Organometallic Chemistry

Hypercoordinated gold(I) compounds
5.* Reactions of complex salts of monovalent gold with bimetallic Li,K derivatives of *o*-cresol and *o*-thiophenol

T. V. Baukova,[a] L. G. Kuz'mina,[b] A. V. Churakov,[b] N. A. Oleinikova,[a] and P. V. Petrovskii[a]*

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085*

[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 117907 Moscow, Russian Federation. Fax: +7 (095) 954 1279*

The reaction of $[O(AuPPh_3)_3]^+BF_4^-$ with a Li,K derivative of *o*-cresol followed by the interaction of the reaction product with CO_2 gave (triphenylphosphine)gold acetate. The reaction of $ClAuPPh_3$ with *o*-LiC_6H_4SLi afforded (triphenylphosphine)gold thiophenoxide. According to the data of X-ray structural analysis, the latter occurs as a dimer formed through an intermolecular secondary Au...Au bond. The reaction of this complex with diazomethane was accompanied by insertion of carbene into the Au—S bond to form a new gold complex, $PhSCH_2AuPPh_3$. The reactions with $PPh_3Au^+BF_4^-$ or HBF_4 yielded a new tetranuclear gold thiocluster, $\{[PhS(AuPPh_3)_2]^{2+}(BF_4^-)\}_2$, which involves Au...Au bonds that differ in strength. The structures of the compounds obtained were established by X-ray structural analysis, ^1H and ^{31}P NMR spectroscopy, and FAB mass spectrometry.

Key words: synthesis, hypercoordinated organogold(I) compounds, (triphenylphosphine)gold thiophenoxide, tetranuclear gold thiocluster, secondary bonds; X-ray diffraction study.

Phosphine-containing hypercoordinated gold(I) σ-complexes in which different types of secondary coordination bonds involving Au atoms (for example, Au...Au, Au...X (X is a heteroatom), Au...H—C (agostic bond), or the Au...π system) occur, are of interest because of their unique structures and properties.[1—8] However, these compounds have not been adequately studied, which hinders the formulation of unified concepts concerning the formation and properties of these compounds.

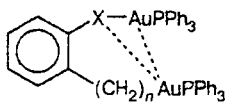
As part of our continuing systematic studies of the chemistry of hypercoordinated gold(I) compounds,[2,8—11] in this work we investigated synthetic approaches to the preparation of a new class of gold

* For Part 4, see *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2244 [*Russ. Chem. Bull.*, 1997, **46**, 2127 (Engl. Transl.)].

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 350—355, February, 1998.

1066-5285/98/4702-0343 $20.00

compounds, namely, binuclear organogold(I) derivatives of *o*-cresol and *o*-thiophenol (of type **A**).



A

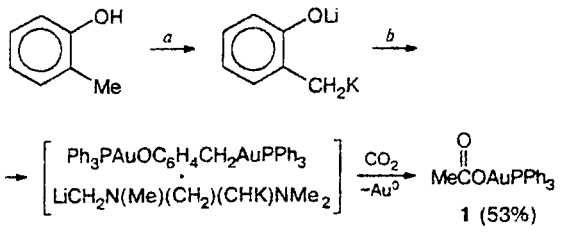
X = O (n = 1), S (n = 0)

These compounds were of interest to us as convenient models for the experimental determination (by means of ^{31}P NMR spectroscopy) of the energy of aurophilic Au...Au interactions. Previously, this energy has been estimated at 6 eV by *ab initio* quantum-chemical calculations.[12] It was suggested that conformational possibilities of binuclear model molecules of type **A** (due to free rotation of substituents about single bonds) are favorable for the formation of intramolecular secondary coordination Au...Au bonds. The presence of these bonds, as in the case of stable (due to the Au...Au bond) *o,o*-bis(triphenylphosphinegold)pyrocatechol,[13] should favor substantial stabilization of presumably unstable phosphine-containing gold complexes of *o*-cresol and thiophenol.

In this work, we studied for the first time the reactions of complex salts of monovalent gold, namely, chloride $ClAuPPh_3$ and tetrafluoroborate $[O(AuPPh_3)_3]^+BF_4^-$, with Li,K derivatives of *o*-cresol and thiophenol (the preparation of these derivatives in high yields has been reported previously[14,15]).

Thus, the reaction of tetrafluoroborate $[O(AuPPh_3)_3]^+BF_4^-$ with the Li,K derivative of *o*-cresol, which has been prepared by successive metallation of *o*-cresol first with the Bu^nLi/TMEDA complex and then with Bu^tOK (see Ref. 14), gave a very unstable digold-containing *o*-cresolate ($Ph_3PAuOC_6H_4CH_2AuPPh_3$) of type **A** as its adduct with a molecule of Li,K-dimetallated tetramethylethylenediamine (TMEDA) $LiCH_2N(Me)(CH_2)(CHK)NMe_2$. The formation of the latter in the reaction agrees with the results of lithiation of other derivatives of the *o*-cresol series with the Bu^nLi/TMEDA complex under analogous conditions.[16] The low-temperature purification of the adduct by repeated reprecipitation from a solution in THF or toluene with petroleum ether under an atmosphere of CO_2 (solutions were cooled with solid carbon dioxide) led to gradual conversion of the adduct into acetate $MeCOOAuPPh_3$ (**1**) accompanied by liberation of metallic gold. In the absence of CO_2 at the stage of purification of the adduct, gold acetate **1** was not formed (Scheme 1).

Scheme 1



Reagents and conditions: *a*. 1) Bu^nLi/TMEDA, 2) Bu^tOK, −50 °C; *b*. $[O(AuPPh_3)_3]BF_4$.

In the reaction under study, it is necessary to use a fivefold excess of the Li,K derivative of *o*-cresol with respect to the aurating agent.

According to the data of elemental analysis, the adduct contains C, H, Au, P, N, Li, and K. The structure of the compound obtained was confirmed by mass spectrometry and IR and ^1H NMR spectroscopy.

The FAB mass spectrum of the adduct has peaks of ions $[CH_2C_6H_4OCH_2(AuPPh_3)_2 + 2H]^+$ at m/z 1040, $[CH_2C_6H_4OCH_2Au(PPh_3)_2]^+$ at m/z 841, and $[CH_2C_6H_4OCH_2AuPPh_3]^+$ at m/z 579. The ^1H NMR spectrum of the adduct (in C_6D_6) shows a complex multiplet of aromatic protons and broadened signals of protons of the CH_3 and CH_2 groups at δ 2.07, 2.20, 2.26, and 2.42.

The structure of compound **1**, which was prepared in this work by a new procedure, was confirmed by X-ray structural analysis. In the $MeCOOAuPPh_3$ molecule, the Au^I atom has a standard linear O—Au—P coordination. The Au—O and Au—P bond lengths are 2.02(2) and 2.205(9) Å, respectively. The angle at the Au atom is 178.5(7)°. The geometric parameters of gold acetate **1** synthesized by us correspond to the values reported in Ref. 17.

The formation of gold acetate **1** in this reaction cannot be unambiguously rationalized. However, by analogy with the published data, it can be suggested that the key step is the reaction of the adduct $[Ph_3PAuOC_6H_4CH_2AuPPh_3 \cdot LiCH_2N(Me)(CH_2)(CHK)NMe_2]$ with CO_2.

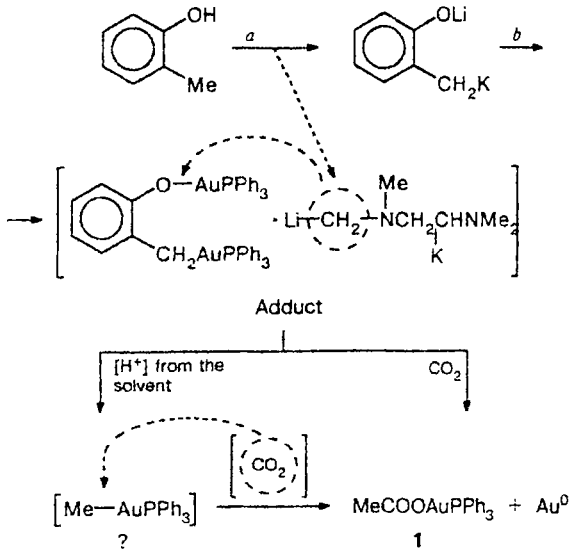
It is known that CO_2 can react with various compounds of metals (Ti, Zr, Rh, Co, Cu, Ag, and Zn) to form both rather stable and unstable molecular complexes. In addition, the CO_2 molecule can be inserted into the C—M and M—H bonds[18] to form carboxylates of transition metals. For example, $Me—Cu(PPh_3)_2$ was converted to $MeCOOCu(PPh_3)_2$ at −40 °C under atmospheric pressure.[19] However, the analogous organogold compound, $Me—AuPPh_3$, does not react with small molecules (CO, CO_2, and CS_2).[20]

Taking into account the facts that the O—Au bond in gold phenoxides is labile[21] and that the insertion of carbene into S—Au bonds[22,23] as well as the insertion of small molecules (including CO_2) into C—M σ-bonds[18–20] proceed readily, the following scheme of formation of gold acetate **1** seems to be the most probable (Scheme 2).

Under the reaction conditions, the methylene CH_2 group of the $LiCH_2N$ fragment of the adduct, which exhibits the carbenoid character (according to the data of X-ray structural analysis)[16] and which can be inserted into the O—Au bond of the adduct, can be the source of the Me group in acetate **1**.

Note that the similar Kolbe—Schmidt reaction, namely, carboxylation of phenoxides of alkali metals with carbon dioxide, proceeded under substantially more

Scheme 2



Reagents and conditions: *a*. 1) Bu^{n}Li/TMEDA, 2) Bu^{t}OK, −50 °C; *b*. $[O(AuPPh_3)_3]BF_4$, −60 °C, Ar.

drastic conditions (upon heating and at high pressure of CO_2).[24]

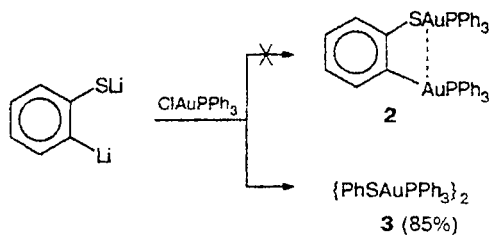
In this work, we studied the reaction of $ClAuPPh_3$ with the dilithium derivative of thiophenol *o*-LiC_6H_4SLi (the latter has been prepared in high yield by the reaction of thiophenol with a Bu^{n}Li/TMEDA complex in cyclohexane according to a known procedure[15]). However, we failed to synthesize a compound of type **A**, namely, the *o*-$Ph_3PAuC_6H_4SAuPPh_3$ complex (**2**), by this method.

The reaction gave the mononuclear (in the crystal, it occurs as a dimer) (triphenylphosphine)gold thiophenoxide (**3**) in high yield. The course of the reaction remained unchanged as the reaction conditions and, in particular, the ratio of the reagents, were changed.

Previoulsy, gold thiophenoxide $PhSAuPPh_3$ was synthesized by the reaction of PhSNa with $ClAuPPh_3$[25] or by the reaction of thiophenol with $MeAuPPh_3$.[26] The molecular weight determination[25] has shown that the compound occurs as a monomer in a solution ($CHCl_3$). The crystal structure of thiophenoxide $PhSAuPPh_3$ has not been studied previously. According to the data of X-ray structural analysis,[27] in the crystal, (triphenylphosphine)gold *p*-nitrothiophenoxide occurs as a monomer.

X-ray diffraction study of gold thiophenoxide **3**, which was synthesized in this work, demonstrated* that in the crystal its dimeric molecule (Fig. 1) is formed through an intermolecular aurophilic Au...Au interaction at a distance of 3.14 Å. Usually, the distances that

Scheme 3



correspond to these interactions vary in the range of 2.7—3.4 Å.[28] The observed mutually staggered arrangement of the linear S—Au—PPh_3 fragments of the molecules of gold thiophenoxide **3** in the dimer corresponds to the C_2 symmetry. The S(1)—Au(1)...Au(2)—S(2) pseudotorsion angle is 96°. An analogous staggered arrangement of two linear X—Au—PPh_3 fragments (where X is a heteroatom or the C atom) was observed in all dimeric derivatives of gold(I) formed through an aurophilic interaction. Such arrangement was also predicted by *ab initio* quantum-chemical calculations.[29] Apparently, it is a necessary condition for the existence of both intra- and intermolecular secondary Au...Au bonds.

It was found that two crystallographically independent monomeric $PhSAuPPh_3$ molecules, which are linked in dimer **3**, differ in the orientation of the phenol rings of the triphenylphosphine ligands. The lengths of the Au—S (2.304 and 2.308 Å) and Au—P (2.267 and 2.265 Å) bonds in two independent molecules of complex **3** have close values and vary within narrow ranges most typical of the corresponding bond lengths.

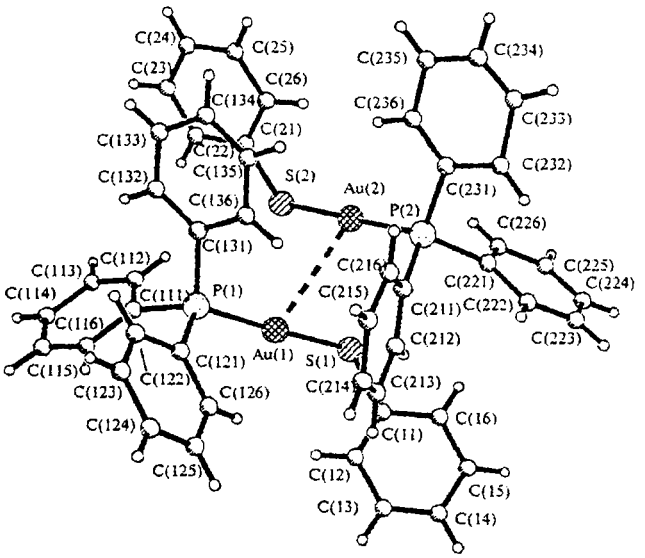
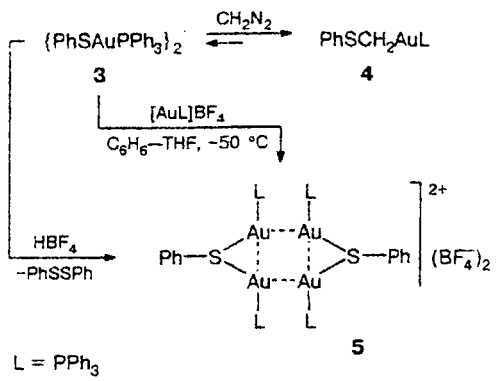


Fig. 1. Structure of the $\{PhSAuPPh_3\}_2$ dimer (**3**) in the crystal.

* The complete data of X-ray diffraction study of complexes **3** and **5** will be published elsewhere.

Scheme 4



The FAB mass spectrum of complex **3** has the molecular ion peak of one $PhSAuPPh_3$ molecular unit at m/z 568 and the peak of a substantially heavier ion $[Ph(SAuPPh_3)_3 + H]^+$ at m/z 1486 as well as peaks of ions of fragmentation products.

The reaction of compound **3** with diazomethane was accompanied by insertion of carbene into the Au—S bond to form a new organogold complex $PhSCH_2AuPPh_3$ (**4**) (Scheme 4).[21] The insertion of carbene into the Au—S bond was first exemplified by the reaction of diazomethane with a cyclic complex, which contains mercury and gold.

The reaction was slow and did not proceed to completion. Under the optimum conditions (monitoring by ^{31}P NMR spectroscopy), the **3** : **4** ratio was 1 : 3.5. We failed to separate these compounds because they are almost equally soluble in organic solvents and are not sufficiently stable in solutions. The presence of gold thiophenoxide **3** did not hinder the identification of complex **4** in the mixture by FAB mass spectrometry and ^1H and ^{31}P NMR spectroscopy.

The mass spectrum of the product of the reaction of complex **3** with diazomethane contains the molecular ion peaks $[PhSAuPPh_3]^+$ (m/z 568) and $[PhSCH_2AuPPh_3]^+$ (m/z 582) as well as peaks of ions corresponding to the products of their successive fragmentation.

The ^1H NMR spectrum of the obtained mixture of complexes **3** and **4** has a doublet signal of the CH_2 group of compound **4** at δ 2.77 ($^3J_{^1H-^{31}P}$ = 7.5 Hz) in addition to a complex multiplet of aromatic protons. The ^{31}P NMR spectrum contains two signals corresponding to complex **3** (δ 37.99) and complex **4** (δ 43.79). The ratio of integrated intensities of the signals is 1 : 3.5.

We have studied for the first time reactions of compound **3** with a coordinatively unsaturated gold complex, namely, tetrafluoroborate $[Ph_3PAu]^+BF_4^-$, which was prepared *in situ* from $ClAuPPh_3$ and $AgBF_4^-$, and with HBF_4. Both reactions afforded a new tetranuclear hypercoordinated gold complex of the sulfonium type, which has a cluster structure, $[PhS(AuPPh_3)_2]_2^{2+}(BF_4^-)_2$ (**5**). When HBF_4 was used, the synthesis of complex **5** occurred with the cleavage of the S—Au bond in the initial compound **3**. In this case, the second reaction product was diphenyl disulfide. Complex **5** is a colorless crystalline compound, which is moderately stable at room temperature and is soluble in $CHCl_3$, THF, and C_6H_6. The complex was characterized by IR and ^{31}P NMR spectroscopy and FAB mass spectrometry. The structure of **5** was established by X-ray diffraction analysis.

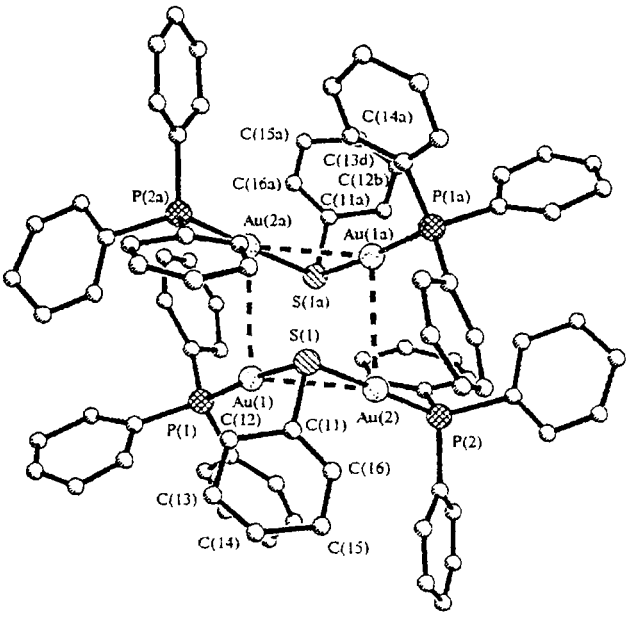


Fig. 2. Structure of the dication of the tetranuclear cluster $[PhS(AuPPh_3)_2]_2$ (**5**).

According to X-ray diffraction study, there are four crystallographically independent molecules of the tetranuclear S-containing gold cluster **5**, which differ in the angles of rotation of the Ph rings of both the Ph—S—Au fragments and of the PPh_3 ligands.

One crystallographically independent structural unit is a centrosymmetrical tetranuclear gold cluster **5** in which two $PhS(AuPPh_3)_2$ monomeric units are linked to each other through two aurophilic interactions (Fig. 2). In the electron-deficient triangular SAu_2 fragment, the angles at the sulfur atom (Au—S—Au) are 79.4, 80.7, 81.1, and 85.4° in four independent molecules, respectively. The Au...Au distances are 2.685, 2.676, 2.766, and 2.775 Å, respectively. The Au...Au distances between the SAu_2 monomeric units in cluster **5** are somewhat larger (3.148, 3.140, 3.150, and 3.118 Å, respectively).

Experimental

The ^1H NMR spectra were recorded on a Bruker WP-200 SY spectrometer (200 MHz, Me_4Si as the internal standard).

The ^{31}P NMR spectrum was obtained on a Bruker CXP 200 instrument (81 MHz, H_3PO_4 as the external standard). The mass spectrum was measured on a Kratos Concept instrument; the energy of bombarding atoms (Cs) was 8 keV; 3-nitrobenzyl alcohol was used as the matrix.

Reaction of an *o*-cresol Li,K derivative with $[O(AuPPh_3)_3]^+BF_4^-$ and synthesis of $MeCOOAuPPh_3$ (1). A cooled suspension of $LiOC_6H_4CH_2K$-*o* in hexane (the organometallic compound was prepared from TMEDA [3.1 mL, 5.70 mmol), *o*-cresol (0.31 g, 2.85 mmol), and Bu^tOK (0.60 g, 5.70 mmol) in anhydrous hexane (10 mL) according to a procedure reported in Ref. 14] was added portionwise with intense stirring to a suspension of $[O(AuPPh_3)_3]^+BF_4^-$ (0.70 g, 0.47 mmol) (see Ref. 30) in anhydrous THF (30 mL) at −60 °C under an atmosphere of argon. The reaction mixture was stirred at −30 °C for 4 h. The resulting solution was decomposed with water (~5 mL) (liberation of metallic gold was observed). The organic layer was separated, dried with two portions of calcined K_2CO_3 for 10 min, and concentrated to dryness *in vacuo*. The residue was treated with cold ether (3×10 mL) at −60 °C and twice reprecipitated with pentane from a solution in tetrahydrofuran at −60 °C. The powdered sand-colored product thus obtained was dried *in vacuo* over P_2O_5. Found (%): C, 48.53; H, 3.66; K, 2.08; Li, 0.56; N, 1.58; P, 5.45. $[Ph_3PAuOC_6H_4CH_2AuPPh_3\times$ $\times LiCH_2N(Me)(CH_2)(CHK)NMe_2)](C_{49}H_{50}Au_2KLiN_2OP_2)$. Calculated (%): C, 49.67; H, 4.25; K, 3.30; Li, 0.59; N, 2.36; P, 5.23. The compound melted above 85 °C (with decomp.). Hydrolysis of the compound afforded TMEDA. MS, *m/z* (I_{rel} (%)): 1498 $[C_6H_4O(CH_2)_2(AuPPh_3)_3]^+$ (10), 1038 $[C_6H_4O(CH_2)_2(AuPPh_3)_2]^+$ (40), 841 $[C_6H_4O(CH_2)_2Au(PPh_3)_2]^+$ (70), 721 $[Au(PPh_3)_2]^+$ (80), 459 $[AuPPh_3]^+$ (40). ^1H NMR (acetone-d_6), δ: 2.01 (br.s); 2.10 (br.s, substituted TMEDA); 2.86 (s, 2 H, CH_2); 6.50—7.50 (m, aromatic protons).

The compound obtained was purified by repeated reprecipitations under an atmosphere of CO_2 first with hexane from a solution in tetrahydrofuran, then with pentane from a solution in toluene, and, finally, with pentane from a solution in CH_2Cl_2 (the solutions were cooled externally with solid CO_2). $MeCOOAuPPh_3$ was obtained as a colorless crystalline compound in a yield of 0.39 g (53% calculated with respect to Au), m.p. 175—177 °C (*cf.* the published data: m.p. >170 °C (with decomp.)[31]; m.p. 185—186 °C [32]). Found (%): C, 46.51; H, 3.57; P, 5.38. $C_{20}H_{18}AuO_2P$. Calculated (%): C, 46.34; H, 3.50; P, 5.98. The IR spectrum of acetate **1** agrees with that reported previously.[32] ^1H NMR (C_6D_6), δ: 2.47 (s, 3 H, CH_3); 6.90—7.40 (m, 15 H, aromatic protons). MS, *m/z* (I_{rel} (%)): 518 $[MeCOOAuPPh_3]^+$ (10).

Reaction of *o*-LiC_6H_4SLi with $ClAuPPh_3$ (synthesis of $\{PhSAuPPh_3\}_2$ (3)). A suspension of *o*-LiC_6H_4SLi [prepared from thiophenol (0.17 mL, 1.6 mmol), a 2.86 *M* Bu^nLi solution in hexane (1.26 mL, 3.6 mmol), and TMEDA (0.52 mL, 3.6 mmol) in cyclohexane (4 mL) according to a known procedure[15]] was added portionwise to a suspension of $ClAuPPh_3$ (1 g, 2.0 mmol) in THF (8 mL) cooled to 0 °C. The reaction mixture was stirred at 0 °C for 2 h (the course of the reaction was monitored by TLC on Silufol plates in benzene; R_f $ClAuPPh_3$ = 0.4). Then the solution was added dropwise with intense stirring to ice water (200 mL). The precipitate that formed was filtered off, washed with ice water (3×10 mL), and dried. After reprecipitation with petroleum ether from a benzene solution, compound **3** was obtained as a yellow powder in a yield of 1.08 g (85%), m.p. 152—154 °C (with decomp.) (*cf.* the published data: m.p. 161—162 °C (with decomp., from $CHCl_3$)[25]; m.p. 154—156 °C (with decomp., from CH_2Cl_2—isopentane)[26]). Found (%): C, 50.71; H, 3.47; P, 5.74; S, 5.55. $C_{48}H_{40}Au_2P_2S_2$. Calculated (%): C, 50.71; H, 3.54; P, 5.45; S, 5.64. IR (Nujol mulls), ν/cm^{-1}: 330 (Au—S). ^1H NMR (C_6D_6), δ: 6.75—8.18 (m, aromatic protons). ^{31}P NMR (C_6D_6), δ: 38.20 (s). MS, *m/z* (I_{rel} (%)): 1486 [M* + $2AuPPh_3]^+$ (10), 1377 $[(AuPPh_3)_3]^+$ (3), 1334 [2M + Au + H]$^+$ (40), 1224 [M + $AuPPh_3$ + Au]$^+$ (5), 1028 [M + $AuPPh_3$ + H]$^+$ (100), 1027 [M + $AuPPh_3$]$^+$ (90), 765 [M + Au] (10), 721 $[Au(PPh_3)_2]^+$ (70), 569 [M + H]$^+$ (20), 568 [M]$^+$ (30), 459 $[AuPPh_3]^+$ (80).

Reaction of $\{PhSAuPPh_3\}_2$ (3) with diazomethane. A solution of diazomethane [prepared from nitrosomethylurea (3.0 g, 29 mmol) and a 40% aqueous solution of KOH (14.4 mL) according to a known procedure[33]] in ether (100 mL) was added with stirring to a solution of compound **3** (0.60 g, 1.05 mmol) in anhydrous benzene (15 mL) at 0 to −5 °C. The reaction mixture was stirred at ~0 °C for 3 days. The course of the reaction was monitored daily by ^{31}P NMR spectroscopy [a sample of the reaction mixture (~10 mL) was concentrated to dryness, the residue was dissolved in chloroform, and the ^{31}P NMR spectrum was recorded; then the solvent was distilled off and the compound was dissolved in a 1 : 1 benzene—ether mixture (10 mL) and added to the reaction mixture]. The reaction mixture was concentrated to dryness *in vacuo*. The residue was washed with a 1 : 1 ether—pentane mixture (3×4 mL), twice reprecipitated with petroleum ether from a benzene solution, and dried. A powder-like beige compound was obtained in a yield of 0.37 g. Found (%): C, 50.98; H, 3.61; P, 5.62. ^1H NMR ($CDCl_3$), δ: 2.77 (d, CH_2, $^2J_{P-H}$ = 7.5 Hz); 7.00—7.75 (m, Ph). ^{31}P NMR ($CDCl_3$), δ: 37.99 (s), 43.79 (s), the ratio of integrated intensities of the signals is 1 : 3.5.

Reaction of $\{PhSAuPPh_3\}_2$ (3) with (triphenylphosphine)gold tetrafluoroborate $[AuPPh_3]^+BF_4^-$ (synthesis of $[PhS(AuPPh_3)_2]_2^{2+}(BF_4^-)_2$ (5)). A solution of $[AuPPh_3]^+BF_4^-$ (prepared from $ClAuPPh_3$ (0.15 g, 0.3 mmol) and $AgBF_4$ (0.07 g, 0.35 mmol)) in THF (5 mL) was added with stirring to a solution of compound **3** (0.17 g, 0.3 mmol) in benzene (3 mL) at 10 °C. The resulting solution was added dropwise with intense stirring to ether (100 mL) cooled to −40 °C. The solid precipitate that formed was filtered off, washed with cold ether and pentane, and dried. After precipitation with an ether—pentane mixture from a solution in a 1 : 1 benzene—THF mixture, $[PhS(AuPPh_3)_2]_2^{2+}(BF_4^-)_2$ was obtained in a yield of 0.17 g (97%), m.p. 136—137 °C (with decomp.). Found (%): C, 45.21; H, 3.17; P, 5.48; S, 3.20. $C_{42}H_{35}Au_2BF_4P_2S$. Calculated (%): C, 45.26; H, 3.17; P, 5.56; S, 2.88. IR (Nujol mulls), ν/cm^{-1}: 1064 (BF_4). ^{31}P NMR (CH_2Cl_2), δ: 35.51 (s). MS, *m/z* (I_{rel} (%)): 1485 [C** + $AuPPh_3$ − H]$^+$ (10), 1377 [C − PhS + $AuPPh_3$]$^+$ (5), 1334 [C + PhS +Au + H]$^+$ (40), 1224 [C + Au]$^+$ (15), 1028 [C + H]$^+$ (90), 1027 [C]$^+$ (100), 917 [C − PhS − H]$^+$ (10), 721 [C − PhS − Au]$^+$ (50), 569 [C − $AuPPh_3$ + H]$^+$ (25), 568 [C − $AuPPh_3$]$^+$ (30), 459 $[AuPPh_3]^+$ (17).

Complex **5** is a colorless crystalline compound, which is moderately stable in solutions, soluble in benzene, THF, and chloroform, and insoluble in ether, petroleum ether, and water.

Reaction of $\{PhSAuPPh_3\}_2$ (3) with HBF_4. A 1 *M* ethereal solution of HBF_4 was added with intense stirring to a solution of compound **3** (0.12 g, 0.2 mmol) at −70 °C until liberation of a precipitate ceased. The precipitate was separated, washed with cold ether (2×10 mL), and dried. Compound **5** was obtained in a yield of 0.10 g (99%), m.p. 136—137 °C (with

* M is the molecular ion $[PhSAuPPh_3]$.

** C is the molecular cation $[PhS(AuPPh_3)_2]^+$.

decomp.) (after reprecipitation with petroleum ether from a solution in CH_2Cl_2). The mother liquor was concentrated to dryness. Diphenyl disulfide was obtained in a yield of 0.02 g (99%), m.p. 59—60 °C (from CH_2Cl_2—hexane) (*cf.* the literature data:[34] m.p. 59.5—60.5 °C).

We thank D. V. Zagorevskii for recording the FAB mass spectra.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-08616a).

References

1. L. G. Kuz'mina, Dr. Sc. (Chem.) Thesis, N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 1990, 394 pp. (in Russian).
2. T. V. Baukova, Dr. Sc. (Chem.) Thesis, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 1996, 24 (in Russian).
3. S. Gambarotta, B. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1305.
4. L. G. Kuz'mina, *Zh. Neorg. Khim.*, 1993, **38**, 994 [*Russ. J. Inorg. Chem.*, 1993, **38** (Engl. Transl.)].
5. H. Schmidbaur, W. Graf, and G. M. G. Vuller, *Angew. Chem., Int. Ed. Engl.*, 1998, **27**, 417.
6. H. Schmidbaur, F. P. Gabbai, A. Schiede, and J. Riede, *Organometallics*, 1995, **14**, 4969.
7. T. V. Baukova, Yu. L. Slovokhotov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1981, **221**, 375.
8. T. V. Baukova, N. A. Oleinikova, D. A. Lemenovskii, and L. G. Kuz'mina, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 729 [*Russ. Chem. Bull.*, 1994, **43**, 681 (Engl. Transl.)].
9. T. V. Baukova, V. P. Dyadchenko, N. A. Oleinikova, D. A. Lemenovskii, and L. G. Kuz'mina, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1125 [*Russ. Chem. Bull.*, 1994, **43**, 1063 (Engl. Transl.)].
10. T. V. Baukova, L. G. Kuz'mina, N. A. Oleinikova, and D. A. Lemenovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2032 [*Russ. Chem. Bull.*, 1995, **44**, 1952 (Engl. Transl.)].
11. T. V. Baukova, L. G. Kuz'mina, N. A. Oleinikova, D. A. Lemenovskii, and A. L. Blumenfel'd, *J. Organometal. Chem.*, 1997, **530**, 27.
12. J. Li and P. Pyykko, *Inorg. Chem.*, 1993, **32**, 2630.
13. L. G. Kuz'mina, N. V. Dvortsova, M. A. Porai-Koshits, E. I. Smyslova, and K. I. Grandberg, *Metalloorg. Khim.*, 1989, **2**, 1179 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
14. H. Andringa and H. D. Verkrnijsse, *J. Organomet. Chem.*, 1990, **393**, 417.
15. G. D. Fignly, C. K. Loop, and J. C. Martin, *J. Am. Chem. Soc.*, 1989, **111**, 654.
16. H. Harder and M. Lutz, *Organometallics*, 1994, **13**, 5173.
17. L. G. Kuz'mina, *Zh. Neorg. Khim.*, 1993, **38**, 990 [*Russ. J. Inorg. Chem.*, 1993, **38** (Engl. Transl.)].
18. I. S. Kolomnikov and M. Kh. Grigoryan, *Usp. Khim.*, 1978, **47**, 603 [*Russ. Chem. Rev.*, 1978, **47** (Engl. Transl.)].
19. A. Miyashito and A. Yamamoto, *J. Organomet. Chem.*, 1973, **49**, 157.
20. A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1977, 1384.
21. E. G. Perevalova, K. I. Grandberg, E. I. Smyslova, Yu. T. Struchkov, L. G. Kuz'mina, D. N. Kravtsov, and T. I. Voevodskaya, *Koord. Khim.*, 1989, **15**, 504 [*Sov. J. Coord. Chem.*, 1989, **15** (Engl. Transl.)].
22. S. Wang and J. P. Fackler, *Organometallics*, 1989, **8**, 1578.
23. A. N. Nesmeyanov, E. G. Perevalova, E. I. Smyslova, V. P. Dyadchenko, and K. I. Grandberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 2610 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26**, 2417 (Engl. Transl.)].
24. K. V. Vatsuro and G. L. Mishchenko, *Imennye reaktsii v organicheskoi khimii* [*Name Reactions in Organic Chemistry*], Nauka, Moscow, 1976, 221 (in Russian).
25. C. Kowala and I. M. Swan, *Aust. J. Chem.*, 1966, **19**, 547.
26. A. Johnson and R. J. Puddephat, *J. Chem. Soc., Dalton Trans.*, 1975, 115.
27. L. G. Kuz'mina, N. V. Dvortsova, O. Yu. Burtseva, M. A. Porai-Koshits, E. I. Smyslova, and K. I. Grandberg, *Metalloorg. Khim.*, 1990, **3**, 364 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
28. P. G. Jones, *Gold Bull.*, 1986, **19**, 46.
29. P. Pyykko and Y. Zhao, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 604.
30. A. N. Nesmeyanov, E. G. Perevalova, D. A. Lemenovskii, V. P. Dyadchenko, and K. I. Grandberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1661 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23** (Engl. Transl.)].
31. E. G. Perevalova, K. I. Grandberg, E. I. Goryunov, and T. V. Baukova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 2148 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1970, **19**, 2031 (Engl. Transl.)].
32. D. I. Nichols and A. S. Charleston, *J. Chem. Soc. (A)*, 1969, **17**, 2581.
33. *Organikum: organisch-chemisches Grundpraktikum*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1976.
34. H. Lecher, *Ber.*, 1920, **53**, 585.

Received June 26, 1997;
in revised form October 10, 1997