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Cationic Gold(I) Phosphanyl Thiolates: Aurophilic Interactions in the Solid State and in Solution

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The aggregation states in solution of gold(I) cationic complexes of the formula $[Au_2(StBu)(L_2)][BF_4]$ (L = PMe_3, PEt_3, $PtBu_3$, PPh_3; L_2 = dppm, dppe) were studied by MS (ESI) and DOSY spectroscopy. These compounds are tetranuclear in the solid state with a core of four gold centres bound together by aurophilic interactions and bridging thiolato groups. Some of these tetranuclear systems are maintained intact in solution depending on the phosphane steric properties or denticity.

Introduction

It is well known that many gold(I) complexes in the solid state adopt structures in which polynuclear systems are stabilized by the presence of relatively short Au···Au distances (aurophilic interactions).[1] In particular, cationic gold(I) phosphanyl thiolates $[Au_2(SR)(L_2)][BF_4]$ (L = phosphane), prepared by Bruce and coworkers by chemical oxidation of the corresponding neutral phosphanyl thiolates [Au(SR)(L)], exist in the solid state as oligomers; most of these structures have a core of four gold atoms associated by aurophilic interactions.[2] It is not clear if such structures survive in solution or are cleaved to give dinuclear species (there is no conclusive evidence on this point in the literature) (Figure 1). We recently prepared a series of related compounds with the formula $[Au_2(SR)(L_2)][BF_4]$ (R = CMe_3, CH_2CMe_3, CH_2CHMe_2, CPh_3; L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) and $[Au_2(SR)(dppe)][BF_4]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane] by following the synthetic strategy of Bruce.[3] In the solid state, the aurophilic interactions build up a structure of four gold atoms with pairs of atoms bound by bridging thiolato ligands, which, at least in the cases studied by X-ray analysis, are generally arranged in an almost perfect square or in an unprecedented zig–zag sequence in the case of $[Au_2(StBu)(dppe)][BF_4]$. The correct formulation for these complexes in the solid state is therefore $[Au_4(SR)_2(L_4)][BF_4]_2$.

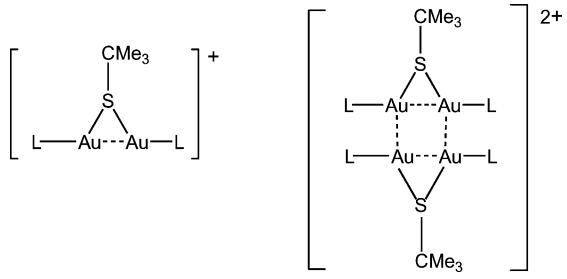

Figure 1. Di- and tetranuclear structural formulae of **2**.

It would be certainly important for a better understanding of the properties and the reactivities of these systems to establish whether the aurophilic interactions unsupported by bridging thiolato groups exist only in the solid state or may survive in the presence of a solvent. Indeed, because of the low energy of such interactions (5–15 kcal mol^{-1}),[2e] an equilibrium dimer/monomer can be postulated, which is possibly influenced by the nature of the solvent (polarity, chemical affinity for the metal centre, etc.) and/or the nature of the phosphane and/or thiolato ligands.

In the literature there is only a limited number of studies estimating the presence of aurophilic interactions in solution, and most of them concern Au^I–Au^I intramolecular contacts often assisted by the presence of a bidentate phosphane.[4] In these cases, the authors demonstrated the partial survival of the Au–Au bonding interactions by using ^1H and ^{31}P VT NMR, UV/Vis and EXAFS spectroscopy. There are a few scattered reports also for the study of the intermolecular interactions in solution: the complexes $[Au_2(dppm)(CH_2)_2S(O)NMe_2][BF_4]$ [dppm = 1,1-bis(diphenylphosphanyl)methane], $[Au_2(dmpm)(CH_2)_2S(O)$-

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$NMe_2][BF_4]$ [dmpm = 1,1-bis(dimethylphenylphosphanyl)-methane][5] and $\{[(PPh_3)Au]_2Cl\}[SbF_6]$,[6] all of which crystallize as dimers because of the formation of two Au^I–Au^I intermolecular bonds, were shown by electronic spectroscopy to maintain at least in part their dimeric structure. Recently, diphosphane gold complexes with Au–Au contacts were studied by EXAFS spectroscopy.[4a]

In consideration of the above, to obtain information on the aggregation state in dissolved cationic phosphanyl thiolates, we began a study of the homogeneous series of gold(I) derivatives with the formula $[Au_2(StBu)(L_2)][BF_4]$ (L = PMe_3 **2a**, PEt_3 **2b**, $PtBu_3$ **2c**, PPh_3 **2d**; L_2 = dppm **2e**, dppe **2f**) by using MS (ESI) and DOSY (Diffusion Ordered SpectroscopY). MS (ESI) was recently used for the characterization of supramolecular organometallic assemblies.[7] DOSY NMR techniques, although very promising,[8a,8b] have not attracted much attention so far[8c,8d] for applications in organometallic and inorganic chemistry in solution. Here we report some conclusions obtained during these studies.

Results and Discussion

Synthesis

Complexes **2a**–**f** were all prepared by chemical oxidation of corresponding thiolates **1a**–**f** with $[FeCp_2]BF_4$. Compounds **1b**,**c**, **1e**, **2b**,**c** and **2e** have not been reported before, and their preparation and characterization can be found in the Experimental Section. The X-ray structures of **2d**[9] and **2f**[3b] are reported in the literature; for the other thiolates with monodentate phosphanes we assume that they exist in the solid state in the usual four-membered square planar arrangement.

Mass Spectrometry Studies

The analyses were carried out in methanol solution. As explained above, the gold(I) complexes here investigated may exist in solution as monocationic dinuclear species and/or as dicationic tetranuclear species. The analysis of the isotopic cluster of the molecular ion is crucial to assess the cationic charge: in fact the $[Au_4(StBu)_2(PR_3)_4]^{2+}$ ion, in addition to the peak corresponding to m/z = M/2, presents other minor peaks at m/z = M/2 + n/2 (n = 1, 2, 3, etc.) due to the minor isotopes of carbon, sulfur and hydrogen), whereas $[Au_2(StBu)(PR_3)_2]^+$ shows signals at M/2+n (n = 0, 1, 2, 3, etc.). Figures 2–6 report the MS (ESI) spectrum of each complex with the corresponding attributions and the enlargement of the isotopic cluster of the molecular ion.

In the case of **2a**, the isotopic cluster (Figure 2b) is rather resolved and allows us to conclude that the dicationic tetranuclear structure observed in the solid state is largely maintained in solution. The MS–MS spectrum of the molecular ion does not give further information on the aggregation state. However it is interesting to note that, under more severe experimental conditions [declustering potential (*DP*) at 120 V], the isotopic cluster of the molecular peak reveals that the dinuclear species arose at the expense of the tetranuclear species (Figure 2c). The Au_6 species responsible for the peak at m/z = 921 most probably formed in the ionization step.

In the case of **2b**, the isotopic cluster is poorly resolved (Figure 3b). It is therefore difficult to draw specific conclusions, but in consideration of the NMR spectroscopic results (vide infra) we suggest that only the dinuclear specie is present in solution. The m/z = 1005 peak may be derived from the aggregation of the dinuclear species during the ionization process. The MS–MS spectrum does not give any additional evidence.

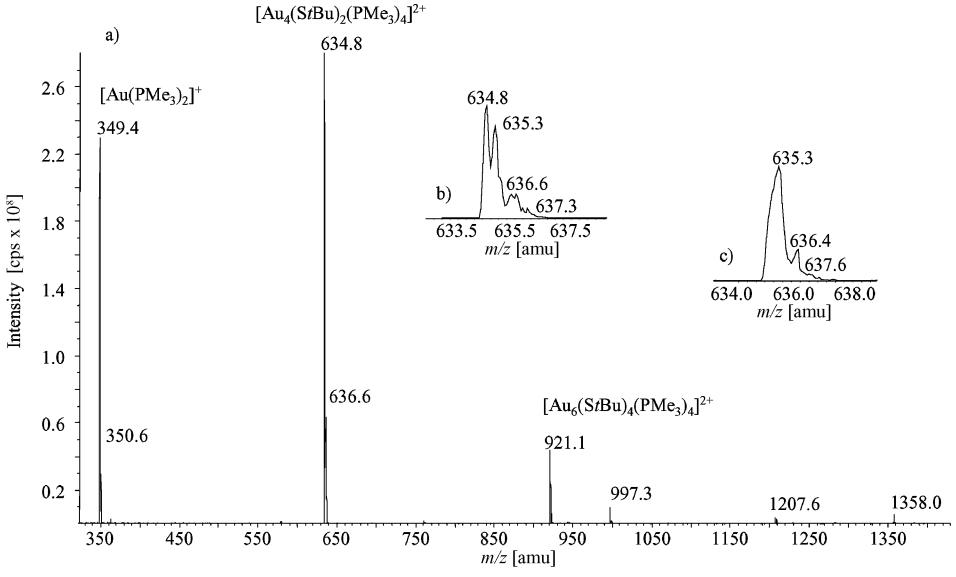

Figure 2. a) MS (ESI+) of **2a**; b) enlargement of the isotopic cluster at m/z = 635 at *DP* = 20 V and c) at *DP* = 120 V.

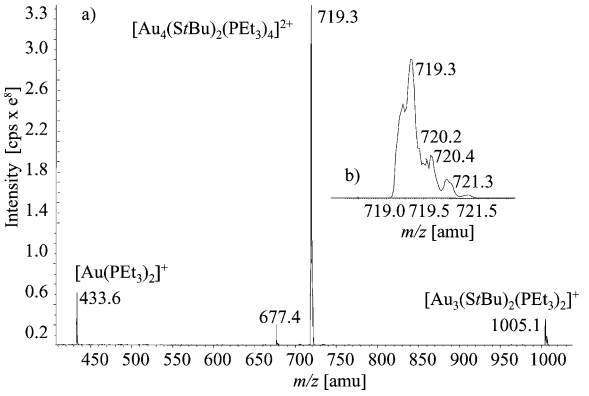

Figure 3. a) MS (ESI+) of **2b**; b) enlargement of the isotopic cluster at *m*/*z* = 719.3.

Alternatively, the mass spectrum recorded for **2c** shows a fairly well-resolved isotopic cluster (Figure 4b), which indicates that only the monocharged dinuclear species is present. The peak at *m*/*z* = 1174 is due to an adduct probably formed during the ionization process.

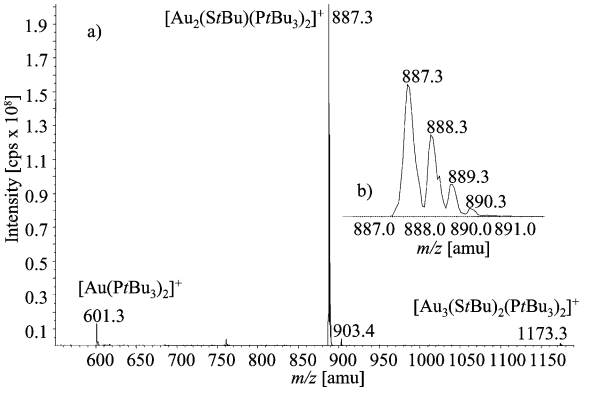

Figure 4. a) MS (ESI+) of **2c**; b) enlargement of the isotopic cluster at *m*/*z* = 887.3.

Similar conclusions can be drawn for **2d** from the analysis of its mass spectrum (Figure 5).

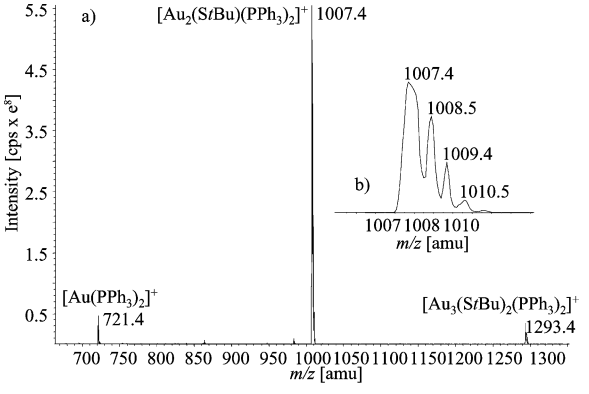

Figure 5. a) MS (ESI+) of **2d**; b) enlargement of the isotopic cluster at *m*/*z* = 1007.4.

Finally, complexes **2e**,**f** containing diphosphanes are present in solution as tetranuclear dications, as was predictable because the diphosphane holds the two dinuclear units firmly together. In the particular case of **2f**, the isotopic cluster is poorly resolved (Figure 6b) and the MS–MS spectrum of the ion at *m*/*z* = 881 shows a small peak at *m*/*z* = 1167 (Figure 6c). Because a species with more gold atoms than the precursor ion is unlikely to form on fragmentation, the presence of a fragment ion at greater *m*/*z* values confirms the tetranuclear nature of **2f**.

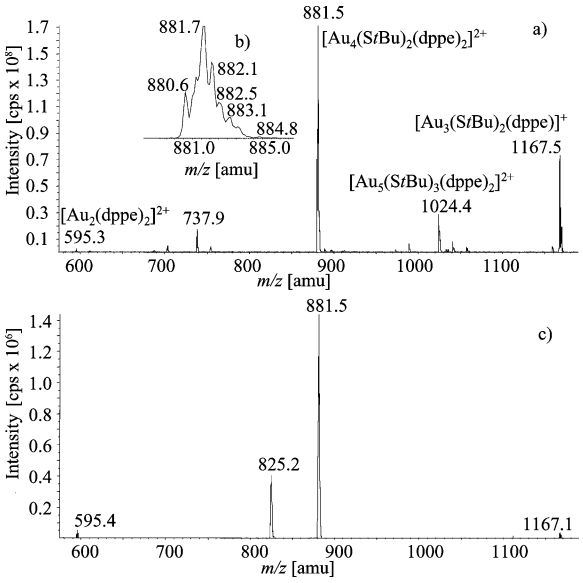

Figure 6. a) MS (ESI+) of **2f**; b) enlargement of the isotopic cluster at *m*/*z* = 881.7; c) MS–MS spectrum of the ion at *m*/*z* = 881.

From these data it is clear that the ability of **2a**–**2d** to maintain totally or partially the aurophilic interactions in solution seems to depend largely on the steric hindrance of the phosphane (then on its cone angle, which is in the order $PMe_3 < PEt_3 < PPh_3 < PtBu_3$).[10] In the case of **2e** and **2f** it is the chelating phosphane, in addition to the thiolato ligand, that binds together the four gold atoms, independently of the survival of the aurophilic interactions.

NMR Spectroscopy

The average diffusion coefficients can be related to hydrodynamic radii r_H by means of the Stokes–Einstein equation [Equation (1)].

$$D = \frac{kT}{c\pi\eta r_H} \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, η the viscosity and c is a numerical factor, which usually approximates to 6 for large-size molecules.

A more accurate estimation of hydrodynamic radius r'_H can be obtained[11] by Equation (2), where the c factor is expressed as a function of the solvent-to-solute ratio of ra-

dii on the basis of the model proposed by Wirtz and coworkers[12] and where r_{solv} is the van der Waals radius of the solvent.

$$D = \frac{kT\left[1+0.695\left(\frac{r_{solv}}{r_H'}\right)^{2.234}\right]}{6\pi\eta r_H'} \quad (2)$$

Valentini et al.[13] used DOSY measurements to determine the diffusion coefficients of some iron and palladium compounds, whose structures in the solid state were known. They obtained the hydrodynamic radii by using the Stokes–Einstein equation and compared these results to the radii of greatest steric hindrance obtained from crystallographic parameters, r_R (rotating the molecule around its geometric centre), and they found very good consistency. The technique was also exploited for the characterization of intermediates in organometallic reactions involving copper,[14] ruthenium,[15] platinum[8b] and zirconium[16] complexes. Finally, some papers report the use of this methodology to study the aggregation state in solution of organolithium[17] and ruthenium complexes.[8c,11]

Several correction factors[17b,18] for the equation, both semiempirical and theoretical have been proposed, by taking into account the dimensions and the nonspherical form of the particle, concentration and so on, but they have been used only rarely as an internal standard is preferred. Some authors[8,19] suggested the use of tetramethylsilane (TMS) as an internal standard to avoid the problems derived from the change in the viscosity due to the variation of the concentration after the addition of the solute to be analyzed and from the temperature.

The spectra were generally performed in deuterated dichloromethane, but in some cases also in methanol and acetone in order to study the influence of the solvent. As the internal standard for viscosity we adopted TMS and all diffusion coefficients were corrected with respect to it.

To test the reliability of the method, our preliminary study was directed towards thiolato phosphanyl compounds **1a**–**f**, as there is no evidence of aurophilic interactions in the solid state and presumably all the more so in solution (Table 1).

Table 1. D ($\times 10^{10}$ m^{2}s^{-1}) and r [Å] values for **1a**–**f** in CD_2Cl_2 at 298 K.

	D	r_H[a]	r'_H[b]	r[c]	r[d]
[Au(S*t*Bu)(PMe$_3$)] (**1a**)	14.6	3.4	4.2	4.8	4.8
[Au(S*t*Bu)(PEt$_3$)] (**1b**)	12.6	4.0	4.7	5.4	5.1
[Au(S*t*Bu)(P*t*Bu$_3$)] (**1c**)	12.2	4.1	4.8	5.5	5.2
[Au(S*t*Bu)(PPh$_3$)] (**1d**)	10.4	4.9	5.4	6.1	6.2
[Au$_2$(S*t*Bu)$_2$(dppm)] (**1e**)	7.3	7.0	7.4	–	6.8
[Au$_2$(S*t*Bu)$_2$(dppe)] (**1f**)	7.2	7.0	7.4	7.4[e]	–

[a] Calculated by using Equation (1), c = 6, T = 298 K, η (CD_2Cl_2, 298 K) = 0.433×10^{-3} kg m^{-1} s^{-1}. [b] Calculated by using Equation (2). [c] Calculated from X-ray structure data. [d] Calculated from the minimized gas-phase structure (PM3/AM1). [e] See ref.[3]

The values of the hydrodynamic radii, calculated by employing Equation (1) with c = 6, were all lower with respect to those obtained from X-ray or PM3 calculations. In the case of **1f**, which is known to be stable in solution as dissociative processes are unlikely, excellent agreement was obtained by the introduction of the Wirtz correction [Equation (2), Table 1), that is, by considering the solvent-to-solute ratio of the radii. However, the corrected hydrodynamic radii of neutral monophosphane derivatives **1a**–**d** were also slightly lower, which suggests a dissociative equilibrium. Actually, like traditional NMR measurements, DOSY techniques, in the presence of rapid exchange, show only one peak resulting from the weighted average of the signals of each species involved. Because it is well known that gold(I) compounds are often involved in rapid phosphane exchange reactions,[20] it is probable that this is the reason for the observed discrepancy between the observed and calculated radii.

We then proceeded with the NMR investigation of the series of cationic clusters **2a**–**f**. X-ray structures in the solid state are known only for [Au$_4$(S*t*Bu)$_2$(dppe)$_2$][BF$_4$]$_2$[3] (which we assume remains tetranuclear in solution) and for [Au$_4$(S*t*Bu)$_2$(PPh$_3$)$_4$][BF$_4$]$_2$;[10] for the other complexes we used data from published structures of similar model compounds or alternatively we performed PM3 calculations using the ArgusLab program.[21] As the only limitation we assumed that the S–Au–P angle had to be as close as possible to 180°. Analysis of the models of **2a**–**d** shows that the radii of greatest steric hindrance of the di- and tetranuclear species do not differ too much (ca 1 or 2 Å), as the only difference in size between the two species is in the third dimension with the assumption that the other two remain roughly constant. In spite of that, the NMR spectroscopic results shown in Table 2 are fairly consistent and point to the same conclusions reached by MS (ESI) spectrometry: the corrected hydrodynamic radius of **2a** is consistent with a tetranuclear species, whereas for **2b** it is intermediate between that of the dinuclear and the tetranuclear species, which indicates that both structures are present in solution (probably involved in rapid equilibrium).

For dppm and dppe derivatives **2e**,**f**, as expected, the radii are nicely consistent with those predicted for the tetranuclear species. Complexes **2c**,**d** gave, in contrast, even smaller r'_H values than those predicted for the dinuclear species from the X-ray structure data, so they probably undergo some dissociation of the phosphane (as is likely from the literature concerning phosphane gold(I) phosphanyl derivatives and from basicity considerations in particular) or even further disruption of the remaining Au–Au interactions.

Finally, to acquire information on the influence of the solvent on the equilibrium involving di- and tetranuclear species, we made some measurements in deuterated methanol and acetone for comparison with the results obtained in dichloromethane. We chose to study triethylphosphane derivative **2b**, which, as reported above, was found to exist as a mixture of the di- and tetranuclear species, and dppe complex **2f** for comparison (Table 3).

The results for complex **2b** in acetone are fairly consistent with a dinuclear monocation formulation, which most probably means that the equilibrium observed in dichloro-

Table 2. D ($\times 10^{10}$ m^{2}s^{-1}) and r [Å] for **2a**–**f** in CD_2Cl_2 at 298 K.

	D	r_H[a]	r'_H[b]	r[c] Au_2	r[c] Au_4	r[d] Au_2	r[d] Au_4	Aggregation degree
$[Au_2(StBu)(PMe_3)_2][BF_4]$ (**2a**)	8.7	5.8	6.3	4.8	6.0	4.8	5.9	tetranuclear
$[Au_2(StBu)(PEt_3)_2][BF_4]$ (**2b**)	9.3	5.5	6.0	5.4	7.3	5.7	7.2	di- and tetranuclear
$[Au_2(StBu)(PtBu_3)_2][BF_4]$ (**2c**)	9.1	5.6	6.1	6.8	7.9	6.8	7.8	dinuclear
$[Au_2(StBu)(PPh_3)_2][BF_4]$ (**2d**)	7.6	6.7	7.1	8.1[e]	9.1[e]	8.4	8.9	dinuclear
$[Au_2(StBu)(dppm)][BF_4]$ (**2e**)	6.1	8.3	8.6	–	8.4	–	8.6	tetranuclear
$[Au_2(StBu)(dppe)][BF_4]$ (**2f**)	6.1	8.2	8.6	–	9.1	–	–	tetranuclear

[a] Calculated by using Equation (1), $c = 6$, η (CD_2Cl_2, 298 K) = 0.433×10^{-3} kg m^{-1} s^{-1}. [b] Calculated by using Equation (2). [c] Calculated from X-ray structure data under the assumption of a spherical shape. [d] Calculated from the minimized gas-phase structure (PM3). [e] See ref.[9]

Table 3. D ($\times 10^{10}$ m^{2}s^{-1}) and r_H [Å] values for **2b** and **2f** in $(CD_3)_2CO$ and CD_3OD.

	Solvent	D	r_H[a]	r'_H[b]	r Au_2[c]	r Au_4[d]
$[Au_2(StBu)(dppe)][BF_4]$ (**2f**)	$(CD_3)_2CO$	8.1	8.9	9.2		9.1
$[Au_2(StBu)(dppe)][BF_4]$ (**2f**)	CD_3OD	5.1	7.9	8.1		9.1
$[Au_2(StBu)(PEt_3)_2][BF_4]$ (**2b**)	$(CD_3)_2CO$	14.7	4.9	5.4	5.4–5.7	
$[Au_2(StBu)(PEt_3)_2][BF_4]$ (**2b**)	CD_3OD	9.1	4.4	4.8	5.4–5.7	

[a] Calculated by using Equation (1), $c = 6$, $T = 298$ K, η_{MeOH} (298 K) = 0.544×10^{-3} kg m^{-1} s^{-1}, $\eta_{acetone}$ (298 K) = 0.306×10^{-3} kg m^{-1} s^{-1}. [b] Calculated by using Equation (2). [c] Calculated from the minimized gas-phase structure (PM3). [d] From X-ray data.[21]

methane is completely shifted towards the rupture of the unsupported aurophilic bonds. In methanol, **2b** shows a hydrodynamic radius that is even lower with respect to that expected for a dinuclear species; thus, some other dissociative process favoured by the polar protic solvent can be invoked. Actually, methanol seems to promote other dissociative processes even in the case of complex **2f**, which, however, maintains its tetranuclear structure in acetone as in dichloromethane.

Conclusions

Table 4 shows our conclusions on the aggregation state of the cationic gold complexes $[Au_2(StBu)(L_2)][BF_4]$ (**2a**–**2f**) on the basis of MS and NMR experiments.

Table 4. Evaluation of the degree of aggregation of **2a**–**f** in solution by MS (ESI) and DOSY techniques.

Complex	MS (MeOH)	DOSY (CD_2Cl_2)	Phosphane cone angle [°]
2a	tetranuclear	tetranuclear	118
2b	dinuclear	di- and tetranuclear	132
2c	dinuclear	dinuclear	182
2d	dinuclear	dinuclear	145
2e	tetranuclear	tetranuclear	–
2f	tetranuclear	tetranuclear	–

In spite of the fact that DOSY spectroscopy and MS (ESI) are performed under rather different conditions (concentration, solvent, etc.), the results are on the whole highly consistent. The main conclusion is that some of the complexes of **2** exist in a tetranuclear form even in dilute solutions, which shows that aurophilic interactions, although not as strong as covalent bonds, are able to maintain the solid state architecture even in solution. Another conclusion seems to be that the survival in solution of the aurophilic interactions depends upon the steric hindrance of the phosphane, because the greater the cone angle, the greater the repulsion between the two monocharged unities connected by aurophilic interactions, and, as a consequence, the dinuclear is preferred to the tetranuclear structure. Moreover, apart from diphosphane derivatives **2e**,**f**, the aurophilic interactions are maintained (at least partially) only when relatively small ligands (trimethyl- and triethylphosphane) are present. Obviously the solvent plays an important role: the polarity and the affinity for gold may determine the aggregation state, as shown by triethylphosphane derivative **2b**, which completely loses its tetranuclear structure in a polar solvent like acetone and methanol, whereas it maintains the dimeric structure in part in the less-polar solvent dichloromethane.

Finally, this work, in addition to the existing literature, shows that NMR and MS techniques may be very useful in the assessment of the degree of aggregation in solution of coordination systems, and they can provide better understanding of the reactivity of species that may exist in a supramolecular aggregation.

Experimental Section

Chemicals: All manipulations and reactions were carried out under an atmosphere of nitrogen or argon by using standard techniques. All solvents were used without any further purification. $[Au(SCMe_3)]_n$ was prepared according to the literature.[22]

Physical Measurements: ^{1}H and ^{31}P NMR spectra were recorded with a Varian Gemini 200 instrument working at 200 MHz. DOSY experiments were performed with a Varian INOVA600 spectrometer operating at 600 MHz for ^{1}H by using a 5 mm broadband inverse probe with z axis gradient; and the sample temperature was maintained at 25 °C. They were carried out by using a stimulated echo sequence with self-compensating gradient schemes, a spectral width of 8000 Hz and 64 K data points. Typically, a value of 100 ms was used for Δ, 1.0 ms for δ and g was varied in 30 steps (16 transients each) to obtain an approximately 90–95% decrease in the resonance intensity at the largest gradient amplitudes. The base-

lines of all arrayed spectra were corrected prior to processing the data. After data acquisition, each FID was apodized with 1.0 Hz line broadening and Fourier transformed. The data were processed with the DOSY macro (involving the determination of the resonance heights of all the signals above a preestablished threshold and the fitting of the decay curve for each resonance to a Gaussian function) to obtain pseudo-two-dimensional spectra with NMR chemical shifts along one axis and calculated diffusion coefficients along the other. Centesimal analysis were carried out in the microanalysis laboratory of Dipartimento di Scienze Farmaceutiche dell'Università di Pisa. The mass spectra were obtained with an Applied Biosystems-MDS Sciex API 4000 triple quadrupole mass spectrometer (Concord, ON, Canada), equipped with Turbo-V Ion-Spray (TIS) source. The operative parameters are as follows: ion-spray 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, 300–1500 *m*/*z*. MS–MS product ions were produced by collision-induced dissociation (CID) of selected precursor ions in the LINAC collision cell (Q2) and mass-analyzed in the second mass filter (Q3). Additional experimental conditions for MS–MS product ions spectra included: collision (CAD) gas, nitrogen; CAD gas pressure, 4 m Pa; collision energy (CE), ramp from 5 to 130 eV (step = 2); collision cell exit potential (CXP), 15 V. Each sample for MS (ESI) was prepared diluting 1:100 with methanol a 5 mg mL^{-1} dichloromethane solution of the target compound and was infused by a syringe pump Harvard Mod. 22 (Harvard Apparatus, Holliston, MA, USA). Melting points were obtained by using a Mel Temp II (Laboratory Devices, USA) equipped with a mercury thermometer as detector of the temperature.

Reaction of [Au(S*t*Bu)]$_n$ with L (L = PMe$_3$, PEt$_3$, P*t*Bu$_3$, PPh$_3$). Formation of [Au(S*t*Bu)(L)] (1a–d): The complexes were all prepared according to the literature method.[3] Compounds **1b**,**c** have not been described before.

Complex 1a: MS (ESI+): *m*/*z* (%) = 349 (45) $[Au(PMe_3)_2]^+$, 363 (15) $[Au(StBu)(PMe_3) + H]^+$, 635 (100) $[Au_4(StBu)_2(PMe_3)_4]^{2+}$, 761 (15) not assigned, 921 (29) $[Au_3(StBu)_2(PMe_3)_2]^+$, 997 (15) $[Au_3(StBu)_2(PMe_3)_3]^+$.

Complex 1b: Small silver flakes from pentane solution. Yield: 0.153 g (80%). M.p. 43 °C. ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 1.19 (dt, $^2J_{P,H}$ = 18.3 Hz, $^3J_{H,H}$ = 7.7 Hz, 6 H, PCH_2), 1.45 (s, 9 H, $SCMe_3$), 1.83 (dq, $^3J_{P,H}$ = 9.3 Hz, $^3J_{H,H}$ = 7.7 Hz, 9 H, $PCCH_3$) ppm. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.63 (dt, $^2J_{P,H}$ = 18.3 Hz, $^3J_{H,H}$ = 7.7 Hz, 9 H, PCH_2), 0.90 (dq, $^3J_{P,H}$ = 9.3 Hz, $^3J_{H,H}$ = 7.7 Hz, 6 H, $PCCH_3$), 1.93 (s, 9 H, $SCMe_3$) ppm. ^{31}P NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 38.64 (s) ppm. ^{31}P NMR (200 MHz, C_6D_6, 25 °C): δ = 38.36 (s) ppm. $C_{10}H_{24}AuPS$ (404.31): calcd. C 29.71, H 5.98; found C 29.77, H 5.92.

Complex 1c: White microcrystals from toluene/pentane solution. Yield: 1.040 g (70%). M.p. 154 °C. ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 1.46 (s, 9 H, $SCMe_3$), 1.51 (d, $^3J_{P,H}$ = 13.2 Hz, 27 H, $PCMe_3$) ppm. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 1.93 (s, 9 H, $SCMe_3$), 1.07 (d, $^3J_{P,H}$ = 13.2 Hz, 27 H, $PCMe_3$) ppm. ^{31}P NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 92.58 (s) ppm. ^{31}P NMR (200 MHz, C_6D_6, 25 °C): δ = 91.46 (s) ppm. MS (ESI+): *m*/*z* (%) = 361 (15) not assigned, 489 (62) $[Au(StBu)(PtBu_3)_4 + H]^+$, 512 (16) $[Au(StBu)(PtBu_3)_4 + Na]^+$, 548 (27) not assigned, 887 (100) $[Au_2(StBu)(PtBu_3)_2]^+$. $C_{16}H_{36}AuPS$ (488.47): calcd. C 39.34, H 7.43; found C 39.12, H 7.38.

Reaction of [Au(S*t*Bu)]$_n$ with L$_2$ (L$_2$ = dppm, dppe). Formation of [Au$_2$(S*t*Bu)$_2$(L$_2$)] (1e,f): Complexes **1f**,**e** were prepared according to a literature procedure described for **1f**.[3]

Complex 1e: Pale yellow microcrystals from toluene/pentane solution. Yield: 0.444 g (93%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.52 (s, 18 H, $SCMe_3$), 2.38 (s, 2 H, PCH_2), 7.2–7.8 (br. m, 20 H, PPh_2) ppm. ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 1.46 (s, 18 H, $SCMe_3$), 3.62 (s, 2 H, PCH_2), 7.3–7.8 (br. m, 20 H, PPh_2) ppm. ^{31}P NMR (200 MHz, $CDCl_3$, 25 °C): δ = 30.11 (s), 28.27 (s) ppm. $C_{33}H_{40}Au_2P_2S_2$ (956.69): calcd. C 41.43, H 4.21; found C 41.40, H 4.16.

Complex 1f: MS (ESI+): *m*/*z* (%) = 881 $[Au_4(StBu)_2(dppe)_2]^{++}$ (100%), 993 $[Au_2(StBu)_2(dppe) + Na]^+$ (25), 1024 $[Au_5(StBu)_3(dppe)_2]^{++}$ (58), 1033 (not assigned, 23), 1167 $[Au_3(StBu)_2(dppe)]^+$ (25).

Reaction of [Au(S*t*Bu)(L)] (L = PMe$_3$, PEt$_3$, P*t*Bu$_3$, PPh$_3$) with [FeCp$_2$][BF$_4$]. Formation of [Au$_2$(S*t*Bu)(L$_2$)][BF$_4$] (2a–d): All complexes were prepared according to the literature.[3]

Complex 2a: MS (ESI+): *m*/*z* (%) = 349 (85) $[Au(PMe_3)_2]^+$, 635 (100) $[Au_4(StBu)_2(PMe_3)_4]^{2+}$, 921 (14) $[Au_6(StBu)_4(PMe_3)_4]^{2+}$. MS–MS 635: *m*/*z* (%)= 273 (65) $[Au(PMe_3)]^+$, 349 (62) $[Au(PMe_3)_2]^+$, 579 (100) $[Au_4(SH)_2(PMe_3)_4]^{2+}$ or $[Au_2(SH)(PMe_3)_2]^+$, 635 (30) $[Au_4(StBu)_2(PMe_3)_4]^{2+}$.

Complex 2b: White microcrystals from dichloromethane solution. Yield: 0.157 g (71%). ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 1.59 (s, 18 H, $SCMe_3$), 1.23 (dt, $^2J_{P,H}$ = 19.1 Hz, $^3J_{H,H}$ = 7.7 Hz, 24 H, PCH_2), 1.94 (dq, $^3J_{P,H}$ = 9.9 Hz, $^3J_{H,H}$ = 7.7 Hz, 36 H, $PCCH_3$) ppm. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 1.55 (s, 18 H, $SCMe_3$), 0.88 (dt, $^2J_{P,H}$ = 19.1 Hz, $^3J_{H,H}$ = 7.7 Hz, 24 H, PCH_2), 1.61 (dq, $^3J_{P,H}$ = 9.9 Hz, $^3J_{H,H}$ = 7.7 Hz, 36 H, $PCCH_3$) ppm. ^{31}P NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 37.93 (s) ppm. ^{31}P NMR (200 MHz, C_6D_6, 25 °C): δ = 38.36 (s) ppm. MS (ESI+): *m*/*z* (%) = 433 (14) $[Au(PEt_3)_2]^+$, 719 (100) $[Au_4(StBu)_2(PEt_3)_4]^{2+}$, 1005 $[Au_3(StBu)_2(PEt_3)_2]^+$. MS–MS 719: *m*/*z* (%) = 315 (100) $[Au(PEt_3)]^+$, 433 (67) $[Au(PEt_3)_2]^+$, 663 (72) $[Au_4(SH)_2(PEt_3)_4]^{2+}$ or $[Au_2(SH)(PEt_3)_2]^+$, 719 (6) $[Au_4(StBu)_2(PEt_3)_4]^{2+}$. $C_{16}H_{39}Au_2BF_4P_2S$: calcd. C 23.84, H 4.88; found C 23.65, H 4.76.

Complex 2c: Light grey microcrystals from dichloromethane solution. Yield: 0.810 g (88%). ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 1.61 (s, 18 H, $SCMe_3$), 1.54 (d, $^3J_{P,H}$ = 13.9 Hz, 108 H, P*t*Bu) ppm. ^{31}P NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 92.74 (s) ppm. MS (ESI+): *m*/*z* (%) = 601 (6) $[Au(PtBu_3)_2]^+$, 887 (100) $[Au_2(StBu)(PtBu_3)_2]^+$, 1173 (6) $[Au_3(StBu)_2(PtBu_3)_2]^+$. MS–MS 887: *m*/*z* (%) = 231 (16) $[Au(PH_3)]^+$, 287 (52) $[Au(PH_2tBu)]^+$, 343 (49) $[Au(PHtBu_2)]^+$, 399 (43) $[Au(PtBu_3)]^+$, 489 (16) not assigned, 493 (14) $[Au_2(SH)(PH_3)_2]^+$, 549 (54) $[Au_2(SH)(PH_3)(PH_2tBu)]^+$, 572 (32) not assigned, 606 (32) $[Au_2(SH)(PH_3)(PHtBu_2)]^+$, 629 (25) not assigned, 647 (16) not assigned, 662 (100) $[Au_2(SH)(PH_3)(PtBu_3)]^+$, 685 (67) not assigned, 703 (83) not assigned, 718 (84) $[Au_2(SH)(PH_2tBu)(PtBu_3)]^+$, 741 (31) not assigned, 759 (36) not assigned, 775 (54) $[Au_2(SH)(PHtBu_2)(PtBu_3)]^+$, 831 (46) $[Au_2(SH)(PtBu_3)_2]^+$, 887 (22) $[Au_2(StBu)(PtBu_3)_2]^+$. $C_{28}H_{63}Au_2BF_4P_2S$ (974.56): calcd. C 34.51, H 6.52; found C 34.63, H 6.71.

Complex 2d: MS (ESI+): *m*/*z* (%) = 721 $[Au(PPh_3)_2]^+$, 1007 (100) $[Au_2(StBu)(PPh_3)_2]^+$, 1293 (7%) $[Au_3(StBu)(PPh_3)_2]^+$. MS–MS 1007: *m*/*z* (%) = 185 (25) $[PPh_2]^+$, 459 (85) $[Au(PPh_3)]^+$, 721 (100) $[Au(PPh_3)_2]^+$, 951 (35) $[Au_2(SH)(PEt_3)_2]^+$, 1008 (15) $[Au_2(StBu)(PPh_3)_2 + H]^+$.

Reaction of [Au$_2$(S*t*Bu)$_2$(L$_2$)] (L$_2$ = dppm, dppe) with [FeCp$_2$][BF$_4$]. Formation of [Au$_4$(S*t*Bu)$_2$(L$_2$)$_2$][BF$_4$]$_2$ (2e,f): The complexes were prepared according to the literature.[3]

Complex 2e: Yellow microcrystals from dichloromethane solution. Yield: 0.235 g (87%). ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ =

1.54 (s, 18 H, $SCMe_3$), 4.35 (t, $^2J_{P,H}$ = 12.0 Hz, 4 H, PCH_2), 7.2–7.6 (br. m, 40 H, PPh_2) ppm. ^{31}P NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 31.28 (br. s), 34.18 (br. s) ppm. MS (ESI+): *m/z* (%) = 581 (9) $[Au_2(dppm)_2]^{2+}$, 867 (100) $[Au_4(StBu)_2(dppm)_2]^{2+}$, 1019 (95) not assigned, 1153 (50) $[Au_3(StBu)_2(dppm)]^+$. MS–MS 867: *m/z* (%) = 185 (30) $[PPh_2]^+$, 397 (31) not assigned, 795 (100) not assigned, 811 (35) $[Au_4(SH)_2(dppm)_2]^{2+}$, 840 (9) $[Au_4(SH)(StBu)(dppm)_2]^{2+}$, 868 (13) $[Au_4(StBu)_2(dppm)_2]^{2+}$. $C_{58}H_{62}Au_4B_2F_8P_4S_2$ (1908.63): calcd. C 36.50, H 3.27; found C 36.88, H 3.19.

Complex 2f: MS (ESI+): *m/z* (%) = 595 $[Au_2(dppe)_2]^{2+}$, 738 (9) not assigned, 881 (100) $[Au_4(StBu)_2(dppe)_2]^{2+}$, 1024 (17) $[Au_5(StBu)_3(dppe)_2]^{2+}$, 1167 (42) $[Au_3(StBu)_2(dppe)]^+$. MS–MS 882: *m/z* (%) = 596 (2) $[Au_2(dppe)_2]^{2+}$, 825 (30) $[Au_4(SH)_2(dppe)_2]^{2+}$, 882 (100) $[Au_4(StBu)_2(dppe)_2]^{2+}$, 1167 (2) $[Au_3(StBu_3)_2(dppe)]^+$.

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