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SYNTHESES OF ORGANOGOLD(1+) COMPOUNDS BY DIRECT AURATION

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Summary

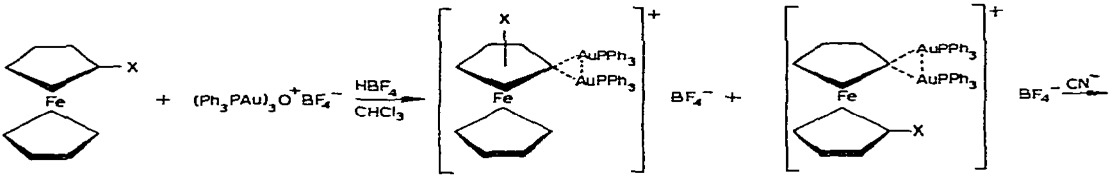
Organogold(1+) compounds have been synthesized by direct auration of cyclopentadiene, cyanoacetic ester and malonitrile with $(Ph_3PAu)_3O^+BF_4^-$. An X-ray structural study (λ Mo, 5062 reflections, $R = 0.039$) of bis(triphenylphosphinegold)malonitrile has been carried out (monoclinic, $a = 12.055(6)$, $b = 14.086(5)$, $c = 20.466(12)$ Å, $\beta = 90.32(4)°$, space group $P2_1/c$, $Z = 4$). The Au—Au bond length is 2.912(1) Å.

Introduction

Metal-containing oxonium salts of several transition and non-transition metals have been synthesized recently, but their metallating ability has not been investigated thus far.

We have obtained gold oxonium salts, $(Ph_3PAu)_3O^+X^-$, [1] and found that they can aurate many organic compounds under mild conditions. Using direct auration we have developed a route to a number of organogold compounds, including some previously unknown.

Tris(triphenylphosphinegold)oxonium salts aurate ferrocene and its derivatives, aliphatic and aliphatic-aromatic ketones and hydrocarbons with an active hydrogen atom and react with enol ethers and ester to form aurated carbonyl



$C_5H_5FeC_5H_3(X)AuPPh_3$ + $XC_5H_4FeC_5H_4AuPPh_3$
(X = H, Me, OMe, C(O)Me, Ph, p-$C_6H_4NO_2$, NO_2, Cl)

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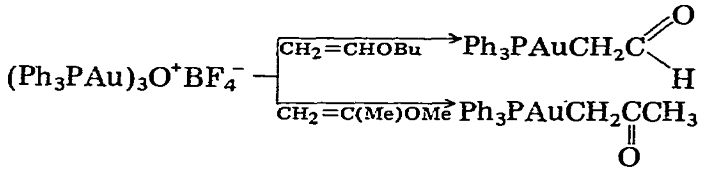
compounds. Auration of ferrocene and its derivatives gives rise to the binuclear organogold complexes $[R(AuPPh_3)_2]^+X^-$, which undergo transformations to the mononuclear compounds $RAuPPh_3$ under the action of nucleophiles (PPh_3, Cl^-, CN^-).

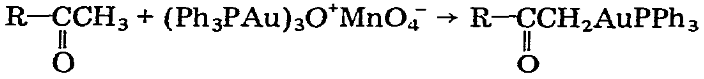
Auration of ferrocene derivatives produces mixtures of homo- and heteroannular isomers, the former predominating [2,3].

Enol ethers react with $(Ph_3PAu)_3O^+BF_4^-$ to give either aurated aldehyde or aurated ketone [4,5].



$$(Ph_3PAu)_3O^+BF_4^- \xrightarrow{CH_2=CHOBu} Ph_3PAuCH_2C(=O)H$$
$$(Ph_3PAu)_3O^+BF_4^- \xrightarrow{CH_2=C(Me)OMe} Ph_3PAuCH_2C(=O)CH_3$$

Under the action of oxonium salts, methyl ketones are aurated in the methyl group [6].



$$R{-}C(=O)CH_3 + (Ph_3PAu)_3O^+MnO_4^- \rightarrow R{-}C(=O)CH_2AuPPh_3$$

($R = Me, Et, Ph, C_5H_5FeC_5H_4$)

In the present paper we report on the interaction of tris(triphenylphosphinegold)oxonium tetrafluoroborate (I) with compounds containing active hydrogen, viz. cyclopentadiene, cyanoacetic ester and malonitrile.

Results and discussion

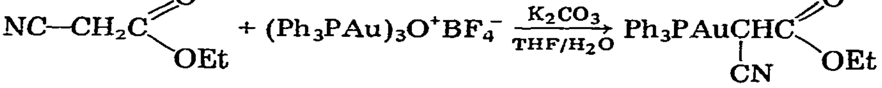
Cyclopentadiene reacts with I in the presence of bases to give cyclopentadienyl(triphenylphosphine)gold. Either potassium carbonate or sodium hydride may be used as base, although the reaction proceeds faster (ca. 15 min) and gives a purer product with sodium hydride.

$$C_5H_6 + (Ph_3PAu)_3O^+BF_4^- \xrightarrow{THF} C_5H_5AuPPh_3$$

(66%)

Earlier $C_5H_5AuPPh_3$ had been obtained by the reaction of C_5H_5Na with Ph_3PAuCl [7].

Ethyl cyanoacetate reacts with I more rapidly (2 min) than does cyclopentadiene to form (triphenylphosphinegold)cyanocarbethoxymethane (II) in a good yield.



$$NC{-}CH_2C(=O)OEt + (Ph_3PAu)_3O^+BF_4^- \xrightarrow[THF/H_2O]{K_2CO_3} Ph_3PAuCH(CN)C(=O)OEt$$

(II; 94%)

The IR CN and CO vibration bands of II (2216 and 1695 cm^{-1}) are lower than those of the parent ester (2265 and 1740 cm^{-1}). The significant decrease of ν(CO) in II is similar to the effect observed in α-metallated carbonyl derivatives [8,9]. It indicates that Au substitutes an α-hydrogen atom of the cyanoacetic ester. Accordingly, the ^{1}H NMR spectrum of II shows a splitting of the methyne proton signal due to interaction with phosphorus (J = 11 Hz).

Malonitrile reacts with I in the presence of base to give the diaurated complex III.

$$H_2C(CN)_2 + (Ph_3PAu)_3O^+BF_4^- \xrightarrow[THF/H_2O]{K_2CO_3} (Ph_3PAu)_2C(CN)_2$$

(III; 97%)

The monoaurated derivative cannot be obtained, even with excess of malonitrile (molar ratio 1.0 : 2.4). In the absence of base the reaction proceeds with the formation of the trinuclear cationic complex IV.

$$H_2C(CN)_2 + (Ph_3PAu)_3O^+BF_4^- \rightarrow [(Ph_3PAu)_3C(CN)_2]^+BF_4^-$$

(IV)

Under the action of an aqueous solution of NaCl or K_2CO_3 complex IV transforms to III, with the loss of one Ph_3PAu^+ group.

$$[(Ph_3PAu)_3C(CN)_2]^+BF_4^- \begin{cases} \xrightarrow{NaCl} \underset{(III)}{(Ph_3PAu)_2C(CN)_2} + Ph_3PAuCl \\ \xrightarrow{K_2CO_3} \underset{(III)}{(Ph_3PAu)_2C(CN)_2} + \underset{(I)}{(Ph_3PAu)_3O^+BF_4^-} \end{cases}$$

The formation of I in the course of the reaction with potassium carbonate is probably due to an in situ interaction of the Ph_3PAu^+ cation with water [5].

On the basis of IR and ^{1}H NMR data it is not possible to distinguish the structure of III with a Au—C σ-bond from the salt-like structure involving a $[(NC)_2C]^{2-}$ dianion, which can be formed from malonitrile [10]. The structure of the diaurated malonitrile III has been established unambiguously by X-ray diffraction. Both gold atoms form covalent bonds with carbon. The metal—metal separation is sufficiently small to indicate the presence of an Au—Au bond (the X-ray crystal structure determination, vide infra).

Compound IV may be described as a complex of III with the Ph_3PAu^+ cation similar to the $[R(AuPPh_3)_2]^+BF_4^-$ derivatives studied earlier, which were interpreted as being complexes of $RAuPPh_3$ with this cation [11]. We proved the formation of IV in the reaction of III with the Ph_3PAu^+ cation generated from chloro(triphenylphosphine)gold under the action of silver tetrafluoroborate.

$$(Ph_3PAu)_2C(CN)_2 + Ph_3Au^+BF_4^- \rightarrow [(Ph_3PAu)_3C(CN)_2]^+BF_4^-$$

(IV)

The structure of IV, however, remains unknown, because in this molecule the Ph_3PAu^+ fragment can be bonded not only to the gold atoms but also to nitrile nitrogen atoms. The IR spectrum of IV contains the characteristic bands of BF_4^- and CN, the CN vibrational frequency (2200 cm^{-1}) being increased by 20 cm^{-1} compared with that of III. The appearance of a positive centre on the carbon atom adjacent to the CN group due to coordination of Ph_3PAu^+ by gold may be responsible for this frequency shift; although it may also result from the Ph_3PAu^+...N coordination. An increase in ν(CN) (by 15 cm^{-1}) was observed in the CuCl malonitrile complex where the copper atom is probably coordinated to nitrogen [12].

Crystal structure of diaurated malonitrile

The molecule of III with the main bond lengths is shown in Fig. 1; bond lengths and bond angles are given in Tables 1 and 2, respectively. Compound III represents a binuclear complex of Au^I with a bridging $C(CN)_2$ fragment. The general configuration of the $(Ph_3PAu)_2C$ moiety in III has much in common with the similar structural unit found in the crystal structure of the binuclear cation $[C_5H_5FeC_5H_4(AuPPh_3)_2]_2^+$ (V) [13] with a bridging C atom of one ferrocene cyclopentadienyl ligand, in spite of the fact that one Au atom in V is additionally bonded to the Fe atom. Each Au atom in molecule III has an unsymmetric trigonal coordination, sums of bond angles at Au(1) and Au(2) being 348.7 and 351.4°, respectively. Thus, the coordination is not strictly planar. The P(1) and P(2) atoms are displaced out of the Au(1)C(37)Au(2) plane to the same side by 0.19 and 0.12 Å, respectively. The P(1)—Au(1) and P(2)—Au(2) bonds form angles of 4.8 and 3.0° with this plane. The Au(1)—P(1) and Au(2)—P(2) bond lengths, 2.269(2) and 2.267(2) Å, are equal within accuracy limits to the values known for triphenylphosphine-gold(I) complexes: 2.275(15) and 2.283-(12) Å in V, 2.279(8) Å in $MeAuPPh_3$ [14], 2.27(1) Å in $C_6F_5AuPPh_3$ [15]. The triphenylphosphine ligands have the usual geometry, P—C bond lengths

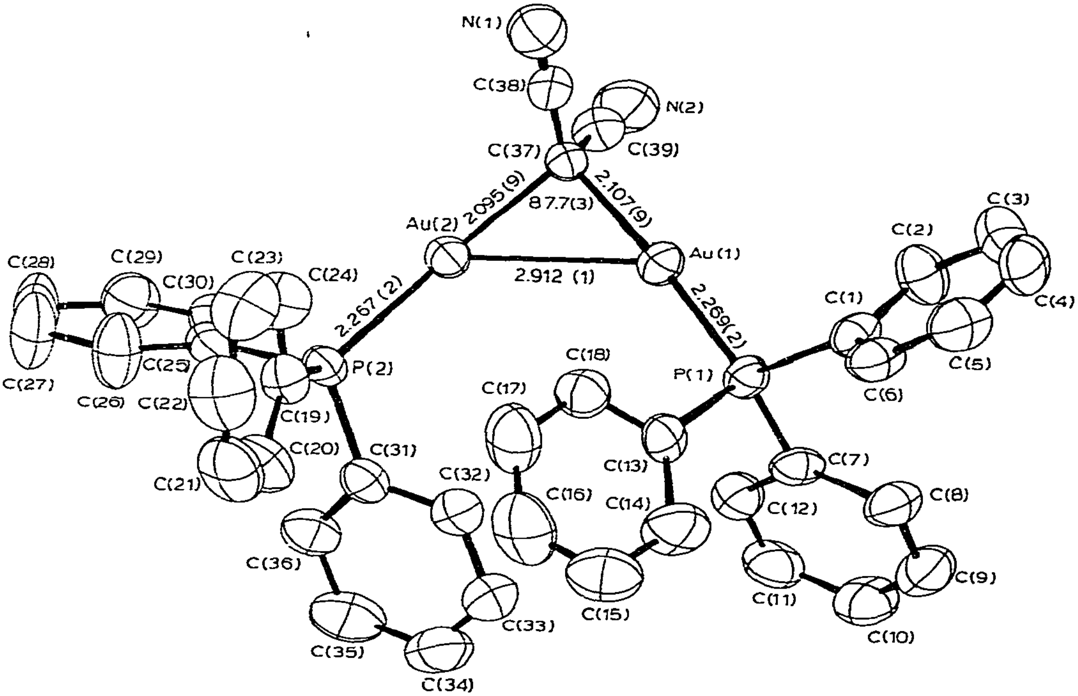


Fig. 1. Molecule III with the most important bond lengths.

TABLE 1

BOND LENGTHS IN THE MOLECULE I

Bond	*d* (Å)	Bond	*d* (Å)
Au(1)—Au(2)	2.912(1)	C(18)—C(13)	1.39(1)
Au(1)—P(1)	2.269(2)	C(19)—C(20)	1.40(1)
Au(2)—P(2)	2.267(2)	C(20)—C(21)	1.38(2)
P(1)—C(1)	1.801(9)	C(21)—C(22)	1.37(2)
P(1)—C(7)	1.811(9)	C(22)—C(23)	1.33(2)
P(1)—C(13)	1.817(9)	C(23)—C(24)	1.40(2)
P(2)—C(19)	1.806(10)	C(24)—C(19)	1.37(1)
P(2)—C(25)	1.824(9)	C(25)—C(26)	1.38(2)
P(2)—C(31)	1.821(10)	C(26)—C(27)	1.42(2)
C(1)—C(2)	1.39(1)	C(27)—C(28)	1.35(2)
C(2)—C(3)	1.37(2)	C(28)—C(29)	1.39(2)
C(3)—C(4)	1.38(2)	C(29)—C(30)	1.38(2)
C(4)—C(5)	1.38(2)	C(30)—C(25)	1.37(2)
C(5)—C(6)	1.37(2)	C(31)—C(32)	1.36(1)
C(6)—C(1)	1.40(1)	C(32)—C(33)	1.38(2)
C(7)—C(8)	1.38(1)	C(33)—C(34)	1.39(2)
C(8)—C(9)	1.37(2)	C(34)—C(35)	1.35(2)
C(9)—C(10)	1.34(2)	C(35)—C(36)	1.39(2)
C(10)—C(11)	1.39(2)	C(36)—C(31)	1.40(2)
C(11)—C(12)	1.39(2)	C(37)—Au(1)	2.107(9)
C(12)—C(7)	1.37(2)	C(37)—Au(2)	2.095(9)
C(13)—C(14)	1.39(1)	C(37)—C(38)	1.43(1)
C(14)—C(15)	1.38(2)	C(37)—C(39)	1.44(1)
C(15)—C(16)	1.35(2)	C(38)—N(1)	1.14(1)
C(16)—C(17)	1.39(2)	C(39)—N(2)	1.16(1)
C(17)—C(18)	1.37(2)		

being 1.806—1.824 Å. The bond distances Au(1)—C(37), 2.107(9), and Au(2)—C(37), 2.095(9) Å, are close to those found in $MeAuPPh_3$, 2.12(3) Å, and $C_6F_5AuPPh_3$, 2.07(2) Å, and also to the distance of 2.12(4) Å between the bridging cyclopentadienyl C atom and one of two Au atoms (uncoordinated by the Fe atom) in V.

As in the case of V, the Au(1)—Au(2) bond in III is almost perpendicular to the bridging $C(CN)_2$ least-squares plane; the dihedral angle between Au(1)-C(37)Au(2) and N(1)C(38)C(37)C(39)N(2) planes being 88.9°. The $C(CN)_2$ moiety is planar within 0.01 Å. Both nitrile groups are linear, the corresponding angles C(37)C(38)N(1) and C(37)C(39)N(2) are 178(1) and 179(1)°, respectively. Within the accuracy limits the bond distances C(38)—N(1), 1.14(1), C(39)—N(2), 1.16(1), C(37)—C(38), 1.43(1), and C(37)—C(39), 1.44(1) Å, are equal to the corresponding values in the tetracyanoethylene molecule [16]. However, the bond angle C(38)C(37)C(39) of 113.4(8)° is somewhat closer to the tetrahedral sp^3 (109.5°) than to the sp^2 (120°) value, so it seems reasonable to consider III as a diaurated dinitrile derivative of methane with additional Au—Au bonding. Actually, the Au(1)—Au(2) distance of 2.912(1) Å, although being slightly longer than the shortest Au—Au distance in metallic gold (2.884 Å [17]), nevertheless corresponds to a metal—metal bond. The considerable decrease of the Au(1)C(37)Au(2) angle to 87.7(3)° in comparison with the tetrahedral value also indicates the presence of Au—Au bonding, while on steric grounds this angle should be increased. It is true that in the cation V, with a

TABLE 2

BOND ANGLES IN THE MOLECULE 1

Angle	ω (°)	Angle	ω (°)
P(1)Au(1)Au(2)	129.34(6)	C(13)C(14)C(15)	120(1)
P(1)Au(1)C(37)	173.4(2)	C(14)C(15)C(16)	121(1)
C(37)Au(1)Au(2)	46.0(2)	C(15)C(16)C(17)	120(1)
P(2)Au(2)Au(1)	129.89(6)	C(16)C(17)C(18)	120(1)
P(2)Au(2)C(37)	175.2(2)	C(17)C(18)C(13)	120(1)
C(37)Au(2)Au(1)	46.3(2)	P(2)C(19)C(20)	119.6(7)
Au(1)P(1)C(1)	112.6(3)	P(2)C(19)C(24)	122.6(8)
Au(1)P(1)C(7)	109.7(3)	C(24)C(19)C(20)	117.8(9)
Au(1)P(1)C(13)	115.3(3)	C(19)C(20)C(21)	121(1)
C(1)P(1)C(7)	108.6(4)	C(20)C(21)C(22)	120(1)
C(1)P(1)C(13)	105.2(4)	C(21)C(22)C(23)	120(1)
C(7)P(1)C(13)	105.0(4)	C(22)C(23)C(24)	122(1)
Au(2)P(2)C(19)	115.3(3)	C(23)C(24)C(19)	119(1)
Au(2)P(2)C(25)	111.1(3)	P(2)C(25)C(26)	121.0(8)
Au(2)P(2)C(31)	113.3(3)	P(2)C(25)C(30)	118.7(8)
C(19)P(2)C(25)	105.1(4)	C(30)C(25)C(26)	120.3(10)
C(19)P(2)C(31)	105.8(4)	C(25)C(26)C(27)	119(1)
C(25)P(2)C(31)	105.5(4)	C(26)C(27)C(28)	120(1)
P(1)C(1)C(2)	123.3(7)	C(27)C(28)C(29)	122(1)
P(1)C(1)C(6)	117.5(7)	C(28)C(29)C(30)	119(1)
C(6)C(1)C(2)	119.2(9)	C(29)C(30)C(25)	121(1)
C(1)C(2)C(3)	119(1)	P(2)C(31)C(32)	123.1(8)
C(2)C(3)C(4)	121(1)	P(2)C(31)C(36)	116.7(8)
C(3)C(4)C(5)	120(1)	C(36)C(31)C(32)	120.1(9)
C(4)C(5)C(6)	120(1)	C(31)C(32)C(33)	119(1)
C(5)C(6)C(1)	120(1)	C(32)C(33)C(34)	121(1)
P(1)C(7)C(8)	119.9(7)	C(33)C(34)C(35)	118(1)
P(1)C(7)C(12)	122.5(8)	C(34)C(35)C(36)	122(1)
C(12)C(7)C(8)	117.5(10)	C(35)C(36)C(31)	118(1)
C(7)C(8)C(9)	121(1)	Au(1)C(37)Au(2)	87.7(3)
C(8)C(9)C(10)	121(1)	Au(1)C(37)C(38)	111.9(6)
C(9)C(10)C(11)	120(1)	Au(1)C(37)C(39)	113.1(6)
C(10)C(11)C(12)	119(1)	Au(2)C(37)C(38)	111.7(6)
C(11)C(12)C(7)	121(1)	Au(2)C(37)C(39)	116.5(6)
P(1)C(13)C(14)	118.3(7)	C(38)C(37)C(39)	113.4(8)
P(1)C(13)C(18)	122.0(7)	C(37)C(38)N(1)	178(1)
C(18)C(13)C(14)	119.7(9)	C(37)C(39)N(2)	179(1)

similar Au_2C (bridge) moiety, the Au—Au bond of 2.768(2) Å is considerably shorter, but Au—Au distances in various bi- and polynuclear gold complexes are found to vary in a wide range, corresponding to several possible types of the metal—metal interaction from the strong Au—Au bond to the weak secondary coordination [18,19].

The small but significant non-linearity of both P—Au—C fragments: P(1)Au(1)C(37) 173.4(2)°, P(2)Au(2)C(37) 175.2(2)°, may also be regarded as an indirect proof of the existence of an Au—Au bond. A similar distortion of the linear Au(1+) coordination environment has also been found in structures of other gold complexes with metal—metal bonding. Namely, in the piperidine complex $[C_5H_{10}NAuCl]_4$ gold atoms form a square with a Au···Au distance of 3.301(5) Å, the N—Au—Cl angle being 176.0(5)° [18]. In the cation V the P—Au—C angle at the gold atom not bonded to the Fe atom is equal to 169(1)°.

However, a similar distortion is not found in the structure of the binuclear complex $[Et_2P(CH_2)_2Au]_2$ with three-membered dimethylenediethylphosphonium bridges. In this case the Au···Au distance is 3.023(1) Å, the C—Au—C angle being 179(1)° [19], perhaps due to steric requirements of the bridging ligands.

The geometry of III therefore reveals the existence of a Au—Au bond. Increase of the P—Au—C angle and the Au—Au distance of III in comparison with those of V indicate that this bonding is weaker in III.

Experimental section

^{1}H NMR spectra were recorded with T-60 and Tesla BS-497 spectrometers; IR spectra were measured with an IKS-29 instrument as oil mulls.

Cell dimensions of the crystals of III and the intensities of 5062 independent reflections with $I > 2\sigma$ were measured with four-circle automatic Syntex $P2_1$ diffractometer (room temperature, λMo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 52°$). Absorption correction taking into account the crystal form was applied according a literature method [20]. Crystals of III are monoclinic, $a = 12.055(6)$, $b = 14.086(5)$, $c = 20.466(12)$ Å, $\beta = 90.32(4)°$, $V = 3475(3)$ Å^3, $Z = 4$, space group $P2_1/c$. The structure was solved by the heavy atom technique and refined by full-matrix least-squares with anisotropic temperature factors for non-hydrogen atoms. H atoms of phenyl rings were included in the refinement with fixed calculated coordinates and isotropic thermal factors ($B_{iso} = 6.0$ Å^2). Finally, $R = 0.039$, $R_w = 0.045$. All calculations were carried out with an Eclipse S/200 computer using modified EXTL programmes *. Coordinates and anisotropic thermal parameters of non-hydrogen atoms are given in Table 3.

Cyclopentadienyl(triphenylphosphine)gold

Cyclopentadiene (4 ml, 48.4 mmol), freshly distilled, was added to a suspension of oxonium salt I (2.00 g, 1.35 mmol) and sodium hydride (0.10 g, 4.14 mmol) in THF (50 ml) under argon atmosphere. The mixture was stirred for 15 min at 0°C; the oxonium salt dissolved completely. Hexane (35 ml) was added to the obtained yellow-brown solution, stirring was continued at 0°C for 15 min and then the precipitate formed was filtered off and discarded. Another portion of hexane (10 ml) was added to the light yellow filtrate and the obtained solution was stirred at 0°C for 10 min. The precipitate formed was filtered off and the filtrate was rapidly added to 500 ml of cold distilled water under vigorous stirring. Cyclopentadienyl(triphenylphosphine)gold was filtered off and washed twice with 15 ml portions of ethanol. Cyclopentadienyl(triphenylphosphine)gold (1.40 g, 66%) was obtained, decomp. above 100°C. ^{1}H NMR ($CDCl_3$): sharp singlet at $\delta = 6.31$ ppm (ref. [7]: sharp singlet at $\delta = 6.3$ ppm).

Triphenylphosphinegold(cyano)carbethoxymethane (II)

Ethylcyanoacetate (0.40 g, 3.54 mmol) and water (0.5 ml) were added to the oxonium salt I (1.00 g, 0.68 mmol) and potassium carbonate (0.20 g, 1.45

(Continued on p. 278)

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* Programmes were modified by A.I. Yanovski and R.G. Gerr in our laboratory.

TABLE 3

COORDINATES OF NON-HYDROGEN ATOMS ($\times 10^4$) WITH THE ANISOTROPIC THERMAL PARAMETERS ($\times 10$) IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Au(1)	1531.5(3)	1973.4(2)	2774.9(2)	36.5(2)	29.9(2)	23.8(1)	2.5(1)	−1.5(1)	0.0(1)
Au(2)	2500.2(3)	676.6(2)	3728.5(2)	36.0(2)	29.0(2)	28.8(2)	6.9(1)	0.8(1)	0.0(1)
P(1)	1504(2)	1875(2)	1668(1)	37.5(9)	32.0(10)	23.1(9)	0.4(8)	−0.6(7)	0.9(8)
P(2)	3381(2)	−728(2)	3576(1)	32.7(9)	28.9(10)	34.5(11)	5.3(8)	1.9(8)	−0.5(9)
C(1)	1401(7)	3020(6)	1281(4)	38(4)	34(4)	28(4)	−9(3)	−5(3)	6(4)
C(2)	2093(8)	3310(8)	777(5)	51(5)	40(5)	36(5)	−8(4)	−2(4)	−1(4)
C(3)	1952(10)	4195(8)	506(6)	75(7)	46(6)	41(5)	−17(5)	4(5)	12(5)
C(4)	1121(11)	4793(8)	721(7)	82(7)	39(5)	56(7)	0(5)	−20(6)	15(5)
C(5)	446(9)	4514(8)	1226(8)	49(5)	36(5)	88(9)	3(4)	−3(5)	10(6)
C(6)	572(8)	3636(7)	1501(6)	43(5)	39(5)	55(6)	5(4)	10(4)	15(4)
C(7)	2755(7)	1296(7)	1387(5)	40(4)	35(4)	30(4)	2(3)	4(3)	8(4)
C(8)	3715(8)	1356(8)	1754(6)	49(5)	49(6)	43(5)	6(4)	2(4)	1(4)
C(9)	4650(9)	858(10)	1584(7)	46(5)	76(8)	60(7)	20(5)	5(5)	9(6)
C(10)	4668(11)	318(11)	1047(8)	57(6)	89(9)	72(9)	24(6)	22(6)	13(8)
C(11)	3721(13)	238(11)	660(7)	89(8)	82(9)	53(7)	27(7)	12(6)	−23(7)
C(12)	2785(10)	762(10)	828(6)	60(6)	82(8)	48(6)	12(6)	5(5)	−18(6)
C(13)	373(7)	1180(6)	1323(4)	41(4)	30(4)	25(4)	−3(3)	5(3)	−1(3)
C(14)	69(8)	349(7)	1637(5)	52(5)	34(4)	42(5)	−2(4)	−4(4)	2(4)
C(15)	−763(10)	−208(8)	1374(6)	68(6)	31(5)	60(7)	−8(4)	1(5)	−1(5)
C(16)	−1315(10)	67(8)	828(6)	60(6)	46(6)	60(7)	−17(5)	−11(5)	−1(5)

C(17)	—1024(10)	903(9)	513(6)	72(7)	53(6)	49(6)	—4(5)	—23(5)	0(5)
C(18)	—184(9)	1458(7)	760(5)	59(5)	35(5)	34(5)	—9(4)	—7(4)	4(4)
C(19)	3606(7)	—1424(6)	4306(5)	37(4)	30(4)	35(4)	4(3)	0(3)	1(3)
C(20)	2721(8)	—1585(8)	4734(5)	44(5)	46(5)	41(5)	5(4)	2(4)	—6(4)
C(21)	2864(10)	—2110(8)	5300(6)	68(6)	50(6)	38(5)	1(5)	7(5)	4(5)
C(22)	3879(11)	—2500(10)	5437(7)	67(7)	66(7)	53(7)	15(6)	—13(6)	17(6)
C(23)	4731(10)	—2326(12)	5045(8)	51(6)	99(10)	69(8)	28(6)	—6(6)	27(8)
C(24)	4618(8)	—1812(9)	4463(6)	36(4)	76(7)	60(7)	15(5)	7(4)	27(6)
C(25)	4759(7)	—548(7)	3234(5)	35(4)	42(5)	41(5)	5(4)	8(4)	7(4)
C(26)	5176(9)	—1157(8)	2770(6)	49(5)	45(5)	64(7)	9(4)	12(5)	—1(5)
C(27)	6263(10)	—1002(10)	2533(7)	49(6)	66(7)	65(7)	23(5)	20(5)	0(6)
C(28)	6862(10)	—267(11)	2762(8)	43(6)	78(8)	78(9)	6(6)	17(6)	20(7)
C(29)	6445(10)	347(10)	3229(7)	48(5)	75(8)	70(8)	—20(5)	2(5)	12(7)
C(30)	5383(8)	202(9)	3455(6)	43(5)	59(6)	61(7)	—6(4)	10(5)	—2(6)
C(31)	2664(7)	—1509(7)	3004(5)	35(4)	35(5)	41(5)	9(3)	—1(4)	—7(4)
C(32)	2415(8)	—2431(7)	3143(6)	50(5)	35(5)	46(6)	—5(4)	9(4)	0(4)
C(33)	1850(9)	—2972(8)	2686(7)	58(6)	41(5)	71(8)	—16(4)	21(5)	—10(6)
C(34)	1542(9)	—2597(10)	2083(7)	47(5)	71(8)	55(7)	6(5)	—5(5)	—27(6)
C(35)	1798(11)	—1686(10)	1956(6)	74(7)	59(7)	47(6)	21(6)	—15(5)	—12(6)
C(36)	2340(10)	—1112(8)	2406(6)	70(6)	30(5)	50(6)	7(5)	—14(5)	0(5)
C(37)	1749(7)	2014(6)	3797(4)	36(4)	35(4)	26(4)	10(3)	—2(3)	—2(3)
C(38)	2528(8)	2732(7)	3992(5)	42(4)	39(5)	34(4)	10(4)	—8(4)	—3(4)
C(39)	719(9)	2057(7)	4147(5)	50(5)	42(5)	31(4)	5(4)	—4(4)	—6(4)
N(1)	3162(7)	3303(7)	4125(5)	53(5)	49(5)	68(6)	0(4)	—17(4)	—5(5)
N(2)	—118(7)	2081(7)	4419(5)	49(4)	66(6)	50(5)	10(4)	5(4)	—15(5)

mmol) in THF (40 ml). The mixture was stirred at 20°C for 2 min; then the solution was dried with potassium carbonate, filtered and evaporated under reduced pressure to the volume of 20 ml. Aurated cyanoacetic ester was precipitated from the solution by addition of hexane (80 ml) and purified by reprecipitation from acetone by hexane. Complex II (1.08 g, 94%) was obtained. m.p. 147—149°C. Found: C, 48.27; H, 3.69. $C_{23}H_{21}AuNO_2P$, calcd.: C, 48.34; H, 3.70%. IR (cm^{-1}): 2214m (CN), 1695s (CO). ^1H NMR ($CDCl_3$), δ, ppm: 7.48 (multiplet, 15 H), 4.18 (quartet, $J = 7$ Hz, 2 H), 3.32 (doublet, $J = 11$ Hz, 1 H), 1.26 (triplet, $J = 7$ Hz, 3 H).

Bis(triphenylphosphinegold)dicyanomethane (III)

Malonitrile (0.10 g, 1.52 mmol) in THF (40 ml) and water (0.5 ml) were added to I (1.00 g, 0.68 mmol) and potassium carbonate (0.20 g, 1.45 mmol). The mixture was stirred for 1 h at 20°C. At first I dissolved, then III gradually precipitated. The precipitate was filtered off, dissolved in chloroform and the solution was dried with potassium carbonate. White crystals of III were precipitated by adding two volumes of ether; yield 0.97 g (97%), m.p. 244—245°C. Found: C, 48.34; H, 3.32; Au, 42.12; N, 2.84. $C_{39}H_{30}Au_2N_2P_2$, calcd.: C, 48.15; H, 3.10; Au, 40.51; N, 2.89%. IR (cm^{-1}): 2180m (CN).

Tris(triphenylphosphinegold)dicyanomethane tetrafluoroborate (IV)

a) Auration of malonitrile. A solution of malonitrile (0.10 g, 1.52 mmol) in THF (40 ml) was added to I (1.00 g, 0.68 mmol). The mixture was stirred at 20°C until I dissolved completely (40 min), then the solution was evaporated under reduced pressure to a volume of 20 ml. Ether (60 ml) was added to the residue and a precipitate of IV formed was separated and washed with ether. Complex IV (0.87 g, 84%) was obtained, decomp. above 162°C (after reprecipitation from acetone with a 1/3 ether/hexane mixture). Found: C, 45.21; H, 2.97; Au, 31.70; F, 5.14; N, 1.80. $C_{57}H_{45}Au_3BF_4N_2P_3$, calcd.: C, 45.07; H, 2.90; Au 32.30; F, 5.00; N, 1.84%. IR (cm^{-1}): 2200m (CN).

b) Reaction of III with $Ph_3PAu^+BF_4^-$. The solution of $Ph_3PAu^+BF_4^-$ prepared from Ph_3PAuCl (0.27 g, 0.55 mmol) and $AgBF_4$ (0.12 g, 0.62 mmol) in THF (30 ml) was added to the suspension of III (0.50 g, 0.51 mmol) in THF (10 ml). The solution of IV so obtained was filtered and evaporated to a volume of 20 ml. Complex IV (0.78 g, 100%) was precipitated from the residual solution with a hexane/ether (1/3) mixture. IR (cm^{-1}): 2200m (CN).

Reaction of IV with NaCl

A solution of IV (0.50 g, 0.33 mmol) in $CHCl_3$ (20 ml) was added to a saturated aqueous solution of NaCl (20 ml) and the mixture was stirred at 20°C for 20 min. The organic layer was separated, washed with water and dried with potassium carbonate. After adding two volumes of ether, diaurated malonitrile (III) precipitated from the solution with an admixture of Ph_3PAuCl, the latter partially remained in the solution. The precipitated III was carefully washed with benzene to remove Ph_3PAuCl, and complex III was obtained (0.32 g, 98%), m.p. 244—245°C. A benzene extract was combined with the mother liquor left after precipitation of III with ether and the solvent was evaporated to dryness under a reduced pressure. Ph_3PAuCl (0.14 g, 88%) was obtained, m.p. 240—241°C (lit. [21]: m.p. 243—244°C).

Reaction of IV with potassium carbonate

Potassium carbonate (0.10 g, 0.73 mmol) and water (0.5 ml) were added to the solution of IV (0.20 g, 0.13 mmol) in THF (20 ml). The mixture was stirred for 30 min at 20°C. The precipitate formed was filtered off, dissolved in $CHCl_3$ and the solution was dried with potassium carbonate. The mixture of I and III was precipitated by adding an excess of ether. The precipitate was washed with acetone (60 ml in 3 portions); III (0.12 g, 94%) was obtained. The acetone extract was evaporated to dryness under reduced pressure, and the residue was dissolved in a small volume of $CHCl_3$. The solution so obtained was treated with an aqueous solution of NaCl. The aqueous layer became alkaline by phenol phtalein indicator and chloro(triphenylphosphine)gold appeared in the organic layer (found by a thin-layer chromatography on Al_2O_3), indicating the presence of oxonium salt I in the residue [1].

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