Auration of Thiophene and Furan: Structures of the 2-Mono- and 2,2-Diaurated Products

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Received August 12, 2003

Thiophene undergoes electrophilic substitution by (triphenylphosphine)gold(I) tetrafluoroborate in tetrahydrofuran under very mild conditions to give directly the 2,2-diaurated cation $\{2,2\text{-}[(Ph_3P)Au]_2C_4H_3S\}^+$ as the BF_4^- salt. The same product is obtained in a two-step process via the monoaurated 2-$[(Ph_3P)Au]C_4H_3S$ molecule, which adds 1 equiv of $[(Ph_3P)Au]BF_4$. Together with the mono- and diaurated furan analogues, which were also prepared via this route, the thiophene compounds have been structurally characterized in single-crystal X-ray studies. The mononuclear complexes of the general formula 2-$[(L)Au]C_4H_3E$, with L = Ph_3P or Ph_3As and E = O or S, were all found to have conventional structures with parameters representing classical types of metalated aromatic heterocycles. Crystals of the arsenic analogue, 2-$[(Ph_3As)Au]C_4H_3O$, are isomorphous with the Ph_3P complex. The products of the second auration step, with the general formula $\{2,2\text{-}[(L)Au]_2C_4H_3E\}^+BF_4^-$ (L = Ph_3P; E = O, S), have the two gold atoms sharing one of the two α-carbon atoms with short intramolecular Au···Au contacts of 2.8134(4) and 2.8461(2) Å and small Au−C−Au angles of 82.5(2)° and 84.5(1)°, respectively. The geometry of the five-membered rings suggests that the aromaticity is strongly reduced upon geminal auration at C-1, which renders this carbon atom tetracoordinated. It is particularly noteworthy that the second auration leaves the sulfur or oxygen donor centers untouched. This observation is one of the most remarkable examples of the strong influence of aurophilic bonding.

Introduction

Geminally diaurated ring systems derived from an aromatic hydrocarbon were first discovered in the 1970s by the Nesmeyanov school in attempts to introduce gold substituents into ferrocene.[1] It was observed that after conventional monometalation to give $(LAuC_5H_4)Fe(C_5H_5)$, with L = Ph_3P, the second ligand-backed electrophile $[(L)Au]^+$ is attached to the same carbon atom to generate a cationic species of the proposed formula $\{1,1\text{-}[(L)Au]_2C_5H_4)Fe(C_5H_5)\}^+$. This unusual substitution pattern was finally confirmed by single-crystal X-ray diffraction studies of the BF_4^- salt.[2]

In this early structural work it was noted that the geminal angle Au−C−Au (78°) at the tetracoordinate *ipso* carbon atom is much smaller than a tetrahedral angle and gives rise to an Au···Au distance of only 2.77 Å, shorter than the interatomic distance in metallic gold.[2]

An early description of the bonding arrangement has pointed to a three-center two-electron (3c, 2e) bond, but positive charge delocalization over the cyclopentadienyl ring, consequently with a loss of aromaticity, is also conceivable. Similar complexes have subsequently been prepared and include the trifluorobenzene complex $[(\mu\text{-}2,4,6\text{-}C_6F_3H_2)(AuPPh_3)_2][ClO_4]$, in which a Au···Au distance of 2.759(1) Å and a small Au−C−Au angle of 79.3(3)° are observed,[3] the tolyl complex $[MeC_6H_4\text{-}\{Au_2(Ph_2PCH_2CH_2)_2\}][BF_4]$, in which two independent PPh_3 groups are replaced by the chelating ligand 1,4-bis(diphenylphosphine)butane,[4] the tetraaurated complexes $[\{C_5H_4(AuPPh_3)_2\}Fe\{C_5H_4(AuPPh_3)_2\}][BF_4]$[5] and $[(CH_2)_2(C_6H_4\text{-}o)_2(AuPPh_3)_4][BF_4]$,[6] in which the even higher accumulation of positive charge within the same molecule does not affect the stability of the complexes, and the unusual trinuclear complex $[Ph_4C_5(AuPPh_3)_3][BF_4]$, in which an additional short Au···Au contact is observed.[7]

Of the 1,1-diaurated aromatic systems containing the $C(AuL)_2$ fragment represented in the literature, no structural evidence has been presented for the class of *hetero*aromatic complexes of this type. The stability of compounds of this stoichiometry was established with the synthesis of $[C_4H_3S(AuPPh_3)_2][BF_4]$. The characterization of this complex, however, was solely by melting point and elemental analysis.[8]

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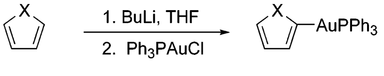
10.1021/om030575f CCC: $25.00

The structural and spectroscopic properties of geminally diaurated heteroarene complexes can be more fully understood on one hand by considering the influence of relativistic effects in gold(I) components[9] and applying the isolobal analogy of $[AuPR_3]^+$ to H^+ on the other.[10] Employing these concepts, the solid state structures of aromatic dinuclear complexes of the type $C(AuL)_2$ should draw parallels to the transition state structures proposed for proton exchange at arenes and more generally to the transition state of electrophilic aromatic substitution.[11] We aim to investigate this relationship by examining heteroarene systems in this work.

Results and Discussion

Direct Auration of Heteroarenes. Two examples of mononuclear heteroaryl gold(I) complexes have been synthesized by the reaction of lithiated aromatic heterocycles[12] with (triphenylphosphine)gold chloride in the molar ratio 1:1 in tetrahydrofuran (eq 1).[13]



(1)

X = S (**1**)
X = O (**2**)

The thiophene (**1**) and furan (**2**) derivatives were isolated as air- and moisture-stable crystalline solids in 60% and 50% yields, respectively. Positive ion fast atom bombardment (FAB) mass spectrometry reveals molecular cations $[M]^+$ for **1** and **2** at $m/z = 542$ and 526 amu. High-intensity peaks with $m/z = 1000$ and 984 for **1** and **2**, respectively, are also observed and are key features of both spectra. These mass peaks correspond to the adducts $[C_4H_3S(AuPPh_3)_2]^+$ and $[C_4H_3O(AuPPh_3)_2]^+$. Although such clustering, which results in dinuclear units, is commonly observed in ion−molecule reactions in the gaseous state, it shows an interesting parallel to the solution chemistry of arylgold complexes (vide infra).[2,6]

Proton NMR spectroscopy of **1** confirms the aromatic nature of the thiophene ligand with an overlap of the thiophene and phenyl resonances between 7.12 and 7.66 ppm. This conclusion is also supported by ^{13}C NMR spectroscopy, where the thiophene carbon resonance signals appear in the aromatic region 126.9−133.3 ppm. The $^{31}P\{^1H\}$ NMR spectrum exhibits a single peak at δ_P 44.3, which is in the field typical of P−Au−Ar bound species.[14] The furan derivative **2** shows NMR spectroscopic data similar to **1**, although the proton NMR spectral resonances occur more upfield, in the range 6.28−7.27 ppm. For the ^{13}C NMR of compound **2**, the spectral range broadens, with signals observed between 108.3 and 144.4 ppm. The geminally disubstituted carbon is not observed in either compound. The arsenic analogue of **2**, 2-$[(Ph_3As)Au]C_4H_3O$ (**2a**), has also been identified in this study. The crystals were found to be isomorphous with those of **2**. The structure showed no anomalies.

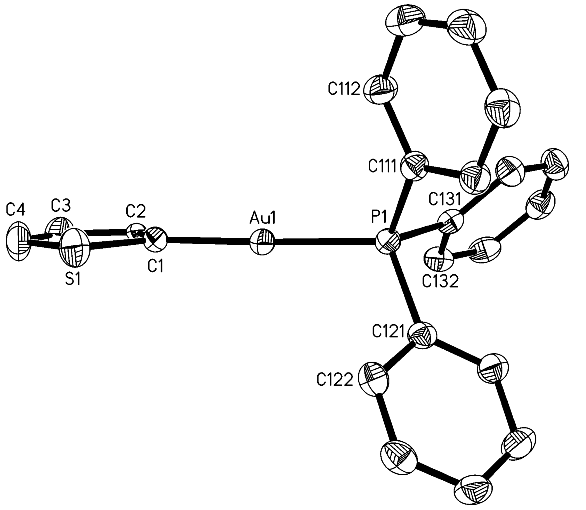


Figure 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−C1 2.038(3), Au1−P1 2.2781(8), Au1···Au1′ 3.977(1); C1−Au1−P1 178.22(9).

Crystals of $C_4H_3SAu(PPh_3)$, **1** (from dichloromethane/pentane at 5 °C), are triclinic, space group $P\bar{1}$, with $Z = 2$ molecules in the unit cell (Figure 1). The gold atom is bound directly to the α-carbon of the thiophene heteroarene and has the usual two-coordinate environment of P(1)−Au(1)−C(11) 178.22(9)°, Au(1)−P(1) 2.2781(8) Å, and Au(1)−C(11) 2.038(3) Å. For comparison, the data for the reference compound $PhAu(PPh_3)$ are 175.5(2)°, 2.296(2) Å, and 2.045(6) Å.[15] The thiophene ring is planar, with the gold atom lying within this plane as shown by the dihedral angles C(11)−S(1)−C(14)−C(13) 0.0(4)° and Au(1)−C(11)−C(12)−C(13) 179.6(3)°. The two molecules per unit cell are organized in pairs with a slightly offset head-to-tail arrangement. The closest intermolecular approach is an Au···S distance of 3.977 Å. There are no discernible intermolecular aurophilic contacts between the molecules on account of the large triphenylphosphine ligands shielding the gold atoms.

Crystals of $C_4H_3OAu(PPh_3)$ (**2**) are triclinic, space group $P\bar{1}$, with $Z = 2$ molecules in the unit cell (Figure 2). The lattice is free of solvent. The distances Au−P 2.2823(8) Å and Au−C 2.032(3) Å and the angle P−Au−C 178.1(1)° are consistent with the thiophene derivative **1** and can be considered normal for an arylgold complex of a triarylphosphine. The two molecules per unit cell are oriented antiparallel to each other, and there are no discernible intermolecular aurophilic or Au···O interactions.

Diaurated Heteroarenes. Tetrafluoroborate salts of diaurated aromatic ligands can be synthesized by treat-

$$2RAuPR_3' + HBF_4 \longrightarrow RH + [R(AuPR_3')_2]BF_4 \qquad (2)$$

$$CH_3AuPPh_3 \xrightarrow{HBF_4} [AuPPh_3]^+$$
$$R_2Hg \xrightarrow{[AuPPh_3]^+} RAuPPh_3 \qquad (3)$$

$$RAuPR'_3 + [AuPR'_3]BF_4 \longrightarrow [R(AuPR'_3)_2]BF_4 \qquad (4)$$

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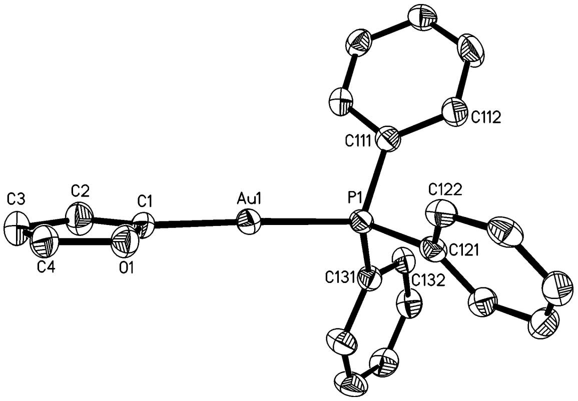
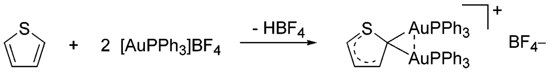


Figure 2. Molecular structure of compound **2** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg] (corresponding values for compound **2a** in square brackets): Au1−C1 2.032(3) [2.028(3)], Au1−P1 2.2823(8) [Au1−As1 2.3882(3)]; C1−Au1−P1 178.1(1) [C1−Au1−As1 177.8(1)].

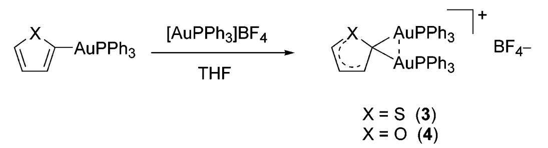
ment of an aryl(triorganophosphine)gold(I) complex with HBF_4, by replacement of mercury in organomercury compounds, or by the direct addition of $[(R_3P)Au]BF_4$ formed in situ from $AgBF_4$ and R_3PAuCl (eqs 2−4).[1−8]

Preparative efforts directed at the synthesis of geminally diaurated heteroarenes in this work focused initially on the last of these three synthetic pathways, but direct auration of thiophene with $[(Ph_3P)Au]^+$ was also considered. Experimental results have shown that thiophene can indeed be diaurated directly by $[(Ph_3P)Au]BF_4$ in tetrahydrofuran even at −60 °C. After a simple workup, the yield was 44% (eq 5).



(5)

The diaurated thiophene complex **3** and furan complex **4** were also prepared via the two-step route as air- and moisture-stable crystalline solids in 63% (mp 163−164 °C) and 50% (mp >147 °C (dec)) yields, by the addition of $[(Ph_3P)Au]BF_4$ to the arene complexes **1** and **2**, respectively (eq 6).



(6)

X = S (**3**)
X = O (**4**)

The $^{31}P\{^1H\}$ NMR spectrum of **3** at room temperature exhibits a sharp singlet at δ_P 36.7, indicating that in solution the triphenylphosphine gold(I) units are in identical stereochemical environments. The ^{13}C NMR spectrum reveals all the expected resonance signals for the thiophene and triphenylphosphine ligands; however the disubstituted carbon is not observed.

The furan derivative **4** exhibits a single resonance at δ_P 36.6 for the equivalent triphenylphosphine gold(I) units at 25 °C. Further evidence for the equivalence of the triphenylphosphine gold(I) units is provided by the ^{13}C NMR spectrum, where only one set of phenyl resonances is observed. The signal of the disubstituted carbon atom is also not detected.

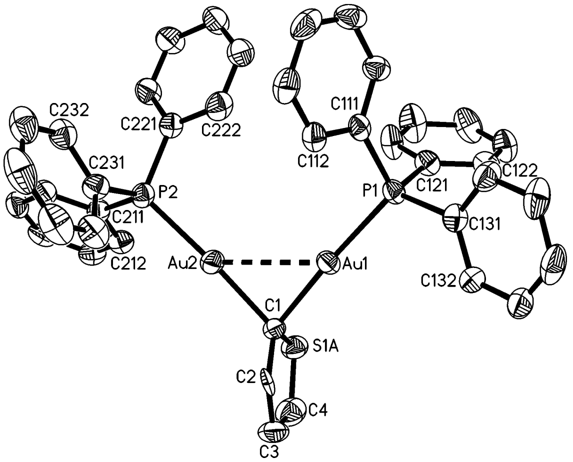


Figure 3. Molecular structure of the cation of compound **3** (ORTEP drawing with 50% probability ellipsoids, H atoms and S/C disorder omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−C1 2.135(7), Au1−P1 2.273(2), Au1···Au2 2.8134(4), Au2−C1 2.133(6), Au2−P2 2.274(2); C1−Au1−P1 175.6(2), C1−Au1···Au2 48.7(2), P1−Au1−Au2 134.64(5), C1−Au2−P2 176.3(2), C1−Au2···Au1 48.8(2), P2−Au2···Au1 134.90(5), Au1−C1−Au2 82.5(2).

Crystals of $[C_4H_3S(AuPPh_3)_2][BF_4]$, **3** (from dichloromethane/pentane at 20 °C), are triclinic, space group $P\bar{1}$, with $Z = 2$ molecules in the unit cell (Figure 3). The lattice contains half a dichloromethane molecule. The two gold atoms share the same α-thiophene carbon atom as a common bonding partner, resulting in a short Au···Au distance of 2.8134(4) Å, which is shorter than that of metallic gold (2.88 Å). The Au(1)−C(1)−Au(2) angle of 82.5(2)° is significantly smaller than the normal tetrahedral angle and agrees with those reported for the ferrocenyl complex $[C_5H_5FeC_5H_4(AuPPh_3)_2][BF_4]$[2] and the trifluorophenyl complex $[C_6H_2F_3(AuPPh_3)_2][ClO_4]$[3] of 78(1)° and 79.3(3)°, respectively. The plane of the triangle Au(1)−C(1)−Au(2) is approximately perpendicular to that defined by the thiophene ring. The thiophene ring is disordered at sulfur and carbon, where the atoms are located in split positions in a ratio of ca. 50:50. The gold centers retain the usual linear two-coordination environment.

Crystals of $[C_4H_3O(AuPPh_3)_2][BF_4]$, **4**, are orthorhombic, space group *Pnma* with $Z = 4$ molecules in the unit cell (Figure 4). The lattice contains no solvent molecules. The α-position of the furan ring is diaurated, yielding a monocation of crystallographically imposed mirror symmetry. The Au(1)−C(1)−Au(1A) angle of 84.5(1)° is similar to the angle observed in **3** of 82.5(2)°. The intramolecular Au···Au distance is 2.8461(2) Å, with the Au(1)−C(1)−Au(1A) triangle perpendicular to the thiophene ring and the usual linear two-coordinate environment of the gold atoms: P(1)−Au(1)−C(1) 176.1(1), Au(1)−P(1) 2.2719(8), and Au(1)−C(1) 2.117(3) Å.

The Au−C distances of 2.135(7) and 2.133(6) Å in **3** and 2.117(3) Å in **4** are significantly longer than those found in the 2c,2e-bonded precursors, **1** and **2**, at 2.038(3) and 2.032(3) Å, respectively. Typically, 2c,2e bonds between gold and aryl groups are reported in the range ca. 2.04−2.08 Å. The compound $PhAu(PPh_3)$ exhibits an Au−C bond benchmark distance of 2.045(6) Å.[15]

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Scheme 1

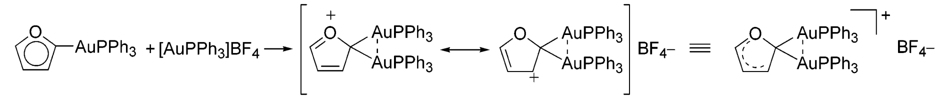
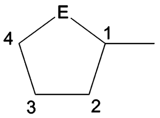


Table 1. C−C and C−Heteroatom Bond Distances (Å) within the Mono- and Diaurated Heteroarenes 1−4

	$C_4H_3S(AuPPh_3)$	$[C_4H_3S(AuPPh_3)_2][BF_4]$	$C_4H_3O(AuPPh_3)$	$[C_4H_3O(AuPPh_3)_2][BF_4]$
	1	**3**	**2**	**4**
	E=S	E=S	E=O	E=O
C1–C2	1.441(5)	1.47(5)	1.358(5)	1.379(6)
C2–C3	1.451(5)	1.42(5)	1.431(5)	1.413(6)
C3–C4	1.362(6)	1.356(12)	1.330(6)	1.332(7)
C4–E	1.696(5)	1.614(17)	1.371(4)	1.353(6)
E–C1	1.708(4)	1.694(14)	1.401(4)	1.415(5)

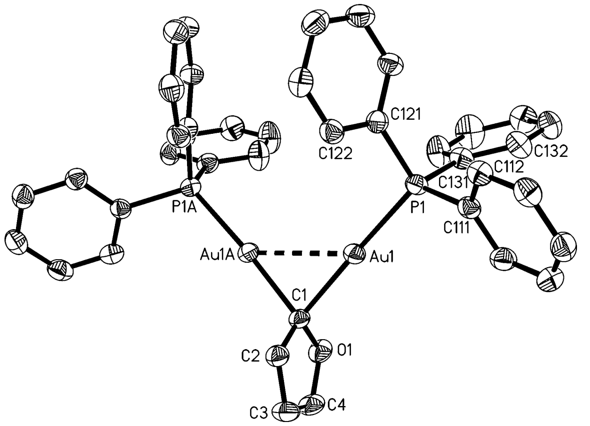


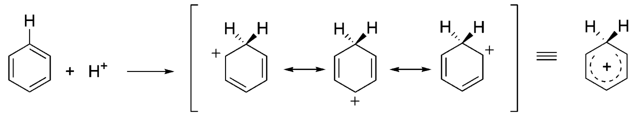
Figure 4. Molecular structure of the cation of compound **4** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−C1 2.117(3), Au1−P1 2.2719(8), Au1···Au1A 2.8461(2); C1−Au1−P1 176.1(1), C1−Au1···Au1A 47.77(7), P1−Au1···Au1A 134.85(2), Au1−C1−Au1A 84.5(1).

By examination of the C−C and C−heteroatom bond lengths in the heteroarene rings of **3** and **4**, it is evident that there is only partial charge delocalization over the ring with loss of aromaticity (Scheme 1).

From the resonance structures attributed to **4**, a lengthening of the C(1)−C(2) and C(1)−O distances is expected on going from a mono- to a diaurated heteroarene system, with concomitant shortening of C(2)−C(3), C(3)−C(4), and C(4)−O. The solid state structure of complex **4** reveals that the C(1)−C(2) and C(1)−O bond distances become longer by 0.021 and 0.014 Å, respectively, relative to those observed in compound **2**, and the C(2)−C(3) and C(4)−O bonds become shorter by 0.018 Å. C(3)−C(4) remains virtually unchanged (Table 1).

Conclusion

Scheme 2



Electrophilic aromatic substitution reactions occurring at an sp^2 carbon center by an addition−elimination mechanism result in the formation of an “arenonium” ion comprised of one arene molecule and one electrophile. For the hydrogen exchange reactions, it is postulated that the hydrogen atom being substituted and the incoming electrophile are both σ-bound to a single carbon atom which is in an sp^3-hybrid state[16−18] (Scheme 2). With the $[AuPPh_3]^+$ unit isolobal with H^+,[10] geminally diaurated arenes are analogues representing stable crystalline intermediates in electrophilic aromatic substitution reactions. The structures observed for **3** and **4** are representative examples for the substitution process at *hetero*arenes.

Experimental Section

All experiments were carried out under an atmosphere of purified nitrogen. All solvents were distilled from an appropriate drying agent and were stored under nitrogen over molecular sieves (4 Å). Mass spectra were recorded on a Finnigan MAT 90 spectrometer using FAB as an ionization method. NMR spectra were obtained at room temperature on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in δ (ppm) values relative to the residual solvent resonance (^{1}H, ^{13}C). ^{31}P{^{1}H} NMR spectra are referenced to external aqueous H_3PO_4 (85%).

2-[(Triphenylphosphine)gold]thiophene, 1.[13] Mp: 165−167 °C (lit.[13] 168−171 °C). MS (FAB): *m/z* 458.5 (100%) $[Ph_3PAu]^+$, 542.4 (35%) $[M]^+$, 720.1 (20%) $[Ph_3PAuPPh_3]^+$, 999.6 (9.3%) $[C_4H_3S(AuPPh_3)_2]^+$. Anal. Calcd for $C_{22}H_{18}AuPS$ (542.39): C, 48.71; H, 3.34. Found: C, 48.73; H, 3.28.

2-[(Triphenylphosphine)gold]furan, 2.[13] Mp: 157−158 °C (lit.[13] 159−160 °C). MS (FAB): *m/z* 458.5 (100%) $[Ph_3PAu]^+$, 526.4 (25%) $[M]^+$, 720.1 (22%) $[Ph_3PAuPPh_3]^+$, 983.6 (7.3%) $[C_4H_3O(AuPPh_3)_2]^+$. Anal. Calcd for $C_{22}H_{18}AuOP$ (526.32): C, 50.21; H, 3.45. Found: C, 50.32; H, 3.44.

2-[(Triphenylarsine)gold]furan, 2a. Furan (0.10 g, 1.5 mmol) was dissolved in tetrahydrofuran (10 mL), and a 1.6 M solution of butyllithium in hexane (1.0 mL, 1.6 mmol) was added. After stirring overnight, (triphenylarsine)gold chloride (0.53 g, 1.0 mmol) was added as a solid, and the resulting solution was stirred for a further 1 h. The solvent was removed

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Table 2. Crystal Data, Data Collection, and Structure Refinement

	1	**2**	**2a**
	Crystal Data		
formula	$C_{22}H_{18}AuPS$	$C_{22}H_{18}AuOP$	$C_{22}H_{18}AsAuO$
M_r	542.36	526.30	570.25
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.7165(1)	7.3914(1)	7.3555(1)
b (Å)	11.2820(2)	11.2957(2)	11.3778(2)
c (Å)	11.5188(2)	11.4679(2)	11.6508(2)
α (deg)	92.328(1)	91.282(1)	91.870(1)
β (deg)	105.206(1)	93.823(1)	93.605(1)
γ (deg)	95.120(1)	103.301(1)	102.582(1)
V (Å^3)	961.7(1)	929.0(1)	948.7(1)
ρ_{calc} (g cm^{-3})	1.873	1.881	1.996
Z	2	2	2
F(000)	520	504	540
μ(Mo Kα) (cm^{-1})	78.42	80.10	94.90
	Data Collection		
T (°C)	-130	-130	-130
no. of measd reflns	23 069	23 453	23 725
no. of unique reflns	3712 [$R_{int} = 0.035$]	3604 [$R_{int} = 0.030$]	3684 [$R_{int} = 0.026$]
abs corr	DELABS	DELABS	DELABS
T_{min}/T_{max}	0.416/0.803	0.438/0.814	0.508/0.844
	Refinement		
no. of refined params	226	226	226
final R values [$I \geq 2\sigma(I)$]			
R1	0.0225	0.0219	0.0192
wR2^a	0.0576	0.0578	0.0481
ρ_{fin}(max/min) (e Å^{-3})	1.229/-1.441	1.302/-1.579	0.480/-0.479

	3$\cdot$0.5CH$_2$Cl$_2$	**4**
	Crystal Data	
formula	$C_{40.5}H_{34}Au_2BClF_4P_2S$	$C_{40}H_{33}Au_2BF_4OP_2$
M_r	1130.87	1072.35
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Pnma$
a (Å)	9.7420(2)	17.3338(2)
b (Å)	14.6798(4)	21.1912(2)
c (Å)	15.5339(4)	9.9489(1)
α (deg)	69.960(1)	90
β (deg)	84.387(1)	90
γ (deg)	73.773(2)	90
V (Å^3)	2003.9(1)	3654.5(1)
ρ_{calc} (g cm^{-3})	1.874	1.949
Z	2	4
F(000)	1078	2040
μ(Mo Kα) (cm^{-1})	75.58	81.59
	Data Collection	
T (°C)	-130	-130
no. of measured reflns	60 748	98 116
no. of unique reflns	7712 [$R_{int} = 0.053$]	4094 [$R_{int} = 0.045$]
abs corr	DELABS	DELABS
T_{min}/T_{max}	0.553/0.862	0.463/0.825
	Refinement	
refined params	497	238
final R values [$I \geq 2\ \sigma(I)$]		
R1	0.0412	0.0221
wR2^a	0.0843	0.0512
ρ_{fin}(max/min) (e Å^{-3})	1.230/-1.808	1.142/-0.644

[a] wR2= $\{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0297 (**1**), 0.0317 (**2**), 0.018 (**2a**), 0.0268 (**3**$\cdot$0.5CH$_2$Cl$_2$), 0.0187 (**4**); b = 1.20 (**1**), 0.68 (**2**), 0.81 (**2a**), 8.90 (**3**$\cdot$0.5CH$_2$Cl$_2$), 6.59 (**4**).

under vacuum and the residue taken up in dichloromethane and extracted with water (10 mL). The organic phase was dried over MgSO$_4$, the solvent reduced in volume (ca. 2 mL), and the product precipitated with *n*-pentane. Yield: 0.20 g, 35%. Mp: 108−109 °C. NMR (CD$_2$Cl$_2$, RT): ^{13}C{^{1}H} 144.4 (s, C_{furan}), 133.5 (s, *m*-C_{phenyl}), 132.7 (s, *ipso*-C_{phenyl}), 130.9 (s, *p*-C_{phenyl}), 129.5 (s, *o*-C_{phenyl}), 118.2 (s, C_{furan}), 108.1 (s, C_{furan}); ^{1}H 7.69−7.24 (m, 16 H, H_{furan} and H_{phenyl}), 6.47 (m, 1H, H_{furan}), 6.38 (m, 1H, H_{furan}). MS (FAB): *m*/*z* 502.4 (100%) [Ph$_3$AsAu]$^+$, 569.3 (36%) [M]$^+$, 807.9 (26%) [Ph$_3$AsAuAsPh$_3$]$^+$, 1071.4 (19%) [C$_4$H$_3$O(AuAsPh$_3$)$_2$]$^+$. Anal. Calcd for $C_{22}H_{18}AsAuO$ (570.27): C, 46.34; H, 3.18. Found: C, 46.45; H, 3.11.

2,2-Bis[(triphenylphosphine)gold]thiophene Tetrafluoroborate, 3. Method A. A solution of [Ph$_3$PAu]BF$_4$ (prepared from Ph$_3$PAuCl (0.25 g, 0.51 mmol) and AgBF$_4$ (0.01 g, 0.51 mmol) in 10 mL of THF) was added to a solution of thiophene (0.02 g, 0.25 mmol) in 5 mL of THF at −60 °C. The reaction mixture was stirred for 2 h at −60 °C and was allowed to warm to room temperature, where it was stirred for another 1 h. The solvent was removed under vacuum, the product was dissolved in dichloromethane, and this solution was filtered to remove any remaining insoluble material. The solvent was reduced in volume (ca. 2 mL), and the product was precipitated on addition of diethyl ether. Yield: 0.14 g, 44%.

Method B. A solution of [Ph_3PAu]BF_4 (prepared from Ph_3PAuCl (0.13 g, 0.26 mmol) and $AgBF_4$ (0.05 g, 0.26 mmol) in 10 mL of THF) was added to a solution of **1** (0.14 g, 0.26 mmol) in 10 mL of THF at −60 °C. The reaction mixture was stirred for 30 min at −60 °C and was allowed to warm to room temperature, where it was stirred for another 30 min. The solvent was removed under vacuum, the product was dissolved in dichloromethane, and this solution was filtered to remove any remaining insoluble material. The solvent was reduced in volume to ca. 2 mL and the product precipitated on addition of diethyl ether. Yield: 0.17 g, 63%. Mp: 163−164 °C. NMR (CD_2Cl_2, RT): $^{31}P\{^1H\}$ 36.7 (s); $^{13}C\{^1H\}$ 157.2 (s, $C_{thiophene}$), 148.7 (s, $C_{thiophene}$), 134.4 (d, $J = 14.0$ Hz, m-C_{phenyl}), 132.7 (s, p-C_{phenyl}), 131.6 (s, $C_{thiophene}$), 129.9 (d, $J = 11.9$ Hz, o-C_{phenyl}), 128.7 (d, $J = 59.2$ Hz, $ipso$-C_{phenyl}); ^1H 5.32 (s, CH_2Cl_2, 1 H), 7.33−7.57 (m, 30 H, H_{phenyl}), 7.85 (t, $J = 3.9$ Hz, 1 H, $H_{thiophene}$), 8.34 (d, $J = 3.5$ Hz, 1 H, $H_{thiophene}$), 8.50 (d, $J = 4.7$ Hz, 1 H, $H_{thiophene}$). MS (FAB): m/z 458.1 (81%) $[Ph_3PAu]^+$, 719.3 (70%) $[Ph_3PAuPPh_3]^+$, 998.4 (100%) $[C_4H_3S(AuPPh_3)_2]^+$. Anal. Calcd for $C_{40}H_{33}Au_2P_2BF_4S$ (1088.45): C, 44.14; H, 3.06. Found: C, 44.04; H, 3.00.

2,2-Bis[(triphenylphosphine)gold]furan Tetrafluoroborate, 4. A solution of [Ph_3PAu]BF_4 (prepared from Ph_3PAuCl (0.19 g, 0.39 mmol) and $AgBF_4$ (0.076 g, 0.39 mmol) in 10 mL of THF) was added to a solution of **2** (0.15 g, 0.28 mmol) in 10 mL of THF at −60 °C. The reaction mixture was stirred for 30 min at −60 °C and for an additional 30 min at room temperature. The solvent was removed under vacuum, and the residual product was dissolved in dichloromethane and was filtered to remove the insoluble impurities. The solvent was reduced in volume to ca. 2 mL, and the product was precipitated by the addition of diethyl ether. Yield: 0.15 g, 50%. Mp: >147 °C (dec). NMR (CD_2Cl_2, RT): $^{31}P\{^1H\}$ 36.6 (s); $^{13}C\{^1H\}$ 162.5 (s, C_{furan}), 154.5 (s, C_{furan}), 134.3 (d, $J = 14.0$ Hz, m-C_{phenyl}), 132.7 (s, p-C_{phenyl}), 129.9 (d, $J = 11.0$ Hz, o-C_{phenyl}), 128.6 (d, $J = 59.0$ Hz, $ipso$-C_{phenyl}), 111.7 (s, C_{furan}); ^1H 6.89 (m, 1 H, H_{furan}), 7.33−7.67 (m, 30 H, H_{phenyl}), 8.16 (m, 1 H, H_{furan}), 8.29 (m, 1 H, H_{furan}). MS (FAB): m/z 458.1 (76%) $[Ph_3PAu]^+$, 719.4 (94%) $[Ph_3PAuPPh_3]^+$, 982.6 (100%) $[C_4H_3O(AuPPh_3)_2]^+$. Anal. Calcd for $C_{40}H_{33}Au_2P_2BF_4O$ (1072.38): C, 44.80; H, 3.10. Found: C, 44.66; H, 3.11.

X-ray Crystallography. Specimens of suitable quality and size were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. The sulfur/C2 atoms in the cation of compound **3** were disordered and refined in split positions with sof's of 50:50. Sof refinement of the solvent molecule in compound **3** led to a value of 0.50, with which it was included into the refinement. Further information on crystal data, data collection, and structure refinement are summarized in Table 2. Important interatomic distances and angles are shown in the corresponding figure captions. Anisotropic thermal parameters and complete lists 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 CCDC 217209−217213.

Acknowledgment. This work was generously supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and Volkswagenstiftung. Donations of chemicals by Heraeus GmbH and Degussa AG are gratefully acknowledged.

Supporting Information Available: Crystallographic data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030575F