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## Neutral or cationic ( $\mu$ -methylene)bisylide digold(III) complexes

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### Abstract

The reaction of  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{I}_2]$  with  $\text{AgC}_6\text{F}_5$  or  $[\text{Ag}(\text{OClO}_3)\text{L}]$  gives the neutral  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2(\text{C}_6\text{F}_5)_2]$  or cationic complexes  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{L}_2(\text{ClO}_4)_2]$  or  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{IL}]\text{ClO}_4$  (L = tetrahydrothiophene,  $\text{PPh}_3$  or  $\text{PPh}_2\text{Me}$ ). Displacement of tetrahydrothiophene gives new cationic (L =  $\text{AsPh}_3$ , py or 1,10-phenanthroline) or neutral complexes,  $(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{X}_2$  (X = SCN or  $\text{S}_2\text{CNMe}_2$ ). The structure of  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2(\text{C}_6\text{F}_5)_2]$  has been established by X-ray crystallography at  $-95^\circ\text{C}$ . The structure has an A-frame geometry with two square-planar gold units.

### Introduction

A few neutral  $\text{CH}_2$ -bridged dinuclear gold(III) complexes have been prepared from dinuclear gold(I) ylidyne complexes by oxidative addition of  $\text{CH}_2\text{X}_2$  [1–5] or by addition of  $\text{CH}_2\text{N}_2$  or  $\text{CH}_3\text{NO}_2$  to gold(II) dimers [6], but no cationic derivatives are known and there is no reported chemistry of these type of compounds.

In the present paper we describe the synthesis of several neutral  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{X}_2]$  (X =  $\text{C}_6\text{F}_5$ , SCN, or  $\text{S}_2\text{CNMe}_2$ ) or cationic  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{L}_2]^{2+}$  or  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{IL}]^+$  (L = tetrahydrothiophene (tht), py, bipy, phen,  $\text{PPh}_3$ , or  $\text{AsPh}_3$ ) ( $\mu$ -methylene)-gold(III) complexes obtained by displacement of iodide or tht from  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2\text{I}_2]$  or  $[(\mu\text{-CH}_2)(\text{Au}(\text{CH}_2)_2\text{PPh}_2)_2(\text{tht})_2(\text{ClO}_4)_2]$  by other neutral or anionic ligands.

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## Results and discussion

$[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  reacts with  $\text{AgC}_6\text{F}_5$  (molar ratio 1:2) to give the pentafluorophenyl complex **1** (Scheme 1) with gold(III) centres bonded only to carbon atoms.

Complex **1** is a white solid, air- and moisture-stable at room temperature, and non-conducting in acetone solutions. The  $^{19}\text{F}$  NMR spectrum confirms the presence of two equivalent  $\text{C}_6\text{F}_5$  groups and shows multiplets at  $-120.10$  (*o*-F),  $-161.46$  (*p*-F) and  $-163.16$  ppm (*m*-F).

The structure of **1** was determined by X-ray diffraction. Crystals of **1** suitable for X-ray studies were obtained from dichloromethane/petroleum ether as colourless plates. The structure is shown in Fig. 1, and has an A-frame geometry with two square-planar gold units (maximum deviation from ideal angles  $3.3^\circ$ ). The methylene group bridges both gold atoms with an angle  $\text{Au}(1)\text{-C}(1)\text{-Au}(2)$   $98.6(3)^\circ$ . The  $\text{Au}\text{-C}(\text{ylide})$  distances lie in the range  $2.091(7)\text{-}2.107(7)$  Å and are similar to those found in other bis-ylide complexes [1–6].

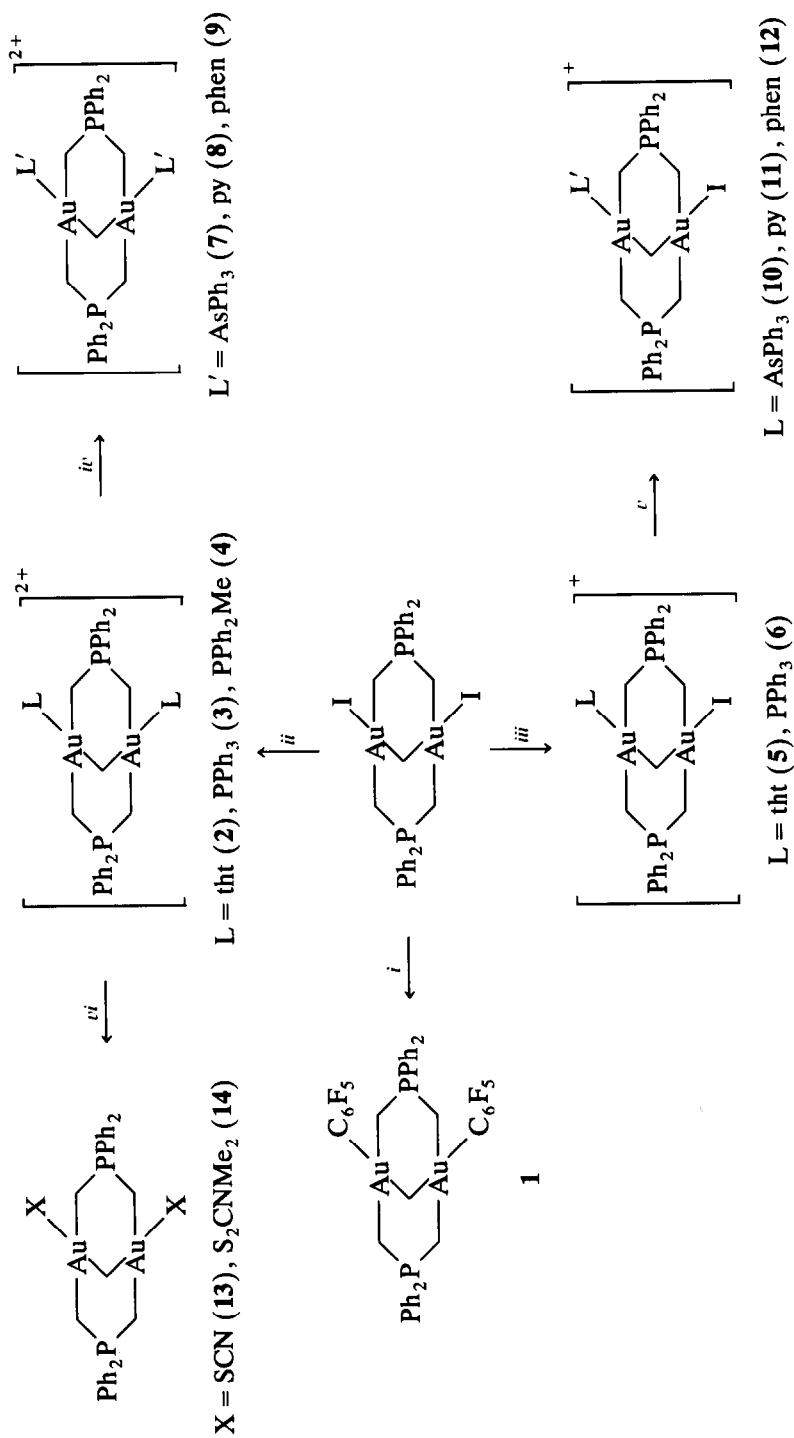
The  $\text{Au}\text{-}\mu\text{CH}_2$  bond lengths are  $2.052(8)$  and  $2.054(7)$  Å, which can be compared to those of other methylene-bridged derivatives characterized by X-ray diffraction  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PR}_2\}_2\text{X}_2]$  ( $\text{X} = \text{Cl}$ ,  $\text{R} = \text{Me}$ ;  $\text{X} = \text{CN}$ ,  $\text{CH}_3$ ,  $\text{R} = \text{Ph}$ ) [3,7,8], in which average  $\text{Au}\text{-CH}_2$  bond lengths of  $2.007$ ,  $2.056(11)$  and  $2.095(10)$  Å, respectively, are observed; these can be rationalised in terms of the structural *trans* influence of the ligand X, with  $\text{Cl} < \text{CN} \sim \text{C}_6\text{F}_5 < \text{CH}_3$ .

The most dramatic difference is the  $\text{Au}\cdots\text{Au}$  distance. In the complex  $[\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2(\text{C}_6\text{F}_5)_2]$  [9] the two  $\text{Au}^{\text{II}}$  centres are only  $2.675(1)$  Å apart, while in **1** the  $\text{Au}\cdots\text{Au}$  distance is  $3.113(1)$  Å, consistent with the absence of an  $\text{Au}\text{-Au}$  bond; this distance is even longer than in the gold(I) precursor  $[\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2]$   $2.977(1)$  Å. The  $\text{Au}\text{-C}(\text{C}_6\text{F}_5)$  bond lengths are both  $2.104(7)$  Å, intermediate between those found in  $[\text{Au}(\text{C}_6\text{F}_5)_4]^-$  [ $2.053(8)\text{-}2.060(8)$  Å] [10] and the gold(II) derivative  $[\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2(\text{C}_6\text{F}_5)_2]$  [ $2.145(8)\text{-}2.164(7)$  Å] [9]. As in the other bridging-methylene gold(III) derivatives, the eight-membered ring possesses a boat configuration, while in the gold(II) pentafluorophenyl complex both chair and boat configurations were found in three independent molecules in the unit cell. The pentafluorophenyl rings of the present compound display angles of  $114.0(7)$  and  $114.3(6)^\circ$  at the *ipso* carbons; such distortions are a common feature of pentafluorophenyl complexes of transition metals [11].

Reaction of  $\text{Ag}(\text{OCIO}_3)\text{L}$  and  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  and removal of the precipitated  $\text{AgI}$  leads to the cationic complexes  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{-L}_2](\text{ClO}_4)_2$  [ $\text{L} = \text{tht}$  (**2**),  $\text{PPh}_3$  (**3**), or  $\text{PPh}_2\text{Me}$  (**4**)] or  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{-IL}](\text{ClO}_4)$  [ $\text{L} = \text{tht}$  (**5**) or  $\text{PPh}_3$  (**6**)], when 2/1 or 1/1 molar ratios, respectively, are used.

It is possible to take advantage of the ease of displacement of *tht* from complexes **2** and **5** to prepare a variety of complexes. Addition of a neutral donor to dichloromethane solutions of **2** or **5** gives cationic complexes  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{L}'_2](\text{ClO}_4)_2$  [ $\text{L}' = \text{AsPh}_3$  (**7**), pyridine (*py*) (**8**), or 1,10-phenanthroline (*phen*) (**9**)] or  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{IL}'](\text{ClO}_4)$  [ $\text{L}' = \text{AsPh}_3$  (**10**), *py* (**11**), or *phen* (**12**)], respectively.

Complexes **5**, **6**, **10–12** are also obtained by reaction of equimolar amounts of  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  and **2**, **3**, **7**, **8** or **9**.



Scheme 1. *i*) 2 AgC<sub>6</sub>F<sub>5</sub>; *ii*) 2 Ag(OClO<sub>3</sub>)L; *iii*) Ag(OClO<sub>3</sub>)L; *iv*) 2 L'; *v*) L'; *vi*) 2 MX.

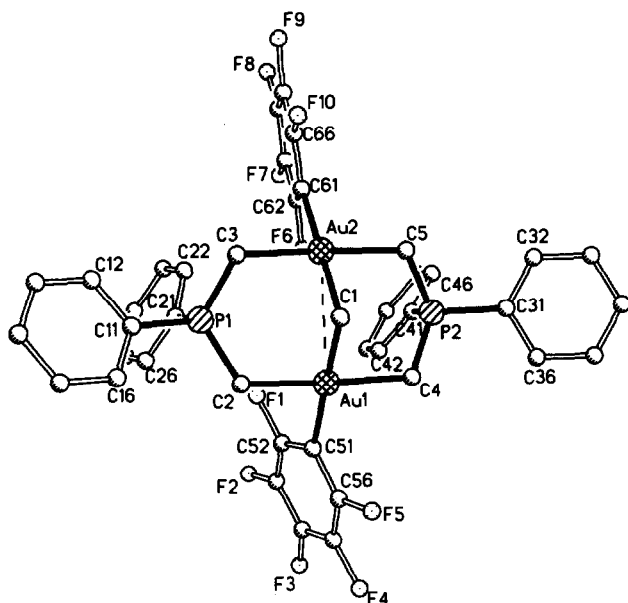


Fig. 1. The molecule of complex 1 in the crystal, showing the atom numbering scheme. Radii arbitrary.

Complexes 2–12 were isolated as white (2–4, 6–11), orange (5) or pale brown (12) solids, air- and moisture-stable at room temperature. They are conducting in acetone solution and behave as 2:1 (complexes 2–4 and 7–9) or 1:1 electrolytes (complexes 5, 6, 10–12) (see Table 1). The mass spectrum (FAB +, nitrobenzyl alcohol as matrix) of complex 6 shows the parent ion of the cation at 1223, but complex 5 shows the highest  $m/z$  ratio at 961 corresponding to the  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}]^+$  fragment, which is also present in the spectrum of 6.

The  $^1\text{H}$  NMR spectra show a signal for the  $\mu\text{-CH}_2$  group (see Table 1) which is normally a singlet but is a triplet for complexes 3 and 4 and a doublet for 6 because of coupling with phosphine ligands. The resonances from  $\text{CH}_2$  ylide groups appear as two pseudo-triplets for complexes 7 and 9 and as four pseudo-triplets for the asymmetrical complexes 5, and 10–12. A more complicated pattern appears when the complex contains one or two phosphines (complexes 3, 4 or 6) (see Experimental). The  $^{31}\text{P}$  NMR spectra show a singlet for the  $\text{PPh}_2$  group in all the complexes, except for 3 and 4 (triplet) and 6 (doublet).

The complex  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2(\text{tht})_2](\text{ClO}_4)_2$  (2) reacts with salts  $\text{MX}$  to give another series of neutral complexes  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{X}_2]$  [ $\text{X} = \text{SCN}$  (13) or  $\text{S}_2\text{CNMe}_2$  (14)]. They are yellow (13) or orange (14) solids and non-conducting in acetone solution.

Their  $^1\text{H}$  NMR spectra show a singlet for the  $\mu\text{-CH}_2$  group, and two pseudo-triplets for the  $\text{CH}_2\text{-P}$  groups. In complex 14 there is a singlet at  $\delta$  3.47 for the methyl groups at room temperature but, at  $-55^\circ\text{C}$ , it splits into two signals at  $\delta$  3.43 and 3.48, which rules out a possible pentacoordination around the gold centres. A singlet is observed in the  $^{31}\text{P}$  NMR spectrum.

## Experimental

Instrumentation and general experimental techniques were as described earlier [12]. Mass spectra were recorded on a VG Autospec. The yields C, H and N analyses and some proton and  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR data are listed in Table 1. All the reactions were at room temperature.

### Preparation of the complexes

$[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2(\text{C}_6\text{F}_5)_2]$  (**1**). To an anhydrous diethyl ether solution of  $\text{AgClO}_4$  (0.023 g, 0.11 mmol) was added  $(\text{NBu}_4)[\text{Ag}(\text{C}_6\text{F}_5)_2]$  [13] (0.075 g, 0.11 mmol). The mixture was stirred for 45 min under  $\text{N}_2$  and protected from light. The precipitated  $[\text{NBu}_4]\text{ClO}_4$  was removed by filtration through diatomaceous earth. A dichloromethane solution of  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  [4] (0.109 g, 0.1 mmol) was added. After stirring for 90 min at room temperature in the dark, the  $\text{AgI}$  was removed and the solution evaporated to ca. 5 ml. Addition of diethyl ether led to precipitation of complex **1**. **1**:  $^1\text{H}$  NMR 7.64–7.23 (m, 20H), 2.02 (m, 8H), 1.81 (s, 2H).

$[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{L}_2](\text{ClO}_4)_2$  [ $\text{L} = \text{tht}$  (**2**),  $\text{PPh}_3$  (**3**), or  $\text{PPh}_2\text{Me}$  (**4**)]. To a dichloromethane solution of  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  [4] (0.163 g, 0.15 mmol) was added  $\text{Ag}(\text{OCIO}_3)\text{L}$  [14,15] [ $\text{L} = \text{tht}$  (0.089 g, 0.3 mmol),  $\text{PPh}_3$  (0.141 g, 0.3 mmol),  $\text{PPh}_2\text{Me}$  (0.122 g, 0.3 mmol)]. After 2 h stirring at room temperature in the dark, the  $\text{AgI}$  was filtered off and the solution evaporated to ca. 5 ml. Addition of diethyl ether (20 ml) gave complexes **2–4** as white solids. **3**:  $^1\text{H}$  NMR 7.90–6.74 (m, 50H), 3.52 (t, 2H,  $^3J(\text{HP}) = 4.0$  Hz), 2.33 (“t”, 4H,  $J = 12.7$  Hz), 1.87 (“c”, 4H,  $J = 11.4$  Hz);  $^{31}\text{P}$  NMR 42.52 ppm (t,  $^3J(\text{PP}) = 7.3$  Hz), 23.18 ppm (t,  $^3J(\text{PP}) = 7.3$  Hz). **4**:  $^1\text{H}$  NMR 7.80–7.32 (m, 40H), 3.00 (“t”, 2H,  $^3J(\text{HP}) = 4.5$  Hz), 2.06 (m, 10H), 1.90 (m, 4H);  $^{31}\text{P}$  NMR 37.82 (t,  $^3J(\text{PP}) = 9.5$  Hz), 10.46 (t,  $^3J(\text{PP}) = 9.5$  Hz).

$[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{IL}]\text{ClO}_4$  [ $\text{L} = \text{tht}$  (**5**) or  $\text{PPh}_3$  (**6**)]. To a dichloromethane solution of  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  [4] (0.109 g, 0.1 mmol) was added  $\text{Ag}(\text{OCIO}_3)\text{L}$  [14,15] ( $\text{L} = \text{tht}$  (0.029 g, 0.1 mmol),  $\text{PPh}_3$  (0.047 g, 0.1 mmol)]. After stirring for 90 min at room temperature in the dark, the  $\text{AgI}$  was filtered off. The solution was evaporated to ca. 5 ml and the addition of diethyl ether gave complexes **5–6**; orange solid and white solid respectively.

Complexes **5–6** were also obtained by the following method. To a solution of  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  [4] (0.054 g, 0.05 mmol) in dichloromethane was added **2** (0.060 g, 0.05 mmol) or **3** (0.078 g, 0.05 mmol). After 90 min, the solution was evaporated to ca. 5 ml and diethyl ether was added. **5**:  $^1\text{H}$  NMR 8.05–7.35 (m, 20H), 3.20 (s, 2H), 2.84 (m, 8H), 2.12–1.75 (m, 8H). **6**:  $^1\text{H}$  NMR 8.00–6.70 (m, 35H), 3.22 (d, 2H,  $^3J(\text{HP}) = 3.2$  Hz), 2.86 (“t”, 2H,  $J = 13.3$  Hz), 2.54 (“t”, 2H,  $J = 13.3$  Hz), 1.80 (m, 4H);  $^{31}\text{P}$  NMR 41.52 ppm (d,  $^3J(\text{PP}) = 4.4$  Hz), 23.07 ppm (t,  $^3J(\text{PP}) = 4.4$  Hz).

$[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{L}'_2](\text{ClO}_4)_2$  [ $\text{L}' = \text{AsPh}_3$  (**7**), pyridine (**8**), or 1,10-phenanthroline (**phen**) (**9**)] and  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{IL}']\text{ClO}_4$  [ $\text{L}' = \text{AsPh}_3$  (**10**), py (**11**), or **phen** (**12**)]. To a solution of **2** (0.060 g, 0.05 mmol) or **3** (0.057 g, 0.05 mmol) in dichloromethane was added an excess of the relevant donor [ $\text{L}' = \text{AsPh}_3$  (0.046 g, 0.15 mmol) **7** or (0.031 g, 0.1 mmol) **10**, py (0.012 ml, 0.15 mmol) **8** or (0.012 ml, 0.15 mmol) **11**, **phen** (0.030 g, 0.15 mmol) **9** or (0.020 g, 0.1 mmol) **12**]. After 2 h stirring at room temperature, the solution was evaporated to

Table 1  
Analytical data for complexes

Complex	Yield (%)	Analysis [Found (calcd.) (%)]				$A_M^a$	$^3P$ NMR ( $\delta$ PPh <sub>2</sub> )	$^1H$ NMR ( $\delta$ $\mu$ -CH <sub>2</sub> )
		C	H	N				
1 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ]	77	41.9 (42.1)	2.7 (2.6)		8	37.79(s)	1.81(s)	
2 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (tht) <sub>2</sub> ClO <sub>4</sub> ) <sub>2</sub>	88	36.9 (36.75)	4.0 (3.85)		223	39.16(s)	<i>b</i>	
3 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (PPh <sub>1</sub> ) <sub>2</sub> ClO <sub>4</sub> ) <sub>2</sub>	86	49.7 (50.1)	4.2 (3.9)		231	42.52(t) [J(PP) 7.3]	3.52(t) [J(PH) 4.0]	
4 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (PPh <sub>2</sub> Me) <sub>2</sub> ClO <sub>4</sub> ) <sub>2</sub>	83	46.25 (46.05)	4.0 (3.95)		235	37.82(t) [J(PP) 9.5]	3.00(t) [J(PH) 4.5]	
5 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> I(tht)ClO <sub>4</sub>	70	34.45 (34.5)	3.15 (3.35)		147	40.68(s)	3.20(s)	
6 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> I(PPh <sub>3</sub> )ClO <sub>4</sub>	75	42.15 (42.65)	3.3 (3.45)		138	41.52(d) [J(PP) 4.4]	3.22(d) [J(PH) 3.2]	
7 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub> ClO <sub>4</sub> ) <sub>2</sub>	79	47.05 (47.45)	3.80 (3.65)		229	42.29(s)	3.69(s)	
8 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (py) <sub>2</sub> ClO <sub>4</sub> ) <sub>2</sub>	70	38.8 (39.3)	3.55 (3.4)	2.25 (2.35)	223	37.44(s)	<i>b</i>	
9 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (phen) <sub>2</sub> ClO <sub>4</sub> ) <sub>2</sub>	86	46.0 (45.65)	3.45 (3.35)	4.2 (4.0)	2.34	35.81(s)	2.81(s)	
10 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> [AsPh <sub>3</sub> ]ClO <sub>4</sub>	67	41.6 (41.3)	3.45 (3.3)		130	41.36(s)	3.27(s)	
11 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> I(py)ClO <sub>4</sub>	76	36.0 (35.8)	3.2 (3.1)	1.45 (1.25)	136	40.48(s)	2.60(s)	
12 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> I(phen)ClO <sub>4</sub>	82	39.6 (39.7)	3.2 (3.1)	2.1 (2.25)	145	39.72(s)	2.69(s)	
13 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (SCN) <sub>2</sub>	67	39.2 (39.15)	3.15 (3.2)	2.7 (2.95)	2	38.03(s)	2.66(s)	
14 [ $\mu$ -CH <sub>2</sub> ] $\lambda$ Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> (S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub> ]	60	38.8 (39.1)	4.0 (3.95)	2.3 (2.6)	17	38.31(s)	2.29(s)	

<sup>a</sup> In acetone, ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. <sup>b</sup> Not soluble enough.

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Au(1)	2220.2(2)	696.6(2)	58.6(2)	196(1)
Au(2)	741.8(2)	2057.2(2)	113.6(2)	192(1)
P(1)	2307(1)	2429(1)	-1174(1)	222(6)
P(2)	944(1)	641(1)	1678(1)	232(6)
C(1)	991(5)	896(4)	-451(5)	275(26)
C(2)	2663(5)	1352(4)	-998(5)	253(25)
C(3)	1192(5)	2622(4)	-997(5)	240(24)
C(4)	1645(5)	21(4)	1049(5)	260(25)
C(5)	229(5)	1364(5)	1121(5)	272(26)
C(12)	2312(3)	3545(3)	-2549(3)	318(19)
C(13)	2492	3791	-3375	401(22)
C(14)	2902	3218	-3909	404(22)
C(15)	3133	2397	-3617	530(26)
C(16)	2953	2151	-2792	475(24)
C(11)	2543	2724	-2258	241(17)
C(22)	2602(3)	3791(3)	-44(3)	346(20)
C(23)	3128	4390	390	400(21)
C(24)	4026	4366	315	382(21)
C(25)	4397	3743	-194	421(22)
C(26)	3871	3144	-629	311(19)
C(21)	2973	3168	-554	247(17)
C(32)	-519(3)	153(3)	2560(3)	343(20)
C(33)	-1017	-429	3007	435(23)
C(34)	-705	-1258	3173	437(23)
C(35)	104	-1505	2893	447(23)
C(36)	602	-922	2447	342(20)
C(31)	290	-93	2280	256(17)
C(42)	2472(3)	1307(3)	2417(3)	377(21)
C(43)	2949	1767	3036	514(25)
C(44)	2527	2166	3696	454(23)
C(45)	1627	2105	3737	501(25)
C(46)	1150	1644	3118	446(23)
C(41)	1572	1245	2458	240(17)
C(51)	3485(5)	463(4)	556(4)	215(23)
C(52)	4041(5)	1080(4)	870(5)	248(25)
C(53)	4850(5)	930(5)	1233(5)	282(26)
C(54)	5143(5)	91(5)	1288(5)	287(26)
C(55)	4623(6)	-562(4)	963(5)	282(26)
C(56)	3811(5)	-363(5)	612(5)	261(25)
C(61)	514(5)	3244(4)	710(4)	237(24)
C(62)	1039(5)	3569(5)	1360(5)	274(25)
C(63)	892(6)	4352(5)	1748(5)	370(30)
C(64)	190(7)	4832(5)	1491(6)	400(32)
C(65)	-360(6)	4533(5)	855(6)	396(31)
C(66)	-166(5)	3759(4)	474(5)	246(24)
F(1)	3785(3)	1921(3)	872(3)	388(16)
F(2)	5366(3)	1559(3)	1552(3)	453(18)
F(3)	5917(3)	-100(3)	1665(3)	430(18)
F(4)	4907(3)	-1383(3)	1017(3)	428(18)
F(5)	3329(3)	-1034(3)	308(3)	376(16)
F(6)	1743(3)	3125(3)	1640(3)	403(17)
F(7)	1443(4)	4640(3)	2363(3)	573(21)
F(8)	26(4)	5600(3)	1851(3)	601(22)
F(9)	-1065(4)	4989(3)	615(4)	570(21)
F(10)	-726(3)	3505(3)	-163(3)	346(15)

<sup>a</sup> Equivalent isotropic *U* defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

ca. 5 ml and addition of diethyl ether led to precipitation of complexes 7–12.

Complexes 10–12 were also obtained by the following method. To a solution of  $[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{I}_2]$  (0.054 g, 0.05 mmol) in dichloromethane was added 7 (0.082 g, 0.05 mmol), 8 (0.059 g, 0.05 mmol), or 9 (0.070 g, 0.05 mmol). After 90 min, the solution was evaporated to ca. 5 ml and diethyl ether was added. 7:  $^1\text{H}$  NMR 8.00–6.89 (m, 50H), 3.69 (s, 2H), 2.33 (“t”, 4H,  $J = 12.7$  Hz), 2.09 (“t”, 4H,  $J = 12.7$  Hz). 9:  $^1\text{H}$  NMR 9.34 (1H), 9.17 (1H), 8.60 (2H), 8.37 (1H), 8.31 (1H), 8.07–7.33 (m, 30H), 2.81 (s, 2H), 2.10 (“t”, 4H,  $J = 13.8$  Hz), 1.76 (“t”, 4H,  $J = 13.8$  Hz). 10:  $^1\text{H}$  NMR 8.05–6.85 (m, 35H), 3.27 (s, 2H), 2.88 (“t”, 2H,  $J = 11.8$  Hz), 2.46 (“t”, 2H,  $J = 11.8$  Hz), 2.10 (“t”, 2H,  $J = 11.8$  Hz), 1.85 (“t”, 2H,  $J = 11.8$  Hz). 11:  $^1\text{H}$  NMR 7.94–7.06 (m, 25H), 2.97 (“t”, 2H,  $J = 12.1$  Hz), 2.60 (s, 2H), 2.16 (“t”, 2H,  $J = 12.1$  Hz), 1.82 (“t”, 2H,  $J = 12.1$  Hz), 1.78 (“t”, 2H,  $J = 12.1$  Hz). 12:  $^1\text{H}$  NMR 9.15 (1H), 8.57 (1H), 8.39 (1H), 8.00–6.90 (m, 24H), 5.9 (1H), 3.00 (“t”, 2H,  $J = 12.3$  Hz), 2.69 (s, 2H), 1.98 (“t”, 2H,  $J = 12.3$  Hz), 1.81 (“t”, 2H,  $J = 12.3$  Hz), 1.56 (“t”, 2H,  $J = 12.3$  Hz).

$[(\mu\text{-CH}_2)\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2\text{X}_2]$  [ $\text{X} = \text{SCN}$  (13) or  $\text{S}_2\text{CNMe}_2$  (14)]. To a solution of 2 (0.060 g, 0.05 mmol) in 15 ml dichloromethane was added an excess of  $\text{NaS}_2\text{CNMe}_2$  (0.054 g, 0.3 mmol) or  $\text{KSCN}$  (0.030 g, 0.3 mmol) in 10 ml  $\text{H}_2\text{O}$ . After stirring for 90 min, the organic phase was separated and the aqueous phase extracted with additional  $\text{CH}_2\text{Cl}_2$ . The organic phase was washed with water, dried over anhydrous  $\text{MgSO}_4$  and concentrated. Addition of diethyl ether led to precipitation of 13 (yellow solid) and 14 (orange solid). 13:  $^1\text{H}$  NMR 7.50–7.24 (m, 20H), 2.66 (s, 2H), 2.14 (“t”, 4H,  $J = 12.9$  Hz), 1.90 (“t”, 4H,  $J = 12.9$  Hz). 14:  $^1\text{H}$  NMR 7.70–7.15 (m, 20H), 3.47 (s, 12H), 2.56 (“t”, 4H,  $J = 12.5$  Hz), 2.29 (s, 2H), 2.08 (“t”, 4H,  $J = 12.5$  Hz).

#### *X-Ray structure determination of 1*

*Crystal data.*  $\text{C}_{41}\text{H}_{30}\text{Au}_2\text{F}_{10}\text{P}_2$ ,  $M_r = 1168.5$ , monoclinic, space group  $\text{P2}_1/\text{n}$ ,  $a = 15.429(5)$ ,  $b = 15.525(5)$ ,  $c = 15.766(4)$  Å,  $\beta = 92.37(2)^\circ$ ,  $U = 3773(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.057$   $\text{Mgm}^{-3}$ ,  $F(000) = 2216$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å,  $\mu = 7.915$   $\text{mm}^{-1}$ ,  $T = -95^\circ\text{C}$ .

*Data collection and reduction.* A Siemens R3 diffractometer with monochromated  $\text{Mo-K}\alpha$  radiation and an LT-2 low-temperature attachment was used. A colourless tablet  $0.4 \times 0.4 \times 0.15$  mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream. 9010 intensities were measured to  $2\theta_{\text{max}}$  of  $50^\circ$ . An absorption correction based on  $\psi$ -scans was applied, with transmission factors 0.35–0.97. Merging equivalents gave 6673 unique reflections ( $R_{\text{int}} 0.029$ ), of which 5272 with  $F > 4\sigma(F)$  were used for all calculations (program system: Siemens SHELXTL PLUS) [16]. Cell constants were refined from setting angles of 50 reflections in the  $2\theta$  range  $20\text{--}23^\circ$ .

*Structure solution and refinement.* The Au atoms were located from the Patterson function and the structure extended by difference syntheses. Au, P, F and C (except phenyl rings) were refined anisotropically. The phenyl groups were refined isotropically with idealised geometry. Hydrogens were included using a riding model. The final  $R$  value was 0.036,  $R_w = 0.037$  for 328 parameters. The weighting scheme was  $w^{-1} = \sigma^2(F) + 0.0002 F^2$ .  $S 1.4$ ; max  $\Delta/\sigma$  0.001; max  $\Delta\rho$  1.45 e Å<sup>-3</sup>. Final atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. Further details of the structure determination (complete bond



Table 3  
Selected bond lengths (Å) and angles (°) for complex 1

Au(1)–Au(2)	3.113(1)	Au(1)–C(1)	2.052(8)
Au(1)–C(2)	2.091(7)	Au(1)–C(4)	2.107(8)
Au(1)–C(51)	2.104(7)	Au(2)–C(1)	2.054(7)
Au(2)–C(3)	2.102(7)	Au(2)–C(5)	2.100(8)
Au(2)–C(61)	2.104(7)	P(1)–C(2)	1.777(7)
P(1)–C(3)	1.781(8)	P(1)–C(11)	1.821(5)
P(1)–C(21)	1.802(5)	P(2)–C(4)	1.780(8)
P(2)–C(5)	1.781(8)	P(2)–C(31)	1.816(5)
P(2)–C(41)	1.799(5)		
Au(2)–Au(1)–C(1)	40.7(2)	Au(2)–Au(1)–C(2)	87.5(2)
C(1)–Au(1)–C(2)	86.7(3)	Au(2)–Au(1)–C(4)	89.2(2)
C(1)–Au(1)–C(4)	87.4(3)	C(2)–Au(1)–C(4)	173.8(3)
Au(2)–Au(1)–C(51)	140.9(2)	C(1)–Au(1)–C(51)	178.4(3)
C(2)–Au(1)–C(51)	93.0(3)	C(4)–Au(1)–C(51)	92.9(3)
Au(1)–Au(2)–C(1)	40.7(2)	Au(1)–Au(2)–C(3)	89.6(2)
C(1)–Au(2)–C(3)	86.0(3)	Au(1)–Au(2)–C(5)	88.4(2)
C(1)–Au(2)–C(5)	87.8(3)	C(3)–Au(2)–C(5)	172.5(3)
Au(1)–Au(2)–C(61)	138.0(2)	C(1)–Au(2)–C(61)	178.6(3)
C(3)–Au(2)–C(61)	94.2(3)	C(5)–Au(2)–C(61)	92.1(3)
C(2)–P(1)–C(3)	115.3(4)	C(2)–P(1)–C(11)	108.1(3)
C(3)–P(1)–C(11)	109.7(3)	C(2)–P(1)–C(21)	110.4(3)
C(3)–P(1)–C(21)	110.0(3)	C(11)–P(1)–C(21)	102.6(2)
C(4)–P(2)–C(5)	116.4(4)	C(4)–P(2)–C(31)	108.4(3)
C(5)–P(2)–C(31)	107.9(3)	C(4)–P(2)–C(41)	109.9(3)
C(5)–P(2)–C(41)	108.3(3)	C(31)–P(2)–C(41)	105.4(2)
Au(1)–C(1)–Au(2)	98.6(3)	Au(1)–C(2)–P(1)	118.2(4)
Au(2)–C(3)–P(1)	114.5(4)	Au(1)–C(4)–P(2)	115.3(3)
Au(2)–C(5)–P(2)	116.8(4)		
C(52)–C(51)–C(56)	114.0(7)		
C(62)–C(61)–C(66)	114.3(6)		

lengths and angles, H atom coordinates structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference CSD-56701.

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### References

- 1 H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 22 (1983) 907.
- 2 P. Jandik and H. Schmidbaur, *Inorg. Chim. Acta*, 74 (1983) 97.
- 3 P. Jandik, U. Schubert and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 21 (1982) 73.
- 4 H.H. Murray, J.P. Fackler, Jr. and A.M. Mazany, *Organometallics*, 3 (1984) 1310.
- 5 H.H. Murray, J.P. Fackler, Jr. and D.A. Tocher, *J. Chem. Soc., Chem. Commun.*, (1985) 1278.
- 6 H.C. Knachel, D.S. Dudis and J.P. Fackler, Jr., *Organometallics*, 3 (1984) 1312.

- 7 H.H. Murray, A.M. Mazany and J.P. Fackler, Jr., *Organometallics*, 4 (1985) 154.
- 8 H. Schmidbaur, C. Hartman, J. Riede, B. Huber and G. Müller, *Organometallics*, 5 (1986) 1652.
- 9 H.H. Murray, J.P. Fackler, Jr., L.C. Porter, D.A. Briggs, M.A. Guerra and R.J. Lagow, *Inorg. Chem.*, 26 (1987) 357.
- 10 P.J. Jones and E. Bembenek, unpublished data.
- 11 P.J. Jones, *J. Organomet. Chem.*, 345 (1988) 405.
- 12 A. Laguna, M. Laguna, J. Jimenez and A.J. Fumanal, *J. Organomet. Chem.*, 396 (1990) 121.
- 13 R. Usón, A. Laguna and J.A. Abab, *J. Organomet. Chem.*, 246 (1983) 341.
- 14 R. Usón, A. Laguna, M. Laguna, J. Jiménez and P.G. Jones, *J. Chem. Soc.*, (1991) 1361.
- 15 F.A. Cotton, L.R. Falvello, R. Usón, J. Forniés, M. Tomás, J.M. Casas and I. Ara, *Inorg. Chem.*, 26 (1987) 1366.
- 16 G.M. Sheldrick, *SHELXTL-PLUS Structure Determination Package*, University of Göttingen, 1990.