Mono- and Bi-nuclear Gold(I) and Gold(III) Complexes with $S_2C–PR_3$ Ligands. *X*-Ray Crystal Structures of $[Au(C_6F_5)_3(S_2C–PEt_3)]$ and $[Au_2(\mu\text{-}S_2C–PEt_3)(C_6F_5)_6]\cdot CH_2Cl_2$*

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Phosphonium dithiocarboxylates $S_2C–PR_3$ displace the neutral ligand in $[Au(C_6F_5)_3(tht)]$ (tht = tetrahydrothiophene) to give monomeric $[Au(C_6F_5)_3(S_2C–PR_3)]$, where the neutral ligand is monodentate. Binuclear singly- or doubly-bridged gold(I) derivatives can be obtained by the reaction (2:1) between suitable gold(I) precursors and $S_2C–PR_3$. Binuclear bridged gold(III) complexes $[Au_2(\mu\text{-}S_2C–PR_3)(C_6F_5)_6]$ have been prepared by reaction of $[Au(C_6F_5)_3(S_2C–PR_3)]$ with $[Au(C_6F_5)_3(OEt_2)]$. The structures of $[Au(C_6F_5)_3(S_2C–PEt_3)]$ and $[Au_2(\mu\text{-}S_2C–PEt_3)(C_6F_5)_6]\cdot CH_2Cl_2$ have been established by *X*-ray crystallography.

We have studied [1,2] some aspects of the chemistry of the versatile ligands $S_2C–PR_3$; however, their role in gold chemistry has not yet been investigated. In the present paper, we describe the synthesis of gold derivatives $[Au(C_6F_5)_3(S_2C–PR_3)]$ containing the unidentate σ-S-bonded ligand. Their reactions with gold(I) or gold(III) compounds lead to binuclear complexes where the $S_2C–PR_3$ ligand uses both S atoms to bridge the metal centres, a situation that has its only precedent in the complex cation $[Ag_2(\mu\text{-}S_2C–PEt_3)_2(S_2C–PEt_3)_2]^{2+}$.[3] Both types of co-ordination have been unambiguously established by single-crystal *X*-ray diffraction studies of $[Au(C_6F_5)_3(S_2C–PEt_3)]$ and $[Au_2(\mu\text{-}S_2C–PEt_3)(C_6F_5)_6]\cdot CH_2Cl_2$.

Results and Discussion

(*a*) *Complexes containing Unidentate* $S_2C–PR_3$.—Reactions of various gold(I) or gold(III) precursors containing a weakly co-ordinating ligand {*viz.* $[Au(C_6F_5)_3(tht)]$, $[Au(C_6F_5)_2Cl(OEt_2)]$, $[Au(C_6F_5)_2(OClO_3)(PPh_3)]$, $[Au(C_6F_5)(tht)]$, or $[AuCl(tht)]$ (tht = tetrahydrothiophene)} with the stoicheiometric amount of $S_2C–PR_3$ [$R_3 = (C_6H_{11})_3$, Et_3, Bu_3, $PhMe_2$, or $PhEt_2$] lead to the expected substitution products only with $[Au(C_6F_5)_3(tht)]$ [equation (1)]; intractable oils [with the other gold(III) derivatives] or mixtures of products [with gold(I)] are obtained in the other cases.

$$[Au(C_6F_5)_3(tht)] + S_2C–PR_3 \longrightarrow [Au(C_6F_5)_3(S_2C–PR_3)] + tht \quad (1)$$

$$R_3 = (C_6H_{11})_3\ (\mathbf{1}),\ Et_3\ (\mathbf{2}),\ Bu_3\ (\mathbf{3}),\ PhMe_2\ (\mathbf{4}),\ PhEt_2\ (\mathbf{5})$$

The reactions are run at −20 °C and in the presence of CS_2 to prevent dissociation of the ligand, since the free phosphine would give $[Au(C_6F_5)_3(PR_3)]$. However, the pink complexes isolated, (**1**)—(**5**) (Table 1), are stable in solution and in the solid state at room temperature. They behave as non-electrolytes in acetone solution and are monomeric (isopiestic method) in dichloromethane solution. Their i.r. spectra show two strong bands in the 800 cm^{-1} region (810s and 790s br cm^{-1}), a pattern which is characteristic for some square-planar complexes of the type $[Au(C_6F_5)_3L]$ (L = unidentate ligand).[4]

The ^1H n.m.r. spectra confirm the purity of the compounds [and, incidentally, that complex (**1**) contains $0.5OEt_2$ of crystallization]. The $^{19}F\text{-}\{^1H\}$ n.m.r. spectrum of complex (**2**) shows the presence of two types of C_6F_5 groups (2:1 ratio) (see Experimental section), compatible with a square-planar structure and unidentate $S_2C–PEt_3$; other five-co-ordinate structures cannot be ruled out from the n.m.r. data alone. The structure of complex (**2**) has thus been established by *X*-ray diffraction studies. Suitable crystals were obtained by slow diffusion of n-hexane into a concentrated dichloromethane solution of (**2**).

The structure analysis (see Figure 1) confirms that the $S_2C–$

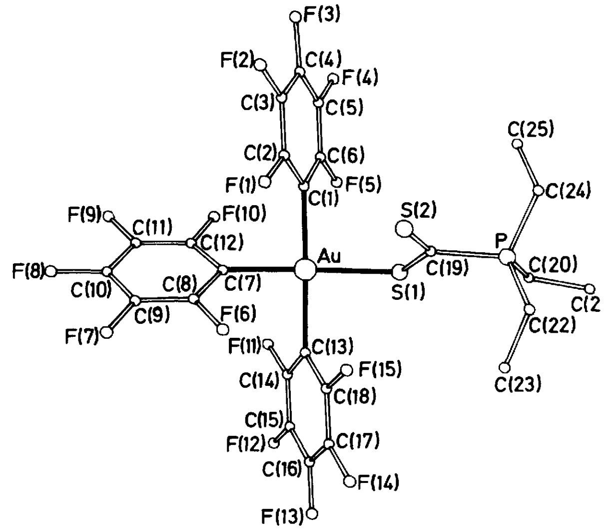

Figure 1. The molecule of $[Au(C_6F_5)_3(S_2C–PEt_3)]$ (**2**) in the crystal, showing the atom numbering scheme. Radii arbitrary, H atoms excluded

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* Tris(pentafluorophenyl)(triethylphosphoniodithioformate-*S*)gold(III) and μ-(triethylphosphoniodithioformate-*S*,*S*′)-bis[tris(pentafluorophenyl)gold(III)]-dichloromethane (1/1) respectively.

Supplementary data available: further details of the crystal-structure determinations have been deposited with Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany. They may be obtained on request, quoting the reference number CSD 52275 and a full literature citation.

Table 1. Analytical[a] and physical data[b]

		Analysis (%)			
Complex	Colour	C	H	Λ_M[c]	M.p./°C
(**1**) $[Au(C_6F_5)_3\{S_2C-P(C_6H_{11})_3\}]\cdot0.5OEt_2$	Pink	42.9 (42.8)	3.5 (3.6)	0.1	206
(**2**) $[Au(C_6F_5)_3(S_2C-PEt_3)]$	Pink	33.65 (33.75)	1.7 (1.6)	0.3	148
(**3**) $[Au(C_6F_5)_3(S_2C-PBu_3)]$	Pink	38.15 (37.7)	2.75 (2.75)	0.6	163
(**4**) $[Au(C_6F_5)_3(S_2C-PPhMe_2)]$	Pink	35.55 (35.8)	1.2 (1.25)	6.1	141
(**5**) $[Au(C_6F_5)_3(S_2C-PPhEt_2)]$	Pink	37.05 (37.15)	1.6 (1.5)	6.1	164
(**6**) $[Au_2\{\mu-S_2C-P(C_6H_{11})_3\}(C_6F_5)_2]$	Brown	34.8 (34.35)	3.25 (3.1)	0.5	149
(**7**) $[Au_2(\mu-S_2C-PEt_3)(C_6F_5)_2]$	Red-brown	24.7 (24.5)	1.65 (1.65)	0.1	144
(**8**) $[Au_2(\mu-S_2C-PBu_3)(C_6F_5)_2]$	Red-brown	29.8 (29.4)	2.85 (2.6)	1.4	130
(**9**) $[Au_2(\mu-S_2C-PPhMe_2)(C_6F_5)_2]$	Brown	26.75 (26.5)	1.15 (1.25)	2.8	154
(**10**) $[Au_2(\mu-S_2C-PPhEt_2)(C_6F_5)_2]$	Brown	28.45 (28.2)	1.55 (1.55)	4.3	163
(**11**) $[Au_2(\mu-S_2C-PEt_3)Cl_2]$	Orange-red	12.7 (12.5)	2.3 (2.1)	5.3	109
(**12**) $[Au_2(\mu-S_2C-PPhMe_2)Cl_2]$	Orange-red	16.05 (16.3)	1.65 (1.6)	3.6	136
(**13**) $[Au_2(\mu-S_2C-PEt_3)_2][ClO_4]_2$	Green-brown	16.85 (17.15)	2.8 (3.1)	165.5	176
(**14**) $[Au_2(\mu-S_2C-PBu_3)_2][ClO_4]_2$	Violet	27.15 (27.05)	4.75 (4.6)	175.5	195
(**15**) $[Au_2(\mu-S_2C-PPhMe_2)_2][ClO_4]_2$	Red-brown	21.4 (21.65)	2.15 (2.25)	161.2[d]	144
(**16**) $[Au_2\{\mu-S_2C-P(C_6H_{11})_3\}(C_6F_5)_6]\cdot CH_2Cl_2$	Yellow	36.6 (36.45)	2.2 (2.45)	*e*	191
(**17**) $[Au_2(\mu-S_2C-PEt_3)(C_6F_5)_6]\cdot CH_2Cl_2$	Yellow	31.55 (31.75)	1.0 (1.1)	*e*	145
(**18**) $[Au_2(\mu-S_2C-PBu_3)(C_6F_5)_6]$	Yellow	35.15 (35.45)	1.6 (1.8)	*e*	152
(**19**) $[Au_2(\mu-S_2C-PPhMe_2)(C_6F_5)_6]$	Yellow	33.55 (33.40)	0.7 (0.8)	*e*	155
(**20**) $[Au_2(\mu-S_2C-PPhEt_2)(C_6F_5)_6]$	Yellow	34.45 (34.2)	0.9 (1.1)	*e*	159

[a] Calculated values are given in parentheses. [b] The molecular weights in $CHCl_3$ solution (calc.) are: (**1**): 1 122(1 091); (**2**): 897(892); (**3**): 943(976); the other compounds are not soluble enough or decompose in $CHCl_3$. [c] In Ω^{-1} cm^2 mol^{-1}; in acetone, 5×10^{-4} molar solutions. [d] In nitromethane, 5×10^{-4} molar solution. [e] Decomposes in acetone or nitromethane (see text).

PEt_3 ligand is monodentate; the Au $\cdots$ S(2) distance is 3.52 Å. The S(1)–C(19)–S(2) angle is *ca.* 4° wider than in the free ligand;[5] this is a general feature of such complexes[1,2] and may reflect some steric repulsion between the non-bonded sulphur atom and the metal. The C–S bond lengths are also consistent with monodentate co-ordination, with C(19)–S(1) 1.690(4) and C(19)–S(2) 1.630(4) Å. The Au–S(1)–C(19) angle of 104.4(2)° suggests sp^3 hybridization at S(1).

The co-ordination geometry at gold is square planar as expected, the largest deviation from the best plane of five atoms being 0.028 Å for Au. The dihedral angle between the co-ordination plane and the plane containing S(1), S(2), C(19), and P is 67.2°. The Au–C(7) bond length of 2.037(3) Å (*trans* to S) is significantly shorter than Au–C(1) and Au–C(13) [2.067(4), 2.076(4) Å], indicating that the sulphur atom exercises a smaller *trans* influence than C_6F_5 itself.

(*b*) *Complexes containing Bridging* S_2C-PR_3.—Neutral or cationic binuclear gold(I) complexes can readily be obtained by reactions [equations (2)—(4)] of suitable gold(I) precursors with the ligands in 2:1 ratio.

$$2\,[Au(C_6F_5)(tht)] + S_2C-PR_3 \longrightarrow [(F_5C_6)Au(\mu-S_2C-PR_3)Au(C_6F_5)] + 2\,tht \quad (2)$$

$R_3 = (C_6H_{11})_3$ (**6**), Et_3 (**7**), Bu_3 (**8**), $PhMe_2$ (**9**), $PhEt_2$ (**10**)

$$2\,[AuCl(tht)] + S_2C-PR_3 \longrightarrow [ClAu(\mu-S_2C-PR_3)AuCl] + 2\,tht \quad (3)$$

$R_3 = Et_3$ (**11**), $PhMe_2$ (**12**)

$$2\,[Au(tht)_2]ClO_4 + 2\,S_2C-PR_3 \longrightarrow [Au_2(\mu-S_2C-PR_3)_2][ClO_4]_2 + 4\,tht \quad (4)$$

$R_3 = Et_3$ (**13**), Bu_3 (**14**), $PhMe_2$ (**15**).

Complexes (**6**)—(**15**) are deeply coloured, air- and moisture-stable solids. They are slightly soluble or insoluble in dichloromethane, chloroform, and acetone and insoluble in diethyl ether and n-hexane.

Complexes (**6**)—(**10**) are non-conducting in acetone solution; their lack of solubility precludes the determination of their molecular weights. Their i.r. spectra show only one band at 800—790 cm^{-1}, in agreement with the proposed structures.[6] Only complex (**7**) is soluble enough to give a ^{19}F-{^{1}H} n.m.r. spectrum, which shows five signals since the hindered rotation of the C_6F_5 rings makes the five fluorine atoms inequivalent.[7]

The chloro derivatives show one i.r. band at 339m [(**11**)] or 337m cm^{-1} [(**12**)] assignable to ν(Au–Cl),[6,8] along with absorptions at 1 070s [(**11**)] and 1 068s cm^{-1} [(**12**)] due to $\nu(C-S)_{asym}$[9,10] which cannot be assigned in other complexes containing C_6F_5 because of overlap with absorptions from the C_6F_5 groups. Acetone solutions of (**11**) and (**12**) are non-conducting; lack of solubility again precludes molecular weight determinations.

Complexes (**13**)—(**15**) show i.r. bands at 1 100s,br and 620s cm^{-1} due to[11] the anion ClO_4^-; their acetone solutions show conductivities within the expected range for 2:1 electrolytes.[12] The broad band at 1 100 cm^{-1} from ClO_4^- masks the $\nu(C-S)_{asym}$ absorptions. Since the only ligand present is S_2C-PR_3, a double bridge must link the two gold(I) centres; short gold–gold contacts cannot be ruled out, but we have so far been unable to obtain crystals suitable for *X*-ray analysis.

The 2:1 reaction between $[Au(C_6F_5)_3(tht)]$ and S_2C-PR_3 leads to the mononuclear derivatives (**1**)—(**5**) described above, with one mol equivalent of the gold(III) starting material remaining unreacted despite the fact that the second S atom of the bidentate ligand is still free. Apparently, S_2C-PR_3 is not a strong enough ligand readily to displace the relatively weak tht ligand in gold(III) complexes (see above).

Tetrahydrothiophene can be more easily displaced from gold(I) complexes; thus $[Au(C_6F_5)(tht)]$ or $[Au(tht)_2]ClO_4$ react with $[Au(C_6F_5)_3(S_2C-PEt_3)]$ affording complexes (**7**) or (**13**) respectively, the gold(III) centre being displaced from the original complex (**2**) [equations (5) and (6)].

$$[Au(C_6F_5)_3(S_2C-PEt_3)] + 2\,[Au(C_6F_5)(tht)] \longrightarrow [(F_5C_6)Au(\mu\text{-}S_2C-PEt_3)Au(C_6F_5)] + [Au(C_6F_5)_3(tht)] + tht \quad (5)$$

$$2\,[Au(C_6F_5)_3(S_2C-PEt_3)] + 2\,[Au(tht)_2]ClO_4 \longrightarrow [Au_2(\mu\text{-}S_2C-PEt_3)_2][ClO_4]_2 + 2\,[Au(C_6F_5)_3(tht)] + 2\,tht \quad (6)$$

In order to prepare gold(III)–gold(III) binuclear complexes with bridging S_2C-PR_3, gold(III) precursors containing a weaker ligand than tht are thus necessary. With gold(III), diethyl ether is a very weak ligand and therefore the 1:1 reaction of the mononuclear complexes (**1**)—(**5**) with $[Au(C_6F_5)_3(OEt_2)]$[13] leads to the expected compounds [equation (7)].

$$[Au(C_6F_5)_3(S_2C-PR_3)] + [Au(C_6F_5)_3(OEt_2)] \longrightarrow [(F_5C_6)_3Au(\mu\text{-}S_2C-PR_3)Au(C_6F_5)_3] + OEt_2 \quad (7)$$

$R_3 = (C_6H_{11})_3$ (**16**), Et_3 (**17**), Bu_3 (**18**), $PhMe_2$ (**19**), $PhEt_2$ (**20**)

Complexes (**16**)—(**20**) are yellow solids, stable at room temperature. They decompose, however, in donor solvents such as acetone, nitromethane, and even diethyl ether.

From diethyl ether solutions of $[(F_5C_6)_3Au(\mu\text{-}S_2C-PEt_3)Au(C_6F_5)_3]$ we have isolated $[Au(C_6F_5)_3(S_2C-PEt_3)]$. This suggests that the decomposition reaction takes place according to equation (8).

$$[Au_2(\mu\text{-}S_2C-PR_3)(C_6F_5)_6] + solvent \longrightarrow [Au(C_6F_5)_3(S_2C-PR_3)] + [Au(C_6F_5)_3(solvent)] \quad (8)$$

One single crystal of $[Au_2(\mu\text{-}S_2C-PEt_3)(C_6F_5)_6]\cdot CH_2Cl_2$ suitable for *X*-ray diffraction studies was obtained by diffusion of n-hexane into a dichloromethane solution of (**17**). The crystal quality was poor because of the solvent of crystallization and its ready loss and the molecular dimensions are therefore of limited accuracy.

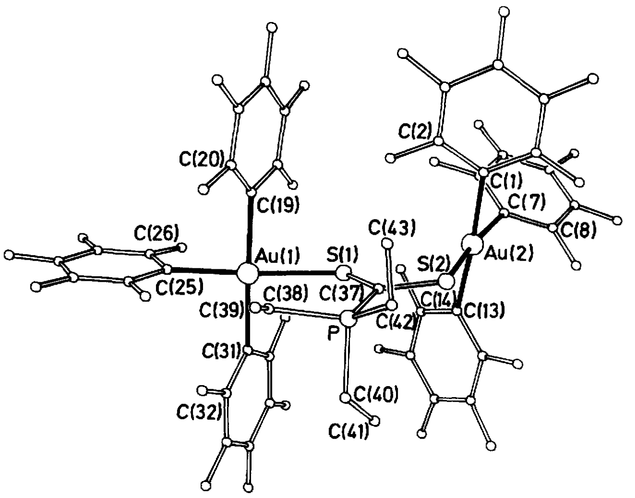

Figure 2. The molecule of $[Au_2(\mu\text{-}S_2C-PEt_3)(C_6F_5)_6]$ (**17**) in the crystal, showing the atom numbering scheme. Radii arbitrary, H atoms excluded

The bridging co-ordination of the S_2C-PEt_3 ligand is confirmed by the *X*-ray structure determination (see Figure 2); this is the first case of a bridging S_2C-PR_3 without ring closure. It is notable that the two P–C–S–Au moieties differ appreciably: Au-S, Au-S-C, and P-C-S are 2.409(8), 2.343(9) Å; 118.7(11), 107.7(12)°; and 125.6(17), 111.2(18)° respectively for S(1) and S(2). It seems that there is little delocalization in the CS_2 group, and that a suitable description of the hybridization is *sp*^{3} for S(1) and *sp*^{2} for S(2). This would imply retention of some double bond character for C(37)–S(2), which cannot be confirmed because of the large e.s.d.s of the C–S bond lengths [C(37)–S(1) 1.666(32), C(37)–S(2) 1.660(30) Å]. It is probable that steric effects (ethyl–C_6F_5 repulsions) are responsible for the widening of the S(1)–C–P angle to 126°, although such assertions are difficult to prove. The co-ordination planes are approximately perpendicular to the PCS_2 plane [dihedral angles 95, 72° for Au(1) and Au(2) respectively]. Of the other complexes with bridging S_2C-PR_3, the ring complex $[Ag_2(\mu\text{-}S_2C-PEt_3)_2(S_2C-PEt_3)_2][ClO_4]_2$[3] displays highly irregular geometry (Ag–S 2.468—2.812 Å) and the chelated *cis*-$[Pt(C_6F_5)_2\{S_2C-P(C_6H_{11})_3\}]$[1] involves a four-membered chelate ring, so no useful comparison is possible. It is clear that several more structures with bridging S_2C-PR_3 will have to be determined to allow a detailed analysis of bonding and structural trends.

Experimental

The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. Infrared spectra (4 000–200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets, n.m.r. spectra on a Varian XL-200 spectrometer. Molecular weights were determined with a Knauer 11.00 vapour-pressure osmometer.

The complexes $[Au(C_6F_5)_3(tht)]$,[4] $[Au(C_6F_5)(tht)]$,[14] $[Au(tht)_2]ClO_4$,[15] and $[Au(C_6F_5)_3(OEt_2)]$[13] were prepared as described elsewhere.

Preparations.—$[Au(C_6F_5)_3(S_2C-PR_3)]$ [$R_3 = (C_6H_{11})_3$ (**1**), Et_3 (**2**), Bu_3 (**3**), $PhMe_2$ (**4**), *or* $PhEt_2$ (**5**)]. To a

Table 2. Atomic co-ordinates ($\times 10^4$) for complex **(2)**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	1 022.6(1)	4 088.4(1)	2 170.4(1)	C(19)	−1 316(4)	5 903(4)	2 772(4)
S(1)	−543(1)	5 675(1)	1 537(1)	C(20)	−2 676(5)	7 908(4)	1 038(4)
S(2)	−1 143(2)	5 216(1)	4 130(1)	C(21)	−3 537(5)	9 096(5)	807(5)
P	−2 484(1)	7 214(1)	2 543(1)	C(22)	−1 993(5)	8 260(5)	3 059(5)
C(1)	−217(3)	2 834(3)	2 993(1)	C(23)	−789(6)	8 710(6)	2 394(6)
C(2)	−317(4)	2 187(4)	4 164(3)	C(24)	−3 916(5)	6 747(6)	3 402(5)
C(3)	−1 115(4)	1 331(4)	4 702(4)	C(25)	−4 357(7)	5 743(7)	3 136(7)
C(4)	−1 858(4)	1 086(4)	4 063(4)	F(1)	396(3)	2 386(3)	4 830(2)
C(5)	−1 781(4)	1 708(4)	2 899(4)	F(2)	−1 177(3)	710(3)	5 850(2)
C(6)	−972(4)	2 562(4)	2 388(3)	F(3)	−2 603(3)	218(3)	4 571(3)
C(7)	2 422(3)	2 752(3)	2 629(3)	F(4)	−2 486(3)	1 452(3)	2 266(3)
C(8)	3 264(4)	2 814(4)	3 285(3)	F(5)	−909(3)	3 113(3)	1 226(2)
C(9)	4 233(4)	1 930(4)	3 594(4)	F(6)	3 174(2)	3 785(2)	3 636(2)
C(10)	4 354(4)	930(4)	3 273(4)	F(7)	5 030(3)	2 055(3)	4 208(3)
C(11)	3 528(4)	815(4)	2 651(4)	F(8)	5 272(3)	39(3)	3 584(3)
C(12)	2 591(4)	1 725(4)	2 329(3)	F(9)	3 653(3)	−186(2)	2 338(3)
C(13)	2 293(4)	5 315(3)	1 309(3)	F(10)	1 822(2)	1 576(2)	1 681(2)
C(14)	3 000(4)	5 306(4)	268(3)	F(11)	2 929(3)	4 447(3)	−180(2)
C(15)	3 796(4)	6 147(4)	—355(4)	F(12)	4 452(3)	6 108(3)	−1 373(3)
C(16)	3 915(5)	7 030(4)	74(4)	F(13)	4 689(3)	7 859(3)	−513(3)
C(17)	3 228(5)	7 066(4)	1 116(5)	F(14)	3 358(4)	7 919(3)	1 541(3)
C(18)	2 430(4)	6 217(4)	1 706(4)	F(15)	1 777(3)	6 286(3)	2 728(3)

Table 3. Selected bond lengths (Å) and angles (°) for complex **(2)**

Au–S(1)	2.366(1)	Au–C(1)	2.067(4)
Au–C(7)	2.037(3)	Au–C(13)	2.076(4)
S(1)–C(19)	1.690(4)	S(2)–C(19)	1.630(4)
P–C(19)	1.829(4)	P–C(20)	1.797(5)
P–C(22)	1.785(7)	P–C(24)	1.796(5)
S(1)–Au–C(1)	93.0(1)	S(1)–Au–C(7)	176.9(1)
C(1)–Au–C(7)	89.2(1)	S(1)–Au–C(13)	87.9(1)
C(1)–Au–C(13)	178.1(2)	C(7)–Au–C(13)	89.9(1)
Au–S(1)–C(19)	104.4(2)	C(19)–P–C(20)	112.3(2)
C(19)–P–C(22)	106.8(2)	C(20)–P–C(22)	110.2(2)
C(19)–P–C(24)	108.8(2)	C(20)–P–C(24)	109.9(3)
C(22)–P–C(24)	108.7(3)	S(1)–C(19)–S(2)	131.4(3)
S(1)–C(19)–P	114.5(2)	S(2)–C(19)–P	114.0(3)
P–C(20)–C(21)	113.0(4)	P–C(22)–C(23)	113.1(5)
P–C(24)–C(25)	113.6(4)		

dichloromethane solution (30 cm^3) containing 0.2 mmol of S_2C-PR_3 [R_3 = $(C_6H_{11})_3$, 0.0712 g; Et_3, 0.0388 g; Bu_3, 0.0556 g; $PhMe_2$, 0.0428 g; or $PhEt_2$, 0.0485 g] and CS_2 (1 cm^3) at −20 °C was added [$Au(C_6F_5)_3$(tht)] (0.1573 g, 0.2 mmol). The solutions turned pink immediately and after stirring for 5 min at −20 °C and 15 min at room temperature, the solvent was partially evaporated (5 cm^3) under vacuum. Hexane (30 cm^3) was added to precipitate pink solids, which were recrystallized by adding n-hexane to diethyl ether solutions.

R_3 = $(C_6H_{11})_3$ **(1)**, 98%; ^{1}H n.m.r. (in $CDCl_3$), δ 3.45 (q, 2 H, CH_2 of Et_2O crystallization), 2.73 (t, 3 H, CH_3 of Et_2O), *ca.* 2 (m, 33 H, C_6H_{11}). R_3 = Et_3 **(2)**, 79%; ^{19}F-{^{1}H} n.m.r. (in $CDCl_3$, reference $CFCl_3$), δ −121.09 (m, 4 F, F_{ortho} of two equivalent C_6F_5), −123.03 (m, 2 F, F_{ortho}), −159.02 (t, *J* 20 Hz, 1 F, F_{para}), −159.33 (t, *J* 20 Hz, 2 F, F_{para} of two equivalent C_6F_5), −163.3 (m, 6 F, F_{meta}).

R_3 = Bu_3 **(3)**, 67; $PPhMe_2$ **(4)**, 75; or $PPhEt_2$ **(5)** 56%.

[$Au_2(\mu-S_2C-PR_3)(C_6F_5)_2$] [$R_3$ = $(C_6H_{11})_3$ **(6)**, Et_3 **(7)**, Bu_3 **(8)**, $PhMe_2$ **(9)** *or* $PhEt_2$ **(10)**]. To a cool (−20 °C) dichloromethane solution (20 cm^3) containing [$Au(C_6F_5)$(tht)] (2 mmol, 0.0904 g) and CS_2 (1 cm^3) was added S_2C-PR_3 (1 mmol). The solutions turned red-brown and after stirring for 10 min at −20 °C and 20 min at room temperature, hexane (30 cm^3) was added to precipitate brown or red-brown solids. Yields: R_3 = $(C_6H_{11})_3$ **(6)**, 60; Et_3 **(7)**, 61; Bu_3 **(8)**, 76; $PhMe_2$ **(9)**, 70; or $PhEt_2$ **(10)**, 54%. ^{19}F-{^{1}H} N.m.r. of **(7)** shows complex signals at −121.0, −123.0, −163.1, and −163.8 p.p.m. and a triplet at −159.4 p.p.m. (*J* 19.8 Hz).

[$Au_2(\mu-S_2C-PR_3)Cl_2$] [R_3 = Et_3 **(11)** *or* $PhMe_2$ **(12)**]. To a cool (−20 °C) dichloromethane solution (15 cm^3) of [AuCl(tht)] (2 mmol, 0.0641 g) containing CS_2 (1 cm^3) was added S_2C-PR_3 (0.1 mmol) and the mixture stirred for 10 min at −20 °C and 20 min at room temperature. The resulting orange-red precipitate was filtered off and washed with hexane (3 × 5 cm^3). Yields: R_3 = Et_3 **(11)**, 63; or $PhMe_2$ **(12)**, 86%. The complexes with R_3 = $(C_6H_{11})_3$, Bu_3, or $PhEt_2$ could not be isolated because addition of hexane to the dichloromethane solutions gave non-crystallizable oils.

[$Au_2(\mu-S_2C-PR_3)_2$][ClO_4]$_2$ [R_3 = Et_3 **(13)**, Bu_3 **(14)**, *or* $PhMe_2$ **(15)**]. To a cool (−20 °C) dichloromethane solution (20 cm^3) of [$Au(tht)_2$][ClO_4]$_2$ (0.0945 g, 0.165 mmol) containing CS_2 (0.1 cm^3) was added S_2C-PR_3 (0.2 mmol) and the mixture stirred for 10 min at −20 °C and 10 min at room temperature. The resulting precipitate (see Colour in Table 1) was filtered off and washed with hexane. Yields: R_3 = Et_3 **(13)**, 54; Bu_3 **(14)**, 71; or $PhMe_2$ **(15)**, 88%.

[$Au_2(\mu-S_2C-PR_3)(C_6F_5)_6$] [$R_3$ = $(C_6H_{11})_3$ **(16)**, Et_3 **(17)**, Bu_3 **(18)**, $PhMe_2$ **(19)**, *or* $PhEt_2$ **(20)**]. To a suspension of 0.1 mmol of [$Au(C_6F_5)_3(S_2C-PR_3)$] **(1)**—**(5)** [0.1091, **(1)**; 0.0892, **(2)**; 0.0976, **(3)**; 0.0912, **(4)**; or 0.0942 g of **(5)**] in hexane (30 cm^3) containing CS_2 (0.1 cm^3) was added [$Au(C_6F_5)_3(OEt_2)$] (1 mmol, 0.0772 g) and the mixture stirred for 3.5 h at room temperature to give a yellow solid of **(18)**, **(19)**, or **(20)**. For R_3 = Et_3 **(17)** 7 h at room temperature were necessary and for R_3 = $(C_6H_{11})_3$ **(16)** 1 h in refluxing hexane. The yellow precipitates were filtered off and washed with hexane (2 × 5 cm^3). Recrystallization was from CH_2Cl_2–hexane. Yields: R_3 = $(C_6H_{11})_3$ **(16)**, 84; Et_3 **(17)**, 77; Bu_3 **(18)**, 90; $PhMe_2$ **(19)**, 82; or $PhEt_2$ **(20)**, 85%.

X-*Ray Structure Determination of* [$Au(C_6F_5)_3(S_2C-PEt_3)$] **(2)**.—*Crystal data.* $C_{25}H_{15}AuF_{15}PS_2$, *M* = 892.44, triclinic, *a* = 11.165(3), *b* = 11.893(4), *c* = 12.405(4) Å, α = 69.54(3), β = 78.64(3), γ = 80.06(3)°, *U* = 1 503.2 Å^3 (by refinement of

Table 4. Atomic co-ordinates (× 10^4) for complex (**17**)

Atom	x	y	z
Au(1)	6 725(1)	7 795.6(5)	6 012.9(4)
Au(2)	7 203(1)	6 250.1(5)	7 728.9(4)
S(1)	6 665(8)	7 041(3)	6 682(3)
S(2)	4 985(9)	6 449(4)	7 362(3)
P	3 427(9)	7 067(4)	6 553(3)
C(2)	6 998(21)	7 828(6)	8 005(4)
C(3)	6 904(21)	8 416(6)	8 304(4)
C(4)	6 684(21)	8 285(6)	8 757(4)
C(5)	6 559(21)	7 567(6)	8 912(4)
C(6)	6 654(21)	6 979(6)	8 613(4)
C(1)	6 873(21)	7 110(6)	8 159(4)
F(2)	7 296(20)	7 958(7)	7 589(6)
F(3)	7 150(24)	9 091(8)	8 177(8)
F(4)	6 567(26)	8 849(9)	9 029(8)
F(5)	6 144(24)	7 486(10)	9 313(6)
F(6)	6 380(21)	6 323(7)	8 760(7)
C(8)	9 044(21)	5 423(8)	8 426(7)
C(9)	10 197(21)	5 298(8)	8 738(7)
C(10)	11 302(21)	5 787(8)	8 767(7)
C(11)	11 254(21)	6 401(8)	8 482(7)
C(12)	10 100(21)	6 526(8)	8 170(7)
C(7)	8 996(21)	6 037(8)	8 142(7)
F(8)	8 065(20)	4 940(8)	8 382(7)
F(9)	10 236(28)	4 703(11)	8 985(8)
F(10)	12 281(30)	5 602(18)	9 080(10)
F(11)	12 236(32)	6 863(15)	8 482(12)
F(12)	10 038(28)	7 118(10)	7 910(8)
C(14)	8 770(19)	5 500(8)	7 007(7)
C(15)	8 979(19)	4 964(8)	6 683(7)
C(16)	8 114(19)	4 353(8)	6 633(7)
C(17)	7 041(19)	4 279(8)	6 907(7)
C(18)	6 832(19)	4 816(8)	7 231(7)
C(13)	7 697(19)	5 426(8)	7 281(7)
F(14)	9 549(18)	6 088(7)	7 079(6)
F(15)	10 074(23)	5 089(10)	6 456(8)
F(16)	8 545(29)	3 879(10)	6 334(8)
F(17)	6 286(27)	3 690(11)	6 824(10)
F(18)	5 753(21)	4 683(10)	7 440(8)
C(20)	6 150(12)	9 278(7)	6 477(4)
C(21)	6 436(12)	9 827(7)	6 805(4)
C(22)	7 628(12)	9 786(7)	7 110(4)
C(23)	8 534(12)	9 198(7)	7 088(4)
C(24)	8 247(12)	8 650(7)	6 761(4)
C(19)	7 055(12)	8 690(7)	6 455(4)
F(20)	5 036(14)	9 350(8)	6 203(5)
F(21)	5 556(19)	10 377(7)	6 820(7)
F(22)	7 890(21)	10 313(8)	7 418(6)
F(23)	9 684(18)	9 198(10)	7 356(6)
F(24)	9 170(17)	8 147(7)	6 747(6)
C(26)	8 285(13)	8 596(8)	5 362(5)
C(27)	8 512(13)	9 049(8)	4 996(5)
C(28)	7 398(13)	9 364(8)	4 729(5)
C(29)	6 058(13)	9 226(8)	4 830(5)
C(30)	5 831(13)	8 773(8)	5 196(5)
C(25)	6 945(13)	8 458(8)	5 463(5)
F(26)	9 341(17)	8 268(8)	5 580(5)
F(27)	9 782(18)	9 165(9)	4 888(7)
F(28)	7 627(22)	9 810(8)	4 402(6)
F(29)	4 992(18)	9 536(9)	4 604(6)
F(30)	4 587(18)	8 655(8)	5 298(7)
C(37)	5 147(31)	6 856(12)	6 866(10)
C(39)	2 187(49)	8 104(19)	6 056(15)
C(40)	2 725(97)	6 319(40)	6 162(30)
C(41)	3 458(68)	5 654(30)	6 216(22)
C(42)	2 025(45)	7 182(17)	6 917(14)
C(43)	2 246(67)	7 845(25)	7 164(21)
C(38)	3 315(50)	7 799(20)	6 092(16)
C(32)	5 607(13)	6 708(7)	5 259(5)
C(33)	5 668(13)	6 079(7)	4 991(5)
C(34)	6 800(13)	5 610(7)	5 061(5)
C(35)	7 872(13)	5 770(7)	5 399(5)
C(36)	7 811(13)	6 398(7)	5 666(5)
C(31)	6 679(13)	6 867(7)	5 596(5)
F(32)	4 544(18)	7 131(9)	5 173(7)
F(33)	4 716(20)	5 911(13)	4 666(7)
F(34)	6 996(29)	5 031(9)	4 800(8)
F(35)	8 994(21)	5 372(11)	5 450(9)
F(36)	8 864(18)	6 572(9)	5 966(6)
C(44)	−1 541(70)	2 286(28)	460(22)
Cl(1)	157(31)	2 528(14)	670(10)
Cl(2)	−891(30)	1 557(12)	62(9)

2θ values of 44 reflections in the range 20—23°), space group $P\bar{1}$, $Z = 2$, $D_c = 1.97$ g cm^{-3}, $F(000) = 852$, deep pink prism, 0.5 × 0.3 × 0.2 mm, $\mu(\text{Mo-}K_\alpha) = 5.2$ mm^{-1}.

Data collection and processing. Stoe-Siemens four-circle diffractomer, monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). 6 317 Profile-fitted[16] intensities ($2\theta_{max.}$ 50°, $+h \pm k \pm l$ and some $-h$ equivalents), 5 283 unique (R_{int} 0.020), 4 859 with $F > 4\sigma(F)$ used for all calculations (SHELXTL[17]). Absorption correction by ψ-scans, transmission factors 0.63—0.92. Three check reflections, no decay.

Structure analysis and refinement. Heavy-atom method. Refinement on F to R 0.025, R' 0.025. All non-H atoms anisotropic, H atoms included using a riding model [C–H 0.96 Å, H–C–H 109.5°, $U(\text{H}) = 1.2U_{eq}(\text{C})$], weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,25\ F^2$, 406 parameters. Final atomic coordinates and derived dimensions are given in Tables 2 and 3.

X-Ray Structure Determination of $[\text{Au}_2(\mu\text{-S}_2\text{C–PEt}_3)(\text{C}_6\text{F}_5)_6]\cdot\text{CH}_2\text{Cl}_2$ (**17**).—*Crystal data.* $\text{C}_{43}\text{H}_{15}\text{Au}_2\text{F}_{30}\text{PS}_2\cdot\text{CH}_2\text{Cl}_2$, $M = 1\,675.5$, monoclinic, $a = 9.765(3)$, $b = 18.218(5)$, $c = 29.429(12)$ Å, $\beta = 96.09(5)°$, $U = 5\,206$ Å^3 (by refinement of 2θ values of 32 reflections in the range 20—23°), space group $P2_1/c$, $Z = 4$, $D_c = 2.14$ g cm^{-3}, yellow plate, 0.35 × 0.25 × 0.08 mm, $\mu(\text{Mo-}K_\alpha) = 5.9$ mm^{-1} $F(000) = 3\,096$.

Data collection and processing. As for complex (**2**) with the following differences: 5 296 unique reflections, 3 142 with $F > 4\sigma(F)$, transmission factors 0.45—0.81.

Structure analysis and refinement. Heavy-atom method. Refinement on F to R 0.077, R' 0.072. Au, S and P anisotropic, H atoms not included. The poor crystal quality, associated with ready loss of solvent of crystallization, resulted in a somewhat

Table 5. Selected bond lengths (Å) and angles (°) for complex (**17**)

Au(1)–S(1)	2.409(8)	Au(1)–C(19)	2.090(13)
Au(1)–C(25)	2.048(16)	Au(1)–C(31)	2.086(15)
Au(2)–S(2)	2.343(9)	Au(2)–C(1)	2.062(14)
Au(2)–C(7)	2.058(20)	Au(2)–C(13)	2.088(19)
C(37)–S(1)	1.666(32)	C(37)–S(2)	1.660(30)
C(37)–P	1.869(30)		
S(1)–Au(1)–C(19)	87.2(5)	S(1)–Au(1)–C(25)	175.2(5)
C(19)–Au(1)–C(25)	90.6(6)	S(1)–Au(1)–C(31)	91.0(5)
C(19)–Au(1)–C(31)	172.1(6)	C(25)–Au(1)–C(31)	90.6(7)
S(2)–Au(2)–C(1)	88.2(7)	S(2)–Au(2)–C(7)	170.8(7)
C(1)–Au(2)–C(7)	87.7(8)	S(2)–Au(2)–C(13)	94.9(6)
C(1)–Au(2)–C(13)	174.9(8)	C(7)–Au(2)–C(13)	89.9(8)
Au(1)–S(1)–C(37)	118.7(11)	Au(2)–S(2)–C(37)	107.7(12)
S(1)–C(37)–S(2)	123.2(18)	S(1)–C(37)–P	125.6(17)
S(2)–C(37)–P	111.2(18)		

unsatisfactory refinement; the C_6F_5 and C_2H_5 groups showed high thermal motion and the solvent was poorly resolved. Aromatic rings were refined as rigid hexagons with C–C 1.395 Å. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0006\ F^2$; 279 parameters. Final atomic co-ordinates and derived dimensions are given in Tables 4 and 5.

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