

Chemistry of Polynuclear Cationic Gold(I) Thiolates of Formula $[\text{Au}_2(\text{StBu})(\text{L}_2)]^+[\text{BF}_4]^-$

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The reactivity of the gold(I) cationic complexes $[\text{Au}_2(\text{StBu})(\text{L}_2)]^+[\text{BF}_4]^-$ [$\text{L} = \text{PMe}_3$, PEt_3 , PtBu_3 ; $\text{L}_2 = \text{dppe}$ [$\text{dppe} = 1,2$ -bis(diphenylphosphanyl)ethane]] was studied. These complexes undergo cleavage of the Au–Au bonds by reaction with phosphanes to give quantitative yields of $[\text{Au}(\text{StBu})(\text{L})_n]$ and $[\text{Au}(\text{L})_n]^+[\text{BF}_4]^-$ ($n = 2$ or 3) in the case of monodentate phosphanes, and $[\text{Au}_2(\text{StBu})_2(\text{dppe})]$ and $[\text{Au}(\text{dppe})_2]^+[\text{BF}_4]^-$ in

the case of the dppe derivative. These compounds also react with $[\text{Au}(\text{StBu})(\text{L})]$ and exchange the neutral moiety bonded to the $[\text{Au}(\text{L})]^+$ cation. In both cases some indication of the nature of the intermediates was reached by mass spectrometry (ESI) and NMR spectroscopy.

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Introduction

Gold(I) complexes in the solid state often adopt structures, in which polynuclear cores of gold centres are bound together by weak bonding interactions (aurophilicity).^[1] In particular, the cationic (phosphane)gold(I) thiolate complexes $[\text{Au}_2(\text{SR})(\text{L}_2)]^+[\text{BF}_4]^-$, studied by the Bruce and Schmidbaur groups, are usually arranged in the solid state as dimeric structures, with a core of four gold atoms bound together by aurophilic interactions.^[2]

In recent papers we reported the preparation of the complexes $[\text{Au}_2(\text{StBu})(\text{L}_2)]^+[\text{BF}_4]^-$ [$\text{L} = \text{PMe}_3$ (**2a**), PEt_3 (**2b**), PtBu_3 (**2c**); $\text{L}_2 = \text{dppm}$, dppe (**2d**)] from the corresponding $[\text{Au}(\text{StBu})(\text{L})]^+$ (**1**) complex using Bruce's method, and we showed by mass spectrometry and NMR spectroscopy that, depending on the nature of the phosphane ligand and the solvent, some of them maintain, in part at least, the tetranuclear structure in solution (Figure 1).^[3,4] In particular, the aurophilic interactions between neighbouring Au atoms survive in solution when the phosphane ligand has a small steric hindrance (PMe_3) or is bidentate, then in the following discussion **2a** and **2d** are better described as tetranuclear dications (Figure 1).

The basic unit of these gold(I) complexes can be considered formally as resulting from the interaction of complex **1** with $[\text{Au}(\text{PR}_3)]^+$, with the thiolato group bridging two gold centres, which are additionally bonded through auro-

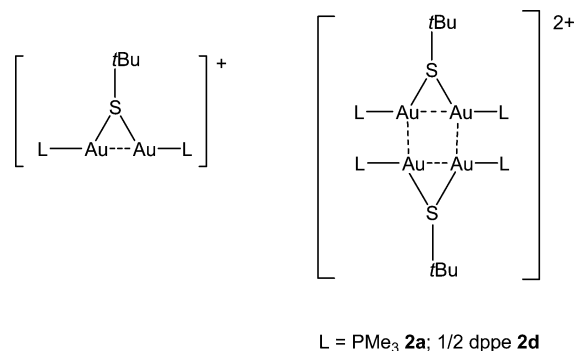


Figure 1. Monomeric (left) and dimeric (right) structures of cations **2**.

philic interactions. It is of some relevance in this context to remember that Schmidbaur has prepared the first prototypical complex of the series, $[\text{Au}_2(\text{SMe})(\text{PMe}_3)_2]^+[\text{BF}_4]^-$, just by the reaction of $[\text{Au}(\text{SMe})(\text{PMe}_3)]^+$ with $[\text{Au}(\text{PMe}_3)]^+$.^[2b]

On the basis of these considerations we studied the behaviour of **2** in the presence of variable amounts of free phosphane or **1**. In the case of the reaction with phosphanes we expected that some exchange should take place since many mononuclear (phosphane)gold(I) derivatives have been reported to rapidly exchange with free phosphane.^[5] Actually, we observed that phosphanes are able to cleave the thiolato-bridged gold–gold interaction, giving the corresponding neutral phosphane thiolato derivatives and cationic phosphane complexes, and that $[\text{Au}(\text{StBu})(\text{L})]$ exchanges with $[\text{Au}_2(\text{StBu})(\text{L}_2)]^+[\text{BF}_4]^-$ or inserts into the Au–Au bond of **2** to give large cyclic cores of Au and S atoms.

Here we describe the results of this investigation together with a combined mass spectrometric and NMR spectroscopic study of the reactions.

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Results and Discussion

Reactivity of Gold(I) Cationic Thiolates with Phosphanes

Reaction of $[\text{Au}_4(\text{StBu})_2(\text{PMe}_3)_4][\text{BF}_4]_2$ (**2a**) with Phosphanes

The first reaction studied was between **2a** and PMe_3 , chosen because of the spectral simplicity of the species involved (Scheme 1). Compound **2a** and trimethylphosphane in a 1:2 ratio were allowed to react in a dichloromethane solution at room temperature. The reaction was almost immediate. The resulting mixture was added dropwise whilst stirring into a large excess of pentane immediately giving an off-white precipitate. The solid was collected by filtration and dried, while the solvent of the filtrate was removed in vacuo to afford a beige solid. The insoluble product was identified as $[\text{Au}(\text{PMe}_3)_2][\text{BF}_4]$ (**3a**) by comparison of the ^1H and ^{31}P NMR spectra with those reported in the literature for $[\text{Au}(\text{PMe}_3)_2]^+[\text{BF}_4]^-$ and by the presence in the mass spectrum of a positive ion peak at $m/z = 349$. Compound **3a** was also prepared from $[\text{AuCl}(\text{PMe}_3)_2]$ and $\text{Ag}[\text{BF}_4]$ according to a published procedure in order to compare the spectroscopic properties of the insoluble product with those of an authentic sample.^[6a]

The product obtained from the pentane solution was identified as $[\text{Au}(\text{StBu})(\text{PMe}_3)]$ (**1a**). The ^1H NMR spectrum in CD_2Cl_2 consists of a singlet at $\delta = 1.46$ ppm from the *StBu* group and a doublet at $\delta = 1.55$ ppm ($J_{\text{P,H}} = 9.9$ Hz) from the PMe_3 group; the ^{31}P NMR spectrum (CD_2Cl_2) shows a singlet at $\delta = 1.40$ ppm. Interestingly, the mass spectrum (ESI; methanol) in the positive ion mode presents, in addition to the peak at $m/z = 363$ $\{[\text{Au}(\text{StBu})(\text{PMe}_3) + \text{H}]^+\}$, peaks at $m/z = 349$ $\{[\text{Au}(\text{PMe}_3)_2]^+\}$, 635 $\{[\text{Au}_4(\text{StBu})_2(\text{PMe}_3)_4]^{2+}\}$ and 921 $\{[\text{Au}_6(\text{StBu})_4(\text{PMe}_3)_4]^{2+}\}$. As already noted,^[4] the peak at $m/z = 635$ arises from the oxidation of the neutral thiolato group during the ionisation process (as confirmed by the absence of $[\text{BF}_4]^-$ in the negative-mode analysis). This compound gives a fragment peak at $m/z = 349$ and an adduct peak at $m/z = 921$. Of course the mass spectrum of **2a** under the

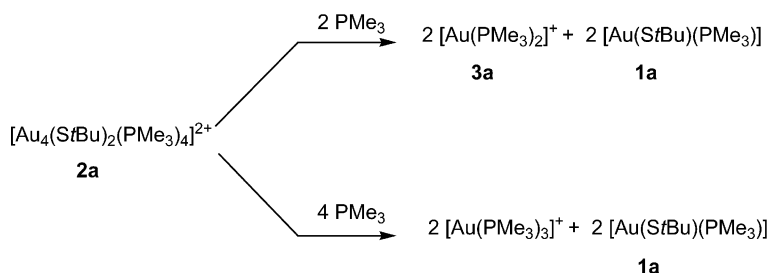
same conditions shows not only the same peaks in the positive-ion mode but also the signal corresponding to $[\text{BF}_4]^-$ in the negative-ion mode.

The NMR spectra in CD_2Cl_2 of the mixture, recorded before the separation of the products by precipitation with pentane, indicates that a dynamic situation is proceeding, since the ^1H NMR spectrum shows two large resonances at $\delta = 1.48$ and 1.61 ppm, and the ^{31}P NMR spectrum one large peak centred at $\delta = 4.64$ ppm. These peaks are roughly the average values of the corresponding signals in the reacting species. It is possible that the equilibrium according to Equation (1) is present {possibly by the formation of the addition intermediate $[\text{Au}_2(\text{StBu})(\text{PMe}_3)_3]^+$ }.

Precipitation of **4a** with pentane should cause the shifting of the equilibrium to the right and leave **1a** as the soluble product. Obviously, this fact implies that mixing $[\text{Au}(\text{PMe}_3)_2][\text{BF}_4]$ and $[\text{Au}(\text{StBu})(\text{PMe}_3)]$ in CD_2Cl_2 in a 1:1 ratio should give the same equilibrium mixture; actually, the spectrum of this mixture is basically identical to that obtained from the reaction of **2a** with trimethylphosphane (signals at $\delta = 1.46$ and 1.59 ppm in the ^1H NMR spectrum; one large signal at $\delta = 5.01$ ppm in the ^{31}P NMR spectrum).

A complex of formula $[\text{Au}_2(\text{SR})(\text{PPh}_3)_3]^+$, similar to the above proposed gold intermediate, is reported in the literature,^[7] and the phosphane ligands were found to compete for the coordination sites at the two gold centres, exhibiting a fluxional behaviour on the NMR scale.

Quite interestingly it turned out that, by using a **2a**/phosphane stoichiometric ratio of 1:4, the neutral product was **1a** as in the previous case, but the ionic product turned out to be spectroscopically different from the expected $[\text{Au}(\text{PMe}_3)_2][\text{BF}_4]$ (**3a**). In fact, the ^1H NMR spectrum in CD_2Cl_2 of the ionic product, dried under reduced pressure (20 Torr), shows a doublet at $\delta = 1.47$ ppm ($J_{\text{H,P}} = 7.7$ Hz), and the ^{31}P NMR spectrum presents a singlet at $\delta = -15.40$ ppm. In CDCl_3 the resonances are similar [^1H NMR: $\delta = 1.50$ ppm (d, $J_{\text{H,P}} = 7.2$ Hz); ^{31}P NMR: $\delta = -15.86$ ppm (s)]. The NMR parameters are different from those reported in the literature for some of the salts of $[\text{Au}(\text{PMe}_3)_2]^+$ (Table 1).



Scheme 1. Reaction of **2a** with PMe_3 .

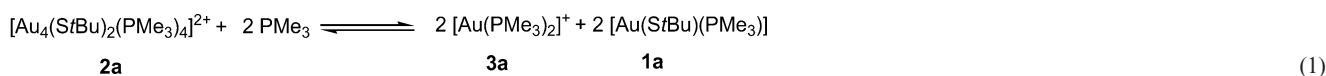


Table 1. ^1H and ^{31}P NMR spectroscopic data for $[\text{Au}(\text{PMe}_3)_2]\text{X}$.

X^-	Solvent	$\delta(^1\text{H})$ [ppm]	$\delta(^{31}\text{P})$ [ppm]	Ref.
Cl^-	CDCl_3	1.6 (s)	3.4 (s)	[6a]
$\text{Cl}^-, \text{Br}^-, \text{I}^-$	$\text{D}_2\text{O}/\text{H}_2\text{O}$	1.6 (br. s)		[6b]
$[\text{NO}_3]^-$, $[\text{BF}_4]^-$	$\text{D}_2\text{O}/\text{H}_2\text{O}$	1.6 (br. s)		[6b]
$[\text{Au}\{\text{P}(\text{O})(\text{OMe})_2\}_2]^+$	CDCl_3	1.69 (d, $J_{\text{H,P}} = 8.5$ Hz)	4.3 (s)	[6c]
$[\text{Au}\{\text{P}(\text{O})(\text{OMe})_2\}_2]^+$	CD_3OD	1.58 (d, $J_{\text{H,P}} = 8.6$ Hz)	7.2 (s)	[6c]
$[\text{BF}_4]^-$	CDCl_3	1.66 (t, $J_{\text{H,P}} = 4.0$ Hz)	8.79 (s)	this work
$[\text{BF}_4]^-$	CD_2Cl_2	1.61 (t, $J_{\text{H,P}} = 4.0$ Hz)	8.70 (s)	this work

Moreover, the integrated area of the phosphane signal in the ^1H NMR spectrum evaluated with respect to an internal standard (ferrocene, hexamethylbenzene) is consistent with the presence of three phosphane ligands per gold centre.

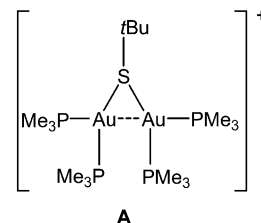
The product was found to be converted into $[\text{Au}(\text{PMe}_3)_2][\text{BF}_4]$ after being kept at 10^{-4} bar overnight, and this explains the contradictory results of the NMR and MS (ESI) data $\{m/z = 349$ corresponding to $[\text{Au}(\text{PMe}_3)_2]^+$, because, under the high-vacuum conditions such as those operating in the mass spectrometer, it is most likely that the product loses a phosphane ligand to give the stable $[\text{Au}(\text{PMe}_3)_2]^+$.

All the $[\text{Au}(\text{PMe}_3)_n]^+$ ($n = 1-4$) cations are reported in the literature.^[6,8,9] $[\text{Au}(\text{PMe}_3)_2]^+$ and $[\text{Au}(\text{PMe}_3)_4]^+$ have been isolated, whereas the existence of $[\text{Au}(\text{PMe}_3)_3][\text{BF}_4]$ is questioned. Actually, on the basis of evidence from IR spectra some authors conclude that $[\text{Au}(\text{PMe}_3)_3][\text{BF}_4]$ does not exist at all, being a 1:1 mixture of $[\text{Au}(\text{PMe}_3)_2][\text{BF}_4]$ and $[\text{Au}(\text{PMe}_3)_4][\text{BF}_4]$.^[6a]

We also added 1 equiv. of phosphane to a CDCl_3 solution of $[\text{Au}(\text{PMe}_3)_2]^+$ in order to achieve the stoichiometric requirements for the formation of $[\text{Au}(\text{PMe}_3)_3]^+$; however, the ^1H NMR spectrum shows a doublet at $\delta = 1.59$ ppm ($J_{\text{H,P}} = 8.8$ Hz) and the ^{31}P NMR a signal at $\delta = -6.96$ ppm, which are different from the values found above for the ionic products of the reaction between **2a** and PMe_3 . Addition of further amounts of PMe_3 shifts the ^{31}P NMR signal progressively to high fields (up to $\delta = -24.44$ ppm), whereas the proton doublet broadens into a large signal. Since these parameters seem to be typical of an exchange between coordinated and free phosphane, and different from those of “ $[\text{Au}(\text{PMe}_3)_3][\text{BF}_4]$ ”, the question of whether the ionic product is indeed the $[\text{Au}(\text{PMe}_3)_3][\text{BF}_4]$ salt is still open.

The reaction of **2a** with PMe_3 in a 1:4 ratio is peculiar in another sense: the reacting mixture, before separation of the products, showed unexpectedly quite narrow NMR signals (a different situation from the one found for the reaction with equimolar amounts) suggesting that a precise species was obtained. In particular the ^1H NMR [singlet at $\delta = 1.47$ ppm and a doublet at $\delta = 1.54$ ppm ($J_{\text{H,P}} = 9.2$ Hz) in a 1:4 ratio] and the ^{31}P NMR spectra (one singlet at $\delta = -3.90$ ppm) could be indicative of a species, in which the PMe_3 ligands are all equivalent or fluxional. We tentatively proposed structure **A** for this intermediate.

Interestingly, this behaviour is strictly peculiar to this stoichiometry since for a higher and lower **2a**/phosphane ratio the resonances are again large and unresolved. In order to detect an addition product, **2a** was treated with an



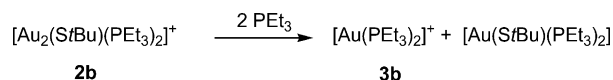
equimolar amount of dppm because of its ability to stabilize two tricoordinate gold atoms bonded together by aurophilic interactions.^[10] Unfortunately, the NMR spectra at room temperature were poorly informative, showing a dynamic behaviour, and the ^{31}P NMR at -70°C was quite complex, showing i.a. a singlet from trimethylphosphane at $\delta = 1.88$ ppm and two singlets at $\delta = 31.78$ and 30.56 ppm from dppm. On the other hand the mass spectrum (ESI) seems to confirm the hypothesis of the above proposed gold intermediate, showing, in addition to the peaks corresponding to $[\text{Au}(\text{PMe}_3)_2]^+$, $[\text{Au}_2(\text{dppm})_2]^{2+}$ and $[\text{Au}_4(\text{StBu})_2(\text{PMe}_3)_4]^{2+}$, a peak at $m/z = 1019$ from the dinuclear complex $[\text{Au}_2(\text{StBu})(\text{PMe}_3)_2(\text{dppm})]^+$. Unfortunately, any attempt to isolate the product has been unsuccessful.

Reaction of $[\text{Au}_2(\text{StBu})(\text{PET}_3)_2][\text{BF}_4]$ (**2b**) with Triethylphosphane

$[\text{Au}_2(\text{StBu})(\text{PET}_3)_2][\text{BF}_4]$ (**2b**) was treated with triethylphosphane by using a **2b**/phosphane molar ratio of 1:1. After the usual workup, the ionic and neutral fractions were separated and it was found that the insoluble fraction contained about half of the starting material **2b** (unreacted) in addition to the expected $[\text{Au}(\text{PET}_3)_2][\text{BF}_4]$ complex. Monitoring by NMR spectroscopy showed that a 1:2 ratio was strictly necessary for the reaction to reach completeness. $[\text{Au}(\text{PET}_3)_2][\text{BF}_4]$ (**3b**) was identified by NMR spectroscopy in CD_2Cl_2 (^1H NMR: two complex resonances, centred at $\delta = 1.97$ and 1.21 ppm for the CH_2 and CH_3 protons, respectively; ^{31}P NMR: singlet at $\delta = 47.3$ ppm) and mass spectrometry (ESI) $\{m/z = 433$ corresponding to $[\text{Au}(\text{PET}_3)_2]^+$. Compounds of the formula $[\text{Au}(\text{PET}_3)_n][\text{PF}_6]$ ($n = 2, 3, 4$) are reported in the literature, but only the dicoordinated cation has been isolated,^[11] and the ^{31}P NMR spectrum of an authentic sample of **3b** prepared according to a literature procedure gives further support for the characterization.^[5a,11]

As for the soluble fraction, the ^1H NMR spectrum in C_6D_6 presents a singlet at $\delta = 1.89$ ppm for the thiolato group, a double quartet at $\delta = 1.15$ ppm ($J_{\text{H,P}} = 8$, $J_{\text{H,H}} =$

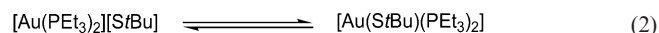
7.7 Hz) and a double triplet at $\delta = 0.75$ ppm ($J_{\text{H,P}} = 17.6$, $J_{\text{H,H}} = 7.7$ Hz) for the triethylphosphane. The ^{31}P NMR spectrum shows one signal at $\delta = 38.22$ ppm, which is fairly consistent with that found for $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$ ($\delta = 38.36$ ppm, C_6D_6). The ^1H NMR spectrum presents some differences: the $\text{S}t\text{Bu}$ chemical shift of $\delta = 1.89$ ppm is quite close to the value found in $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$ ($\delta = 1.93$ ppm), but the phosphane resonances are different ($\delta = 0.63$ and 0.90 ppm). In particular, the 1:2 thiolato/phosphane ratio of the integrated areas are consistent with the formula $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)_2]$ (Scheme 2). This was supported by the reaction of a C_6D_6 solution of $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$ with triethylphosphane in a 1:1 ratio in an NMR tube that gave the same spectroscopic parameters observed in the case of the soluble fraction.



Scheme 2. Reaction of **2b** with PET_3 .

Alternatively, the neutral compound could consist of $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$ containing PET_3 , trapped in the crystals of the solid, so that dissolving the complex could cause the phosphane to be lost and rapidly exchange with coordinated phosphane. In order to clarify this point some variable-temperature NMR experiments were performed in deuterated toluene. Whereas the signals in the ^1H NMR spectrum broadened from -10 to -80 °C, the ^{31}P NMR spectrum ($\delta = 39.93$ ppm at 25 °C) was more informative. Between -10 and -30 °C the signal shifts gradually to $\delta = 37.95$ ppm. A second peak appears below -30 °C and at -80 °C in addition to the major peak ($\delta = 37.04$ ppm), and a second singlet arises at $\delta = 41.90$ ppm (Figure S1 in the Supporting Information). No signal corresponding to free phosphane was found. The resonance at $\delta = 41.90$ ppm is not far (considering the different solvent and anionic ligand) from the value reported for $[\text{Au}(\text{PET}_3)_2]\text{PF}_6$ ($\delta = 43.3$ ppm, CD_2Cl_2).^[5a]

Then, since no evidence for the presence of free exchanging phosphane was found, we are inclined to propose the equilibrium according to Equation (2) to explain these data.

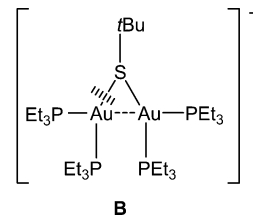


The mass spectrum analysis is not clear-cut showing a peak at $m/z = 405$ $\{[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3) + \text{H}]^+\}$ in addition to other minor signals from secondary reactions. There are in fact peaks at $m/z = 433$ $\{[\text{Au}(\text{PET}_3)_2]^+\}$, 719 $\{[\text{Au}_2(\text{S}t\text{Bu})(\text{PET}_3)_2]^+\}$ and at higher m/z values arising from adducts of **2b** with $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$ (**1b**) formed in the gas phase during MS (ESI) analysis ($m/z = 1005$ $\{[\text{Au}_3(\text{S}t\text{Bu})_2(\text{PET}_3)_2]^+\}$ and $m/z = 1123$ $\{[\text{Au}_3(\text{S}t\text{Bu})_2(\text{PET}_3)_3]^+\}$). The $[\text{Au}(\text{PET}_3)_2]^+$ ion derives from the fragmentation of **2b**, which is formed by electrochemical oxidation of the neutral compound during the ionization process by electrospray. However, these results do not invalidate the hypothesis of a tricoordinate complex, since in the gas phase under high-

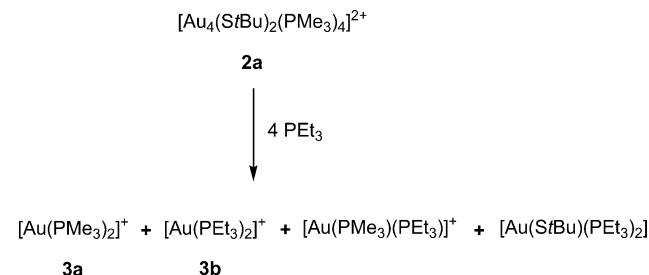
vacuum conditions $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)_2]$ could lose a phosphane ligand to give the more stable $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$. In fact the product, when kept at 10^{-3} Torr pressure for some hours, changed into $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$, preventing elemental analysis.

There are several literature papers on related tricoordinate gold(I) complexes. For example, the triphenylphosphane derivatives $[\text{Au}(\text{SR})(\text{PPh}_3)_2]$ ($\text{R} = \text{S}_2\text{COCH}_2\text{CH}_3$, SC_6F_5 , $\text{C}_5\text{Me}_5\text{CS}_2$, etc.)^[12] in the solid state exhibit longer Au–P distances than in the corresponding phosphanyl–gold dicoordinated complexes.

In an effort to understand some mechanistic aspects the reaction was monitored by NMR spectroscopy in CD_2Cl_2 solution. The ^{31}P NMR spectrum of the reaction mixture before separation of the products presented one sharp singlet at $\delta = 39.48$ ppm, and the ^1H NMR showed well-resolved signals: a singlet at $\delta = 1.51$ ppm for the thiolato group, a double quartet at $\delta = 1.9$ ppm ($J_{\text{H,P}} = 8$, $J_{\text{H,H}} = 7.7$ Hz) and a structured signal centred at $\delta = 1.18$ ppm for the phosphane CH_2 and CH_3 groups. The spectrum is quite similar to that of the starting cation **2b** [apart from the fact that the presence of some benzene (the phosphane was added as a benzene solution) caused a small change (0.07 ppm) of the chemical shifts compared to those observed in pure CD_2Cl_2]. A structure like **B**, which derives from the addition of a triethylphosphane ligand to each gold atom, could explain the above results provided that the phosphane ligands are all equivalent.



The formation of a tricoordinate gold thiolate seems to be peculiar to triethylphosphane. This product was also obtained when treating **2a** with triethylphosphane by using **2a**/phosphane in a 1:4 ratio. After the usual workup, roughly equal amounts of **3a** and $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)_2]$ were formed together with minor amounts of **3b** and $[\text{Au}(\text{PMe}_3)(\text{PET}_3)]^+$ (Scheme 3).



Scheme 3. Reaction of **2a** with PET_3 .

In fact, the ^1H NMR spectrum of the insoluble fraction in CD_2Cl_2 presents a triplet at $\delta = 1.61$ ppm ($J_{\text{H,P}} = 4.0$ Hz) (PMe_3) as the major signal, which together with the ^{31}P

NMR major singlet at $\delta = 8.73$ ppm is indicative of the presence of $[\text{Au}(\text{PMe}_3)_2][\text{BF}_4]$ (**3a**). A double triplet at $\delta = 1.23$ ppm ($J_{\text{H,H}} = 8$, $J_{\text{H,P}} = 18.7$ Hz) and a large structured signal at $\delta = 1.94$ ppm for PEt_3 are also present in the ^1H NMR spectrum as minor peaks. The ^{31}P NMR spectrum shows minor signals, a singlet at $\delta = 47.20$ ppm (s) for $[\text{Au}(\text{PEt}_3)_2][\text{BF}_4]$ (**3b**) and two doublets at $\delta = 44.93$ (d, $J_{\text{P,P}} = 335.5$ Hz) and 11.01 ppm (d, $J_{\text{P,P}} = 335.5$ Hz) for $[\text{Au}(\text{PMe}_3)(\text{PEt}_3)][\text{BF}_4]$. The mass spectrum (ESI) confirms this assignment by showing peaks at $m/z = 349$ $\{[\text{Au}(\text{PMe}_3)_2]^+\}$, $m/z = 391$ $\{[\text{Au}(\text{PMe}_3)(\text{PEt}_3)]^+\}$ and $m/z = 433$ $\{[\text{Au}(\text{PEt}_3)_2]^+\}$.

In contrast, only one pentane-soluble product was detected and isolated, which was characterized as $[\text{Au}(\text{StBu})(\text{PEt}_3)_2]$ by NMR spectroscopy in C_6D_6 and MS (ESI) (see above for discussion).

A point that remains to be explained is the apparent selectivity of this reaction since $[\text{Au}(\text{StBu})(\text{PEt}_3)_2]$ is the only neutral product and **3a** is largely predominant with only small amounts of the other possible (phosphane)gold cations. This is particularly remarkable since it is well known that gold(I) compounds are often involved in phosphane exchange reactions;^[5] this happens, for instance, for compounds like $[\text{Au}(\text{PR}_3)_n]^+$.

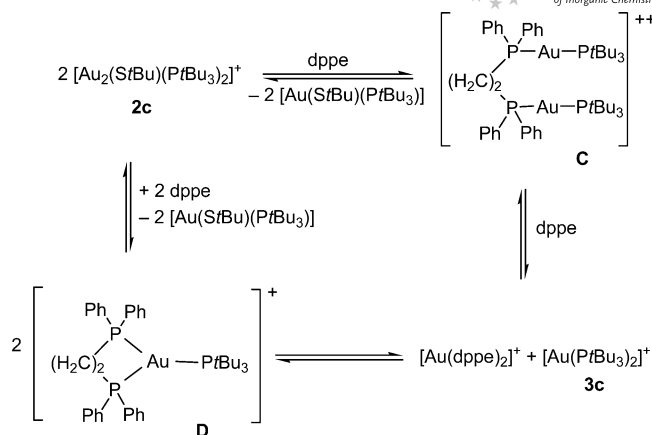
Reaction of $[\text{Au}_2(\text{StBu})(\text{PtBu}_3)_2][\text{BF}_4]$ (**2c**) with Phosphanes

The reaction between $[\text{Au}_2(\text{StBu})(\text{PtBu}_3)_2][\text{BF}_4]$ (**2c**) and PtBu_3 gives $[\text{Au}(\text{PtBu}_3)_2][\text{BF}_4]$ (**5c**) and $[\text{Au}(\text{StBu})(\text{PtBu}_3)]$ (**1c**) in roughly equal amounts.

The ^{31}P NMR spectrum of the ionic product (one singlet at $\delta = 97.00$ ppm) is quite close to the value of $\delta = 97.4$ ppm in CDCl_3 reported by Schmidbaur et al. for **3c**.^[13] The mass spectrum (ESI) confirmed this formulation: $m/z = 601$ $\{[\text{Au}(\text{PtBu}_3)_2]^+\}$. The ^1H NMR spectrum in CD_2Cl_2 (which was not previously reported, as far as we know) presents the phosphane resonance as a double doublet centred at $\delta = 1.55$ ppm ($J_{\text{H,P}} = 7$ Hz); in principle this would be consistent with the presence of two nonequivalent PtBu_3 ligands, but the X-ray structure reported in the literature shows a linear coordination around the gold centre with the two *tert*-butyl groups staggered and equivalent.^[13b] At the moment we have no satisfactory explanation for this observation.

The NMR parameters in C_6D_6 of the pentane-soluble fraction are consistent with those found for **1c**, prepared by a different route, and the mass spectrum (ESI), as expected, presents a peak at $m/z = 489$ assigned to $[\text{Au}(\text{StBu})(\text{PtBu}_3) + \text{H}]^+$ and the oxidation product at $m/z = 601$ $\{[\text{Au}(\text{PtBu}_3)_2]^+\}$ and $m/z = 887$ $\{[\text{Au}_2(\text{StBu})(\text{PtBu}_3)_2]^{2+}\}$ (no BF_4^- is present, see discussion above).

Since **2c** has been shown to exist in solution only as a monocationic dinuclear species,^[4] it appeared interesting to study the feasibility of the addition of dppe to the thiolato-bridged gold–gold moiety. The reaction, carried out by using equimolar amounts of **2c** and dppe, proceeded in an unexpected way to give $[\text{Au}(\text{StBu})(\text{PtBu}_3)]$ (**1c**) and a mixture of $[\text{Au}(\text{dppe})_2][\text{BF}_4]$ and $[\text{Au}(\text{PtBu}_3)_2][\text{BF}_4]$ in a 1:1 ratio as shown in Scheme 4.



Scheme 4. Proposed mechanisms for the reaction of **2c** with dppe.

The two cationic species were easily identified on the basis of their spectroscopic behaviour by comparison with the above reported data and the literature.^[13,14] In particular the ^{31}P NMR spectrum in CD_2Cl_2 shows the two phosphane resonances at $\delta = 97.09$ and 21.93 ppm, assigned to **3c** and $[\text{Au}(\text{dppe})_2]^+$, respectively. Accordingly, mass spectrometry (ESI) shows peaks at $m/z = 601$ $\{[\text{Au}(\text{PtBu}_3)_2]^+\}$ and 993 $\{[\text{Au}(\text{dppe})_2]^+\}$ (positive-ion mode) and at $m/z = 87$ $([\text{BF}_4]^-)$ (negative-ion mode).

The pentane-soluble neutral compound was identified as $[\text{Au}(\text{StBu})(\text{PtBu}_3)]$ (**1c**) from ^1H NMR [singlet at $\delta = 1.93$ ppm and a doublet at $\delta = 1.06$ ppm ($J_{\text{H,P}} = 13.2$ Hz)] and ^{31}P NMR ($\delta = 91.48$ ppm) spectroscopy in C_6D_6 . The mass spectrum (ESI) of the positive ions confirmed the structure by showing a peak at $m/z = 489$ $\{[\text{Au}(\text{StBu})(\text{PtBu}_3) + \text{H}]^+\}$, in addition to other peaks deriving from in situ oxidation during the ionization process as discussed elsewhere.^[4]

Interestingly, dppe does not give any neutral derivative, being completely consumed to afford $[\text{Au}(\text{dppe})_2][\text{BF}_4]$.

Two rational mechanisms are depicted in Scheme 4. The trapping by the diphosphane of the $[\text{Au}(\text{PtBu}_3)]^+$ species, formed after the displacement of the neutral $[\text{Au}(\text{StBu})(\text{PtBu}_3)]$, could result in two possible intermediates: a dinuclear dicoordinated (phosphane)gold cation (**C**) or a tricoordinated gold cation (**D**). In both cases disproportionation of one of these intermediates gives the final cationic products $[\text{Au}(\text{dppe})_2][\text{BF}_4]$ and **3c**.

Both intermediates have some support in the literature: for instance several examples of tricoordinate gold(I) compounds containing a di- and a monophosphane ligand of the type $[\text{Au}(\text{PPh}_3)(\text{dppe})][\text{Co}(\text{CO})_4]$,^[15] $[\text{Au}(\text{PPh}_3)(\text{dppe})][\text{X}]$ ($\text{X} = \text{Cl}, \text{CN}$),^[16] and $[\text{AuCl}(\text{PPh}_3)(\text{dppe})]$ ^[17] have been reported.

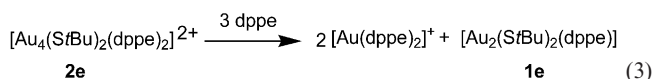
Reaction of $[\text{Au}_4(\text{StBu})_2(\text{dppe})_2][\text{BF}_4]_2$ (**2d**) with Bis(1,2-diphenylphosphanyl)ethane

When equimolar amounts of dppe and **2d** were used the reaction did not run to completeness, as shown by the presence of the starting complex in the insoluble pentane fraction. However, in the same fraction $[\text{Au}(\text{dppe})_2][\text{BF}_4]$ was

isolated and identified by comparison of the spectroscopic data. MS analysis showed positive ion peaks at $m/z = 993$ $\{[\text{Au}(\text{dppe})_2]^+\}$, 881 $\{[\text{Au}_4(\text{S}t\text{Bu})_2(\text{dppe})_2]^{2+}\}$ and 1168 $\{[\text{Au}_3(\text{S}t\text{Bu})_2(\text{dppe})]^+\}$ and 87 $[\text{BF}_4^-]$ as the negative ion.

^1H NMR spectra recorded in C_6D_6 of the pentane-soluble fraction show a singlet at $\delta = 1.88$ ppm for the thiolato ligand, a signal centred at $\delta = 2.62$ ppm for the dppe CH_2 group and two large signals between $\delta = 6.8$ and 7.6 ppm for the aromatic protons. The ^{31}P NMR spectrum shows a signal at $\delta = 37.90$ ppm. This compound was identified as $[\text{Au}_2(\text{S}t\text{Bu})_2(\text{dppe})]$ by comparison of its spectroscopic data with those of a pure sample prepared by an alternative route.^[3,4] The MS (ESI) analysis confirms the attribution, showing the diagnostic peak at $m/z = 993$ $\{[\text{Au}_2(\text{S}t\text{Bu})_2(\text{dppe}) + \text{Na}]^+\}$ in addition to peaks at $m/z = 881$ $\{[\text{Au}_4(\text{S}t\text{Bu})_2(\text{dppe})_2]^{2+}\}$, 1024 $\{[\text{Au}_5(\text{S}t\text{Bu})_3(\text{dppe})_2]^{2+}\}$ and 1168 $\{[\text{Au}_3(\text{S}t\text{Bu})_2(\text{dppe})]^+\}$ deriving from the electrospray process (see above for discussion).

The presence of unreacted $[\text{Au}_4(\text{S}t\text{Bu})_2(\text{dppe})_2][\text{BF}_4]_2$ indicates that in this case a different stoichiometry with respect to that used in the above reactions is required in order to drive the reaction to completeness. Indeed, by using the right stoichiometry {3 equiv. of dppe per equiv. of $[\text{Au}_4(\text{S}t\text{Bu})_2(\text{dppe})_2][\text{BF}_4]_2$ }, $[\text{Au}(\text{dppe})_2][\text{BF}_4]$ and $[\text{Au}_2(\text{S}t\text{Bu})_2(\text{dppe})]$ were obtained in almost quantitative yields according to Equation (3).



Reactivity of Gold(I) Cationic Thiolates in the Presence of Neutral Precursors

As a further aspect of the chemistry of the $[\text{Au}_2(\text{S}t\text{Bu})(\text{L})_2][\text{BF}_4]$ systems, the reaction of the cationic complexes **2a** with neutral phosphane thiolates $[\text{Au}(\text{S}t\text{Bu})(\text{L})]$ was investigated. This mixture resembles the situation that occurs during the preparation of **2**, when $[\text{FeCp}_2]^+$ is gradually added to a solution of $[\text{Au}(\text{S}t\text{Bu})(\text{L})]$ in dichloromethane.

$[\text{Au}_4(\text{S}t\text{Bu})_2(\text{PMe}_3)_4][\text{BF}_4]_2$ (**2a**) + $[\text{Au}(\text{S}t\text{Bu})(\text{PMe}_3)]$ (**1a**)

The ^1H NMR spectrum of **2a** in CD_2Cl_2 shows a singlet at $\delta = 1.58$ ppm and a doublet at $\delta = 1.67$ ppm ($J_{\text{P,H}} = 11.4$ Hz) and the ^{31}P NMR spectrum a singlet at $\delta = -1.91$ ppm.

After addition of even small amounts of $[\text{Au}(\text{S}t\text{Bu})(\text{PMe}_3)]$ (**1a**) to this solution, partial coalescence of the trimethylphosphane doublet and broadening of the ^{31}P NMR resonance (without significant changes in the chemical shifts) occurs. Further broadening in the ^1H NMR spectrum is observed upon addition of more **1a**. When 2 equiv. of the neutral thiolate per equiv. of **2a** were added, the phosphane appeared as quite a broad signal. Accordingly, the ^{31}P resonance at $\delta = -1.99$ ppm resulted in quite a broad signal (ca. 80 Hz). The fact that broadening in-

creases with the amount of **1a** added indicates that the exchange is in the "slow-exchange" regime. Variable-temperature ^1H NMR experiments showed that the signals become resolved starting from -20 °C; below -40 °C a singlet at $\delta = 1.48$ ppm {close to the corresponding signal at $\delta = 1.46$ ppm in $[\text{Au}(\text{S}t\text{Bu})(\text{PMe}_3)]$ } and a doublet at $\delta = 1.65$ ppm ($J_{\text{H,P}} = 11.0$ Hz) for PMe_3 are observed. The ^{31}P NMR spectrum shows a sharp resonance at $\delta = -3.07$ ppm, which remained as the only signal even at -70 °C. This is a result that is difficult to rationalize unless suggesting (at high temperature) a slow scrambling of free and coordinated $[\text{Au}(\text{S}t\text{Bu})(\text{PMe}_3)]$, and (at low temperature) a symmetric or quasi-symmetric stabilized intermediate.

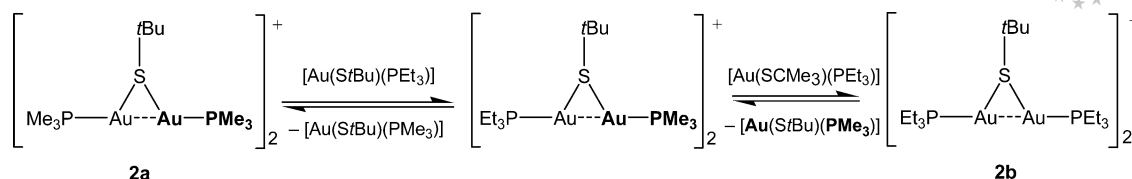
The mass spectrum (ESI) of this solution gives some support for a trinuclear intermediate, because it shows an ion peak at m/z (%) = 997 $\{[\text{Au}_3(\text{S}t\text{Bu})_2(\text{PMe}_3)_3]^+ (52)\}$, in addition to the ion peaks at m/z (%) = 349 $\{[\text{Au}(\text{PMe}_3)_2]^+ (83)\}$, 363 $\{[\text{Au}(\text{S}t\text{Bu})(\text{PMe}_3) + \text{H}]^+ (40)\}$, 635 $\{[\text{Au}_4(\text{S}t\text{Bu})_2(\text{PMe}_3)_4]^{2+} (100)\}$ and 921 $\{[\text{Au}_6(\text{S}t\text{Bu})_4(\text{PMe}_3)_4]^{2+} (72)\}$. The intensity of the peak at $m/z = 997$ and its persistence under different experimental conditions should rule out instrumental artefacts. It is perhaps of some relevance to remember that the trinuclear complex $[(\text{CH}_2\text{S})_2(\text{AuPPh}_3)_3]^+$ prepared by Schmidbaur and coworkers presents a similar NMR behaviour showing even at -60 °C the equivalence of the phosphane groups.^[2b] In this case the authors propose a low-energy mechanism that exchanges the three $\text{Au}(\text{PPh}_3)$ groups for the two sulfur donors. Then it is possible that a similar situation may arise in our case.

Interestingly, by using a 1:4 $[\text{Au}_4(\text{S}t\text{Bu})_2(\text{PMe}_3)_4][\text{BF}_4]_2/[\text{Au}(\text{S}t\text{Bu})(\text{PMe}_3)]$ ratio, the ^1H and ^{31}P NMR spectra are well resolved even at room temperature, indicating that a rapid exchange occurs. The NMR parameters are not very different from those reported above for the precedent experiment [^1H NMR: $\delta = 1.46$ ppm (s) and 1.61 ppm (d); ^{31}P NMR: $\delta = -0.09$ ppm].

However, any attempt to isolate some ionic intermediates by adding pentane to the CH_2Cl_2 solution resulted only in the recovery of **2a** leaving the neutral thiolate in solution.

$[\text{Au}_4(\text{S}t\text{Bu})_2(\text{PMe}_3)_4][\text{BF}_4]_2$ (**2a**) + $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$ (**1b**)

The reaction between $[\text{Au}_4(\text{S}t\text{Bu})_2(\text{PMe}_3)_4][\text{BF}_4]_2$ and $[\text{Au}(\text{S}t\text{Bu})(\text{PET}_3)]$ in CD_2Cl_2 in a 1:1, 1:2 and 1:4 ratio was studied. After addition of the neutral compound to the ionic one, all the NMR signals became increasingly broad (in particular the resonance from the PMe_3 protons) until the signals appeared well resolved when the 1:4 ratio was reached; the ^1H NMR spectrum shows a singlet at $\delta = 1.53$ ppm for the thiolato group, a doublet at $\delta = 1.64$ ppm ($J_{\text{H,H}} = 11.0$ Hz) for PMe_3 , a double quartet at $\delta = 1.95$ ppm ($J_{\text{H,P}} = 9.9$, $J_{\text{H,H}} = 7.7$ Hz) and a double triplet at $\delta = 1.25$ ppm ($J_{\text{H,P}} = 9.9$, $J_{\text{H,H}} = 18.7$ Hz) for PET_3 . In the ^{31}P NMR spectrum two signals are present at $\delta = 38.26$ and -0.09 ppm, which were assigned to PET_3 and PMe_3 , respectively, by comparison with the spectra of other (phosphane)gold derivatives. The chemical shifts are about the same as those of **2a** and **2b**, and the behaviour is quite sim-

Scheme 5. Reaction of **2a** with **1b**.

ilar to that observed for the **2a/1a** reaction, supporting the idea that a rapid exchange between coordinated $[\text{Au}(\text{SiBu})(\text{PMe}_3)]$ and $[\text{Au}(\text{SiBu})(\text{PEt}_3)]$ takes place.

The MS (ESI) data of the solutions (Table S1 in the Supporting Information) show the presence of gold species of various nuclearity and in particular **2a**, **2b** and $[\text{Au}_2(\text{SiBu})(\text{PMe}_3)(\text{PEt}_3)]^+$. The attribution of the ion $[\text{Au}_2(\text{SiBu})(\text{PMe}_3)(\text{PEt}_3)]^+$ was confirmed by comparison with an authentic sample, prepared from $[\text{Au}(\text{PMe}_3)]\text{BF}_4$ by reaction with $[\text{Au}(\text{SiBu})(\text{PEt}_3)]$ according to a procedure described by Bruce et al.^[2f] $[\text{Au}(\text{PMe}_3)]\text{BF}_4$ was generated by the reaction of $[\text{Au}(\text{Cl})(\text{PMe}_3)]$ with $\text{Ag}[\text{BF}_4]$ in CH_2Cl_2 and used without isolating it. The mass spectrum of the mixture shows a peak at $m/z = 635$ corresponding to the tetranuclear species $[\text{Au}_4(\text{SiBu})_2(\text{PMe}_3)_4]^{2+}$ and peaks at $m/z = 677$ and 719 relative to the dinuclear monocationic species $[\text{Au}_2(\text{SiBu})(\text{PMe}_3)(\text{PEt}_3)]^+$ and $[\text{Au}_2(\text{SiBu})(\text{PEt}_3)_2]^+$, respectively. Recalling that the tetranuclear core is maintained in solution only when the phosphane is relatively small,^[3,4] it seems that the presence of one PEt_3 ligand in the $[\text{Au}_2(\text{SiBu})(\text{PMe}_3)(\text{PEt}_3)]^+$ is sufficient to cause the compound to exist in the dinuclear form.

By increasing the amounts of $[\text{Au}(\text{SiBu})(\text{PEt}_3)]$, the intensity of the peaks corresponding to $[\text{Au}_2(\text{SiBu})(\text{PMe}_3)(\text{PEt}_3)]^+$ and $[\text{Au}_2(\text{SiBu})(\text{PEt}_3)_2]^+$ increases and, as a consequence, the intensity of the signal relative to $[\text{Au}_4(\text{SiBu})_2(\text{PMe}_3)_4]^{2+}$ decreases (Table S1).

In addition to these peaks there are signals at $m/z = 997$, 1039 and 1081 corresponding to phosphane trinuclear clusters of Au^I , already proposed for the reaction of **2a** with **1a**. The presence of these species, although in principle could be of some support for the involvement of such intermediates for all the reactions between **2** and **1**.

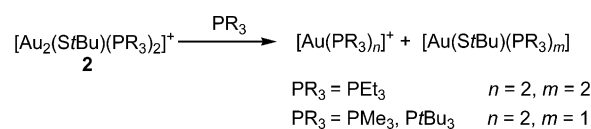
The spectroscopic behaviour is consistent with a dynamic situation involving **2a**, **2b** and the corresponding derivative containing two different phosphanes (at least in the hypothesis that the PEt_3 protons of the different species resonate at roughly the same frequency and that the PMe_3 signals are more sensitive to the environment) (Scheme 5).

By raising further the $[\text{Au}(\text{SiBu})(\text{PEt}_3)]/2\text{a}$ ratio there is no significant change in the NMR and mass spectra of the solution, thus supporting the idea that the molar ratio 2 has a special meaning in terms of the mechanistic requirements.

Conclusions

The results of this study show that the complexes **2** indeed react as a sort of $[\text{Au}(\text{phosphane})]^+$ fragment sup-

ported by $[\text{Au}(\text{SR})(\text{phosphane})]$ (**1**). The phosphane traps the $[\text{Au}(\text{phosphane})]^+$ moiety cleaving a gold–thiolato bond with concurrent loss of neutral **1**, while free and coordinated $[\text{Au}(\text{SR})(\text{phosphane})]$ exchange. However, the different combinations of **2** and phosphane may produce gold complexes that have different coordination numbers, as shown in Scheme 6 in the case of the monophosphane derivatives.

Scheme 6. General scheme for the reaction of **2** with monophosphanes.

The exchange reactions of **1** with complexes **2** may have in principle useful synthetic applications for the preparation of new derivatives **2**, by using $[\text{Au}(\text{SR})(\text{phosphane})]$ systems, different from the corresponding coordinated moiety in **1**.

Finally the reactivity does not seem to be influenced by the aggregation state of **2** in solution since, as we have shown in a previous paper, **2a**, **2b** and **2c** exist in solution as a dimer, a mixture of a dimer and monomer and a monomer, respectively.^[4]

Experimental Section

Chemicals: All manipulations and reactions were carried out under dinitrogen or argon by using standard techniques. All solvents were used without any further purifications. The following compounds were prepared according to literature procedures: $[\text{Au}(\text{SiBu})(\text{L})]$ ($\text{L} = \text{PMe}_3$, PEt_3 , PtBu_3 ; **1a**, **1b**, **1c**),^[3] $[\text{Au}_2(\text{SiBu})_2(\text{L}_2)]$ ($\text{L}_2 = \text{dppe}$; **1d**),^[4] $[\text{Au}_2(\text{SiBu})(\text{L}_2)][\text{BF}_4]$ ($\text{L} = \text{PMe}_3$, PEt_3 , PtBu_3 ; **2a**, **2b**, **2c**; $\text{L}_2 = \text{dppe}$; **2d**)^[4] and $[\text{Au}(\text{Cl})(\text{L})]$ ($\text{L} = \text{PMe}_3$, PEt_3 , PtBu_3).^[18]

Physical Measurements: ^1H and ^{31}P NMR spectra were recorded with a Varian Gemini 200 instrument, working at 200 MHz. Carbon and hydrogen elemental analyses were performed in the microanalysis laboratory of the Dipartimento di Scienze Farmaceutiche dell'Università di Pisa. Mass spectra were obtained from an Applied Biosystems-MDS Sciex API 4000 triple quadrupole mass spectrometer (Concord, Ont., Canada), equipped with a Turbo-V ionspray (TIS) source. The operative parameters used were as follows: ionspray voltage (IS), 5.0 kV; gas source 1 (GS1), 25; gas source 2 (GS2), 25; turbo temperature (TEM), 0 °C; entrance potential (EP), 10 V; declustering potential (DP), 20 V; scan range, $m/z = 300$ – 1500 . Each sample for MS (ESI) was prepared by a 1:100 dilution of a dichloromethane solution (5 mg/mL) of the target compound with methanol, and it was infused by a syringe

pump Harvard Mod. 22 (Harvard Apparatus, Holliston, MA, USA).

Reaction of [Au(Cl)(L)] with L (L = PMe₃, PEt₃, PrBu₃). Formation of [Au(Cl)(L)₂]: The complexes were prepared according to the procedure described in the literature.^[5a,6b] [Au(Cl)(PrBu₃)₂] has not been reported before.

[Au(Cl)(PrBu₃)₂]: White microcrystals were obtained from a dichloromethane solution. Yield: 0.370 g (85%). C₂₄H₅₄AuClP₂ (637.06): calcd. C 45.3, H 8.5; found C 45.7, H 8.6. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.60 (dd, ³J_{PH} = 7 Hz, PrBu₃) ppm. ³¹P NMR (200 MHz, CDCl₃, 25 °C): δ = 98.89 (s) ppm.

Reaction of [Au(Cl)(L)₂] (L = PMe₃, PEt₃, PrBu₃) with Ag[BF₄]. Formation of [Au(L)₂][BF₄] (L = 3a, 3b, 3c): All the complexes were prepared according to the same procedure adopted for the reaction of [Au(Cl)(PMe₃)₂] with Ag[BF₄], which is reported as an example. Ag[BF₄] (0.097 g, 0.5 mmol) was added to a solution of [Au(Cl)(PMe₃)₂] (0.100 g, 0.276 mmol) in dichloromethane (10 mL), and the mixture was stirred in the dark for 2 h. The precipitate of AgCl was removed by filtration. The solvent was then evaporated, and the solid residue was washed with pentane (2 × 10 mL), dried in vacuo and crystallized from dichloromethane as white microcrystals. Yield: 0.214 g (98%). C₆H₁₈AuBF₄P₂ (435.93): calcd. C 16.5, H 4.2; found C 16.7, H 4.1. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.66 (t, ²J_{PH} = 4.0 Hz, PMe₃) ppm. ³¹P NMR (200 MHz, CDCl₃, 25 °C): δ = 8.79 (s) ppm. MS (ESI+): *m/z* = 349 [Au(PMe₃)₂]⁺.

Complex 3b: Light-grey microcrystals were obtained from a dichloromethane solution. Yield: 0.253 g (97%). C₁₂H₃₀AuBF₄P₂ (520.09): calcd. C 27.7, H 5.8; found C 27.6, H 5.6. ¹H NMR (200 MHz, CD₂Cl₂, 25 °C): δ = 1.21 (br. m, 18 H, Me), 1.97 (br. m, 12 H, CH₂) ppm. ³¹P NMR (200 MHz, CD₂Cl₂, 25 °C): δ = 47.30 (s) ppm. MS (ESI+): *m/z* = 433 [Au(PEt₃)₂]⁺.

Complex 3c: Light-grey microcrystals were obtained from a dichloromethane solution. Yield: 0.340 g (99%). C₂₄H₅₄AuBF₄P₂ (688.41): calcd. C 41.9, H 7.9; found C 41.2, H 7.7. ¹H NMR (200 MHz, CD₂Cl₂, 25 °C): δ = 1.55 (dd, ³J_{PH} = 7.0 Hz, Me) ppm. ³¹P NMR (200 MHz, CD₂Cl₂, 25 °C): δ = 97.00 (s) ppm. MS (ESI+): *m/z* = 601 [Au(PrBu₃)₂]⁺.

Reaction of [Au₂(SrBu)(L)₂][BF₄] (L = PMe₃, PEt₃, PrBu₃, PPh₃; L₂ = dppe) with Phosphanes: The reaction of [Au₄(SrBu)₂(PMe₃)₄][BF₄]₂ (2a) with PMe₃ is described as an example. [Au₄(SrBu)₂(PMe₃)₄][BF₄]₂ (0.122 g, 0.168 mmol) was dissolved in dichloromethane (5 mL) and added to a toluene solution of trimethylphosphane (1 M, 0.17 mL, 0.17 mmol). After being stirred for ca. 1 h, the solution was added dropwise whilst stirring to pentane (100 mL), immediately giving a white solid. After stirring for 15 min, the solid was collected by filtration and dried. This was washed with pentane (2 × 5 mL), dried and identified as [Au(PMe₃)₂][BF₄] (3a). Yield: 70 mg (96%). ¹H NMR (CDCl₃): δ = 1.66 (br. s, 18 H, PMe₃) ppm. ³¹P NMR (CDCl₃): δ = 8.96 ppm. MS (ESI+): *m/z* (%) = 349 (100) [Au(PMe₃)₂]⁺. The pentane solution obtained after separation of 3a was concentrated to dryness in vacuo leaving a white solid. This was dissolved in pentane and crystallized by cooling the solution to –20 °C. White crystals of [Au(SrBu)(PMe₃)] (1a) were obtained. Yield: 50 mg (82%). ¹H NMR (C₆D₆): δ = 1.91 (s, 9 H, SrBu), 0.54 (d, *J*_{PH} = 9.9 Hz, 9 H, PMe) ppm. ³¹P NMR (C₆D₆): δ = 0.72 ppm. MS (ESI+): *m/z* (%) = 349 (45) [Au(PMe₃)₂]⁺, 363 (15) [Au(SrBu)(PMe₃) + H]⁺, 635 (100) [Au₄(SrBu)₂(PMe₃)₄]²⁺, 761 (15 not assigned), 921 (29) [Au₆(SrBu)₄(PMe₃)₄]²⁺.

Reaction of [Au₂(SrBu)(PEt₃)₂][BF₄] (2b) with PEt₃: [Au₂(SrBu)(PEt₃)₂][BF₄] (2b) (0.086 g, 0.107 mmol) was treated with PEt₃ in CH₂Cl₂ (0.89 M, 0.23 mL, 0.21 mmol) to give:

[Au(PEt₃)₂][BF₄] (3b): Off white crystals. Yield: 0.045 g (80%).

[Au(SrBu)(PEt₃)₂]: Colourless oil. Yield: 0.045 g (79%). ¹H NMR (C₆D₆): δ = 1.89 (s, 9 H, SrBu), 1.15 (dq, *J*_{PH} = 8, *J*_{H,H} = 7.7 Hz, 12 H, PCH₂), 0.75 (dt, *J*_{PH} = 17.6, *J*_{H,H} = 7.7 Hz, 18 H, PCMe) ppm. ³¹P NMR (C₆D₆): δ = 38.22 ppm. MS (ESI+): *m/z* (%) = 405 (17) [Au(SrBu)(PEt₃) + H]⁺, 433 (92) [Au(PEt₃)₂]⁺, 718 (100) [Au₂(SrBu)(PEt₃)₂]⁺, 1005 (37) [Au₃(SrBu)₂(PEt₃)₂]⁺.

Reaction of [Au₂(SrBu)(PrBu₃)₂][BF₄] (2c) with PrBu₃: [Au₂(SrBu)(PrBu₃)₂][BF₄] (2c) (0.165 g, 0.17 mmol) was treated in CH₂Cl₂ with PrBu₃ (0.082 mL, 0.34 mmol) to give:

[Au(PrBu₃)₂][BF₄] (3c): White crystals. Yield: 0.114 g (100%).

[Au(SrBu)(PrBu₃)] (1c): Colourless oil. Yield: 0.081 g (98%). ¹H NMR (C₆D₆): δ = 1.88 (s, 9 H, SrBu), 1.09 (d, *J*_{PH} = 13.2 Hz, 27 H, PrBu), 1–1.4 (br. m) ppm. ³¹P NMR (C₆D₆): δ = 91.44 (s), 96.13 (s), 63.22 (s), 62.55 (s), 61.57 (s) ppm. MS (ESI+): *m/z* (%) = 489 (24) [Au(SrBu)(PrBu₃) + H]⁺, 601 (68) [Au(PrBu₃)₂]⁺, 887 (100) [Au₂(SrBu)(PrBu₃)₂]⁺.

Reaction of [Au₂(SrBu)(dppe)][BF₄] (2d) with dppe: [Au₂(SrBu)(dppe)][BF₄] (2d) (0.065 g, 0.067 mmol) was treated with dppe (40.1 mg, 0.10 mmol) to give:

[Au(dppe)₂][BF₄]: White crystals. Yield: 0.070 g (97%). ¹H NMR (CD₂Cl₂): δ = 2.44 (br. s, 8 H, PCH₂), 7.0–7.4 (br. m, 40 H, PPh) ppm. ³¹P NMR (CD₂Cl₂): δ = 21.96 ppm. MS (ESI+): *m/z* (%) = 993 (100) [Au(dppe)₂]⁺.

[Au₂(SrBu)₂(dppe)] (1d): Colourless oil. Yield: 0.063 g (97%). ¹H NMR (C₆D₆): δ = 1.91 (s, 18 H, SrBu), 2.51 (br. s, 4 H, PCH₂), 6.8–7.5 (br. m, 20 H, PPh₂) ppm. ³¹P NMR (C₆D₆): δ = 30.29 ppm. MS (ESI+): *m/z* (%) = 881 (100) [Au₄(SrBu)₂(dppe)]²⁺, 993 (25) [Au₂(SrBu)₂(dppe) + Na]⁺, 1024 (58) [Au₅(SrBu)₃(dppe)]²⁺, 1167 (25) [Au₃(SrBu)₂(dppe)]⁺.

Reaction of [Au₂(SrBu)(L)₂][BF₄] (L = PMe₃, PEt₃, PrBu₃, PPh₃) with [Au(SrBu)(L)]: The reaction of [Au₄(SrBu)₂(PMe₃)₄][BF₄]₂ (2a) with [Au(SrBu)(PMe₃)] (1a) is reported as an example. A solution of 2a (0.008 g, 11.0 × 10^{–3} mmol) in CD₂Cl₂ (1 mL) was placed in an NMR tube and ¹H NMR, ³¹P NMR and mass spectra were recorded. The desired amount of [Au(SrBu)(PMe₃)] (1a) was then added, and, after dissolution of the solid, the resulting solution was left for 1 h to reach equilibrium. This solution was then re-examined by ¹H NMR and ³¹P NMR spectroscopic and MS analyses.

Preparation of [Au₂(SrBu)(PMe₃)(PEt₃)] [BF₄]: A solution of Ag[BF₄] (0.097 g, 0.50 mmol) in ethanol (5 mL) was added slowly at 0 °C in the darkness to [Au(Cl)(PMe₃)] (0.145 g, 0.50 mmol) in CH₂Cl₂ (5 mL). The solution was stirred in the darkness for a further 30 min and was then filtered through Celite and dried. The residue was dissolved in CH₂Cl₂ (5 mL), and the solution was added dropwise into a solution of CH₂Cl₂ (5 mL) containing [Au(SrBu)(PEt₃)] (1b) (0.202 g, 0.50 mmol) in the darkness whilst stirring. The stirring was continued for 30 min, after which the solution was concentrated to ca. 3 mL, and pentane was added, layer on layer. A light sensitive solid was obtained, which was washed with pentane (3 × 3 mL), and the solvent was removed in vacuo. Yield: 0.29 g (72%). ¹H NMR (200 MHz, CD₂Cl₂, 25 °C): δ = 1.58 (s, 18 H, SrBu), 1.66 (d, *J*_{PH} = 11.0 Hz, 18 H, PMe₃), 1.95 (dq, *J*_{PH} = 9.5, *J*_{H,H} = 7.7 Hz, 12 H, PCH₂Me), 1.23 (dt, *J*_{PH} = 19.0, *J*_{H,H} = 7.7 Hz, 18 H, PCH₂Me) ppm. ³¹P NMR (CD₂Cl₂, 25 °C): δ = 38.07 (s), –1.96 (s) ppm. MS (ESI+): *m/z* (%) = 349 (71) [Au(PMe₃)₂]⁺, 391 (50) [Au(PMe₃)(PEt₃)]⁺, 433 (26) [Au-

(PEt₃)₂]⁺, 635 (58) [Au₄(S_tBu)₂(PMe₃)₄]²⁺, 677 (100) [Au₂(S_tBu)-(PMe₃)(PEt₃)]⁺, 719 (71) [Au(S_tBu)(PEt₃)₂]⁺. C₁₃H₃₃Au₂BF₄P₂S (764.15): calcd. C 20.4, H 4.4; found C 20.1, H 4.1.

Supporting Information (see footnote on the first page of this article): Additional figure showing the VT NMR spectra for the reaction between [Au(PEt₃)₂][S_tBu] and [Au(S_tBu)(PEt₃)₂] and table reporting the MS (ESI) data of the solutions containing [Au₄(S_tBu)₂-(PMe₃)₄][BF₄]₂ and [Au(S_tBu)(PEt₃)].

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