

Acta Cryst. (1993). **C49**, 131–132

Structure of $[\text{Au}(\text{PPh}_3)_2][\text{C}(\text{CN})_3]$

JU-CHUN WANG* AND YU WANG†

Department of Chemistry, Soochow University, Taipei, Taiwan 11102

(Received 4 June 1992; accepted 5 August 1992)

Abstract

Bis(triphenylphosphine)gold(I) tricyanomethanide, $[\text{Au}(\text{PPh}_3)_2][\text{C}(\text{CN})_3]$ or $\text{Au}(\text{PPh}_3)_2(\text{TCM})$, 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 $\text{C}(\text{CN})_3^-$ (TCM) group when it complexes with transition metals (Wang, 1987; Wang *et al.*, 1992). The structure of one crystal form of $\text{Au}(\text{PPh}_3)_2(\text{TCM})$ (space group $C2/c$) has been reported (Baukova *et al.*, 1989). Here we report the structure of another form (space group $P2_1/c$) 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-

† Department of Chemistry, National Taiwan University, Taipei, Taiwan.

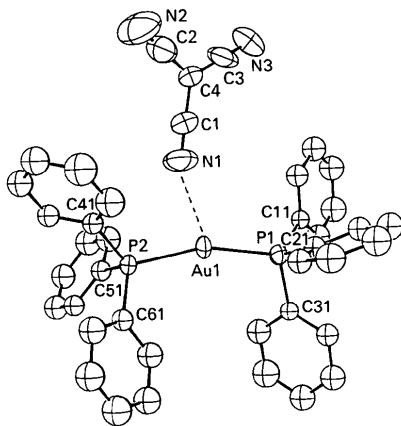


Fig. 1. ORTEP drawing of the title compound with 50% probability ellipsoids for non-H atoms.

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

$\text{Au}[(\text{C}_{18}\text{H}_{15}\text{P})_2](\text{C}_4\text{N}_3)$
 $M_r = 811.62$
 Monoclinic
 $P2_1/c$
 $a = 12.336$ (2) Å
 $b = 14.108$ (2) Å
 $c = 19.875$ (8) Å
 $\beta = 97.44$ (2)°
 $V = 3429.9$ (23) Å³
 $Z = 4$

$D_x = 1.572$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 9.5$ – 14 °

$\mu = 4.40$ mm⁻¹

$T = 298$ K

$0.40 \times 0.30 \times 0.25$ mm

Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction: empirical

$T_{\min} = 0.6788$, $T_{\max} = 1.0000$

6301 measured reflections

6014 independent reflections

2890 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 25.0$ °

$h = -14 \rightarrow 14$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 23$

3 standard reflections

frequency: 120 min

intensity variation: 3%

Refinement

Refinement on F

Final $R = 0.033$

$wR = 0.037$

$S = 0.495$

2890 reflections

236 parameters

H-atom parameters not refined

$w = 4F_o^2 / [\sigma^2(I) + (0.02F_o)^2]$
 $(\Delta/\sigma)_{\max} = 0.05$

$\Delta\rho_{\max} = 0.616$ e Å⁻³

$\Delta\rho_{\min} = -0.586$ e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

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

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

	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(PPh₃)₂Cl with 0.2251 g (3.81 mmol) potassium tricyanomethanide (KTCM) in CH₂Cl₂ (DCM) overnight. 0.1884 g (0.23 mmol, yield 86%) ivory precipitate of Au(PPh₃)₂TCM was formed by adding a large amount of diethyl ether (Et₂O) to the reaction solution. Colorless crystals of Au(PPh₃)₂TCM were grown from DCM/Et₂O 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.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55409 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1016]

These studies were supported by the National Science Council (NSC81-0208-M031-03) of the Republic of China on Taiwan.

References

- B. A. Frenz & Associates, Inc. (1989). *Personal SDP Structure Determination Package*. College Station, Texas, USA.
 Baukova, T. V., Kravtsov, D. N., Kuz'mina, L. G., Dvortsova, N. V., Poray-Koshits, M. A. & Perevalova, E. G. (1989). *J. Organomet. Chem.* **372**, 465–471.
 Johnson, C. K. (1970). *ORTEP*. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee, USA.
 Wang, J. C. (1987). PhD dissertation. Louisiana State Univ., Baton Rouge, Louisiana, USA.
 Wang, J. C., Shih, L. J., Chen, Y. J., Wang, Y., Fronczek, F. R. & Watkins, S. F. (1992). *Acta Cryst.* Submitted.

Acta Cryst. (1993). **C49**, 132–135

Structure of the Tetrakis(2,2',5,5'-tetra-thiafulvalene) Hexatungstate Acetonitrile Solvate Salt (TTF)₄W₆O₁₉·0.5(CH₃CN)

SMAÏL TRIKI, LAHCÈNE OUAHAB* AND DANIEL GRANDJEAN

Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA 254 CNRS, Université de Rennes I, 35042 Rennes CEDEX, France

(Received 28 May 1992; accepted 10 August 1992)

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 W₆O₁₉²⁻ units, two different organic chains and two isolated TTF molecules. The geometrical parameters of the two W₆O₁₉²⁻ units are very similar and compare well with those found in other radical cation salts containing W₆O₁₉²⁻, for example (TMTTF)₂W₆O₁₉ (Triki, Ouahab, Grandjean & Fabre, 1991) and (TTF)₃W₆O₁₉ (Triki,