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Preparation, Structure and Reactivity of Polynuclear Gold(I) Phosphanyl Alkanethiolates

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The homoleptic gold(I) thiolates of formula $[Au(SR)]_n$ (R = CMe_3, CH_2CMe_3, CH_2CHMe_2, CPh_3) have been converted into their phosphane derivatives of general formula [Au(SR)(L)] (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) and $[Au_2(SR)_2(dppe)]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane], which have been characterized by elemental analysis, mass spectrometry, ^1H and ^{31}P NMR spectroscopy and cyclic voltammetry. Complexes $[Au(SCMe_3)(PMePh_2)]$ (**1c**), $[Au_2(SCMe_3)_2(dppe)]$ (**1e**) and $[Au(SCH_2CMe_3)(PPh_3)]$ (**3d**) have been characterized in the solid state by X-ray diffraction: no aurophilic interactions have been found. The electrochemical behaviour of these phosphane thiolato derivatives shows two irreversible oxidation processes, the first of which involves 0.5 electrons per Au–SR. Chemical oxidation by $[FeCp_2]BF_4$ produces disulfide and cationic gold(I) complexes of formula $[Au_2(SR)(L)_2][BF_4]$ and $[Au_2(SR)(dppe)][BF_4]$, characterized by elemental analysis, mass spectrometry and ^1H and ^{31}P NMR spectroscopy. All the complexes are presumably dimeric in the solid state as shown in the case of $[Au_4(SCMe_3)_2(dppe)_2][BF_4]_2$ (**5e**) and $[Au_4(SCH_2CMe_3)_2(PMe_3)_4][BF_4]_2$ (**7a**), which have been fully characterized by X-ray diffraction. The aurophilic interactions form a structure of four gold atoms with pairs of atoms bonded by bridging thiolato ligands, which are arranged in an almost perfect square in the case of **7a** and in an unprecedented zigzag sequence in the case of **5e**. Complex **4a** reacts with $HSCMe_3$ under basic conditions to give $[Au(SCMe_3)(PMe_3)]$ and with LiX (X = Me, CH_2CMe_3) to give a 1:1 mixture of $[AuX(PMe_3)]$ and $[Au(SCMe_3)(PMe_3)]$.

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Introduction

Research on gold(I) thiolate complexes has produced numerous reports over the past few decades, because of their various practical applications such as, i.a., in gilding technology,[1] in the treatment of rheumatoid arthritis and in cancer chemotherapy.[2] In fact some phosphane gold(I) thiolates are the active principles of Auranofin and other antiarthritic products,[3] whose therapeutic activity seems to be correlated to their oxidation products in vivo. In particular Bruce et al., by thoroughly investigating the oxidation of such thiolato-phosphane derivatives, have been able to show that the final products are cationic gold clusters stabilized in the solid state by aurophilic interactions.[3]

In spite of many literature reports on the synthesis and properties of gold thiolates,[4] complexes containing simple aliphatic groups have been limited to some scattered scientific reports[4a–4c,4g,4h] and some information deriving from patents.[5] So far attention has mostly been dedicated to the few homoleptic thiolates, which are soluble in organic solvents,[4k] and to the phosphane-thiolato derivatives carrying biologically interesting substrates.[3d]

In this paper we describe the synthesis, the characterization and the redox behaviour of a series of gold(I) thiolate complexes derived from simple sterically demanding alkanethiols, where the alkyl group is the *tert*-butyl, *sec*-butyl and neopentyl group. We have also studied triphenylmethanethiol derivatives for comparison purposes. We have prepared homoleptic, neutral derivatives with phosphanes, and the corresponding cationic products prepared according to the Bruce oxidative procedure[3] as a strategy for building gold–gold interactions in the solid state. We report also the structural characterization and a preliminary investigation on the reactivity of these polynuclear cations.

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Results and Discussion

Syntheses

The homoleptic thiolates $[Au(SR)]_n$ (R = CMe_3, CH_2CHMe_2, CH_2CMe_3, CPh_3) have been prepared following essentially two literature methods: addition of an excess

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(3:1) of the thiol to a solution of aqueous tetrachloroauric acid, or alternatively the use of bis(2-hydroxyethyl) sulfide as the auxiliary reducing agent before adding the thiol.[4c] The two methods give similar yields (almost quantitative), but the latter was preferred in the case of the neopentanethiolate, owing to the necessity of saving the starting thiol. In this case care must be used in controlling the temperature to avoid the formation of metallic gold. The thiolates have good stability either in the air or in the light and are generally insoluble at room temperature in the most common organic solvents, apart from the neopentanethiolate that is slightly soluble in benzene and dichloromethane after it has been kept for a while at 40–45 °C. Owing to their insolubility the complexes were characterized only by elemental analysis. They react easily with stoichiometric amounts of the appropriate phosphane to yield the corresponding gold(I) phosphane thiolates of formula [Au(SR)(L)] (R = *tert*-butyl, L = PMe_3 **1a**, PMe_2Ph **1b**, $PMePh_2$ **1c**, PPh_3 **1d**; R = isobutyl, L = PMe_3 **2a**, PMe_2Ph **2b**, $PMePh_2$ **2c**, PPh_3 **2d**; R = neopentyl, L = PMe_3 **3a**, PMe_2Ph **3b**, $PMePh_2$ **3c**, PPh_3 **3d**; R = trityl, L = PMe_3 **4a**, PMe_2Ph **4b**, $PMePh_2$ **4c**, PPh_3 **4d**).[4e,4h,4i] As far as we know, only [Au($SCMe_3$)(PPh_3)] (**1d**) and [Au(SCH_2CHMe_2)(PPh_3)] (**2d**) have already been reported in the literature, **1d** having been prepared by the reaction of [AuCl(PPh_3)] with [Pb($SCMe_3$)$_2$][4c] and **2d** by the reaction of [AuCl(PPh_3)] with the thiol in the presence of a base.[4a]

The reactions were carried out in benzene at room temperature, the yields varying from 80 to 95%. The compounds are crystalline colourless solids, stable in the air and humidity, soluble in aromatic and chlorinated solvents and insoluble in aliphatic hydrocarbons.

The gold(I) dppe thiolates [Au_2(SR)$_2$(dppe)] (R = CMe_3 **1e**; CH_2CHMe_2 **2e**; CH_2CMe_3 **3e**), have been prepared in the same way by using a phosphane/Au = 1/2 molar ratio. All the compounds have been characterized by elemental analysis and NMR spectroscopy.

Well-formed crystals suitable for X-ray determination have been obtained for [Au($SCMe_3$)($PMePh_2$)] (**1c**), [Au_2($SCMe_3$)$_2$(dppe)] (**1e**) and [Au(SCH_2CMe_3)(PPh_3)] (**3d**) by crystallization from toluene at low temperature. None of these complexes show the presence of aurophilic interactions. The molecular structure of **1c** is shown in Figure 1, the most relevant distances and angles are also listed in Table 1. The gold atom shows the expected linear coordination and Au–S and Au–P distances are very similar to those observed in many other structurally characterized gold(I) phosphanyl-thiolate complexes that are reported in the literature,[6] and closely correspond to those reported for other gold(I) methyldiphenylphosphane derivatives.[6c]

Figure 2 shows the centrosymmetric structure of compound **1e** whose geometrical parameters around the gold atom are listed in Table 1. The observed conformation of the dppe ligand is a normal feature in almost all the gold(I) diphosphanyl-thiolate complexes studied hitherto,[7] apart from the cases with bidentate thiolate ligands, which result in cyclic complexes.[8]

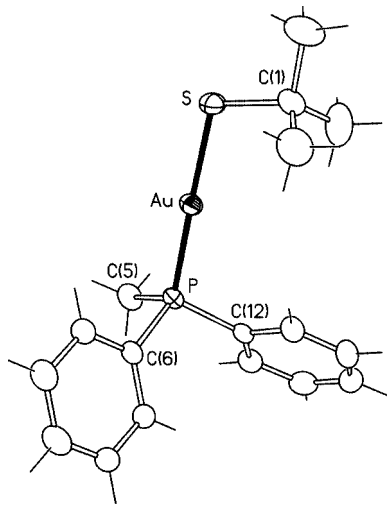

Figure 1. View of the molecular structure of **1c**. Ellipsoids are at 30% probability.

Table 1. Selected bond lenghts [Å] and angles [°] in **1c**, **1e** and **3d**.

1c			
Au–P	2.261(2)	Au–S	2.288(2)
P–Au–S	175.94(6)	C(5)–P–Au	113.9(3)
C(6)–P–Au	115.6(2)	C(12)–P–Au	109.7(2)
C(1)–S–Au	107.0(2)		
1e			
Au–P	2.264(2)	Au–S	2.290(3)
P–Au–S	176.9(1)	C(1)–P–Au	109.9(3)
C(2)–P–Au	116.2(3)	C(8)–P–Au	115.6(3)
C(14)–S–Au	107.3(4)		
3d			
Au–P	2.261(2)	Au–S	2.285(3)
P–Au–S	177.2(1)	C(1P)–P–Au	112.1(4)
C(7P)–P–Au	113.3(4)	C(13P)–P–Au	114.7(3)
C(1)–S–Au	107.0(4)		

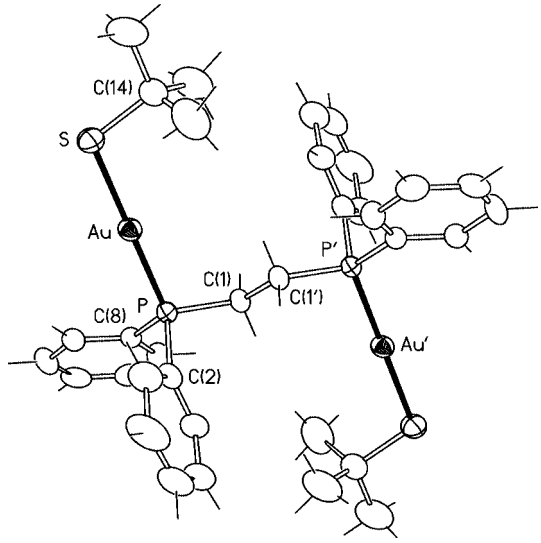

Figure 2. Projection of the molecular structure of **1e**. Thermal ellipsoids are at 30% probability. ′ = 1−*x*, 1−*y*, 1−*z*.

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Finally, the most relevant distances and angles of **3d** (the molecular structure is shown in Figure S1 in the Supporting Information) are listed in Table 1. The gold coordination is very similar to that found in **1e** and **3d** and corresponds very closely to that which has been found in the neutral phosphanyl-thiolato complexes of gold(I) with triphenylphosphane.[7f,9]

Oxidation of Gold Thiolates

In spite of the widespread use in several decomposition techniques and some applications in galvanic processes, the electrochemistry of gold complexes was until recently rather poorly explored. A review summarizes the results of the redox behaviour of gold and silver compounds.[11] In particular the Bruce group has found that gold phosphane thiolates undergo two irreversible oxidation processes, that, in agreement to theoretical studies, were assigned as sulfur- and gold-centred, respectively.[3] Chemical complications following oxidation have been elucidated by studying the reaction with ferrocenium tetrafluoroborate.[3] The oxidation process ultimately gives disulfide and a cationic cluster that in the solid state appears to be constituted by a dicationic tetragold system with gold–gold distances that are in the range of typical distances for aurophilic interactions.[3,10] Such reactivity has been observed in a variety of phosphane and diphosphane gold thiolates, and in particular in the case of those derivatives that are the active principles of Auranofin and of other antiarthritic drugs.[3]

The present study is aimed at elucidating the behaviour of our systems towards both electrochemical and chemical oxidation and exploiting the Bruce reaction in order to build up polynuclear structures, and possibly to understand how the structure and the geometry depend on the nature of the ligands.

Electrochemical Studies

As representatively shown in Figure 3, which refers to [Au(SCH$_2$CMe$_3$)(PMe$_3$)], the gold thiolates with monophosphanes undergo two oxidation processes, both having features of chemical irreversibility.[12] Indeed, also limited to the first oxidation (peak **A**), it lacks the directly associated return peak even at high scan rates (2.0 V s^{-1}), thus indicating that the oxidized product undergoes rapid chemical complications.

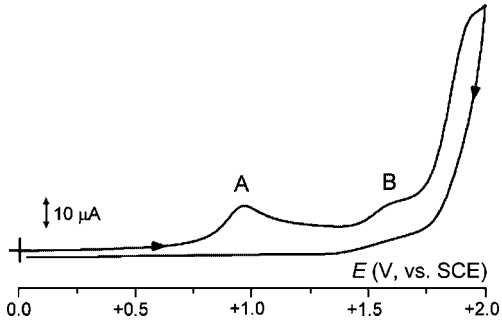

Figure 3. Cyclic voltammogram recorded at a platinum electrode in CH_2Cl_2 solution containing [Au(SCH$_2$CMe$_3$)(PMe$_3$)] (1.8×10^{-3} mol dm^{-3}) and [NBu$_4$][PF$_6$] (0.2 mol dm^{-3}). Scan rate: 0.2 V s^{-1}.

In agreement with the literature,[3] exhaustive oxidation that corresponds to the first oxidation (E_w = +1.2 V) consumes ca. half an electron per molecule, confirming that the ligand centred[9] first process is coupled to fast chemical reactions. Because of the partial overlapping of the solvent discharge no attempts to identify the product arising from the second gold-centred process have been carried out (the standard reduction potential of the couple Au^{I}/Au^{0} in water is +1.69 V).

Table 2 consists of the electrode potentials from the first oxidation of all the compounds studied: An attempt to account for the influence of the electronic effects from the different substituents present in the phosphane or the thiolate groups[12] on the location of the oxidation processes (Table S1 in the Supporting Information) suggests that the main contribution would arise from the inductive effects of the substituents of the phosphane moieties. In fact, they display the highest correlation coefficients, whereas the contribution of the thiolate substituents greatly departs from linearity. However, it has been considered that, given the irreversibility of the electron removals, the potentials for the first oxidation might have a thermodynamic meaning only under the assumption that the kinetics of the coupled chemical complications proceed with similar rates.[13]

In fact, as in the case of the mononuclear complexes, exhaustive oxidation at the first anodic process consumes half an electron per gold atom, which means one electron per molecule. The peak potentials for the first oxidation of the dinuclear derivatives are reported in Table 2.

Since in the mononuclear derivatives the SCMe$_3$ group seems to be a more efficient electron donor than the

Table 2. Peak potentials (V vs. SCE) for the first oxidation process exhibited by the present mono- and digold thiolates in CH_2Cl_2 solution.

Complex	E_p[a]	Complex	E_p[a]	Complex	E_p[a]
[Au(SCMe$_3$)(PMe$_3$)] (**1a**)	+0.97	[Au(SCH$_2$CHMe$_2$)(PMe$_3$)] (**2a**)	+0.97	[Au(SCPh$_3$)(PMe$_3$)] (**4a**)	+0.91
[Au(SCMe$_3$)(^{m}e2Ph)] (**1b**)	+0.95	[Au(SCH$_2$CHMe$_2$)(PPh$_3$)] (**2d**)	+1.09	[Au(SCPh$_3$)(PMe$_2$Ph)] (**4b**)	+0.96
[Au(SCMe$_3$)(PMePh$_2$)] (**1c**)	+1.03	[Au(SCH$_2$CMe$_3$)(PMe$_3$)] (**3a**)	+1.00	[Au(SCPh$_3$)(PMePh$_2$)] (**4c**)	+1.04
[Au(SCMe$_3$)(PPh$_3$)] (**1d**)	+1.04	[Au(SCH$_2$CMe$_3$)(PPh$_3$)] (**3d**)	+1.22	[Au(SCPh$_3$)(PPh$_3$)] (**4d**)	+1.07
[Au$_2$(SCMe$_3$)$_2$(dppe)] (**1e**)	+0.90				
[Au$_2$(SCH$_2$CHMe$_2$)$_2$(dppe)] (**2e**)	+1.10				
[Au$_2$(SCH$_2$CMe$_3$)$_2$(dppe)] (**3e**)	+0.75				

[a] Measured at 0.2 V s^{-1}. In turn the dinuclear derivatives exhibit a voltammetric profile qualitatively similar to those of the mononuclear complexes {the cyclic voltammetric behaviour of [Au$_2$(SCH$_2$CMe$_3$)$_2$(dppe)] (**3e**) is illustrated in Figure S2 in the Supporting Information}.

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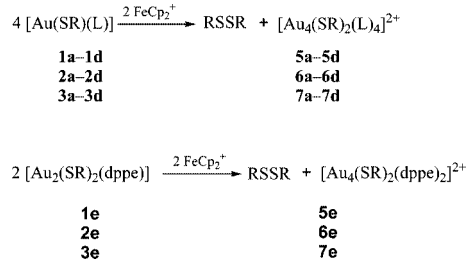
SCH_2CMe_3 ligand, it is puzzling that $[Au_2(SCMe_3)_2(dppe)]$ is oxidized less easily than $[Au_2(SCH_2CMe_3)_2(dppe)]$, unless a different relative arrangement of the thiolato groups in the complexes with dppe might be operative.

Chemical Oxidation

Following previous reaction conditions,[3] the phosphane gold thiolates **1**–**3** have been reacted with $[FeCp_2][BF_4]$ (Scheme 1). In all cases (apart from the thiolates **4**, which react giving uncharacterized products) the reaction proceeds by consuming one mol of ferrocenium salt per two mol of gold thiolate moiety, as shown by colour changes at the equivalence point (the persistence of the green colour of the ferrocenium ion indicates that the reaction is complete).



Scheme 1.

The solid residue, after evaporation of the solvent, is washed with diethyl ether in order to extract ferrocene and the disulfide (RSSR) (the oxidation product of the thiolato ligand), which were identified by NMR spectroscopy. The residue was crystallized from dichloromethane/hexane to give grey to pale yellow crystals of **5**–**7**, which are stable in the air and insoluble in aliphatic and aromatic hydrocarbons, and fairly soluble in acetone and dichloromethane. All the products present satisfactory elemental analyses and have been characterized by NMR spectroscopy and mass spectrometry. On the basis of the relative 2:1 ratio of the ^1H NMR signals from the phosphane and the thiolato groups we have attributed a general formula $[Au_2(SR)(L)_2][BF_4]$. Actually, for similar compounds, the literature reports[3] structures in the solid state that generally result from the aggregation of the monocations in dimers of the formula $[Au_4(SR)_2(phosphane)_4][BF_4]_2$, where the tetranuclear arrangement of the gold atoms is due to aurophilic interactions.

Well-formed crystals suitable for structural determination have been obtained in the case of **5e** and **7a** by crystallization from dichloromethane/hexane or dichloromethane/diethyl ether solutions.

The structure of the tetranuclear cation $[Au_4(SCH_2CMe_3)_2(PMe_3)_4]^{2+}$ is sketched in Figure 4 and the most significant bond lengths and angles are listed in Table 3. The four gold atoms make a square ring by means of four aurophilic interactions. Such an arrangement is very frequent in phosphanyl-thiolato complexes of gold(I), notably with the trimethylphosphane.[6e,14] The cation belongs to the point group 2/*m* (C_{2h}), possessing the inversion centre in the middle of the square of the four gold atoms, the twofold axis lying in the gold plane in the middle between the atoms Au and Au′ and the mirror perpendicular to the axis passing through the S and C(1) atoms. It is a common feature of the gold derivatives with this framework that the PSP plane makes a dihedral angle with the Au_4 plane acute from the side of the sulfur atom. Our cation conforms to this feature showing a torsion angle Au′–Au–Au′′–S of 85.2°. The methyl groups of the phosphanes do not comply with the high symmetry of the molecule, resulting in a statistical disorder between two limit conformations almost equally populated and corresponding to different torsion angles Au′–Au–P–C(5). For the sake of simplicity, only the A conformation of the methyl groups, as marked by the labels, has been drawn in the figure because of its slightly higher frequency.

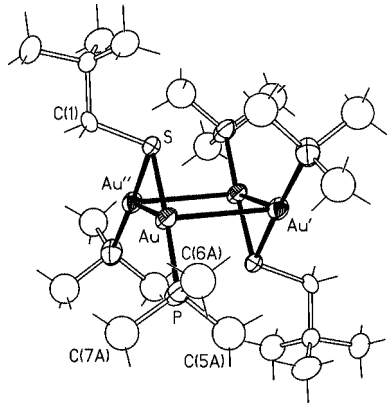


Figure 4. View of the structure of the cationic part of **7a**. Only the most populated positions of the disordered phosphanes have been represented. Thermal ellipsoids are at 30% probability. ′ = $1-x$, $1-y$, z; ′′ = x, y, $-z$.

Table 3. Selected bond lenghts [Å] and angles [°] in **7a**. The apexes in the atom labels have the same meaning as in Figure 4.

Au–Au′	3.112(1)	Au–Au′′	3.138(1)
Au–P	2.259(5)	Au–S	2.332(4)
Au′–Au–Au′′	90.0	S–Au–Au′	86.4(1)
S–Au–Au′′	47.72(9)	P–Au–Au′	96.1(1)
P–Au–Au′′	132.7(2)	Au–S–Au′′	84.6(2)
Au–S–C(1)	104.3(5)	Au–P–C(5A)	117(1)
Au–P–C(6A)	113(1)	Au–P–C(7A)	115(1)

This structure is similar to those reported for $[Au_4(SMe)_2(PMe_3)_4]^{2+}$[6d] and $[Au_4(SCMe_3)_2(PPh_3)_4]^{2+}$,[15] prepared by different routes.

The structure of the tetranuclear cation present in the crystal of **5e**·CH_2Cl_2 is shown in Figure 5 and the bond lengths and angles around the metal are listed in Table 4. The projection has been done down the twofold axis, which relates the two moieties of the cation, point group 2 (C_2 in the Schoenflies notation). The gold atoms are arranged in a sort of zigzag chain. A similar metal arrangement has been found in Ag,[16a,16b] Ag–Pd[16c] Ni,[16d] Mo[16e] and Ta[16f] derivatives, but it has never been reported for gold. Different from almost all these examples, where the metal chain is lying on a plane, the chain of gold atoms is mark-

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edly puckered so that it may be described as a tetrahedron heavily distorted by the stretching of some edges. The three shortest edges correspond to the drawn bonds Au(1)–Au(2), Au(2)–Au(2′) and Au(2′)–Au(1′), while the other three, Au(1)···Au(2′) and Au(2)···Au(1′), 3.717 Å, and Au(1)···Au(1′), 4.903 Å, correspond to non-bonding distances. The torsion angle Au(1)–Au(2)–Au(2′)–Au(1′), which in an undistorted tetrahedron is 70.5°, in our chain rises to 107.8° and only one of the twofold axes of the ideal tetrahedron is preserved.

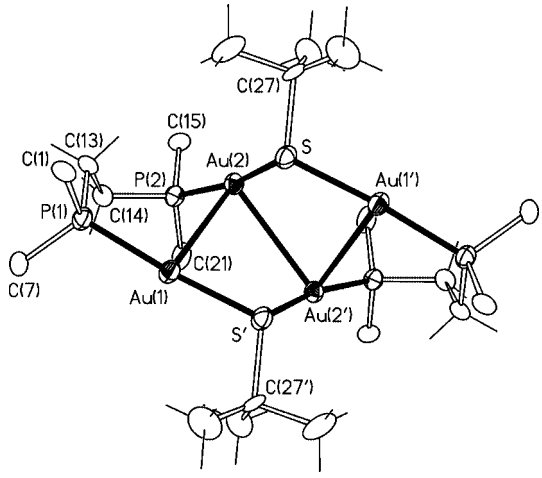

Figure 5. View of the structure of the cationic part of **5e** projected down the twofold axis. The phenyl groups of dppe have been omitted apart from the carbon atoms connected to the phosphorus atoms. Thermal ellipsoids are at 30% probability. ′ = –*x*, *y*, 1/2 – *z*.

Table 4. Selected bond lenghts [Å] and angles [°] in **3d**. The apexes in the atom labels have the same meaning as in Figure 4.

Au(1)–Au(2)	2.986(1)	Au(2)–Au(2′)	3.152(1)
Au(1)–P(1)	2.281(4)	Au(2)–P(2)	2.285(5)
Au(1)–S′	2.320(4)	Au(2)–S	2.346(5)
Au(2)–Au(1)–P(1)	92.3(1)	Au(2)–Au(1)–S′	87.0(1)
P(1)–Au(1)–S′	172.8(2)	Au(1)–Au(2)–Au(2′)	74.49(3)
P(2)–Au(2)–S	168.4(2)	P(2)–Au(2)–Au(1)	92.6(1)
S–Au(2)–Au(1)	85.4(1)	S–Au(2)–Au(2′)	82.7(1)
P(2)–Au(2)–Au(2′)	107.8(1)	Au(1)–S′–Au(2′)	105.6(2)
Au(1)–S′–C(27′)	111.3(6)	Au(2)–S–C(27)	107.3(7)
Au(1)–P(1)–C(1)	111.2(7)	Au(1)–P(1)–C(7)	113.8(6)
Au(1)–P(1)–C(13)	112.5(6)	Au(2)–P(2)–C(14)	110.3(6)
Au(2)–P(2)–C(15)	112.2(7)	Au(2)–P(2)–C(21)	118.0(6)

Although both Au(1)–Au(2) and Au(2)–Au(2′) distances fall within the aurophilic bond range, the second one, 3.152 Å, suggests a rather weak interaction and being associated with a wide Au–S–Au angle, 105.6°, is in keeping with the suggested relationship between this angle and the strength of the gold–gold interaction.[15]

Hence, the corrected formulations for the complexes in the solid state are $[Au_4(SR)_2(L)_4][BF_4]_2$. On the basis of these results and on the literature reports we think that the other cationic compounds prepared have a similar structure, based on a core of four gold atoms associated by aurophilic interactions.

It is not clear if such structures will survive in solution (the literature is not conclusive in this regard). ESI-MS spectra of these complexes in methanol show peaks that can be attributed both to the corresponding dinuclear monocation and to the tetranuclear dication. However, in the case of $[Au_4(SCH_2CHMe_2)_2(PMe_3)_4][BF_4]_2$ (**6a**) and $[Au_4(SCH_2CHMe_2)_2(PPh_3)_4][BF_4]_2$ (**6d**), the spectra show, in addition to the peaks at *m*/*z* = 635 and 1007 for $[Au_2(SR)(PMe_3)_2]^+$ and $[Au_4(SR)_2(PMe_3)_4]^{2+}$, respectively, species at high molecular weights, e.g. $[Au_3(SR)_3(PMe_3)_2]^+$, $[Au_3(SR)_2(PMe_3)_2]^+$ and $[Au_3(SR)(PMe_3)_3]^+$, but it is not certain if those species derive from fragmentation of the tetranuclear species or from the aggregation of small fragments. Moreover, close inspection of the peak corresponding to $[Au_2(SR)(PMe_3)_2]^+$ shows that, in addition to the expected M, M + 1, M + 2 peaks, signals at M + 1/2 are present, which are assigned to the dicationic species $[Au_4(SR)_2(PMe_3)_4]^{2+}$. These observations suggest that tetranuclear species are present in solution (perhaps together with the dinuclear ones) although further experimental evidences are necessary in order to draw clear-cut conclusions.

Reactions with Nucleophiles

Thiolate Anions

The cationic gold clusters can be converted back to the neutral thiolates by reaction with the thiolato anion generated in situ: in fact reacting $[Au_4(SCMe_3)_2(PMe_3)_4][BF_4]_2$ (**4a**) with 2 equiv. of 2-methyl-2-propanethiol in the presence of a base (ethanolamine) produces almost quantitatively $[Au(SCMe_3)(PMe_3)]$ (**2a**). The reaction can easily be followed by ^{1}H NMR spectroscopy. By adding a stoichiometric amount of 2-methyl-2-propanethiol and ethanolamine in a 1:1 molar ratio to a CD_2Cl_2 solution of the dication the signals from the initial cationic complex **4a** disappear immediately and the resonances from the protons of the neutral thiolate **2a** arise.

$$[Au_4(SCMe_3)_2(PMe_3)_4]^{2+} \xrightarrow[Me_3CSH/ethanolamine]{CH_2Cl_2} [Au_2(SCMe_3)_2(PMe_3)_4]$$

Lithium Alkyls

We decided to study the reaction of $[Au_4(SCMe_3)_2(PMe_3)_4][BF_4]_2$ with LiMe and $LiCH_2CMe_3$ because of the spectral simplicity of the expected alkyl derivatives.

The reactions have been carried out with an excess of the alkylating agent in dichloromethane. When $[Au_4(SCMe_3)(PMe_3)_4][BF_4]_2$ was reacted with LiMe, after hydrolysis and extraction with benzene, a solid was obtained whose ^{1}H NMR spectrum shows, in addition to the signals of $[Au(SCMe_3)(PMe_3)]$, two doublets at δ = 0.59 ppm (J = 8.8 Hz) and 1.23 ppm (J = 8.4 Hz). These signals, having a relative intensity of 3:1, could be attributed quite naturally to the PMe_3 and AuMe protons in $[Au(Me)(PMe_3)]$. Accordingly the ^{31}P NMR spectrum of the reaction mixture shows the presence of signals at δ =

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–3.51 ppm, corresponding to the gold phosphanyl thiolate $[Au(SCMe_3)(PMe_3)]$, and δ = 10.74 ppm, which seems logical to attribute to $[Au(Me)(PMe_3)]$.

Surprisingly our NMR spectroscopic data are not in agreement with those reported in the literature for $[Au(Me)(PMe_3)]$, prepared from $[Au(Cl)(PMe_3)]$ by alkylation with LiMe in diethyl ether (δ = 0.21 ppm, $J_{P,H}$ = 8.9 Hz and δ = 0.57 ppm, $J_{H,H}$ = 8.7 Hz).[17] We have prepared $[Au(Me)(PMe_3)]$ following the reported procedure,[18] and we found the same ^1H NMR signals as the methyl derivative formed by reacting $[Au_4(SCH_2CHMe_2)_2(PMe_3)_4][BF_4]_2$ with LiMe. The ^{31}P NMR spectrum showing a signal at δ = 12.35 ppm is rather consistent with the above value of δ = 10.74 ppm. The product reacts rapidly and quantitatively in deuterated benzene with an excess of trifluoroacetic acid, forming methane and $[Au(OOCF_3)(PMe_3)]$ as shown by the immediate appearance in the ^1H NMR spectrum of a singlet at δ = 0.14 ppm (methane) and in the ^{31}P NMR spectrum of a signal at δ = –16.14 ppm, to be attributed to $[Au(OOCF_3)(PMe_3)]$. This was unequivocally identified by purification and comparison of the ^1H NMR spectrum in $CDCl_3$ with that reported in the same solvent (δ = 1.68 ppm, d, $J_{P,H}$ = 11.36 Hz).[19]

Only an X-ray single-crystal determination could positively clarify this point but so far we have not been able to prepare suitable crystals.

$[Au_4(SCMe_3)_2(PMe_3)_4][BF_4]_2$ was similarly reacted with $LiCH_2CMe_3$ yielding an equimolar mixture of $[Au(SCMe_3)(PMe_3)]$ and $[Au(CH_2CMe_3)(PMe_3)]$. The neopentylgold derivative, which has not been reported in the literature thus far, was prepared by alkylation of the corresponding chloro derivative with $LiCH_2CMe_3$ in diethyl ether. The product was isolated as a white crystalline solid, which, even when stored under nitrogen at room temperature and out of light, becomes gradually grey after a few weeks. However, the complex shows well resolved NMR spectra in CD_2Cl_2. The ^1H NMR spectrum shows a singlet at δ = 1.01 ppm and a doublet at δ = 1.22 ppm ($J_{H,H}$ = 8.4 Hz) corresponding to the methyl and methylene protons, respectively, of the neopentyl group and a doublet at δ = 1.41 ppm ($J_{P,H}$ = 8.4 Hz) corresponding to the trimethylphosphane; accordingly the ^{31}P NMR spectrum shows a singlet at δ = 16.60 ppm. The reaction with trifluoroacetic acid in deuteriobenzene gave neopentane (singlet at δ = 0.89 ppm) and $[Au(OOCF_3)(PMe_3)]$, as expected.

These results show that, from the reaction of the above cationic gold thiolates with alkyllithium reagents, half of the metal centres undergo alkylation and the other half are released as a neutral phosphane thiolate:

$$[Au_4(SCMe_3)(PMe_3)_4]^{2+} \xrightarrow{LiR} [Au(SCMe_3)(PMe_3)] + 2\,[Au(R)(PMe_3)]$$

$R = Me, CH_2CMe_3$

Conclusions

We report here the synthesis and characterization of a series of gold(I) thiolates, in which the thiolato ligands contain aliphatic C_4 and C_5 alkyls with different steric hindrance, or a trityl group. The aliphatic thiols give neutral gold thiolates that do not exhibit any Au–Au bonding interactions in the solid state, but upon oxidation afford cationic derivatives that at least in the solid state dimerize to dicationic tetranuclear species with pairs of gold atoms bonded by aurophilic interactions. As in the majority of the literature reports, the arrangement was found to be almost square in the case of **7a** but in the case of **5e**, where dppe is the phosphane supporting ligand, an unusual zigzag organization has been found. It is obviously premature to make a pertinent theory but we are attempting to attribute this peculiar structure to the presence of a chelating phosphane.

Apart from this dinuclear–tetranuclear issue, these cationic thiolates behave towards nucleophiles as $[Au(SR)(PMe_3)]$-stabilized $[Au(PMe_3)]^+$ cations losing the neutral complex and adding the nucleophile. This reactivity confirms that the aurophilic interactions and also the bridging thiolato ligands, which are responsible for the variety of structures in the solid state for gold(I), are easily disrupted in solution.

Experimental Section

All manipulations and reactions were carried out under dinitrogen or argon using standard techniques. Diethyl ether and benzene were distilled prior to use, first over K/benzophenone and later over $LiAlH_4$. *n*-Pentane, CH_2Cl_2 and ethanol were dried under vacuum over molecular sieves. ^1H and ^{31}P NMR spectra were recorded with a Varian Gemini 200 instrument, working at 200 MHz. Centesimal analysis have been executed in the microanalysis laboratory of Dipartimento di Scienze Farmaceutiche dell'Università di Pisa. The mass spectra were obtained by an Ion Spray technique with the Perkin–Elmer instrument SCIEX API III, in methanol solution. Material and apparatus for electrochemistry have been described elsewhere.[20] All of the potential values refer to the Saturated Calomel Electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at +0.39 V. $[Au(SCMe_3)]_n$ was prepared according to the literature.[3a] $[Au(SCH_2CHMe_2)]_n$ was prepared in the same way (yield 93%). C_4H_9AuS (286.15): calcd. C 16.79, H 3.17; found C 16.64, H 3.20. Neopentanethiol was prepared by a literature procedure[21] from the corresponding neopentyl tosylate, obtained from neopentyl alcohol and tosyl chloride in pyridine [yield 95%. ^1H NMR ($CDCl_3$): δ = 0.91 (s, 9 H, CMe_3), 2.46 (s, 3 H, MePh), 3.67 (s, 2 H, CH_2S) ppm] by treatment with NaSH in methoxyethanol [yield 21%. ^1H NMR ($CDCl_3$): δ = 0.96 (s, 9 H, Me), 1.20 (t, 1 H, $J_{H,H}$ = 8.8 Hz, SH), 2.41 (d, 2 H, $J_{H,H}$ = 8.8 Hz, CH_2S) ppm].

Preparation of $[Au(SCH_2CMe_3)]_n$

Method A: Neopentanethiol (0.327 g, 3.14 mmol) was added dropwise to an aqueous solution of $H[AuCl_4]$ (29.34 wt.-% Au) (0.676 g, 1 mmol Au) in EtOH (2.6 mL). An exothermic reaction occurred with the formation of a brown solid that turned white in 30 min. The mixture was heated at 50 °C for 10 min, and the white solid was then separated from the solvent by settling, washed first with

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EtOH (2 × 10 mL) and then with Et_2O (2 × 10 mL). The residual solvent was removed under vacuum to give a solid product (0.294 g, 98%), which is insoluble in the most common organic solvent. $C_5H_{11}AuS$ (300.17): calcd. C 20.01, H 3.69; found C 20.0, H 4.0.

Method B: An aqueous solution of bis(2-hydroxyethyl) sulfide (2 mL, 2.0 mmol) was added dropwise at 0 °C to a solution of $H[AuCl_4]\cdot xH_2O$ (1.05 mmol) in water (1 mL) and EtOH (2.6 mL). The stirring was maintained until the solution turned colourless. Neopentanethiol (0.109 g, 1.05 mmol) was added and a white solid began to precipitate immediately from the solution. After stirring for 30 min, the solid product was separated, washed as described above and dried under vacuum (0.234 g, 78%).

Reaction of $[Au(SCMe_3)]_n$ with L (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, dppe). Formation of $[Au(SCMe_3)(L)]$ (1a, 1b, 1c, 1d, 1e): The reaction of $[Au(SCMe_3)]_n$ with PMe_3 is reported as an example. Trimethylphosphane (0.6 mL of a 1 M solution in toluene, 0.6 mmol) was added to a suspension of $[Au(SCMe_3)]_n$ (0.152 g, 0.53 mmol) in toluene (10 mL) while stirring. The solid immediately dissolved to give a clear colourless solution, which was kept stirring for a further 30 min. The solution was concentrated under vacuum to ca 3 mL and pentane (15 mL) was added causing a white solid to precipitate. The solid was washed twice with pentane (15 mL) and recrystallized from toluene to give 0.187 g (98%) of **1a**. $C_7H_{18}AuPS$ (362.23): calcd. C 23.21, H 5.01; found C 23.3, H 5.3. ^1H NMR (C_6D_6): δ = 1.90 (s, 9 H, CMe_3), 0.55 (d, 9 H, $J_{H,P}$ = 9.5 Hz, PMe_3) ppm. ^{31}P NMR (C_6D_6): δ = 0.61 ppm.

The complexes **1b**–**1e** were prepared in a similar manner to that of $[Au(SCMe_3)]_n$ by reaction with the appropriate phosphane.

Complex 1b: Yield 90%. $C_{12}H_{20}AuPS$ (424.30): calcd. C 33.97, H 4.75; found C 33.52, H 4.95. ^1H NMR (C_6D_6): δ = 1.95 (s, 9 H, CMe_3), 0.81 (d, 6 H, $J_{H,P}$ = 9.5 Hz PMe_2), 7.02 (5 H, br. m, PPh) ppm. ^{31}P NMR (C_6D_6): δ = 13.01 ppm.

Complex 1c: Yield 97%. $C_{17}H_{22}AuPS$ (486.37): calcd. C 41.98, H 4.56; found C 41.79, H 4.45. ^1H NMR (C_6D_6): δ = 1.94 (s, 9 H, CMe_3), 1.21 (d, 3 H, $J_{H,P}$ = 8.8 Hz, PMe), 7.10 (10 H, br. m, PPh_2) ppm. ^{31}P NMR (C_6D_6): δ = 25.00 ppm.

Complex 1d: Yield 95%. $C_{22}H_{24}AuPS$ (548.44): calcd. C 48.18, H 4.41; found C 47.96, H 4.27. ^1H NMR (C_6D_6): δ = 1.92 (s, 9 H, CMe_3), 6.80–6.92 (9 H, br. m, PPh_3), 7.25–7.40 (6 H, br. m, PPh_3) ppm. ^{31}P NMR (C_6D_6): δ = 38.77 ppm.

Complex 1e: Yield 89%. $C_{34}H_{42}Au_2P_2S_2$ (970.72): calcd. C 42.07, H 4.36; found C 41.95, H 4.28. ^1H NMR (C_6D_6): δ = 1.90 (s, 9 H, CMe_3), 2.68 (s, 4 H, PCH_2), 6.8–7.0, 7.4–7.6 (20 H, br. m, PPh_2) ppm. ^{31}P NMR (C_6D_6): δ = 37.64 ppm.

Reaction of $[Au(SCH_2CHMe_2)]_n$ with L (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, dppe). Formation of $[Au(SCH_2CHMe_2)(L)]$ (2a, 2b, 2c, 2d, 2e): The following complexes were prepared as described before.

Complex 2a: White solid. Yield 79%. $C_7H_{18}AuPS$ (362.23): calcd. C 23.21, H 5.01; found C 22.97, H 4.88. ^1H NMR (C_6D_6): δ = 0.45 (d, 9 H, $J_{H,P}$ = 9.9 Hz, PMe_3), 1.23 (d, 6 H, $J_{H,H}$ = 6.6 Hz, Me_2), 2.10 (m, 1 H, $J_{H,H}$ = 6.6 Hz, CH), 3.32 (d, 2 H, $J_{H,H}$ = 6.6 Hz, SCH_2) ppm. ^{31}P NMR (C_6D_6): δ = –0.40 ppm.

Complex 2b: Grey oil. Yield 77%. $C_{12}H_{20}AuPS$ (424.30): calcd. C 33.97, H 4.75; found C 33.77, H 4.53. ^1H NMR (C_6D_6): δ = 0.86 (d, 6 H, $J_{H,P}$ = 9.9 Hz, PMe_2), 1.30 (d, 6 H, $J_{H,H}$ = 6.6 Hz, Me_2), 2.14 (m, 1 H, $J_{H,H}$ = 6.6 Hz, CH), 3.37 (d, 2 H, $J_{H,H}$ = 6.6 Hz, SCH_2), 6.8–7.3 (5 H, br. m, PPh) ppm. ^{31}P NMR (C_6D_6): δ = 11.31 ppm.

Complex 2c: Grey oil. Yield 81%. $C_{17}H_{22}AuPS$ (486.37): calcd. C 41.98, H 4.56; found C 41.78, H 4.25. ^1H NMR (C_6D_6): δ = 1.26 (d, 6 H, $J_{H,H}$ = 6.2 Hz, Me_2), 1.34 (d, 3 H, $J_{H,P}$ = 9.5 Hz, PMe), 2.11 (m, 1 H, $J_{H,H}$ = 6.4 Hz, CH), 3.38 (d, 2 H, $J_{H,H}$ = 6.2 Hz, CH_2), 6.8–7.4 (10 H, br. m, PPh_2) ppm. ^{31}P NMR (C_6D_6): δ = 23.53 ppm.

Complex 2d: White crystals. Yield 75%. $C_{22}H_{24}AuPS$ (548.44): calcd. C 48.18, H 4.41; found C 48.0, H 4.3. ^1H NMR (C_6D_6): δ = 1.27 (d, 6 H, $J_{H,H}$ = 6.6 Hz, Me_2), 2.10 (m, 1 H, $J_{H,H}$ = 6.6 Hz, CH), 3.37 (d, 2 H, $J_{H,H}$ = 6.6 Hz, SCH_2), 6.7–7.4 (15 H, br. m, PPh_3) ppm. ^{31}P NMR (C_6D_6): δ = 38.64 ppm.

Complex 2e: White solid. Yield 65%. $C_{34}H_{42}Au_2P_2S_2$ (970.72): calcd. C 42.07, H 4.36; found C 41.8, H 4.2. ^1H NMR (C_6D_6): δ = 1.25 (d, 12 H, $J_{H,H}$ = 6.6 Hz, Me_2), 2.09 (m, 2 H, $J_{H,H}$ = 6,6 Hz, CH), 2.57 (br. s, 4 H, PCH_2), 3.37 (d, 4 H, $J_{H,H}$ = 6.6 Hz, CH_2), 6.7–7.5 (20 H, br. m, PPh_2) ppm. ^{31}P NMR (C_6D_6): δ = 37.60 ppm.

Reaction of $[Au(SCH_2CMe_3)]_n$ with L (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, dppe). Formation of $[Au(SCH_2CMe_3)(L)]$ (3a, 3b, 3c, 3d, 3e): The following complexes were prepared as described above.

Complex 3a: White crystals. Yield 99%. $C_8H_{20}AuPS$ (376.25): calcd. C 25.5, H 5.4; found C 25.54, H 5.36. ^1H NMR (CD_2Cl_2): δ = 1.02 (s, 9 H, CMe_3), 1.56 (d, 9 H, $J_{H,P}$ = 10.3 Hz, PMe_3), 2.80 (s, 2 H, SCH_2) ppm. ^1H NMR (C_6D_6): δ = 0.62 (d, 9 H, $J_{H,P}$ = 10.3 Hz, PMe_3), 1.33 (s, 9 H, CMe_3), 3.37 (s, 2 H, SCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ = 0.10 ppm. ^{31}P NMR (C_6D_6): δ = –1.03 ppm.

Complex 3b: Crystallized from Et_2O. Yield 85%. $C_{13}H_{22}AuPS$ (438.32): calcd. C 35.62, H 5.06; found C 35.52, H 5.4. ^1H NMR (C_6D_6): δ = 0.98 (d, 6 H, $J_{H,P}$ = 7.3 Hz 1.34, PMe_2), (s, 9 H, CMe_3); 3.42 (s, 2 H, CH_2S), 7.00 (3 H, br. m, PPh), 7.27 (2 H, br. m, PPh) ppm. ^{31}P NMR (C_6D_6): δ = 3.53 ppm.

Complex 3c: Crystallized from Et_2O. Yield 90%. $C_{18}H_{24}AuPS$ (500.39): calcd. C 43.21, H 4.83; found C 43.10; H 5.01. ^1H NMR (C_6D_6): δ = 1.29 (d, 3 H, PMe), 1.32 (s, 9 H, CMe_3); 3.41 (s, 2 H, CH_2S); 6.92 (6 H, br. m, PPh); 7.28 (m, 4 H, PPh_2) ppm. ^{31}P NMR (C_6D_6): δ = 16.64 ppm.

Complex 3d: White crystals from toluene at –5 °C. Yield 97%. $C_{23}H_{26}AuPS$ (562.47): calcd. C 49.11, H 4.66; found C 48.93, H 4.8. ^1H NMR (CD_2Cl_2): δ = 1.05 (s, 9 H, CMe_3), 2.92 (s, 2 H, SCH_2), 7.53–7.54 (15 H, br. m, PPh_3) ppm. ^1H NMR (C_6D_6): δ = 1.31 (s, 9 H, CMe_3), 3,40 (s, 2 H, SCH_2), 6.88 (m, 9 H, PPh_3), 7.29 (6 H, br. m, PPh_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 39.26 ppm. ^{31}P NMR (C_6D_6): δ = 36.21 ppm.

Complex 3e: Crystallized from toluene at –5 °C. Yield 90%. $C_{36}H_{46}P_2S_2Au_2$ (998.77): calcd. C 43.29, H 4.64; found C 43.09, H 4.47. ^1H NMR ($CDCl_3$): δ = 1.07 (s, 18 H, CMe_3), 2.71 (s, 4 H, CH_2S), 3.02 (s, 4 H, PCH_2), 7.29–7.67 (20 H, br. m, PPh_2) ppm. ^1H NMR (C_6D_6): δ = 1.29 (s, 18 H, CMe_3), 2.68 (s, 4 H, PCH_2), 3.41(s, 4 H, CH_2S), 6.91 (12 H, br. m, PPh_2), 7.51 (8 H, br. m, PPh_2) ppm. ^{31}P NMR (C_6D_6): δ = 37.38 ppm.

Preparation of $[Au(SCPh_3)]_n$. Method A: Triphenylmethanethiol (1.076 g, 3.9 mmol) suspended in EtOH (10 mL) was added slowly to a solution of $H[AuCl_4]\cdot xH_2O$ (1.3 mmol) in water (1 mL) and EtOH (5 mL): the mixture was stirred for 3 h and a beige solid was formed. The solid was separated and washed with water (2 × 30 mL), EtOH (20 mL) and Et_2O (20 mL). A beige solid was obtained (0.565 g, 92%). $C_{19}H_{15}AuS$ (472.36): calcd. C 48.31, H 3.20; found C 46.7, H 2.9. Mp: 128° (dec).

Method B: Bis(2-hydroxyethyl) sulfide (0.3 mL, 3 mmol) was added dropwise whilst stirring to 0.671 g of a solution of $H[AuCl_4]\cdot xH_2O$

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(1.0 mmol) in water (10 mL) at 0 °C, causing a precipitate to form. Triphenylmethanethiol (0.276 g, 1 mmol) in $CHCl_3$ (20 mL) was added slowly in ca. 20 min and the reaction mixture stirred for 1 hour giving a grey precipitate. After addition of MeOH (40 mL), the solid was separated, washed with MeOH (2 × 40 mL) and dried (0.40 g, 85%).

Reaction of $[Au(SCPh_3)]_n$ with L (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, dppe): Formation of $[Au(SCPh_3)(L)]$ (4a, 4b, 4c, 4d, 4e)

Complex 4a: pale yellow crystals. Yield 61%. $C_{21}H_{24}AuPS$ (536.43): calcd. C 46.0, H 4.4; found C 45.7, H 4.2. Mp = 118 °C (dec). ^1H NMR (C_6D_6): δ = 0.37 (d, 9 H, J_{PH} = 10.2 Hz, PMe_3), 6.8–7.4 (9 H, br. m, CPh_3), 8.06 (d, 6 H, $J_{H,H}$ = 7.3 Hz, CPh_3) ppm.^{31}P NMR (C_6D_6): δ = 6.41 ppm.

Complex 4b: Pale yellow crystals. Yield 46%. $C_{26}H_{26}AuPS$ (598.50): calcd. C 51.1, H 4.3; found C 50.7, H 4.1. ^1H NMR (C_6D_6): δ = 0.69 (d, 6 H, $J_{H,P}$ = 9.9 Hz, PMe_2), 6.8–8.2 (m, 14 H, CPh_3 + PPh), 8.08 (d, 6 H, $J_{H,H}$ = 7.3 Hz, CPh_3) ppm. ^{31}P NMR (C_6D_6): δ = 40.18 ppm.

Complex 4c: Pale yellow microcrystals. Yield 52%. $C_{31}H_{28}AuPS$ (660.57): calcd. C 55.4, H 4.2; found C 55.2, H 4.1. ^1H NMR (C_6D_6): δ = 1.07 (d, 3 H, $J_{H,P}$ = 9.2 Hz, PMe), 6.8–8.2 (m, 19 H, CPh_3 + PPh_2), 8.09 (d, 6 H, $J_{H,H}$ = 7.7 Hz, CPh_3) ppm.^{31}P NMR (C_6D_6): δ = 42.07 ppm.

Complex 4d: White solid. Yield 71%. $C_{36}H_{30}AuPS$ (722.64): calcd. C 59.0, H 4.1; found C 58.7, H 3.9. Mp = 140 °C (dec). ^1H NMR (C_6D_6): δ = 6.8–7.3 (m, 24 H, PPh_3 + CPh_3), 8.08 (d, 6 H, $J_{H,H}$ = 7.3 Hz, CPh_3) ppm. ^{31}P NMR (C_6D_6): δ = 48.22 ppm.

Complex 4e: Pale yellow microcrystals. Yield 87%. $C_{64}H_{54}Au_2P_2S_2$ (1343.14): calcd. C 57.2, H 4.0; found C 56.8, H 4.2. ^1H NMR (C_6D_6): δ = 2.0–2.5 (4 H, br. m, PCH_2), 6.8–7.4 (m, 50 H, PPh_2 + CPh_3), 8.05 (d, 12 H, $J_{H,H}$ = 7.7 Hz, CPh_3) ppm. ^{31}P NMR (C_6D_6): δ = 42.88 ppm.

Reaction of $[Au(SCMe_3)(L)]$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) with $[FeCp_2][BF_4]$. Formation of $[Au_4(SCMe_3)_2(L)_4][BF_4]_2$ (L = 5a, 5b, 5c, 5d): The reaction of $[Au(SCMe_3)(PMe_3)]$ with $[FeCp_2][BF_4]$ is reported as an example. $[FeCp_2][BF_4]$ (0.037 g, 0.136 mmol) was added to a solution of $[Au(SCMe_3)(PMe_3)]$ (0.100 g, 0.276 mmol) in dichloromethane (10 mL) and the mixture was stirred for 30 min giving a deep yellow solution. The solvent was evaporated and the solid residue was washed with Et_2O (2 × 10 mL), followed by benzene (10 mL), dried under vacuum and crystallized from dichloromethane at –5 °C as colourless crystals (0.094 g, 94%). $C_{20}H_{54}Au_4B_2F_8P_4S_2$ (1444.15): calcd. C 16.6, H 3.8; found C 16.9, H 3.4. ^1H NMR (CD_3COCD_3): δ = 1.60 (s, 18 H, CMe_3), 1.83 (d, 36 H, $J_{H,P}$ = 11.7 Hz, PMe_3) ppm. ^1H NMR (CD_2Cl_2): δ = 1.60 (s, 18 H, CMe_3), 1.71 (d, 36 H, $J_{H,P}$ = 11.0 Hz, PMe_3) ppm. ^{31}P NMR (CD_2Cl_2): δ = 4.58 ppm. ESI-MS (methanol): *m/z* = 635 $[Au_2(SCMe_3)(PMe_3)_2]^+$, 579 $\{[Au_2(SCMe_3)(PMe_3)_2]^+ - C_4H_8\}$, 273 $[Au(PMe_3)]^+$, 87 $[BF_4]^-$. The organic phase was evaporated to dryness giving a solid from which ferrocene sublimates as yellow-orange crystals at 40 °C under high vacuum. ^1H NMR (CD_2Cl_2): δ = 4.18 ppm. The white residue was identified as $(SCMe_3)_2$. ^1H NMR(CD_2Cl_2): δ = 1.31 ppm.

Complex 5b: Colourless crystals. Yield 92%. $C_{40}H_{62}Au_4B_2F_8P_4S_2$ (1692.43): calcd. C 28.4, H 3.7; found C 28.1, H 3.5. ^1H NMR (CD_3COCD_3): δ = 1.65 (s, 18 H, CMe_3); 7.60 (m, 12 H, PPh); 7.95 (m, 8 H, PPh) ppm. ^1H NMR (CD_2Cl_2): δ = 1.67 (s, 18 H, CMe_3), 1.93 (d, 24 H, $J_{H,P}$ = 11.0 Hz, PMe_2), 7.62 (m, 20 H, PPh) ppm. ^{31}P NMR (CD_2Cl_2): δ = 15.92 ppm. ESI-MS (methanol): *m/z* = 759 $[Au_2(SCMe_3)(PMe_2Ph)_2]^+$, 703 $\{[Au_2(SCMe_3)(PMe_2Ph)_2]^+ - C_4H_8\}$.

Complex 5c: Colourless crystals. Yield 95%. $C_{60}H_{70}Au_4B_2F_8P_4S_2$ (1940.72): calcd. C 37.1, H 3.6; found C 37.4, H 3.7. ^1H NMR (CD_3COCD_3): δ = 1.68 (s, 18 H, CMe_3), 2.42 (d, 12 H, $J_{H,P}$ = 10,3 Hz, PMe), 7.58 (m, 24 H, PPh), 7.84 (m, 16 H, PPh) ppm. ^1H NMR (CD_2Cl_2): δ = 1.67 (s, 18 H, CMe_2Ph_3), 2.20 (d, 12 H, $J_{H,P}$ = 10.3 Hz, PMe), 7.52 (40 H, br. m, PPh) ppm. ^{31}P NMR (CD_2Cl_2): δ = 27.51 ppm. ESI-MS (methanol): *m/z* = 883 $[Au_2(SCMe_3)(PMePh_2)_2]^+$, 817 $\{[Au_2(SCMe_3)(PMePh_2)_2]^+ - C_4H_8\}$.

Complex 5d: Colourless crystals. Yield 96%. $C_{80}H_{78}Au_4B_2F_8P_4S_2$ (2189.00): calcd. C 43.9, H 3.6; found C 43.6, H 3.4. ^1H NMR (CD_3COCD_3): δ = 1.70 (s, 9 H, CMe_3), 7.62 (15 H, br. m, PPh_3) ppm. ^1H NMR (200 MHz, CD_2Cl_2): δ = 1.75 (s, 9 H, CMe_3), 7.48 (15 H, br. m, PPh_3) ppm. ^1H NMR (CD_3OD): δ = 1.64 (s, 9 H, CMe_3), 7.49 (15 H, br. m, PPh_3) ppm. ^{31}P NMR (CD_2Cl_2): δ = 43.02 ppm. ESI-MS (methanol): *m/z* = 1007.3 $[Au_2(SCMe_3)(PPh_3)_2]^+$, 87 $[BF_4]^-$.

Reaction of $[Au(SCH_2CHMe_2)(L)]$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) with $[FeCp_2][BF_4]$. Formation of $[Au_4(SCH_2CHMe_2)_2(L)_4][BF_4]_2$ (6a, 6b, 6c, 6d): Following the above procedure $[Au(SCH_2CHMe_2)(PMe_3)]$ (0.130 g, 0.36 mmol) in CH_2Cl_2 (10 mL) was treated with $[FeCp_2][BF_4]$ (0.050 g, 0.18 mmol). The solvent was evaporated under vacuum and the residue was washed with pentane (2 × 30 mL) and benzene (2 × 30 mL). Crystallization from CH_2Cl_2/Et_2O afforded a white solid (0.111 g, 86%). $C_{20}H_{54}Au_4B_2F_8P_4S_2$ (1444.15): calcd. C 16.6, H 3.7; found C 16.5, H 3.7. ^1H NMR (CD_3COCD_3): δ = 1.22 (d, 12 H, $J_{H,H}$ = 6.6 Hz, Me_2), 1.81 (d, 36 H, J_{PH} = 11.7 Hz, PMe_3), 3.17 (d, 4 H, $J_{H,H}$ = 6,6 Hz, CH_2) ppm. ^{31}P NMR (CD_3COCD_3): δ = 2.80 ppm. ESI (MeOH): *m/z* = 635 $[Au_2(SCH_2CHMe_2)(PMe_3)_2]^+$, 349 $[Au(PMe_3)_2]^+$, 273 $[Au(PMe_3)]^+$. From the hydrocarbon extracts the solvent was evaporated leaving a solid residue, from which ferrocene [^1H NMR (CD_2Cl_2): δ = 4.12 ppm] was obtained by sublimation under vacuum at 40 °C leaving a residue identified as $(SCH_2CHMe_2)_2$ [^1H NMR (200 MHz, CD_2Cl_2): δ = 0.99 (d, 12 H, $J_{H,H}$ = 6.6 Hz, Me_2), 1.83 (m, 2 H, $J_{H,H}$ = 6.6 Hz, CH), 2.59 (d, 4 H, $J_{H,H}$ = 6.6 Hz, CH_2) ppm].

Complex 6b: Off-white crystals. Yield 55%. $C_{40}H_{62}Au_4B_2F_8P_4S_2$ (1692.43): calcd. C 28.4, H 3.7; found C 28.2, H 3.5. ^1H NMR (CD_3COCD_3): δ = 1.12 (d, 12 H, $J_{H,H}$ = 6.6 Hz, Me_2), 2.06 (d, 24 H, J_{PH} = 11.0 Hz, PMe_2), 3.21 (d, 4 H, $J_{H,H}$ = 6.2 Hz, CH_2), 7.6–8.0 (20 H, br. m, PPh) ppm. ^{31}P NMR (CD_3COCD_3): δ = 14.83 ppm.

Complex 6c: Pale yellow solid. Yield 57%. $C_{60}H_{70}Au_4B_2F_8P_4S_2$ (1940.72): calcd. C 37.1, H 3.6; found C 36.8, H 3.4. ^1H NMR (CD_3COCD_3): δ = 1.16 (d, 12 H, $J_{H,H}$ = 6.6 Hz, Me_2); 3.26 (d, 4 H, $J_{H,H}$ = 6.2 Hz, CH_2), 2.39 (d, 12 H, J_{PH} = 10.3 Hz, PMe), 7.2–8.0 (40 H, br. m, PPh_2) ppm. ^{31}P NMR (CD_3COCD_3): δ = 27.86 ppm.

Complex 6d: Grey solid. Yield 79%. $C_{80}H_{78}Au_4B_2F_8P_4S_2$ (2189.00): calcd. C 43.9, H 3.6; found C 43.8, H 3.3. ^1H NMR (CD_3COCD_3): δ = 1.06 (d, 12 H, $J_{H,H}$ = 6.2 Hz, Me_2), 1.86 (m, 2 H, $J_{H,H}$ = 6.4 Hz, CH), 3.13 (d, 4 H, $J_{H,H}$ = 6.2 Hz, CH_2), 7.3–7.8 (60 H, br. m, PPh_3) ppm. ^{31}P NMR (CD_3COCD_3): δ = 35.00 ppm. ESI-MS (MeOH): *m/z* = 1007 $[Au_2(SCH_2CHMe_2)(PPh_3)_2]^+$, 721 $[Au(PPh_3)_2]^+$, 459 $[Au(PPh_3)]^+$.

Reaction of $[Au(SCH_2CMe_3)(L)]$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) with $[FeCp_2][BF_4]$. Formation of $[Au_4(SCH_2CMe_3)_2(L)_4][BF_4]_2$ (7a, 7b, 7c, 7d)

Complex 7a: crystallized from dichloromethane/n-hexane to give a beige product. Yield 90%. $C_{22}H_{58}Au_4B_2F_8P_4S_2$ (1472.20): calcd. C 17.9, H 4.0; found C 17.7, H 3.8. ^1H NMR (CD_2Cl_2): δ = 1.11 (s,

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18 H, CMe_3), 1.69 (d, 36 H, $J_{H,P}$ = 10,8 Hz, PMe_3), 3.10 (s, 4 H, CH_2S) ppm. ^{1}H NMR (CD_3COCD_3): δ = 1.12 (s, 18 H, CMe_3), 1.82 (d, 36 H, $J_{H,P}$ = 11.3 Hz, PMe_3), 3.19 (s, 4 H, CH_2S) ppm. ^{31}P NMR (CD_2Cl_2): δ = 2.96 ppm. ESI-MS (methanol): *m/z* 649 $[Au_2(SCH_2CMe_3)(PMe_3)_2]^+$, 349.1 $[Au(PMe_3)_2]^+$, 87 $[BF_4]^-$ ppm. From the ethereal phase ferrocene and $(SCH_2CMe_3)_2$ were isolated.

Complex 7b: Crystallized as off-white crystals from CH_2Cl_2. Yield 86%. $C_{42}H_{66}Au_4B_2F_8P_4S_2$ (1720.49): calcd. C 29.3, H 3.9; found C 29.5, H 4.2. ^{1}H NMR (CD_2Cl_2): δ = 1.15 (s, 18 H, CMe_3), 1.93 (d, 6 H, $J_{H,P}$ = 12.8 Hz, PMe_2), 3.20 (s, 4 H, CH_2S), 7.67 (5 H, br. m, PPh) ppm. ^{1}H NMR (CD_3COCD_3): δ = 1.12 (s, 18 H, CMe_3), 3.22 (s, 4 H, CH_2S), 7.63 (3 H, br. m, PPh), 7.94 (2 H, br. m, PPh) ppm. ^{31}P NMR (CD_2Cl_2): δ = 15.23 ppm.

Complex 7c: Crystallized from CH_2Cl_2. Yield 82%. $C_{62}H_{74}Au_4B_2F_8P_4S_2$ (1968.77): calcd. C 37.8, H 3.8; found C 37.7, H 3.6. ^{1}H NMR (CD_2Cl_2): δ = 1.17 (s, 18 H, CMe_3), 2.19 (d, 3 H, $J_{H,P}$ = 9.2 Hz, PMe), 3.26 (s, 4 H, CH_2S); 7.60 (10 H, br. m, PPh_2) ppm. ^{1}H NMR (CD_3COCD_3): δ = 1.14 (s, 18 H, CMe_3); 2.41 (s, 3 H, PMe), 3.37 (s, 4 H, CH_2S), 7.58 (6 H, br. m, PPh_2), 7.84 (4 H, br. m, PPh_2) ppm. ^{31}P NMR (CD_2Cl_2): δ = 28.32 ppm.

Complex 7d: Yellow crystals from dichloromethane/hexane. Yield 90%. $C_{82}H_{82}Au_4B_2F_8P_4S_2$ (2217.05): calcd. C 44.4, H 3.7; found C 44.5, H 3.9. ^{1}H NMR (CD_2Cl_2): δ = 1.19 (s, 18 H, CMe_3), 3.32 (s, 4 H, CH_2S), 7.44 (m, 15 H, PPh_3) ppm.^{1}H NMR (CD_3COCD_3): δ = 1.16 (s, 18 H, CMe_3), 3.46 (s, 4 H, CH_2S), 7.51 (m, 15 H, PPh_3) ppm. ^{31}P NMR (CD_2Cl_2): δ = 42.90 ppm.

Reaction of $[Au_2(SR)_2(dppe)]$ (R = CMe_3, CH_2CHMe_2, CH_2CMe_3) with $[FeCp_2][BF_4]$. Formation of $[Au_4(SR)_2(dppe)_2][BF_4]_2$ (5e, 6e, 7e)

Complex 5e: pale yellow crystals. Yield 93%. $C_{60}H_{66}Au_4B_2F_8P_4S_2$ (1936.69): calcd. C 37.2, H 3.4; found C 36.7, H 3.0. ^{1}H NMR (CD_3COCD_3): δ = 1.65 (s, 18 H, CMe_3), 3.28 (d, 8 H, $J_{H,P}$ = 13.2 Hz, PCH_2), 7.72 (20 H, br. m, PPh_2) ppm. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.58 (s, 18 H, CMe_3), 2.97 (d, 8 H, $J_{H,P}$ = 12.8 Hz, PCH_2), 7.60 (20 H, br. m, PPh_2) ppm. ^{1}H NMR (CD_3OD): δ = 1.57 (s, 18 H, CMe_3), 3.04 (d, 8 H, $J_{H,P}$ = 13.2 Hz, PCH_2), 7.62 (15 H, br. m, PPh_2) ppm. ^{31}P NMR (CD_2Cl_2): δ = 37.87 ppm. ESI-MS (methanol): *m/z* = 880.9 ($[Au_2(SCMe_3)$-$(dppe)]^+$), 1167 $[Au_3(SCMe_3)_2(dppe)]^+$, 87 $[BF_4]^-$.

Complex 6e: Pale grey solid. Yield 82%. $C_{60}H_{66}Au_4B_2F_8P_4S_2$ (1936.69): calcd. C 37.2, H 3.4; found C 36.8, H 3.3. ^{1}H NMR (CD_3COCD_3): δ = 1.00 (d, 12 H, $J_{H,H}$ = 6.6 Hz, Me_2), 1.84 (m, 2 H, $J_{H,H}$ = 6.6 Hz, CH), 2.84 (d, 4 H, $J_{H,H}$ = 5.9 Hz, CH_2), 3.17 (m, 8 H, PCH_2), 7.2–8.0 (40 H, br. m, PPh_2) ppm. ^{31}P NMR (CD_3COCD_3): δ = 37.91 ppm.

Complex 7e: Clear beige crystals. Yield 89%. $C_{62}H_{70}Au_4B_2F_8P_4S_2$ (1964.74): calcd. C 37.9, H 3.6; found C 38.0, H 4.0. ^{1}H NMR (CD_2Cl_2): δ = 1.13 (s, 18 H, CMe_3), 2.94 (d, 8 H, $J_{H,P}$ = 12.5 Hz CH_2P), 3.36 (s, 4 H, CH_2S), 7.50 (20 H, br. m, PPh_2) ppm. ^{1}H NMR (CD_3COCD_3): δ = 1.10 (s, 18 H, CMe_3), 3.15 (d, 8 H, $J_{H,P}$ = 13.2 Hz CH_2P), 3.60 (s, 4 H, CH_2S), 7.48 (m, 20 H, PPh_2) ppm. ^{31}P NMR (CD_2Cl_2): δ = 39.11 ppm. ESI-MS (methanol): *m/z* = 895 $[Au_2(SCMe_3)(dppe)]^+$, 87 $[BF_4]^-$.

Reaction of $[Au_4(SC_4H_9)_2(PMe_3)_4][BF_4]_2$ with 2-Methyl-2-propanethiol in the Presence of Ethanolamine: The reaction was monitored by ^{1}H NMR spectroscopy. Two NMR tubes were prepared containing a solution of $[Au_4(SC_4H_9)_2(PMe_3)_4][BF_4]_2$ (0.010 g, 0.0069 mmol) in CD_2Cl_2 (0.5 mL) and a solution of 2-methyl-2-propanethiol (0.0138 mmol) and ethanolamine (0.0138 mmol) in CD_2Cl_2 (0.5 mL). After recording the NMR spectra of the two samples as a blank the two solutions were added together and after a few minutes the resulting spectra showed the disappearance of the starting products and the presence of the signals of pure $[Au(SC_4H_9)(PMe_3)]$.

[Au(Me)(PMe$_3$)]: LiMe (0.3 mL of a 1.6 M solution in Et_2O, 0.5 mmol) was added to a suspension of $[Au(Cl)(PMe_3)]$ (0.150 g, 0.5 mmol) in Et_2O (10 mL) and kept at –10 °C. The solution became yellow, then returned slowly to colourless. The reaction mixture was kept for 30 min at –10 °C and then for 2 h at room temperature. The mixture was cooled to 0 °C and was hydrolyzed with H_2O (10 mL). The ethereal phase was separated, desiccated over anhydrous sodium sulfate and the solvents evaporated to dryness under vacuum. A light grey solid was recovered (0.094 g, 65%), which was stored away from the light. $C_4H_{12}AuP$ (288.08): calcd. C 16.68, H 4.20; found C 16.49, H 4.05. ^{1}H NMR (C_6D_6): δ = 0.55 (9 H, d, $J_{H,P}$ = 8.4 Hz, PMe_3), 1.26 (3 H, d, $J_{H,H}$ = 8.4 Hz, CH_3) ppm. ^{31}P NMR (C_6D_6): δ = 12.35 ppm.

[Au(CH$_2$CMe$_3$)(PMe$_3$)]: $Li(CH_2CMe_3)$ (0.038 g, 0.49 mmol) was added to a suspension of $[Au(Cl)(PMe_3)]$ (0.150 g, 0.49 mmol) in diethyl ether (15 mL) and the reaction was carried out as above. The mixture was then hydrolyzed with water (10 mL), the organic phase was dried with Na_2SO_4, concentrated and kept overnight at –20 °C. A white solid was obtained (0.149 g, 89%). $C_8H_{20}AuP$ (344.19): calcd. C 27.92, H 5.86; found C 27.65, H 5.90. ^{1}H NMR (C_6D_6): δ = 0.53 (d, 9 H, $J_{H,P}$ = 8.8 Hz, PMe_3), 1.55 (s, 9 H, CH_3), 2.10 (d, 2 H, $J_{H,H}$ = 8.8 Hz, CH_2) ppm. ^{1}H NMR (CD_2Cl_2): δ = 1.01 (s, 9 H, CH_3), 1.23 (d, 2 H, $J_{H,H}$ = 8.4 Hz, CH_2), 1.41 (d, 9 H, $J_{H,P}$ = 8.4 Hz, PMe_3) ppm. ^{31}P NMR (C_6D_6): δ = 13.16 ppm.

Reaction of $[Au_4(SCMe_3)_2(PMe_3)_4][BF_4]_2$ with Methyllithium. Formation of [Au(SCMe$_3$)(PMe$_3$)] and [Au(Me)(PMe$_3$)]: A large excess of LiMe (0.5 mL of a 1.6 M solution in Et_2O, 0.8 mmol), was added to a solution of $[Au_4(SCH_2CHMe_2)_2(PMe_3)_4][BF_4]_2$ (0.052 g, 0.04 mmol) in CH_2Cl_2 (15 mL). A white precipitate formed immediately. The mixture was stirred for 2 h, and then water (10 mL) was added. The organic layer was separated, desiccated over anhydrous sodium sulfate, and was then evaporated to dryness to leave a light yellow solid showing NMR spectra that are the sum of of both the signals of $[Au(SCMe_3)(PMe_3)]$ and $[Au(Me)(PMe_3)]$. ^{1}H NMR (C_6D_6): δ = 0.62 (d, 9 H, $J_{P,H}$ = 8.8 Hz, $[Au(Me)PMe_3]$, 1.20 (d, 3 H, $J_{H,H}$ = 8.4 Hz, CH_3) $[Au(Me)(PMe_3)]$, 1.48 (s, 9 H, $SCMe_3$), 1.57 (d, 9 H, $J_{H,P}$ = 10.3 Hz, $SAuPMe_3$) ppm. ^{31}P NMR (C_6D_6): δ = 10.74 ($[Au(Me)(PMe_3)]$), 2.95 ($[Au(SCMe_3)(PMe_3)]$) ppm.

Reaction of $[Au_4(SCMe_3)_2(PMe_3)_4][BF_4]_2$ with Neopentyllithium. Formation of [Au(SCMe$_3$)(PMe$_3$)] and [Au(CH$_2$CMe$_3$)(PMe$_3$)]: Solid $LiCH_2CMe_3$ (0.004 g, 0.05 mmol) was added to a solution of $[Au_4(SCMe_3)_2(PMe_3)_4][BF_4]_2$ (0.034 g, 0.025 mmol) in CH_2Cl_2 (15 mL) kept at –20 °C. The mixture was warmed to room temperature. After stirring for 2 h water (10 mL) was added dropwise, the organic phase was separated, dried with anhydrous sodium sulfate and the solvents evaporated to dryness to give a light yellow solid whose NMR spectra show both the signals of $[Au(SCMe_3)(PMe_3)]$ and $[Au(CH_2CMe_3)(PMe_3)]$. ^{1}H NMR (CD_2Cl_2): δ = 1.01 (s, 9 H, $CCMe_3$), 1.23 (d, 2 H, $J_{H,H}$ = 8.8 Hz, CH_2), 1.41 (d, 9 H, $J_{H,P}$ = 8.4 Hz, $CAuPMe_3$), 1.48 (s, 9 H, $SCMe_3$), 1.57 (d, 9 H, $J_{H,P}$ = 10.3 Hz, $SAuPMe_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 2.95 ($[Au(SCMe_3)(PMe_3)]$); 16.58 ($[Au(CH_2CMe_3)(PMe_3)]$) ppm.

X-ray Diffraction: Crystals of **1c**, **1e** and **3d** were obtained by cooling toluene solutions, and **5e** and **7a** were obtained from dichloromethane/pentane solutions. The X-ray diffraction experiments were carried out at room temperature (T = 293 K) by means of a Bruker P4 diffractometer by operating with a graphite-monochromated Mo-K_α radiation. The samples were sealed in glass capillaries under an atmosphere of dinitrogen. The intensity data collection was car-

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Table 5. Crystal data and structure refinements.

	1c	**1e**·diethyl ether	**3d**	**5e**·CH_2Cl_2	**7a**
Empirical formula	$C_{17}H_{22}AuPS$	$C_{38}H_{52}Au_2OP_2S_2$	$C_{23}H_{26}AuPS$	$C_{61}H_{68}Au_4B_2Cl_2F_8P_4S_2$	$C_{22}H_{58}Au_4B_2F_8P_4S_2$
Formula mass [g mol^{-1}]	486.34	1044.79	562.43	2021.54	1472.17
Crystal system	triclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	*Pnnm* (No. 58)
a [Å]	7.881(1)	8.986(2)	12.896(2)	23.652(4)	10.320(1)
b [Å]	11.149(1)	10.837(1)	14.001(3)	17.030(2)	10.511(1)
c [Å]	12.122(1)	11.449(2)	12.958(2)	19.806(3)	20.637(2)
α [°]	106.701(7)	94.423(9)	–	–	–
β [°]	105.168(9)	90.51(1)	109.43(1)	121.96(1)	–
γ [°]	106.092(9)	109.33(1)	–	–	–
V [Å^3]	910.3(2)	1048.2(3)	2206.4(7)	6768.4(17)	2238.6(4)
Z	2	1	4	4	2
D_{calc} [Mg m^{-3}]	1.774	1.655	1.693	1.984	2.184
μ [mm^{-1}]	8.272	7.192	6.839	8.937	13.349
No. measured	4082	4700	4834	7672	3107
No. unique [R_{int}]	3306 [0.0431]	3897 [0.0313]	3982 [0.0496]	6654 [0.0694]	2382 [0.0570]
No. parameters	185	195	236	343	73
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0305, 0.0696	0.0436, 0.1042	0.0510, 0.1077	0.0662, 0.1199	0.0565, 0.1196
R_1, wR_2 [all data][a]	0.0386, 0.0729	0.0687, 0.1147	0.0976, 0.1268	0.1619, 0.1533	0.1194, 0.1454
Goodness of fit[a] on F^2	1.042	1.071	1.012	0.979	1.003

[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $Rw(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [MAX(F_o^2,0) + 2F_c^2]/3$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N - P)\}1/2$, where N, P are the numbers of observations and parameters, respectively.

ried out with the $\omega/2\theta$ scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to for check sample decay. The intensities were corrected for Lorentz and polarization effects and for absorption. In the case of **1e** and **7a** the absorption correction was made by means of an integration method based on the crystal habit.[22] For **1e**, **3d** and **5e**, the crystal fragments used in the data collection were rather irregular, therefore a precise numerical correction was impossible and a semi-empirical method was used.[22] The structure solutions were obtained by means of the automatic direct methods contained in the SHELXS97 program.[23] The refinement, based on full-matrix least-squares on F^2, were done by means of the SHELXL97 program.[22] Some other utilities contained in the WINGX suite were also used.[24] The more relevant crystal parameters are listed in Table 1.

The asymmetric unit of compound **1c** consists of one molecule [Au(S*t*Bu)($PMePh_2$)]. The hydrogen atoms were placed in calculated positions and during the refinement were allowed to "ride" on the connected carbon atoms. In the last of the refinement cycles all the heavy atoms were refined with anisotropic thermal parameters obtaining the reliability factors listed in Table 5.

The asymmetric unit of compound **1e** consists of one half of the molecule [Au_2(S*t*Bu)$_2$(dppe)] riding the inversion centre. A series of maxima around another inversion centre was interpreted as a disordered ethyl ether molecule. The maxima were fitted with the positional parameters of a well-refined ethyl ether molecule from the literature and were refined as a rigid group with isotropic thermal parameters. The hydrogen atoms were placed in calculated positions and anisotropic thermal parameters were used for the heavy atoms of the main molecule. The reliability factors obtained in the last refinement cycle are listed in Table 5.

The asymmetric unit of compound **3d** consists of one molecule [Au(SCH_2tBu)(PPh_3)]. The hydrogen atoms were placed in calculated positions and during the refinement were allowed to "ride" on the connected carbon atoms. In the last of the refinement cycles all the heavy atoms were refined with anisotropic thermal parameters thus obtaining the reliability factors listed in Table 5.

The asymmetric unit of compound **5e** is made up of one half of the cation $[Au_4(StBu)_2(dppe)_2]^{2+}$ located on the twofold axis, one half of a dichloromethane molecule similarly located on the twofold axis and one BF_4^- anion. The BF_4^- anion presents a remarkable disorder and was refined as a rigid group distributed on two limit positions with variable occupancy, fixing the total occupancy to 1.0. The hydrogen atoms were placed in calculated positions and were allowed to "ride" on the connected carbon atoms. Anisotropic thermal parameters were used for all the heavy atoms, excluding those of the disordered anion. The reliability factors obtained in the last refinement cycle are listed in Table 5.

The asymmetric unit of compound **7a** is made up of one fourth of the cation $[Au_4(SCH_2tBu)_2(PMe_3)_4]^{2+}$, with 2/*m* symmetry and one BF_4^- anion located on the twofold axis. Both the $-PMe_3$ group and the anion present a remarkable disorder. The $-PMe_3$ group was refined as a rigid group distributed, with different occupancy, on two positions related by rotation around the Au–P bond; the occupancies were refined fixing the total occupancy to 1.0. The disorder of the tetrahedral anion was instead due to a misalignment between the twofold axis of the crystal and the corresponding operator of the group. The BF_4^- unit was therefore simply introduced in the model with occupancy 1/2. The hydrogen atoms were placed in calculated positions and were allowed to "ride" on the connected carbon atoms. Anisotropic thermal parameters were used for all the heavy atoms, excluding those of the disordered groups. The reliability factors obtained in the last refinement cycle are listed in Table 5.

CCDC-603883 (for **1c**), -603884 (for **1e**), -603885 (for **3d**), -603886 (for **5e**) and -603887 (for **7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Additional figures for compounds **1c**, **1e**, **3d**, **5e** and **7a** (crystal structure, cyclic voltammogram) and a table relating electrochemical behaviour and the inductive electronic effects of the ligands are available.

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