

# Organogold(I) complexes: Synthesis, X-ray crystal structures and aurophilicity

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## Abstract

The synthesis of  $\text{RAuPPh}_3$  ( $\text{R} = \text{aryl}$ ) from  $\text{ClAuPPh}_3$  and Grignard RM reagents ( $\text{M} = \text{Li}$  or  $\text{MgX}$ ) is described. New (vinyl-phenyl)gold(I) and other arylgold(I) complexes were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{19}\text{F}$  NMR, melting point determination, and X-ray diffraction. Crystallographic studies of some organogold(I) complexes indicate an aurophilic  $\text{Au(I)} \cdots \text{Au(I)}$  attraction.

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## 1. Introduction

Inertial confinement fusion (ICF) is a subject of intense investigations. In ICF, energetic driver beams from high power laser (Laser MégaJoule) and X-ray heat a target containing specific materials in some parts. Organic and organometallic materials (polymers or alveolar materials also called foams) are frequently used as parts of targets for various experiments of plasma physics: plasma propagation, laser interaction with matter, etc). In this field, the development of polymerizable monomers containing specific atoms such as group XIV (Si, Ge and Sn) or group XI transition metals is a very important theme [1]. In this new study, the “gold” atom must be introduced by covalent bond into the monomers structure. Such monomers containing gold must be further polymerized or introduced in foams

with high level of homogeneity [2] for producing various doped materials.

These doped materials must answer to several requirements as follows: (1) a composition including carbon, hydrogen and a controlled amount of gold atom, with tolerance of phosphorous atom, (2) an homogeneous repartition of gold into the polymer or foams (3) controlled physical properties. To reach these materials, it was essential to prepare monomers containing gold that were “air and water stable” then could be easily handled.

The substituted polystyrenes family was excellent candidate for such applications because of their atomic composition and the large chemistry that it offers. We have previously described the synthesis of polymerizable monomers: some substituted styrene derivatives and their corresponding polymers containing silicium, germanium and tin [1]. Then in this work, we choose to synthesize substituted styrenes derivatives containing gold that must be easily copolymerized via radical

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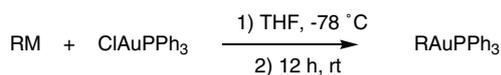
polymerization process: with styrene to prepare various polymers or with a mixture of styrene/DVB to prepare foams by an high internal phase emulsion (HIPE) [3].

The organometallic chemistry of gold has attracted much attention [4–6] during past decades. Two types of organogold compounds can be used for our application:  $R_3Au$  or  $RAuL$  compounds. The  $RAuL$  complexes were preferred for their higher stability than  $R_3Au$  [7,8]. The major improvement in the field was the preparation of mono and polyfluoro aryl gold compounds, especially neutral complexes of the “ $Ar_F AuL$ ” [9] type. Many reports in the literature concern fluorinated derivatives such as 2,4,6-tris(trifluoromethyl)phenylgold(I) complexes [8,10–13] with various ligands like triphenylarsine or diphosphines for examples. The presence of a “ $Ar_F$ ” fluoroaryl group provides greater stability compared to aryl analogs. But as part of our study, fluorine atoms were not desirable in polymers.

At the beginning of the eighties, some studies were performed on more classical aryl groups like anisole and as ligand, the triphenylphosphine. In 1980, van Kotten et al. [14] prepared 2,6-dimethoxy- and 2,4,6-trimethoxy-phenyl(triphenylphosphine)gold(I) complexes with classic organometallic synthesis. Then, the 2,6-dimethoxyphenyl(triphenylphosphine)gold(I) complex was fully characterized by X-ray diffraction analysis by Riley and Davis [15].

For our purpose, we choose to prepare derivatives analogs to aryl(triphenylphosphine)gold(I) complexes because of their easy handling. We report here the synthesis of new vinylphenyl(triphenylphosphine)gold(I) derivatives that are very important compounds for the preparation of new doped materials with gold (e.g. by copolymerization). We have applied the same procedure to the synthesis of other gold derivatives: [i.e. 2,4,6-tris(trimethyl)- [16–18], 4-(methoxy)-, 3-methoxy, 4-fluoro-, 3-fluoro-, 3,5-difluoro-phenyl(triphenylphosphine)gold(I)]. All these derivatives are characterized by  $^1H$ ,  $^{13}C$ ,  $^{31}P$ ,  $^{19}F$  NMR, melting point determination, and X-ray diffraction analysis. There is experimental evidence of aurophilic  $Au(I) \cdots Au(I)$  [19–23] attraction from crystallography.

A series of gold complexes of the general type  $[AuR(PPh_3)]$  (Fig. 1) were prepared by standard methods in high yields (Table 1).

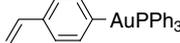
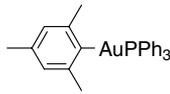
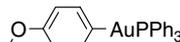
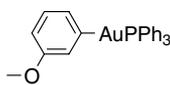
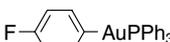
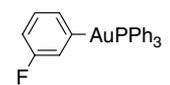
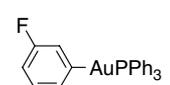
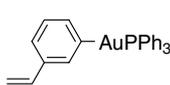
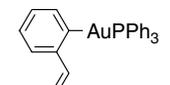


$M = Li$ ;  $R = 4-CH_2=CHPh$  (**1**),  $3-CH_2=CHPh$  (**8**),  $2-CH_2=CHPh$  (**9**)

$M = MgBr$ ;  $R =$  mesityl (**2**), 4-MeOPh (**3**), 3-MeOPh (**4**), 4-FPh (**5**), 3-FPh (**6**), 3,5-F<sub>2</sub>Ph (**7**)

Fig. 1. Synthesis of  $RAuPPh_3$  with RM reagents.

Table 1  
Structures of gold complexes

Entry	$RAuPPh_3$	Yield (%)	Mp ( $^\circ C$ )
1		89	152–153
2		91	196–197
3		90	137–138
4		96	136–137
5		85	140–141
6		96	148–149
7		88	132–133
8		89	156–157
9		89	156–157

These derivatives were prepared by classical organometallic synthesis under inert atmospheres. They were isolated by standard methods and purified by crystallization in chloroform. It is important to note that all these derivatives were air and water stable. In a matter of fact, this stability allowed to study the vinyl substituted gold(I) complexes in different polymerization procedures. We can note that for these gold(I) complexes the melting point is close to the temperature of decomposition. For example the differential scanning calorimetry (DSC) of complex **6** shows a melting point of ca. 149  $^\circ C$  and a temperature of beginning decomposition of ca. 160  $^\circ C$ .

All these complexes were characterized by complete NMR analysis. The  $^{13}\text{C}$  NMR spectra of complexes **1**, **2**, **4**, **6**, **7** and **8** were specific: a doublet (Fig. 2), was observed for the carbon that was attached to the gold atom. There was coupling between the *ipso*-carbon and the phosphorus. This coupling was very extensive (approximately 110 Hz) and has rarely been reported in the literature [24,25]. This *ipso*-carbon was not observed in complexes **3** and **5**. To establish this coupling, it was necessary that the  $\text{CDCl}_3$  solution in the NMR tube must be very concentrated (in the range of 100 to 120 mg of complex).

In order to confirm the structures of these complexes, an X-ray diffraction analysis was performed to determine their molecular structure. Crystal data and refinement details for major complexes are presented in Table 8. Figs. 3–8 show the molecular structure of **1**, **2**, **3**, **4**, **6** and **7**, respectively, with selected bond lengths and angles in Tables 2–7. Complex **5** could not be analyzed because it was not a monocrystal.

All the complexes proved to have molecular structures that we have expected; however, some differences were observed. Molecular structures of complexes **1**, **2**, and **4** were confirmed by X-ray diffraction analysis and these three complexes were monomers.

Studies of X-ray diffraction of complexes **3**, **6** and **7** (Figs. 5, 7 and 8; Tables 4, 6 and 7) reveals that the

$\text{Au}\cdots\text{Au}$  distance, respectively, of 3.135, 3.120 and 3.108 Å. These distances are in conformity with direct aurophilic interaction:  $\text{Au}\cdots\text{Au}$  separations must be less than 3.6 Å [20,21].

Tables 2–7 summarize selected bond lengths and angles for complexes **1**, **2**, **3**, **4**, **6** and **7**.

We initially compared dimeric compounds. In complexes **3**, **6** and **7**,  $\text{Au}-\text{C}$  bond lengths were between 2.049(5) and 2.118(5) Å, thus essentially equal and similar to related distances in other arylgold complexes [9,15]. These bond lengths were substantially shorter than the predicted single bond length of approximately 2.44 Å ( $r_{\text{Au}} = 1.34$  Å,  $r_{\text{P}} = 1.10$  Å) and may indicate some degree of  $\text{Au}(\text{d}_{\pi}) \rightarrow \text{P}(\text{d}_{\pi})$  back bonding in these linear complexes [26]. In the case of dimers, it was interesting to note that the two  $\text{Au}-\text{C}$  distances in each complex were very homogeneous and similar. These  $\text{Au}-\text{C}$  bond lengths were a little longer than in ethynyl gold(I) complexes [27] which  $\text{Au}-\text{C}$  bond lengths are in the range 1.983(8)–2.03(2) Å.

Comparison of NMR and X-ray diffraction analysis revealed that as complexes were close to linearity, there is coupling by bonds in  $^{13}\text{C}$  NMR and not spatial coupling as previously supposed.

A classical synthesis method was used to prepare stable new vinylphenyl(triphenylphosphine)gold(I) complexes. We report the synthesis of gold(I) complexes

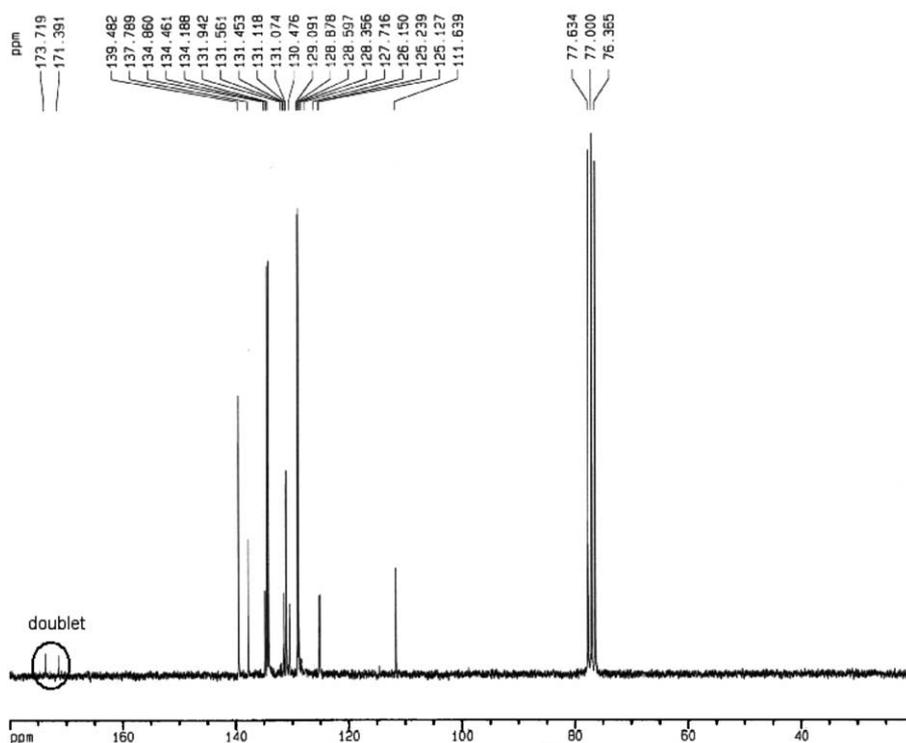


Fig. 2.  $^{13}\text{C}$  NMR spectrum of complex **1**. To establish this coupling by  $^{13}\text{C}$  NMR, the  $\text{CDCl}_3$  solution in the NMR tube must be very concentrated (100 to 120 mg of the complex to reveal this small doublet).

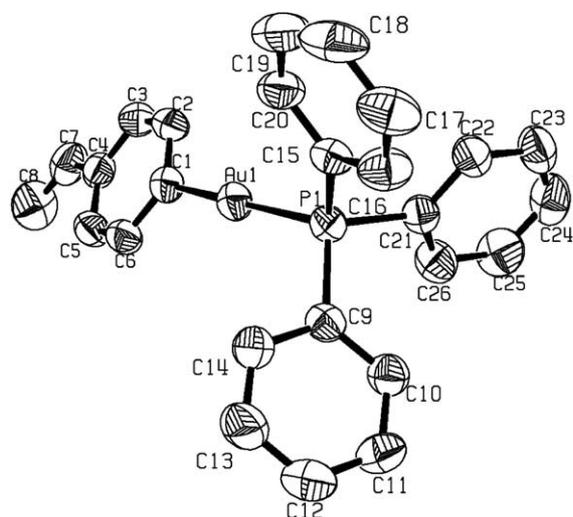


Fig. 3. ORTEP view of complex 1. Displacement parameter ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

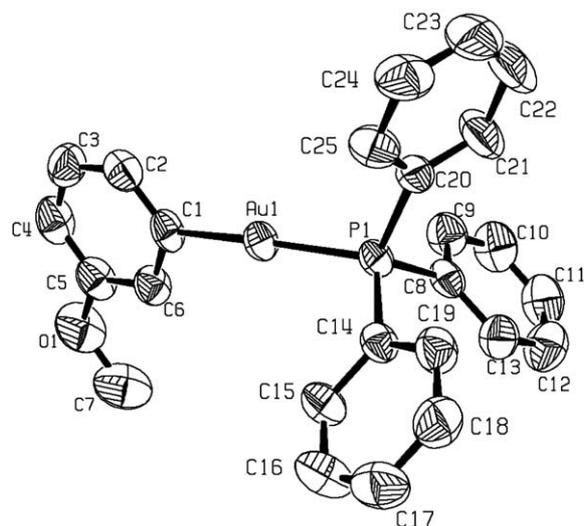


Fig. 6. ORTEP view of complex 4. Displacement parameter ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

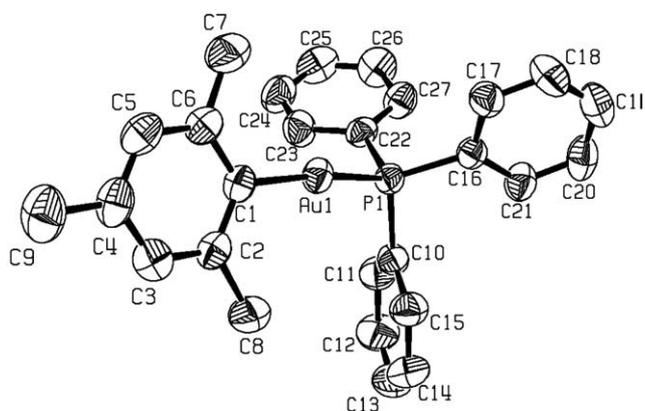


Fig. 4. ORTEP view of complex 2. Displacement parameter ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

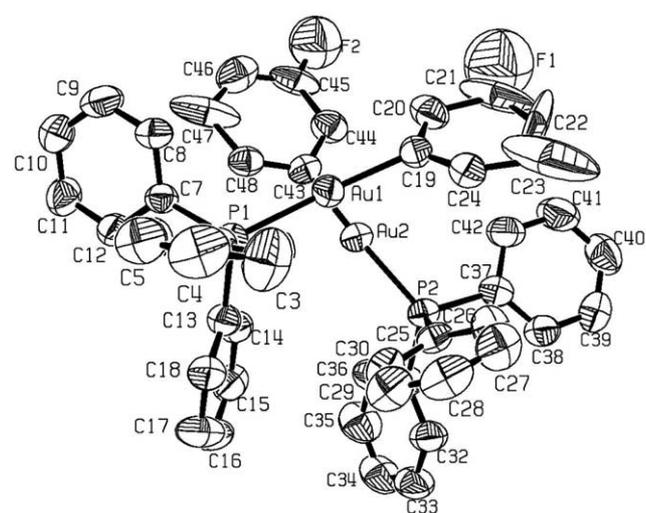


Fig. 7. ORTEP view of complex 6. Displacement parameter ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

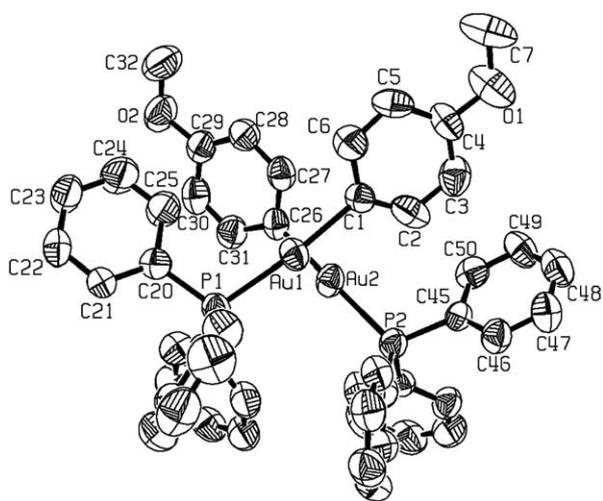


Fig. 5. ORTEP view of complex 3. Displacement parameter ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

with good overall yields from commercially available chloro(triphenylphosphine)gold(I).  $^{13}\text{C}$  NMR spectra properties for complexes **1**, **2**, **4**, **6**, **7** and **8** had particular features, with a large coupling constant between the *ipso*-carbon and the phosphorous atom. However, in complexes **3** and **5** the *ipso*-carbon could not be identified. The structures of **1**, **2** and **4** were also confirmed by X-ray crystal structure determination. On the other hand, the complexes **3**, **6** and **7** were dimeric. The radical polymerization of the three vinylphenyl(triphenylphosphine)gold(I) (**1**, **8** and **9**) are in progress and preliminary results are very promising for the application. The synthesis of various complexes with other ligands like triethylphosphine is also in progress in order to increase reactivity toward polymerization.

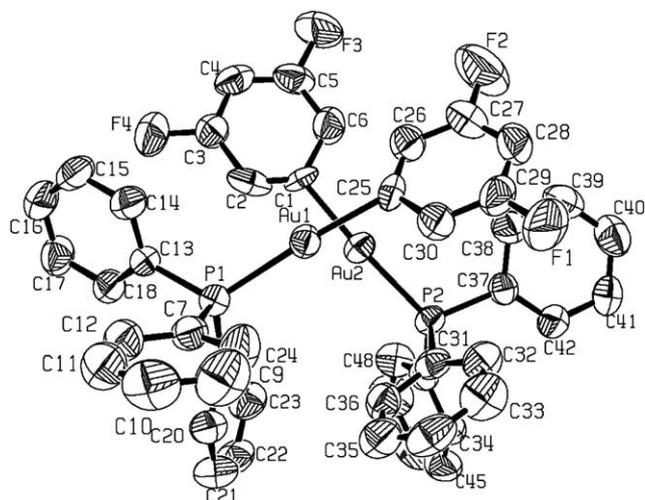


Fig. 8. ORTEP view of complex 7. Displacement parameter ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

Table 2  
Selected bond lengths (Å) and angles (°) for complex 1

Bond lengths (Å)	
Au(1)–P(1)	2.2937(11)
Au(1)–C(1)	2.046(4)
C(1)–C(2)	1.384(6)
C(1)–C(6)	1.393(6)
C(2)–C(3)	1.390(7)
C(3)–C(4)	1.374(6)
C(4)–C(5)	1.394(6)
C(5)–C(6)	1.381(6)
Bond angles (°)	
P(1)–Au(1)–C(1)	173.53(12)
C(2)–C(1)–Au(1)	122.0(3)
C(6)–C(1)–Au(1)	122.3(3)
C(2)–C(1)–C(6)	115.1(4)
C(1)–C(2)–C(3)	123.0(4)
C(4)–C(3)–C(2)	121.2(4)
C(3)–C(4)–C(5)	116.8(4)
C(6)–C(5)–C(4)	121.3(4)
C(1)–C(6)–C(5)	122.6(4)

## 2. Experimental

### 2.1. Instrumentation, materials and reagents

All reactions were carried out using standard Schlenk techniques under an inert atmosphere (Ar).  $^1\text{H}$  (200 MHz),  $^{13}\text{C}$  (50 MHz),  $^{31}\text{P}$  (81 MHz),  $^{19}\text{F}$  (188 MHz) NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker AC 200. The findings were as follows (in order): chemical shift ( $\delta$  in ppm), multiplicity (s, d, t, m for singlet, doublet, triplet, multiplet, respectively) and coupling constant ( $J$  in Hz).  $\text{ClAuPPh}_3$ , 4-bromostyrene, *n*-butyllithium, mesitylmagnesium bromide, 4-methoxyphenylmagnesium bromide, 4-fluoromagnesium bromide, 3-methoxyphenylmagnesium bromide,

Table 3  
Selected bond lengths (Å) and angles (°) for complex 2

Bond lengths (Å)	
Au(1)–P(1)	2.2891(12)
Au(1)–C(1)	2.061(5)
C(1)–C(2)	1.404(7)
C(1)–C(6)	1.397(7)
C(2)–C(3)	1.390(7)
C(3)–C(4)	1.367(8)
C(4)–C(5)	1.391(9)
C(5)–C(6)	1.397(7)
Bond angles (°)	
P(1)–Au(1)–C(1)	171.08(14)
C(2)–C(1)–Au(1)	118.9(3)
C(6)–C(1)–Au(1)	123.0(4)
C(2)–C(1)–C(6)	117.9(5)
C(1)–C(2)–C(3)	120.5(5)
C(4)–C(3)–C(2)	122.0(6)
C(3)–C(4)–C(5)	117.8(5)
C(6)–C(5)–C(4)	121.8(5)
C(1)–C(6)–C(5)	120.0(5)

Table 4  
Selected bond lengths (Å) and angles (°) for complex 3

Bond lengths (Å)	
Au(1)–P(1)	2.2953(19)
Au(1)–C(1)	2.100(7)
Au(1)–Au(2)	3.1352(4)
Au(2)–P(2)	2.299(2)
Au(2)–C(26)	2.063(8)
C(1)–C(2)	1.289(11)
C(1)–C(6)	1.363(11)
C(2)–C(3)	1.375(12)
C(3)–C(4)	1.352(13)
C(4)–C(5)	1.396(13)
C(5)–C(6)	1.385(12)
C(26)–C(31)	1.372(11)
C(26)–C(27)	1.393(11)
C(27)–C(28)	1.394(12)
C(28)–C(29)	1.356(12)
C(29)–C(30)	1.378(12)
C(30)–C(31)	1.367(13)
Bond angles (°)	
P(1)–Au(1)–C(1)	173.1(2)
C(1)–Au(1)–Au(2)	88.94(19)
P(1)–Au(1)–Au(2)	96.46(19)
P(2)–Au(2)–C(26)	177.2(2)
C(26)–Au(2)–Au(1)	80.4(2)
P(2)–Au(2)–Au(1)	102.29(5)
C(2)–C(1)–C(6)	116.7(8)
C(1)–C(2)–C(3)	125.6(9)
C(4)–C(3)–C(2)	118.2(9)
C(3)–C(4)–C(5)	119.3(8)
C(6)–C(5)–C(4)	117.8(8)
C(1)–C(6)–C(5)	122.4(9)
C(31)–C(26)–C(27)	114.8(8)
C(28)–C(27)–C(26)	122.8(8)
C(29)–C(28)–C(27)	119.8(9)
C(28)–C(29)–C(30)	118.6(9)
C(31)–C(30)–C(29)	120.6(8)
C(30)–C(31)–C(26)	123.3(9)

Table 5  
Selected bond lengths (Å) and angles (°) for complex 4

<i>Bond lengths (Å)</i>	
Au(1)–P(1)	2.2956(8)
Au(1)–C(1)	2.056(3)
C(1)–C(2)	1.362(5)
C(1)–C(6)	1.401(5)
C(2)–C(3)	1.400(6)
C(3)–C(4)	1.376(6)
C(4)–C(5)	1.362(6)
C(5)–C(6)	1.391(5)
<i>Bond angles (°)</i>	
P(1)–Au(1)–C(1)	175.51(10)
C(2)–C(1)–Au(1)	123.0(3)
C(6)–C(1)–Au(1)	118.7(3)
C(2)–C(1)–C(6)	118.2(3)
C(1)–C(2)–C(3)	120.8(4)
C(4)–C(3)–C(2)	120.6(4)
C(3)–C(4)–C(5)	119.1(4)
C(6)–C(5)–C(4)	120.7(4)
C(1)–C(6)–C(5)	120.5(4)

Table 6  
Selected bond lengths (Å) and angles (°) for complex 6

<i>Bond lengths (Å)</i>	
Au(1)–P(1)	2.2963(14)
Au(1)–C(19)	2.049(5)
Au(1)–Au(2)	3.1203(3)
Au(2)–P(2)	2.3085(13)
Au(2)–C(43)	2.057(5)
C(19)–C(20)	1.368(8)
C(19)–C(24)	1.403(9)
C(20)–C(21)	1.504(14)
C(21)–C(22)	1.444(19)
C(22)–C(23)	1.24(2)
C(23)–C(24)	1.72(2)
C(43)–C(48)	1.386(7)
C(43)–C(44)	1.400(8)
C(44)–C(45)	1.396(10)
C(45)–C(46)	1.378(12)
C(46)–C(47)	1.407(12)
C(47)–C(48)	1.510(11)
<i>Bond angles (°)</i>	
P(1)–Au(1)–C(19)	173.41(17)
C(19)–Au(1)–Au(2)	80.29(15)
P(1)–Au(1)–Au(2)	104.68(3)
P(2)–Au(2)–C(43)	173.62(15)
C(43)–Au(2)–Au(1)	86.57(13)
P(2)–Au(2)–Au(1)	98.27(3)
C(20)–C(19)–C(24)	116.3(6)
C(19)–C(20)–C(21)	113.5(7)
C(22)–C(21)–C(20)	113.3(9)
C(23)–C(22)–C(21)	156(2)
C(22)–C(23)–C(24)	82.2(19)
C(19)–C(24)–C(23)	138.4(9)
C(48)–C(43)–C(44)	116.2(5)
C(45)–C(44)–C(43)	117.8(6)
C(46)–C(45)–C(44)	124.6(6)
C(45)–C(46)–C(47)	124.2(8)
C(46)–C(47)–C(48)	107.8(9)
C(43)–C(48)–C(47)	129.4(6)

Table 7  
Selected bond lengths (Å) and angles (°) for complex 7

<i>Bond lengths (Å)</i>	
Au(1)–P(1)	2.2957(14)
Au(1)–C(25)	2.111(5)
Au(1)–Au(2)	3.1080(3)
Au(2)–P(2)	2.2988(13)
Au(2)–C(1)	2.118(5)
C(1)–C(2)	1.184(8)
C(1)–C(6)	1.437(8)
C(2)–C(3)	1.472(9)
C(3)–C(4)	1.345(9)
C(4)–C(5)	1.378(10)
C(5)–C(6)	1.378(9)
C(25)–C(26)	1.334(8)
C(25)–C(30)	1.364(8)
C(26)–C(27)	1.362(9)
C(27)–C(28)	1.366(10)
C(28)–C(29)	1.352(10)
C(29)–C(30)	1.364(9)
<i>Bond angles (°)</i>	
P(1)–Au(1)–C(25)	172.52(15)
C(25)–Au(1)–Au(2)	79.98(14)
P(1)–Au(1)–Au(2)	105.55(4)
P(2)–Au(2)–C(1)	173.99(14)
C(1)–Au(2)–Au(1)	85.87(12)
P(2)–Au(2)–Au(1)	99.57(3)
C(2)–C(1)–C(6)	121.6(5)
C(1)–C(2)–C(3)	121.3(5)
C(4)–C(3)–C(2)	121.7(6)
C(3)–C(4)–C(5)	114.7(6)
C(6)–C(5)–C(4)	123.5(6)
C(5)–C(6)–C(1)	117.1(6)
C(26)–C(25)–C(30)	120.5(5)
C(25)–C(26)–C(27)	118.8(6)
C(26)–C(27)–C(28)	123.5(7)
C(29)–C(28)–C(27)	115.4(6)
C(28)–C(29)–C(30)	123.0(6)
C(25)–C(30)–C(29)	118.8(6)

3-fluoromagnesium bromide, 3,5-difluoromagnesium bromide and all solvents were all purchased from Aldrich.

## 2.2. General procedure with $M = Li$

To a solution of 4-bromostyrene (0.18 g, 1 mmol) in THF (2 mL), 0.4 mL of *n*-BuLi 2.5 M (1 mmol) was added dropwise at  $-78\text{ }^{\circ}\text{C}$ . The mixture was stirred for 10 min, and a solution of ClAuPPh<sub>3</sub> (0.5 g, 1 mmol) in THF (15 mL) was added to the “*para*-vinyl(phenyl)lithium”. The mixture was allowed to warm to room temperature, and mixed for 16 h. The mixture was treated with a saturated solution of ammonium chloride and extracted with diethylether. The organic layers were washed with a saturated solution of sodium chloride. The organic layers were dried over magnesium sulphate; and solvents were removed under reduced pressure. The crude product was obtained as a lightly yellow powder through removal

of the solvent in vacuo. **1–9** were obtained as white crystals via crystallization from  $\text{CHCl}_3$ .

#### 2.2.1. *p*-Vinylphenyl(triphenylphosphine)Au(I) (**1**)

Yield: 89% (0.5 g), m.p.: 152–153 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 5.15 (1H, d,  $J = 10.8$  Hz), 5.73 (1H, d,  $J = 17.6$  Hz), 6.73 (1H, dd,  $J = 10.9$  Hz,  $J = 17.6$  Hz), 7.47–7.76 (19  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 111.6 (1C), 125.2 (1C, d,  $J_{\text{C-P}} = 5.2$  Hz), 129 (6C, d,  $J_{\text{C-P}} = 10.7$  Hz), 131 (3C, d,  $J_{\text{C-P}} = 49$  Hz), 131.1 (3C, d,  $J_{\text{C-P}} = 5.3$  Hz), 134.3 (6C,  $J_{\text{C-P}} = 13.7$  Hz), 134.9 (1C), 137.8 (1C), 139.5 (1C), 172.6 (1C, d,  $J_{\text{C-P}} = 116$  Hz);  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 45.

#### 2.2.2. *m*-Vinylphenyl(triphenylphosphine)Au(I) (**8**)

Yield: 89% (0.5 g), m.p.: 156–157 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 5.19 (1H, d,  $J = 10.9$  Hz), 5.76 (1H, d,  $J = 17.6$  Hz), 6.76 (1H, dd,  $J = 10.9$  Hz,  $J = 17.6$  Hz), 7.24–7.70 (19  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 112.0 (1C), 123.7 (1C), 127.4 (1C), 129.0 (6C, d,  $J_{\text{C-P}} = 10.9$  Hz), 131.2 (3C), 134.3 (6C,  $J_{\text{C-P}} = 13.6$  Hz), 136.1 (1C), 137.5 (1C), 138.4 (1C), 139.2 (1C), 171.9 (1C, d,  $J_{\text{C-P}} = 112.9$  Hz);  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 45.

#### 2.2.3. *o*-Vinylphenyl(triphenylphosphine)Au(I) (**9**) [28]

Yield: 89% (0.5 g), m.p.: 156–157 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 5.20 (1H, d,  $J = 10.8$  Hz), 5.82 (1H, d,  $J = 17.5$  Hz), 7.16–7.48 (2H, m), 7.47–7.70 (18  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 110.8 (1C), 124.4 (1C), 125.6 (1C), 126.4 (1C), 129.0 (6C, d,  $J_{\text{C-P}} = 10.9$  Hz), 131.2 (3C), 134.2 (6C,  $J_{\text{C-P}} = 13.7$  Hz), 139.6 (1C), 137.5 (1C), 143.8 (1C), 139.2 (1C), 146.1 (1C);  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 45.

### 2.3. General procedure with $M = \text{MgBr}$

The appropriate organomagnesium bromide derivatives (1 mmol) were added dropwise to a solution of  $\text{ClAuPPh}_3$  (0.5 g, 1 mmol) in THF (15 mL) at  $-78$  °C. The mixture was allowed to warm to room temperature and was mixed for 16 h. Treatment was the same as for compound **1**.

#### 2.3.1. 2,4,6-Trimethylphenyl(triphenylphosphine)Au(I) (**2**)

Yield: 91%, m.p.: 196–197 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 2.27 (3H, s), 2.66 (6H, s), 6.98 (2H, s), 7.49–7.71 (15  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 21.1 (1C), 26.8 (2C), 126.3 (2C, d,  $J_{\text{C-P}} = 6.6$  Hz), 129 (6C,  $J_{\text{C-P}} = 10.6$  Hz), 130.8 (3C,  $J_{\text{C-P}} = 2.2$  Hz), 131.3 (3C,  $J_{\text{P-C}} = 48.2$  Hz), 134.3 (6C,  $J_{\text{P-C}} = 13.8$  Hz), 135.0 (1C), 145.7 (1C), 169.8 (1C,  $J_{\text{P-C}} = 111.1$  Hz);  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 46.

#### 2.3.2. *p*-Methoxyphenyl(triphenylphosphine)Au(I) (**3**)

Yield: 90%, m.p.: 137–138 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 3.82 (3H, s), 6.95 (2H, d), 7.47–7.68 (17  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 55.0 (1C), 113.5 (2C), 129.0 (6C,  $J_{\text{C-P}} = 10.7$  Hz), 130.9 (3C,  $J_{\text{P-C}} = 49.7$  Hz), 131.1 (3C,  $J_{\text{C-P}} = 2.0$  Hz), 134.3 (6C,  $J_{\text{P-C}} = 13.7$  Hz), 139.9 (2C), 157.8 (1C);  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 45.

#### 2.3.3. *m*-Methoxyphenyl(triphenylphosphine)Au(I) (**4**)

Yield: 96%, m.p.: 136–137 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 3.85 (3H, s), 6.74 (1H, m), 7.20 (3H, m), 7.47–7.70 (15  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 55.0 (1C), 111.9 (1C), 124.1 (1C), 128.0 (1C), 129.0 (6C,  $J_{\text{C-P}} = 10.7$  Hz), 130.9 (3C,  $J_{\text{C-P}} = 48.4$  Hz), 131.1 (3C), 134.3 (6C,  $J_{\text{P-C}} = 13.6$  Hz), 158.7 (1C), 173.2 (1C,  $J_{\text{C-P}} = 115.9$  Hz);  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 45.

#### 2.3.4. *p*-Fluorophenyl(triphenylphosphine)Au(I) (**5**)

Yield: 85%, m.p.: 140–141 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 7.03 (2H, m), 7.47–7.73 (17  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 114.1 (2C,  $J_{\text{C-F}} = 17.7$  Hz), 129.0 (6C,  $J_{\text{C-P}} = 10.8$  Hz), 131.3 (3C), 134.3 (6C,  $J_{\text{P-C}} = 13.6$  Hz), 140.1 (2C,  $J_{\text{C-F}} = 5.4$  Hz), 161.6 (1C,  $J_{\text{C-F}} = 241.2$  Hz),  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 45;  $^{19}\text{F}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 188 MHz):  $-119.40$  (m, 1F).

#### 2.3.5. *m*-Fluorophenyl(triphenylphosphine)Au(I) (**6**)

Yield: 96%, m.p.: 148–149 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 6.81 (1H, m), 7.36–7.68 (18  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 112.3 (1C,  $J_{\text{C-F}} = 20.7$  Hz), 125.2 (1C,  $J_{\text{C-F}} = 15.0$  Hz), 128.3 (1C), 129.1 (6C,  $J_{\text{C-P}} = 10.7$  Hz), 130.2 (3C), 131.2 (3C), 134.3 (6C,  $J_{\text{P-C}} = 13.6$  Hz), 134.9 (1C), 162.8 (1C,  $J_{\text{C-F}} = 246.5$  Hz), 174.5 (1C,  $J_{\text{C-P}} = 115.2$  Hz);  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 45;  $^{19}\text{F}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 188 MHz):  $-118.43$  (m, 1F).

#### 2.3.6. 3,5-Difluorophenyl(triphenylphosphine)Au(I) (**7**)

Yield: 88%, m.p.: 132–133 °C.  $^1\text{H}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 200 MHz): 6.55 (1H, m), 7.14 (2H, m), 7.46–7.65 (15  $\text{H}_{\text{ar}}$ , m);  $^{13}\text{C}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 50 MHz): 100.7 (1C,  $J_{\text{C-F}} = 25.1$  Hz), 120.6 (2C,  $J_{\text{C-F}} = 12.0$  Hz), 129.1 (6C,  $J_{\text{C-P}} = 10.8$  Hz), 130.5 (3C,  $J_{\text{C-P}} = 50.6$  Hz), 131.3 (3C), 134.3 (6C,  $J_{\text{P-C}} = 13.6$  Hz), 162.6 (1C,  $J_{\text{C-F}} = 249.4$  Hz), 176.1 (1C,  $J_{\text{C-P}} = 117.7$  Hz),  $^{31}\text{P}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 81 MHz): 44;  $^{19}\text{F}$  NMR  $\delta$  ppm ( $\text{CDCl}_3$ , 188 MHz):  $-116.8$  (m, 1F).

### 3. X-ray crystal structure determination

Suitable single crystals of **1**, **2**, **3**, **4**, **6** and **7** were mounted on a glass fiber. Data collections were carried

Table 8  
Crystal and refinement data for complexes **1**, **2**, **3**, **4**, **6**, and **7**

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>6</b>	<b>7</b>
Formula	C <sub>26</sub> H <sub>22</sub> AuP	C <sub>27</sub> H <sub>26</sub> AuP	C <sub>50</sub> H <sub>44</sub> Au <sub>2</sub> P <sub>2</sub> O <sub>2</sub>	C <sub>25</sub> H <sub>22</sub> AuOP	C <sub>48</sub> H <sub>38</sub> Au <sub>2</sub> F <sub>2</sub> P <sub>2</sub>	C <sub>48</sub> H <sub>36</sub> Au <sub>2</sub> F <sub>4</sub> P <sub>2</sub>
Formula weight	562.37	578.41	1132.72	566.36	1108.66	1144.64
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	9.3850(4)	9.0251(1)	13.5515(3)	8.8659(4)	13.6700(2)	13.7647(2)
<i>b</i> (Å)	9.6898(6)	14.3916(2)	11.9963(2)	10.7086(3)	11.6510(2)	11.7638(2)
<i>c</i> (Å)	12.9710(8)	17.8986(3)	26.9017(7)	12.7905(6)	25.8010(6)	25.6862(6)
$\alpha$ (°)	75.959(3)			72.921(3)		
$\beta$ (°)	70.290(3)	91.9775(6)	101.6633(7)	71.059(2)	97.6010(7)	98.2129(6)
$\gamma$ (°)	86.859(4)			80.279(3)		
<i>V</i> (Å <sup>3</sup> )	1076.83(10)	2323.48(6)	4283.16(16)	1094.32(8)	4073.20(11)	4116.71(10)
<i>Z</i>	2	4	4	2	4	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.734	1.654	1.757	1.719	1.808	1.847
$\mu$ (mm <sup>-1</sup> )	9.913	6.411	6.956	6.807	7.316	7.249
<i>F</i> (000)	544	1128	2192	548	2128	2192
$\theta$ Range (°)	2.17; 28.59	1.82; 28.57	1.55; 28.52	2.97; 28.79	2.37; 28.67	2.35; 28.69
Reflections collected	12278	32711	51125	22242	52495	47878
Independent reflections	5227	5802	10565	5434	9978	10338
<i>R</i> <sub>int</sub>	0.039	0.053	0.096	0.046	0.081	0.085
Maximum/minimum transmission	0.419/0.518	0.250/0.294	0.348/0.516	0.208/0.279	0.134/0.271	0.366/0.701
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0313	0.0275	0.0495	0.0253	0.0351	0.0369
<i>wR</i> <sub>2</sub> (all data)	0.0701	0.0983	0.1188	0.0613	0.0909	0.0869

out at room temperature on a Bruker-Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo (K $\alpha$ ) radiation ( $\lambda = 0.71073$  Å). Cell parameters were retrieved and refined using DENZO-SMN [29] software on all reflections. Data reductions were performed with the DENZO-SMN [29] software. An empirical absorption correction based on the symmetry-equivalent reflections was applied to each data set using the SORTAV [30] program. The structure were solved either by SIR92 [31] or SHELXS-97 [32] and refined with the SHELXL-97 program [33]. The hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. Detailed crystal data are listed in Table 8.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 267455 (compound **1**), 267456 (compound **2**), 267457 (compound **3**), 267458 (compound **4**), 267459 (compound **6**), 267460 (compound **7**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the web <http://www.ccdc.cam.ac.uk>.

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