Structure of [Au(PPh₃)₂][C(CN)₃]

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Abstract

Bis(triphenylphosphine)gold(I) tricyanomethanide, [Au(PPh₃)₂][C(CN)₃] or Au(PPh₃)₂(TCM), has been synthesized and its structure determined. The Au—P distances are 2.290 (2) and 2.300 (2) Å. One TCM N atom is weakly coordinated to the Au atom with an Au—N distance of 2.726 (11) Å. As a result of this weak interaction, the angle P—Au—P is 161.23 (9)° rather than linear (180°). The geometry of TCM is trigonal planar (D_{3h}) with average C—N and C—C distances of 1.14 (2) and 1.40 (2) Å respectively.

Comment

We have recently been interested in the geometric deformation of the C(CN)₃⁻ (TCM) group when it complexes with transition metals (Wang, 1987; Wang *et al.*, 1992). The structure of one crystal form of Au(PPh₃)₂(TCM) (space group C2/c) has been reported (Baukova *et al.*, 1989). Here we report the structure of another form (space group P2₁/c) in which the molecular structure and the geometry are quite different. The Au—P distances are 2.290 (2) and 2.300 (2) Å. One N atom is weakly coordinated to Au with Au—N1 2.726 (11) Å; this weak interac-

tion affects the P1—Au—P2 angle. Final positional parameters are presented in Table 1, and selected bond lengths and angles are listed in Table 2. Fig. 1 is an *ORTEP* drawing (Johnson, 1970) of the molecule showing the atomic labelling scheme.

Experimental

Crystal data

Au[(C₁₈H₁₅P)₂](C₄N₃)	D_x = 1.572 Mg m⁻³
M_r = 811.62	Mo Kα radiation
Monoclinic	λ = 0.71073 Å
P2₁/c	Cell parameters from 25
a = 12.336 (2) Å	reflections
b = 14.108 (2) Å	θ = 9.5–14°
c = 19.875 (8) Å	μ = 4.40 mm⁻¹
β = 97.44 (2)°	T = 298 K
V = 3429.9 (23) Å³	0.40 × 0.30 × 0.25 mm
Z = 4	Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer	2890 observed reflections [I>3σ(I)]
θ/2θ scans	θ_max = 25.0°
Absorption correction: empirical	h = −14 → 14
	k = 0 → 16
T_{min} = 0.6788, T_{max} = 1.0000	l = 0 → 23
	3 standard reflections
6301 measured reflections	frequency: 120 min
6014 independent reflections	intensity variation: 3%

Refinement

Refinement on F	$w = 4F_o^2/[\sigma^2(I)+(0.02F_o^2)^2]$
Final R = 0.033	(Δ/σ)_max = 0.05
wR = 0.037	Δρ_max = 0.616 e Å⁻³
S = 0.495	Δρ_min = −0.586 e Å⁻³
2890 reflections	Atomic scattering factors
236 parameters	from *International Tables*
H-atom parameters not refined	*for X-ray Crystallography* (1974, Vol. IV)

Fig. 1. *ORTEP* drawing of the title compound with 50% probability ellipsoids for non-H atoms.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

$B_{eq} = (4/3)[a^2 B(1,1)+b^2 B(2,2)+c^2 B(3,3)+ab(\cos \gamma)B(1,2)$
$+ac(\cos \beta)B(1,3)+bc(\cos \alpha)B(2,3)]$.

	x	y	z	B_{eq}
Au1	0.24956 (5)	0.09032 (3)	0.25351 (2)	3.310 (6)
P1	0.1478 (2)	0.0657 (2)	0.1502 (1)	2.93 (5)
P2	0.3562 (2)	0.0621 (2)	0.3552 (1)	2.96 (5)
N1	0.230 (1)	0.2758 (8)	0.2884 (6)	7.9 (4)
N2	0.417 (1)	0.544 (1)	0.3024 (9)	11.1 (5)
N3	0.076 (1)	0.5249 (9)	0.1945 (7)	9.0 (4)
C1	0.238 (1)	0.3545 (9)	0.2767 (6)	5.6 (3)
C2	0.340 (1)	0.504 (1)	0.2860 (7)	6.4 (4)
C3	0.152 (1)	0.4910 (9)	0.2246 (6)	6.3 (4)
C4	0.244 (1)	0.4499 (7)	0.2618 (6)	4.8 (3)
C11	0.0243 (7)	0.1346 (7)	0.1316 (4)	2.67 (16)*
C12	0.0326 (9)	0.2317 (8)	0.1319 (5)	3.89 (21)*
C13	−0.0591 (9)	0.2898 (9)	0.1158 (5)	4.55 (23)*
C14	−0.159 (1)	0.2449 (9)	0.1019 (6)	5.16 (26)*
C15	−0.170 (1)	0.1497 (9)	0.1035 (6)	5.40 (27)*
C16	−0.0773 (9)	0.0929 (9)	0.1180 (5)	4.32 (21)*
C21	0.2249 (8)	0.0844 (8)	0.0796 (4)	3.19 (17)*

C22	0.3337 (9)	0.0626 (8)	0.0876 (5)	4.00 (22)*
C23	0.393 (1)	0.0707 (9)	0.0327 (6)	5.57 (28)*
C24	0.341 (1)	0.0994 (9)	−0.0290 (6)	5.42 (26)*
C25	0.233 (1)	0.1225 (9)	−0.0375 (6)	4.78 (25)*
C26	0.1724 (9)	0.1171 (7)	0.0170 (5)	3.78 (21)*
C31	0.1095 (7)	−0.0578 (6)	0.1432 (4)	2.52 (16)*
C32	0.1110 (8)	−0.1084 (7)	0.0830 (5)	3.62 (19)*
C33	0.0887 (9)	−0.2036 (9)	0.0809 (6)	4.57 (24)*
C34	0.062 (1)	−0.2524 (9)	0.1361 (6)	5.10 (26)*
C35	0.057 (1)	−0.202 (1)	0.1959 (7)	6.01 (30)*
C36	0.0812 (9)	−0.1048 (9)	0.2000 (6)	4.65 (23)*
C41	0.4543 (8)	0.1532 (7)	0.3857 (5)	3.04 (18)*
C42	0.4760 (9)	0.1731 (7)	0.4539 (5)	3.52 (19)*
C43	0.5540 (9)	0.2427 (8)	0.4760 (6)	4.63 (24)*
C44	0.609 (1)	0.2863 (9)	0.4325 (6)	5.33 (27)*
C45	0.593 (1)	0.265 (1)	0.3641 (7)	6.92 (34)*
C46	0.512 (1)	0.197 (1)	0.3411 (6)	5.66 (29)*
C51	0.2725 (8)	0.0455 (7)	0.4230 (5)	3.11 (18)*
C52	0.188 (1)	0.1099 (9)	0.4283 (6)	4.90 (25)*
C53	0.126 (1)	0.101 (1)	0.4812 (6)	5.24 (25)*
C54	0.145 (1)	0.0262 (9)	0.5256 (6)	4.97 (25)*
C55	0.225 (1)	−0.0381 (9)	0.5202 (6)	4.69 (24)*
C56	0.2903 (8)	−0.0281 (7)	0.4687 (5)	3.38 (19)*
C61	0.4333 (8)	−0.0462 (7)	0.3506 (5)	3.23 (18)*
C62	0.374 (1)	−0.1254 (8)	0.3229 (5)	4.65 (24)*
C63	0.424 (1)	−0.2133 (9)	0.3200 (6)	5.11 (26)*
C64	0.534 (1)	−0.219 (1)	0.3430 (6)	5.93 (30)*
C65	0.593 (1)	−0.1430 (9)	0.3679 (6)	5.47 (28)*
C66	0.541 (1)	−0.0565 (9)	0.3733 (6)	4.83 (25)*

*Refined isotropically.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Au1—P1	2.290 (2)	P2—C61	1.81 (1)
Au1—P2	2.300 (2)	N1—C1	1.14 (2)
Au1—N1	2.726 (11)	N2—C2	1.12 (2)
P1—C11	1.805 (9)	N3—C3	1.16 (2)
P1—C21	1.81 (1)	C1—C4	1.38 (2)
P1—C31	1.806 (9)	C2—C4	1.44 (2)
P2—C41	1.81 (1)	C3—C4	1.39 (2)
P2—C51	1.81 (1)		
P1—Au1—P2	161.23 (9)	C41—P2—C51	105.2 (4)
Au1—P1—C11	116.9 (3)	C41—P2—C61	106.4 (5)
Au1—P1—C21	113.0 (3)	C51—P2—C61	106.4 (5)
Au1—P1—C31	108.8 (3)	N1—C1—C4	177. (2)
C11—P1—C21	106.1 (4)	N2—C2—C4	177. (2)
C11—P1—C31	107.3 (4)	N3—C3—C4	179. (2)
C21—P1—C31	103.8 (5)	C1—C4—C2	120. (1)
Au1—P2—C41	116.8 (3)	C1—C4—C3	118. (1)
Au1—P2—C51	111.0 (3)	C2—C4—C3	122. (1)
Au1—P2—C61	110.3 (3)		

The title compound was synthesized by reacting 0.2008 g (0.27 mmol) Au(PPh$_3$)$_2$Cl with 0.2251 g (3.81 mmol) potassium tricyanomethanide (KTCM) in CH$_2$Cl$_2$ (DCM) overnight. 0.1884 g (0.23 mmol, yield 86%) ivory precipitate of Au(PPh$_3$)$_2$TCM was formed by adding a large amount of diethyl ether (Et$_2$O) to the reaction solution. Colorless crystals of Au(PPh$_3$)$_2$TCM were grown from DCM/Et$_2$O mixed solvents. The structure was solved by Patterson methods using *Personal SDP* (B. A. Frenz & Associates, Inc., 1989). H atoms were placed at idealized positions; these were included in the structure-factor calculations but not in the least-squares calculations. All calculations were carried out on a 80386-based IBM-compatible PC.

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Structure of the Tetrakis(2,2',5,5'-tetrathiafulvalene) Hexatungstate Acetonitrile Solvate Salt (TTF)$_4$W$_6$O$_{19}$.0.5(CH$_3$CN)

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Abstract

The organic lattice is built from two different TTF chains which develop along the [010] direction. Each chain is formed by dimers separated by isolated molecules. Short intradimer S⋯S contacts [S1⋯S4 3.416 (7), S2⋯S3 3.411 (7), S11⋯S11 3.430 (7), S12⋯S12 3.446 (8), S13⋯S13 3.464 (9), S14⋯S14 3.338 (8) Å] and short anion–cation contacts [O2⋯S1 2.87 (1), O6⋯S4 2.86 (1), O16⋯S16 3.16 (2) Å] are observed.

Comment

The crystal structure represented in Fig. 2 is built from two discrete W$_6$O$_{19}^{2-}$ units, two different organic chains and two isolated TTF molecules. The geometrical parameters of the two W$_6$O$_{19}^{2-}$ units are very similar and compare well with those found in other radical cation salts containing W$_6$O$_{19}^{2-}$, for example (TMTTF)$_2$W$_6$O$_{19}$ (Triki, Ouahab, Grandjean & Fabre, 1991) and (TTF)$_3$W$_6$O$_{19}$ (Triki,