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Gold complexes of 3,4-bis(diphenylphosphinoamino)toluene and 1,2-bis(diphenylphosphinoamino)benzene. A comparative study †

Pedro A. Bella,[a] Olga Crespo,[b] Eduardo J. Fernández,[a] Axel K. Fischer,[c] Peter G. Jones,[d] Antonio Laguna,*[b] José M. López-de-Luzuriaga[a] and Miguel Monge[a]

[a] *Departamento de Química, Universidad de La Rioja, Obispo Bustamante 3, E-26001 Logroño, Spain*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain. E-mail: alaguna@posta.unizar.es*
[c] *Institüt für Chemie, Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany*
[d] *Institüt für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany*

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The reaction of the diphosphines 3,4-$(NHPPh_2)_2MeC_6H_3$ and 1,2-$(NHPPh_2)_2C_6H_4$ with gold(I) and gold(III) substrates such as $[Au(C_6F_5)_n(tht)]$ or $[Au(tht)_2]X$ in various molar ratios led to the dinuclear $[RC_6H_3\{NHPPh_2Au(C_6F_5)_n\}_2]$ (R = Me, n = 1 **1** or 3 **6**; R = H, n = 1 **2** or 3 **7**) and $[\{RC_6H_3(NHPPh_2)_2Au\}_2][O_3SCF_3]_2$ (R = Me **3** or H **5**) or the mononuclear $[MeC_6H_3(NHPPh_2)_2Au(C_6F_5)_3]$ **8** and $[\{MeC_6H_3(NHPPh_2)_2\}_2Au]X$ (X = O_3SCF_3 **4a** or ClO_4 **4b**) complexes, showing different selectivity depending on the phosphine. Reaction of **8** with gold(I) compounds gave the mixed neutral gold(I)–gold(III) $[MeC_6H_3(NHPPh_2)_2Au(C_6F_5)_3AuX]$ (X = Cl **9** or C_6F_5 **10**) derivatives. When the pentafluorophenyl gold precursors are treated with the disulfides 3,4-$(NHPPh_2S)_2MeC_6H_3$ and 1,2-$(NHPPh_2S)_2C_6H_4$ only the dinuclear complexes $[RC_6H_3(NHPPh_2SAu(C_6F_5)_n)_2]$ (R = Me, n = 1 **11** or 3 **12**; R = H, n = 1 **13** or 3 **14**) are obtained. Mononuclear cationic complexes $[RC_6H_3(NHPPh_2S)_2Au(C_6F_5)_2]ClO_4$ (R = Me **15** or H **16**) have also been obtained by reaction of the phosphinosulfides with the gold(III) precursor $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$. The addition of the deprotonating agent $NBu_4(acac)$ to **1**, **2** and **7** removes one aminic proton, yielding the dinuclear anionic complexes $[NBu_4][RC_6H_3\{NHPPh_2Au(C_6F_5)_n\}\{NPPh_2Au(C_6F_5)_n\}]$ (R = Me, n = 1 **17**; R = H, n = 1 **18** or 3 **19**). Addition of the aurating agent $[Au(OClO_3)(PPh_3)]$ to complex **19** led to the neutral trinuclear complex $[C_6H_4\{NHPPh_2Au(C_6F_5)_3\}\{N(AuPPh_3)PPh_2Au(C_6F_5)_3\}]$ **20**, containing a P,P,N-tridentate ligand. The crystal structures of complexes **1**, **3**, **4b**, **6**, **12** and **20** have been established by X-ray diffraction studies.

Introduction

The presence of small and apparently unimportant substituent groups in an organic molecule often goes unnoticed; nevertheless, they can be responsible for very different chemical and physical properties, either of the molecule itself or of the complexes that result from its co-ordination to metal centres. Examples of such behaviour are common in the literature. For instance, the presence or absence of a methyl group in the pyrimidine bases uracil and thymine seems to be responsible for the high selectivity in the constitution of the nucleic acids RNA and DNA respectively.[1] In the field of pharmacology the methyl group can confer markedly different properties. Thus, morphine, codeine and thebaine have the same skeleton but differ by various methyl groups. Whereas the first acts as a sedative, the second is employed againsts coughs and colds and the third is innocuous in the human body.[2–4]

In the last few years the application of gold-based drugs (chrysotherapy) has been the subject of considerable interest; their field of application was not limited to the treatment of rheumatoid arthritis, but they were also screened against tumors. The most effective molecules in cancer therapy contain bidentate phosphine ligands and their co-ordination to gold(I) centres is tetrahedral;[5,6] nevertheless, these complexes show several problems of toxicity.[7] In these molecules it seems that the choice of the ligand is of capital importance and thus an appropriate molecule can enforce tetrahedral co-ordination, not common in gold(I). Some gold(III) complexes have also been shown to display significant antitumor properties.[8–10]

Here we report a comparative study of 3,4-bis(diphenylphosphinoamino)toluene and 1,2-bis(diphenylphosphinoamino)-benzene in their reactions with gold(I) and gold(III) complexes. The presence of a methyl group in the former confers different donor properties on the phosphorus atoms, leading to a selectivity in their reactions with gold substrates.

Results and discussion

The tetrahydrothiophene (tht) ligand in $[Au(C_6F_5)(tht)]$ can easily be displaced by the diphosphines 3,4-$(NHPPh_2)_2MeC_6H_3$ and 1,2-$(NHPPh_2)_2C_6H_4$ (molar ratio 2:1) to give the dinuclear complexes $[RC_6H_3(NHPPh_2AuC_6F_5)_2]$ (R = Me **1** or H **2**) in which the co-ordination of the ligands takes place through the phosphorus atoms. This assignment is in accordance with the spectroscopic data obtained. Thus, in the ^{31}P-$\{^1H\}$ NMR spectrum of **1** two singlets at δ 77.5 and 74.8 appear, which are shifted to lower field compared with the free diphosphine (δ 29.9 and 33.9) and, as in the rest of complexes in this manuscript with the same phosphine, no coupling between the inequivalent phosphorus atoms was observed. We assign the signal at higher frequency to the phosphorus in position 3 because this atom is less shielded when compared with that at position 4 as a consequence of the inductive effect of the methyl

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4009/

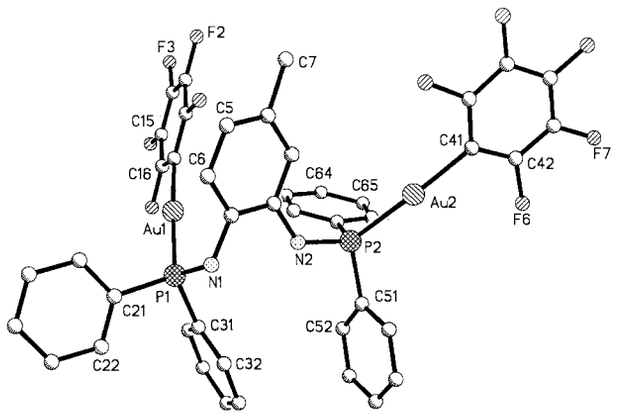


Fig. 1 Molecular structure of complex **1**; H atoms omitted for clarity.

Table 1 Selected bond lengths [Å] and angles [°] for complex **1**

Au(1)–C(11)	2.056(9)	P(1)–N(1)	1.690(8)
Au(1)–P(1)	2.263(2)	P(2)–N(2)	1.664(8)
Au(2)–C(41)	2.041(9)	N(1)–C(1)	1.418(11)
Au(2)–P(2)	2.275(3)	N(2)–C(2)	1.413(12)
C(11)–Au(1)–P(1)	177.1(3)	C(61)–P(2)–Au(2)	106.7(3)
C(41)–Au(2)–P(2)	170.0(2)	C(1)–N(1)–P(1)	117.8(6)
N(1)–P(1)–C(31)	107.0(4)	C(2)–N(2)–P(2)	128.8(7)
N(1)–P(1)–C(21)	105.0(4)	C(6)–C(1)–N(1)	122.1(10)
N(1)–P(1)–Au(1)	110.8(3)	C(2)–C(1)–N(1)	119.1(9)
C(31)–P(1)–Au(1)	112.0(3)	C(1)–C(2)–N(2)	118.1(8)
C(21)–P(1)–Au(1)	116.6(3)	C(3)–C(2)–N(2)	122.2(10)
N(2)–P(2)–C(51)	99.8(4)	C(12)–C(11)–Au(1)	123.8(7)
N(2)–P(2)–C(61)	107.3(4)	C(16)–C(11)–Au(1)	121.8(6)

group. A similar shift to low field is also observed in case of complex **2** (from δ 32 in the "free" ligand to 76.4). The ^{1}H NMR spectrum of **1** shows the non-equivalent aminic protons at δ 4.43 (s) and 4.90 (s) and for **2** the corresponding signal of the equivalent protons appears at δ 4.90 (s). Their mass spectra and other analytical data are also in accordance with the proposed stoichiometry (see Experimental section).

When the same reactions are carried out with equimolar amounts of the starting materials a mixture of compounds is obtained that cannot be separated because of their similar solubility in common organic solvents.

The crystal structure of complex **1** has been determined by X-ray analysis. Compound **1** is a dinuclear derivative in which the gold atoms exhibit slightly distorted linear geometries (Fig. 1). Table 1 shows a selection of bond lengths and angles. The Au–P distances of 2.263(2) and 2.275(3) Å compare well with those observed in other gold(I) dinuclear derivatives such as $[Au_2(PPh_2CH_2SPh)_2][O_3SCF_3]_2$[11] (2.2721(11) Å) or $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-P–P})]$[12] (P–P = dppe, 1,2-bis(diphenylphosphinoethane); dpph, *o*-phenylenebis(diphenylphosphine) (2.249(2), 2.265(2), 2.257(2), 2.267(2) Å). The Au–C distances (2.056(9), 2.041(9) Å) are slightly shorter than those found in other gold(I) derivatives such as $[Au(C_6F_5)(PPh_3)]$[13] (2.07(2) Å), or in the derivatives $[Au_2(C_6F_5)_2(\mu\text{-dppm})]$[14] (dppm = bis-(diphenylphosphino)methane) (2.063, 2.058(12) Å) and $[Au_2(C_6F_5)(PPh_3)(\mu\text{-}7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})]$[15] (2.068(8) Å). Selected torsion angles from the ligand backbone are collected in Table 2.

These results show a similar co-ordination behavior in the reaction of these ligands with the above-mentioned gold(I) precursor. However, when the gold(I) starting material is $[Au(tht)_2]X$ (X = non-co-ordinated anion), with two labile groups bonded to gold, the reactions with the ligands in different molar ratios reveal a difference in their co-ordinative possibilities. Thus, the toluene ligand 3,4-$(NHPPh_2)_2MeC_6H_3$ reacts with $[Au(tht)_2][O_3SCF_3]$ in equimolecular amounts to afford the expected dinuclear derivative **3** in high yield,

Table 2 Selected torsion angles (rounded to nearest degree) from the ligand backbones

Compound **1**:

Au1	P1	N1	C1	C2	N2	P2	Au2
	6	−84	−8	−170	34		

Compound **3**:

Au	P2	N2	C2	C1	N1	P1	Au′
	31	−140	−1	154	40		

Compound **4b** (chelate rings):

Au	P2	N2	C56	C51	N1	P1	Au
−63	11	54	−6	−91	60	28	

Au	P4	N4	C101	C106	N3	P3	Au
	−61	9	49	2	−99	59	26

Compound **6**:

Au1	P1	N1	C1	C2	N2	P2	Au2
	177	−102	2	−143	62		

Compound **12**:

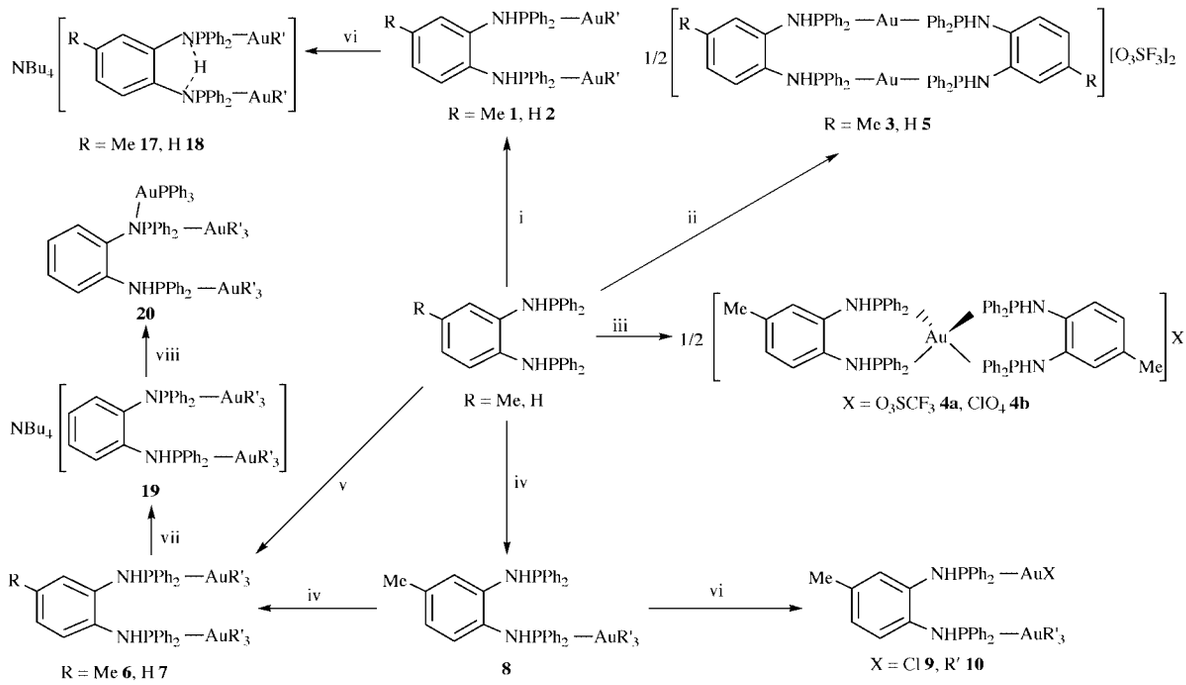
Au1	S1	P1	N1	C11	C12	N2	P2	S2	Au2
	−42	−53	177	6	176	−56	−47		

Compound **20**:

Au2	P2	N1	C1	C2	N2	P3	Au3
	−53	125	−3	169	−69		

replacing the tht ligands by two phosphines (Scheme 1). The isolated complex is the *trans* isomer as was detected in the solid state (see below) and probably retains this conformation in solution because the ^{31}P-{^{1}H} spectrum shows two singlets at δ 75.8 and 75.2 suggesting a deceptively simple second order system. The same reaction in a 2:1 molar ratio leads to a new cationic complex **4** (X = O_3SCF_3 **4a** or ClO_4 **4b**), whose analytical and spectroscopic data are in accordance with a stoichiometry in which two diphosphines are bonded to one gold centre in a tetrahedral environment. In its ^{31}P-{^{1}H} NMR spectrum a very complicated pattern centred at δ 61.7 can be observed at room temperature (Fig. 2). This pattern can be assigned to an AA′BB′ spin system in which the difference between the chemical shifts of the non-equivalent phosphorus present in the molecule is similar to their coupling constant, thus generating the second order spin system. When the spectrum is recorded at 223 K the AA′BB′ system disappears and two pseudotriplets centred at δ 66.7 and 56.5 appear. This new pattern can now be assigned to an AA′XX′ spin system showing a difference in the coupling constants between the non-equivalent phosphorus present in the molecule. This result can be explained accepting that the coupling changes at high/low temperature are due to a break in the Au–P bonds more rapidly/slowly on the NMR timescale, although recent studies on gold and silver complexes with symmetric diphosphines suggest an equilibrium between a monomeric $[M(P–P)]^+$ and dimeric $\{[M(P\text{-}P)_2]_2\}^{2+}$ species.[16] In both cases the resolution of the spectra does not allow a complete assignment of coupling constants.

The crystal structures of complexes **3** (Fig. 3, Table 3) and **4b** (Fig. 4, Table 4) have been determined. In the dinuclear cation of compound **3**, which exhibits crystallographic inversion symmetry, each ligand co-ordinates to both gold centers *via* its phosphorus atoms; the geometry at the metallic centers is essentially linear. The separation of the gold centers is 5.954(2) Å. The Au–P distances are 2.309(2) and 2.312(2) Å, longer than those found in **1**. The independent NH groups both form hydrogen bonds to atom O1 of the triflate anion. In compound **4b**, with its 1:2 stoichiometry, the gold centre is co-ordinated by four phosphorus atoms of two different ligands, thus displaying somewhat distorted tetrahedral geometry. The dis-



Scheme 1 R′ = C_6F_5; (i) 2 [AuR′(tht)]; (ii) $[Au(tht)_2][O_3SCF_3]$; (iii) 1 $[Au(tht)_2]X$; (iv) $[AuR'_3(tht)]$; (v) 2 $[AuR'_3(tht)]$; (vi) [AuX(tht)]; (vii) $NBu_4(acac)$; (viii) $[Au(PPh_3)]ClO_4$.

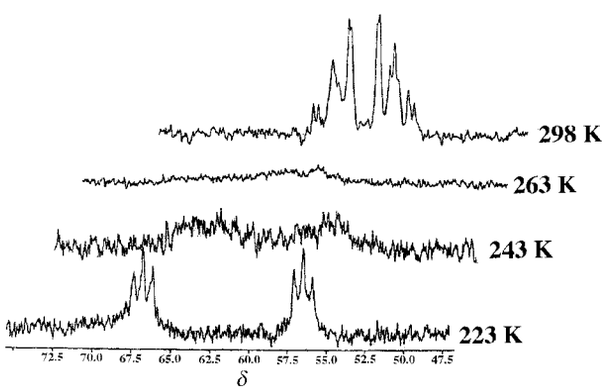


Fig. 2 Variable temperature $^{31}P-\{^1H\}$ NMR spectra for complex **4b** in $CDCl_3$ at 223, 243, 263 and 298 K.

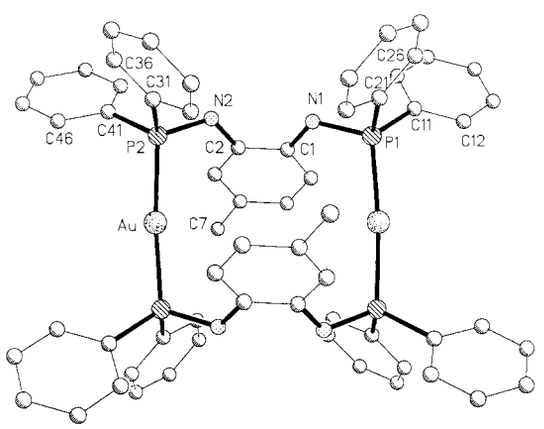


Fig. 3 Structure of the cation of complex **3**; H atoms omitted for clarity.

tortions arise first from the restricted bite of the diphosphine (P1–Au–P2 92.51(13), P3–Au–P4 92.74(13)°), and secondly from the presence of one shorter (2.401, 2.408(4) Å) and one longer (2.435, 2.437(4) Å) Au–P bond to each ligand. These distances compare well with those of $[Au(dppe)_2]^+$ (2.389(3)–2.416(3) Å),[17] $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(SPPh_2)_2CH_2\}]ClO_4$[18] (2.380(2), 2.389(2) Å) and $[Au(PMePh_2)_4]PF_6$[19] (2.449(1) Å).

Table 3 Selected bond lengths [Å] and angles [°] for complex **3**

Au–P(1)[1]	2.309(2)	P(2)–N(2)	1.650(7)
Au–P(2)	2.312(2)	P(2)–C(31)	1.807(9)
P(1)–N(1)	1.659(6)	P(2)–C(41)	1.817(8)
P(1)–C(21)	1.806(8)	N(1)–C(1)	1.421(9)
P(1)–C(11)	1.808(8)	N(2)–C(2)	1.417(10)
P(1)[1]–Au–P(2)	174.70(7)	C(31)–P(2)–Au	113.6(3)
N(1)–P(1)–C(21)	102.7(3)	C(41)–P(2)–Au	113.6(2)
N(1)–P(1)–C(11)	108.8(3)	C(1)–N(1)–P(1)	125.2(6)
C(21)–P(1)–C(11)	105.4(3)	C(2)–N(2)–P(2)	125.8(5)
N(1)–P(1)–Au[1]	109.3(2)	C(6)–C(1)–C(2)	118.5(8)
C(21)–P(1)–Au[1]	114.3(2)	C(6)–C(1)–N(1)	121.3(7)
C(11)–P(1)–Au[1]	115.4(2)	C(2)–C(1)–N(1)	120.2(7)
N(2)–P(2)–C(31)	104.0(3)	C(3)–C(2)–C(1)	118.7(8)
N(2)–P(2)–C(41)	108.7(3)	C(3)–C(2)–N(2)	120.6(7)
C(31)–P(2)–C(41)	106.4(4)	C(1)–C(2)–N(2)	120.7(7)
N(2)–P(2)–Au	110.1(2)		

Symmetry transformation used to generate equivalent atoms: $1-x+1$, $-y+1$, $-z+1$.

Both seven-membered chelate rings are closely similar in conformation (Table 2). A hydrogen bond is observed from N4–H4 to O2 of the anion.

When the benzene derivative is employed as ligand in the reaction with the same gold(I) complex the result is different. The reaction in equimolecular amounts led to the synthesis of the corresponding 1:1 complex **5**, but when the reaction is carried out in 2:1 molar ratio (diphosphine: gold(I)) after 30 min the same complex **5** is isolated, the excess of phosphine remaining in the solvent.

The difference in the co-ordinative properties of the phosphorus atoms in both ligands can also be observed in their reactions with gold(III) complexes. Thus, the reaction of 3,4-$(NHPPh_2)_2MeC_6H_3$ or 1,2-$C_6H_4(NHPPh_2)_2$ with $[Au(C_6F_5)_3(tht)]$ in a 2:1 molar ratio proceeds in a similar manner with substitution of the tetrahydrothiophene ligands and formation of the dinuclear complexes $[RC_6H_3\{NHPPh_2Au(C_6F_5)_3\}_2]$ (R = Me **6** or H **7**). This result differs from those previously described for other diphosphines, such as bis(diphenylphosphino)methane or vinylidenebis(diphenylphosphine), in that the same molar ratio only induces the co-ordination of one gold(III) atom, the other phosphorus remaining unsaturated.[20–22]

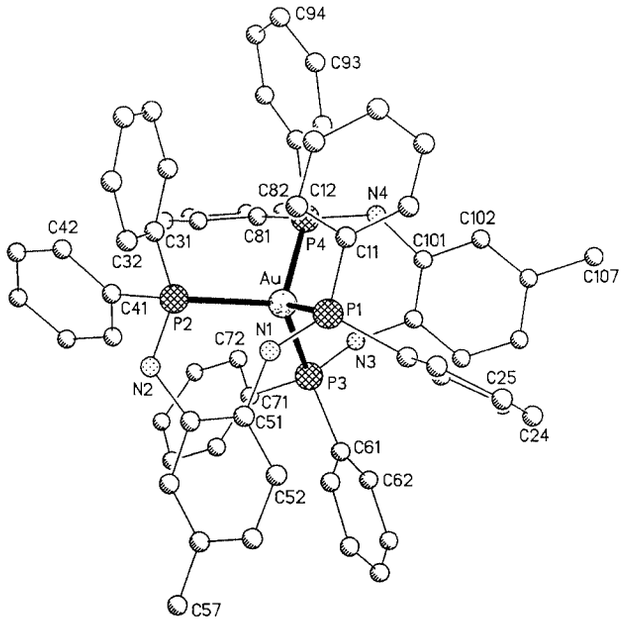


Fig. 4 Structure of the cation of complex **4b**; H atoms omitted for clarity.

Table 4 Selected bond lengths [Å] and angles [°] for complex **4b**

Au–P(1)	2.401(4)	P(2)–C(41)	1.814(13)
Au–P(3)	2.408(4)	P(2)–C(31)	1.827(13)
Au–P(4)	2.435(4)	P(3)–N(3)	1.682(12)
Au–P(2)	2.437(4)	P(3)–C(71)	1.825(13)
P(1)–N(1)	1.689(12)	P(3)–C(61)	1.829(14)
P(1)–C(21)	1.82(2)	P(4)–N(4)	1.682(12)
P(1)–C(11)	1.829(13)	P(4)–C(91)	1.815(14)
P(2)–N(2)	1.676(12)	P(4)–C(81)	1.840(15)
P(1)–Au–P(3)	120.27(13)	C(31)–P(2)–Au	115.1(4)
P(1)–Au–P(4)	122.87(13)	N(3)–P(3)–C(71)	101.4(6)
P(3)–Au–P(4)	92.74(13)	N(3)–P(3)–C(61)	107.2(5)
P(1)–Au–P(2)	92.51(13)	C(71)–P(3)–C(61)	98.9(5)
P(3)–Au–P(2)	119.11(12)	N(3)–P(3)–Au	106.6(4)
P(4)–Au–P(2)	111.39(13)	C(71)–P(3)–Au	117.5(4)
N(1)–P(1)–C(21)	107.3(6)	C(61)–P(3)–Au	123.1(4)
N(1)–P(1)–C(11)	100.6(6)	N(4)–P(4)–C(91)	101.0(6)
C(21)–P(1)–C(11)	99.9(6)	N(4)–P(4)–C(81)	105.6(6)
N(1)–P(1)–Au	108.2(4)	C(91)–P(4)–C(81)	102.2(6)
C(21)–P(1)–Au	119.5(4)	N(4)–P(4)–Au	115.6(5)
C(11)–P(1)–Au	119.3(4)	C(91)–P(4)–Au	116.3(4)
N(2)–P(2)–C(41)	98.0(6)	C(81)–P(4)–Au	114.3(4)
N(2)–P(2)–C(31)	105.4(5)	C(51)–N(1)–P(1)	119.5(9)
C(41)–P(2)–C(31)	102.5(5)	C(56)–N(2)–P(2)	128.3(9)
N(2)–P(2)–Au	112.0(4)	C(106)–N(3)–P(3)	119.5(9)
C(41)–P(2)–Au	121.6(4)	C(101)–N(4)–P(4)	127.7(9)

These complexes are air- and moisture-stable white solids at room temperature. They have been readily characterised by NMR spectroscopy. Their ^{31}P-{^{1}H} NMR spectra show resonances at δ 48.9 and 48.6 for **6** and 48.4 for **7**, which are shifted to lower field from those of the "free" ligands. All the signals are broadened because of the long distance coupling of the phosphorus with the fluorine atoms in *trans* position, which confirms that the co-ordination takes place through the phosphorus atoms. Other analytical and spectroscopic data are also in accordance with the proposed stoichiometry (see Experimental section). The crystal structure of complex **6** (Fig. 5, Table 5) has been determined by X-ray diffraction studies. The compound is a dinuclear gold(III) derivative with the expected square planar co-ordination geometry; the mean deviations of the five atoms Au, P and three *ipso* C from the respective least-squares plane are 0.092 and 0.080 Å. The Au · · · Au separation is 7.631(3) Å and the interplanar angle is 60°. The Au–P distances of 2.346(2) and 2.358(3) Å are in the

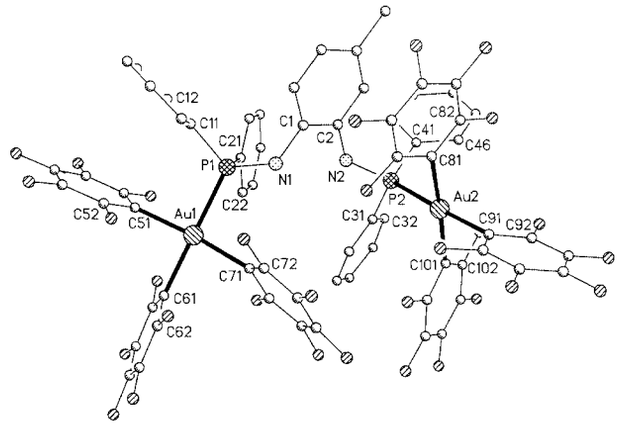


Fig. 5 Molecular structure of complex **6**; H atoms omitted for clarity.

Table 5 Selected bond lengths [Å] and angles [°] for complex **6**

Au(1)–C(71)	2.064(10)	P(1)–N(1)	1.673(8)
Au(1)–C(51)	2.071(10)	P(1)–C(21)	1.798(10)
Au(1)–C(61)	2.088(9)	P(1)–C(11)	1.803(9)
Au(1)–P(1)	2.346(2)	P(2)–N(2)	1.670(8)
Au(2)–C(101)	2.062(10)	P(2)–C(41)	1.800(9)
Au(2)–C(91)	2.070(10)	P(2)–C(31)	1.834(10)
Au(2)–C(81)	2.076(10)	N(1)–C(1)	1.430(11)
Au(2)–P(2)	2.358(3)	N(2)–C(2)	1.398(12)
C(71)–Au(1)–C(51)	171.9(3)	N(1)–P(1)–C(11)	109.4(4)
C(71)–Au(1)–C(61)	86.9(3)	C(21)–P(1)–C(11)	109.1(4)
C(51)–Au(1)–C(61)	87.9(3)	N(1)–P(1)–Au(1)	113.7(3)
C(71)–Au(1)–P(1)	95.3(2)	C(21)–P(1)–Au(1)	109.3(3)
C(51)–Au(1)–P(1)	90.6(2)	C(11)–P(1)–Au(1)	110.7(3)
C(61)–Au(1)–P(1)	173.1(2)	N(2)–P(2)–C(41)	108.5(4)
C(101)–Au(2)–C(91)	87.3(3)	N(2)–P(2)–C(31)	101.7(4)
C(101)–Au(2)–C(81)	172.6(3)	C(41)–P(2)–C(31)	105.8(4)
C(91)–Au(2)–C(81)	89.0(3)	N(2)–P(2)–Au(2)	117.1(3)
C(101)–Au(2)–P(2)	91.3(2)	C(41)–P(2)–Au(2)	110.1(3)
C(91)–Au(2)–P(2)	175.6(2)	C(31)–P(2)–Au(2)	112.9(3)
C(81)–Au(2)–P(2)	92.8(2)	C(1)–N(1)–P(1)	123.1(6)
N(1)–P(1)–C(21)	104.4(4)	C(2)–N(2)–P(2)	130.3(6)

range of those found in phosphinogold(III) derivatives such as $[NBu_4][\{Au(C_6F_5)_3(PPh_2CHPPh_2)\}_2Au]$[23] (2.367(2) Å) or $[AuMe_3(PPh_3)]$[24] ((2.347(6) Å), and longer than those found in $[Au(C_6F_5)(S_2C_6H_4)(PPh_3)]$[25] (2.340(1) Å) or $[AuCl_3(PPh_3)]$[26] (2.335(4) Å). These values are consistent with a higher *trans* influence of the C donor ligands. The Au–C distances are in the range 2.062(10)–2.088(9) Å, and are similar to those in other tris(pentafluorophenyl)gold(III) derivatives.[27]

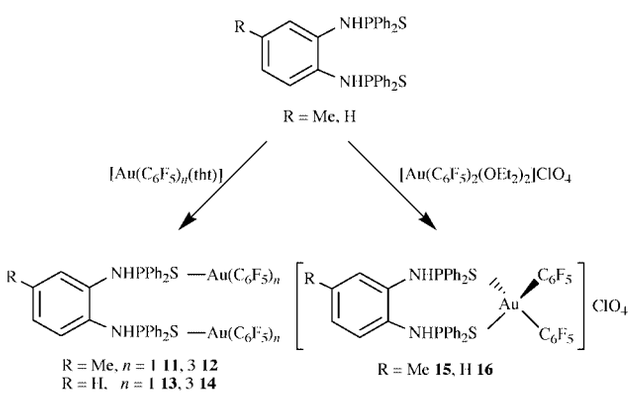
When the molar ratio of the reagents is 1 : 1 the result differs for the two ligands. Thus, while for 3,4-$(NHPPh_2)_2MeC_6H_3$ the spectroscopic data are in accordance with the formation of the desired mononuclear product **8** (see below), in the case of 1,2-$C_6H_4(NHPPh_2)_2$ the previously described complex **7** is isolated again, even with a great excess of the diphosphine (3 : 1). This result seems to indicate a difference in the donor properties of the phosphorus atoms in the toluene derivative. The ^{31}P-{^{1}H} NMR spectrum of complex **8** shows unequivocally that the co-ordination only takes place at one phosphorus atom because only one of the signals of the "free" ligand is shifted to lower field (δ 46.4) and its position is in the same range as those found for complexes **6** and **7**, in which the gold(III) precursor is the same. Taking into account the inductive effect of the methyl group, the gold(III) centre should be bonded to the phosphorus placed *para* to this group. The ^{1}H NMR spectrum of **8** shows in the aminic region two doublets at δ 4.24 [^{2}J(H–P) = 7.45] and 5.16 [^{2}J(H–P) = 15.6 Hz]. Owing to the decrease of electron density that the gold(III) centre induces in the groups bonded to it, we assign the latter to the proton of the aminic group *trans* to the gold atom. It is furthermore well established that in the case of ^{2}J coupling constants the electron density on one atom is

negatively correlated with the coupling constant to that centre.[28] In contrast, the signal corresponding to the other aminic proton retains a value similar to that of the "free" ligand.

The presence of a free PPh_2 group in complex **8** can be also confirmed in its reactions with gold(I) derivatives containing one weakly co-ordinated ligand, such as tetrahydrothiophene {*e.g.* [AuX(tht)] (X = Cl or C_6F_5)}, which afford the neutral dinuclear complexes **9** and **10** (Scheme 1). The co-ordination of the new gold(I) fragments can be confirmed by their IR spectra, which display the vibrations from the new group at 328 (ν(Au–Cl) for **9**) and 952 cm^{-1} (C_6F_5-Au^I for **10**), and by their NMR spectra which show the displacement of the signal of one of the phosphorus from δ 29.6 to 62.4 in **9** or 75.2 in **10**, arising from its co-ordination to the new metallic fragment. The signal of the phosphorus bonded to the gold(III) centre remains approximately the same as for the precursor complex.

In order to test the thermal stability of these new complexes we recorded their ^{31}P-{^1H} NMR spectra at different temperatures (293, 303 and 323 K) but no signs of dissociative equilibrium that could change gold(I) and gold(III) between the two inequivalent P atoms were detected. All other analytical and spectroscopic data are also in accordance with the proposed stoichiometry (see Experimental section).

Extending the comparative study of these diphosphines, we prepared their sulfide derivatives in order to investigate any influence on their co-ordinative properties by an extra bond between the ring and the donor atoms. In the case of $C_6H_4(NHPPh_2S)_2$-1,2 the preparation had been previously described.[29] The same process was employed to synthesize the toluene derivative $MeC_6H_3(NHPPh_2S)_2$-3,4. The reaction of the sulfurated ligands with gold(I) or gold(III) complexes in different molar ratios shows loss of selectivity. Thus, reaction with $[Au(C_6F_5)_n(tht)]$ (n = 1 or 3) in 1 : 1 or 1 : 2 molar ratio yielded in all the cases the dinuclear derivatives $[RC_6H_3(NHPPh_2SAu(C_6F_5)_n)_2]$ (R = Me, n = 1 **11** or n = 3 **12**; R = H, n = 1 **13** or 3 **14**), even in the presence of a great excess of ligand (4 : 1). The ^{31}P-{^1H} NMR spectra of **11**–**14** display the resonances of the phosphorus at δ 59.8 and 59.7 (**11**), 55.7 and 54.9 (**12**), 59.9 (**13**) or 55.5 (**14**), *i.e.* almost in the same position as for the starting materials (δ 57.7 and 56.5 for $MeC_6H_3(NHPPh_2S)_2$-3,4 or 57.0 for $C_6H_4(NHPPh_2S)_2$-1,2). This effect is attributable to the presence of the sulfur donor atom, avoiding the major change in electron density at phosphorus on co-ordination to a gold center (*cf.* complexes **1**, **2**, **6** and **7** lacking these sulfur atoms). The reaction of the phosphine sulfides with the gold(III) precursor $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ also involves identical behaviour of both ligands, leading to the mononuclear derivatives $[RC_6H_3(NHPPh_2S)_2Au(C_6F_5)_2]ClO_4$ (R = Me **15** or H **16**) (Scheme 2). Complexes **11**–**16** display analytical and spectroscopic data in accordance with the proposed stoichiometry, and, once again, almost no displacement of the signals of the phosphorus is observed in the ^{31}P-{^1H} NMR spectra of **15** (δ 56.8 and 56.7) and **16** (56.7).



Scheme 2

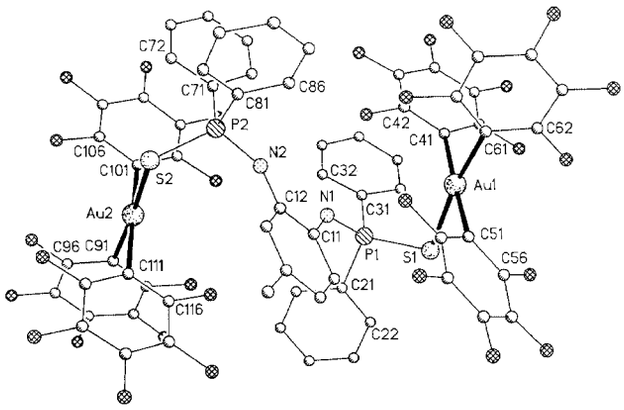


Fig. 6 Molecular structure of complex **12**; H atoms omitted for clarity.

Table 6 Selected bond lengths [Å] and angles [°] for complex **12**

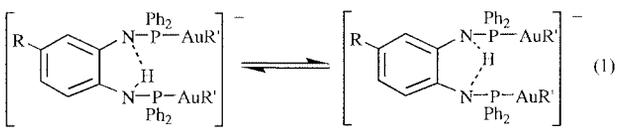
Au(1)–C(61)	2.048(19)	P(1)–N(1)	1.655(17)
Au(1)–C(51)	2.06(2)	P(1)–C(21)	1.76(2)
Au(1)–C(41)	2.08(2)	P(1)–C(31)	1.79(2)
Au(1)–S(1)	2.403(5)	P(1)–S(1)	2.005(8)
Au(2)–C(91)	2.039(19)	P(2)–N(2)	1.674(17)
Au(2)–C(101)	2.04(2)	P(2)–C(71)	1.78(2)
Au(2)–C(111)	2.09(2)	P(2)–C(81)	1.80(2)
Au(2)–S(2)	2.400(5)	P(2)–S(2)	2.013(8)
C(61)–Au(1)–C(51)	87.7(6)	N(1)–P(1)–C(31)	102.8(8)
C(61)–Au(1)–C(41)	89.2(6)	C(21)–P(1)–C(31)	108.6(8)
C(51)–Au(1)–C(41)	176.9(6)	N(1)–P(1)–S(1)	117.0(6)
C(61)–Au(1)–S(1)	172.3(4)	C(21)–P(1)–S(1)	106.8(6)
C(51)–Au(1)–S(1)	86.5(4)	C(31)–P(1)–S(1)	113.7(6)
C(41)–Au(1)–S(1)	96.5(4)	N(2)–P(2)–C(71)	101.6(8)
C(91)–Au(2)–C(101)	88.1(6)	N(2)–P(2)–C(81)	108.5(8)
C(91)–Au(2)–C(111)	87.8(6)	C(71)–P(2)–C(81)	107.6(8)
C(101)–Au(2)–C(111)	175.6(6)	N(2)–P(2)–S(2)	117.0(7)
C(91)–Au(2)–S(2)	173.7(4)	C(71)–P(2)–S(2)	114.9(6)
C(101)–Au(2)–S(2)	96.2(4)	C(81)–P(2)–S(2)	106.9(7)
C(111)–Au(2)–S(2)	88.0(5)	P(1)–S(1)–Au(1)	106.3(3)
N(1)–P(1)–C(21)	107.7(8)	P(2)–S(2)–Au(2)	107.4(3)

The crystal structure of complex **12** has been determined (Fig. 6, Table 6) and is similar in principle to that of **6**, although the backbone conformation (Table 2) is much more regular, with approximate twofold symmetry. The Au · · · Au separation is 8.972(2) Å. Each gold atom is co-ordinated to three carbon atoms of different pentafluorophenyl rings and one sulfur atom of the toluene disulfide ligand; thus, the environment of the gold centres is square planar with mean deviations (as above) of 0.047 and 0.049 Å from the best planes, which are nearly parallel (interplanar angle 4°). The Au–S distances are 2.400(5) and 2.403(5) Å, longer than those found in $[Au(PPh_3)_2][Au(C_3S_5)_2]$[30] (2.321(2)–2.326(2) Å) (C_3S_5 = 4,5-disulfanyl-1,3-dithiole-2-thionate) or $[(PClPh_3)[Au\{S_2C_2(CF_3)_2\}_2]$,[31] 2.288 Å.

All the complexes so far presented exhibit co-ordination of metallic fragments at one or both phosphorus atoms or, in the case of the disulfides, at both sulfur atoms. Nevertheless, in both ligands the nuclearity could be increased, as the nitrogen atoms represent potential donors to new metal centres. The co-ordination of these to gold is in principle not easy[32] but deprotonation would increase the basicity and therefore co-ordination would be favored. We therefore tested the reaction of some derivatives of 3,4-$(NHPPh_2)_2MeC_6H_3$ and 1,2-$(NHPPh_2)_2C_6H_4$ with deprotonating agents such as NBu_4(acac) (acac = acetylacetonate) and the further reactivity of some of the products thus obtained with gold substrates.

The reaction of complexes **1** and **2** with NBu_4(acac) in equimolecular amounts leads to the synthesis of the anionic amide derivatives $[NBu_4][RC_6H_3\{NHPPh_2Au(C_6F_5)\}\{NPPh_2Au(C_6F_5)\}]$ (R = Me **17** or H **18**) as air-stable yellow solids (Scheme 1). They display analytical data in accordance with the

proposed stoichiometry (see Experimental section). Their ^{31}P-$\{^1H\}$ spectra at room temperature show two or one broad signals at δ 62.7 and 59.5 (**17**) or 61.6 (**18**), respectively, all located at higher field than their corresponding precursor **1** or **2**. These shifts are in accordance with an increase of electron density at the phosphorus when the aminic proton is removed. The presence of only one signal for **18** and the fact that for **17** both signals are shifted as compared with its precursor **1** could be explained by the existence of a rapid exchange equilibrium in solution, in which the aminic proton changes its position from one nitrogen to the other, eqn. (1). Unfortunately, when the



spectra are recorded at lower temperatures (223 K) no better resolution is obtained, indicating that the exchange is fast on the NMR timescale, even at lower temperatures. In the ^1H NMR spectra of these species the aminic proton appears at δ 6.23 (**17**) or 6.39 (**18**) as a broad signal that is not well resolved when the temperature is decreased. The mass spectra (FAB^-) show the peak corresponding to the molecular anion at *m/z* = 1217 (40, **17**) or 1203 (7%, **18**).

Even when the same reaction is carried out with an excess of deprotonating agent, no further deprotonation is observed and the same products **17** and **18** are always obtained. However, when **17** is treated with $[Au(ClO_4)(PPh_3)]$ in order to coordinate the $AuPPh_3$ fragment to the unsaturated nitrogen a mixture, which we were not able to separate, was obtained. This is in accordance with the idea of a rapid exchange equilibrium in which the aminic proton is delocalised between both nitrogen atoms.

We have also treated the gold(III) derivative **7** with the same deprotonating agent $NBu_4(acac)$ (1 : 1) in dichloromethane. This reaction led to the synthesis of the new anionic amide derivative $[NBu_4][C_6H_4\{NHPPh_2Au(C_6F_5)_3\}\{NPPh_2Au(C_6F_5)_3\}]$ **19** as an air-stable yellow solid with analytical and spectroscopic data in accordance with the proposed stoichiometry. Its ^{31}P-$\{^1H\}$ NMR spectrum displays, as for **18**, only one broad signal for both non-equivalent phosphorus at δ 29.4, also shifted to higher field as compared with its precursor **7**. In this case, when the spectrum is recorded at −70 °C in hexadeuteroacetone, the signal is split into two at δ 34.6 and 17.0, showing the expected inequivalence and confirming the existence of a rapid equilibrium in solution which would make both phosphorus equivalent at room temperature. In its mass spectrum (FAB^-) the molecular ion is also detected at *m/z* = 1871 (10%). Attempts at a double deprotonation using a 1 : 2 molar ratio were unsuccessful and the same compound is obtained.

The excess of electron density at one nitrogen atom does indeed permit the introduction of new metallic centres, thus, treatment of complex **19** with one equivalent of $[Au(ClO_4)(PPh_3)]$ led to the neutral complex $[C_6H_4\{NHPPh_2Au(C_6F_5)_3\}\{N(AuPPh_3)PPh_2Au(C_6F_5)_3\}]$ **20** as a white solid. Its ^{31}P-$\{^1H\}$ NMR spectrum does not show the previously described equilibrium phenomena, and thus three signals, one from each non-equivalent phosphorus, are clearly observed at room temperature. The positions of the phosphorus bonded to gold(III) (δ 48.4 and 47.5) are similar to those found for the precursor complex **7** and the second signal is broader than the first one, which could mean that the resonance at δ 47.5 corresponds to the phosphorus of the diphosphine bonded to the N–$AuPPh_3$ fragment. A third signal, from the PPh_3 group, appears at δ 29.7; this chemical shift is in accordance with data previously reported for N–Au^I–P compounds.[33] All other analytical and spectroscopic data are in accordance with this stoichiometry.

The crystal structure of compound **20** (Fig. 7, Table 7) has

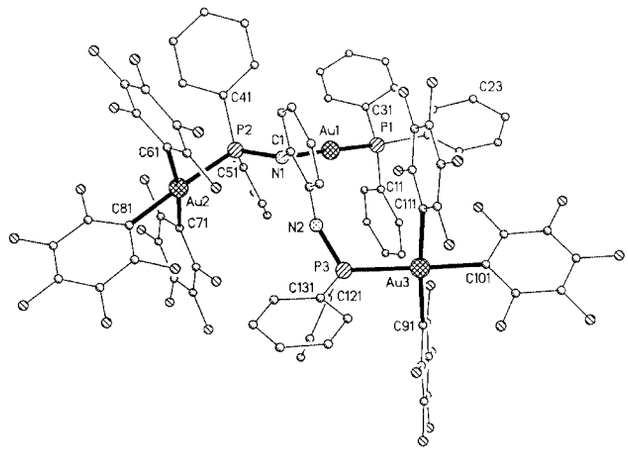


Fig. 7 Molecular structure of complex **20**; H atoms omitted for clarity.

Table 7 Selected bond lengths [Å] and angles [°] for complex **20**

Au(1)–N(1)	2.096(4)	P(1)–C(21)	1.814(6)
Au(1)–P(1)	2.2404(16)	P(1)–C(11)	1.828(6)
Au(2)–C(81)	2.062(6)	P(2)–N(1)	1.648(5)
Au(2)–C(61)	2.070(5)	P(2)–C(41)	1.816(6)
Au(2)–C(71)	2.069(5)	P(2)–C(51)	1.827(5)
Au(2)–P(2)	2.3829(15)	P(3)–N(2)	1.657(5)
Au(3)–C(101)	2.061(6)	P(3)–C(131)	1.801(6)
Au(3)–C(111)	2.074(5)	P(3)–C(121)	1.800(6)
Au(3)–C(91)	2.079(6)	N(2)–C(2)	1.416(7)
Au(3)–P(3)	2.3615(16)	N(1)–C(1)	1.440(6)
P(1)–C(31)	1.813(6)		
N(1)–Au(1)–P(1)	176.85(12)	C(11)–P(1)–Au(1)	112.44(19)
C(81)–Au(2)–C(61)	86.1(2)	N(1)–P(2)–C(41)	112.0(2)
C(81)–Au(2)–C(71)	85.9(2)	N(1)–P(2)–C(51)	103.1(2)
C(61)–Au(2)–C(71)	170.9(2)	C(41)–P(2)–C(51)	103.6(2)
C(81)–Au(2)–P(2)	176.22(15)	N(1)–P(2)–Au(2)	114.86(17)
C(61)–Au(2)–P(2)	97.38(14)	C(41)–P(2)–Au(2)	111.72(19)
C(71)–Au(2)–P(2)	90.76(15)	C(51)–P(2)–Au(2)	110.65(17)
C(101)–Au(3)–C(111)	87.3(2)	N(2)–P(3)–C(131)	107.2(3)
C(101)–Au(3)–C(91)	88.0(2)	N(2)–P(3)–C(121)	99.0(2)
C(111)–Au(3)–C(91)	175.2(2)	C(131)–P(3)–C(121)	108.8(3)
C(101)–Au(3)–P(3)	175.93(15)	N(2)–P(3)–Au(3)	119.32(18)
C(111)–Au(3)–P(3)	93.64(15)	C(131)–P(3)–Au(3)	112.43(19)
C(91)–Au(3)–P(3)	91.15(15)	C(121)–P(3)–Au(3)	109.02(19)
C(31)–P(1)–C(21)	106.3(3)	C(2)–N(2)–P(3)	132.2(4)
C(31)–P(1)–C(11)	105.1(3)	C(1)–N(1)–P(2)	122.2(3)
C(21)–P(1)–C(11)	105.5(3)	C(1)–N(1)–Au(1)	118.5(3)
C(31)–P(1)–Au(1)	112.4(2)	P(2)–N(1)–Au(1)	114.5(2)
C(21)–P(1)–Au(1)	114.33(18)		

been determined by X-ray studies. It is a trinuclear derivative with the gold centers in different oxidation states. Two gold(III) centres (Au2 and Au3) exhibit square planar geometries in which the mean deviations (as defined above) are 0.045 and 0.039 Å. The Au^{III}–P distances are 2.3829(15) and 2.3615(16) Å, somewhat longer than in **6**, and the Au–C distances lie in the range 2.061(6) to 2.079(6) Å, similar to those in **6**. The third gold center Au1 shows a linear geometry consistent with the oxidation state +I; the distance Au1–P is 2.2404(16) Å, shorter than those found in **1** or **3**, which is presumably attributable to the weak *trans* influence of the nitrogen donor (Au1–N1 2.096(4) Å). Intramolecular gold–gold distances are Au1 · · · Au2 5.292, Au1 · · · Au3 5.553 and Au2 · · · Au3 8.029(1) Å. A probable intramolecular hydrogen bond is indicated by the contact distances N1 · · · N2 2.719, H2 · · · N1 2.29 Å.

Experimental

Reagents

The compounds $[AuCl(tht)]$,[34] $[Au(tht)_2]X$[35] (X = ClO_4 or SO_3CF_3), $[Au(C_6F_5)(tht)]$,[35] $[Au(C_6F_5)_3(tht)]$,[20] $[Au(C_6F_5)_2(OEt_2)_2]$-

Table 8 Details of data collection and structure refinement for complexes **1**, **3**, **4b**, **6**, **12** and **20**

	1	**3**	**4b**	**6**	**12**	**20**
Chemical formula	$C_{46}H_{32}Au_2F_{10}N_2P_2$	$C_{66}H_{60}Au_2Cl_4F_6N_4O_6P_4S_2$	$C_{66}H_{64}AuCl_9N_4O_4P_4$	$C_{73}H_{42}Au_2F_{30}N_2P_2$	$C_{72}H_{35}Au_2Cl_4F_{30}N_2P_2S_2$	$C_{98}H_{68}Au_3F_{30}N_2O_2P_3$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.3178(18)	12.155(4)	13.641(4)	11.342(3)	13.651(2)	15.0004(10)
b/Å	16.640(4)	20.020(5)	29.735(8)	14.518(3)	16.877(2)	15.307(2)
c/Å	25.407(5)	15.609(4)	17.361(6)	22.250(5)	17.226(2)	23.393(3)
α/°				94.10(2)	104.44(2)	87.517(10)
β/°	90.651(14)	110.08(3)	98.26(3)	102.22(2)	104.18(2)	72.928(10)
λ/°				106.32(2)	90.93(2)	62.925(10)
U/Å^3	4361.7(15)	3568(2)	6969(4)	3402.8(14)	3713.5(8)	4546.2(9)
Z	4	2	4	2	2	2
M	1258.61	1842.91	1617.11	1972.96	2159.81	2535.33
T/°C	−130	−100	−130	−100	−100	−100
μ(Mo-Kα)/cm^{-1}	68.71	44.73	25.97	44.83	43.10	49.94
No. of reflections measured	11090	11040	9581	11892	18143	47095
No. of unique reflections	7698	6240	9138	11.837	12191	20440
R_{int}	0.0408	0.0545	0.0501	0.0331	0.1145	0.0517
R ($F > 4\sigma(F)$)	0.0488	0.0468	0.0760	0.0518	0.0939	0.0445
wR (F^2, all refl.)	0.1141	0.1002	0.1945	0.1250	0.2291	0.0836

ClO_4,[36] 3,4-$(NHPPh_2)_2MeC_6H_3$, and 1,2-$(NHPPh_2)_2C_6H_4$[29] were prepared by literature methods. **CAUTION**: perchlorate salts with organic cations may be explosive.

General procedure

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer and on a FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5×10^{-4} M acetone solutions with a Jenway 4010 conductimeter. The C, H, N and S analyses were carried out with a Perkin-Elmer 240C microanalyser. Mass spectra were recorded on a VG Autospec instrument using liquid secondary ion techniques and 3-nitrobenzyl alcohol as matrix and on a HP59987A ELECTROSPRAY. The ^{1}H, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker ARX 300 spectrometer in $CDCl_3$ or hexadeuteroacetone (HDA) solutions. Chemical shifts are quoted relative to $SiMe_4$ (^{1}H, external), $CFCl_3$ (^{19}F, external) and H_3PO_4 (85%) (^{31}P, external).

Syntheses

[$RC_6H_3(NHPPh_2AuC_6F_5)_2$] (R = Me 1 or H 2). To a dichloromethane solution (20 mL) of 3,4-$(NHPPh_2)_2MeC_6H_3$ (0.1 mmol, 0.05 g) or $C_6H_4(NHPPh_2)$1,2 (0.1 mmol, 0.05 g) under N_2 was added [$Au(C_6F_5)$(tht)] (0.2 mmol; 0.1 g). The reaction mixture was stirred for 1 h and evaporated to *ca.* 5 mL. Addition of hexane (20 mL) led to precipitation of complexes **1**, **2** as white solids. Yield: 76 (**1**), 40% (**2**). Mass spectra: $[M]^+$ at m/z = 1218 (4, **1**), 1204 (4%, **2**). Calc. for $C_{43}H_{28}Au_2F_{10}N_2P_2$ (**1**): C, 42.4; H, 2.3; N, 2.3. Found: C, 42.5; H, 2.1; N, 2.25. $C_{21}H_{13}AuF_5NP$ (**2**): C, 41.9; H, 2.15; N, 2.3. Found: C, 42.55; H, 1.85 ; N, 2.3%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ (**1**) 77.5 (s) and 74.8(s); (**2**) 76.4 (s). ^{1}H NMR ($CDCl_3$): δ (**1**) 6.73–7.73 [m, 23 H, Ph], 4.43 [s, 1 H, NH], 4.90 [s, 1 H, NH] and 2.20 [s, 3 H, CH_3]; (**2**) 6.98–7.96 [m, 24 H, Ph] and 4.77 [s, 2 H, NH]. ^{19}F NMR ($CDCl_3$): δ **1** −116.15 [m, 2F, F_o], −116.40 [m, 2F, F_o]; −158.22 [t, 1F, $J(F_p–F_m)$ = 19.6, Fp], −158.29 [t, 1F, $J(F_p$-$F_m)$ = 19.7 Hz, Fp], −162.41 [m, 2F, F_m] and −162.44 [m, 2F, F_m]; (**2**) −116.25 [m, 4F, F_o], −158.16 [t, 2F, $J(F_p–F_m)$ = 20.1 Hz, Fp] and −162.36 [m, 4F, F_m].

[{$RC_6H_3(NHPPh_2)_2Au$)}$_2$] [O_3SCF_3]$_2$ (R = Me 3 or H 5). To a solution of 3,4-$(NHPPh_2)_2MeC_6H_3$ (0.1 mmol, 0.05 g) or 1,2-$(NHPPh_2)_2C_6H_4$ (0.1 mmol, 0.05 g) in dichloromethane (20 mL) under N_2 was added $[Au(tht)_2][O_3SCF_3]$ (0.1 mmol; 0.05 g). The reaction mixture was stirred for 1 h and evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) gave complexes **3** and **5** as white solids. Yield: 94 (**3**), 65% (**5**). Mass spectra: $[M + O_3SCF_3]^+$ at m/z = 1523 (25, **3**), 1495 (47%, **5**). Calc. for $C_{31}H_{26}AuF_3N_2O_3P_2S$ (**3**): C, 45.95; H, 3.4; N, 3.35. Found: C, 45.80; H, 3.0; N, 3.25. $C_{32}H_{28}AuF_3N_2O_3P_2S$ (**5**): C, 45.3; H, 3.20; N, 3.4. Found: C, 44.9; H, 3.0 ; N, 3.4%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ (**3**) 75.8 (s) and 75.2(s); (**5**) 76.2 (s). ^{1}H NMR ($CDCl_3$): δ (**3**) 6.98–7.89 [m, 46 H, Ph], 5.3 [m, 4 H, N–H] and 2.08 [s, 6 H, CH_3]; (**5**) 7.05–7.89 [m, 48 H, Ph] and 5.29 [s, 4 H, NH].

[{$MeC_6H_3(NHPPh_2)_2$}$_2$Au]X (X = O_3SCF_3 4a or ClO_4 4b). To a solution of $MeC_6H_3(NHPPh_2)_2$-3,4 (0.4 mmol, 0.2g) in dichloromethane (20 mL) under N_2 was added $[Au(tht)_2]$ X (0.2 mmol; 0.1 (X = O_3SCF_3), 0.09 g (X = ClO_4)). The reaction mixture was stirred for 1 h and evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) gave complexes **4a** and **4b** as white solids. Yield: 98 (**4a**), 95% (**4b**). Mass spectra: $[M]^+$ at m/z = 1177 (46, **4a**; 25%, **4b**). Calc. for $C_{63}H_{56}AuF_3N_4O_3P_4S{\cdot}CH_2Cl_2$ (**4a**): C, 54.45; H, 4.15; N, 4.0. Found: C, 54.8; H, 4.3; N, 4.1. $C_{62}H_{56}AuClN_4O_4P_4{\cdot}CH_2Cl_2$ (**4b**): C, 55.55; H, 4.3; N, 4.1. Found: C, 55.1; H, 4.0 ; N, 4.1%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ (**4a**, **4b**) 61.7 [AA′BB′ (298 K), 4P, Ph_2P], 56.5, 66.7 [AA′XX′

(223 K), 4P, Ph_2P]. ^1H NMR ($CDCl_3$): δ (**4a**, **4b**) 6.5–7.8 [m, 46 H, Ph], 4.4 [m, 4 H, NH] and 2.06 [s, 6 H, CH_3].

[RC_6H_3{$NHPPh_2Au(C_6F_5)_3$}$_2$] (R = Me 6 or H 7). To a dichloromethane solution (20 mL) of 3,4-$(NHPPh_2)_2MeC_6H_3$ (0.1mmol, 0.05g) or $C_6H_4(NHPPh_2)_2$-1,2 (0.1 mmol, 0.05 g) under N_2 was added $[Au(C_6F_5)_3(tht)]$ (0.2 mmol; 0.17 g). The reaction mixture was stirred for 1 h and evaporated to *ca*. 5 mL. Addition of hexane (20 mL) led to precipitation of complexes **6** and **7** as white solids. Yield: 91 (**6**), 63% (**7**). Mass spectra: $[M]^+$ at *m/z* = 1887 (25, **6**) and 1872 (4%, **7**). Calc. for: $C_{67}H_{28}Au_2F_{30}N_2P_2$ (**6**): C, 42.65; H, 1.5; N, 1.5. Found: C, 42.0; H, 1.5; N, 1.3. $C_{33}H_{13}AuF_{15}NP$ (**7**): C, 42.35; H, 1.4; N, 1.5. Found: C, 42.25; H, 1.25 ; N, 1.5%. ^{31}P-{^1H} NMR ($CDCl_3$): δ (**6**) 48.9 (m) and 48,6 (m); (**7**) 48.4 (m). ^1H NMR ($CDCl_3$): δ (**6**) 6.11–7.64 [m, 23 H, Ph], 4.93 [m, 2 H, NH] and 1.79 [s, 3 H, CH_3]; (**7**) 6.37–7.62 [m, 24 H, Ph] and 5.18 [d, 2H, *J*(H–P) = 10.2 Hz, NH]. ^{19}F NMR ($CDCl_3$): δ (**6**) −120.86 [m, 8F, F_o], −121.64 [m, 4F, F_o], −156.22 [t, 2F, $J(F_p\text{-}F_m)$ = 20.1, F*p*], −156.48 [t, 2F, $J(F_p\text{-}F_m)$ = 19.5, F*p*], −156.82 [t, 1F, $J(F_p\text{-}F_m)$ = 20.2, F*p*], −156.89 [t, 1F, $J(F_p\text{-}F_m)$ = 20.9 Hz, F*p*], −160.22 [m, 8F, F_m] and −161.02 [m, 4F, F_m]; (**7**) −120.87 [m, 8F, F_o], −121.44 [m, 4F, F_o], −156.24 [t, 4F, $J(F_p\text{-}F_m)$ = 19.4, F*p*], −156.78 [t, 2F, $J(F_p\text{-}F_m)$ = 19.4 Hz, F*p*], −160.24 [m, 8F, F_m] and −161.07 [m, 4F, F_m].

[$MeC_6H_3(NHPPh_2)Au(C_6F_5)_3$] 8. To a solution of 3,4-$(NHPPh_2)_2MeC_6H_3$ (0.1 mmol, 0.05 g) in dichloromethane (5 mL) under N_2 was added $[Au(C_6F_5)_3(tht)]$ (0.1 mmol; 0.09 g). The reaction mixture was immediately evaporated to *ca*. 1 mL. Addition of hexane (10 mL) led to precipitation of complex **8** as a white solid. Yield: 41%. Mass spectrum: $[M]^+$ at *m/z* = 1188 (40%). Calc. for $C_{49}H_{28}AuF_{15}N_2P_2$: C, 49.50; H, 2.35; N, 2.35. Found: C, 48.95; H, 2.35; N, 2.0%. ^{31}P-{^1H} NMR ($CDCl_3$): δ 46.4 (m) and 29.6 (s). ^1H NMR ($CDCl_3$): δ 6.21–7.58 [m, 23 H, Ph], 5.16 [d, 1 H, *J*(H-P) = 15.6, NH], 4.24 [d, 1 H, *J*(H-P) = 7.45 Hz, NH] and 2.09 [s, 3 H, CH_3]. ^{19}F NMR ($CDCl_3$): δ −120.54 [m, 4F, F_o], −121.29 [m, 2F, F_o], −156.55 [t, 2F, $J(F_p\text{-}F_m)$ = 19.9, F*p*], −157.20 [t, 1F, $J(F_p\text{-}F_m)$ = 20.0 Hz, F*p*], −160.15 [m, 4F, F_m] and −161.26 [m, 2F, F_m].

[$MeC_6H_3(NHPPh_2)_2Au(C_6F_5)_3AuX$] (X = Cl 9 or C_6F_5 10). To a dichloromethane solution (20 mL) of complex **8** (0.1 mmol, 0.12 g) under N_2 was added [AuX(tht)] (0.1 mmol, 0.03 (X = Cl) or 0.04g (X = C_6F_5)). After 1 h of reaction the solution was evaporated to *ca*. 5 mL. Addition of hexane (20 mL) led to the precipitation of complexes **9**, **10** as white solids. Yield: 56 (**9**), 50% (**10**). Mass spectra: $[M - C_6F_5]^+$ at *m/z* = 1252 (17%, **9**); $[M]^+$ at *m/z* = 1552 (4%, **10**). Calc. for $C_{49}H_{28}Au_2ClF_{15}N_2P_2$ (**9**): C, 41.4; H, 1.95; N, 1.95. Found: C, 40.95; H, 1.65; N, 1.95. $C_{55}H_{28}Au_2F_{20}N_2P_2$ (**10**): C, 42.55; H, 1.8; N, 1.8. Found: C, 41.95; H, 1.45 ; N, 1.8%. ^{31}P-{^1H} NMR ($CDCl_3$): δ (**9**) 62.4 (s) and 45.4 (m); (**10**) 75.2 (m) and 46.9 (m). ^1H NMR ($CDCl_3$): δ (**9**) 6.30–7.77 [m, 23 H, Ph], 5.37 [d, 1 H, *J*(H–P) = 15 Hz, NH], 4.44 [m, 1 H, NH] and 2.03 [s, 3 H, CH_3]; (**10**) 6.36–7.73 [m, 23H, Ph], 5.10 [d, 1 H, *J*(H-P) = 15 Hz, NH], 4.51 [m, 1 H, NH] and 2.09 [s, 3 H, CH_3]. ^{19}F NMR ($CDCl_3$): δ (**9**) −120.90 [m, 4F, F_o], −121.43 [m, 2F, F_o], −156.07 [t, 2F, $J(F_p\text{-}F_m)$ = 19.8, F*p*], −156.86 [t, 1F, $J(F_p\text{-}F_m)$ = 19.8 Hz, F*p*], −159.75 [m, 4F, F_m] and −161.11 [m, 2F, F_m]; (**10**) −116.48 [m, 2F, F_o, Au^I], −120.83 [m, 4F, F_o, Au^{III}], −121.45 [m, 2F, F_o, Au^{III}]; −156.00 [t, 2F, $J(F_p\text{-}F_m)$ = 20.0, F*p*, Au^{III})], −156.81 [t, 1F, $J(F_p\text{-}F_m)$ = 19.6, F_p, Au^{III}], −157.96 [t, 1F, $J(F_p\text{-}F_m)$ = 20.1 Hz, F*p*, Au^I]; −159.81 [m, 4F, F_m, Au^{III}], −161.06 [m, 2F, F_m, Au^{III}] and −162.27 [m, 2F, F_m, Au^I].

[$RC_6H_3(NHPPh_2SAu(C_6F_5)_n)_2$] (R = Me, *n* = 1 11 or 3 12; R = H, *n* = 1 13 or 3 14). To a solution of MeC_6H_3-$(NHPPh_2S)_2$-3,4 (0.1 mmol, 0.06 g) or $C_6H_4(NHPPh_2S)_2$-1,2 (0.1 mmol, 0.05 g) in dichloromethane (20 mL) under N_2 $[Au(C_6F_5)(tht)]$ (0.2 mmol; 0.07 g) or $[Au(C_6F_5)_3(tht)]$ (0.2 mmol, 0.17 g) was added. After 1 h of stirring, the reaction mixture was evaporated to *ca*. 5 mL. Addition of hexane (20 mL) led to precipitation of complexes **11**, **12**, **13** and **14** as white solids. Yield: 67 (**11**), 62 (**12**), 80 (**13**), 73% (**14**). Mass spectra: $[M - C_6F_5]^+$ at *m/z* = 1115 (4%, **11**); $[M]^+$ at *m/z* = 1950 (22%, **12**); $[M - C_6F_5]^+$ at *m/z* = 1101 (90%, **13**). Calc. for $C_{43}H_{28}$-$Au_2F_{10}N_2P_2S_2$ (**11**): C, 40.25; H, 2.20; N, 2.15. Found: C, 40.5; H, 2.10; N, 2.15. $C_{67}H_{28}Au_2F_{30}N_2P_2S_2$ (**12**): C, 41.25; H, 1.45; N, 1.45. Found: C, 41.25; H, 1.30; N, 1.4. $C_{21}H_{13}AuF_5NPS$ (**13**): C, 39.75; H, 2.05; N, 2.20. Found: C, 39.45; H, 1.80; N, 2.30. $C_{33}H_{13}AuF_{15}NPS$ (**14**): C, 40.95; H, 1.35; N, 1.45. Found: C, 41.05; H, 1.7; N, 1.45%. ^{31}P-{^1H} NMR ($CDCl_3$): δ (**11**) 59.8 (s) and 59.7 (s); (**12**) 55,7(s) and 54.9 (s); (**13**) 59.9 (s); (**14**) 55.5 (s). ^1H NMR ($CDCl_3$): δ (**11**) 6.56–7.97 [m, 23 H, Ph], 5.92 [d, 1 H, *J*(H-P) = 10.9, NH], 5.76 [d, 1 H, *J*(H-P) = 11.8 Hz, NH] and 2.01 [s, 3 H, CH_3]; (**12**) 6.5–7.86 [m, 23 H, Ph], 5.62 [m, 1 H, NH], 5.47 [m, 1 H, NH] and 1.88 [s, 3 H, CH_3]; (**13**) 6.80–7.90 [m, 24 H, Ph] and 5.90 [d, 2 H, *J*(H-P) = 10.7 Hz, NH]; (**14**) 6.73–8.03 [m, 24 H, Ph] and 5.61 [m, 2 H, NH]. ^{19}F NMR ($CDCl_3$): δ (**11**) −115.39 [m, 4F, F_o], −159.29 [t, 1F, $J(F_p\text{-}F_m)$ = 20.2, F_p], −159.46 [t, 1F, $J(F_p\text{-}F_m)$ = 20.1 Hz, F*p*], −161.99 [m, 2F, F_m] and −162.12 [m, 2F, F_m]; (**12**) −121.63 [m, 8F, F_o], −122.35 [m, 4F, F_o], −156.68 [t, 1F, $J(F_p\text{-}F_m)$ = 20.2, F_p], −156.71 [t, 1F, $J(F_p–F_m)$ = 20.2, F_p], −157.07 [t, 2F, $J(F_p\text{-}F_m)$ = 19.8, F_p], −157.09 [t, 2F, $J(F_p–F_m)$ = 20.2 Hz, F_p], −160.40 [m, 8F, F_m] and −160.93 [m, 4F, F_m]; (**13**) −115.35 [m, 4F, F_o], −159.24 [t, 2F, $J(F_p\text{-}F_m)$ = 20.1 Hz, F_p] and −161.92 [m, 4F, F_m]; (**14**) −121.68 [m, 8F, F_o], −122.36 [m, 4F, F_o], −156.65 [t, 2F, $J(F_p\text{-}F_m)$ = 20.1, F_p], −156.95 [t, 4F, $J(F_p\text{-}F_m)$ = 20.0 Hz, F_p], −160.29 [m, 8F, F_m] and −160.92 [m, 4F, F_m].

[$RC_6H_3(NHPPh_2S)_2Au(C_6F_5)_2$] ClO_4 (R = Me 15 or H 16). To a freshly prepared solution of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ (0.1 mmol) in diethyl ether (20 mL) and under N_2 was added $MeC_6H_3(NHPPh_2S)_2$-3,4 (0.1 mmol, 0.06 g) or C_6H_4-$(NHPPh_2S)_2$-1,2 (0.1 mmol, 0.05 g). After 6 h of stirring a cloudy precipitate was filtered off. Evaporation of the solvent to *ca*. 5mL and addition of 20 mL of hexane led to the precipitation of complexes **15** and **16** as yellow solids. Yield: 74 (**15**), 50% (**16**). Mass spectra: $[M]^+$ at *m/z* = 1085 (17, **15**) and 1071 (15%, **16**). Calc. for $C_{43}H_{28}AuClF_{10}N_2O_4P_2S_2$ (**15**): C, 43.6; H, 2.4; N, 2.35. Found: C, 43.2; H, 2.1; N, 2.2. $C_{42}H_{26}AuClF_{10}$-$N_2O_4P_2S_2$ (**16**): C, 43.05; H, 2.25; N, 2.40. Found: C, 43.25; H, 2.20; N, 2.5%. ^{31}P-{^1H} NMR ($CDCl_3$): δ (**15**) 56.8 (s) and 56.7 (s); (**16**) 56.7(s). ^1H NMR ($CDCl_3$): δ (**15**) 6.91–7.89 [m, 23 H, Ph; 2 H, NH] and 2.26 [s, 3 H, CH_3]; (**16**) 6.38–7.97 [m, 24 H, Ph; 2 H, NH]. ^{19}F NMR ($CDCl_3$): δ (**15**) −121.11 [m, 2F, F_o], −121.45 [m, 2F, F_o], −154.85 [t, 1F, $J(F_p\text{-}F_m)$ = 20.2, F_p], −155.12 [t, 1F, $J(F_p\text{-}F_m)$ = 20.2 Hz, F_p] and −160.04 [m, 4F, F_m]; (**16**) −121.10 [m, 4F, F_o], −154.90 [t, 2F, $J(F_p\text{-}F_m)$ = 20.3 Hz, F_p] and −159.93 [m, 4F, F_m].

[NBu_4][$RC_6H_3(NHPPh_2)(NPPh_2)Au_2(C_6F_5)_n$] (R = Me, *n* = 2 (17); R = H, *n* = 2 (18) or 6 (19)) To a solution of complex **1** (0.1 mmol, 0.12 g), **2** (0.1 mmol, 0.12 g) or **7** (0.1 mmol, 0.2 g) in dichloromethane (20 mL) and under N_2 was added $NBu_4(acac)$ (0.1 mmol, 0.03 g). After 2 min the solutions became yellow, and were stirred for 1 h. Evaporation of the solvents to *ca*. 5 mL and addition of 20 mL of hexane gave complexes **17**–**19** as yellow solids. Yield: 63 (**17**), 56 (**18**), 77% (**19**). Mass spectra: $[M]^-$ at *m/z* = 1217 (40, **17**); 1203 (7, **18**) and 1871(10%, **19**). Calc. for $C_{59}H_{63}Au_2F_{10}N_3P_2{\cdot}C_6H_{14}$ (**17**): C, 50.45; H, 5.0; N, 2.70. Found: C, 49.9; H, 4.95; N, 3.0. $C_{58}H_{61}Au_2F_{10}N_3P_2$ (**18**): C, 48.2; H, 4.25: N, 2.90. Found: C, 48.3; H, 4.5; N, 2.8. $C_{82}H_{61}Au_2F_{30}N_3P_2$ (**19**): C, 46.6; H, 2.90; N, 2.0. Found: C, 46.65; H, 3.0; N, 1.9%. ^{31}P-{^1H} NMR ($CDCl_3$): δ (**17**) 62.7 (m), 59.5 (m); (**18**) 61.6 (m); (**19**) 29.4 [m (298 K), 2P, Ph_2P]; (HDA) 34.6, 17.0 [m (203 K), 2P, PPh_2]. ^1H NMR (anions) ($CDCl_3$): δ (**17**) 7.25–7.96 [m, 23 H, Ph], 6.23 [m, 1 H, NH] and 2.08 [s, 3 H, CH_3]; (**18**) 7.16–7.99 [m, 24 H, Ph] and 6.39 [m, 1 H, NH]; (**19**)

7.18–7.75 [m, 24 H, Ph] and 6.08 [m, 1 H, NH]. ^{19}F NMR ($CDCl_3$): δ (**17**) −115.80 [m, 4F, F_o], −158.71 [t, 1F, $J(F_p\text{-}F_m) = 19.0$, F_p], −159.05 [t, 1F, $J(F_p\text{-}F_m) = 18.4$ Hz, F_p] and −162.27 [m, 4F, F_m]; (**18**) −115.40 [m, 4F, F_o], −160.71 [t, 2F, $J(F_p\text{-}F_m) = 19.3$ Hz, F_p] and −163.26 [m, 4F, F_m]; (**19**) −119.67 [m, 8F, F_o], −120.22 [m, 4F, F_o], −159.84 [t, 2F, $J(F_p\text{-}F_m) = 19.7$, F_p], −160.58 [t, 4F, $J(F_p\text{-}F_m) = 19.7$ Hz, F_p], −162.85 [m, 8F, F_m] and −162.92 [m, 4F, F_m].

$[C_6H_4\{NHPPh_2Au(C_6F_5)_3\}\{N(AuPPh_3)PPh_2Au(C_6F_5)_3\}]$ 20. To a freshly prepared solution (20 mL) of $[Au(ClO_4)(PPh_3)]$ (0.1mmol) in tetrahydrofuran, complex **19** was added (0.1 mmol, 0.21 g) under N_2. The solution became colorless immediately and was stirred for 1 h. Evaporation to dryness and addition of diethyl ether gave a precipitate identified as $[NBu_4]ClO_4$, which was filtered off. The solution was evaporated to *ca*. 5 mL and addition of hexane (20 mL) led to precipitation of complex **20** as a white solid. Yield: 60%. Mass spectrum: $[M - C_6F_5]^+$ at m/z = 2163 (5%). Calc. for $C_{84}H_{40}Au_3F_{30}N_2P_3$: C, 43.3; H, 1.75; N, 1.2. Found: C, 43.3; H, 2.0; N, 1.2%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 48.4 [m, 1P, PPh_2], 47.5 [m, 1P, PPh_2] and 29.7 [m, 1P, PPh_3]. ^{1}H NMR ($CDCl_3$): δ 6.21–7.53 [m, 39 H, Ph] and 5.18 [m, 1 H, NH]. ^{19}F NMR ($CDCl_3$): δ −120.89 [m, 8F, F_o], −121.69 [m, 4F, F_o], −156.23 [t, 2F, $J(F_p\text{-}F_m) = 19.5$, F_p], −157.32 [m, 2F, F*p*], −156.78 [t, 1F, $J(F_p\text{-}F_m) = 20.5$, F_p], −158.04 [t, 1F, $J(F_p\text{-}F_m) = 18.3$ Hz, F_p], −160.23 [m, 4F, F_m] and −161.39 [m, 8F, F_m].

Crystal structure determinations

The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Siemens P4 (**3**, **6**), Stoe-STADI4 (**1**, **4b**), or Siemens SMART (**12**, **20**) diffractometers. Program SHELXL-97 [38] was used for the refinement. Crystallographic data are summarised in Table 8.

Special details of refinement. For all structures, methyl H of tolyl groups were not located. Complex **1** crystallises with half a molecule of hexane, badly resolved across an inversion centre. The NH hydrogens were located in difference syntheses and found to complete planar geometry at nitrogen; they were constrained to this ideal geometry. Complex **3** is a dichloromethane disolvate; the solvent is disordered over two positions. The H atoms bonded to N were not located, but were set geometrically assuming planar geometry at nitrogen. Complex **4** is a dichloromethane tetrasolvate. The NH was treated as for **3**; carbon atoms refined isotropically. Complex **6** crystallises with two hexane molecules, each badly resolved over an inversion centre. The NH were treated as for **3**. Complex **12** crystallises with two molecules of dichloromethane and one of hexane, the latter across an inversion centre. The small crystal provided weak intensity data, in view of which the N and C atoms were refined isotropically. Complex **20** crystallises with two molecules of diisopropyl ether, one of which is disordered (one methyl group at two alternative positions).

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See http://www.rsc.org/suppdata/dt/1999/4009/ for crystallographic files in .cif format.

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References

1 L. Stryer, *in Biochemistry*, 4th edn., Freeman and Company, New York, 1995, chs. 4 and 5.
2 A. I. Basbcum and J. D. Levina, *N. Engl. J. Med.*, 1991, **325**, 326.
3 P. J. Hoskin and G. M. Hanks, *Drugs,* 1991, **41**, 326.
4 A. Manjour, H. Khachaturian, M. E. Lewis, H. Akil and S. J. Watson, *Trends Neurosci.*, 1988, **11**, 308.
5 S. J. Berners-Price, C. K. Mirabelli, R. K. Johnson, M. R. Mattern, F. L. McCabe, L. F. Faucette, C. M. Sung, S. M. Mong, P. J. Sadler and S. T. Crooke, *Cancer Res.*, 1986, **45**, 5486.
6 S. J. Berners-Price, G. R. Girard, D. T. Hill, B. M. Sutton, P. S. Jarret, L. F. Faucette, R. K Johnson, C. K. Mirabelli and P. J. Sadler, *J. Med. Chem.*, 1990, **33**, 1386; S. J. Berners-Price and P. J. Sadler, *Struct. Bonding* (*Berlin*), 1988, **70**, 27.
7 G. D. Hoke, R. A. Macia, P. C. Meunier, P. G. Bugelsky, C. K. Mirabelli, G. F. Rush and W. D. Matthews, *Toxicol. Appl. Pharmacol.*, 1989, **100**, 293.
8 P. J. Sadler and R. E. Sue, *Metal-Based Drugs,* 1994, **1**, 107.
9 S. Carotti, A. Guerri, T. Mazzei, L. Messori, E. Mini and P. Orioli, *Inorg. Chim. Acta*, 1998, **281**, 90.
10 M. C. Gimeno and A. Laguna, *Chem. Rev.*, 1997, **97**, 511.
11 E. J. Fernandez, J. M. Lopez-de Luzuriaga, M. Monge, M. A. Rodriguez, O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *Inorg. Chem.*, 1998, **37**, 6002.
12 O. Crespo, M. C. Gimeno, P. G. Jones, B. Ahrens and A. Laguna, *Inorg. Chem.*, 1997, **36**, 496.
13 R. W. Baker and J. P. Pauling, *J. Chem Soc.*, *Dalton Trans.*, 1972, 2264.
14 P. G. Jones and C. Thöne, *Acta Crystallogr.*, *Sect. C*, 1992, **48**, 1312.
15 O. Crespo, M. C. Gimeno, A. Laguna and M. D. Villacampa, *Acta Crystallogr.*, *Sect. C*, 1998, **54**, 203.
16 S. J. Berners-Price, R. J. Bowen, T. W. Hambley and P. C. Healy, *J. Chem Soc.*, *Dalton Trans.*, 1999, 1337; S. J. Berners-Price, R. J. Bowen, P. J. Harvey, P. C. Healy and G. A. Koutsantonis, *J. Chem Soc.*, *Dalton Trans.*, 1998, 1743.
17 S. I. Berners-Price, M. A. Mazid and P. J. Sadler, *J. Chem Soc.*, *Dalton Trans.*, 1984, 969; P. A. Bates and J. M. Waters, *Inorg. Chim. Acta*, 1984, **81**, 151.
18 O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Inorg. Chem.*, 1994, **33**, 6328.
19 R. C. Elder, E. H. Keller, M. Zieher, M. Onady and R. R. White, *J. Chem. Soc.*, *Chem. Commun.*, 1981, 900.
20 R. Usón, A. Laguna, M. Laguna, E. J. Fernández, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 1971.
21 R. Usón, A. Laguna, M. Laguna and E. J. Fernandez, *Inorg. Chim. Acta*, 1980, **45**, L 177.
22 E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga and M. E. Olmos, *Chem. Ber.*, 1997, **130**, 1513.
23 E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna and J. M. López-de-Luzuriaga, *Organometallics*, 1995, **14**, 2918.
24 J. Stein, J. P. Fackler, Jr., C. Paparizos and H. W. Chen, *J. Am. Chem. Soc.*, 1981, **103**, 2192.
25 E. Cerrada, E. J. Fernandez, M. C. Gimeno, A. Laguna, M. Laguna, R. Terroba and M. D. Villacampa, *J. Organomet. Chem.*, 1995, **492**, 105.
26 G. Bandali, D. A. Clemente, G. Marangoni and L. J. Cattalini, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 886.
27 R. Usón, A. Laguna, M. Laguna, M. L. Castilla, P. G. Jones and C. Fittschen, *J. Chem. Soc. Dalton Trans.*, 1987, 3017.
28 H. Günther, *NMR Spectroscopy, 2nd edn.*, Wiley, New York, 1996, p. 110.
29 T. Q. Ly, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc.*. *Dalton Trans.*, 1997, 1611.
30 P. G. Jones, E. Cerrada, M. C. Gimeno and M. Laguna, *Z. Kristallogr.*, 1994, **209**, 827.
31 J. H. Enmark and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2636.
32 J. M. López-de-Luzuriaga, A. Schier and H. Schmidbaur, *Chem. Ber.*, 1997, **130**, 221.
33 J. M. López-de-Luzuriaga, A. Sladek, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1997, **36**, 966.
34 R. Usón, A. Laguna and M. Laguna, *Inorg. Synth.*, 1989, **26**, 85.
35 R. Usón, A. Laguna, M. Laguna, J. Jiménez, M. P. Gómez, A. Sainz and P. G. Jones, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 3457.
36 R. Usón, A. Laguna and J. Vicente, *J. Chem. Soc.*, *Chem. Commun.*, 1973, 353.
37 R. Usón, A. Laguna and M. L. Arrese, *Synth. React. Inorg. Metal Org. Chem.*, 1984, **14**, 557.
38 G. M. Sheldrick, SHELXL-97, A program for crystal structure refinement, University of Göttingen, 1997.

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