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FULL PAPER

Gold(I) organosulfinate and organosulfonate complexes

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(Phosphine)gold(I) organosulfonates and organosulfinates $(R_3P)Au–OS(O)_2R'$ (**A**) and $(R_3P)Au–S(O)_2R'$ (**B**), respectively, are active catalysts for the addition of alcohols to alkynes. A series of compounds of type **A** (R = Ph and Me, R′ = *p*-Tol; R = Ph, R′ = *p*-Py; R = Ph and Me, R′ = Et) and type **B** (R = Ph, R′ = *p*-Tol; R = Ph and Me, R′ = Me) were prepared and characterized by analytical and spectroscopic data. The crystal structure of $[p\text{-TolS(O)}_2O–Au(PPh_3)]\cdot CH_2Cl_2$ was determined by single crystal X-ray diffraction. The molecules are aggregated into pairs with O-bonded gold atoms and short Au · · · Au contacts [3.1770(3) Å]. By contrast, crystals of "*p*-TolS(O)O–Au(PPh_3)" contain intimately aggregated ion pairs of the homoleptic components $[(Ph_3P)_2Au]^+[\{p\text{-TolS(O)}_2\}_2Au]^-$ with a short Au · · · Au contact [2.9249(2) Å] and a strongly bent P–Au–P axis [156.66(4)°]. The sulfinate ligands are both S-bonded to the gold atom. Analogous *p*-tolylsulfinate complexes were also prepared with the isocyanide ligands ^{t}BuNC and 2,6-$Me_2C_6H_3NC$. Their spectroscopic data indicate ionic solid state structures with homoleptic cations and anions.

Introduction

Gold chemistry is dominated largely by the coordination of soft (polarizable) ligands to the closed-shell ($5d^{10}$) univalent state Au(I).[1] This is not only true for the classical cyanide, isocyanide and thiolate ligands, but also for the ever-growing family of polyfunctional tertiary phosphines.[2] By contrast the coordination chemistry of gold(I) with hard (less polarizable) ligands has developed very slowly, and compounds with fluorine, oxygen or nitrogen donor atoms are still very limited in number.[3]

Recent work has shown, however, that mixed ligand combinations L–Au–X, with L being very soft and X being extremely hard lead to catalytic activity previously unprecedented in gold(I) chemistry.[4] While the neutral ligand L may be selected from the large variety of tertiary phosphines, the anionic component X can be derived mainly from oxo-acids of sulfur. This group of acids comprises the large family of sulfuric, sulfurous, sulfinic, and sulfonic acids, which range from hard sulfur(VI) compounds, like the highly electronegative fluorosulfuric and fluoroalkylsulfonic acids,[5] to softer sulfur(IV) compounds, such as sulfinic acids.

It is obvious from the literature that gold(I) sulfates, sulfonates and sulfinates have never been investigated in detail, and that their structural chemistry was left largely unexplored.[6–8] This situation parallels the state of affairs with the corresponding phosphonates and phosphinates, which have been studied more extensively only very recently.[9–12] As a continuation of our previous endeavours in this area,[8–11] and driven by the new incentive from catalysis,[4] we have now investigated a few representative examples of the general formulae $(L)Au–S(O)_2R$ and $(L)Au–OS(O)_2R$.

Preparative studies

Gold(I) arylsulfonate complexes can be prepared using the silver salt method as applied to (phosphine)gold(I) chloride precursors. Thus, treatment of (triphenylphosphine)gold(I) chloride with equimolar quantities of silver *p*-tolylsulfonate in dichloromethane at room temperature leads to a precipitate of silver chloride and, from the mother liquor after filtration, a 78% yield of (triphenylphosphine)gold *p*-tolylsulfonate (**1**) is isolated as colourless crystals; m.p. 162 °C with decomposition. The trimethylphosphine analogue **2** is generated in 75% yield from $(Me_3P)AuCl$ and $p\text{-MeC}_6H_4SO_3Ag$ following the same procedure (m.p. 129 °C with decomposition). $(Ph_3P)AuCl$ was also converted into the *p*-pyridylsulfonate (**3**) using the corresponding reagents (77% yield). Silver ethylsulfonate was employed for the synthesis of $(Me_3P)Au–OSO_2Et$ (**4**) and $(Ph_3P)Au–OSO_2Et$ (**5**) in 85 and 90% yields, respectively.

$$(R_3P)AuCl + AgOS(O)_2R' \xrightarrow[-AgCl]{} (R_3P)AuOS(O)_2R' \quad (1)$$

1–5

Complex	R	R′
1	Ph	*p*-Tol
2	Me	*p*-Tol
3	Ph	*p*-Py
4	Me	Et
5	Ph	Et

All (phosphine)gold sulfonates were identified through their analytical and spectroscopic data. Their ^{31}P NMR chemical shifts suggest that the compounds are present as LAuX molecules in solution, since $[L_2Au]^+$ cations in an ionic form with $[AuX_2]^-$ anions are known to have larger downfield shifts.[8,13] Similar arguments can be derived from the IR data (see Experimental).[7] (Phosphine)gold organosulfonates have previously been prepared *in situ* for catalytic purposes, but their properties were not disclosed.[4]

Gold(I) arylsulfinates can be synthesized following a similar route to that employed for the preparation of the sulfonates. Silver *p*-tolylsulfinate reacts with (triphenylphosphine)gold chloride in tetrahydrofuran at −70 °C to give an AgCl precipitate and $p\text{-TolS(O)O–Au(PPh}_3)$ (**6**, m.p. 98 °C with decomposition) in 94.5% yield. Colourless needles of the products can be grown from solutions in dichloromethane upon addition of pentane at −30 °C.

For the preparation of the (triphenylphosphine)gold(I) and (trimethylphosphine)gold(I) methylsulfinate complexes (**7**, m.p.

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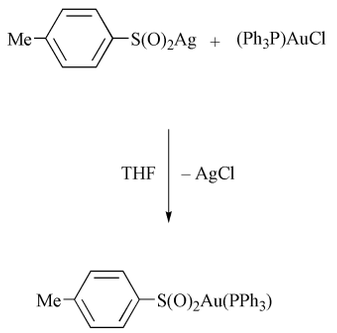


(2)

6

79 °C with decomposition, 84.5% yield; **8**, m.p. 68 °C with decomposition, 83% yield), the $(R_3P)AuCl$ complexes were first converted into the trifluoroacetates $(R_3P)AuOC(O)CF_3$ by reaction with CF_3COOAg in CH_2Cl_2. These intermediates were then reacted with MeS(O)ONa in methanol at −78 °C. The pale-yellow compounds could not be crystallized. Solutions in dichloromethane, chloroform or tetrahydrofuran undergo rapid decomposition at room temperature.

$$(R_3P)AuCl \xrightarrow[-AgCl]{+CF_3COOAg} (R_3P)AuOC(O)CF_3 \xrightarrow[-CF_3COONa]{+MeSO_2Na} (R_3P)AuS(O)_2Me \quad (3)$$

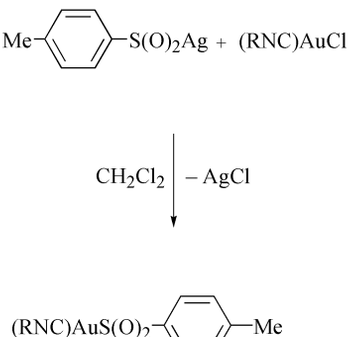
7; R = Ph
8; R = Me

$$2\,(L)AuS(O)_2R' \rightleftharpoons [(L)_2Au]^+\,[Au(S(O)_2R')_2]^- \quad (4)$$

6–10

Complex	L	R′
6	Ph_3P	*p*-Tol
7	Ph_3P	Me
8	Me_3P	Me
9	XyNC	*p*-Tol
10	^{t}BuNC	*p*-Tol

Two gold(I) sulfinate complexes were also prepared with isocyanide ligands. (2,6-dimethylphenyl isocyanide)gold(I) ["(*m*-xylylisocyanide)gold(I)"] *p*-tolylsulfinate *p*-$TolS(O)_2$–Au-(CNXy), **9**, was obtained from (XyNC)AuCl and *p*-$TolS(O)_2Ag$ in dichloromethane at −70 °C in 92% yield; m.p. 112 °C with decomposition. The analogous ^{t}butyl isocyanide complex *p*-$TolS(O)_2Au(CN^tBu)$ **10** was synthesized accordingly from (^{t}BuNC)AuCl in 86% yield; m.p. 98 °C with decomposition.



(5)

9, R = Xy
10, R = ^{t}Bu

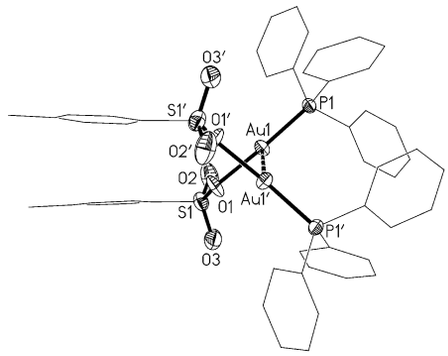


Fig. 1 Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids for the core atoms; H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–O1 2.086(2), Au1–P1 2.2123(8), Au1 · · · Au′ 3.1770(3); P1–Au1–O1 175.47(8).

The complexes show CN stretching vibrations in their IR spectra at 2217 and 2246 cm^{-1}, respectively. The high abundance of the ions $[L_2Au]^+$ (L = XyNC, ^{t}Bu) in the mass spectra of these compounds suggests ionic structures with homoleptic cations and anions, but no single crystals could be grown for structure determinations.

Crystal structure analyses

Crystals of the sulfonate complex **1** (colourless rods from CH_2Cl_2–n-C_5H_{12} at −30 °C) are monoclinic, space group *C*2/*c* with $Z = 8$ formula units and dichloromethane molecules in the unit cell. The complexes are aggregated into pairs through aurophilic bonding [Au–Au1 3.1770(3) Å]. In the dimers, the components are related by a crystallographically imposed two-fold axis. Through the mutual approach of the monomers, the P–Au–O axes are bent and deviate significantly from linearity [175.47(8)°]. The gold atoms are oxygen-bonded [Au1–O1 2.086(2) Å, S1–O1–Au1 118.6(2)°]. The corresponding sulfur–oxygen bond thus represents a single bond with S1–O1 1.491(3) Å and is longer than the two remaining S–O bonds [S1–O2 1.441(4), S1–O3 1.425(4) Å] (Fig. 1).

Crystals of complex **5** (from tetrahydrofuran–diethylether at −30 °C) were also investigated by X-ray methods, but the crystallinity of the specimens was not good enough to allow a satisfactory refinement of the structure. From the preliminary results, however, there can be no doubt that the sulfonate compound **5** also has the proposed heteroleptic structure, *i.e.* $(Ph_3P)AuOS(O)_2Et$, and not a homoleptic ion-pair structure as observed for the sulfinate **6**. The latter appears to be favoured only for gold(I) sulfinates.

Crystals of complex **6** (from CH_2Cl_2–n-C_5H_{12} at −30 °C) are triclinic, space group $P\bar{1}$ with $Z = 2$ formula units in the unit cell. The asymmetric unit contains an ion pair with no crystallographically imposed symmetry. As already derived from mass spectrometric results, this dinuclear unit contains the two homoleptic ions with quasi-linear configurations at both metal centers (Fig. 2). The molecular axes of the two ions are crossed and have a short metal–metal contact of 2.9429(2) Å. Obviously, in order to allow a very close approach, the two axes are bent very significantly to reach an unprecedentedly small P1–Au2–P2 angle of only 156.66(4)° in the cation, and 176.50(4)° for S1–Au1–S2 in the anion. This result strongly supports the idea of aurophilic bonding in **6**, because such a strong bending of a P–Au–P axis is observed only for species where a strong neutral donor ligand or a soft anion are present to increase the coordination number of the metal atom from 2 to 3. Examples of such cases include $[(Ph_3P)_3Au]^+$ and $[Au(GeCl_3)_3]^-$.[14,15] From the structure of **6**, it appears that in the ion pair, the di(sulfinato)aurate(I) anion plays the role of a donor ligand for the cation, *with its gold atom as the donor center*!

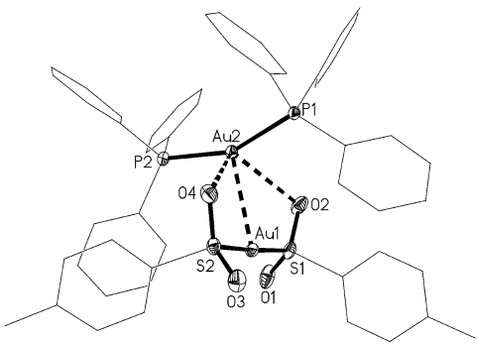


Fig. 2 Molecular structure of compound **6** (ORTEP drawing with 50% probability ellipsoids for the core atoms; H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–S1 2.293(1), Au1–S2 2.295(1), Au2–P1 2.311(1), Au2–P2 2.305(1), Au1···Au2 2.9429(2), Au2···O2 3.218(2), Au2···O4 3.239(2); S1–Au1–S2 176.50(4), P1–Au2–P2 156.66(4).

In the anion of **6**, the two sulfinate ligands are sulfur-bonded, in agreement with the principle of hard and soft acids and bases which predicts a preference of soft gold(I) for soft sulfur(IV) over oxygen. This arrangement is reminiscent of the structure of the analogous phosphinate or phosphite complexes of the types $[Au\{P(O)R_2\}_2]^-$ and $[\{(RO)_3P\}_2Au]^+$ where the gold atoms are exclusively phosphorus-bonded, not oxygen-bonded.[9–12] There are two Au–O contacts (O2, O4) which may also influence the bonding geometry at Au2, but the effect is expected to be small. As perhaps should be expected, only the sulfonate complexes show the molecular structure LAuX which, upon dissociation of the leaving group X^-, will yield the cationic unit $[LAu]^+$ which is considered the catalytically active species.[4] The sulfinate complexes have homoleptic, ionic structures, from which the generation of $[LAu]^+$ species is less obvious, and in fact unlikely.

Experimental

All experiments were carried out in an atmosphere of pure dry nitrogen. Solvents were dried and saturated with nitrogen. Glassware was oven-dried and flushed with nitrogen. Standard equipment was used throughout. Starting materials were commercially available or were prepared using literature methods: $(Me_3P)AuCl$,[16] $(Ph_3P)AuCl$,[17] $(Ph_3P)AuOC(O)CF_3$,[8] ^tBuNC and 2,6-$Me_2C_6H_3NC$,[18] (^{t}BuNC)AuCl and (2,6-$Me_2C_6H_3NC$)-AuCl.[19] The silver sulfonates and sulfinates were prepared following the procedure disclosed in the patent literature.[20]

(Triphenylphosphine)gold(I) *p*-tolylsulfonate, 1

A suspension of silver *p*-tolylsulfonate (300 mg, 1.1 mmol) in dichloromethane (20 mL) was treated with a solution of $(Ph_3P)AuCl$ (500 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) at 20 °C for 3 h with stirring. The AgCl precipitate was filtered off and the product was precipitated from the clear filtrate by addition of pentane. The product was filtered, washed with toluene and crystallized from CH_2Cl_2–pentane at −30 °C; colourless rods containing dichloromethane, m.p. 162 °C with decomposition; 490 mg (78% yield). NMR ($CDCl_3$, 20 °C), ^{1}H: δ 7.9–7.1 (m, 19H, C_6H_5/C_6H_4); 2.41 (s, 3H, Me); 5.3 (s, 2H, CH_2Cl_2). $^{31}P\{^1H\}$: δ 27.9 (s); $^{13}C\{^1H\}$: δ 134.1 (d, J = 14.0 Hz); 132.2 (s); 129.3 (d, J = 12.3 Hz); 127.6 (d, J = 64.9 Hz) for *o*, *p*, *m* and *ipso* in C_6H_5; 141.7, 139.2, 129.0 and 126.5 all s for *ipso*, *o*, *m* and *p* in C_6H_4; 53.3 (s) for CH_2Cl_2; 21.3 (s) for Me. IR (KBr): 1261, 1184, 1146, 1100, 954 cm^{-1} ν(SO_3R). MS (FAB): *m*/*z* 721 (11%) $[(Ph_3P)_2Au]^+$; 631 (3) $[M + 1]^+$; 459 (100) $[(Ph_3P)Au]^+$; 262 (6) $[Ph_3P]^+$. $C_{26}H_{24}AuCl_2O_3PS$ (715.35): calcd. C 43.6, H 3.4, S 4.5; found C 44.1, H 3.3, S 4.4%.

(Trimethylphosphine)gold(I) *p*-tolylsulfonate, 2

The compound was prepared similarly to **1** from *p*-$TolSO_3Ag$ (600 mg, 2.2 mmol) and $(Me_3P)AuCl$ (400 mg, 1.3 mmol) in dichloromethane (20 mL) in 75% yield (430 mg); m.p. 129 °C with decomposition. NMR ($CDCl_3$, 20 °C), ^{1}H: δ 7.81 and 7.21 (4H, m, C_6H_4); 2.36 (s, 3H, *Me*C); 1.62 (d, J = 2.2 Hz, 9H, MeP). $^{31}P\{^1H\}$; δ −15.8 (s). $^{13}C\{^1H\}$: δ 141.7, 139.3, 129.1 and 126.4 all s for *ipso*, *o*, *m*, and *p* in C_6H_4; 21.5 (s, *Me*C); 15.9 (d, J = 51.5 Hz, MeP). MS (FAB): *m*/*z* 445 (14%) $[M + 1]^+$; 444 (0.5) $[M]^+$; 349 (16) $[(Me_3P)_2Au]^+$; 273 (100) $[(Me_3P)Au]^+$. $C_{10}H_{16}AuO_3PS$ (560.38): calcd. C 27.1, H 3.6, S 7.2; found C 27.1, H 3.4, S 7.2%.

(Triphenylphosphine)gold(I) *p*-pyridylsulfonate, 3[21]

The compound was prepared similarly to **1** from silver *p*-pyridylsulfonate (260 mg, 0.97 mmol) and $(Ph_3P)AuCl$ (400 mg, 0.8 mmol) in 30 mL of CH_2Cl_2 in 77% yield (380 mg); m.p. 156 °C with decomposition. NMR ($CDCl_3$, 20 °C), ^{1}H: δ 8.7–8.3 (m, 4H, Pyr); 7.7–7.4 (m, 15H, Ph). $^{31}P\{^1H\}$: δ 30.5 (s). MS (FAB): *m*/*z* 974 (5%) $[(Ph_3P)_2Au_2SO_3Py]^+$; 721 (2) $[(Ph_3P)_2Au]^+$; 619 (16) $[M + 1]^+$; 618 (59) $[M]^+$; 459 (100) $[(Ph_3P)Au]^+$; 262 (7) $[Ph_3P]^+$. $C_{23}H_{19}AuNO_3PS$ (618.25): calcd. C 44.6, H 3.1, N 2.4, S 5.2; found C 44.2, H 3.3, N 2.0, S 5.0%.

(Trimethylphosphine)gold(I) ethylsulfonate, 4

The compound was prepared similarly to **1** from silver ethylsulfonate (170 mg, 0.78 mmol) and $(Me_3P)AuCl$ (200 mg, 0.65 mmol) in 20 mL of tetrahydrofuran in 85% yield (210 mg); m.p. 122 °C with decomposition. NMR ($CDCl_3$, 20 °C), ^{1}H: δ 3.02 (q, J = 7 Hz, 2H, CH_2); 1.38 (t, J = 8 Hz, 3H, *Me*C); 1.64 (d, J = 12.1 Hz, 9H, MeP). $^{31}P\{^1H\}$: δ −12.5, s. $^{13}C\{^1H\}$: δ 46.0 (s, CH_2); 8.9 (s, *Me*C); 16.0 (d, J = 68 Hz, MeP). MS (FAB): *m*/*z* 655 (42%) $[(Me_3P)_2Au_2OSO_2Et]^+$; 579 (56) $[Me_3PAu_2OSO_2Et]^+$; 383 (8) $[M + 1]^+$; 273 (100) $[(Me_3P)Au]^+$. $C_5H_4AuO_3PS$ (382.17): calcd. C 15.7, H 3.7; found C 15.4, H 3.5%.

(Triphenylphosphine)gold(I) ethylsulfonate, 5

The compound was obtained as above from $EtSO_3Ag$ (216 mg, 1.0 mmol) and $(Ph_3P)AuCl$ (400 mg, 0.81 mmol) in 40 mL of tetrahydrofuran in 90% yield (412 mg): m.p. 135 °C with decomposition. NMR ($CDCl_3$, 20 °C), ^{1}H: δ 7.6–7.2 (m, 15H, Ph); 3.05 (q, J = 7 Hz, 2H, CH_2); 1.42 (t, J = 8 Hz 3H, Me). $^{31}P\{^1H\}$: δ 29.6 (s). $^{13}C\{^1H\}$: δ 134.3 (d, J = 15 Hz), 132.5 (s), 129.5 (d, J = 13.9 Hz) and 127.9 (d, J = 65.3 Hz) for *o*, *p*, *m* and *ipso* in C_6H_5; 46.3 (s, CH_2); 9.5 (s, Me). IR (KBr): 1275, 1270 ν_a (SO_2R), 1170 cm^{-1} ν_s (SO_2R). MS (FAB): *m*/*z* 721 (16%) $[(Ph_3P)_2Au]^+$; 569 (2) $[M + 1]^+$; 459 (100) $[(Ph_3P)Au]^+$, 262 (4) $[Ph_3P]^+$. $C_{20}H_{20}AuO_3PS$ (568.38): calcd. C 42.2, H 3.5, S 5.6; found C 41.4, H 3.7, S 5.1%.

(Triphenylphosphine)gold(I) *p*-tolylsulfinate, 6

Silver *p*-tolylsulfinate (213 mg, 0.81 mmol) was suspended in 20 mL of tetrahydrofuran, cooled to −70 °C and treated with a solution of $(Ph_3P)AuCl$ (400 mg, 0.81 mmol) in 20 mL of tetrahydrofuran. The reaction mixture was filtered after 2 h of vigorous stirring. The filtrate was concentrated in a vacuum and precooled pentane added (at −70 °C); colourless needles, m.p. 98 °C with decomposition; 470 mg (94.5% yield). NMR ($CDCl_3$, 20 °C), ^{1}H: δ 7.9–7.1 (m, 19H, C_6H_5/C_6H_4); 2.39 (s, 3H, Me). $^{31}P\{^1H\}$: δ 30.4 (s). MS (FAB): 721 (100%) $[(Ph_3P)_2Au]^+$, 615 (3) $[M + 1]^+$, 459 (57) $[(Ph_3P)Au]^+$, 262 (4) $[Ph_3P]^+$. $C_{25}H_{22}AuO_2PS$ (614.45): calcd. C 48.9, H 3.6, S 5.2; found C 49.4, H 4.2, S 4.3%.

(Triphenylphosphine)gold(I) methylsulfinate, 7

$(Ph_3P)AuCl$ (400 mg, 0.81 mmol) was converted into $(Ph_3P)AuOC(O)CF_3$ by treatment with CF_3COOAg (180 mg, 0.81 mmol) in 20 mL of CH_2Cl_2 at −78 °C for 30 min. The

Table 1 Crystal data, data collection and structure refinement for compounds **1** and **6**

	p-TolS(O)$_2$–Au(PPh$_3$)·CH$_2$Cl$_2$ **6**	*p*-TolS(O)$_2$O–Au(PPh$_3$)·CH$_2$Cl$_2$ **1**
Crystal data		
Formula	$C_{51}H_{46}Au_2Cl_2O_4P_2S_2$	$C_{26}H_{24}AuCl_2O_3PS$
M_r	1313.77	715.35
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	12.4984(2)	18.7637(2)
b/Å	13.1125(3)	16.5719(2)
c/Å	15.9587(3)	17.9879(2)
α/°	90.213(1)	
β/°	91.173(1)	111.590(1)
γ/°	101.733(1)	
V/Å^3	2562.1(1)	5200.9(1)
Z	2	8
Data collection		
T/K	143	143
Measured reflections	37101	41169
Unique reflections	9698 [R_{int} = 0.0435]	5720 [R_{int} = 0.0409]
Refls. used for refinement	9046	5331
Refinement		
Refined parameters	568	307
Final R values [$I > 2\sigma(I)$]		
$R1$ [a]	0.0307	0.0276
$wR2$ [b]	0.0717	0.0633
(shift/error)$_{max}$	<0.001	<0.001
ρ_{fin}(max/min)/e Å^{-3}	1.172/ −1.198	0.842/ −0.870

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0129 (**1**), 0.00 (**6**); b = 16.87 (**1**), 6.74 (**6**).

reaction mixture was filtered and the filtrate added to a suspension of $MeSO_2Na$ (160 mg, 1.6 mmol) in 20 mL of methanol and stirred for 8 h at −78 °C. After filtration, the product was precipitated from the filtrate by addition of pentane; 84.5% yield (370 mg); m.p. 79 °C with decomposition. NMR ($CDCl_3$, 20 °C), ^{1}H: δ 7.6–7.4 (m, 15H, Ph); 2.94 (s, 3H, Me). ^{31}P{^{1}H}: δ 30.9 (s). MS (FAB): *m*/*z* 721 (23%) [(Ph$_3$P)$_2$Au]$^+$; 459 (100) [(Ph$_3$P)Au]$^+$, 262 (9) [Ph$_3$P]$^+$. $C_{19}H_{18}AuO_2PS$ (538.36): calcd. C 42.4, H 3.3; found C 42.1, H 3.0%.

(Trimethylphosphine)gold(I) methylsulfinate, 8

The compound was obtained similarly to **7** from (Me$_3$P)AuCl (200 mg, 0.65 mmol), CF_3CO_2Ag (160 mg, 0.72 mmol) and $MeSO_2Na$ (130 mg, 1.3 mmol) in 20 mL of CH_2Cl_2 and 20 mL of methanol, respectively; 83% yield (190 mg); m.p. 68 °C with decomposition. NMR ($CDCl_3$, 20 °C), ^{1}H: δ 3.21 (s, 3H, MeS); 1.87 (d, J = 17.6 Hz, 9H, MeP); ^{31}P{^{1}H}: δ −14.1 (s). ^{13}C{^{1}H}: δ 37.4 (s, MeS); 15.9 (d, J = 42.3, MeP). MS (FAB): *m*/*z* 349 (100%) [(Me$_3$P)$_2$Au]$^+$; 272 (49) [(Me$_3$P)Au]$^+$. $C_4H_{12}AuO_2PS$ (352.15): calcd. C 13.6, H 3.4; found C 14.1, H 3.1%.

(2,6-Dimethylphenylisocyanide)gold(I) *p*-tolylsulfinate, 9

(XyNC)AuCl (230 mg, 0.63 mmol) was treated with *p*-TolSO$_2$Ag (180 mg, 0.68 mmol) in dichloromethane (20 mL) at −70 °C for 3 h with stirring. The reaction mixture was filtered and the product precipitated from the filtrate by addition of precooled pentane (−70 °C); yellow solid, m.p. 112 °C with decomposition; 280 mg (92% yield). NMR ($CDCl_3$, 20 °C), ^{1}H: δ 7.9–7.1 (m, 7H, C_6H_4/C_6H_3); 2.4 (s, 6H, *Me*$_2$Xy); 1.6 (s, 3H, *Me*Tol). IR (KBr): 2217 cm^{-1}. MS (FAB): *m*/*z* 484 (4%) [M]$^+$; 459 (100) [(XyNC)$_2$Au]$^+$; 328 (13) [(XyNC)Au]$^+$. $C_{16}H_{16}AuNO_2S$ (483.34): calcd. C 39.7, H 3.3, N 2.9; found C 39.3, H 3.2, N 2.8%.

(^{t}Butylisocyanide)gold(I) *p*-tolylsulfinate, 10

The compound was obtained similarly to **9** from (^{t}BuNC)AuCl (110 mg, 0.35 mmol) and *p*-TolSO$_2$Ag (110 mg, 0.42 mmol) in 10 mL of CH_2Cl_2; yellow solid, m.p. 98 °C with decomposition; 130 mg (86% yield). NMR ($CDCl_3$, 20 °C), ^{1}H: δ 8.0–7.0 (m, 4H, C_6H_4); 1.90 (s, 3H, *Me*Tol); 1.57 (s, 9H, ^{t}Bu). ^{13}C{^{1}H}: δ 130.7, 130.4, 129.2 and 127.5 all s for *o*, *p*, *m*, *ipso* of C_6H_4; 59.8 (t, J = 7.3 Hz, *Me*$_3$*C*); 30.2 (s, Me$_3$*C*); 22.3 (s, *Me*Tol); CAu not detected. IR (KBr): 2246 cm^{-1}. MS (FAB): *m*/*z* 549 (5%) [Au$_2$SO$_2$-*p*-Tol]$^+$; 363 (2) [(^{t}BuNC)$_2$Au]$^+$, 155 (100) [*p*-TolSO$_2$]$^+$. $C_{12}H_{16}AuNO_2S$ (435.30): calcd. C 33.0, H 3.6, N 3.2; found C 32.2, H 3.4, N 2.8%.

X-Ray crystallography

Specimens of compounds **1** and **6** 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. Intensity data were corrected for absorption effects (DELABS from PLATON). The structures were solved by a combination of direct methods (SHELXS-97)[22] and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97).[22] 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. Crystals of compound **6** contained some additional disordered and unidentified solvent in the lattice, which was not included in the refinement but was taken care of by the 'SQUEEZE'-procedure (from PLATON).[23] The volume occupied by the solvent is 236 Å^3, the number of electrons per unit cell deduced by squeeze is 21. 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.

CCDC reference numbers 165245 and 165246.

See http://www.rsc.org/suppdata/dt/b1/b104001b/ for crystallographic data in CIF or other electronic format.

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