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(Phosphine)gold(I) trifluoromethanesulfonates, trifluoroacetates and trichlorothioacetates †

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Stable, crystalline (phosphine)gold(I) trifluoroacetates of the type $(R_3P)AuOC(O)CF_3$ have been prepared in high yield from the corresponding chloro complexes with $AgOC(O)CF_3$ in tetrahydrofuran for R = Me, Ph or *o*-Tol. The crystal structure of $(Me_3P)AuOC(O)CF_3$ features trimers with two short aurophilic Au · · · Au contacts in an angular Au · · · Au · · · Au unit. Trichlorothioacetic acid has been aurated (in high yield) using $\{[(R_3P)Au]_3O\}^+BF_4^-$ and $NaBF_4$ in dichloromethane to give equally stable compounds $(R_3P)AuSC(O)CCl_3$ with R = Me, Ph or *o*-Tol. In these products the trichlorothioacetate group is exclusively sulfur bonded to the gold atom. The methyl and *o*-tolyl compounds are dimers in the solid state, but association is based on only very long intermolecular Au · · · S and Au · · · Cl contacts, respectively. (Triphenylphosphine)gold thioacetate was prepared similarly, but the product is thermally unstable in both the solid and solution state. It thus appears that the presence of the halogen substituents is essential for the stability of the present compounds, which are useful aurating agents and can be employed for the controlled deposition of gold. [Tri(*o*-tolyl)phosphine]gold chloride was converted into the trifluoromethanesulfonate (triflate) in 95% yield by treatment with $AgOS(O)_2CF_3$ in tetrahydrofuran. The crystal structure determination of the CH_2Cl_2 solvate revealed non-ionic, molecular components [Au–O 2.110(3) Å, S–O–Au 120.4(2)°], which are associated into dimers *via* hydrogen bonds [O · · · H–C 170.2°, C–H 0.969 Å, H · · · O 2.575 Å] with two CH_2Cl_2 molecules.

Introduction

(Phosphine)gold(I) complexes $(R_3P)AuX$ are among the key reagents in gold chemistry. Apart from the conventional halide and pseudohalide compounds (X = Cl, Br, I, CN or SCN),[1–4] which have been used most extensively in the past, more recent work has also included several new reagents. Prominent examples are oxonium salts $[(R_3P)Au]_3O^+X^-$,[5] but alkoxides,[6] siloxides,[7,8] and aryl oxides[9–11] of the general type $(R_3P)AuOR$ are also of increasing importance. There is generally a need for $(R_3P)AuX$ complexes with X representing a good leaving group (a poor donor and nucleophile). With these counter ions, the cationic agents $[(R_3P)Au]^+$ can perform as extremely strong electrophiles as required in most "auration" reactions, including applications in homogeneous catalysis.[12,13] However, some of the ideal candidates $(R_3P)AuX$ with X = fluoride, tetrafluoroborate, hexafluorophosphate or trifluoromethanesulfonate (triflate) are of very limited stability.[14] They often cannot be isolated and have to be handled in solution at low temperature.

In this context we have resumed investigations of the trifluoromethanesulfonates, trihalogenocarboxylates and thiocarboxylates, which have not been studied much in the past.[15–17] Complexes of this family may have many advantages owing to their higher thermal stability and good solubility in acceptable solvents. There is also reason to expect that the compounds follow a clean thermal decomposition pattern involving decarboxylation as the initial step under mild conditions. This could offer advantages for gold deposition processes from solution or even from the vapour.[18]

In the scattered literature about previous work in this area there are several prototypes with simple carboxylate ligands,[19–25] but no more systematic investigations have been carried out.[17]

† Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

Results and discussion

Preparation and characterization of the compounds

The trifluoroacetates are readily prepared from (phosphine)-gold halides and silver trifluoroacetate [eqn. (1)]. For the

$$(R_3P)AuCl + AgOC(O)CF_3 \longrightarrow AgCl + (R_3P)AuOC(O)CF_3 \quad (1)$$

1: R = Me
2: R = Ph
3: R = *o*-Tol

auration of trichlorothioacetic acid, tris[(phosphine)gold] oxonium salts (in the presence of an excess of $NaBF_4$ as counter ion supplier) have been used [eqn. (2)]. The products can be

$$\{[(R_3P)Au]_3O\}^+BF_4^- + 3\,Cl_3CC(O)SH \longrightarrow 3\,(R_3P)AuSC(O)CCl_3 + H_2O + HBF_4 \quad (2)$$

4: R = Me
5: R = Ph
6: R = *o*-Tol

isolated in high yields as colourless, crystalline materials, readily soluble in most common polar organic solvents (di- and trichloromethane, tetrahydrofuran), but insoluble in pentane or diethyl ether. The composition was confirmed by elemental analysis, mass spectrometry and NMR spectroscopy (Experimental section). It is interesting that for almost all complexes the most prominent peak in the mass spectra is the $[(R_3P)Au]^+$ adduct of the parent compound. Cations of the formula $\{CX_3CO_2[Au(PR_3)]_2\}^+$ appear to be highly favoured upon ionization under high vacuum conditions.

In an exploratory experiment, thioacetic acid has also been subjected to auration with trigold oxonium tetrafluoroborate under similar conditions to give $(Ph_3P)AuSC(O)CH_3$ **7**. This product has much lower thermal stability as compared to the

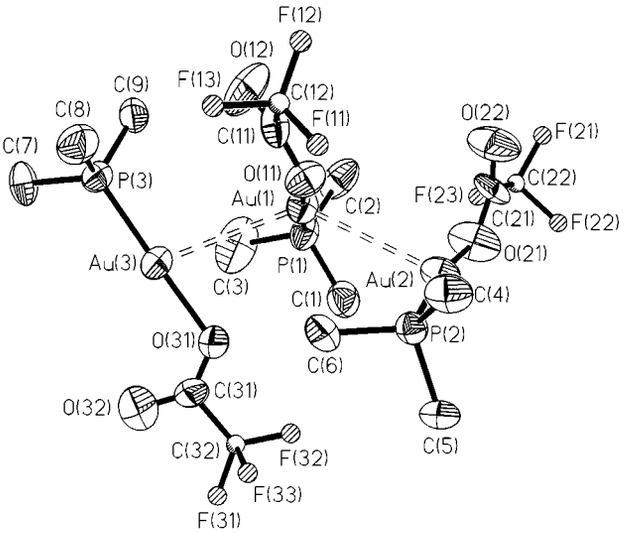

Fig. 1 Molecular structure of compound **1** (ORTEP[26] drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au(1)–O(11) 2.057(14), Au(1)–P(1) 2.204(5), O(11)–Au(1)–P(1) 177.0(5), C(11)–O(11)–Au(1) 118.5(13); Au(2)–O(21) 2.09(2), Au(2)–P(2) 2.217(5), O(21)–Au(2)–P(2) 168.9(5), C(21)–O(21)–Au(2) 124(2); Au(3)–O(31) 2.08(2), Au(3)–P(3) 2.214(5), O(31)–Au(3)–P(3) 178.9(5), C(31)–O(31)–Au(3) 121(2); Au(1)···Au(2) 3.3136(13), Au(1)···Au(3) 3.3326(13), Au(2)···Au(1)···Au(3) 129.81(3), O(11)–Au(1)···Au(2) 81.5(4), O(11)–Au(1)···Au(3) 92.1(4), O(21)–Au(2)···Au(1) 92.4(6), O(31)–Au(3)···Au(1) 75.3(5), P(1)–Au(1)···Au(2) 95.73(14), P(1)–Au(1)···Au(3) 90.6(2), P(2)–Au(2)···Au(1) 96.28(14), P(3)–Au(3)···Au(1) 103.6(2).

trichlorothioacetate. It must be handled in solution at temperatures well below 0 °C to avoid rapid decomposition.

(Triphenylphosphine)- and [tri(*o*-tolyl)phosphine]-gold triflate **8** and **9** are prepared from the corresponding chlorides by treatment with $AgOS(O)_2CF_3$ in tetrahydrofuran, eqn. (3). The

$$(R_3P)AuCl + AgOS(O)_2CF_3 \longrightarrow AgCl + (R_3P)AuOS(O)_2CF_3 \quad (3)$$

8: R = Ph
9: R = *o*-Tol

solutions obtained after filtration from the AgCl precipitate are stable at ambient temperature in the dark, but **8** readily decomposes upon evaporation of the solvent. Colourless, solid residues can be kept below −20 °C for some time, however, especially so if the thf is not removed completely. The *o*-tolyl homologue **9** is more robust and the solution and the solid are stable at temperatures below 0 °C. Single crystals of a $\mathbf{9}\cdot CH_2Cl_2$ solvate are obtained from dichloromethane–pentane at 0 °C.

Crystal and molecular structures

Crystals of (trimethylphosphine)gold trifluoroacetate **1**, mp 118 °C, from tetrahydrofuran–pentane are monoclinic (space group $P2_1/n$, $Z = 12$, at −78 °C). The asymmetric unit contains three crystallographically independent molecules. These three molecules [with the gold atoms Au(1), Au(2) and Au(3), Fig. 1], are associated into a trimer *via* two short aurophilic Au···Au contacts: Au(1)···Au(2) 3.3136(13) Å, Au(1)···Au(3) 3.3326(13) Å, Au(2)···Au(1)···Au(3) 129.81(3)°. These trimers are part of a spiral chain of molecules running along the *x*-axis of the crystal (Figs. 2, 3). However, the Au···Au contacts between the trimers are much longer and well in excess of the sum of the van der Waals radii [Au(3)···Au(2′) 4.322(6) Å].

The individual monomers have a linear configuration at the gold atoms with angles O–Au–P all close to 180° (caption to Fig. 1), while the angles O–Au–Au and P–Au–Au range from 75.3 to 103.6°. These pattern details are rather common in aggregates of linear gold(I) complexes L–Au–X, as is the "crossed swords" arrangement of neighbouring P–Au–O units

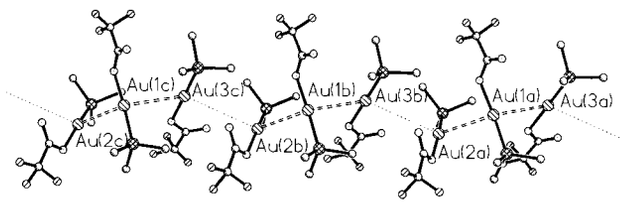

Fig. 2 Chain formation of the trimers of compound **1** through Au···Au contacts [Au(3)···Au(2′) 4.322(6) Å].

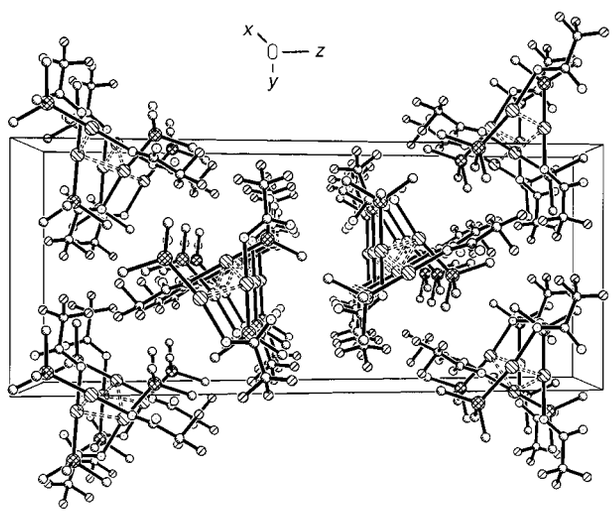

Fig. 3 Cell plot of compound **1** with the chains running along the *x* axis.

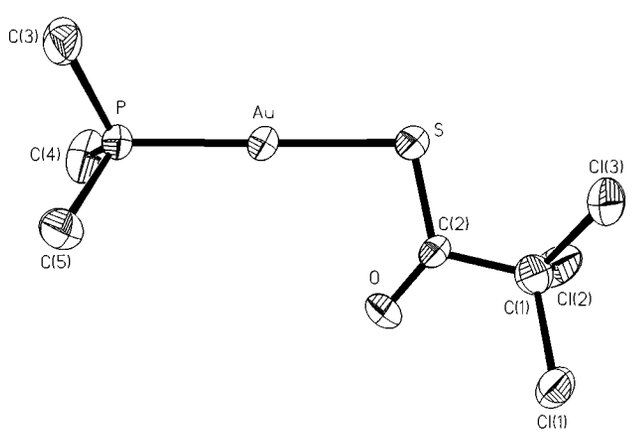

Fig. 4 Molecular structure of compound **4** (ORTEP[26] drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–P 2.248(4), Au–S 2.315(4); P–Au–S 176.0(2), Au–S–C(2) 101.7(5).

(Figs. 1–3). The internal dimensions of the tertiary phosphine and the trifluoroacetate groups are not unusual and mutually consistent for the three monomers.

The Au–O bond lengths are in the narrow range from 2.06(1) to 2.09(2) Å with angles Au–O–C between 119(1) and 124(2)°. The former are to be considered rather long and may indicate the poor donor properties of the trifluoroacetate group as compared *e.g.* with the trimethylsiloxide group in $(R_3P)AuOSiR_3$ molecules.[7,8]

Crystals of (trimethylphosphine)gold trichlorothioacetate **4**, mp 143 °C, from dichloromethane–diethyl ether, are also monoclinic (space group $P2_1/c$, $Z = 4$, at −110 °C), but the lattice is composed of dimers, the monomeric units of which are related by a crystallographically imposed centre of inversion (Figs. 4 and 5). In the monomer the gold atom is attached to the sulfur atom of the trichlorothioacetate group with a rather long Au–S distance of 2.315(4) Å, but a narrow angle Au–S–C of

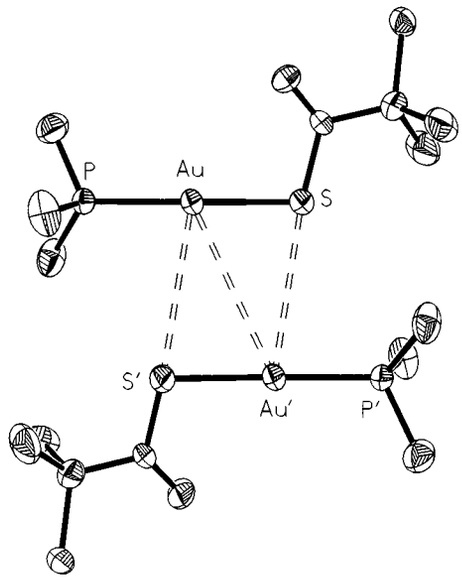

Fig. 5 Association of monomers of compound **4** into dimers, based on weak Au · · · Au′ [4.012 Å] and Au · · · S′ [3.722 Å] contacts.

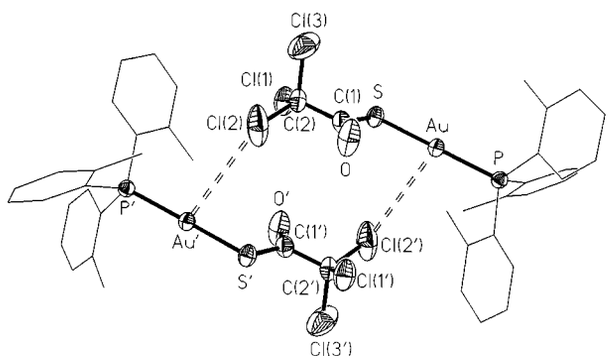

Fig. 6 Dimeric structure of compound **6** (ORTEP[26] drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–P 2.2722(13), Au–S 2.3104(13); P–Au–S 173.34(4), C(1)–S–Au 104.1(2), Au · · · Cl(2′) 3.720(1).

101.7(5)°. It should be noted that the O and Au atoms are not drawn together: The S–Au–P axis is close to linear [176.0(2)°] and the small deviation from 180° is in the opposite direction. The internal geometry of the phosphine and the $SC(O)CCl_3$ ligands is not exceptional.

Surprisingly, the intermolecular bonding is not based on Au · · · Au interactions, but rather on Au–S′ contacts: Au · · · Au′ 4.012; Au · · · S′ 3.722 Å. These values are in the range of van der Waals distances and are probably associated with only very weak forces. A similar rhomboid array of atoms (AuSAu′S′, Fig. 5) has recently also been detected in the structure of gold(I) thiophosph(in)ate complexes.[27,28] However weak, these interactions are still determining quite significantly the organization of molecules in the crystal.

Crystals of [tri(*o*-tolyl)phosphine]gold trichlorothioacetate **6**, mp 154 °C, from dichloromethane–diethyl ether are also monoclinic (space group $P2_1/n$, $Z = 4$, at −79 °C). The lattice contains equivalent molecules loosely aggregated to give centrosymmetrical dimers (Fig. 6). The intermolecular forces are only based on long Cl · · · Au contacts (3.720 Å). As in **4** (above) the trichlorothioacetate unit is attached to the gold atom *via* the sulfur atom with an Au–S distance of 2.3104(13) Å and angles C–S–Au 104.1(2) and P–Au–S 173.34(4)°. The former is wider than in **4**, probably owing to the steric congestion arising through the bulky tri(*o*-tolyl)phosphine ligand. Both this distortion and the bending at Au rule out any intramolecular O · · · Au contacts. However, the P–Au–S bending is in favour of the intermolecular Cl · · · Au contact which

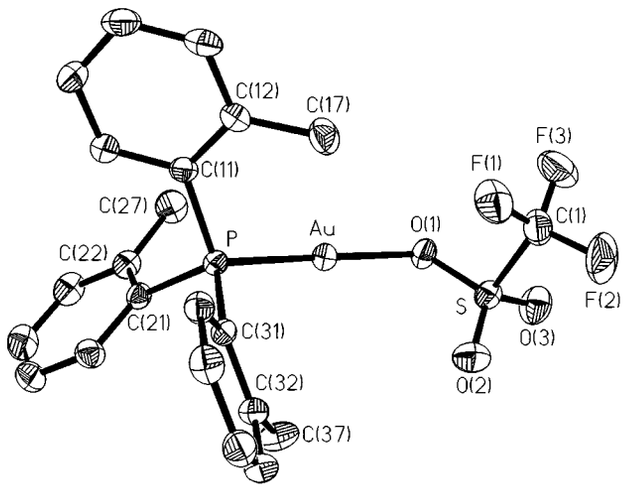

Fig. 7 Molecular structure of compound **9** (ORTEP[26] drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–P 2.225(1), Au–O(1) 2.110(3), S–O(1) 1.470(3), S–O(2) 1.432(4), S–O(3) 1.426(3), S–C(1) 1.823(5), C(1)–F(1) 1.330(6), C(1)–F(2) 1.319(6), C(1)–F(3) 1.322(6); P–Au–O(1) 176.50(8), Au–O(1)–S 120.4(2), O(1)–S–O(2) 113.0(2), O(1)–S–O(3) 112.2(2), O(1)–S–C(1) 101.8(2), O(2)–S–O(3) 118.9(2), O(2)–S–C(1) 104.7(2), O(3)–S–C(1) 103.9(2), S–C(1)–F(1) 111.0(3), S–C(1)–F(2) 110.4(4), S–C(1)–F(3) 111.6(4), F(1)–C(1)–F(2) 108.0(5), F(1)–C(1)–F(3) 107.5(4), F(2)–C(1)–F(3) 108.1(4).

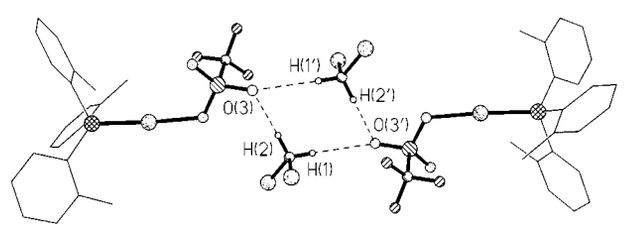

Fig. 8 Hydrogen bonding between compound **9** and the CH_2Cl_2 solvent molecules [C–H(1) 0.969 Å, H(1) · · · O(3′) 2.575 Å; C–H(1) · · · O(3′) 170.2°; C–H(2) 0.964 Å, H(2) · · · O(3) 2.556 Å; C–H(2) · · · O(3) 142.9°].

is similar to the observations made recently for Cl_3Ge–Au–P(*o*-Tol)$_3$.[29]

Crystals of compound **9**·CH_2Cl_2 are triclinic (space group $P\bar{1}$, $Z = 2$, at −80 °C). The asymmetric unit contains one monomer **9** and one solvent molecule (Fig. 7). These components are associated into dimeric units *via* weak hydrogen bonds as drawn in Fig. 8.[30] The two complexes and the two solvent molecules are related by a crystallographic centre of inversion.

The configuration at the gold atom is close to linear [P–Au–O(1) 176.50(8)°]. The triflate anion is strongly coordinated to the gold atom *via* one oxygen atom [O(1)] as witnessed by a short Au–O contact of only 2.110(3) Å and by a lengthening of the S–O(1) bond to 1.470(3) Å as compared to S–O(2) and S–O(3) with 1.432(4) and 1.426(3) Å, respectively. The angle at the oxygen atom O(1) [120.4(2)°] is rather small and also indicative of covalent Au–O bonding. The geometry of the CF_3SO_3 and Ph_3P moieties is otherwise unexceptional.

In the structural chemistry of gold there is only one precedent for gold–triflate bonding:[31] dimethylgold(III) triflate hydrate contains a CF_3SO_3 unit bound to gold(III) unidentately with an Au–O contact of 2.201(6) Å and an Au–O–S angle of 128.7(4)°. The S–O bonds show only small variations [1.456(6) *versus* 2 × 1.439(4) Å] suggesting a weaker bonding than in **9**. Fully ionic triflate anions have S–O bond lengths smaller than 1.420 Å, as recently measured for the gold compound $(CH_2)_2[PPh_2SAu(PPh_3)]_2^{2+}$ 2 $(CF_3SO_3^-)$, where no Au–O contact is discernible.[32]

Conclusion

The present study has shown that (phosphine)gold(I) trihalogeno(thio)acetates are readily available from standard reagents as stable compounds, which are easy to handle owing to their good solubility. They are a useful addition to the arsenals of aurating agents and of precursors for gold deposition processes. Work following up these opportunities is in progress.

Experimental

General

The experiments were routinely carried out in an atmosphere of dry and pure nitrogen. Standard equipment was used throughout. Glassware and solvents were purified, dried and filled/saturated with nitrogen. Starting materials were either commercially available or synthesized *via* published procedures: $\{[(Ph_3P)Au]_3O\}^+BF_4^-$,[5] $\{[(Me_3P)Au]_3O\}^+BF_4^-$,[33] $\{[(o\text{-Tol})_3PAu]_3O\}^+BF_4^-$,[34] $(Ph_3P)AuCl$,[35] $(Me_3P)AuCl$,[33] $(o\text{-Tol})_3PAuCl$,[36] $Cl_3CC(O)SH$.[37]

Syntheses

$(Me_3P)AuOC(O)CF_3$ 1. To a solution of $(Me_3P)AuCl$ (120 mg, 0.39 mmol) in thf (30 ml) was added $AgOC(O)CF_3$ (86 mg, 0.39 mmol) dissolved in thf (20 ml). After stirring for 1 h the reaction mixture was filtered. Evaporation of the solvent from the filtrate *in vacuo* to leave a volume of *ca*. 5 ml and addition of pentane led to the precipitation of 135 mg (90%) of complex **1** as a white solid. The compound is air-stable as a solid and in solution, soluble in dichloromethane and tetrahydrofuran, but insoluble in pentane and diethyl ether. Colourless crystals suitable for X-ray analysis could be obtained from tetrahydrofuran solution by layering with pentane, mp 118 °C (decomp.) (Found: C, 15.28; H, 2.17. $C_5H_9AuF_3O_2P$ requires C, 15.56; H, 2.35%). NMR ($CDCl_3$): ^1H, δ 1.69 [d, J(HP) 10 Hz, Me]; $^{13}C\text{-}\{^1H\}$, δ 119.3 [q, J(CF) 297, CF_3], 158.5 [q, J(CF) 44, CO_2] and 14.7 [d, J(CP) 38 Hz, Me]; $^{31}P\text{-}\{^1H\}$, δ −15.3 (s). FAB mass spectrum: *m*/*z* 658 (11%, $[M + AuPMe_3]^+$).

$(Ph_3P)AuOC(O)CF_3$ 2. The synthesis was analogous to that of complex **1** with $(Ph_3P)AuCl$ (120 mg, 0.24 mmol) and $AgOC(O)CF_3$ (54 mg, 0.24 mmol) to give 131 mg (94%) of **2**. Stability and solubility as for **1**, mp 128 °C (decomp.) (Found: C, 41.78; H, 2.80. $C_{20}H_{15}AuF_3O_2P$ requires C, 41.98; H, 2.64%). NMR ($CDCl_3$): ^1H, δ 7.28–7.81 (m, Ph); $^{13}C\text{-}\{^1H\}$, δ 119.7 [q, J(CF) 293, CF_3], 164.2 [q, J(CF) 48, CO_2], 133.9 [d, J(CP) 13], 132.0 [d, J(CP) 3], 129.1 [d, J(CP) 12] and 127.8 [d, J(CP) 59 Hz] (*ortho*-, *para*-, *meta*-, *ipso*-C of Ph); $^{31}P\text{-}\{^1H\}$, δ 27.5 (s). FAB mass spectrum: *m*/*z* 1031 (5%, $[M + AuPPh_3]^+$).

$(o\text{-Tol})_3PAuOC(O)CF_3$ 3. The synthesis was analogous to that of complex **1** with $(o\text{-Tol})_3PAuCl$ (170 mg, 0.32 mmol) and $AgOC(O)CF_3$ (70 mg, 0.32 mmol) to give 177 mg (91%) of **3**. Stability and solubility as for **1**, mp 136 °C (decomp.) (Found: C, 44.85; H, 3.47. $C_{23}H_{21}AuF_3O_2P$ requires C, 44.97; H, 3.45%). NMR ($CDCl_3$): ^1H, δ 6.84–7.71 (m, 12 H, C_6H_4) and 2.58 (s, 9 H, Me); $^{13}C\text{-}\{^1H\}$, δ 118.2 [q, J(CF) 290, CF_3], 161.0 [q, J(CF) 47, CO_2], 142.8 [d, J(CP) 11, C2], 133.2 [d, J(CP) 10, C6], 132.3 [d, J(CP) 3, C3], 132.0 [d, J(CP) 2, C4], 126.5 [d, J(CP) 10, C5], 123.9 [d, J(CP) 66, C1] and 22.6 [d, J(CP) 11 Hz, Me]; $^{31}P\text{-}\{^1H\}$, δ 0.4 (s). FAB mass spectrum: *m*/*z*: 1115 (4%, $[M + AuP(o\text{-Tol})_3]^+$).

$(Me_3P)AuSC(O)CCl_3$ 4. To a solution of $Cl_3CC(O)SH$ (40 µl, 0.36 mmol) in dichloromethane (10 ml) were added at 0 °C $NaBF_4$ (100 mg, 0.91 mmol) and $\{[(Me_3P)Au]_3O\}^+BF_4^-$ (110 mg, 0.12 mmol) in dichloromethane (10 ml). The solution was stirred for 2 h at 0 °C and afterwards the solvent removed *in vacuo* to leave a volume of 5 ml. Addition of diethyl ether led to the precipitation of 142 mg (88%) of complex **4** as a white solid. The compound is air-stable and stable in solution, soluble in dichloromethane and chloroform, but insoluble in pentane and diethyl ether. Colourless crystals suitable for X-ray analysis could be obtained from dichloromethane solution by layering with diethyl ether, mp 143 °C (decomp.) (Found: C, 13.19; H, 2.30; S, 7.00. $C_5H_9AuCl_3OPS$ requires C, 13.30; H, 2.01; S, 7.10%). NMR ($CDCl_3$): ^1H, δ 1.71 [d, J(HP) 9 Hz, Me]; $^{13}C\text{-}\{^1H\}$, δ 101.6 (s, CCl_3), 192.9 [s, C(O)S] and 15.1 [d, J(CP) 36 Hz, Me]; $^{31}P\text{-}\{^1H\}$, δ −2.0 (s). FAB mass spectrum: *m*/*z* 451 (4%, $[M + 1]^+$).

$(Ph_3P)AuSC(O)CCl_3$ 5. The synthesis was analogous to that of compound **4** with $\{[(Ph_3P)Au]_3O\}^+BF_4^-$ (114 mg, 0.08 mmol), $NaBF_4$ (100 mg, 0.91 mmol) and $Cl_3CC(O)SH$ (26 µl, 0.23 mmol) to give 137 mg (93%) of **5**. Stability and solubility as for **4**, mp 161 °C (decomp.) (Found: C, 37.91; H, 2.49; S, 4.88. $C_{20}H_{15}AuCl_3OPS$ requires C, 37.67; H, 2.37; S, 5.03%). NMR ($CDCl_3$): ^1H, δ 7.35–7.77 (m, Ph); $^{13}C\text{-}\{^1H\}$, δ 101.4 (s, CCl_3), 193.8 [s, C(O)S], 134.0 [d, J(CP) 16], 131.7 [d, J(CP) 3], 129.1 [d, J(CP) 12] and 128.6 [d, J(CP) 63 Hz] (*ortho*-, *para*-, *meta*-, *ipso*-C of Ph); $^{31}P\text{-}\{^1H\}$, δ 37.9 (s). FAB mass spectrum: *m*/*z* 637 (7%, $[M + 1]^+$).

$(o\text{-Tol})_3PAuSC(O)CCl_3$ 6. The synthesis was analogous to that of compound **4** with $\{[(o\text{-Tol})_3PAu]_3O\}^+BF_4^-$ (167 mg, 0.10 mmol), $NaBF_4$ (100 mg, 0.91 mmol) and $Cl_3CC(O)SH$ (35 µl, 0.31 mmol) to give 203 mg (96%) of **6**. Stability and solubility as for **4**. Colourless crystals suitable for X-ray analysis could be obtained from dichloromethane solution by layering with diethyl ether, mp 154 °C (decomp.) (Found: C, 40.60; H, 3.13. $C_{23}H_{21}AuCl_3OPS$ requires C, 40.64; H, 3.11%). NMR ($CDCl_3$): ^1H, δ 6.91–7.88 (m, 12 H, C_6H_4) and 2.61 (s, 9 H, Me); $^{13}C\text{-}\{^1H\}$, δ 100.4 (s, CCl_3), 193.5 [s, C(O)S], 142.8 [d, J(CP) 12, C2], 133.3 [d, J(CP) 9, C6], 132.1 [d, J(CP) 9, C3], 131.7 [d, J(CP) 2, C4], 126.6 [d, J(CP) 10, C5], 125.0 [d, J(CP) 58, C1] and 22.7 [d, J(CP) 11 Hz, Me]; $^{31}P\text{-}\{^1H\}$, δ 16.1 (s). FAB mass spectrum: *m*/*z* 679 (3%, $[M + 1]^+$).

$(Ph_3P)AuSC(O)CH_3$ 7. To a solution of $CH_3C(O)SH$ (40 µl, 0.53 mmol) in thf (10 ml) was added slowly at −30 °C a solution of $\{[(Ph_3P)Au]_3O\}^+BF_4^-$ (260 mg, 0.18 mmol) in dichloromethane (20 ml), followed by $NaBF_4$ (100 mg, 0.91 mmol). After stirring for 2 h at −30 °C the solution was filtered. Evaporation of the solvent from the filtrate *in vacuo* at −20 °C to leave a volume of *ca*. 5 ml and addition of pentane led to the precipitation of 231 mg (82%) of complex **7** as a white solid. The complex decomposes at 0 °C and is stable in solution only below −30 °C (Found: C, 45.41; H, 3.78. $C_{20}H_{18}AuOPS$ requires C, 44.95; H, 3.40%). NMR (CD_2Cl_2, −30 °C): ^1H, δ 7.17–7.69 (m, Ph) and 2.51 (s, Me); $^{13}C\text{-}\{^1H\}$, δ 186.8 [s, C(O)S], 134.0 [d, J(CP) 14], 131.5 [d, J(CP) 2], 129.0 [d, J(CP) 12] and 128.9 [d, J(CP) 58 Hz] (*ortho*-, *para*-, *meta*-, *ipso*-C of Ph); $^{31}P\text{-}\{^1H\}$, δ 37.9 (s).

$(Ph_3P)AuOS(O)_2CF_3$ 8. A solution of $(Ph_3P)AuCl$ (372 mg, 0.75 mmol) in 100 ml of thf was treated with a solution of $AgOS(O)_2CF_3$ (192 mg, 0.75 mmol) in 30 ml of the same solvent. The precipitate of AgCl formed was separated by filtration. The solvent was removed from the filtrate in a vacuum at −20 °C. The colourless, flaky residue decomposes above −20 °C; yield 456 mg (100%). NMR ($CDCl_3$, −20 °C): ^1H, δ 7.58–7.45 (m, Ph); $^{13}C\text{-}\{^1H\}$, δ 134.0 [d, J(CP) 14, C2/6)], 132.7 [d, J(CP) 3, C4], 129.5 [d, J(CP) 12, C3/5], 127.0 [d, J(CP) 68, C1] and 120.3 [q, J(CF) 317 Hz, CF_3]; $^{31}P\text{-}\{^1H\}$, δ 28.1 (s).

$(o\text{-Tol})_3PAuOS(O)_2CF_3$ 9. To a solution of $(o\text{-Tol})_3PAuCl$ (115 mg, 0.22 mmol) in thf (30 ml) was added at 0 °C AgO-

Table 1 Crystal data, data collection, and structure refinement for compounds **1**, **4**, **6** and **9**

	1	**4**	**6**	**9**·CH_2Cl_2
Formula	$C_5H_9AuF_3O_2P$	$C_5H_9AuCl_3OPS$	$C_{23}H_{21}AuCl_3OPS$	$C_{23}H_{23}AlCl_2F_3O_3PS$
M_r	386.06	451.47	679.74	735.31
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	9.759(1)	6.208(1)	11.229(2)	10.637(1)
b/Å	11.362(2)	10.216(1)	14.256(1)	11.303(1)
c/Å	27.183(3)	19.180(2)	15.642	11.785(1)
α/°				67.80(1)
β/°	99.35(1)	98.70(1)	103.91(1)	81.99(1)
γ/°				76.01(1)
V/Å^3	2974.1(7)	1202.4(3)	2430.6(6)	1271.1(2)
D_c/g cm^{-3}	2.587	2.494	1.858	1.921
Z	12	4	4	2
F(000)	2112	832	1312	712
μ(Mo-Kα)/cm^{-1}	150.07	131.64	65.48	61.88
T/°C	−78	−110	−79	−80
Measured reflections	5834	2374	5527	10959
Unique reflections	5716 [R_{int} = 0.0528]	2374	5270 [R_{int} = 0.0181]	5509 [R_{int} = 0.0200]
Reflections for refinement	4797	2222	4721	5410
Refined parameters	275	109	271	307
Final R values [$I > 2\sigma(I)$]				
$R1$	0.0656	0.0507	0.0304	0.0312
$wR2$	0.1687	0.1207	0.0717	0.0796
ρ_{fin}(max./min.)[a]/e Å^{-3}	3.140/−3.606	2.330/−2.249	1.192/−2.111	1.791/−2.924

[a] The residual electron densities were located around Au atoms (compounds **4** and **6**) and around the CF_3 unit (**1**), respectively. Absorption correction by ψ scans was prevented by cooling problems at the end of the measurements.

$S(O)_2CF_3$ (55 mg, 0.22 mmol) dissolved in thf (10 ml). After stirring for 15 min the reaction mixture was filtered. Evaporation of the solvent from the filtrate *in vacuo* to leave a volume of *ca*. 5 ml and addition of pentane led to the precipitation of 136 mg (95%) of complex **9** as a white solid. The compound is stable in solution only below 0 °C, soluble in dichloromethane and tetrahydrofuran, but insoluble in pentane and diethyl ether. Colourless crystals suitable for X-ray analysis could be obtained from dichloromethane solution by layering with pentane at 0 °C (Found: C, 37.90; H, 3.24. $C_{22}H_{21}AuF_3O_3PS$·CH_2Cl_2 requires C, 37.57; H, 3.15%). NMR ($CDCl_3$, 0 °C): ^{1}H, δ 6.88–7.74 (m, 12 H, C_6H_4) and 2.55 (s, 9 H, Me); ^{13}C-{^{1}H}, δ 142.6 [d, J(CP) 13, C2], 133.2 [d, J(CP) 9, C6], 132.0 [d, J(CP) 8, C3], 131.6 [d, J(CP) 3, C4], 126.6 [d, J(CP) 10, C5], 124.6 [d, J(CP) 60, C1], 121.0 [q, J(CF) 325, CF_3] and 22.5 [d, J(CP) 12 Hz, Me]; ^{31}P-{^{1}H}, δ 1.6 (s).

Crystal structure determinations

Specimens of suitable quality and size of compounds **1**, **4**, **6** and **9**·CH_2Cl_2 were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å). During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lorentz-polarization correction was applied and intensity data were corrected for absorption effects (DIFABS).[38] The structures were solved by direct methods (SHELXS 86) and completed by full-matrix least squares techniques against F^2 (SHELXL 93).[39] The thermal motion of all non-hydrogen atoms of compounds **4** and **6** was treated anisotropically. The CF_3 group in **1** was slightly disordered and was refined with isotropic thermal parameters. The hydrogen atoms of the solvent molecule CH_2Cl_2 in the crystal of **9** were located, whereas all other hydrogen atoms of compounds **1**, **4**, **6** and **9** were placed in idealized calculated positions. All hydrogen atoms were allowed to ride on their corresponding carbon atoms with fixed isotropic contributions [$U_{iso(fix)} = 1.5U_{eq}$ of the attached C atom]. Further information on crystal data, data collection and structure refinement is summarized in Table 1.

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See http://www.rsc.org/suppdata/1999/1645/ for crystallographic files in .cif format.

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