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The Quest for Complexes with a Coordinative Gold−Bismuth Bond

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In attempts to prepare gold(I) bismuthine compounds of the type $R_3Bi{-}AuX$ with a coordinative Au−Bi bond, the complexes $(C_4H_8S)AuCl$, $(Me_2S)AuCl$, $(C_4H_8S)AuC_6F_5$, $(Ph_3P)AuCl$, and $[(Ph_3P)Au]BF_4$ were reacted with the tertiary bismuthines Me_3Bi, $MePh_2Bi$, Ph_3Bi, $(2\text{-}MeO\text{-}C_6H_4)_3Bi$, and $(2\text{-}Me_2NCH_2\text{-}C_6H_4)_3Bi$ in different molar ratios in dichloromethane at low temperatures. In all reactions the bismuthines acted as alkylating or arylating agents for gold to give organogold complexes. The products with the sulfur ligands were generally unstable and decomposed above −50 °C. With phosphine ligands, the organogold(I) complexes can be traced in the reaction mixtures by NMR spectroscopy. The primary product $(Ph_3P)AuPh$ is aurated further by $[(Ph_3P)Au]BF_4$ to give $C_6H_5[Au(PPh_3)]_2BF_4$. A stable dinuclear arylgold complex was obtained in the reactions of the thioether complexes with tris(2-((dimethylamino)methyl)phenyl)bismuthine, and the structure of this 10-membered metallacyclic compound has been determined: $[-Au-C_6H_4CH_2NMe_2-]_2$. The molecules feature strong transannular aurophilic interactions. The crystal structure of tris(2-methoxyphenyl)bismuthine has also been determined.

Introduction

Tertiary *phosphines,* R_3P, are the most widely employed ligands in late-transition-metal chemistry.[1] In contrast, the coordination chemistry with tertiary *arsines*, R_3As, and *stibines* R_3Sb is much less developed,[2] even though the introduction of these ligands may have certain advantages, regarding in particular the stereochemistry and the trans influence or trans effect in their complexes.[3] Finally, tertiary *bismuthines* R_3Bi were only rarely used as donor components in any donor/acceptor complexes,[2] and less than half a dozen coordination compounds have been fully characterized.[4−6]

In the course of extensive studies in the molecular and supramolecular chemistry of gold(I) complexes, we have investigated a large number of prototypes with tertiary amines, phosphines, and arsines mainly of the general formula $(R_3E)AuX$ with E = N, P, As and X = (pseudo)halide, alkoxide, siloxide, mercaptide, etc.[7,8] A literature survey has shown that the number of related compounds with tertiary stibines is very small indeed[2,9−11] and that no gold(I) complex with a tertiary bismuthine ligand—featuring a discrete Au−Bi donor/acceptor bond—has ever been reported. There is generally a paucity of data on gold−bismuth compounds other than binary or polynary alloys.[12]

In the present study we have therefore probed a series of seemingly straightforward synthetic pathways which could lead to gold(I) bismuthine complexes. It was expected that compounds with an Au−Bi donor/acceptor bond should exhibit properties very different from those of the N, P, As, and Sb analogues, owing (a) to the unique character of the bismuth atom as the most electropositive group V element, (b) to the large atomic radius of the heaviest stable element in the periodic table, and (c) to strong relativistic effects.

Our attempts to prepare a complex of the type $(R_3Bi)AuX$ were not successful. All pertinent reactions took a different course, but from the nature of the products the true reactivity pattern could be elucidated. It turned out that tertiary bismuthines are powerful alkylating or arylating agents for gold(I). Any bismuthine complex intermediate which may be generated will immediately be subject to heterolytic Bi−C cleavage and Au−C bond formation with concomitant Au−Bi separation. Tertiary bismuthines R_3Bi thus are genuine organometallic reagents comparable in their mode of reactivity to Grignard, organolithium, or organozinc compounds, which are all known to alkylate or arylate gold(I) complexes.[7]

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Results and Discussion

Synthesis. The most common standard reagents for the preparation of gold(I) complexes of the type L−Au−X were used, including (tetrahydrothiophene)gold chloride, (tht)AuCl, (dimethyl sulfide)gold chloride, $(Me_2S)AuCl$, pentafluorophenyl(tetrahydrothiophene)gold, $(tht)AuC_6F_5$, (triphenylphosphine)gold chloride, $(Ph_3P)AuCl$, and (triphenylphosphine)gold tetrafluoroborate, $(Ph_3P)Au^+BF_4^-$. The bismuth components were trimethyl-, diphenylmethyl-, triphenyl-, tris(2-methoxyphenyl)- and tris-(2-((dimethylamino)methyl)phenyl)bismuthine. The reactions were generally carried out under very mild conditions (−78 to −50 °C, inert gas blanket, protection against light) to minimize thermal and photochemical decomposition. The bismuthines were used in stoichiometric quantities (1:1) or in large excess (e.g. 1:4). Even so, most experiments led to extensive decomposition, as noted from the formation of deep purple colloids in solution followed by the appearance of black precipitates containing almost all of the heavy metal (Au, Bi) introduced into the reaction mixture.

The reaction of (tht)AuCl with $BiPh_3$ (1:4, 1:2, and 1:1) may serve as an example: at room temperature and in CD_2Cl_2 as a solvent, immediate decomposition was observed, while at −78 °C a yellow color developed which turned to deep purple with formation of a dark precipitate upon removal of the solvent. Attempts made with $MePh_2Bi$ gave similar results. If the temperature did not exceed −50 °C, the dark products could be redissolved in CD_2Cl_2. These solutions showed ^1H NMR resonances that could be assigned to (tht)AuPh in both cases, but the products could not be isolated, owing to the limited stability.

When $(Me_2S)AuCl$ was introduced instead of (tht)-AuCl and treated with $BiPh_3$, $BiPh_2Me$, or $Bi(C_6H_4OMe\text{-}2)_3$, the results indicated the formation of thermally unstable $(Me_2S)AuPh$ or $(Me_2S)Au(C_6H_4OMe\text{-}2)$, respectively. The above reactions are therefore formulated as arylation reactions (Scheme 1) which leave the corresponding diarylbismuth chlorides Ar_2BiCl as byproducts.

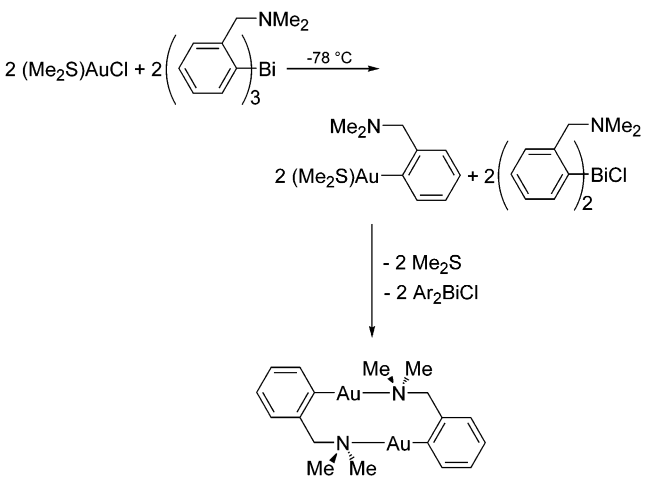
Scheme 1

$$(Me_2S)AuCl + Ar_2RBi \xrightarrow{-78\ °C} (Me_2S)AuAr + ArRBiCl$$

It was only the reaction of $(Me_2S)AuCl$ with equimolar quantities of $Bi(C_6H_4CH_2NMe_2\text{-}2)_3$ that led to a stable product, which was identified as $[-Au-(C_6H_4CH_2NMe_2\text{-}2)-]_2$. This compound (melting point 119 °C) was obtained previously using the corresponding lithium reagent and (triphenylarsine)gold chloride, (Ph_3As)-AuCl,[13] but its structure had not been determined. It appears that in this reaction (Scheme 2) the arylbismuth compound again acts as an arylating agent (like an aryllithium compound), but the amino group of the side chain is then able to substitute the thioether of a neighboring molecule with ring closure.

The same product was obtained from the reaction of tris(2-((dimethylamino)methyl)phenyl)bismuth with (tht)-AuC_6F_5 in dichloromethane at −78 °C.

Scheme 2



It should be noted that analogous reactions with $SbPh_3$ are known to give a stable 1:4 complex, $[Au(SbPh_3)_4]^+X^-$.[9,11] The corresponding bismuth compounds have never been observed in any of the above experiments.

The arylation products generated from (thioether)gold chlorides are all inherently unstable because of the poor ligand properties of the R_2S donor molecules. In contrast, (phosphine)gold alkyls and aryls are known to be stable compounds.[7] In subsequent experiments, therefore, $(R_3P)AuCl$ complexes were also employed as reagents for R_3Bi substrates. The reaction of $(Ph_3P)AuCl$ with $BiPh_2Me$ in dichloromethane at −78 °C was found to be very slow, while upon warming to room temperature it led to decomposition. Only small amounts of $(Ph_3P)AuPh$ were detected in the reaction mixture by NMR spectroscopy.

To enhance the reactivity of the gold complex, the chloride was converted into the tetrafluoroborate by metathesis with $AgBF_4$ to produce $[(Ph_3P)Au]^+BF_4^-$ (in dichloromethane at −78 °C). These solutions reacted rapidly with $BiMe_3$, $BiPh_2Me$, and $BiPh_3$, but only the bismuthines containing phenyl groups gave a stable arylation product, which was identified as $\{C_6H_5[Au(PPh_3)]_2\}^+BF_4^-$ by NMR spectroscopy and mass spectrometry. From the reaction mixture obtained with $BiMe_3$ only $[Au(PPh_3)_2]BF_4$ could be isolated as a decomposition product (Scheme 3).

The results show that the triorganobismuthines R_3-Bi perform as organylating agents for the strong acceptor $[(Ph_3P)Au]^+BF_4^-$, but the primary products of the type $(Ph_3P)AuR$ are aurated further by the excess of the gold component.[14] This leads to decomposition in the gold methyl case but to a stable product for the gold phenyl case.

Structural Studies. In the course of the present investigations two structures have been determined in order to support the assignments based on analytical and spectral data for one arylgold and one arylbismuth compound.

Crystals of $[Au(C_6H_4CH_2NMe_2\text{-}2)]_2$ are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units (two dimers) in the unit cell. The dinuclear molecules were found to

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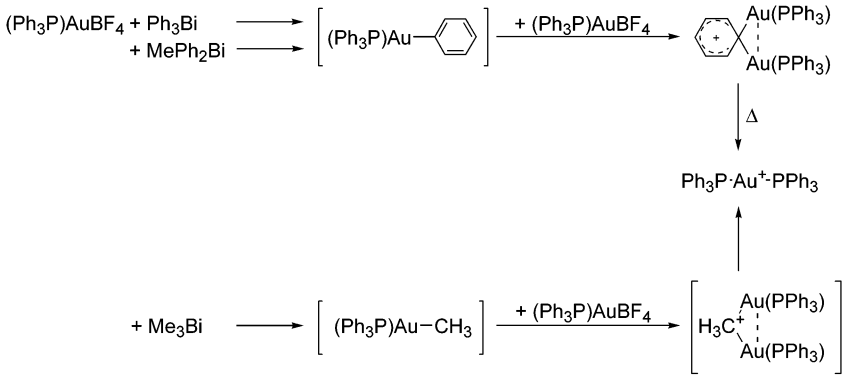
Scheme 3



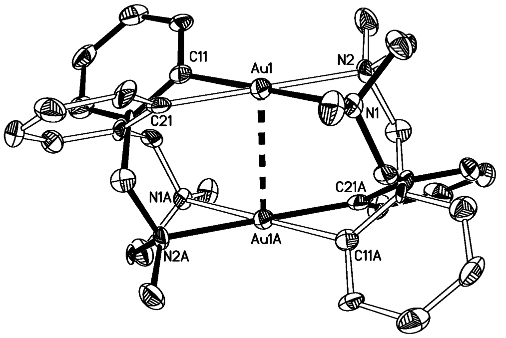


Figure 1. Disordered molecular structure of the compound $[Au(C_6H_4CH_2NMe_2\text{-}2)]_2$ (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity; sof 50/50). Selected bond lengths (Å) and angles (deg): Au1−N1 = 2.152(10), Au1−C11 = 2.042(15), Au1−N2 = 2.1371(2), Au1−C21 = 2.034(14), Au1⋯Au1A = 2.9176(5); N1−Au1−C11 = 179.7(5), N2−Au1−C21 = 179.4(4).

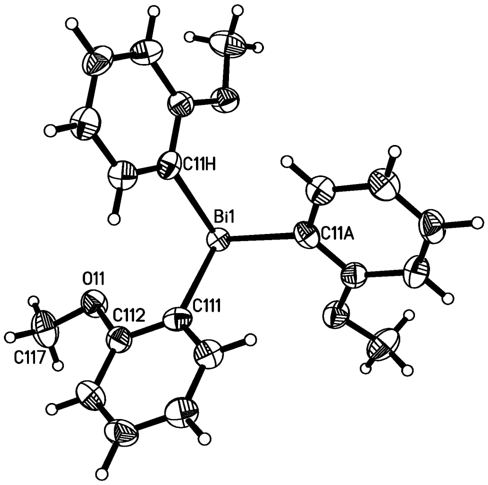


Figure 2. Molecular structure of the compound $Bi(C_6H_4\text{-}OMe\text{-}2)_3$ (ORTEP drawing with 50% probability ellipsoids; only one of the two crystallographically independent molecules is shown). Selected bond lengths (Å) and angles (deg): Bi1−C111 = 2.248(7); B1−O11 = 3.097; C111−Bi−C11A = 93.5(2).

be disordered, and the structure was solved using a model illustrated in Figure 1. The dinuclear units are based on a ten-membered ring with a transannular Au−Au contact of 2.9176(5) Å, representing significant aurophilic bonding. The compound is a rare case where linearly two-coordinate gold has an aryl group trans to an amine ligand. This situation is generally not expected to be very stable, but obviously the support by the ring structure and by the transannular metal−metal interaction leads to a more robust configuration.

Crystals of $Bi(C_6H_4OMe\text{-}2)_3$ are rhombohedral, space group $R\bar{3}$, with $Z = 24$ molecules in the unit cell. The bismuth atom of one of the two independent molecules resides on a 3-fold axis which relates the three aryl substituents in what can be described as a propeller conformation (Figure 2). The second molecule has no crystallographically imposed symmetry and is disordered. Superpositions show that the differences in the molecular structures are not great and that both right- and left-handed propellers are present in the unit cell. The C−Bi−C angles are found in the narrow range between 92.6(3) and 95.4(3)° and the Bi−C distances between 2.248(7) and 2.269(9) Å. These parameters are in good agreement with published data.[15] The atomic distances between the oxygen and bismuth atoms (3.079−3.118 Å) are longer than standard covalent Bi−O bond lengths (2.08−2.80 Å)[16] but considerably shortened as compared with the sum of estimated van der Waals radii (>3.60 Å),[17] suggesting weak Bi−O donor/acceptor interactions of the metal center with the methoxy groups.

Conclusions

All attempts to prepare gold(I) bismuthine compounds with a Au−Bi coordinative bond were unsuccessful. Reactions of a series of complexes of the type L−Au−X (with L = thioether, phosphine ligands and with X = Cl, BF_4, C_6F_5 anions) with trialkyl, triaryl, or mixed alkyl/aryl bismuthines gave organogold complexes which are the products of transmetalation processes. Bismuthines thus act as organometallic reagents for gold in all cases. The products with thioether ligands $R{-}Au(SR_2)$ were found to be unstable above −50 °C; those with phosphine ligands $R{-}Au(PR_3)$ could be detected in solution by NMR spectroscopy but were not separated from the diorganobismuthine compounds R_2BiX. The primary phenylation product $PhAu(PPh_3)$ was aurated further with $[(Ph_3P)Au]BF_4$ to give the known phenyl-bridged dinuclear complex $\{C_6H_5[Au(PPh_3)]_2\}^+BF_4^-$.[14] It was only with the tris(2-((dimethylamino)methyl)-

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phenyl)bismuthine that a stable arylgold complex could be isolated. Its crystal and molecular structure has been determined. The 10-membered dimetallacycle features short transannular aurophilic contacts.

In summary, it appears that tertiary bismuthines cannot be employed as donor ligands for gold(I) complexes, because the reaction intermediates are subject to rapid trans-organylation processes to give organogold complexes. The bismuthines thus react like standard organometallic reagents such as organolithium, organozinc, and Grignard reagents. The organogold compounds produced are either thermally unstable (e.g. with sulfur donors) or stable (as with phosphine donors) but are difficult to separate from the organobismuth byproducts. A robust product has only been successfully isolated in a case where head-to-tail dimerization in a ten-membered dimetallacyclic system with transannular aurophilic bonding can lend sufficient stability to the arylgold complex: $[-Au-C_6H_4CH_2NMe_2-]_2$. This compound had been prepared previously via a standard organometallic route and the correct structure predicted.[13] It is surprising that in this example even a nitrogen donor is sufficient to afford a stable substituent/ligand combination.

Experimental Section

General Procedure. All organometallic syntheses were performed under a dry deoxygenated dinitrogen atmosphere using standard Schlenk techniques. All solvents were distilled from an appropriate drying agent and stored over molecular sieves (4 Å) and under nitrogen. Solutions were handled at −78 °C unless otherwise stated and protected against light.

All standard chemicals and $Bi(C_6H_4\text{-}OMe\text{-}2)_3$ were purchased from Aldrich or Fluka and used without further purification. (tht)AuCl,[18] $(Me_2S)AuCl$,[18] $(tht)AuC_6F_5$,[18] $(Ph_3P)AuCl$,[19] Me_3Bi,[20] $MePh_2Bi$,[21] and $Bi(C_6H_4CH_2NMe_2\text{-}2)_3$[22] were prepared as described in the literature.

Mass spectra were recorded on a Finnigan MAT 90 spectrometer using FAB as an ionization method. NMR spectra were obtained at various temperatures on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonances converted to TMS (^1H). $^{31}P\{^1H\}$ NMR spectra are referenced to external aqueous H_3PO_4 (85%). The single-crystal X-ray diffraction measurements were performed at −130 °C on a Nonius DIP 2020 diffractometer using graphite-monochromated Mo Kα radiation.

Phenyl(tetrahydrothiophene)gold(I), (tht)AuPh. To a stirred suspension of (tht)AuCl (158 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added, at −78 °C, $BiPh_3$ (220 mg, 0.5 mmol). The resulting yellow solution was stirred for 5 h at this temperature. Removal of the solvent (−78 °C!) yielded an extremely thermolabile deep purple solid containing (tht)AuPh and byproducts. ^1H NMR (CD_2Cl_2, −60 °C): δ 1.9−2.2 (br s, 4H, SCH_2CH_2), 3.0−3.4 (br s, 4H, SCH_2CH_2), 7.1−7.9 (m, 5H, C_6H_5). Introducing 2 or 4 equiv of $BiPh_3$ or $BiPh_2Me$ afforded product mixtures, the NMR spectra of which also contained this set of resonances. Decomposition started upon warming above −50 °C with deposition of purple-black precipitates.

Table 1. Crystal Data and Data Collection and Structure Refinement Details

	$[Au(C_6H_4CH_2NMe_2\text{-}2)]_2$	$Bi(C_6H_4OMe\text{-}2)_3$
Crystal Data		
formula	$C_9H_{12}AuN$	$C_{21}H_{21}BiO_3$
M_r	331.16	530.36
cryst syst	monoclinic	rhombohedral
space group	$P2_1/c$	$R\bar{3}$
a (Å)	11.5252(3)	23.160(3)
b (Å)	7.7649(2)	23.160(3)
c (Å)	11.3199(2)	25.418(5)
α (deg)	90	90
β (deg)	119.416(1)	90
γ (deg)	90	120
V (Å^3)	882.4(1)	11807(3)
ρ_{calcd} (gcm^{-3})	2.493	1.790
Z	4	24
F(000)	608	6096
μ(Mo Kα) (cm^{-1})	166.04	89.75
Data Collection		
T (°C)	−130	−130
no. of measd rflns	23 915	114 079
no. of unique rflns	1949 (R_{int} = 0.045)	5791 (R_{int} = 0.073)
abs cor	DELABS[23]	DELABS[23]
T_{min}/T_{max}	0.452/0.820	0.692/0.912
Refinement		
no. of refined params	172	358
final R values ($I > 2\sigma(I)$)		
R1	0.0279	0.0487
wR2[a]	0.0754	0.0953
a/b	0.000/6.76	0.000/280.60
ρ_{fin}(max/min) (e Å^{-3})		1.903/−1.243

[a] $wR2 = \{[\sum w(F_o^2\text{-}F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p = (F_o^2 + 2F_c^2)/3$.

(Dimethyl sulfide)phenylgold(I), $(Me_2S)AuPh$. To a suspension of $(Me_2S)AuCl$ (29.5 mg, 0.1 mmol) in CD_2Cl_2 (1 mL) was added with stirring, at −78 °C, $BiPh_2Me$ (37.8 mg, 0.1 mmol). Stirring of the resulting yellow solution was continued for 5 h at this temperature. The thermolabile product $(Me_2S)AuPh$ contained in the reaction mixture was identified by its ^1H NMR resonances. ^1H NMR (CD_2Cl_2, −60 °C): δ 2.34 (s, 6H, SCH_3), 7.1−7.7 (m, 5H, C_6H_5). The products decomposed upon warming of the solution above −50 °C with deposition of dark precipitates.

(Dimethyl sulfide)(2-methoxyphenyl)gold(I), $(Me_2S)AuC_6H_4\text{-}OMe\text{-}2$. The reaction was carried out as described above, using $(Me_2S)AuCl$ (29.5 mg, 0.1 mmol) and $Bi(C_6H_4\text{-}OMe\text{-}2)_3$ (62.5 mg, 0.1 mmol), to yield thermolabile $(Me_2S)AuC_6H_4OMe\text{-}2$ and byproducts. ^1H NMR (CD_2Cl_2, −60 °C): 2.57 (s, 6H, SCH_3), 3.69 (s, 3H, OCH_3), 6.7−7.5 (m, 4H, C_6H_4).

Bis(*μ*-*C*,*N*-2-((dimethylamino)methyl)phenyl)digold(I), $[-Au-(C_6H_4CH_2NMe_2\text{-}2)-]_2$. To a suspension of $(Me_2S)AuCl$ (29.5 mg, 0.1 mmol) in CD_2Cl_2 (1 mL) was added with stirring, at −78 °C, $Bi(C_6H_4CH_2NMe_2\text{-}2)_3$ (61.2 mg, 0.1 mmol). The resulting solution was warmed to −30 °C and developed a pale yellow color as it was stirred for 5 h at this temperature. Layering the reaction mixture with *n*-pentane afforded colorless crystals; mp 119 °C. ^1H NMR (CD_2Cl_2, room temperature): δ 2.84 (s, 6H, NCH_3), 4.08 (s, 2H, CH_2), 6.8−7.8 (m, 4H, C_6H_4). ^1H NMR (CD_2Cl_2, −60 °C): δ 2.66 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 3.46 (d, $^2J_{HH}$ = 11.2 Hz, 1H, CH_2), 4.62 (d, $^2J_{HH}$ = 11.2 Hz, 1H, CH_2), 6.8−7.8 (m, 4H, C_6H_4). The analogous procedure with $(tht)AuC_6F_5$ as a precursor also yields $[-Au-(C_6H_4CH_2NMe_2\text{-}2)-]_2$.

(*μ*-*C*1,*C*1-Phenyl)bis[(triphenylphosphine)gold(I)] Tetrafluoroborate, $\{C_6H_5[Au(PPh_3)]_2\}^+BF_4^-$. A solution of $[(Ph_3P)Au]^+BF_4^-$ was prepared from $(Ph_3P)AuCl$ (99.0 mg, 0.2 mmol) and $AgBF_4$ (42.6 mg, 0.22 mol) in CD_2Cl_2 (3 mL) at −78 °C. After filtration from the silver salts, the cold solution was added to triphenylbismuthine (88.1 mg, 0.2 mmol). After 4 h of stirring at this temperature and upon addition of *n*-pentane, a thermostable white precipitate was formed, which was collected, washed with toluene, and dried (127 mg, 48% yield). ^1H NMR (CD_2Cl_2, −60 °C): δ 7.2−7.8 (m, AuC_6H_5 and m, PC_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 36.3 (s, $AuPPh_3$).

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MS (FAB): *m*/*z* 995 (70%) [M]$^+$, 722 (98%) [$(Ph_3P)_2Au$]$^+$, 459 (100%) [$(Ph_3P)Au$]$^+$, 262 (7%) [Ph_3P]$^+$. Introducing $BiPh_2Me$ into the same procedure afforded a product which gave similar spectra. The values agree with literature data.[14]

Crystal Structure Determinations. The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected using a Nonius DIP2020 system with monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation at −130 °C. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[23] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions. One of the two crystallographically independent molecules of $Bi(C_6H_4\text{-}OMe\text{-}2)_3$ was disordered and refined in two split positions (sof 88/12). All atoms except for the bismuth atom of the part with the lower occupancy were refined with isotropic contributions. One of the three OMe groups of this part could not be located in the Fourier map. Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions. Complete lists of displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. The data are available on request on quoting CCDS-215633, 215634.

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Supporting Information Available: Tables giving details of crystal data, data collection, and structure refinement, atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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