Auration of the Sulfones $MeSO_2CH_2CN$ and $CH_2(CH_2SO_2)_2CH_2$

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$MeSO_2CH_2CN$ shows considerable C-H acidity at its methylene group. Through lithiation followed by reaction with $(Ph_3P)AuCl$ it can therefore be readily converted into the dinuclear, geminally substituted product $MeSO_2C[Au(PPh_3)]_2CN$. With an excess of aurating reagents, a third $[(Ph_3P)Au]$ group becomes N-bonded to the nitrile unit to give an ionic trinuclear compound $\{MeSO_2C[Au(PPh_3)]_2CNAu(PPh_3)\}^+BF_4{}^-$. The same product is obtained by direct reaction of $MeSO_2CH_2CN$ with $[(Ph_3P)Au]BF_4$. The crystal structures of the two products have been determined. The diaurated sulfone parts of the molecule and the cation are virtually superimposible. Small Au-C-Au angles and short Au–Au contacts suggest significant aurophilic interactions ("A-frame" structures). The small $-C{\equiv}N$-Au angle of $165.6(5)°$ in the cation indicates that the strong $[(Ph_3P)Au]^+$ acceptor causes substantial changes in the bonding of the nitrile group. Dilithiation of 1,3-dithiane-S,S'-tetroxide followed by reaction with 2 equivalents of $(Ph_3P)AuCl$ affords the geminally diaurated compound $CH_2(CH_2SO_2)_2C[Au(PPh_3)]_2$.

Key words: Gold(I) Complexes, Auration, Sulfones, Nitriles, 2,6-Dithiane-S,S'-tetroxide

Introduction

Auration of organic substrates by strong gold(I) or gold(III) electrophiles is one of the most attractive methods of synthesis for organogold compounds [1 – 3]. The procedure is generally most efficient with organic compounds exhibiting *C-H acidity*. Treatment of precursors of this type with simple gold(I) reagents $[(L)Au]^+ BF_4{}^-$ or with the oxonium salts $\{[(L)Au]_3O\}^+BF_4{}^-$ leads to an exchange of protons by the isolobal $[(L)Au]^+$ cations. In most of the cases documented in the literature, L represents a tertiary phosphine or arsine. Prominent and classical examples among the substrates employed are strong C-H acids like *e. g.* malodinitrile [4] or 1,3-diketones [5], but also moderately activated solvents like acetonitrile [6].

Ever since this reaction was discovered, evidence has accumulated that *geminal diauration* is a particularly facile process, with the second substitution often more rapid – and irreversible – than the preceding first step [1, 2]. Even *triauration* of methyl groups was observed with suitable substrates such as methylphosphonium and –sulf(ox)onium salts or phosphonium/sulf(ox)onium methylides [7, 8]. Typically, in these cases one methyl group is fully aurated, while others remain untouched.

Structural studies of the products have shown that in the di- or tri-aurated products the Au-C-Au angles are much smaller than expected for a tetrahedral configuration of tetrasubstituted carbon atoms, in most cases only *ca.* 90° instead of the 109.5° standard. These small angles are associated with short intramolecular Au–Au contacts in the range from 2.9 to 3.1 Å, very close to the Au-Au distance in metallic gold and well below the sum of van der Waals radii, suggesting significant "*aurophilic*" bonding [9].

As part of a series of studies oriented at an exploitation of these phenomena for the preparation of new classes of organogold compounds we have investigated *i. a.* the auration of *sulfones* [5]. With sulfones physiologically acceptable, gold-substituted sulfones may be of interest in pharmacology. Moreover, polynuclear gold compounds with short gold-gold contacts are known to show intriguing photophysical properties, most notably luminescence, which – owing to the complexity of the phenomenon – calls for an extended investigation of complexes with a variety of hitherto unexplored substituents. The literature has only two reports of previous successful attempts to aurate sulfones [5, 10], in which both mono- and diauration have been documented.

The present report focuses on the behaviour of *cyanomethyl(methyl)sulfone*, $CH_3SO_2CH_2CN$, in which the methylene group is activated by both the nitrile and the sulfone function. For polyauration, the methyl group potentially offers an alternative site for substitution, which could give access to gold-rich products. However, the new results show that geminal diauration at the methylene group and coordination to the nitrile group are the preferred modes of reaction. A cyclic disulfone derived from 1,3-dithiane was also included in the auration studies.

Preparative Results

Cyanomethyl(methyl)sulfone was dilithiated at its methylene group using two equivalents of ^{n}butyllithium in a tetrahydrofuran/hexane mixed solvent at -78 °C and then treated with two equivalents of (triphenylphosphine)gold(I) chloride. After non-aqueous work-up following standard procedures a colourless crystalline product was obtained in 82% yield (m. p. 175 °C with decomposition). The dinuclear compound was readily identified by analytical and spectroscopic data (Experimental Section and eq. (1)).

A solution of this diaurated material in tetrahydrofuran was further treated (at -78 °C) with a solution of an excess of $[(Ph_3P)Au]BF_4$, prepared *in situ* from $AgBF_4$ and $(Ph_3P)AuCl$. Extraction of the residue left

$$(1)$$
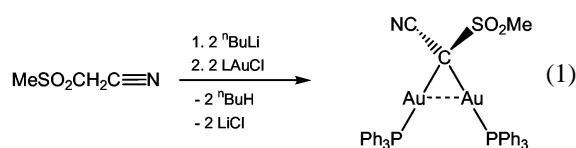
upon evaporation of the tetrahydrofuran solvent with dichloromethane gave a 52% yield of the trinuclear compound (m. p. 186 °C).

The same product was obtained in almost quantitative yield by treating $MeSO_2CH_2CN$ with an equimolar quantity of $[(Ph_3P)Au]BF_4$ in tetrahydrofuran at -78 °C (eq. (2, 3)).

This result was unexpected, because the 1:1 stoichiometry (in the absence of an auxiliary base) was chosen for the experiment in order to obtain a 1:1 complex with the $[(Ph_3P)Au]$ unit attached to the nitrile group. Obviously the auration of the methylene group is faster and irreversible and competes successfully with the simple C≡N-Au complex formation. With the chosen 1:1 molar ratio of the reactants, two out of three sulfone substrates remain unchanged. The results are in agreement with the course of the auration of the cyanomethyl(triphenyl)phosphonium cation, which affords the cation $\{Ph_3PC[Au(PPh_3)]_2C\equiv N-Au(PPh_3)\}^{2+}$ (as the bis-perchlorate salt) [11].

The analytical data of the trinuclear product confirmed the proposed composition, and the spec-

$$(2)$$

$$(3)$$

$$(4)$$
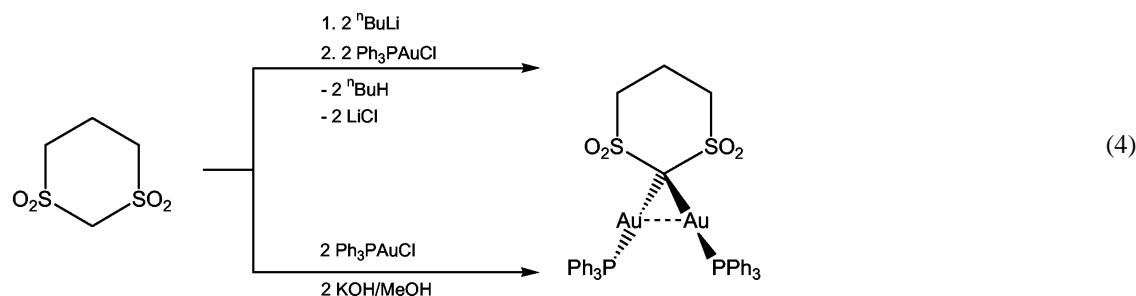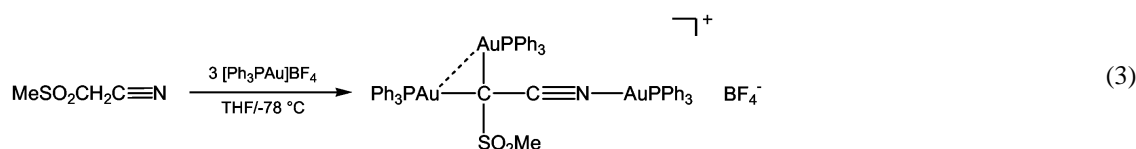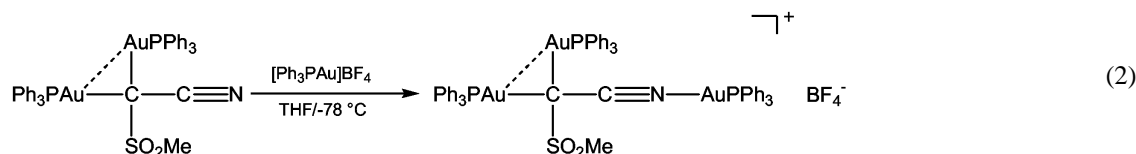
troscopic characteristics indicated that the third [(Ph$_3$P)Au] unit [$\delta\,^{31}P$ 30.0 ppm] was in a different environment as compared to the first two [$\delta\,^{31}P$ 37.1 ppm]. The chemical shift of the latter is in excellent agreement with that of the dinuclear precursor [$\delta\,^{31}P$ 37.7 ppm]. Together with the ^{1}H and ^{13}C NMR data, this observation suggests that the sulfone part of the substrate did not undergo major changes in the last auration step. Surprisingly, however, the nitrile part also showed only very minor changes in the IR spectrum, with ν(C≡N) at 2167 cm^{-1} (trinuclear) as compared to 2161 cm^{-1} (dinuclear). The two structures were finally determined by single crystal X-ray diffraction studies.

Open-chain 1,3-disulfones have been subjected to auration in a previous study [5]. This investigation was now extended to the cyclic 1,3-disulfone derived from 1,3-dithiane. This heterocycle was dilithiated using two equivalents of ^{n}butyllithium and subsequently treated with two equivalents of (Ph$_3$P)AuCl in tetrahydrofuran at -78 °C to give after standard work-up an 87% yield of the geminally diaurated product. The same compound was obtained by using methanolic potassium methoxide as a base with a similar yield (88%) (eq. (4)). The new diaurated disulfone was isolated as a colourless solid (m.p. 181 °C with decomposition), but could not be crystallized. It was identified by analytical and spectroscopic data.

Structural Results

MeSO$_2$C[Au(PPh$_3$)]$_2$CN

Crystals of the *dinuclear compound* obtained from acetone solutions as the 1:1 solvate are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ formula units in the unit cell (measured at 143 K). The asymmetric unit contains one independent molecule with no crystallographically imposed symmetry together with one acetone molecule, which has no unusual intermolecular contacts. The structure is shown in Fig. 1.

The two gold atoms have become attached to the carbon atom C1 bridging the sulfone sulfur atom S1 and the cyano carbon atom C2, replacing the two hydrogen atoms of the precursor substrate. The coordination geometry at the gold atoms is almost linear, and the two phosphorus atoms and the sulfur atom have the standard tetrahedral configuration. Carbon atom C1 is also in a quasi-tetrahedral environment, but the geometry is strongly distorted with an Au1-C1-Au2 angle of only 90.4(2)°, a deviation of almost twenty degrees
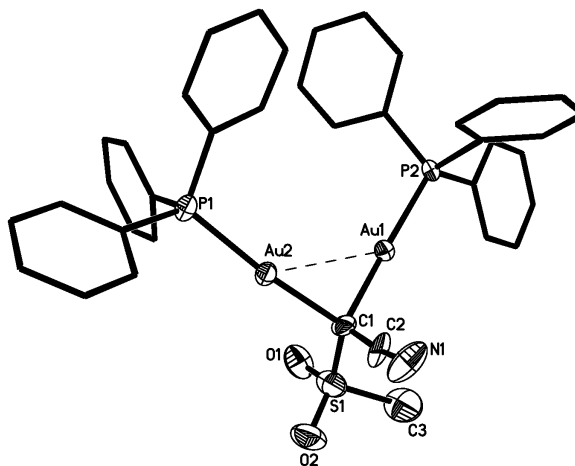

Fig. 1. Molecular structure of MeSO$_2$C[Au(PPh$_3$)]$_2$CN in its 1:1 acetone solvate (ORTEP, 50% probability ellipsoids for the core atoms, hydrogen atoms and solvent molecule omitted). Selected bond lengths [Å] and angles [°]: C1-C2 1.440(10), C2-N1 1.129(10); C1-S1 1.724(7), C3-S1 1.809(10), O1-S1 1.431(6), O2-S1 1.458(6); C1-Au1 2.10787), C1-Au2 2.102(6); C2-C1-S1 106,5(5), C2-C1-Au1 111.4(5), C2-C1-Au2 117.0(5), S1-C1-Au1 116.7(4), S1-C1-Au2 114.6(4), Au1-C1-Au2 90.4(2).

from the tetrahedral reference. All other angles at C1 are in the range from 106.5(5) to 117.0(5)°. This distorted tetrahedron is in a staggered conformation relative to the tetrahedron about the sulfur atom.

The bond lengths show no anomalies, including a C≡N distance of 1.129(10) Å and S=O distances of 1.431(6) and 1.458(6) Å. Associated with the small Au1-C1-Au2 angle is a short Au1–Au2 contact of 2.9861(3) Å which is indicative of significant aurophilic bonding ("A-frame structure") [9].

{MeSO$_2$C[Au(PPh$_3$)]$_2$CNAu(PPh$_3$)}$^+$ BF$_4^-$
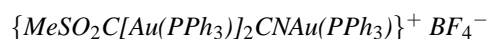
Crystals of the 1:1 solvate of the trinuclear complex with acetone are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The asymmetric unit contains the complex cation, the BF$_4^-$ anion and one acetone molecule (Fig. 2). Between these components there are no unusual sub-van der Waals contacts. The part of the cation which represents the dinuclear precursor molecule is virtually superimposible with this substrate. Notable examples are the small Au1-C1-Au2 angle of 89.08(19)° and the short Au–Au contact of 2.9587(3) Å, as well as the staggered conformation of the tetrahedra centered by the atoms C1 and S1. As for the dinuclear precursor complex, the maximum attainable (mirror) symmetry is not reached
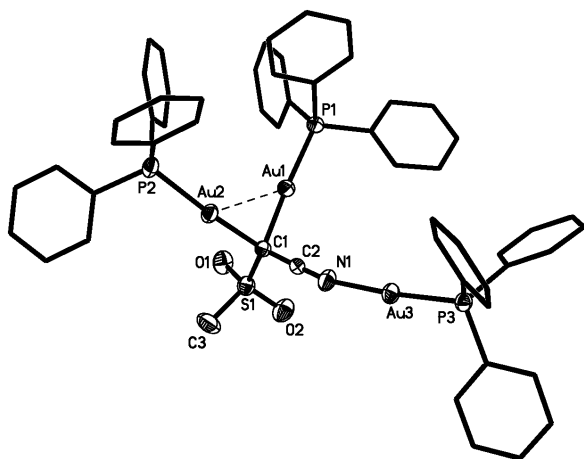
Fig. 2. Structure of the cation in crystals of {MeSO$_2$C [Au(PPh$_3$)]$_2$CNAu(PPh$_3$)}BF$_4$·Me$_2$CO (ORTEP, 50% probability ellipsoids for the core atoms, hydrogen atoms, solvent molecule and counterion omitted). Selected bond lengths [Å] and angles [°]: C1-C2 1.386(7), C2-N1 1.146(7); C1-S1 1.747(5), C3-S1 1.777(6), O1-S1 1.440(4), O2-S1 1.446/4); Au1-C1 2.125(5), Au2-C1 2.093(5); Au3-N1 2.032(5); C2-C1-S1 112.2(4), C2-C1-Au1 107.0(4), C2-C1-Au2 118.4(4), S1-C1-Au1 113.6(3), S1-C1-Au2 114.3(3), Au1-C1-Au2 89.08(19); C2-N1-Au3 165.6(5).

owing to this conformation, which places one oxygen atom (O1) between the two gold atoms. This leaves O2 and C3 on the two sides of the potential mirror plane, instead of the idealized array with O1 and O2 as mirror images.

The third gold atom is attached to the nitrile nitrogen atom, but while the angle C1-C2-N1 remains linear [178.5(6)°] the newly formed C≡N-Au angle (C2-N1-Au3) is much smaller at only 165.6(5)°. This result is in agreement with findings for the complex cation of the related phenylsulfone, which is associated into a hexanuclear dication: Its C≡N-Au angles are even smaller at 153.6(5) and 162.6(5)° [5]. Because of the consistent results for different substitution patterns it is unlikely that the deviations of these angles from the 180° standard are due to packing forces in the crystal, but are an intrinsic structural motif. And in fact this suggestion is supported by structural data for [(Ph$_3$P)Au] complexes of quite different substrates such as {(^{t}BuNC)$_2$Ru[(Ph$_2$P)$_2$CC≡NAu(PPh$_3$)]$_2$}$^{2+}$ or 2-Me-C$_6$H$_4$SO$_2$C(CN)C≡NAu(PPh$_3$) with C≡N-Au angles of 166.8(13) and 166.3(3)°, respectively [12, 13].

The data are indicative of a significant change in the nitrile bonding upon terminal complexation with a build-up of stereochemically active electron density at the nitrogen atom. However, surprisingly, this change is not reflected by the C≡N distances and by the ν(C≡N) stretching frequencies, which show only slight differences upon auration, not really reaching out of the standard deviations of the experiments.

Further selected details of the two structures are given in the figure captions.

Conclusions

The present studies have shown that methyl(cyanomethyl)sulfone is readily and selectively aurated by standard gold(I) electrophiles at the methylene group to give the geminally dinuclear complex. With excess reagent, no trinuclear products with hypercoordinate carbon atoms [9, 14, 15] or with an aurated methyl group are obtained. Terminal complexation at the nitrile group occurs instead. The reaction pathways thus resembles that observed for (cyanomethyl)phenylsulfone [5]. The structures of the two products are indicative of significant intramolecular/intraionic aurophilic bonding and a substantial modification of the nitrile bonding characteristics upon auration, which is in agreement with literature data of quite different classes of compounds [12, 13]. The auration of the cyclic disulfone followed the pattern already established for open-chain sulfones.

Experimental Section

General: The experiments were carried out in an atmosphere of dry nitrogen. Glassware was oven-dried and filled with nitrogen, and solvents were distilled, dried and saturated with nitrogen. Standard equipment was used throughout. CH$_2$(CH$_2$SO$_2$)$_2$CH$_2$ was prepared as described in the literature [16].

{1,1-Bis[(triphenylphosphine)gold(I)](cyano)methyl}-(methyl)sulfone

MeSO$_2$CH$_2$CN (24.1 mg, 0.20 mmol) was dissolved in 20 ml of tetrahydrofuran and cooled to −78 °C. 25 ml of a 1.6 M solution of ^{n}BuLi in hexane was added with stirring, followed after 2 h by a solution of (Ph$_3$P)AuCl (200 mg, 0.40 mmol) in tetrahydrofuran (20 ml). Stirring was continued over night and over this period the mixture was allowed to warm to room temperature. The solvents were removed in a vacuum and the product extracted from the residue with 10 ml of dichloromethane. Evaporation of the solution gave a colourless microcrystalline precipitate (170 mg, 82% yield). Single crystals of a 1:1 solvate could be grown by slow dif-

	MeSO$_2$C[Au(PPh$_3$)]$_2$-CN · Me$_2$CO	{MeSO$_2$C[Au(PPh$_3$)]$_2$CNAu(PPh$_3$)}-BF$_4$·Me$_2$CO	
Empirical formula	C$_{42}$H$_{39}$Au$_2$NO$_3$S	C$_{60}$H$_{54}$Au$_3$BF$_4$NO$_3$S	Table 1. Crystal Data, Data Collection and Structure Refinement Details for MeSO$_2$C-[Au(PPh$_3$)]$_2$CN · Me$_2$CO and {MeSO$_2$C[Au(PPh$_3$)]$_2$CNAu-(PPh$_3$)}BF$_4$ · C$_3$H$_9$O.
M	1093.69	1639.72	
Crystal system	orthorhombic	monoclinic	
Space group	$P2_12_12_1$	$P2_1/c$	
a [Å]	9.8263(1)	13.6038(1)	
b [Å]	19.0183(2)	23.4226(3)	[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.
c [Å]	20.8216(3)	19.6767(3)	
β [°]	90	99.8731(15)	
V [Å^3]	3891.13(8)	6176.86(13)	
ρ_{calc} [g cm^{-3}]	1.867	1.763	
Z	4	4	
$F(000)$	2104	3136	
μ (Mo-K$_\alpha$) [cm^{-1}]	77.07	72.73	
T [K]	143	143	
Refls. Measured	84668	135423	
Refls. Unique	7123 [$R_{int} = 0.079$]	10933 [$R_{int} = 0.065$]	
Refined param. /restraints	463 / 0	640 / 0	
$R1[I \geq 2\sigma(I)]$	0.0273	0.0338	
$wR2$[a]	0.0572	0.0675	
Absolute structure factor	0.005(7)		
Weighting scheme	$a = 0.0084$	$a = 0.0147$	
	$b = 11.4973$	$b = 23.7971$	
σ_{fin}(max/min) [eÅ^{-3}]	0.890 / −0.617	1.067 / −0.857	

fusion of pentane vapour into a solution of the compound in *acetone* at −10 °C.

NMR (CD$_2$Cl$_2$, 20 °C), ^{1}H: $\delta = 7.11 - 7.85$ (m, 30 H, Ph); 3.20 (s, 3 H, Me); ^{13}C{^{1}H}: $\delta = 134.6$ (d, $J = 14$ Hz, C2/6), 131.9 (s, C4), 128.6 (d, $J = 54.5$ Hz, C1), 129.2 (d, $J = 11$ Hz, C3/5), 46.9 (s, Me), *C*N and *C*Au2 not detected; ^{31}P{^{1}H}: $\delta = 37.7$ (s). MS (FAB): *m/z* 1492 (7%) [M + AuL]$^+$; 1034 (39) [M]$^+$; 720 (72) [L$_2$Au]$^+$; 458 (100) [LAu]$^+$ (L = Ph$_3$P). IR (KBr): 2161.5 cm^{-1}, ν(C≡N). C$_{30}$H$_{33}$Au$_2$NO$_2$P$_2$S·Me$_2$CO (1093.68): calcd. C 46.12, H 3.59; found C 45.74, H 3.41.

{1,1-Bis[(triphenylphosphine)gold(I)](N-[(triphenylphosphine)gold(I)]cyano)methyl}-(methyl)sulfon tetrafluoroborate

Method 1: A solution of [(Ph$_3$P)Au]BF$_4$ was prepared by reacting AgBF$_4$ (56 mg, 0.29 mmol) and (Ph$_3$P)AuCl (143 mg, 0.29 mmol) in tetrahydrofuran (10 ml) at −78 °C with stirring for 2 h. Subsequently a solution of MeSO$_2$C[Au(PPh$_3$)]$_2$CN (150 mg, 0.14 mmol) in 10 ml of tetrahydrofuran was added and the reaction mixture stirred over night while it was allowed to warm to room temperature. The solvents were evaporated and the residue extracted with dichloromethane (10 ml). The solvent was again evaporated and the residue washed with pentane to leave 119 mg (52% yield) of a colourless microcrystalline product.

Method 2: MeSO$_2$CH$_2$CN (36 mg, 0.30 mmol), dissolved in 10 ml of tetrahydrofuran, was added to a solution of [(Ph$_3$P)Au]BF$_4$ in tetrahydrofuran, prepared from AgBF$_4$

(58 mg, 0.30 mmol) and (Ph$_3$P)AuCl (150 mg, 0.30 mmol) in 10 ml of the same solvent at −78 °C with stirring. The reaction mixture was stirred over night while it warmed up to room temperature. Evaporation of the solvent and extraction of the residue afforded a solution of the product, which was recovered upon evaporation of the dichloromethane solvent as a colourless solid (m.p. 186 °C with decomposition) in an almost quantitative yield (158 mg, 98%). Single crystals could be grown by slow diffusion of pentane vapour into a solution of the compound in *acetone* at −10 °C.

NMR (CD$_2$Cl$_2$, 25 °C), ^{1}H: $\delta = 7.23 - 8.15$ (m, 45 H, Ph); 3.23 (s, 3 H, Me); ^{13}C{^{1}H}: $\delta = 129.4 - 135.1$ (Ph), 48.5 (s, Me), *C*N and *C*Au$_2$ not detected; ^{31}P{^{1}H}: 37.1 (s, 2 P), 30.0 (s, 1 P). MS (FAB): *m/z* 1494 (3%) [M-BF$_4$]$^-$, 720 (88) [L$_2$Au]$^+$, 459 (100) [LAu]$^+$, 262 (4) [L]$^+$. IR (KBr): 2167 cm-1, ν(C≡N). C$_{57}$H$_{48}$Au$_3$BF$_4$NO$_2$P$_3$S·Me$_2$CO (1639.72), calcd. C 43.95, H 3.32; found C 42.86, H 3.13.

1,1-Bis[(triphenylphosphine)gold(I)]-2,6-dithiane-S,S'-tetroxide

Method 1: A solution of 1,3-dithiane-S,S'-tetroxide (37 mg, 0.20 mmol) [16] in 10 ml of tetrahydrofuran was lithiated with 0.25 ml of a 1.6 M solution of ^{n}BuLi in hexane at −78 °C for 2 h. Subsequently a solution of (Ph$_3$P)AuCl (200 mg, 0.40 mmol) in 10 ml of tetrahydrofuran was added at −78 °C and the reaction mixture stirred for 3 h while it was allowed to warm up to room temperature. After evaporation of the solvent the residue was extracted with

dichloromethane and the product isolated as a colourless solid by evaporation of the solvent from the extract (185 mg, 87% yield, m. p. 181 °C with decomposition).

Method 2: The same quantities of the disulfone and the gold(I) complex (above) were dissolved in a solution of KOH (23 mg, 0.40 mmol) in 10 ml of methanol and the reaction mixture stirred for 3 h at room temperature. Removal of the methanol in a vacuum and extraction of the residue with dichloromethane gave 193 mg of the product (88% yield).

NMR (CD$_2$Cl$_2$, 20 °C), ^{1}H: $\delta = 7.15 - 7.90$ (m, 30 H, Ph), 3.17 (m, 4 H, CCH$_2$), 2.42 (m, 2 H, CH$_2$); ^{13}C$\{^1$H$\}$: $\delta = 134.6$ (d, $J = 14.0$ Hz, C2/6), 132.1 (s, C4), 131.5 (d, $J = 54.5$ Hz, C1), 129.6 (d, $J = 11.9$ Hz, C3/5), 52.3 (s, SCH$_2$), 38.7 (s, CH$_2$); ^{31}P$\{^1$H$\}$: $\delta = 38.7$ (s). MS (FAB) *m/z* = 1100 (9.8%) [M]$^+$; 721 (50.6) [L$_2$Au]$^+$; 459 (100) [LAu]$^+$. C$_{40}$H$_{36}$Au$_2$O$_4$P$_2$S$_2$ (1100.72), calcd. C 44.71, H 3.30; found C 44.71, H 3.42.

Crystal structure determination

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 DIP 2020 diffractometer, employing graphite-monochromated Mo-K$_\alpha$ radiation. Intensity data were corrected for absorption effects (DELABS from PLATON). 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) [17]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions.

Further information on crystal data, data collection and structure refinement are summarized in Table 1. Anisotropic displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-250555 & 250556.

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