Hypercoordinated compounds of gold(I)
1. Synthesis and properties of mono- and binuclear organogold(I) derivatives of diphenyl ether

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Mono- and binuclear gold(I) derivatives of *ortho*-substituted diphenyl ether, $C_6H_5OC_6H_4AuPPh_3$ and $O(C_6H_4)_2(AuPPh_3)_2$, were prepared by the reaction of the 2,2'-dilithium derivative of diphenyl ether with $ClAuPPh_3$. X-Ray structural study has shown that these compounds contain secondary intramolecular bonds between the gold and oxygen atoms. The interaction of $C_6H_5OC_6H_4AuPPh_3$ with $(AuPPh_3)BF_4$ affords the $[C_6H_5OC_6H_4(AuPPh_3)_2]BF_4$ cationic complex. The latter reacts with PPh_3 to give the starting $C_6H_5OC_6H_4AuPPh_3$ complex.

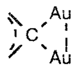
Key words: synthesis, diphenyl ether, hypercoordinated organogold(I) compounds, secondary bonds, X-ray diffraction analysis.

The most typical coordination of a single-charged gold cation in compounds is linear coordination, which can be described in terms of the interaction of the 6sp hybrid orbital of the gold atom with the σ-orbitals of ligands. The possibility of increasing the coordination number of the metal atom (up to a 16- or 18-electron configuration) in 14-electron complexes with a filled 5d sublevel (the d^{10} electron configuration) is mainly determined by the outer vacant 6p orbitals and the minimum implication of 5d orbitals into additional interactions.[1,2] Since the outer orbitals of the gold atom are diffuse and are located at rather high energy levels, their interaction with the localized orbitals of ligands may only result in the formation of relatively weak bonds. Bonds of this type are commonly said to be secondary, and a compound in which the secondary bonds occur is referred to as a hypercoordinated compound.

Various secondary bonds have been found in complexes of monovalent gold, for example, Au···X (X is a heteroatom), Au···H—C (agostic bond), Au···π-system, and Au···Au.[3] These weak interactions have a crucial effect on the structure and properties of gold(I) compounds. The so-called aurophilic Au···Au interactions, which are particularly typical of the chemistry of Au(I), are of the greatest interest. These interactions sometimes result in structures that cannot be described in terms of classical views of the theory of structure and chemical bonds. Among these structures are, for example, «A-shaped» complexes (containing structural fragments A) of the type $[E(AuPR_3)_n]^{q+}$ (E = C, O, S, P, Se, Cl).[4] In some of these complexes the formal valency of element E is violated.

A

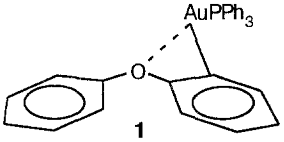
Hypercoordinated σ-organogold(I) compounds of the aromatic series are the most interesting and convenient for a detailed investigation of the secondary bonds of a gold atom. They are normally rather stable, which is important when investigating them by physical methods. It is in this class of compounds that new types of structures have been discovered. These new structures are unusual for organometallic compounds and include structures with three-center two-electron bonds (**B**) found, for example, in the pentanuclear cyclic mesityl complex of gold, $[AuMes]_5$,[5] and structures in which the gold(I) atom is coordinated to the carbon atoms of the cyclopentadienyl ligand in a fashion intermediate between the η^1- and η^3-types of coordination.[6] However, the hypercoordinated organogold(I) compounds have not yet been adequately investigated.



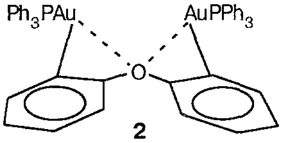
B

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 729—736, April, 1994.

In the present paper we synthesized for the first time a novel class of functionally substituted hypercoordinated organogold(I) compounds consisting of three different types of mono- and diaurated derivatives of diphenyl ether (**1**, **2**, and **3**), and carried out a comparative study of their molecular and electronic structures by X-ray diffraction analysis (for **1** and **2**), X-ray absorption fine structure spectra (EXSAFS, for **3**), fast atom bombardment (FAB) mass spectrometry, and ^{31}P NMR spectroscopy.



1



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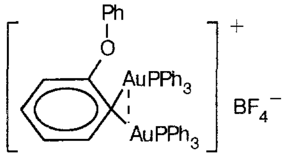
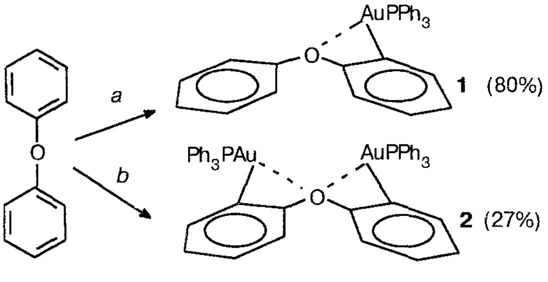


3

The characteristic features of the structures of complexes **1** and **2** were analyzed in comparison with the data obtained by optimization of the geometry of a diphenyl ether molecule by semiempirical quantum-chemical MNDO calculations and by the conformational analysis of a diphenyl ether molecule and a type **2** molecule carried out using molecular mechanics.

We have synthesized mono- and diaurated *ortho*-derivatives of diphenyl ether, **1** and **2**, by the reaction of (triphenylphosphine)gold chloride with the 2,2′-dilithium derivative of diphenyl ether prepared by metallation of diphenyl ether with Bu^nLi in an ether—THF solution.[7] Since both steps of the synthesis of complexes **1** and **2**, *i.e.*, lithiation of diphenyl ether and the subsequent transmetallation (the replacement of the lithium atoms by gold), are reversible, preparation of compounds **1** and **2** is difficult to control and depends on a variety of factors, mainly, on the ratio between the Li derivative of diphenyl ether and $ClAuPPh_3$.*

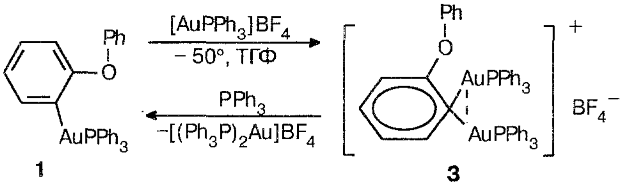


a. 1. *n*-BuLi, 2. $ClAuPPh_3$

b. 1. *n*-BuLi, 2. exc. $ClAuPPh_3$

Monoaurated complex **1** was prepared in a high yield, when an excess of the organolithium derivative of diphenyl ether with respect to $ClAuPPh_3$ was used. Diaurated complex **2** could only be obtained with a deficiency of the organolithium derivative of diphenyl ether with respect to $ClAuPPh_3$. In this case, a mixture of products **1** and **2** is initially formed in the reaction and some $ClAuPPh_3$ remains unreacted. $ClAuPPh_3$ was removed by treating this mixture with an aqueous solution of KCN, which does not react with organogold complexes (on brief contact) but does convert the admixture of $ClAuPPh_3$ to the water-soluble complex $K[Au(CN)_2]$. After treatment with KCN the mixture of **1** and **2** was separated by crystallization.

As other σ-organogold compounds of the aromatic series,[8] compound **1** readily reacts with the coordination unsaturated complex of gold, $(AuPPh_3)BF_4$ (prepared *in situ* from $ClAuPPh_3$ and $AgBF_4$), to give a novel cationic *ortho*-diauated derivative of diphenyl ether, compound **3**.



According to tentative data of the EXSAFS investigation of complex **3**, the bond lengths in the nearest coordination environment of gold atoms are the following: Au—C 2.11, Au—P 2.30, and Au—Au 2.73 Å, and the most probable number of the Au—Au bonds per metal atom n_{Au-Au} is 1. These data are in good agreement with the structural formula suggested for compound **3**.

Like other cationic binuclear organogold derivatives of the aromatic series,[8] complex **3** reacts with nucleophilic reagents with the recovery of the corresponding organogold compound. For example, the reaction of complex **3** with PPh_3 affords compound **1** and the complex $[(Ph_3P)_2Au]BF_4$.

Compounds **1**—**3** are yellowish crystalline solids. Compound **1** is stable, while **2** and **3** are of limited stability in air in the solid state and in solution. Complex **2** reacts with oxygen-containing solvents (THF, acetone) with evolution of heat to give brown oils or polymeric products of unknown structure.

The structures of all of the organogold derivatives of diphenyl ether synthesized (**1**—**3**) were confirmed by elemental analysis, IR and ^{31}P NMR spectroscopy, and

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* Unfortunately, as far as we know, no efficient procedures for controlled mono- and dilithiation of diphenyl ether have been developed yet.

FAB mass spectroscopy. The structures of complexes **1** and **2** were established by X-ray diffraction analysis.

The results of the X-ray structural study of complexes 1 and 2

Molecular structures of complexes **1** and **2** are shown in Figs 1 and 2, the bond lengths are listed in Tables 1 and 2, and the bond angles are given in Tables 3 and 4, respectively.

The Au—C bond lengths in molecules **1** and **2** lie within the interval of normal values for the Au—C(sp^2) bonds (2.05 Å, on the average),[9] and the Au—P bond lengths are close to the average length of these bonds (2.28 Å)[9] in complexes incorporating an C—Au—P fragment.

The most important structural characteristics of molecules **1** and **2** are their specific conformations, which allow one to judge the structural features of these compounds.

The C(2′)O(1)C(7′) ether fragment in complex **1** (see Fig. 1) is nearly coplanar with the C(7′)· · ·C(12′) benzene ring that does not contain the AuPPh$_3$ substituent (the dihedral angle is 4.95°) and is practically perpendicular to the second benzene ring (the corresponding dihedral angle is 86.10°). This geometry of the molecule is favorable for the conjugation of the unshared electron pair at the π-orbital of the oxygen atom with the C(7′)· · ·C(12′) benzene ring. In fact, the length of the O(1)—C(7′) bond bearing the unsubstituted Ph group(1.39 Å) is equal to the standard C(Ph)—O bond length in derivatives of anisole in which the occurrence of the above-mentioned conjugation has been shown by calculations.[10–12]

The second unshared electron pair of the oxygen atom located at the sp^2 orbital cannot efficiently interact with the π-system of the C(1′)· · ·C(6′) benzene ring since it is arranged at an angle of 120° with respect to the O(1)· · ·C(2) bond. Consequently, this bond is substantially lengthened (1.45 Å) compared with the O(1)—C(7′) bond, and the orientation of the Au-substituted benzene ring is not prescribed by the above-

Table 1. Bond lengths (*d*/Å) in compound **1**

Bond	*d*	Bond	*d*
Au(1)—P(1)	2.288(2)	Au(1)—C(1')	2.04(1)
P(1)—C(11)	1.81(1)	P(1)—C(21)	1.82(1)
P(1)—C(31)	1.82(1)	O(1)—C(2')	1.41(1)
O(1)—C(7')	1.37(2)	C(1')—C(2')	1.37(2)
C(1')—C(6')	1.40(2)	C(2')—C(3')	1.39(2)
C(3')—C(4')	1.37(2)	C(4')—C(5')	1.36(2)
C(5')—C(6')	1.37(2)	C(7')—C(8')	1.37(2)
C(7')—C(12')	1.38(2)	C(8')—C(9')	1.37(2)
C(9')—C(10')	1.40(2)	C(10')—C(11')	1.39(2)
C(11')—C(12')	1.36(2)	C(11)—C(12)	1.41(2)
C(11)—C(16)	1.38(2)	C(12)—C(13)	1.39(2)
C(13)—C(14)	1.36(2)	C(14)—C(15)	1.37(2)
C(15)—C(16)	1.37(2)	C(21)—C(22)	1.38(2)
C(21)—C(26)	1.40(2)	C(22)—C(23)	1.38(2)
C(23)—C(24)	1.38(2)	C(24)—C(25)	1.39(3)
C(25)—C(26)	1.41(2)	C(31)—C(32)	1.39(2)
C(31)—C(36)	1.37(2)	C(32)—C(33)	1.39(2)
C(33)—C(34)	1.32(3)	C(34)—C(35)	1.41(3)
C(35)—C(36)	1.38(2)		

Table 2. Bond lengths (*d*/Å) in compound **2**

Bond	*d*	Bond	*d*
Au(1)—P(1)	2.268(6)	Au(1)—C(11)	2.06(2)
Au(2)—P(2)	2.289(6)	Au(2)—C(21)	2.03(2)
P(1)—C(111)	1.81(2)	P(1)—C(121)	1.82(1)
P(1)—C(131)	1.81(2)	P(2)—C(211)	1.80(1)
P(2)—C(221)	1.80(2)	P(2)—C(231)	1.82(1)
O—C(16)	1.43(3)	O—C(26)	1.41(3)
C(11)—C(12)	1.40(4)	C(11)—C(16)	1.36(3)
C(12)—C(13)	1.34(4)	C(13)—C(14)	1.35(4)
C(14)—C(15)	1.41(4)	C(15)—C(16)	1.30(4)
C(21)—C(22)	1.39(4)	C(21)—C(26)	1.39(3)
C(22)—C(23)	1.38(4)	C(23)—C(24)	1.38(4)
C(24)—C(25)	1.38(5)	C(25)—C(26)	1.42(4)
C(111)—C(112)	1.40(2)	C(111)—C(116)	1.40(2)
C(112)—C(113)	1.39(2)	C(113)—C(114)	1.40(2)
C(114)—C(115)	1.39(2)	C(115)—C(116)	1.39(2)
C(121)—C(122)	1.40(2)	C(121)—C(126)	1.40(2)
C(122)—C(123)	1.39(2)	C(123)—C(124)	1.39(2)
C(124)—C(125)	1.39(2)	C(125)—C(126)	1.39(2)
C(131)—C(132)	1.40(2)	C(131)—C(136)	1.40(2)
C(132)—C(133)	1.40(2)	C(133)—C(134)	1.40(2)
C(134)—C(135)	1.40(2)	C(135)—C(136)	1.39(2)
C(211)—C(212)	1.40(2)	C(211)—C(216)	1.39(2)
C(212)—C(213)	1.39(1)	C(213)—C(214)	1.40(2)
C(214)—C(215)	1.39(2)	C(215)—C(216)	1.39(1)
C(221)—C(222)	1.39(3)	C(221)—C(226)	1.40(3)
C(222)—C(223)	1.39(3)	C(223)—C(224)	1.40(3)
C(224)—C(225)	1.39(3)	C(225)—C(226)	1.39(3)
C(231)—C(232)	1.40(2)	C(231)—C(236)	1.39(2)
C(232)—C(233)	1.39(2)	C(233)—C(234)	1.39(2)
C(234)—C(235)	1.40(2)	C(235)—C(236)	1.39(2)

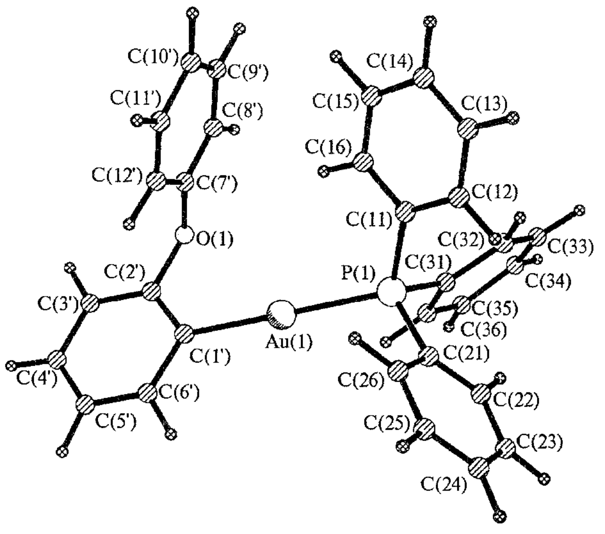


Fig. 1. Molecular structure of $C_6H_5OC_6H_4AuPPh_3$ (**1**).

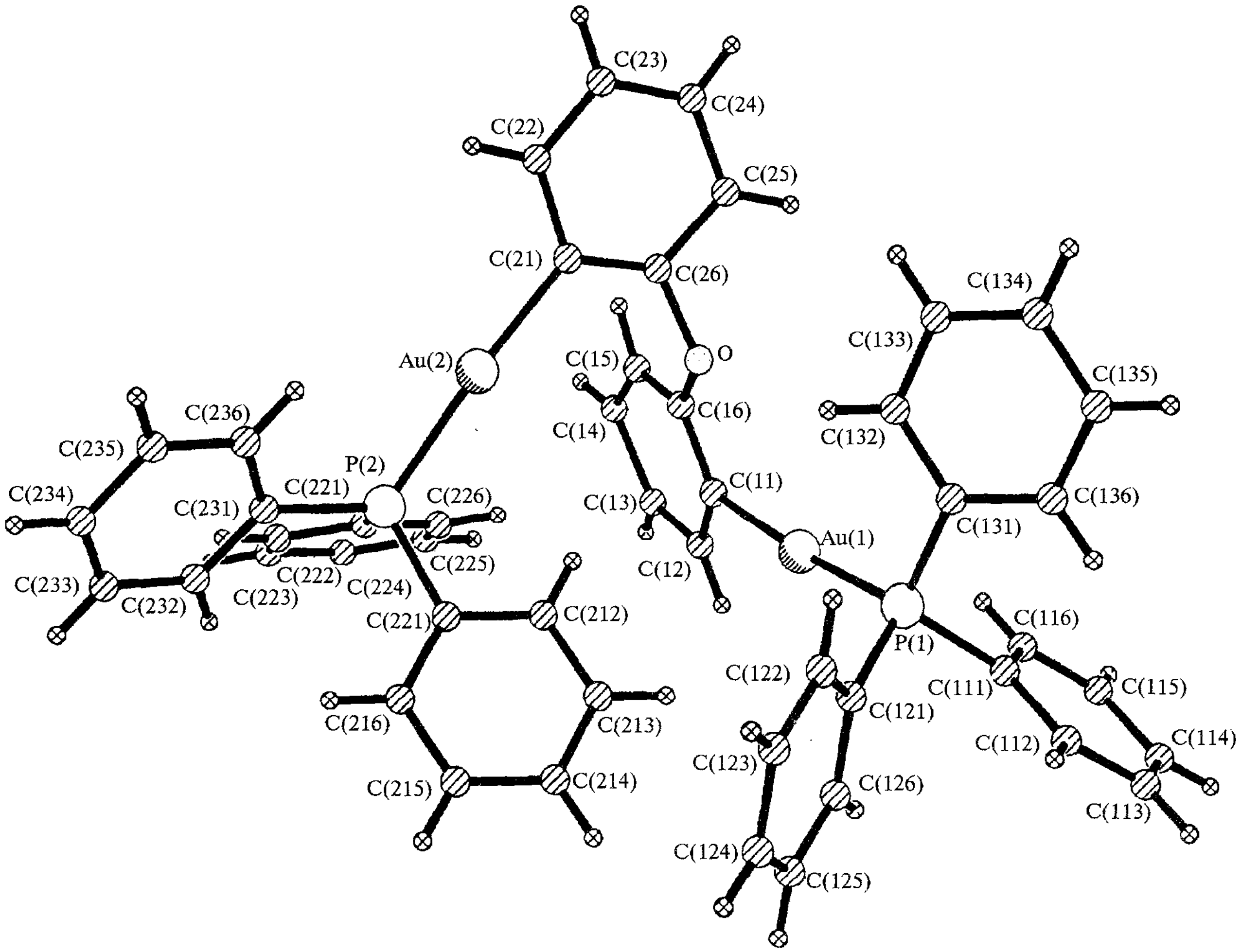
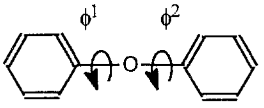


Fig. 2 Molecular structure of $O(C_6H_4)_2(AuPPh_3)_2$ (**2**).

considered *n*—π-conjugation effects. Optimization of the geometry of the molecule of free diphenyl ether by semiempirical quantum-chemical MNDO calculations affords values of the torsional angles ϕ^1 and ϕ^2 close to those obtained for complex **1** (0 and 90°, respectively):



The calculation of the conformation of this molecule by molecular mechanics using the MMX program showed that at the fixed value $\phi^1 = 0°$, a minimum of the potential energy occurs at $\phi^2 = 90°$. However, the increase in the conformational energy of the molecule that occurs when the ϕ^2 angle varies ±40° from 90° does not exceed 4 kcal mol^{-1}. Thus, though the perpendicular orientation of the Au-substituted benzene ring in compound **1** corresponds to minimum steric interactions, it is unlikely that this orientation is determined by steric conditions in the molecule, since the conformational energy minimum is rather broad. At the same time, at the orientation of the C(1′)···C(6′) benzene ring with respect to the O(1)—C(2′) bond found in molecule **1**, the p-orbital of the unshared electron pair of the O atom is directed at the gold atom (more precisely, at the 6p-orbital of the gold atom). The Au···O distance equal to 3.09 Å is comparable with the sum of the van der Waals radii, therefore, the occurrence of a secondary Au···O bond is quite possible. The geometric conditions for the existence of this secondary bond apparently determine the perpendicular orientation of the C(1′)···C(6′) benzene ring with respect to the COC ether fragment.

Thus, the unshared electron pair at the p-orbital of the oxygen atom in the molecule of compound **1** is arranged so that it can be simultaneously involved in two weak interactions: with the π-system of the benzene ring (π-type) and with the vacant 6p-orbital of the gold atom (σ-type), *i.e.*, the whole system of weak electronic interactions incorporates the Ph···O···Au fragment.

The conformation of the diphenyl ether moiety in the molecule of 2,2′-diaurated derivative **2** (see Fig. 2) is close to that found in monoaurated derivative **1**. The dihedral angles between the plane of the C(16)OC(26) ether fragment and the planes of the two

Table 3. Bond angles ω (degrees) in compound **1**

Angle	ω	Angle	ω	Angle	ω
P(1)—Au(1)—C(1')	179.5(3)	O(1)—C(7')—C(12')	124.0(1)	C(1')—C(6')—C(5')	122.0(1)
Au(1)—P(1)—C(21)	113.8(4)	P(1)—C(21)—C(22)	122.3(9)	C(7')—C(8')—C(9')	120.0(1)
C(11)—P(1)—C(21)	106.7(5)	C(22)—C(21)—C(26)	120(1)	C(9')—C(10')—C(11')	117.0(1)
C(21)—P(1)—C(31)	106.0(5)	C(22)—C(23)—C(24)	120(1)	C(7')—C(12')—C(11')	119.0(1)
Au(1)—C(1')—C(2')	122.8(8)	C(24)—C(25)—C(26)	120(2)	P(1)—C(11)—C(16)	118.3(8)
C(2')—C(1')—C(6')	115(1)	P(1)—C(31)—C(32)	121.9(9)	C(11)—C(12)—C(13)	119.0(1)
O(1)—C(2')—C(3')	115(1)	C(32)—C(31)—C(36)	119(1)	C(13)—C(14)—C(15)	119.0(1)
C(2')—C(3')—C(4')	119(1)	C(32)—C(33)—C(34)	120(2)	C(11)—C(16)—C(15)	121.0(1)
C(4')—C(5')—C(6')	121(1)	C(34)—C(35)—C(36)	118(2)	P(1)—C(21)—C(26)	117.4(9)
O(1)—C(7')—C(8')	115(1)	Au(1)—P(1)—C(11)	112.0(4)	C(21)—C(22)—C(23)	120.0(1)
C(8')—C(7')—C(12')	121(1)	Au(1)—P(1)—C(31)	112.8(4)	C(23)—C(24)—C(25)	120.0(2)
C(8')—C(9')—C(10')	121(1)	C(11)—P(1)—C(31)	104.8(5)	C(21)—C(26)—C(25)	119.0(1)
C(10')—C(11')—C(12')	123(1)	C(2')—O(1)—C(7')	118.7(9)	P(1)—C(31)—C(36)	119.1(9)
P(1)—C(11)—C(12)	123.4(9)	Au(1)—C(1')—C(6')	122.4(8)	C(31)—C(32)—C(33)	120.0(1)
C(12)—C(11)—C(16)	118(1)	O(1)—C(2')—C(1')	120.0(1)	C(33)—C(34)—C(35)	121.0(2)
C(12)—C(13)—C(14)	121(2)	C(1')—C(2')—C(3')	124.0(1)	C(31)—C(36)—C(35)	121.0(1)
C(14)—C(15)—C(16)	121(1)	C(3')—C(4')—C(5')	119.0(1)		

Table 4. Bond angles ω (degrees) in compound **2**

Angle	ω	Angle	ω	Angle	ω
P(1)—Au(1)—C(11)	174.6(7)	C(22)—C(23)—C(24)	121(3)	C(12)—C(11)—C(16)	115(2)
Au(1)—P(1)—C(111)	113.0(6)	C(24)—C(25)—C(26)	116(3)	P(2)—C(231)—C(232)	123(1)
Au(1)—P(1)—C(131)	108.8(5)	O—C(26)—C(25)	110(2)	C(232)—C(231)—C(236)	120(1)
C(111)—P(1)—C(131)	105.9(7)	P(1)—C(111)—C(112)	123(1)	C(232)—C(233)—C(234)	120(1)
Au(2)—P(2)—C(211)	110.9(5)	C(131)—C(132)—C(133)	120(1)	C(234)—C(235)—C(236)	120(1)
Au(2)—P(2)—C(231)	117.4(6)	C(133)—C(134)—C(135)	120(1)	C(12)—C(13)—C(14)	121(3)
C(211)—P(2)—C(231)	106.8(7)	C(131)—C(136)—C(135)	120(1)	C(14)—C(15)—C(16)	122(3)
C(16)—O—C(26)	116(2)	P(2)—C(211)—C(216)	124(1)	O—C(16)—C(15)	125(2)
Au(1)—C(11)—C(16)	123(2)	C(211)—C(212)—C(213)	120(1)	Au(2)—C(21)—C(22)	126(2)
C(11)—C(12)—C(13)	123(3)	C(213)—C(214)—C(215)	120(1)	C(112)—C(111)—C(116)	120(1)
C(13)—C(14)—C(15)	116(3)	C(211)—C(216)—C(215)	120(1)	C(112)—C(113)—C(114)	120(1)
O—C(16)—C(11)	112(2)	P(2)—C(221)—C(226)	116(2)	C(114)—C(115)—C(116)	120(1)
C(11)—C(16)—C(15)	123(2)	C(221)—C(222)—C(223)	120(2)	P(1)—C(121)—C(122)	124(1)
Au(2)—C(21)—C(26)	120(2)	C(223)—C(224)—C(225)	120(2)	C(122)—C(121)—C(126)	120(1)
C(21)—C(22)—C(23)	123(2)	C(221)—C(226)—C(225)	120(2)	C(122)—C(123)—C(124)	120(1)
C(23)—C(24)—C(25)	120(3)	P(2)—C(231)—C(236)	117(1)	C(124)—C(125)—C(126)	120(1)
O—C(26)—C(21)	123(2)	C(231)—C(232)—C(233)	120(1)	P(1)—C(131)—C(132)	119(1)
C(21)—C(26)—C(25)	126(2)	C(233)—C(234)—C(235)	120(1)	C(132)—C(131)—C(136)	120(1)
P(1)—C(111)—C(116)	117(1)	P(2)—Au(2)—C(21)	174.7(7)	C(132)—C(133)—C(134)	120(1)
C(111)—C(112)—C(113)	120(1)	Au(1)—P(1)—C(121)	115.2(5)	C(134)—C(135)—C(136)	120(1)
C(113)—C(114)—C(115)	120(1)	C(111)—P(1)—C(121)	105.4(7)	P(2)—C(211)—C(212)	116(1)
C(111)—C(116)—C(115)	120(1)	C(121)—P(1)—C(131)	108.0(7)	C(212)—C(211)—C(216)	120(1)
P(1)—C(121)—C(126)	116(1)	Au(2)—P(2)—C(221)	112.5(8)	C(212)—C(213)—C(214)	120(1)
C(121)—C(122)—C(123)	120(1)	C(211)—P(2)—C(221)	104.0(9)	C(214)—C(215)—C(216)	120(1)
C(123)—C(124)—C(125)	120(1)	C(221)—P(2)—C(231)	104.3(9)	P(2)—C(221)—C(222)	124(2)
C(121)—C(126)—C(125)	120(1)	Au(1)—C(11)—C(12)	122(2)	C(222)—C(221)—C(226)	120(2)
P(1)—C(131)—C(136)	121(1)	C(222)—C(223)—C(224)	120(2)	C(224)—C(225)—C(226)	120(2)
C(22)—C(21)—C(26)	114(2)				

phenyl rings are 7.05° (with the C(11) · · · C(16) phenyl ring) and 75.99° (with the C(21) · · · C(26) phenyl ring). The lower accuracy in the structural determination does not allow one to determine whether the C—O bonds in compound **2** are unequal, as was found for compound **1**. At the conformation of diphenyl ether found in molecule **2**, the unshared electron pair at the p-orbital of the oxygen atom is directed at the Au(2) atom and the electron pair at the sp^2-orbital of the oxygen atom is aimed at Au(1). The Au(1) · · · O distance (3.04(2) Å) is shorter than the Au(2) · · · O distance (3.25(2) Å). Thus, in molecule **2** the interaction of the vacant 6p-orbital of the Au(1) atom with the hybrid sp^2-orbital of the oxygen atom is stronger than the interaction of the similar orbital of the Au(2) atom with the unhybridized p-orbital of oxygen. The interaction of Au with the hybridized sp^2-orbital of oxygen in molecule **1** does not occur, since it requires the sterically unfavorable nearly coplanar conformation of the diphenyl oxide moiety. The reasons why the secondary Au · · · O bond involving the hybridized orbital of the O atom is stronger are unclear and cannot be elucidated on the basis of the geometric parameters of molecules **1** and **2** in the crystal, because the electronic effects under consideration are weak and may be «masked» by conformational and packing effects. It should only be noted that the hybrid sp^2-orbital is longer and therefore can more efficiently overlap with the 6p-orbital of gold. However, it is directed at the gold atom to a lesser extent than the p-orbital (in the former case the corresponding angle is 120°, and in the latter case it is 90°).

The conformation in which the Au atoms are close to one another (interact) does not occur in the molecule of 2,2′-diaurated complex **2**. The Au(1)···Au(2) distance in **2**, equal to 5.238 Å, is too great for an «aurophilic» Au···Au interaction to exist.

To find out whether there is conformational hindrance in molecule **2** that prevents gold atoms from approaching each other to distances (about 3 Å) corresponding to Au···Au interactions, we carried out the following version of the calculations using the molecular mechanics method. $AuPH_3$ substituents were introduced in the *ortho*-position of both phenyl rings (the Au—P and Au—C distances were taken to be standard and the CAuP angle was taken to be 180°), and the distances between the gold atoms (and between the CH-groups in the unsubstituted *ortho*-positions) in the sterically allowed conformations of the diphenyl oxide moiety were calculated. The results of these calculations are given below ($\phi^1 = 0°$):

ϕ^2 (degr.)	Au···Au (Å)	H···H (Å)
−90	3.99	4.74
−80	3.71	4.79
−70	3.42	4.84
−60	3.13	5.98
−55	2.95	6.12
−50	2.83	6.21

One can see that the gold—gold distances corresponding to aurophilic interactions (~2.8 to ~3.4 Å)[3] may be attained in sterically allowed conformations of the diphenyl oxide moiety. In these cases the distances between the phosphine fragments are so great (more than 6 Å) that their effect on the conformation of the diaurated complex may be ignored.

Thus, the calculations show that there are no steric restrictions in molecule **2** preventing Au···Au aurophilic interactions. This allows us to conclude that stabilization of molecule **2** due to two secondary Au···O bonds is better than that due to Au···Au interaction.

Experimental

IR spectra (KBr) were recorded on an UR-20 spectrometer. ^{31}P NMR spectra were obtained on a Bruker CXP 200 instrument (81 MHz) in CH_2Cl_2 with 85 % H_3PO_4 as the external standard. Mass spectra were measured on a KRATOS CONSEPT mass spectrometer with an energy of bombarding atoms (Cs) of 8 keV using 2-nitrobenzyl alcohol as the matrix.

Complexes **1—3** were prepared under dry argon. Solvents were distilled just prior to use over benzophenonesodium ketyl under argon.

The course of the reactions was monitored by TLC on Silufol UV-254 plates (Czechoslovakia). Visualization was carried out by heating the plates.

The X-ray structural study of compound **1** was carried out on an Enraf-Nonius CAD-4 four-circle automatic K-diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ-scanning, $\theta_{max} = 25°$) at 20 °C, that of compound **2** was carried out at −100 °C.

Crystals of $(C_6H_5OC_6H_4)AuP(C_6H_5)_3$ **1** are triclinic, $a = 9.119(1)$, $b = 10.482(1)$, $c = 13.413(4)$ Å, $\alpha = 96.42(2)$, $\beta = 103.87(2)$, $\gamma = 93.97(1)°$, $V = 1230.6(5)$ Å^3, $d_{calc} = 1.69$ g cm^{-3}, Z = 2, space group $P\bar{1}$.

The complete set of 5984 experimental reflections (3183 of which with $I > 2\sigma(I)$) was acquired from three crystals, since the crystals decomposed after approximately 24 hours of measurement. Decomposition of crystals occurred over a very brief period. Therefore, we applied no corrections for drift in the standard reflections within each of the three blocks of the experimental reflections, and just rejected those about ≈200 values in each of the blocks, which were recorded from a decomposing crystal. All three of the crystals used for the measurements had identical shapes and similar sizes, which was confirmed by the fact that the same standard reflections from these crystals differ by only 5—7 %. The final F^2 set contained 3183 reflections and consisted of three blocks having 1120, 1116, and 947 reflections, respectively.

The structure was solved by the heavy atom method and refined by the least squares method in the full-matrix isotropic approximation. At this stage of the refinement a correction for absorption of X rays by the crystal was applied according to the DIFABS procedure[13] (μ(Mo-Kα) = 34.2 cm^{-1}). The correction was introduced separately for each of the three F blocks taking into account the corresponding matrix of the crystal orientation.

The final refinement was carried out by the least squares method in the full-matrix anisotropic approximation. The coordinates of the H atoms were calculated geometrically and included into the final refinement with fixed positional and temperature ($B_{iso} = 7$ Å^2) parameters. Finally: $R = 0.042$, $R_w = 0.045$ over 3183 reflections with $F \geq 4\sigma(F)$; the weight scheme $w = 1.9381/(\sigma^2 F_0 + 0.001093 F_0^2)$ was used. The maximum and minimum residual electron densities on the electron density differential map are 2.15 and −2.15 e/Å^3 and are almost entirely localized in the vicinity of the metal atom.

Crystals of $O(C_6H_4)_2[AuP(C_6H_5)_3]_2$ **2** are monoclinic, at −100°C, $a = 9.437(7)$, $b = 16.26(2)$, $c = 25.16(3)$ Å, $\beta = 93.99(8)°$, $V = 3849.98(6)$ Å^3, $Z = 4$, $d_{calc} = 1.87$ g cm^{-3}, space group $P2_1/c$.

Intensities of 5024 reflections (2508 of which with $I > 2\sigma(I)$) were mesaured.

The structure of **2** was solved by the heavy atom method and refined by the least squares method in the isotropic approximation. At this stage of the refinement a correction for absorption of X rays by the crystal was applied according to the DIFABS procedure[13] (μ(Mo-Kα) = 43.5 cm^{-1}).

Further refinement of the structure was carried out by the least squares method in the full-matrix anisotropic approximation. The coordinates of the H atoms were calculated geometrically and included into the final refinement with fixed

Table 5. Coordinates of nonhydrogen atoms and their isotropic equivalent temperature parameters (B_{eq}, A^2) in compound **1**

Atom	x	y	z	B_{eq}
Au(1)	0.5064(0)	0.4363(0)	0.2833(0)	3.5
P(1)	0.3791(3)	0.3643(2)	0.6390(2)	3.5
O(1)	0.3658(9)	0.8052(8)	0.8288(7)	4.5
C(1')	0.596(1)	0.741(1)	0.7872(8)	3.8
C(2')	0.522(1)	0.830(1)	0.8341(8)	3.8
C(3')	0.587(2)	0.953(1)	0.8810(9)	4.9
C(4')	0.736(2)	0.988(1)	0.882(1)	5.7
C(5')	0.814(2)	0.902(1)	0.838(1)	5.9
C(6')	0.747(1)	0.782(1)	0.791(1)	4.7
C(7')	0.324(1)	0.739(1)	0.9017(9)	4.3
C(8')	0.171(1)	0.727(1)	0.896(1)	4.9
C(9')	0.118(2)	0.663(2)	0.966(1)	6.1
C(10')	0.216(2)	0.606(2)	1.041(1)	6.4
C(11')	0.370(2)	0.621(2)	1.044(1)	5.8
C(12')	0.425(1)	0.687(1)	0.9774(9)	4.4
C(11)	0.292(1)	0.280(1)	0.7243(8)	3.7
C(12)	0.283(2)	0.145(1)	0.723(1)	5.1
C(13)	0.213(2)	0.090(1)	0.790(1)	6.5
C(14)	0.154(2)	0.162(2)	0.858(1)	5.9
C(15)	0.165(2)	0.293(2)	0.861(1)	6.1
C(16)	0.234(1)	0.352(1)	0.796(1)	4.7
C(21)	0.507(1)	0.258(1)	0.5956(8)	3.8
C(22)	0.493(1)	0.216(1)	0.4920(9)	4.6
C(23)	0.599(2)	0.142(1)	0.462(1)	5.4
C(24)	0.719(2)	0.108(2)	0.536(1)	6.2
C(25)	0.734(2)	0.148(2)	0.640(1)	7.0
C(26)	0.628(2)	0.224(2)	0.671(1)	5.8
C(31)	0.225(1)	0.372(1)	0.5257(8)	3.9
C(32)	0.103(2)	0.278(2)	0.494(1)	5.5
C(33)	−0.016(2)	0.291(2)	0.410(1)	6.6
C(34)	−0.013(2)	0.392(2)	0.360(1)	6.9
C(35)	0.112(2)	0.487(2)	0.386(1)	7.0
C(36)	0.230(2)	0.474(1)	0.470(1)	5.7

Table 6. Coordinates of nonhydrogen atoms and their equivalent or isotropic temperature parameters (B_{eq}/B_{iso}) in compound **2**

Atom	x	y	z	B_{eq}/B_{iso}
Au(1)	0.2881(1)	0.3992(1)	0.3779(0)	1.8
Au(2)	0.1584(1)	0.1639(1)	0.5082(0)	2.1
P(1)	0.1675(6)	0.5183(4)	0.3617(2)	1.8
P(2)	0.3065(7)	0.2049(4)	0.5792(2)	1.9
O	0.158(2)	0.229(1)	0.3859(7)	2.5
C(11)	0.382(3)	0.286(1)	0.3884(9)	2.0(4)
C(12)	0.531(3)	0.276(2)	0.393(1)	3.3(5)
C(13)	0.593(3)	0.202(2)	0.396(1)	2.5(4)
C(14)	0.515(3)	0.132(2)	0.397(1)	3.6(5)
C(15)	0.366(3)	0.143(2)	0.392(1)	3.0(5)
C(16)	0.307(2)	0.215(1)	0.3901(8)	1.4(4)
C(21)	0.043(3)	0.127(2)	0.4414(9)	2.4(4)
C(22)	−0.058(3)	0.065(2)	0.4389(9)	2.6(5)
C(23)	−0.124(3)	0.038(2)	0.391(1)	3.6(5)
C(24)	−0.094(4)	0.072(2)	0.344(1)	4.3(6)
C(25)	−0.001(3)	0.138(2)	0.343(1)	3.5(6)
C(26)	0.070(3)	0.159(1)	0.3921(9)	2.2(4)
C(111)	0.252(2)	0.5854(9)	0.3157(6)	2.6(5)
C(112)	0.225(2)	0.6698(9)	0.3129(6)	3.5(5)
C(113)	0.290(2)	0.7180(9)	0.2757(6)	5.9(8)
C(114)	0.381(2)	0.6819(9)	0.2412(6)	4.8(7)
C(115)	0.408(2)	0.5976(9)	0.2440(6)	3.7(5)
C(116)	0.343(2)	0.5493(9)	0.2812(6)	3.1(5)
C(121)	0.143(2)	0.5811(9)	0.4202(5)	1.3(4)
C(122)	0.016(2)	0.5843(9)	0.4457(5)	3.0(5)
C(123)	0.009(2)	0.6294(9)	0.4926(5)	4.3(6)
C(124)	0.129(2)	0.6714(9)	0.5140(5)	3.0(5)
C(125)	0.255(2)	0.6682(9)	0.4886(5)	3.2(5)
C(126)	0.262(2)	0.6231(9)	0.4417(5)	3.0(5)
C(131)	−0.006(2)	0.4944(9)	0.3303(6)	2.5(5)
C(132)	−0.067(2)	0.4182(9)	0.3405(6)	2.6(5)
C(133)	−0.194(2)	0.3951(9)	0.3132(6)	3.9(6)
C(134)	−0.261(2)	0.4482(9)	0.2758(6)	4.9(7)
C(135)	−0.201(2)	0.5244(9)	0.2657(6)	4.8(7)
C(136)	−0.073(2)	0.5475(9)	0.2929(6)	3.1(5)
C(211)	0.344(2)	0.3132(6)	0.5755(5)	1.7(4)
C(212)	0.346(2)	0.3466(6)	0.5244(5)	2.0(4)
C(213)	0.365(2)	0.4310(6)	0.5180(5)	2.4(4)
C(214)	0.383(2)	0.4820(6)	0.5626(5)	2.2(4)
C(215)	0.381(2)	0.4485(6)	0.6136(5)	2.4(4)
C(216)	0.362(2)	0.3642(6)	0.6200(5)	2.0(4)
C(221)	0.479(2)	0.157(2)	0.5798(9)	3.1(5)
C(222)	0.544(2)	0.117(2)	0.6240(9)	7.0(1)
C(223)	0.677(2)	0.081(2)	0.6208(9)	10.0(2)
C(224)	0.745(2)	0.084(2)	0.5732(9)	4.1(6)
C(225)	0.679(2)	0.124(2)	0.5290(9)	11.0(2)
C(226)	0.546(2)	0.160(2)	0.5322(9)	15.0(2)
C(231)	0.249(2)	0.186(1)	0.6455(5)	1.8(4)
C(232)	0.338(2)	0.195(1)	0.6916(5)	5.8(8)
C(233)	0.283(2)	0.191(1)	0.7415(5)	8.0(1)
C(234)	0.138(2)	0.177(1)	0.7454(5)	3.6(5)
C(235)	0.049(2)	0.167(1)	0.6993(5)	4.8(7)
C(236)	0.104(2)	0.172(1)	0.6494(5)	4.2(6)

positional and temperature (B_{iso} = 7 Å^2) parameters. The final refinement was carried out in the anisotropic approximation for the Au, P, and O atoms and the phenyl C atoms of the diphenyl ether and in the isotropic approximation for the phenyl C atoms in the PPh_3 ligands and brought to $R = 0.0534$ and $R_w = 0.0558$ over 2470 reflections with $F \geq 5\sigma(F)$ using the weight scheme $w = 42.788/(\sigma^2 F_0 + 0.000064 F_0{}^2)$. The maximum and minimum residual electron densities on the electron density differential map were 2.06 and −1.16 e/Å^3.

All of the calculations were carried out using SHELX programs on an IBM PC/AT personal computer. The coordinates of the atoms in compounds **1** and **2** are listed in Tables 5 and 6.

Synthesis of compounds 1—3

2-(Triphenylphosphineaurio)diphenyl oxide (1). A solution of the 2,2′-dilithium derivative of diphenyl ether,[7] prepared by the reaction of 5.44 mL (11 mmol) of a 2.0 *N* hexane solution of BuLi in 12 mL of ether with 0.75 g (4 mmol) of diphenyl ether in 6 mL of THF (5 h, 50 °C), was cooled to −20 °C and poured portionwise into a suspension of 2 g (4 mmol) of $ClAuPPh_3$ in 25 mL of THF (until $ClAuPPh_3$ disappeared according to TLC).* The reaction mixture was quenched with 5 mL of water. The organic phase was dried with calcined

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* The yield of the 2,2′-dilithium derivative of diphenyl ether under these conditions was ~50 % (determined in a blank experiment by carboxylation).[7]

K_2CO_3 and evaporated until dry. The residue was dissolved in ~10 mL of THF and diluted with 15 mL of ether and ~20 mL of hexane (this results in the formation of a viscous precipitate). The solvent was separated from the precipitate and evaporated *in vacuo* to dryness. The residue was treated with pentane (3 × 10 mL) and dried to give 2.00 g (80 %) of compound **1**, m.p. 158—159 °C (dec.) after reiterated reprecipitation from a solution in THF with an ether—hexane mixture (1:2). Found (%): C, 57.75; H, 3.84; P, 4.83. $C_{30}H_{24}AuOP$. Calculated (%): C, 57.33; H,3.85; P, 4.93. ^{31}P NMR, δ: 43.45. MS, *m/z* (I_{rel}(%)): 1545 $[M + (AuPPh_3)_2 + H]^+$ (7), 1087 $[M + AuPPh_3 + H]^+$ (10), 721 $[M-PhOPh + PPh_3]^+$ (12), 629 $[M + H]^+$ (19), 628 $[M]^+$ (20), 459 $[M-PhOPh]^+$ (100).

2,2′-Bis(triphenylphosphineaurio)diphenyl oxide (2). A solution of the 2,2′-dilithium derivative of diphenyl ether (prepared from 1.2 mL (2.1 mmol) of a 1.8 *N* hexane solution of BuLi in 4 mL of ether and 0.16 g (9 mmol) of diphenyl ether in 2 mL of THF as described above) was added portionwise to a suspension of 0.5 g (1 mmol) of $ClAuPPh_3$ in 10 mL of THF. The resulting reaction mixture was stirred for 1 h and quenched with water (~5 mL). The organic layer was separated, dried with calcined K_2CO_3 for 5 min, and evaporated *in vacuo* to dryness. The oily residue was treated with ether and pentane and reprecipitated twice from a THF solution with an ether—hexane mixture (1:1) at −20 °C. The resulting solid (0.29 g) was dissolved in 4 mL of $CHCl_3$ and the solution was shaken with a solution of 0.03 g (4.6 mmol) of KCN in 3 mL of water for 2 min. The organic layer was separated,* dried with calcined K_2CO_3, and evaporated *in vacuo* to dryness. The residue was reprecipitated from a THF—ether—hexane (1:1:1) mixture at −20 °C to give 0.10 g (27 %) of compound **2**, m.p. 206—208 °C (dec.). Found (%): C, 53.18; H, 3.69; P, 5.31. $C_{48}H_{38}Au_2OP_2$. Calculated (%): C, 53.18; H, 3.52; P, 5.70. MS, *m/z* (I_{rel}(%)): 1545 $[M + AuPPh_3]^+$ (55), 721 $[M-PhOPh]^+$ (40), and 459 $[M-PhOPh(AuPPh_3)]^+$ (100).

From mother liquors (after the separation of compound **2**), 0.03 g (14 %) of compound **1** was isolated, m.p. 158—159 °C (dec.).

2,2-Bis(triphenylphosphineaurio)diphenyl oxide tetrafluoroborate (3). A solution of $(AuPPh_3)BF_4$ (prepared from 0.2 g (0.4 mmol) of $ClAuPPh_3$ and 0.08 g (0.4 mmol) of $AgBF_4$ in 2 mL of THF) was added dropwise at −40 °C to a solution of 0.25 g (0.4 mmol) of compound **1** in 1 mL of THF. The solution was filtered and added dropwise with stirring to ~20 mL of ether cooled to −50 °C. The precipitate was filtered off, washed with cold ether, and dried *in vacuo* over P_2O_5 to afford 0.27 g (58 %) of compound **3**, m.p. 125—126 °C (dec.). Found (%): C, 49.17; H, 3.31; P, 5.46. $C_{48}H_{39}Au_2BF_4OP_2$. Calculated, (%): C, 49.08; H, 3.35; P, 5.27. IR, ν/cm^{-1}: 1064 (BF_4). ^{31}P NMR, δ: 37.89. MS, *m/z* (I_{rel}(%))**: 1087 $[C + H]^+$ (100), 1546 $[C + AuPPh_3 + H]^+$ (30), 1377 $[C + AuPPh_3-PhOPh]^+$ (10), 841 $[C + H-Au]^+$ (7), 721 [C—PhOPh—Au] (55), 629 $[C + H-AuPPh_3]^+$ (5) and 459 $[C-AuPPh_3]^+$ (53).

The reaction of compound 3 with PPh_3. A solution of 0.025 g (0.09 mmol) of PPh_3 in 2 mL of benzene was added to a suspension of 0.10 g (0.085 mmol) of compound **3** in 3 mL of benzene. The reaction mixture was kept for 26 days at 10 °C. The solvent was removed *in vacuo* and the residue was extracted with cold ether to give 0.05 g (93 %) of compound **1**, m.p. 158—160 °C. The residue after extraction was bis(triphenylphosphine)gold tetrafluoroborate obtained in quantitative yield, m.p. 224—225 °C (from a methanol—hexane mixture).[15]

The authors wish to thank A. L. Blyumenfel'd for recording ^{31}P NMR spectra, D. V. Zagorevskii and K. V. Kazakov who obtained mass spectra, and Yu.L. Slovokhotov who carried out the EXSAFS study.

The study described in the present paper was partly supported by the International Scientific Fund, grant № Ch_1 002479.

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Received May 24, 1993;
in revised form December 28, 1993

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* Concentration of aqueous extracts and subsequent extraction with methyl ethyl ketone affords $K[Au(CN)_2]$, νC≡N 2142 cm^{-1}.[14]

** C is the molecular cation.