# Gold Clustering at Dimethylsulfoximine Me<sub>2</sub>S(O)NH

Armin Hamel, Christian Hollatz, Annette Schier, and Hubert Schmidbaur

Anorganisch-chemisches Institut, Technische Universität München, D-85747 Garching, Germany

Reprint requests to Prof. H. Schmidbaur. E-mail: H.Schmidbaur@lrz.tum.de

Dedicated to Prof. Dr. Dr. h. c. Max Schmidt on the occasion of his 75th birthday

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Polyaurated complexes of the dimethylsulfoximide anion  $[Me_2S(O)N]^-$  have been prepared by reacting N-trimethylsilyl-dimethylsulfoximide with  $[(Ph_3P)Au]BF_4$  in various molar ratios. With one or two equivalents of the gold(I) reagent only the dinuclear complex is obtained in high yield:  $\{[(Ph_3P)Au]_2NS(O)Me_2\}^+ BF_4^-$ . With three or four equivalents only the trinuclear complex is produced:  $\{[(Ph_3P)Au]_3NS(O)Me_2\}^{2+} 2 BF_4^-$ . No mono- or tetra-auration was observed, respectively. The composition of the compounds has been confirmed by analytical and spectroscopic data, and the crystal structure of the dinuclear compound has been determined by single crystal X-ray diffraction of the dichloromethane solvate. The two gold atoms are found to be coordinated to the nitrogen atom with a small Au-N-Au angle of only 92.3(3)° and a short Au-Au distance of 2.9900(5) Å. The nitrogen atom is in a distorted trigonal pyramidal configuration which allows an intramolecular SO-Au contact. For the trinuclear complex a structure with a tetracoordinate nitrogen atom [SNAu<sub>3</sub>] is proposed which is analogous to the corresponding complexes of phosphinimines R<sub>3</sub>P=NH. With the ditertiary phosphine Ph<sub>2</sub>PCH<sub>2</sub>Ch<sub>2</sub>PPh<sub>2</sub> (dppe) a cyclic dinuclear complex (dppe)Au<sub>2</sub>[NS(O)Me<sub>2</sub>]BF<sub>4</sub> can be synthesized starting from (dppe)Au2Cl2. The reaction of the phosphine-rich precursor [(Ph<sub>3</sub>P)<sub>2</sub>Au]BF<sub>4</sub> with Me<sub>3</sub>SiNS(O)Me<sub>2</sub> in the molar ratio 2:1 affords a binuclear complex  $\{[(Ph_3P)_2Au]_2NS(O)Me_2\}BF_4$  of an as yet unknown structure.

# Introduction

Owing to their unique electron characteristics [1 - 3] complex gold(I) units  $[LAu]^+$  (L = donor ligand) show many unexpected bonding phenomena. One of the most striking observations made in recent years in many laboratories has been the clustering of such units around boron, carbon, nitrogen / phosphorus / arsenic, and oxygen / sulfur / selenium donor centres [4]. Homoleptic substitution to give polycations like  $[(LAu)_nC]^{m+}$ ,  $[(LAu)_nN/P/As]^{m+}$  or  $[(LAu)_nO/S/Se]^{m+}$  is complemented by clustering at partially substituted heteroatoms as in species like  $[RC(AuL)_n]^{m+}$ ,  $[RN(AuL)_n]^{m+}$  or  $[RO(AuL)_n]^{m+}$  or their phosphorus and sulfur/selenium analogues [5].

Clustering at nitrogen [6] is particularly common and was found to occur readily at ammonia [7], hydrazine [8], hydroxylamine [9], primary and secondary amines and amides [10], and a variety of *imines* [11]. This chemistry not only includes standard aldimines and ketimines (Schiff bases RR'C=NH), but also carbodiimines [12] and phosphinimines  $R_3P=NH$  [13]. Up to three [LAu]<sup>+</sup> units could be assembled at the nitrogen atom of such phosphinimines to give dications  $[R_3PN(AuL)_3]^{2+}$ .

In the present study the clustering of  $[LAu]^+$  moieties at the nitrogen atom of a sulfoximine  $R_2S(O)=NH$  has been investigated in order to probe the influence of a neighbouring oxo centre on the donor capabilities of the imines.

The organometallic chemistry of dialkylsulfoximines was studied in this laboratory in the past [14], but gold was not considered as a partner element in this earlier program.

# Preparative, Analytical and Spectroscopic Results

Dimethylsulfoximine is readily prepared from dimethylsulfoxide an hydrazoic acid, the latter being generated in situ from sodium azide and an acid in chloroform. The product can be converted into the N-trimethylsilyl derivative by treatment with trimethylchlorosilane in the presence of a base (triethylamine) in toluene (eq. (1)). N-Trimethylsilyldimethylsulfoximide is a distillable liquid, which

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is a very convenient reagent in sulfoximine chemistry [14]. It was also used exclusively in the present study.

 $\begin{array}{l} Me_2SO + NaN_3 \xrightarrow{H^+/CHCl_3} & Me_2S(O)NH \\ Me_2S(O)NH + Me_3SiCl \xrightarrow{NEt_3/toluene} & Me_2S(O)NSiMe_3 \end{array}$ (1)

The most common and most powerful aurating agents for the introduction of  $[LAu]^+$  units with L = PPh<sub>3</sub> are (triphenylphosphine)gold tetrafluoroborate [which cannot be isolated and is prepared in situ from (triphenylphosphine)gold chloride [15] and silver tetrafluoroborate], or {tris[(triphenylphosphine)gold]oxonium} tetrafluoroborate (which can be isolated and stored) [16]. Both reagents were used successfully in the present investigation, but the preparations with [(Ph<sub>3</sub>P)Au]BF<sub>4</sub> were more convenient.

Treatment of  $Me_2S(O)=NSiMe_3$  with

 $[(Ph_3P)Au]BF_4$  in the molar ratio of 1:1 in dichloromethane at room temperature gave a colourless product in less than 50% yield, which was shown to be the *di*nuclear (below) instead of the expected *mon*onuclear complex. It therefore appears that the *di*auration of the sulfoximine is at least faster or even thermodynamically more favoured than complete *mono*auration. From reactions with the 1:1 stoichiometry of reagents one half of the sulfoximine is recovered unchanged.

For the 1:2 stoichiometry of reagents very high yields (89%) of the *di*nuclear complex were isolated (eq. (2)). The product is a robust, colourless, crystalline solid (m. p. 122 °C with decomposition).

$$\begin{split} Me_2S(O)NSiMe_3 + 2 \left[(Ph_3P)Au\right]BF_4 \qquad (2) \\ & \underline{}^{NaBF_4} \rightarrow \left\{ Me_2S(O)N[AuPPh_3]_2 \right\}BF_4 \end{split}$$

The product is stable in moist air as a solid and in solution (di- and trichloromethane, tetrahydrofuran). It is readily identified by its analytical and spectroscopic data. The mass spectrum shows the parent cation (m/z 1010) in high abundance. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum has a singlet resonance at  $\delta$  32.0 ppm (CDCl<sub>3</sub>), and the <sup>1</sup>H NMR spectrum a singlet at  $\delta$  3.42 for the methyl and a multiplet for the phenyl protons (7.35 - 7.65). The anion gives rise to a <sup>11</sup>B resonance at  $\delta$  –1.25 ppm. The NMR data indicate that the two phosphine ligands and the two methyl groups are equivalent, ruling out a structure with one [LAu]<sup>+</sup> at nitrogen and the other at oxygen (or carbon) for the solution state. This conclusion is also supported by the IR data (for Nujol mulls), which show the  $\nu$ (S=O) vibration to be largely unchanged as compared to the starting material. The crystal structure of the compound has been determined and the results verify the structural model with both gold atoms coordinated to the nitrogen centre also for the solid state (below).

From experiments with the reagents in the molar ratio 1:3 in dichloromethane (at -20 °C) a different product was obtained in high yield (83%, m. p. 115 °C with decomposition), which is also colourless and has similar solubility properties (eq. (3)).

$$\frac{\text{Me}_2S(O)\text{NSiMe}_3 + 3 [(Ph_3P)\text{Au}]\text{BF}_4}{\frac{\text{NaBF}_4}{\text{Me}_2S(O)\text{N}[\text{AuPPh}_3]_3}[\text{BF}_4]_2}$$
(3)

The analytical data (Exp. Part) indicate that the expected *tri*nuclear compound has been formed. Again only a singlet <sup>31</sup>P resonance is observed (29.6 ppm) which suggests that all three Ph<sub>3</sub>P ligands are equivalent. The <sup>1</sup>H resonance of the methyl groups is shifted to 3.72 ppm, while the phenyl multiplet is largely unchanged as compared to the dinuclear product. The <sup>13</sup>C{<sup>1</sup>H} spectrum has a single set of phenyl resonances proving that all 9 aryl groups are equivalent. The mass spectrum (FAB) does not show the complete trinuclear *di*cation, but features [(Ph<sub>3</sub>P)<sub>2</sub>Au]<sup>+</sup> and [(Ph<sub>3</sub>P)Au]<sup>+</sup> as the main fragments.

The crystals of the *tri*nuclear compound did not have the quality to allow the determination of the solid state structure by X-ray diffraction. It should be noted, however, that crystal structures of the corresponding triorgano*phosphinimines* (**A**) have been determined. The three gold atoms are always bound to one common nitrogen atom of the *di*cations [13]. Based on this analogy, a structure (**B**) is proposed for the trinuclear sulfoximide complex which has a tetrahedrally four-coordinated nitrogen atom.

Attempts to aurate the sulfoximine further by applying an even greater molar ratio of reactants (1:4) under similar conditions gave only the *tri*nuclear



compound. The excess of the gold fluoroborate was found to decompose upon work-up causing low yields and poorer quality of the product. It should be noted that the quadruply aurated species  $\{Me_2S(O)N[Au(PPh_3)]_4\}^{3+}$  would bear a very high positive charge (3+) which is likely to destabilise the system even if the oxo centre is employed as an auxiliary donor. Homoleptic pentacoordination of nitrogen by gold atoms is however well established [6].

Monoauration of the nitrogen function in dimethylsulfoximine with  $[(Ph_3P)Au]^+$  units proved impossible. The diauration appears to be kinetically or – more likely – thermodynamically more favoured (above). The open coordination sphere at *two-coordinate* gold(I) leads to significant Au–Au interactions which induce polyauration. At sterically more crowded gold centres (with *two* phosphine ligands) this tendency should be reduced. Therefore Me<sub>2</sub>S(O)=NSiMe<sub>3</sub> was also reacted with [(Ph<sub>3</sub>P)<sub>2</sub>Au]<sup>+</sup>BF<sub>4</sub><sup>-</sup> [17] in the molar ratio 1:1 in the presence of NaBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> (Eq. (4)).

$$2 [(Ph_3P)_2Au]BF_4 + Me_2S(O)NSiMe_3 \qquad (4)$$
  
$$\rightarrow \{ [(PPh_3)_2Au]_2NS(O)Me_2 \}BF_4 \qquad (4)$$

According to microanalytical data the product obtained did not have the composition of a mononuclear complex, but appeared to be the corresponding dinuclear complex. This compound was indeed formed in high yield from the analogous reaction with the reagents in the molar ratio 1:2 (85% yield, m. p. 112 °C with decomposition). The product has a singlet <sup>31</sup>P (27.6 ppm) and a singlet <sup>11</sup>B resonance (-1.19 ppm), a singlet <sup>1</sup>H signal at 3.74 ppm (Me) and a multiplet at 7.25 - 7.55 ppm (Ph). The mass spectrum shows the ions [(Ph<sub>3</sub>P)<sub>2</sub>Au]<sup>+</sup> and [(Ph<sub>3</sub>P)Au]<sup>+</sup>. The structure of this compound is unknown. No single crystals could be grown for X-ray diffraction analysis.

The preference for *di*auration is also confirmed by the course of the reaction of Me<sub>2</sub>S(O)=NSiMe<sub>3</sub> with the dinuclear gold complex of the ditertiary phosphine Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (dppe). A bistetrafluoroborate was first prepared in situ from (dppe)(AuCl)<sub>2</sub> [18] and two equivalents of AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C and then treated with the Ntrimethylsilylsulfoximide in the presence of NaBF<sub>4</sub> (Eq. 5).

A colourless crystalline product was obtained in 81% yield (mp. 109°C with decomposition). Solu-



tions in CDCl<sub>3</sub> show a <sup>31</sup>P resonance at 27.6 ppm, a <sup>11</sup>B resonance at -1.19 ppm and <sup>1</sup>H resonances at 3.74 (s, Me), 2.78 ( $A_2A'_2XX'$ ) and 7.25 - 7.55 (Ph). The mass spectrum shows the ion [(dppe)Au]<sup>+</sup>. A cyclic structure is proposed for this compound, but there is no proof as yet from X-ray diffraction analysis.

# The Structural Chemistry of {Me<sub>2</sub>S(O)N[Au(PPh<sub>3</sub>)]<sub>2</sub>}+BF<sub>4</sub>-

Crystals of the dinuclear compound (from dichloromethane / pentane) are monoclinic, space group  $P2_1/n$ , with Z = 4 molecular units and four molecules of dichloromethane in the unit cell. The lattice contains cations, anions and solvent molecules well separated with no significant sub-van-der-Waals contacts. The cation has no crystallo-graphically imposed symmetry and the coordinates of the atoms deviate strongly from the maximum possible symmetry operation, a mirror plane passing through N, S and O and bisecting the Au-N-Au angle.

Both gold atoms are coordinated to the nitrogen atom with an angle Au1-N-Au2 of only 92.3(3)°. This small angle is associated with a short aurophilic contact Au1-Au2 of 2.9900(5) Å. The configuration at the gold atoms is close to linear [N-Au1-P2 175.4(2), N-Au2-P1 173.1(2)°]. Most significantly, the configuration at the nitrogen atom is not planar. The sum of the angles Au1/2-N-S 114.5(5)/121.5(5)° and Au1-N-Au2 92.3(3)° is only 328.3° indicating a large deviation from planarity. The sulfoxide unit O=SMe<sub>2</sub> is clearly tilted towards one of the gold atoms (Au1) (Fig. 1). This structural detail is at variance with the characteristics of the analogous dinuclear phosphinimine cation,  $\{Ph_3P-N[Au(PPh_3)]_2\}^+$  where the imine nitrogen atom has been found to be in a planar configuration and the  $R_3P$  group in a symmetrical position [13].



Fig. 1. Molecular structure of the cation of

 $\{ \dot{M}e_2S(O)N[Au(PPh_3)]_2 \} BF_4 \times CH_2Cl_2. (ORTEP drawing with 50\% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1-N 2.087(8), Au1-P2 2.233(2), Au1-M2 2.9900(5), Au2-N 2.061(8), Au2-P1 2.234(2), N-S 1.522(8), S-O 1.453(8), S-C1 1.754(10), S-C2 1.748(10); N-Au1-P2 175.4(2), N-Au2-P1 173.1(2), S-N-Au2 121.5(5), S-N-Au1 114.5(5), Au2-N-Au1 92.3(3).$ 

The differences probably arise from a weak interaction of the oxo function S=O with one of the two gold atoms (Au1). Both the pyramidalization of the N(S,Au,Au) unit and the tilt of the Me<sub>2</sub>SO unit bring the two atoms (Au1, O) closer together [Au1–O 3.485 Å].

### Conclusions

The imine function in a sulfoximine is readily aurated with the usual aurating agents  $[LAu]^+ X^-$  to give di- and trinuclear complexes. The gold atoms are coordinated to the nitrogen atoms with small angles Au-N-Au which favour aurophilic bonding (Au–Au). In the example for which a detailed structure analysis is available, the sulfoxide group is oriented towards one of the gold atoms and maintains a significant Au–O contact. The nitrogen atom attains a pyramidal configuration and the tilt of the sulfoxide group reduces the symmetry of the cationic unit.

#### **Experimental Part**

All experiments were routinely carried out in an atmosphere of pure and dry nitrogen. Solvents and glassware were dried and saturated / filled with nitrogen. Standard equipment was used throughout. N-Trimethylsilyl-dimethylsulfoximide [14], (triphenylgold(I) chloride [15], bis(triphenylphosphine)gold(I) chloride [17], and [1,2-bis(diphenylphosphino)ethane]dichlorodi-

gold(I) [18] were prepared following literature methods. NaBF<sub>4</sub> and AgBF<sub>4</sub> were commercially available.

# *N*,*N*-*Bis*[(triphenylphosphine)gold(I)]dimethylsulfoximide(+) tetrafluoroborate(-)

From Ph<sub>3</sub>AuCl (0.297 g, 0.60 mmol) and AgBF<sub>4</sub> (0.117 g, 0.6 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> a solution of [(Ph<sub>3</sub>P)Au]BF<sub>4</sub> is prepared and treated with a solution of Me<sub>3</sub>SiNS(O)Me<sub>2</sub> (0.049 g, 0.3 mmol) in the same volume of the same solvent. After addition of a small amount of solid NaBF<sub>4</sub> the reaction mixture is stirred for 2 h at r.t. The solution turns pink. It is filtered and the volume of the filtrate is reduced to 3 ml in a vacuum. Addition of diethylether (30 ml) gives a colourless precipitate of the product, which is filtered and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> / pentane (0.293 g, 89% yield, m. p. 122 °C with decomp.). NMR, <sup>1</sup>H:  $\delta$  3.42 (s, 6H, Me), 7.35 - 7.65 (m, 30H, Ph); <sup>11</sup>B: -1.25 (s); <sup>31</sup>P{<sup>1</sup>H}: 32.0 (s). MS(FAB): m/z  $1010 [M-BF_4]^+, 459 [(Ph_3P)Au]^+. C_{38}H_{36}Au_2BF_4NOP_2S$ (1097.47) calcd. C 41.59, H 3.31, N 1.28; found C 41.49, H 3.66, N 1.04.

The same dinuclear product is obtained from  $Me_3SiNS(O)Me_2$  (0,049 g), (Ph<sub>3</sub>P)AuCl (0.148 g) and  $AgBF_4$  (0.059 g, 0.3 mmol each) in 20 ml of  $CH_2Cl_2$  (0.07 g yield; same analytical and spectroscopic data).

### *N*,*N*,*N*-*Tris*[(triphenylphosphine)gold(I)]dimethylsulfoximide(2+) bis[tetrafluoroborate(-)]

A solution of the silylsulfoximide (0.049 g, 0.3 mmol) in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> is treated (at -20 °C) with a solution of [(Ph<sub>3</sub>P)Au]BF<sub>4</sub> prepared from 0.9 mmol each of (Ph<sub>3</sub>P)AuCl (0.445 g) and AgBF<sub>4</sub> (0.175 g) in 30 ml of the same solvent containing some NaBF4. After 30 min the mixture is allowed to warm to room temperature and is stirred for 2 h. The mixture is filtered, the filtrate concentrated to a volume of 5 ml and layered with petroleum ether. A fine colourless precipitate is obtained (0.41 g, 83% yield, m.p. 115 °C with decomp.). NMR, <sup>1</sup>H: 3.74 (s, 6H, Me), 7.25-7.55 (m, 45 H, Ph); <sup>11</sup>B: -1.31 (s);  ${}^{13}C{}^{1}H$ : 77.1 (s, Me), 126.5 (d, C<sub>ipso</sub>, J = 66 Hz), 129.7 (d,  $C_{meta}$ , J = 13 Hz), 132.8 (d,  $C_{para}$ , J = 3 Hz), 133.9 (d,  $C_{\text{ortho}}$ , J = 14 Hz; <sup>31</sup>P{<sup>1</sup>H}: 29.6 (s). MS(FAB): m/z 720  $[(Ph_3P)_2Au]^+$ , 459  $[(Ph_3P)Au]^+$ . C<sub>56</sub>H<sub>51</sub>Au<sub>3</sub>B<sub>2</sub>F<sub>8</sub>NOP<sub>3</sub>S (1643.53) calcd. C 40.83, H 3.34, N 0.85; found C 40.02, H 3.2. N 0.8.

The same trinuclear product is obtained from the reagents in a 1:4 ratio: Me<sub>3</sub>SiNS(O)Me<sub>2</sub> (0.049 g, 0.3 mmol), (Ph<sub>3</sub>P)AuCl (0.594 g), AgBF<sub>4</sub> (0.236 g, 1.2 mmol each); 20 + 40 ml of CH<sub>2</sub>Cl<sub>2</sub>, -20 °C, 0.5 + 2 h (0.39 g yield; same analytical and spectroscopic data).

### *Bis[bis(triphenylphosphine)gold(I)]dimethylsulfoximide(+) tetrafluoroborate(-)*

A solution of  $[(Ph_3P)_2Au]BF_4$  is prepared from  $(Ph_3P)_2AuCl (0.378 g)$  and  $AgBF_4 (0.097 g, 0.5 mmol each)$  in 40 ml of  $CH_2Cl_2$  at -20 °C and filtered into a solution of Me<sub>3</sub>SiNS(O)Me<sub>2</sub> (0.041 g, 0.25 mmol) in 10 ml of the same solvent containing some NaBF<sub>4</sub>. The mixture is allowed to warm up to room temperature and is then stirred for another 2 h. After filtration the volume of the filtrate is reduced to 5 ml and petroleum ether is added to precipitate the colourless product (0.657 g, 84% yield, m. p. 112 °C with decomp.). NMR, <sup>1</sup>H: 3.06 (s, 6H, Me), 7.37 - 7.73 (m, 60 H, Ph); <sup>11</sup>B: -1.27 (s); <sup>31</sup>P{<sup>1</sup>H}: 30.8 (s). MS(FAB): m/z 720  $[(Ph_3P)_2Au]^+$ , 459  $[(Ph_3P)Au]^+$ .  $C_{74}H_{66}Au_2BF_4NOP_4S$  (1622.08): calcd. C 54.79, H 4.10, N 0.86; found C 54.21, H 4.14, N 0.81.

The same dinuclear product is obtained from the reagents in a 1:1 molar ratio:  $Me_3SiNS(O)Me_2$  (0.082 g),  $(Ph_3P)_2AuCl$  (0.378 g),  $AgBF_4$  (0.097 g, 0.5 mmol each), 20 + 40 ml of  $CH_2Cl_2$ , -20 °C, 0.5 + 2 h (0.34 g yield, same analytical and spectroscopic data).

#### [1,2-Bis(diphenylphosphino)ethane]digold(1)-µ-N,Ndimethylsulfoximide(+) tetrafluoroborate(-)

A solution of [bis(diphenylphosphino)ethane]digold(I) bis(tetrafluoroborate), (dppe)Au<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>, is prepared from (dppe)Au<sub>2</sub>Cl<sub>2</sub> (0.036 g, 0.041 mmol) and AgBF<sub>4</sub> (0.0156 g, 0,082 mmol) in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> at -20 °C and filtered into a solution of Me<sub>3</sub>SiNS(O)Me<sub>2</sub> (0.0067 g, 0.041 mmol) in 10 ml of the same solvent containing some NaBF<sub>4</sub>. After 30 min the reaction mixture is allowed to warm to room temperature and stirred for 2 h. After filtration the filtrate is concentrated to a volume of 3 ml and layered with petroleum ether to give a white microcrystalline precipitate (0.03 g, 80.6% yield, m. p. 109 °C with decomp.) NMR, <sup>1</sup>H: 2.78 (m, 4H, CH<sub>2</sub>), 3.74 (s, 6H, Me), 7.25 - 7.55 (m, 20 H, Ph); <sup>11</sup>B: -1.19 (s); <sup>31</sup>P{<sup>1</sup>H}: 27.6 (s). MS(FAB): 595 [(dppe)Au]<sup>+</sup>. C<sub>28</sub>H<sub>30</sub>Au<sub>2</sub>BF<sub>4</sub>NOP<sub>2</sub>S

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(971.29): calcd. C 34.62, H 3.11, N 1.44; found C 34.13, H 3.21, N 1.50.

#### Crystal structure analysis

The data were collected on a Nonius KappaCCD area detector equipped with a rotating anode (Nonius FR591). Graphite-monochromated Mo-K<sub> $\alpha$ </sub> radiation was used. The structure was solved by a combination of direct methods and difference-Fourier syntheses and refined by full matrix least-squares calculations on  $F^2$ . The thermal motion was treated anisotropically for all non-hydrogen atoms. Hydrogen atoms were calculated and allowed to ride on their corresponding C atoms with fixed isotropic contributions.

Crystal data for  $C_{39}H_{38}Au_2BCl_2F_4NOP_2S$ :  $M_r =$ 1182.35, colorless crystals, monoclinic, a = 9.881(1), b =24.490(1), c = 17.468(1) Å,  $\beta = 102.234(1)^{\circ}$ , space group  $P2_1/n, Z = 4, V = 4131.06(11) \text{ Å}^3, \rho_{\text{calc}} = 1.901 \text{ g cm}^{-3}$ F(000) = 2264; T = 0 °C. 70534 measured and 8426 unique reflections [ $R_{int} = 0.0865$ ]; 478 refined parameters, wR2 = 0.1264, R = 0.0554 for 8426 reflections used for refinement. Residual electron densities: +2.40/-2.14 e/Å<sup>3</sup> (located around the gold atoms). The function minimized was:  $wR2 = \{ [\Sigma w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2] \}^{1/2}; w =$  $1/[\sigma^{2}(F_{o}^{2}) + (ap)^{2} + bp]; p = (F_{o}^{2} + 2F_{c}^{2})/3; a = 0.0264,$ b = 67.93. Important interatomic distances and angles are given in the figure caption. Anisotropic thermal parameters and complete lists of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC-148154.

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