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# THE SYNTHESIS OF PALLADIUM-GOLD AND PLATINUM-GOLD BIMETALLIC COMPLEXES BASED UPON BIS(DIPHENYLARSINO)METHANE: CRYSTAL STRUCTURE OF *TRANS*-[Pd(μ-Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>AuCl)<sub>2</sub>Cl<sub>2</sub>] · xCH<sub>2</sub>Cl<sub>2</sub>

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Abstract—The reaction of trans-[M( $\eta^1$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] (M = Pd or Pt) with Au(tht)Cl (tht = tetrahydrothiophen) formed trans-[M( $\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>AuCl)<sub>2</sub>Cl<sub>2</sub>], from which the corresponding bromides were made by reaction with LiBr. Oxidative addition of the appropriate dihalogen formed trans-[M( $\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>AuX<sub>3</sub>)<sub>2</sub>X<sub>n</sub>] (M = Pd, n = 2; M = Pt, n = 4). The structure of the complex trans-[Pd( $\mu$ -Ph<sub>2</sub>As CH<sub>2</sub>AsPh<sub>2</sub>AuCl)<sub>2</sub>Cl<sub>2</sub>] • xCH<sub>2</sub>Cl<sub>2</sub> has been determined and shown to contain trans square planar palladium atoms [Pd—Cl 2.291 (av), Pd—As 2.416(2), 2.400(2) Å]. Each bis(diphenylarsino)methane ligand coordinates to palladium and gold [As—Au 2.331(2), 2.340(2) Å], but there are no significant Pd···Au interactions. The ligand Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub> formed only insoluble, probably polymeric, 1 : 1 complexes [{MCl<sub>2</sub>(Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub>)<sub>n</sub>], whilst reaction of [PdCl<sub>2</sub>(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)<sub>2</sub>] with [Au(tht)Cl] produced [PdCl<sub>2</sub> (Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)]<sub>2</sub> and [ClAu(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)AuCl].

The syntheses of homo- and heteronuclear bimetallic complexes using methylene backboned phosphine ligands such as  $Ph_2PCH_2PPh_2$  (dppm) or  $Ph_2PCH_2P(Ph)CH_2PPh_2$  have been extensively studied.<sup>1-3</sup> Our current interest is in the production of hetero-bimetallic complexes containing soft metals as catalyst precursors, and we have reported elsewhere<sup>4</sup> studies of palladium and platinum complexes of the group 16 ligands RECH<sub>2</sub>ER (R = Me or Ph, E = S, Se or Te). These complexes are too labile to form bimetallic species conveniently, and hence we have examined the ligands  $Ph_2As$  $CH_2AsPh_2$  (dpam) and  $Ph_2SbCH_2SbPh_2$  (dpsbm), and report the results below.

## **RESULTS AND DISCUSSION**

Bis(diphenylphosphino)methane (dppm) is known to preferentially chelate to  $Pd^{II}$  and  $Pt^{II}$ 

complexes such as  $[M(dppm)Cl_2]$ in and  $[M(dppm)_2]Cl_2^{1,2,5}$  (M = Pd or Pt), although with strong binding co-ligands such as  $\sigma$ -C<sub>6</sub>F<sub>5</sub><sup>6</sup> or C = CR,<sup>5</sup> the  $\eta^1$  coordination mode is found as in  $[M(\eta^1-dppm)_2R_2]$  (R = C<sub>6</sub>F<sub>5</sub> or C=CR). These complexes have been used to construct bimetallics by binding a second metal to the uncoordinated ---PPh<sub>2</sub> group in the  $\eta^1$ -dppm. For our purposes the presence of "exotic" groups such as acetylides or perfluoroaryls was undesirable, and hence we replaced dppm by the heavier analogues dpam and dpsbm, in which the larger donor atoms significantly increase the ring strain on chelation and hence favour the  $\eta^1$  bonding mode.<sup>7,8</sup>

The reaction of M(MeCN)<sub>2</sub>Cl<sub>2</sub> (M = Pd or Pt) with dpam in acetonitrile in a 1:2 ratio afforded the complex [M(dpam)<sub>2</sub>Cl<sub>2</sub>]. The platinum complex has been described previously,<sup>7</sup> and formulated as a *trans* isomer on the basis of the far-IR spectrum. The <sup>195</sup>Pt NMR shift at  $\delta$  -3659 confirms the geometry as *trans*, since *cis* PtAs<sub>2</sub>Cl<sub>2</sub> donor sets resonate at substantially lower frequencies.<sup>9</sup>

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 $[Pd(dpam)_2Cl_2]$  exhibits v(Pd-Cl) at 354 cm<sup>-1</sup>, consistent with a trans geometry in this case also. Treatment of the [M(dpam)<sub>2</sub>Cl<sub>2</sub>] complexes with two equivalents of [Au(tht)Cl] (tht = tetrahydrothiophen) in  $CH_2Cl_2$  produced yellow solids which contained M, gold, arsenic and chlorine by EDX, and had analyses consistent with the formula [M(dpam)<sub>2</sub>Au<sub>2</sub>Cl<sub>4</sub>]. The <sup>1</sup>H NMR spectra of these complexes revealed the absence of tht, and that the  $\delta(CH_2)$  resonances of the dpam ligand had shifted to high frequency by  $\geq 0.6$  ppm. The v(M-Cl) vibrations, and in the platinum case the <sup>195</sup>Pt chemical shift, were only slightly different from those of the starting materials. Overall, this suggests that the gold has bound to the uncoordinated -AsPh<sub>2</sub> groups with no major change at the M centres, and that a probable formulation is  $[M(\mu$ dpamAuCl)<sub>2</sub>Cl<sub>2</sub>]. This was confirmed by an X-ray study of the palladium-gold complex.

The crystal structure of trans-[Pd( $\mu$ -Ph<sub>2</sub>As CH<sub>2</sub>AsPh<sub>2</sub>AuCl)<sub>2</sub>Cl<sub>2</sub>] · xCH<sub>2</sub>Cl<sub>2</sub> consists of discrete molecules with the unit cell containing two very similar but crystallographically distinct molecules. Each molecule is centrosymmetric, with a palladium atom positioned on the centre of symmetry and with a *trans* square planar coordination geometry (Fig. 1 and Table 1). Bis(diphenylarsino)methane (dpam) has been characterized crystallographically a number of times and several coordination modes have been established. In the present example, one arsenic atom coordinates to Pd<sup>II</sup> and the other to Au<sup>I</sup>, but with a Pd···Au distance [3.56 (av) Å] too long to be



Fig. 1. View of molecule 2 showing the atom labelling scheme. Thermal ellipsoids are drawn at the 35% probability level and hydrogen atoms are omitted for clarity. Molecule 1 has a similar geometry and a related numbering scheme.

regarded as a significant interaction. In the same vein, the Pd $\cdots$ Cl(Au) distance (>3.6 Å) means that the palladium is in a clear cut square planar coordination geometry. The Pd-As distances [2.416(2), 2.400(2) Å] are in good agreement with a much earlier study<sup>10</sup> of [Pd(dpam)Cl]<sub>2</sub>CO (2.40-2.46 Å) and the Pd-Cl distances [2.291 (av) Å] may be compared to that, for example, in  $(NH_4)_2$ [PdCl<sub>4</sub>] [2.299(4) Å].<sup>11</sup> The As—Au distances [2.331(2), 2.340(2) Å] are shorter than those found<sup>12</sup> in the Au<sup>III</sup> species [{ $R_3Au(dpam)$ } Ag(OClO<sub>3</sub>)] (R = C<sub>6</sub>F<sub>5</sub>) [2.457(2), 2.469(2) Å] and similar to that in [Ph3AsAuBr] [2.342(5) Å].<sup>13</sup> The ligand geometry is unexceptional, with one of the phenyl groups showing some disorder as evidenced by the thermal parameters, and the crystal contains methylene chloride of solvation, which showed a partial occupancy of 0.17(2). As found in other systems with coordinated Au-Cl, the As—Au—Cl angle is close to linear.

The  $[M(\mu-dpamAuCl)_2Cl_2]$  complexes are stable in solution in chlorinated solvents, and reaction with LiBr in refluxing ethanol converts them to the corresponding bimetallic bromides, which are assigned a similar structure on the basis of the spectroscopic data (Experimental section). Treatment of  $[Pt(\mu-dpamAuX)_2X_2]$  (X = Cl or Br) in CH<sub>2</sub>Cl<sub>2</sub> solution with a small excess of the corresponding dihalogen in CCl<sub>4</sub> resulted in precipitation of deep yellow (X = Cl) or orange (X = Br) solids, which analysed as  $[Pt(\mu-dpamAuX_3)_2X_4]$ , corresponding to oxidation of both metal centres. The <sup>195</sup>Pt NMR spectrum of the bromocomplex in CH<sub>2</sub>Cl<sub>2</sub> showed a single resonance at  $\delta$  – 3147, consistent with Pt<sup>IV</sup>, but the dark orange solution paled rapidly and a new resonance at  $\delta - 4075$  appeared and the Pt<sup>IV</sup> resonance disappeared. The new resonance was in the region expected for a Pt<sup>II</sup> complex, but differed from that of either  $[Pt(\mu-dpamAuBr)_2Br_2]$  or  $[Pt(\eta^{1}$ dpam)<sub>2</sub>Br<sub>2</sub>], and is tentatively assigned to [Pt( $\mu$ dpamAuBr<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>], the product of reductive elimination at the platinum, with the gold centre remaining as  $Au^{III}$ . The corresponding [Pt( $\mu$ dpamAuCl<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>] had a <sup>195</sup>Pt NMR resonance at  $\delta - 2286$ , and the decomposition product  $[Pt(\mu-dpamAuCl_3)_2Cl_2]$  had a signal at  $\delta-3335$ . On further standing, this solution also developed a resonance at  $\delta$ -1615 attributable to [PtCl<sub>4</sub>]<sup>2-</sup>. Addition of dihalogen in CCl<sub>4</sub> to CH<sub>2</sub>Cl<sub>2</sub> solutions of  $[Pd(\mu-dpamAuX)_2X_2]$  produced yellow materials which we formulate as  $[Pd(\mu-dpamAuX_3)_2X_2]$ , where the palladium remains as Pd<sup>11</sup>, but the gold has oxidized to Au<sup>III</sup>. The UV-vis spectra consist of several overlapping bands with poorly defined maxima, but by comparison with the spectra of the Pd<sup>II</sup>-Au<sup>I</sup> starting materials, new absorptions were

Molecule 1		Molecule 2		
Pd(1)-Cl(11) 2.289(5)		Pd(2)-Cl(21)	2.293(5)	
Pd(1)—As(11) 2.416(2)		Pd(2)As(21)	2.400(2)	
Au(1)—As(12) 2.331(2)		Au(2)—As(22)	2.340(2)	
Au(1)-Cl(12) 2.260(5)		Au(2)Cl(22)	2.267(5)	
As(11) - C(1) = 1.94(2)		As(21) - C(2)	1.97(2)	
As(11) - C(11) = 1.97(2)		As(21)C(51)	1.94(2)	
As(11) - C(21) = 1.91(2)		As(21)C(61)	1.95(2)	
As(12) - C(1) = 1.91(2)		As(22) - C(2)	1.94(2)	
As(12)—C(31) 1.93(2)		As(22)—C(71)	1.92(2)	
As(12) - C(41) = 1.90(2)		As(22)C(81)	1.93(2)	
$As(11) \cdots As(12) = 3.233$		$As(21) \cdots As(22)$	3.192	
$Pd(1) \cdots Au(1) = 3.636$		$Pd(2)\cdots Au(2)$	3.494	
C—C (phenyl) min. 1.3	1(3)	max. 1.53(4)		
Cl(11)Pd(1)As(11)	91.8(1)	Cl(21)— $Pd(2)$ — $A$	as(21)	90.8(1)
Cl(12)— $Au(1)$ — $As(12)$	176.8(2)	Cl(22)—Au(2)—A	As(22)	175.0(2)
Pd(1) - As(11) - C(1)	114.9(6)	Pd(2)-As(21)-C	C(2)	112.6(6)
Pd(1) - As(11) - C(11)	117.0(6)	Pd(2)-As(21)-C	C(51)	115.4(5)
Pd(1) - As(11) - C(21)	116.5(6)	Pd(2)—As(21)—C	C(61)	118.2(6)
Au(1) - As(12) - C(1)	111.9(6)	Au(2)As(22)	C(2)	117.9(6)
Au(1) - As(12) - C(31)	110.2(6)	Au(2)—As(22)—4	C(71)	114.6(6)
Au(1) - As(12) - C(41)	115.9(6)	Au(2)—As(22)—4	C(81)	110.8(6)
C(1)— $As(11)$ — $C(11)$	102.6(8)	C(2)—As(21)—C	(51)	104.0(8)
C(1)— $As(11)$ — $C(21)$	100.6(8)	C(2)As(21)C	(61)	101.6(8)
C(11)— $As(11)$ — $C(21)$	103.0(8)	C(51)-As(21)-C	C(61)	103.1(8)
C(1) $As(12)$ $C(31)$	106.4(9)	C(2)As(22)C	(71)	106.6(8)
C(1)— $As(12)$ — $C(41)$	105.4(9)	C(2) - As(22) - C	(81)	101.2(8)
C(31)— $As(12)$ — $C(41)$	106.5(9)	C(71)—As(22)—O	C(81)	104.2(8)
As(11) - C(1) - As(12)	114(1)	As(21)-C(2)-A	s(22)	110(1)
CC (phenyl)	min. 111(3)	max. 126(3)		

Table 1. Selected bond lengths (Å) and angles (°)

identified at *ca* 30,000 (X = Cl) or *ca* 25,000 (X = Br) cm<sup>-1</sup>, regions where [AuX<sub>3</sub>(AsR<sub>3</sub>)] complexes absorb.<sup>14</sup> The spectra lack absorptions at lower energy ( $\ge ca$  20,000 cm<sup>-1</sup>) reported for Pd<sup>TV</sup> complexes of type [Pd(AsR<sub>3</sub>)<sub>2</sub>X<sub>4</sub>].<sup>15</sup> The latter are highly unstable deep orange-red complexes, and few have been obtained in a pure state.<sup>15</sup> Our failure to convert the Pd<sup>TI</sup> centres to Pd<sup>TV</sup> is not particularly surprising, and even in the platinum analogues the Pt<sup>TV</sup> centres readily reductively eliminate X<sub>2</sub> in solution.

In marked contrast to dpam or Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub>,<sup>2</sup> the coordination chemistry of the ligand Me<sub>2</sub>As CH<sub>2</sub>AsMe<sub>2</sub> has not been investigated. We found that reaction of Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub> with MCl<sub>2</sub> (MeCN)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> gave only 1:1 complexes {MCl<sub>2</sub>(Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub>)}<sub>n</sub>, which were insoluble in common organic solvents. The tentative identification of two  $\nu$ (M—Cl) stretching modes in the far-IR spectrum of each complex suggests the chlorines are *cis*, but whether the complexes are mono-, di- or polymeric is unclear. The corresponding  $\{PtCl_2(Me_2PCH_2PMe_2)\}_n$  is also insoluble in common solvents, and is thought<sup>16</sup> to be a *cis*-diphosphine-bridged dimer. dithioether The and diselencether complexes  $\{M(MeECH_2EMe)Cl_2\}_{\mu}$  $(E = S \text{ or } Se)^4$  (but not the corresponding ditelluroether complexes) dissolve in chlorocarbons in the presence of excess MeECH<sub>2</sub>EMe to give  $[MCl_2(\eta^1-MeECH_2EMe)_2]$ . However, no reaction occurred between the  $\{MCl_2(Me_2AsCH_2AsMe_2)\}_n$ and excess Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub>. The difference between dpam and Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub> is consistent with the expected greater donor ability of Me<sub>2</sub>As groups which, combined with the insolubility of the 1:1 complexes, disfavour the formation of  $\eta^{1}$ coordinated Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub> complexes.

The palladium ditertiary stibine complex  $[Pd(dpsbm)_2Cl_2]$ , which is probably a *cis* isomer on the basis of its far-IR spectrum,<sup>8</sup> was treated with [Au(tht)Cl], resulting in a red-brown solid. However, this contained gold, antimony and chlor-

ine but no palladium (EDX data) and was identified<sup>8</sup> as ClAu(dpsbm)AuCl by comparison with a sample prepared directly from Au(tht)Cl and dpsbm in CH<sub>2</sub>Cl<sub>2</sub>. The palladium product from this reaction was identified by chemical analysis as  $[Pd(dpsbm)Cl_2]_2$ .<sup>8</sup> Hence, in the case of dpsbm, the gold reagent abstracts one dpsbm ligand in preference to forming a bimetallic complex.

#### **EXPERIMENTAL**

Physical measurements were made as described previously.<sup>4</sup>

#### Preparations and characterizations

Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>. A solution of Ph<sub>2</sub>As CH<sub>2</sub>AsPh<sub>2</sub> (1.92 g, 4.1 mmol) in MeCN (10 cm<sup>3</sup>) was added to PdCl<sub>2</sub>(MeCN)<sub>2</sub> (0.52 g, 2.0 mmol) suspended in MeCN (30 cm<sup>3</sup>). The mixture was refluxed for 5 h. The yellow precipitate that formed was filtered off and rinsed with MeCN (10 cm<sup>3</sup>). The crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>. Yield 0.20 g (89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) :  $\delta$  3.15 (CH<sub>2</sub>), 7.0–7.6 (phenyl).  $\nu$ (Pd—Cl) = 354 cm<sup>-1</sup>.  $E_{max}/10^3$  cm<sup>-1</sup> ( $\epsilon$  mol/mol<sup>-1</sup>cm<sup>-1</sup> dm<sup>3</sup>) : 28.4 (12,700), 34.1 (6300).

Pt(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>. This was prepared in an analogous manner, in 80% yield, using PtCl<sub>2</sub>(MeCN)<sub>2</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) :  $\delta$  2.97 (CH<sub>2</sub>), 7.0–7.6 (phenyl). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>, 77.8 MHz) :  $\delta$  – 3659.  $\nu$ (Pt––Cl) = 329 cm<sup>-1</sup>.  $E_{max}$  ( $\epsilon$ mol) : 32.5 (3600).

Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuCl)<sub>2</sub>Cl<sub>2</sub>. A solution of Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> (0.17 g, 0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was treated with AuCl (tetrahydrothiophen) (0.10 g, 0.31 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>). The mixture was stirred for 3 h, concentrated (2 cm<sup>3</sup>) and precipitated with Et<sub>2</sub>O (20 cm<sup>3</sup>). The yellow solid that formed was separated, washed thoroughly with Et<sub>2</sub>O and dried *in vacuo*. Yield 0.20 g (83%). Found: C, 38.0; H, 2.7. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub>Cl<sub>4</sub>Pd: C, 37.8; H, 2.8%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  3.75 (CH<sub>2</sub>), 7.0–7.6 (phenyl).  $\nu$ (Pd—Cl) = 354 cm<sup>-1</sup>,  $\nu$ (Au—Cl) = 326 cm<sup>-1</sup>.  $E_{max}$  ( $\epsilon$  mol): 27.9 (13,300), 38.2 (20,300).

Pt(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuCl)<sub>2</sub>Cl<sub>2</sub>. This was prepared in an analogous manner, in 79% yield, using Pt(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>. Found : C, 35.9 ; H, 2.5. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub>Cl<sub>4</sub>Pt : C, 35.8 ; H, 2.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) :  $\delta$  3.73 (CH<sub>2</sub>), 7.0-7.6 (phenyl). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>, 77.8 MHz) :  $\delta$ - 3685. v(Pt—Cl) = 326 cm<sup>-1</sup>.  $E_{max}$  ( $\varepsilon$  mol) : 35.5 (17,600), 37.7 (22,100).

The bromo complexes were prepared by refluxing the analogous chloro complexes with a large excess

of LiBr in ethanol for 4 h. The resulting materials were filtered off, washed with a little diethyl ether and dried *in vacuo*.

Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuBr)<sub>2</sub>Br<sub>2</sub>. Found : C, 33.7; H, 1.6. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub>Br<sub>4</sub>Pd : C, 34.0; H, 2.5%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) :  $\delta$  3.95 (CH<sub>2</sub>), 7.0–7.6 (phenyl). v(Pd—Br) = 278 cm<sup>-1</sup>.  $E_{max}$  ( $\epsilon$  mol) : 26.1 (17,300), 32.3 (11,300).

Pt(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuBr)<sub>2</sub>Br<sub>2</sub>. Found: C, 30.1; H, 2.0. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub>Br<sub>4</sub>Pt: C, 32.4; H, 2.4%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  3.91 (CH<sub>2</sub>), 7.0–7.6 (phenyl). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>, 77.8 MHz):  $\delta$  –4304. v(Pt—Br) = 279 cm<sup>-1</sup>.  $E_{max}$  ( $\epsilon$  mol): 33.1 (14,200), 37.9 (25,500).

Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuCl<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. A solution of Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuCl)<sub>2</sub>Cl<sub>2</sub> (0.20 g, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was treated with a saturated solution of chlorine in CCl<sub>4</sub> (1 cm<sup>3</sup>). The solution was stirred for 5 min, concentrated (2 cm<sup>3</sup>) and precipitated with Et<sub>2</sub>O (10 cm<sup>3</sup>). The yellow solid produced was filtered off and dried *in vacuo*. Found: C, 35.0; H, 2.6. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub> Cl<sub>8</sub>Pd: C, 34.7; H, 2.5%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz):  $\delta$  3.48 (CH<sub>2</sub>), 7.2–7.7 (phenyl).  $E_{max}$  ( $\epsilon$  mol): 29.3 (13,500), 32.2 (16,100).

Pt(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuCl<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>. This was prepared in an analogous manner using Pt(Ph<sub>2</sub>As CH<sub>2</sub>AsPh<sub>2</sub>—AuCl)<sub>2</sub>Cl<sub>2</sub>. Found: C, 32.7; H, 2.4. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub>Cl<sub>10</sub>Pt: C, 31.8; H, 2.3%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz):  $\delta$  3.72 (CH<sub>2</sub>), 7.2–7.7 (phenyl). *E*<sub>max</sub> ( $\epsilon$  mol): 29.0 (33,800), 37.5 (23,400). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>, 77.8 MHz):  $\delta$  –2286 (Pt<sup>1V</sup>), –3335 (Pt<sup>11</sup>).

Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuBr<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>. A solution of Pd(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuBr)<sub>2</sub>Br<sub>2</sub> (0.22 g, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was treated with a solution of bromine in CCl<sub>4</sub> (1 cm<sup>3</sup> of 10 cm<sup>3</sup> Br<sub>2</sub> in 50 cm<sup>3</sup> CCl<sub>4</sub>). The solution was stirred for 5 min, concentrated (2 cm<sup>3</sup>) and precipitated with Et<sub>2</sub>O (10 cm<sup>3</sup>). The orange solid that formed was filtered off and dried *in vacuo*. Found: C, 28.5; H, 1.5. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub>Br<sub>8</sub>Pd: C, 28.8; H, 2.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz):  $\delta$  3.73 (CH<sub>2</sub>), 7.2–7.7 (phenyl). *E*<sub>max</sub> ( $\epsilon$  mol): 26.3 (5100), 28.4 (5200), 38.8 (32,200).

Pt(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>—AuBr<sub>3</sub>)<sub>2</sub>Br<sub>4</sub>. This was prepared in an analogous manner using Pt(Ph<sub>2</sub>As CH<sub>2</sub>AsPh<sub>2</sub>—AuBr)<sub>2</sub>Br<sub>2</sub>. Found: C, 25.0; H, 1.7. Calc. for C<sub>50</sub>H<sub>44</sub>As<sub>4</sub>Au<sub>2</sub>Br<sub>10</sub>Pt: C, 25.7; H, 1.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz):  $\delta$  3.55 (CH<sub>2</sub>), 7.2–7.7 (phenyl). *E*<sub>max</sub> ( $\epsilon$  mol): 26.5 (4200), 29.7 (6700), 33.1 (10.900), 38.8 (28,000). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>, 77.8 MHz):  $\delta$  –3147 (Pt<sup>IV</sup>), –4075 (Pt<sup>II</sup>).

 $Me_2AsCH_2AsMe_2$ . Sodium metal (4.2 g, 0.18 mol) in THF (150 cm<sup>3</sup>) was treated dropwise with  $Me_2AsI$  (20.4 g, 0.84 mol) with gentle heating to

initiate the reaction. After stirring for 30 min,  $CH_2Cl_2$  (2.0 cm<sup>3</sup>, 0.03 mol) was added dropwise over 1 h, then the mixture was stirred overnight. Excess sodium was hydrolysed with ethanol (10 cm<sup>3</sup>) and the reaction mixture was hydrolysed with  $H_2O$  (60 cm<sup>3</sup>). The organic layer was separated and dried over MgSO<sub>4</sub>. The solvents were removed and the crude product distilled *in vacuo*, giving 1.4 g (21% based on CH<sub>2</sub>Cl<sub>2</sub>) of Me<sub>2</sub>AsCH<sub>2</sub>AsMe<sub>2</sub>, b.p. 30°C (1.0 mm Hg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) :  $\delta$  1.1 (CH<sub>3</sub>), 1.6 (CH<sub>2</sub>).

Pd(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>. This was made as described.<sup>8</sup> Found: C, 45.6; H, 3.4. Calc. for  $C_{50}H_{44}Cl_2PdSb_4$ : C, 45.9; H, 3.4%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  2.44 (CH<sub>2</sub>), 7.0–7.6 (phenyl).

Reaction of  $Pd(Ph_2SbCH_2SbPh_2)_2Cl_2$  with Au(tht)Cl. A solution of Au(tht)Cl (0.04 g, 0.12 mmol) in  $CH_2Cl_2$  (5 cm<sup>3</sup>) was added to  $Pd(Ph_2SbCH_2SbPh_2)_2Cl_2$  (0.08 g, 0.06 mmol) in  $CH_2Cl_2$  (10 cm<sup>3</sup>), and the mixture stirred for 30 min. The solution was concentrated *in vacuo* to *ca* 5 cm<sup>3</sup>, diethyl ether (10 cm<sup>3</sup>) added, and the redbrown solid (A) produced filtered off and dried *in vacuo*. The yellow filtrate was taken to dryness *in vacuo* (B).

(A) Found: C, 28.2; H, 2.1. Calc. for  $C_{25}H_{22}$ Au<sub>2</sub>Cl<sub>2</sub>Sb<sub>2</sub>: C, 29.1; H, 2.1% <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  2.93 (CH<sub>2</sub>), 7.0–7.6 (phenyl).  $v(Au-Cl) = 320 \text{ cm}^{-1}$ . (B) Found: C, 40.4; H, 3.0. Calc. for  $C_{50}H_{44}Cl_4Pd_2Sb_4$ : C, 40.4; H, 3.0%.

Au<sub>2</sub>Cl<sub>2</sub>(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>). To Au(tht)Cl (0.07 g, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added to a solution of Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub> (0.06 g, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>). The mixture was stirred for 30 min, concentrated to 2 cm<sup>3</sup> and treated with diethyl ether (15 cm<sup>3</sup>). The dark red–brown precipitate was filtered, washed with diethyl ether (10 cm<sup>3</sup>) and dried *in vacuo*. Yield 0.08 g (73%). Found : C, 28.1 ; H, 2.2. Calc. for C<sub>25</sub>H<sub>22</sub>Au<sub>2</sub>Cl<sub>2</sub>Sb<sub>2</sub>: C, 29.1 ; H, 2.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) :  $\delta$  2.93 (CH<sub>2</sub>), 7.3–7.6 (phenyl). v(Au–Cl) = 319 cm<sup>-1</sup>.

#### Crystal structure determination

Crystals were grown by vapour diffusion from  $CH_2Cl_2$ -Et<sub>2</sub>O and mounted in glass capillaries. Data were collected using a Stoe Stadi-4 diffractometer fitted with Mo radiation and a graphite monochromator. Cell dimensions were determined from 11 reflections ( $24 \le 2\theta \le 25^\circ$ ) using a yellow needle crystal. The three standard reflections showed some decay during the experiment, which was allowed for in the data processing along with the usual Lorentz and polarization corrections. An empirical  $\psi$ -scan absorption correction was applied. The structure was solved using SHELXS86<sup>17</sup> and refined using SHELX76.<sup>18</sup> Weak

features in the difference electron density map showed the presence of a dichloromethane solvate molecule, which was allowed to refine with a variable population. Hydrogen atoms were introduced in calculated positions [d(C-H) = 1.08 Å] with a common refined thermal parameter, and the palladium, gold, arsenic and chlorine (not solvate) atoms given anisotropic thermal parameters. One of the phenyl rings [C(4J), J = 1, 6] refined poorly, giving unreasonable bond lengths and large thermal parameters, and during the final refinement this was constrained to be a regular hexagon [d(C-C) = 1.395 Å]. Full-matrix least-squares refinement minimizing  $\Sigma w \Delta^2$  using neutral atom complex scattering factors taken from SHELX76 (Cl, C, H) and ref. 19 (Pd, Au, As) converged satisfactorily and the residual electron density was in the range +1.32 to -1.38 e Å<sup>-3</sup>, with the largest peak close to Au(1). Details of the structure solution are given in Table 2. Additional material available from the Cambridge Crystallographic Data

Table 2. Crystal data for *trans*- $[Pd(\mu-Ph_2AsCH_2AsPh_2AuCl)_2Cl_2] \cdot xCH_2Cl_2$ 

Formula	$C_{50}H_{44}As_4Au_2Cl_4Pd \cdot xCH_2Cl_2$		
	[x = 0.17(2)]		
M <sub>r</sub>	1586.76 + 84.92x		
Crystal system	Triclinic		
Space group	РĪ		
a (Å)	13.435(7)		
$b(\mathbf{A})$	11.458(7)		
$c(\mathbf{\hat{A}})$	18.595(9)		
α (°)	90.53(4)		
$\beta$ (°)	100.38(4)		
γ (°)	89.83(5)		
$V(Å^3)$	2815.5		
$T(\mathbf{K})$	295		
Density (calc.; $g cm^{-3}$ )	1.871 ( $x = 0$ ) to 1.971 ( $x = 1$ )		
Z	2		
F(000) (e)	1496 + 84x		
Crystal size (mm <sup>3</sup> )	$0.10 \times 0.10 \times 0.78$		
Type of data collection	$\omega$ -2 $\theta$		
Measured reflections	7272		
Unique reflections	$6432 \ (R_{\rm int} = 0.034)$		
Absorption correction	$\psi$ -scan		
$2\theta$ range (°)	5-45		
Index range $(h; k; l)$	-14 to 14, $-12$ to 12, 0 to 20		
Observed reflections	5160 $[F > 3\sigma(F)]$		
Number of parameters	302		
Weighting scheme $(w^{-1})$	$\sigma^2(F) + 0.001F^2$		
$\lambda$ , Å (Mo- $K_{\alpha}$ )	0.71073		
$\mu ({\rm cm}^{-1})$	80.1 (x = 0)		
Max.  shift/e.s.d.	0.09		
R"	0.059		
$R_{w}^{a}$	0.081		

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; R_{w} = [\Sigma w (F_{o} - F_{c})^{2} / \Sigma w F_{o}^{2}]^{1/2}.$ 

Centre comprises the fractional atomic coordinates, thermal parameters and a full listing of bond lengths and angles.

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