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Synthesis and crystal structure of bis(triphenylphosphine)gold tricyanomethanide, $[(PPh_3)_2Au]^+ [C(CN)_3]^-$

T.V. Baukova, D.N. Kravtsov *

A.N. Nesmeyanov Institute of Organoelement Compounds, U.S.S.R. Academy of Sciences, Vavilov St., 28, Moscow 117813 (U.S.S.R.)

L.G. Kuz'mina, N.V. Dvortsova, M.A. Poray-Koshits

N.S. Kurnakov Institute of General and Inorganic Chemistry, U.S.S.R. Academy of Sciences, Leninsky Prospekt, 31, Moscow 117907 (U.S.S.R.)

E.G. Perevalova

Chemistry Department Moscow State University, Leninskie Gory, Moscow 117234 (U.S.S.R.)

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Abstract

A new unusual transformation of tetracyanoethylene (TCE) into a tricyanomethanide anion $[C(CN)_3]^-$ has been found. This transformation occurs as a result of action of tris(triphenylphosphinegold)oxonium tetrafluoroborate $[O(AuPPh_3)_3]^+BF_4^-$ on TCE or its donor-acceptor complexes with toluene and 2.4-dihydro-1.3-diphenylcyclopenta(b)indene, to give $[(PPh_3)_2Au]^+[C(CN)_3]^-$ (I). The X-ray diffraction study of I (20 °C, λMo-K_α, 1569 reflections, space group $C2/c$, $Z = 4$, $R = 0.0296$) has revealed that the cations $[Au(PPh_3)_2]^+$ occupy specific positions in the inversion centres and the anions $[C(CN)_3]^-$ are located on the '2' axes. No Au · · · N interaction in I has been found. Complex I has been characterized by ^1H and ^{31}P NMR and IR spectroscopy. The conductivity of I in CH_3OH-CH_3CN solutions has been measured.

Introduction

As has been previously reported $ClAuPPh_3$ does not react with TCE because of the reduced electron density at the gold atom bonded to the electronegative chlorine atom [1]. Interaction of TCE with $[O(AuPPh_3)_3]^+BF_4^-$ [2], in which the univalent atom of gold is bonded to the electron-deficient atom, has not as yet been studied.

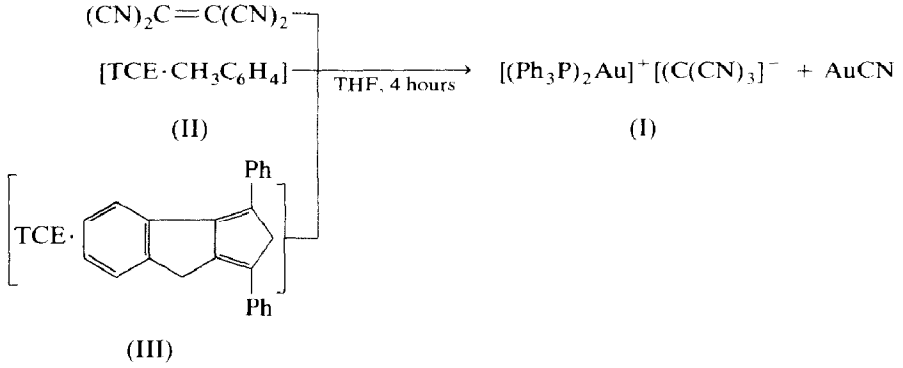
An unusual transformation of TCE under the action of $[O(Au(PPh_3)]^+BF_4^-$ into $[(PPh_3)_2Au]^+[C(CN)_3]^-$ is described here. The reaction takes place with a noncoordinated TCE, as well as with the TCE participating in the formation of a weak

donor-accepting, charge transfer complex ($TCE \cdot CH_3C_6H_5$) (II) [3] or a strongly-bonded complex with 2,4-dihydro-1,3-diphenylcyclopenta(b)indene [4] (III), which does not dissociate in solution.

We have performed conductivity and X-ray diffraction studies of I.

Results and Discussion

TCE and its donor–acceptor complexes II and III react with $[O(AuPPh_3)_3]^+ BF_4^-$ in THF at room temperature to give I in 42–80% yields. In all cases AuCN is the second product of this reaction



(III)

The colourless crystals of complex I are soluble in polar solvents, and are stable up to 230 °C. Complex I is a strong electrolyte which dissociates completely in solution (CH_3OH-CH_3CN 1 : 1) at room temperature (at a concentration of $0.150–1.550 \cdot 10^{-3}$ mol $\cdot l^{-1}$), as its conductivity does not depend on its concentration ($\lambda = 130 \pm 4$ ohm $\cdot$ cm$^2 \cdot$ mol^{-1}).

Crystal structure

The X-ray diffraction study of I has revealed that the $[Au(PPh_3)_2]^+$ cations are located in the inversion centres while the $[C(CN)_3]^-$ anions are located on the '2' axes. The tricyanomethanide anion is planar and the sum of the bond angles at the

Table 1

Bond lengths (Å)

Au–P	2.315(2)	C(10)–C(11)	1.40(3)
P–C(1)	1.802(9)	C(11)–C(12)	1.37(2)
P–C(7)	1.81(1)	C(12)–C(7)	1.35(2)
P–C(13)	1.81(1)	C(13)–C(14)	1.38(1)
C(1)–C(2)	1.48(3)	C(14)–C(15)	1.40(2)
C(2)–C(3)	1.27(3)	C(15)–C(16)	1.27(7)
C(3)–C(4)	1.37(2)	C(16)–C(17)	1.51(1)
C(4)–C(5)	1.39(2)	C(17)–C(18)	1.32(2)
C(5)–C(6)	1.37(2)	C(18)–C(13)	1.39(1)
C(6)–C(1)	1.38(1)	N(1)–C(20)	1.04(2)
C(7)–C(8)	1.47(2)	N(2)–C(21)	1.29(1)
C(8)–C(9)	1.38(3)	C(19)–C(20)	1.33(4)
C(9)–C(10)	1.23(4)	C(19)–C(21)	1.47(7)

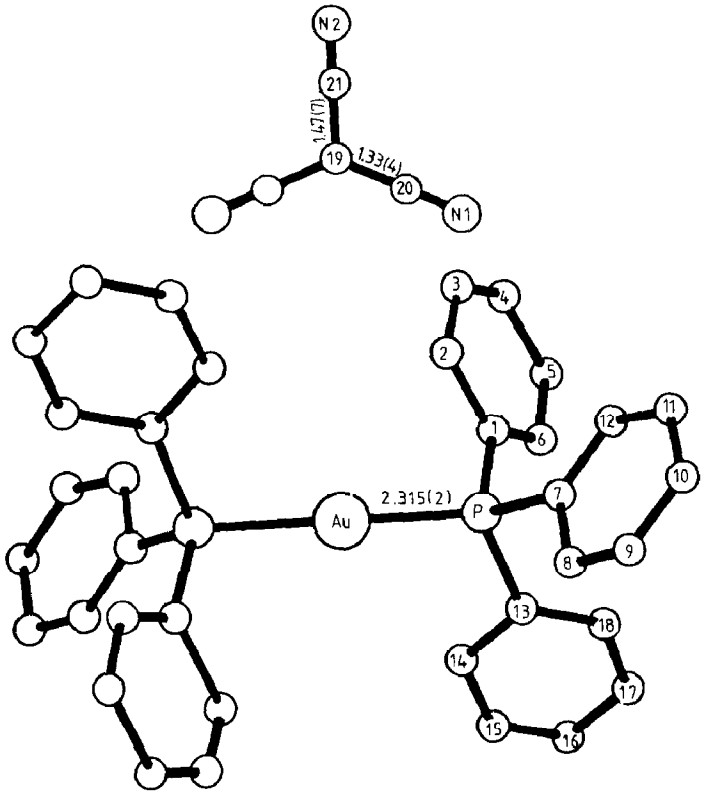


Fig. 1. The structures of the cation and the anion.

central carbon atom is equal to 360°. No Au · · · N interaction was found in the crystal of I. The structures of the cation and anion are depicted in the Fig. 1, bond lengths and bond angles are given in the Tables 1 and 2.

The nature of the $[C(CN)_3]^-$ anion and the coordination of gold with nitrogen atom in cation I are of special interest.

In all the known tricyanomethanide structures [5 – 13] the N atom of anion $[C(CN_3)]^-$ is either coordinated with the metal atom or takes part in the hydrogen bond of the N · · · H–N type (as in the case of NH_4^+ as a counterion [7]).

The quantum-chemical calculation allows two possible structures for the $[C(CN_3)]^-$ anion with D_{3h} or C_{2v} symmetry, the first being somewhat more attractive [12]. Nevertheless both possibilities can be realized in the crystals of tricyanomethanides. The averaged geometrical parameters for the TCM anion in the various complexes as well as the symmetry type of anion in each structure are given in Table 3.

Owing to the low degree of experimental accuracy in determining the geometrical parameters of TCM anion in the structure I detailed discussions about them are not possible, however comparison of the results obtained with from the literature does allow some conclusions to be drawn in terms of the geometry of this anion. The type of symmetry realized by the $[C(CN)_3]^-$ anion is probably determined by the crystal field symmetry—in all cases where C_{2v} symmetry of the anion is realized, it is

Table 2

Bond angles (°)

PAuP	180	C(7)C(8)C(9)	115(2)
AuPC(1)	110.4(3)	C(8)C(9)C(10)	127(3)
AuPC(7)	114.4(4)	C(9)C(10)C(11)	118(2)
AuPC(13)	113.6(4)	C(10)C(11)C(12)	120(2)
C(1)PC(7)	106.2(6)	C(11)C(12)C(7)	122(2)
C(1)PC(13)	106.7(5)	PC(13)C(14)	118.8(8)
C(7)PC(13)	105.1(5)	PC(13)C(18)	121.8(8)
PC(1)C(2)	121(2)	C(18)C(13)C(14)	119(1)
PC(1)C(6)	124.8(7)	C(13)C(14)C(15)	118(1)
C(6)C(1)C(2)	112(3)	C(14)C(15)C(16)	125(4)
C(1)C(2)C(3)	121(1)	C(15)C(16)C(17)	117(4)
C(2)C(3)C(4)	119(2)	C(16)C(17)C(18)	118(2)
C(3)C(4)C(5)	120(1)	C(17)C(18)C(13)	122(1)
C(4)C(5)C(6)	119(1)	C(20)C(19)C(21)	114(4)
C(5)C(6)C(1)	122(1)	C(20)C(19)C(20)	133(8)
PC(7)C(8)	119(1)	N(1)C(20)C(19)	166(4)
PC(7)C(12)	125(1)	N(2)C(21)C(19)	180
C(12)C(7)C(8)	116(2)		

located in the crystal at a specific position on the '2' axis. In most of the complexes the C–C bonds of the anion lie between 1.38–1.41 Å, only in the structure of Ag · TCM) where the errors are rather high, is this bond much longer (1.48 Å) [6]. However, it is noteworthy that the Ag · TCM is the only structure in which the nitrogen atoms of the TCM anion are bonded to the Ag atom by strong coordinate bonds thus giving a polymer framework.

It is clear that the averaged C–C bond lengths in the tricyanomethanide complexes (excluding Ag · TCM) are shorter than the average C(sp)–C(sp^2) in the TCNQ complexes (1.427 Å, 280 cases, between 1.420–1.433 [14]), but longer than the C(sp)–C(sp) bond lengths (1.183, 119 cases [14]). The C–N bond lengths in the tricyanomethanides are in the range 1.15–1.17 Å (1.13 Å in the Ag · TCM structure) and are somewhat longer than the average 1.144 Å for the C–N bond in the TCNQ

Table 3

The averaged geometrical parameters of the TCM anion in the various complexes and the type of symmetry in each structure

Complex	Symmetry	C–C (mean, Å)	C–N (mean, Å)	Reference
Me_2Tl·TCM	C_{2v}	1.38	1.17	5
Ag·TCM	C_{2v}	1.48	1.13	6
NH_4·TCM	D_{3h}	1.40	1.15	7
Na·TCM	D_{3h}	1.405	1.153	8
K·TCM	D_{3h}	1.39	1.17	9
K·TCM	D_{3h}	1.40	1.15	10
Cu·(TCM)	C_{2v}	1.41	1.15	11
$Au(PPh_3)_2$·TCM	C_{2v}	1.40	1.15	This work
Fer^+·TCM	D_{3h}	1.402	1.159	12
$SnMe_3$·TCM·H_2O	D_{3h}	1.40	1.15	13

complexes (284 cases, between 1.139–1.149 Å [14]). These data suggest that while the multiplicity of the C–C bond is enhanced, the multiplicity of C–N bond is lowered in all the $[C(CN)_3]^-$ anions with the exception of the $Ag^+[C(CN)_3]^-$ complex.

In cation I, gold has strictly linear coordination. The Au–P bondlength is 2.315 Å. In other structures with the same cation [15–18], the Au–P bond length is in the range 2.30–2.34 Å.

Experimental

The IR spectrum of I was recorded with an UR-20 spectrometer in nujol, the ^1H NMR spectrum was recorded with a T-60 (60 MHz) instrument with TMS as an internal standard, and the ^{31}P NMR spectra were recorded with a CFT-20 instrument. Conductivity was measured by use of a conductivity apparatus MM34-04 at a constant frequency of 1000 MHz in a cell with planar parallel platinum electrodes in absolute solvents (CH_3OH and CH_2CN).

Crystals of $[Au(PPh_3)_2]^+[C(CN)_3]^-$ are monoclinic, at 20 °C $a = 20.895(4)$, $b = 8.822(2)$, $c = 20.584(4)$ Å, $\beta = 111.09(2)°$, $Z = 4$, space group $C2/c$, both the anion and cation occupy special positions; the anion on the second order axis and the cation in the centre of symmetry).

The unit cell parameters and intensities of 1569 reflections with $I > 2.5\sigma(I)$ were measured by use of an Enraf–Nonius CAD-4 four-circle diffractometer (λ Mo-K_α, graphite monochromator, $\omega/5/3\theta$-scan, $2\theta \leqslant 50°$).

Absorption correction was applied using the curves of azimuthal scans. The crystal decomposes during the course of the measurements; by the end of the measurements the intensities of the standard reflections had fallen by 30%.

The structure was solved by the heavy atom technique and refined by the least squares technique first isotropically and then anisotropically. A continuous shifting of the atoms of the C–CN fragment, of the anion located on the second order axis, from their positions in the electron density syntheses was observed during the refinement. Thus further least squares refinement was carried out for the fixed x, y, z coordinates of this fragment. The H atom coordinates were calculated geometrically and their contribution was included in the last stages of the refinement. Final discrepancy factors were $R = 0.0296$, $R_w = 0.038$.

Atomic coordinates and their isotropic equivalent temperature parameters are listed in Table 4.

Reaction of TCE with $[O(AuPPh_3)_3]^+BF_4^-$

To a solution of 0.026 g (0.203 mmol) of TCE in 10 ml of absolute THF was added 0.100 g (0.067 mmol) of $[O(AuPPh_3)_3]^+BF_4^-$. The mixture was stirred for 4 hours. The yellow precipitate that formed was isolated, washed with acetone, and dried to give 0.010 g (20% relative to Au) of AuCN, identified in the form of $AuCN \cdot PPh_3$ (after treatment of AuCN with a solution of PPh_3 in chloroform) m.p. 202–203 °C (lit. [19]: m.p. 203–204 °C).

The combined organic solutions were evaporated to dryness. The solid residue was recrystallized from acetone by pentane, to give 0.07 g (80% relative to Au) of I, m.p. 231–232 °C. Analysis. Found: C, 59.07; H, 3.42; N, 5.21; Au, 24.36; P, 7.43. $C_{41}H_{30}N_3P_2Au$ calc.: C, 59.26; H, 3.37; N, 5.18; Au, 24.30; P, 7.52%. IR spectrum

Table 4

Atomic coordinates ($\times 10^4$) and their isotropic equivalent temperature parameters ($Å^2$)

Atom	x	y	z	B_{iso}^{eq}
Au	0	0	0	3.296(7)
P	−1045(1)	1037(3)	−84(1)	3.02(5)
N(1)	5556(7)	2269(21)	6863(7)	5.8(3)
N(2)	5000	−2161	7500	5
C(1)	−1326(4)	257(8)	580(4)	2.9(2)
C(2)	−842(5)	41(40)	1258(5)	5.6(2)
C(3)	−1018(8)	−411(21)	1781(6)	6.4(5)
C(4)	−1671(3)	−939(22)	1664(6)	5.7(3)
C(5)	−2156(7)	−918(23)	973(9)	6.3(4)
C(6)	−1975(5)	−316(14)	456(5)	3.9(3)
C(7)	−1033(5)	3069(11)	27(6)	3.2(2)
C(8)	−877(6)	4006(22)	−487(5)	4.5(2)
C(9)	−841(8)	5557(23)	−342(9)	7.1(4)
C(10)	−983(8)	6218(23)	115(9)	5.6(3)
C(11)	−1119(7)	5342(13)	611(7)	5.3(3)
C(12)	−1142(6)	3796(13)	553(6)	4.1(2)
C(13)	−1723(5)	680(12)	−913(6)	3.5(2)
C(14)	−1653(6)	−519(14)	−1322(6)	4.5(3)
C(15)	−2210(10)	834(24)	−1940(7)	6.2(4)
C(16)	−2779(6)	−199(41)	−2147(6)	5.2(3)
C(17)	−2832(7)	1242(22)	−1731(7)	5.3(3)
C(18)	−2336(6)	1510(23)	−1139(7)	4.3(3)
C(19)	5000	547	7500	5
C(20)	5333(5)	1548(11)	7123(5)	2.9(2)
C(21)	5000	−1050	7500	5

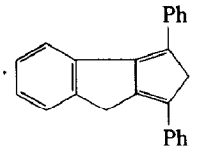
(ν, cm^{-1}): 22015 w, 2205 w, 2168 w, 1607 m., 1332 w, 1100 m, 1030 w, 1000 w, 948 w, 850 w, 750 w, 715 m, 699 m, 525 m, 512 m, 500 m. ^1H NMR spectrum ($(CD_3)_2CO$, δ, ppm): 7.63 m aromatic protons. ^{31}P NMR spectrum ($CDCl_3$, δ, ppm): −42.35 s.

Reaction of $(TCE \cdot CH_3C_6H_5)$ (II) with $[O(AuPPh_3)_3]^+BF_4^-$

A solution of 0.075 g (0.580 mmol) of TCE in 6 ml of absolute toluene was added to a suspension of 0.300 g (0.200 mmol) of $[O(AuPPh_3)_3]^+BF_4^-$ in 17 ml of absolute THF. The mixture was stirred for 4 hours. The residue was isolated from the solution, washed (4 × 1 ml) with acetone, and dried, to give 0.050 g (35% relative to Au) of AuCN, identified in the form of $AuCN \cdot PPh_3$ as described above.

The solution obtained after washing of the AuCN precipitate was combined with the acetone extracts and was evaporated to dryness. 0.31 g of residue was dissolved in 3ml of acetone and diluted by petroleum ether to slight cloudiness. The yellow precipitate was isolated and washed with pentane, yield 0.06 g. IR spectroscopy and TLC (on Silufol in ether) indicate that this residue is a mixture of I and $(PPh_3)_2Au^+BF_4^-$ [20].

A new portion of petroleum ether was added to the mother liquor to cloudiness. The precipitated crystals were isolated, washed with pentane and dried in vacuo to give 0.21 g (42% relative to Au) of I, m.p. 231–232 °C.

Reaction of [$^{TCE\cdot}$ ] *(III) with* $[O(AuPPh_3)_3]^+BF_4^-$

To a solution of 0.20 g (0.046 mmol) of III in 7 ml of absolute THF was added 0.020 g (0.014 mmol) of $[O(AuPPh_3)_3]^+BF_4^-$ and stirred for 4 hours. The precipitate was isolated, washed with THF, and dried, to give 0.030 g (33% relative to Au) of AuCN, identified as described earlier, in the form of $AuCN \cdot PPh_3$.

The combined THF extracts were evaporated to dryness. The residue was extracted with benzene. The benzene extracts were evaporated to dryness to give 0.010 g (100%) of 2.4-dihydro-1.3-diphenylcyclopenta(b)indene, m.p. 176–178°C (from a mixture of C_6H_6 and C_2H_5OH) (lit. [4]: m.p. 176–178°C).

After the extraction with benzene the residue was recrystallized from an acetone-hexane mixture, to give 0.020 g (59% relative to Au) of I was obtained, m.p. 231–232°C.

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