6022 (8)	0.105 (7)
C(8)	0.3423 (11)	0.5430 (7)	0.6381 (12)	0.164 (11)
C(9)	0.0386 (9)	0.7957 (3)	0.5425 (7)	0.095 (7)
C(10)	0.0884 (13)	0.8356 (3)	0.6189 (8)	0.160 (11)
C(11)	0.1209 (25)	0.9053 (8)	0.6228 (26)	0.183 (25)
C(12)	0.0194 (26)	0.9353 (14)	0.5915 (27)	0.201 (25)
C(11′)	0.0512 (26)	0.9028 (7)	0.5908 (18)	0.155 (20)
C(12′)	0.0591 (32)	0.9517 (17)	0.6591 (20)	0.189 (24)
P(2)	−0.0488 (2)	0.6583 (2)	0.7906 (2)	0.104 (2)
C(13)	−0.1190 (11)	0.7225 (6)	0.8190 (10)	0.144 (10)
C(14)	−0.0614 (11)	0.7844 (7)	0.8433 (12)	0.175 (12)
C(15)	−0.1216 (16)	0.8272 (11)	0.8820 (15)	0.215 (16)
C(16)	−0.0707 (20)	0.8916 (13)	0.9031 (21)	0.296 (22)
C(17)	−0.1343 (5)	0.5907 (4)	0.7651 (5)	0.122 (8)
C(18)	−0.2209 (5)	0.6072 (5)	0.6898 (6)	0.129 (8)
C(19)	−0.2981 (6)	0.5553 (5)	0.6797 (8)	0.170 (11)
C(20)	−0.3941 (16)	0.5546 (15)	0.6094 (18)	0.178 (21)
C(20′)	−0.3761 (19)	0.5874 (13)	0.6091 (20)	0.209 (24)
C(21)	0.0316 (16)	0.6517 (11)	0.8971 (6)	0.298 (21)
C(22)	0.1033 (11)	0.6004 (11)	0.8897 (15)	0.258 (20)
C(23)	0.1948 (6)	0.6247 (4)	0.8719 (11)	0.229 (14)
C(24)	0.2663 (11)	0.5688 (7)	0.8947 (14)	0.230 (14)
B(1)	0.4841 (9)	0.1508 (7)	0.3100 (7)	0.071 (6)
C(31)	0.4753 (7)	0.0947 (3)	0.2391 (4)	0.063 (5)
C(32)	0.5542 (7)	0.0551 (3)	0.2427 (4)	0.081 (6)
C(33)	0.5482 (7)	0.0113 (3)	0.1798 (4)	0.097 (7)
C(34)	0.4633 (7)	0.0070 (3)	0.1134 (4)	0.110 (8)
C(35)	0.3844 (7)	0.0465 (3)	0.1097 (4)	0.106 (7)
C(36)	0.3904 (7)	0.0904 (3)	0.1726 (4)	0.082 (6)
C(41)	0.3854 (6)	0.1593 (5)	0.3401 (5)	0.080 (6)
C(42)	0.3712 (6)	0.2151 (5)	0.3794 (5)	0.102 (7)
C(43)	0.2887 (6)	0.2218 (5)	0.4051 (5)	0.132 (9)
C(44)	0.2205 (6)	0.1728 (5)	0.3915 (5)	0.155 (12)
C(45)	0.2346 (6)	0.1170 (5)	0.3523 (5)	0.138 (10)
C(46)	0.3171 (6)	0.1102 (5)	0.3266 (5)	0.104 (7)
C(51)	0.5095 (8)	0.2177 (4)	0.2653 (4)	0.072 (5)
C(52)	0.6033 (8)	0.2242 (4)	0.2593 (4)	0.085 (6)
C(53)	0.6267 (8)	0.2768 (4)	0.2190 (4)	0.110 (8)
C(54)	0.5563 (8)	0.3228 (4)	0.1846 (4)	0.127 (9)
C(55)	0.4625 (8)	0.3163 (4)	0.1906 (4)	0.123 (9)
C(56)	0.4391 (8)	0.2637 (4)	0.2309 (4)	0.089 (6)
C(61)	0.5696 (5)	0.1335 (5)	0.3987 (4)	0.064 (5)
C(62)	0.5692 (5)	0.0723 (6)	0.4305 (4)	0.084 (6)
C(63)	0.6404 (5)	0.0547 (5)	0.5031 (4)	0.108 (8)
C(64)	0.7119 (5)	0.0983 (5)	0.5438 (4)	0.109 (8)
C(65)	0.7122 (5)	0.1595 (5)	0.5120 (4)	0.109 (8)
C(66)	0.6410 (5)	0.1771 (5)	0.4395 (4)	0.090 (6)

Table 2. *Selected geometric parameters* (Å, °)

Au—P(1)	2.310 (3)	Au—P(2)	2.305 (4)
P(1)—C(1)	1.837 (8)	P(1)—C(5)	1.837 (8)
P(1)—C(9)	1.837 (7)	C(1)—C(2)	1.533 (13)
C(2)—C(3)	1.533 (17)	C(3)—C(4)	1.531 (18)
C(5)—C(6)	1.532 (15)	C(6)—C(7)	1.535 (16)
C(7)—C(8)	1.532 (20)	C(9)—C(10)	1.531 (14)
C(10)—C(11)	1.532 (21)	C(11′)—C(12′)	1.532 (44)
C(11)—C(12)	1.532 (47)	B(1)—C(31)	1.666 (15)
C(11)—C(12′)	1.569 (57)	B(1)—C(41)	1.664 (17)
B(1)—C(61)	1.675 (13)	C(23)—C(24)	1.532 (17)
P(2)—C(13)	1.838 (16)	P(2)—C(17)	1.843 (8)
P(2)—C(21)	1.838 (12)	C(13)—C(14)	1.530 (20)
C(14)—C(15)	1.533 (32)	C(15)—C(16)	1.528 (34)
C(17)—C(18)	1.533 (11)	C(18)—C(19)	1.531 (13)
C(19)—C(20)	1.531 (24)	C(19)—C(20′)	1.531 (28)
B(1)—C(51)	1.690 (17)	C(21)—C(22)	1.525 (32)
C(22)—C(23)	1.530 (24)	C(10)—C(11′)	1.532 (19)
P(1)—Au—P(2)	176.1 (1)	Au—P(1)—C(1)	112.0 (3)
Au—P(1)—C(5)	116.1 (4)	C(1)—P(1)—C(5)	104.6 (5)
Au—P(1)—C(9)	112.4 (5)	C(1)—P(1)—C(9)	105.7 (5)
C(5)—P(1)—C(9)	105.2 (6)	P(1)—C(1)—C(2)	110.7 (7)
C(1)—C(2)—C(3)	110.5 (10)	C(2)—C(3)—C(4)	110 (1)
P(1)—C(5)—C(6)	113.2 (7)	C(5)—C(6)—C(7)	109.3 (9)
C(6)—C(7)—C(8)	110 (1)	P(1)—C(9)—C(10)	111.4 (7)
C(9)—C(10)—C(11)	128.1 (9)	C(9)—C(10)—C(11′)	102.1 (8)
C(10)—C(11)—C(12′)	114 (2)	C(10)—C(11)—C(12)	97 (2)
Au—P(2)—C(17)	111.2 (3)	C(13)—P(2)—C(21)	91.6 (9)
Au—P(2)—C(21)	123.3 (7)	C(10)—C(11′)—C(12)	154 (3)
C(17)—P(2)—C(21)	110.5 (8)	C(10)—C(11′)—C(12′)	116 (2)
C(13)—C(14)—C(15)	106 (1)	Au—P(2)—C(13)	113.1 (5)
P(2)—C(17)—C(18)	109.8 (6)	C(13)—P(2)—C(17)	104.1 (5)
C(18)—C(19)—C(20)	123 (1)	P(2)—C(13)—C(14)	113.4 (9)
C(19)—C(20′)—C(20)	76 (3)	C(17)—C(18)—C(19)	108.2 (8)
C(21)—C(22)—C(23)	115 (1)	C(18)—C(19)—C(20′)	96 (1)
C(31)—B(1)—C(41)	114.7 (9)	C(14)—C(15)—C(16)	109 (2)
C(41)—B(1)—C(51)	112.0 (9)	P(2)—C(21)—C(22)	102 (1)
C(41)—B(1)—C(61)	102.0 (8)	C(22)—C(23)—C(24)	104 (1)
B(1)—C(31)—C(32)	120.6 (5)	C(31)—B(1)—C(51)	103.9 (8)
B(1)—C(41)—C(42)	120.2 (6)	C(31)—B(1)—C(61)	112.0 (9)
B(1)—C(51)—C(52)	117.6 (6)	C(51)—B(1)—C(61)	112.7 (8)
B(1)—C(61)—C(62)	117.5 (6)	B(1)—C(31)—C(36)	119.3 (5)
B(1)—C(41)—C(46)	119.8 (6)	B(1)—C(51)—C(56)	122.3 (6)
B(1)—C(61)—C(66)	122.5 (6)		

Crystals of $[Au\{P(n\text{-butyl})_3\}_2][BPh_4]$ were grown by the diffusion of ether into a dichloromethane solution of the compound. A crystal was mounted on a glass fiber for data collection; axial dimensions and monoclinic symmetry were verified by axial-rotation photographs. Au(1) was located by the Patterson technique and all other non-H atoms were located by repeated Fourier syntheses. The phenyl rings were idealized as regular hexagons (C—C—C = 120°, C—C = 1.39 Å) and refined as rigid bodies. Because of severe disorder, it was necessary to constrain the C—C bond lengths within the phosphine ligands. For C(11), C(12) and C(20) two alternate positions with 50% site occupancies were distinguishable and were refined as such. The positions of the H atoms attached to the phenyl rings were idealized (C—H = 0.96 Å) and assigned constrained isotropic displacement parameters $U(H) = 1.2U_{eq}(C)$. No attempt was made either to locate, or to include within the refinement, the H atoms on the phosphine ligand; non-H atoms were refined anisotropically. The maximum and minimum residual electron densities in the final difference Fourier map were less than 0.7 e Å^{-3}. All computations were performed using *SHELXTL* (Sheldrick, 1984).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71492 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1037]

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Hybrid Ligands. Structure of a Palladium(II) Complex Containing a Pyrazolol-Derived Phosphine Ligand, [(*o*-$C_6H_4CH_2NMe_2$)Pd($Ph_2P\{\overline{C{=}C(O)N(Ph)N{=}C}(Me)\}$)]

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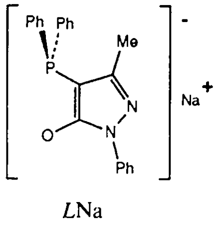
Abstract

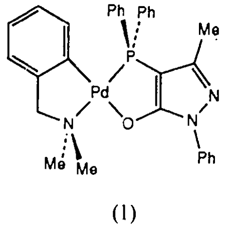
In the title compound, {2-[(dimethylamino-κ*N*)methyl]phenyl-κ*C*}(4-diphenylphosphino-κ*P*-3-methyl-1-phenyl-5-pyrazololato-κ*O*)palladium(II) 0.5-benzene solvate, $[Pd(C_{22}H_{18}N_2OP)(C_9H_{12}N)].0.5C_6H_6$, the Pd atom, which is in a quasi-planar environment, is complexed by two chelating three-electron-donor ligands, with P and N atoms occupying *trans* positions. The plane defined by the aromatic pyrazole ring is coplanar with the metal plane. The angle between the N-bonded phenyl ring and the metal plane is 8°.

Comment

Chelating *P*,*O*-ligands have demonstrated an extremely rich coordination chemistry, the most striking examples being some β-keto and β-ether phosphines which have been used successfully in catalytic processes of industrial relevance (Bader & Lindner, 1991; Keim, Behr, Gruber, Hoffmann, Kowaldt, Kürschner, Limbäcker & Sistig, 1986; Dupont, Gomes Carneiro, Luke & Matt, 1988; Knowles, Sabacky & Vineyard, 1974). In a number of catalytic reactions such unsymmetrical ligands induce high selectivities which cannot be achieved with symmetrical chelates (Behr, Freudenberg & Keim, 1986). It is also well established that phosphines which contain functional substituents based on oxygen-donor atoms may often efficiently enhance the reactivity of transition-metal complexes, in particular when the functional ligand is acting as a semi-labile ligand (Werner, Stark, Schulz & Wolf, 1992) or when the functional group is capable of selective binding to the substrates which will be transformed in the coordination sphere (Powell, Kuksis, May, Nyberg & Smith, 1981). As a part of our studies on hybrid ligands, we recently developed a synthesis of the pyrazolone-derived phosphine salt *L*Na, which is suitable for the formation of *P*,*O*-chelate complexes (Matt, Sutter-Beydoun, Brunette, Balegroune & Grandjean, 1993). The main features of pyrazole moieties are their high stability in acidic and neutral media as well as their strong electron-withdrawing character, which is superior to the CF_3 group in strength (Stary & Freiser, 1975). This latter property may, in principle, affect the coordination behaviour of donor atoms connected to the pyrazole ring and allow the synthesis of electron-poor *P*,*O*-chelate systems. In this paper we present the synthesis and structure of the palladium(II) complex (1), containing two chelating ligands: the pyrazololato ligand L^- and an anion derived from dimethylbenzylamine.



*L*Na



(1)