N-Metallation of MS_2N_2 rings. X-ray crystal structures of $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)Au(PPh_3)][ClO_4]$, $[\{(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)Au\}_2(\mu_2\text{-dppm})][ClO_4]_2$ and $[Au(dppeS\text{-}P)Cl]_2$

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Bimetallic complexes $[(\eta^5\text{-}C_5R_5)M(S_2N_2)Au(PPh_3)][ClO_4]$ and tetrametallic species $[\{(\eta^5\text{-}C_5R_5)M(S_2N_2)Au\}_2(\mu_2\text{-P^\wedge P})][ClO_4]_2$ (R = H, M = Co; R = Me, M = Ir; P^P = dppm or dppe) can be prepared by treatment of $[(\eta^5\text{-}C_5R_5)M(S_2N_2)]$ with gold(I) electrophiles generated by chloride abstraction from $[AuCl(PPh_3)]$ or $[(AuCl)_2(\mu_2\text{-P^\wedge P})]$. X-Ray crystallography of $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)Au(PPh_3)][ClO_4]$ and $[\{(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)Au\}_2(\mu_2\text{-dppm})][ClO_4]_2$ confirms auration of the metal-bound nitrogen atom of the MS_2N_2 ring. π-Stacking of theMS_2N_2 rings occurs within both structures.

Introduction

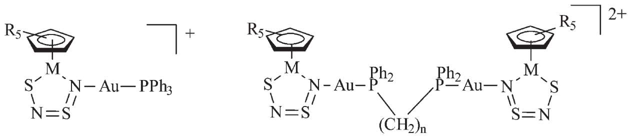
The chemistry of sulfur–nitrogen heterocycle and cage systems has elicited considerable attention from both theoretical and synthetic standpoints. The general development of this fascinating area has been hampered by the paucity of stable and easily handled S–N reagents. Thus, despite its renowned explosive tendencies, tetrasulfur tetranitride (S_4N_4) has been the most commonly used material for the synthesis of binary S–N systems,[1] organic heterocycles[2] and metalla-sulfur–nitrogen complexes.[3,4]

We recently reported the preparation of the tin(IV) disulfurdinitrido complex $[^nBu_2Sn(S_2N_2)]_2$, which shows great promise as a metathesis reagent for the synthesis of ES_2N_2 (E = metal or non-metal) rings.[5,6] For example $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)]$, only the second crystallographically characterised metal cyclopentadienyl S_2N_2 complex, is accessible from $[(\eta^5\text{-}C_5Me_5)IrCl_2(PPh_3)]$ or $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$.[6] Moreover $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)]$ undergoes metallation at the *non metal-bound nitrogen atom* by $[(\eta^5\text{-}C_5Me_5)IrCl(PPh_3)]^+$ to give $[(\eta^5\text{-}C_5Me_5)_2Ir_2(S_2N_2)Cl(PPh_3)]^+$. Conversely, the metal-bound nitrogen atom is the site of protonation in metal–$[S_2N_2H]^-$ complexes[7,8] and of metallation in $[M(S_2N_2)(PPh_3)]_2$ (M = Pt or Pd),[9] $[R_2Sn(S_2N_2)]_2$ (R = ^{n}Bu, Me or ^{t}Bu)[6,10,11] and $[Ph_4P]_2[Ni_3(S_2N_2)_2]$,[12] which contain $M_2(\mu_2\text{-}N)_2$ cores.

Auration of MS_2N_2 rings by gold(I) electrophiles has not been previously reported. In this paper we describe the *N*-metallation of $[(\eta^5\text{-}C_5H_5)Co(S_2N_2)]$ and $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)]$ by cations generated by halide abstraction from gold(I)-chloride precursors, including representative X-ray crystal structures.

Results and discussion

Chloride abstraction from $[AuCl(PPh_3)]$ and $[(AuCl)_2(\mu_2\text{-P^\wedge P})]$ (P^P = dppm or dppe) with silver(I) perchlorate in dichloromethane, followed by addition of stoichiometric quantities of $[(\eta^5\text{-}C_5H_5)Co(S_2N_2)]$ or $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)]$ generated the heterometallic complexes **1**–**6** (Fig. 1) in 24–68% yields, the dppe complexes **5**, **6** being isolated in lowest yields. The air- and moisture- stable complexes are soluble in dichloromethane, thf and acetone. The X-ray crystal structures of $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)Au(PPh_3)][ClO_4]$ and $[\{(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)Au\}_2(\mu_2\text{-dppm})][ClO_4]_2$ (see below) confirm that metallation occurs, as expected, at the more electron-rich metal-bound nitrogen atom. An attempt to metallate both nitrogen centres of $[(\eta^5\text{-}C_5H_5)Co(S_2N_2)]$ with two equivalents of $[Au(PPh_3)]^+$ in dichloromethane led to an intractable mixture of products. FAB$^+$ MS for **1** and **2** contained peaks for $[(arene)M(S_2N_2)Au(PPh_3)]^+$ at *m*/*z* 879 and 675 respectively, but the dicationic complexes **3**–**6** were less straightforward. Peaks at *m*/*z* 813 for **3**, **4** and *m*/*z* 827 for **5**, **6** corresponded to $[Au_2(P^\wedge P)Cl]^+$, with higher mass peaks of weaker intensity for **3**–**5** assigned to $[(P^\wedge P)Au_2Cl(S_2N_2)M(arene)]^+$ (*m*/*z* 1233, 1030 and 1246 respectively). Since elemental analyses and NMR spectroscopy have indisputably established the purity of **1**–**6**, we cannot explain the peculiar mass spectrometric data for **3**–**6**. The IR spectra of the complexes are dominated by bands arising from the phosphine co-ligands and the perchlorate anions (*ca.* 1100, 625 cm^{-1}), bands from the S_2N_2 groups could not be assigned with certainty.



	M	R	n
1	Ir	Me	
2	Co	H	
3	Ir	Me	1
4	Co	H	1
5	Ir	Me	2
6	Co	H	2

Fig. 1 Structures of complexes **1**–**6**.

The crystal structure of **1** (Fig. 2) confirms metallation of the metal-bound nitrogen atom N(1). The IrS_2N_2 ring retains its planarity,[6] the N(1)–Au(1)–P(1) axis is approximately linear

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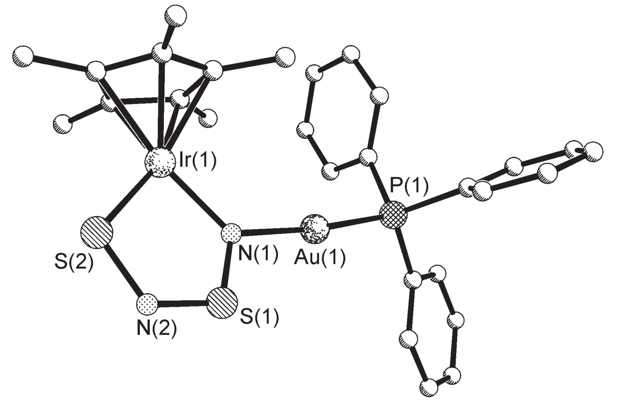

Fig. 2 X-Ray crystal structure of **1** (C–H bonds and perchlorate counterion omitted for clarity). Selected bond lengths (Å) and angles (°) (esd's in parentheses): Au(1)–N(1) 2.059(4), Au(1)–P(1) 2.2400(15), N(1)–S(1) 1.584(4), N(1)–Ir(1) 2.984(4), S(1)–N(2) 1.568(5), N(2)–S(2) 1.664(5), S(2)–Ir(1) 2.2060(15), N(1)–Au(1)–P(1) 173.71(12), S(1)–N(1)–Ir(1) 120.0(3), S(1)–N(1)–Au(1) 115.4(2), Ir(1)–N(1)–Au(1) 124.6(2), N(2)–S(1)–N(1) 110.5(2), S(1)–N(2)–S(2) 116.2(3), N(2)–S(2)–Ir(1) 107.42(18), N(1)–Ir(1)–S(2) 85.81(13).

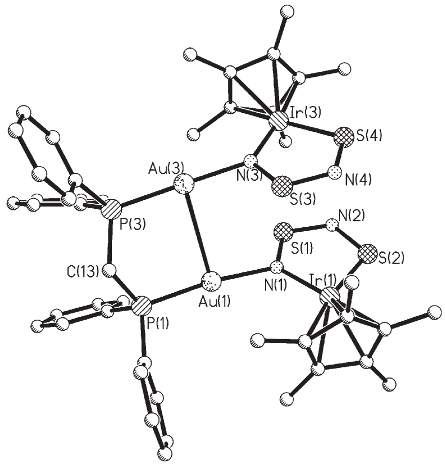

Fig. 3 X-Ray crystal structure of **3**·CH_2Cl_2 (C–H bonds, solvent molecule and perchlorate counterions omitted for clarity).

[173.71(12)°] with Au(1)–N(1) and Au(1)–P(1) distances of 2.059(4) and 2.2400(15) Å respectively. The IrS_2N_2 rings are stacked [interplanar separation *ca.* 3.4 Å] in the manner of other MS_2N_2 structures,[7,13] but intermolecular Au···Au interactions or close cation–anion contacts are absent.

A comparison of metallacycle bond lengths for [(η^5-C_5Me_5)Ir(S_2N_2)], **1** and [(η^5-C_5Me_5)$_2$$Ir_2$($S_2N_2$)Cl($PPh_3$)][$PF_6$] (Table 1), indicates that metallation appears to change the IrS_2N_2 bond lengths and angles in a similar fashion to protonation.[8] The Ir–S(2) distances in **1** is 0.02 Å longer than in [(η^5-C_5Me_5)Ir(S_2N_2)], with N(1)–S(1) *ca.* 0.05–0.07 Å longer in the bimetallic complexes compared to [(η^5-C_5Me_5)Ir(S_2N_2)]. N(2)–S(2) is also lengthened in the binuclear complexes.

The crystal structure of **3**·CH_2Cl_2 shows two [(η^5-C_5Me_5)Ir(S_2N_2)] units linked by [Au_2(μ_2-dppm)]$^{2+}$ (Fig. 3), selected bond lengths and angles appearing in Table 2. The two N–Au–P axes [N(1)–P(1)–Au(1) 172.1(3)°, N(3)–Au(3)–P(3) 174.9(2)°] are parallel, the IrS_2N_2 rings adopting a head-to-tail stacking arrangement with respect to one another. The Au(1)–Au(3) distance [3.1931(9) Å] is slightly longer than generally found for digold(I) complexes containing a bridging diphosphine ligand [2.576–3.173 Å].[14–22] The molecular conformation enforced by the Au···Au interaction results in a rare intramolecular example of MS_2N_2 ring π-stacking, the N(1)···N(3) and S(2)···S(4) distances being 3.56 and 3.90 Å respectively, additionally the face-to-face phenyl rings have an interplanar separation of 3.77 Å. There is one short Au···O interaction with a perchlorate anion [Au(1)···O(2) 3.31 Å], but no significant intercation contacts. Compound **3** represents an interesting oligomer or building subunit for polymeric M–S–N organometallic chains.

We have demonstrated that [^{n}Bu_2Sn(S_2N_2)]$_2$ can form MS_2N_2 chelate rings by metathetical exchange of *cis*-chloride ligands from a metal centre;[5,6] we were intrigued as to whether the gold(I) centres of [(AuCl)$_2$(μ_2-P^P)] (P^P = dppm or dppe) could be linked with an [S_2N_2]$^{2-}$ unit to give nine- or ten-membered rings. To this end, [^{n}Bu_2Sn(S_2N_2)]$_2$ and [(AuCl)$_2$(μ_2-P^P)] (1 : 1 molar ratio) were refluxed together in thf for four hours. ^{31}P{^{1}H} NMR spectra of crude reaction mixtures contained one major component, characterised by two doublets (J_{PP} 16 Hz for dppm, 63 Hz for dppe) and several weaker singlets. Gel permeation chromatography (Biobeads SX-8, dichloromethane eluant) enabled purification of the mixtures, monitored by ^{31}P{^{1}H} NMR spectroscopy of 1 cm^3 fractions collected prior to, and including, the yellow eluate. Fractions whose ^{31}P{^{1}H} NMR spectra did not contain doublets were not studied further. For the dppe complex, colourless crystals were grown from dichloromethane–hexane by solvent diffusion. X-Ray crystallography revealed, unexpectedly, a dimeric structure [Au(dppeS-*P*)Cl]$_2$ (Fig. 4) *i.e.* one AuCl unit had been abstracted from [(AuCl)$_2$(μ_2-dppe)] and the uncoordinated phosphorus(III) centre converted into the phosphorus(V) sulfide by reaction with [S_2N_2]$^{2-}$, two such [Au(dppeS-*P*)Cl] units being linked by an Au–Au interaction. The structure of [Au(dppeS-*P*)Cl]$_2$ contains approximately linear P–Au–Cl units [P(1)–Au(1)–Cl(1) 174.93(8)°, P(3)–Au(2)–Cl(2) 172.69(8)°] whose axes are *gauche* to one another [P(1)–Au(1)–Au(2)–Cl(2) −58°, P(3)–Au(2)–Au(1)–Cl(1) −62°]. The Au(1)–Au(2) separation [3.2626(5) Å] is at the upper limit of the range observed for unsupported (*i.e.* without bridging ligands) Au(I)–Au(I) contacts [3.031(1)–3.264(2) Å].[24–31] FAB$^+$ MS for the dppm and dppe complexes contained strong peaks at *m*/*z* 613 and 627 respectively for [Au(P^PS)]$^+$.

Table 1 A comparison of metallacycle bond lengths in [(η^5-C_5Me_5)Ir(S_2N_2)], **1** and [(η^5-C_5Me_5)$_2$$Ir_2$($S_2N_2$)Cl($PPh_3$)][$PF_6$].[a]

	[(η^5-C_5Me_5)Ir(S_2N_2)]	**1**	[(η^5-C_5Me_5)$_2$$Ir_2$ (S_2N_2)Cl(PPh_3)]$^+$
Ir–N(1)	1.962(6)	1.983(4)	1.961(1)
Ir–S(2)	2.175(2)	2.206(1)	2.179(2)
N(1)–S(1)	1.509(7)	1.584(4)	1.558(10)
S(1)–N(2)	1.563(9)	1.568(4)	1.531(9)
N(2)–S(2)	1.632(8)	1.664(4)	1.685(9)

[a] N(1) and S(2) are the metal-bound atoms of the [S_2N_2]$^{2-}$ chain

In conclusion, metallation of [(η^5-C_5H_5)Co(S_2N_2)] and [(η^5-C_5Me_5)Ir(S_2N_2)] by gold(I) electrophiles takes place at the more electron-rich metal-bound nitrogen atom; we have obtained bimetallic and tetrametallic complexes. X-Ray crystallography reveals that the metallacycle experiences some distortion upon *N*-metallation but planarity of the MS_2N_2 ring is retained. Furthermore, intramolecular π-stacking of the MS_2N_2 rings occurs in the tetrametallic systems.

Experimental

Reactions were conducted under dinitrogen, subsequent procedures were performed in air. Dichloromethane was dried and distilled from calcium hydride prior to use, all other solvents and reagents were used as received. [(η^5-C_5Me_5)Ir(S_2N_2)] and [(η^5-C_5H_5)Co(S_2N_2)] were prepared by literature methods,[6,23] chlorogold(I)–phosphine complexes were prepared by treating

Table 2 Selected bond lengths (Å) and angles (°) for **3**.CH_2Cl_2 (esd's in parentheses)

N(1)–S(1)	1.584(9)	N(3)–S(3)	1.608(8)
N(1)–Ir(1)	1.983(8)	N(3)–Ir(3)	1.984(8)
N(1)–Au(1)	2.066(7)	N(3)–Au(3)	2.057(7)
Ir(1)–S(2)	2.184(3)	Ir(3)–S(4)	2.203(3)
S(2)–N(2)	1.664(9)	N(4)–S(4)	1.668(9)
N(2)–S(1)	1.561(9)	N(4)–S(3)	1.563(8)
Au(1)–P(1)	2.252(3)	Au(3)–P(3)	2.249(3)
S(1)–N(1)–Ir(1)	119.8(4)	S(3)–N(3)–Ir(3)	119.7(4)
S(1)–N(1)–Au(1)	115.4(4)	S(3)–N(3)–Au(3)	110.8(4)
Ir(1)–N(1)–Au(1)	124.8(4)	Ir(3)–N(3)–Au(3)	129.3(4)
N(1)–Ir(1)–S(2)	86.1(2)	N(3)–Ir(3)–S(4)	85.8(2)
N(2)–S(2)–Ir(1)	107.6(3)	N(4)–S(4)–Ir(3)	107.9(3)
S(1)–N(2)–S(2)	116.3(5)	S(3)–N(4)–S(4)	116.1(5)
N(2)–S(1)–N(1)	110.2(4)	N(4)–S(3)–N(3)	110.4(5)
N(1)–Au(1)–P(1)	172.1(2)	N(3)–Au(3)–P(3)	174.9(2)
N(1)–Au(1)–Au(3)	97.2(2)	N(3)–Au(3)–N(1)	92.9(2)
P(1)–Au(1)–Au(3)	88.45(7)	Au(3)–Au(1)–P(1)	88.13(7)

[AuCl(tht)] (tht = tetrahydrothiophen) with stoichiometric quantities of the phosphine in dichloromethane. $^{31}P\{^1H\}$ and ^1H NMR spectra (109.4 and 270.0 MHz respectively, d_2-dichloromethane) were recorded on a JEOL GSX 270 spectrometer, FAB$^+$ mass spectra (3-nitrobenzyl alcohol matrix) were carried out by the EPSRC National Mass Spectrometry Service Centre (Swansea).

CAUTION! Perchlorate salts are potentially explosive and should be handled with care.

The general procedure employed is illustrated for **3**.

To $[(AuCl)_2(\mu_2\text{-dppm})]$ (41 mg, 0.05 mmol) in dichloromethane (5 cm^3) was added silver(I) perchlorate (21 mg, 0.1 mmol) and the solution stirred in the dark for 1.5 h. $[(\eta^5\text{-}C_5Me_5)Ir(S_2N_2)]$ (42 mg, 0.1 mmol) was added as a solid in one portion and the mixture stirred for 18 h in the dark. The grey-black mixture was filtered through Celite, which was washed further with dichloromethane (20 cm^3). The filtrate was concentrated to *ca.* 1 cm^3, vapour diffusion of diethyl ether into this solution afforded 54 mg (59%) of **3** as red crystals. Complexes **5**, **6** were crystallised from dichloromethane–diethyl ether by solvent diffusion.

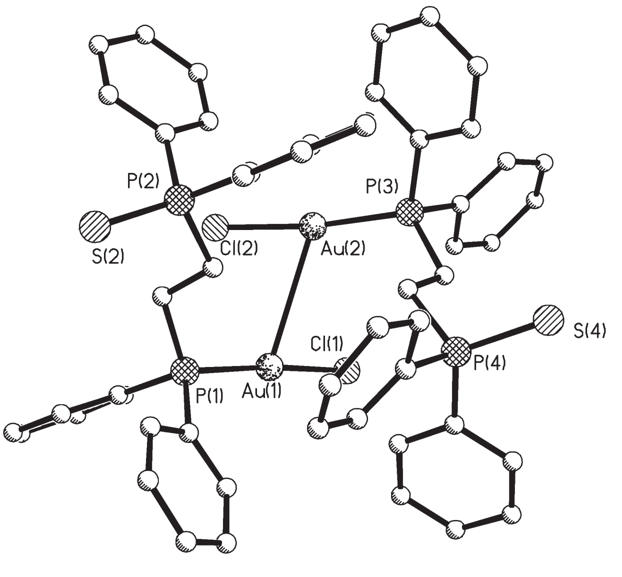

Fig. 4 X-Ray crystal structure of $[Au(dppeS\text{-}P)Cl]_2$(C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°) (esd's in parentheses): Au(1)–P(1) 2.245(2), Au(1)–Cl(1) 2.292(2), Au(1)–Au(2) 3.2626(5), S(2)–P(2) 1.958(3), Au(2)–P(3) 2.2359(19), Au(2)–Cl(2) 2.2974(17), S(4)–P(4) 1.961(3), P(1)–Au(1)–Cl(1) 174.93(8), P(1)–Au(1)–Au(2) 108.71(6), Cl(1)–Au(1)–Au(2) 75.86(6), P(3)–Au(2)–Cl(2) 172.69(8), P(3)–Au(2)–Au(1) 110.80(5), Cl(2)–Au(2)–Au(1) 76.11(5).

1 Red crystals, yield 34%. Found (calc. for $C_{28}H_{30}AuClIrN_2O_4PS_2$): C 34.2 (34.3), H 2.7 (3.1), N 2.7 (2.9)%. δ_P: 31.7 (s). δ_H: 7.70–7.57 (m, 18H, Ph), 1.51 (s, 15H, C_5Me_5). FAB$^+$ MS: m/z 879, $[M^+ - ClO_4]$.

2 Purple crystals, yield 68%. Found (calc. for $C_{23}H_{20}AuClCoN_2O_4PS_2$): C 35.8 (35.6), H 2.45 (2.6), N 3.6 (3.6)%. δ_P: 30.0 (s). δ_H: 7.80–7.61 (m, 18H, Ph), 6.01 (s, 5H, C_5H_5). FAB$^+$ MS: m/z 675, $[M^+ - ClO_4]$.

3 Red crystals, yield 59%. Found (calc. for $C_{45}H_{52}Au_2Cl_2Ir_2N_4O_8P_2S_4$): C 29.8 (29.8), H 2.5 (2.9), N 2.8 (3.1)%. δ_P: 26.8 (s). δ_H: 7.70–7.44 (m, 20H, Ph), 4.43 (t, 2H, J = 15 Hz, CH_2), 2.04 (s, 30H, C_5Me_5). FAB$^+$ MS: m/z, 813 $[Au_2(dppm)Cl]^+$, 1233 $[Au_2(dppm)Cl(S_2N_2)Ir(C_5Me_5)]^+$.

4 Purple crystals, yield 60%. Found (calc. for $C_{35}H_{32}Au_2Cl_2Co_2N_4O_8P_2S_4$): C 29.8 (29.8), H 2.2 (2.3), N 3.7 (4.0)%. δ_P: 26.4 (s). δ_H: 7.90 (m, 8H, Ph), 7.51 (m, 12H, Ph), 5.86 (s, 1H, C_5H_5), 4.50 (t, 2H, J = 13 Hz, CH_2). FAB$^+$ MS: m/z 813 $[Au_2(dppm)Cl]^+$, 1030 $[Au_2(dppm)Cl(S_2N_2)Co(C_5H_5)]^+$.

5 Red blocks, yield 24%. Found (calc. for $C_{46}H_{52}Au_2Cl_2Ir_2N_4O_8P_2S_4$): C 31.05 (30.18), H 2.40 (2.97), N 2.89 (3.06)%. δ_P: 27.5 (s). δ_H: 7.73–7.47 (m, 20H, Ph), 3.22 (d, 4H, J = 6 Hz, CH_2), 2.01 (s, 30H, C_5Me_5). FAB$^+$ MS: m/z 827 $[Au_2(dppe)Cl]^+$, 1246 $[Au_2(dppe)Cl(S_2N_2)Ir(C_5Me_5)]^+$.

6 Purple crystals, yield 24%. Found (calc. for $C_{36}H_{34}Au_2Cl_2Co_2N_4O_8P_2S_4$): C 30.24 (30.38), H 2.32 (2.41), N 3.43 (3.94)%. δ_P: 28.7 (s). δ_H: 7.86 (m, 8H, Ph), 7.54 (m, 12H, Ph), 6.04 (s, 10H, C_5H_5), 3.29 (s, 4H, CH_2). FAB$^+$ MS: m/z 827 $[Au_2(dppe)Cl]^+$.

Reaction between $[(AuCl)_2(\mu_2\text{-}P\char`^P)]$ *and* $[^nBu_2Sn(S_2N_2)]_2$; $[(AuCl)_2(\mu_2\text{-}P\char`^P)]$ (0.17 mmol) and $[^nBu_2Sn(S_2N_2)]_2$ (0.17 mmol) were refluxed in thf (8 cm^3) for four hours. The solvent was evaporated *in vacuo*, the products extracted into dichloromethane (2 cm^3) and purified by gel permeation chromatography (Biobeads SX-8, dichloromethane eluant), 1 cm^3 fractions collected prior to, and including, the yellow eluate were monitored by $^{31}P(^1H)$ NMR spectroscopy. Fractions giving singlets in their $^{31}P\{^1H\}$ NMR spectra were discarded, those containing a pair of doublets were combined. From the reaction using $[(AuCl)_2(\mu_2\text{-dppe})]$, colourless needles of $[Au(dppeS\text{-}P)Cl]_2$ were grown by layering dichloromethane solutions of the appropriate fractions with hexane.

$\mathbf{[Au(dppmS\text{-}P)Cl]_2}$ δ_P: 36.7 (d, J = 16), 16.9 (d, J = 16 Hz). FAB$^+$ MS: m/z 613, $[Au(dppmS)]^+$.

$\mathbf{[Au(dppeS\text{-}P)Cl]_2}$ δ_P: 43.9 (d, J = 63), 32.5 (d, J = 63 Hz). FAB$^+$ MS: m/z 627, $[Au(dppeS)]^+$.

X-ray crystallography

Single crystal diffraction studies on **1**, **3**·CH_2Cl_2 and $[Au(dppeS\text{-}P)Cl]_2$ were performed on a Bruker SMART CCD diffractometer at 125 K with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Details of data collections and structural refinements are given in Table 3. The structures were solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms bound to carbon were idealised and fixed (C–H 0.95 Å). Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL.[32] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Database Centre.†

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† CCDC reference numbers 213795–213798. See http://www.rsc.org/suppdata/nj/b3/b306847a/ for crystallographic data in .cif or other electronic format.

Table 3 Details of X-ray data collections and structural refinements for **1**, **3**.CH_2Cl_2 and **[Au(dppeS-*P*)Cl]$_2$**

	1	**3**.CH_2Cl_2	[Au(dppeS-*P*)Cl]$_2$
Empirical Formula	$C_{28}H_{30}AuClIrN_2O_4PS_2$	$C_{46}H_{54}Au_2Cl_4Ir_2N_4O_8P_2S_4$	$C_{52}H_{48}Au_2Cl_2P_4S_2$
M	978.25	1901.24	1325.74
T/K	125(2)	125(2)	125(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2(1)/c$	$Pca2(1)$	$P\bar{1}$
a/Å	13.0057(17)	32.363(8)	11.0993(8)
b/Å	11.2301(15)	10.367(3)	13.0681(10)
c/Å	21.098(3)	16.838(4)	19.3948(14)
α/°	90	90	84.735(1)
β/°	98.213(2)	90	76.483(1)
γ/°	90	90	64.900(1)
U/Å^3, Z	3049.9(7), 4	5649(3), 4	2476.9(3), 2
D_c/Mg m^{-3}	2.130	2.235	1.778
μ/mm^{-1}	9.477	10.321	6.273
F(000)	1856	3584	1288
Crystal size/mm	0.1 × 0.1 × 0.1	0.25 × 0.15 × 0.06	0.18 × 0.1 × 0.1
θ range/°	1.58–23.29	1.96–23.33	2.02–23.36
Reflections collected	14 834	23 332	12 636
Independent reflections (R_{int})	4361 (0.0470)	7349 (0.0473)	7038 (0.0410)
Goodness-of-fit on F^2	0.955	0.952	0.900
$R1$, $wR2$	0.0233, 0.0464	0.0259, 0.0632	0.0364, 0.0713

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