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Mesityl gold(III) complexes. X-ray structure of mononuclear $[Au(mes)_2Cl(PPh_3)]$ and the dimer $[Au(mes)_2Cl]_2$

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Dedicated to Prof. Martin A. Bennett in recognition of his outstanding contributions to organometallic and inorganic chemistry, on the occasion of his 65th birthday.

Abstract

The reaction between $PPN[AuCl_4]$ and $[Hg(mes)_2]$ gives the anionic complex *cis*-$PPN[Au(mes)_2Cl_2]$ (**1**) and [Hg(mes)Cl] as side-product. Complex **1** is a precursor to other compounds both neutral and cationic. Removal of one chloride ligand affords the mononuclear neutral complexes *cis*-$[Au(mes)_2ClL]$ ($L = PPh_3$ (**2**), $P\{p\text{-tol}\}_3$ (**3**), $AsPh_3$ (**4**), $SPPh_3$ (**5**)) by addition of a neutral ligand or, alternatively if no ligand is added, dimeric *cis*-$[Au(mes)_2Cl]_2$ (**6**). If both chloride groups in **1** are removed, cationic compounds can be obtained by addition of a potentially bidentate ligand affording *cis*-$[Au(mes)_2(L–L)]X$ complexes ($X = ClO_4$, L–L = bipy (**7**), L–L = phen (**8**), L–L = dppe (**9**) $X = SO_3CF_3$, L–L = dppm (**10**)). Dithiocarbamate- or acetate salts can be added to solutions of '$Au(mes)_2X$' (obtained by removal of two chloride anions in **1**) leading to the neutral compounds *cis*-$[Au(mes)_2(L–L)]$ (L–L = S_2CNR_2 (R = Me (**11**), Et (**12**), Bz (**13**)), O_2CCF_3 (**14**)). The structures of *cis*-$[Au(mes)_2Cl(PPh_3)]$ (**2**) and *cis*-$[Au(mes)_2Cl]_2$ (**6**) have been established by an X-ray diffraction study.

Keywords: Gold(III); Mercury; Mesityl

1. Introduction

Gold(III) complexes with two gold-carbon bonds have been known for a long time, particularly those containing methyl or pentafluorophenyl groups as ligands [1–4]. The traditional synthesis with Grignard or organolithium reagents lead generally to very low yields. Improved synthetic methods involved the use of organotin [5], organothalium [6] and organomercury [7,8] reagents or, in a few cases, the oxidative addition of halogen to the corresponding organogold(I) complexes $[AuR_2]^-$ [9,10].

We have been reporting on the chemistry of mesityl gold(I) derivatives [11–13]. The radical mesityl $[(C_6H_2Me_3)–]$ can act as a simple (terminal) ligand or as a bridge between two metalic centres affording a three-centre two-electron bond. Mesityl gold(I) derivatives of the type [AuRL] have proven to be useful precursors to homo- and hetero-polynuclear compounds [11,12] that have displayed interesting metal-metal interactions. We wanted to extend this chemistry to gold(III) complexes and study the behaviour of such compounds.

Gold(III) componds containing the mesityl group as a terminal ligand have been obtained by reaction between the Grignard reagent and $[AuCl_2(L–L)]ClO_4$ [L–L = bipy (2,2′-bipyridine), phen (1,10-phenantroline), dpphen (4,7-diphenylphenantroline)] [14] and by oxidative addition of halogens to mesityl gold(I)

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Q[Au(mes)X] complexes (Q = $P(CH_2Ph)PPh_3$, $N(PPh_3)_2$) [11]. However, both methods have restrictions. The first one is limited by the range of available gold(III) starting materials stable towards the derivative Mg(mes)Br. The second only affords gold(III) complexes with one mesityl group. It was, therefore, desirable to obtain a mesityl gold(III) compound that could be used as a precursor to other gold(III) products in a wider range.

In this paper we describe the synthesis of the compound *cis*-PPN[Au(mes)$_2$Cl$_2$] (**1**) (PPN$^+$: $N(PPh_3)_2$, bis(triphenylphosphine)iminium)) which is obtained via the organomercury reagent [Hg(mes)$_2$] [15] according to an earlier procedure for transferring one or two aryl groups to gold(III) centres [7,8,16–24]. Attempts to prepare **1** via Grignard or lithiated reagents and PPN[AuCl$_4$] failed due to predominant reduction to PPN[Au(mes)Cl] previously reported [11]. Complex **1** behaves as a precursor to other mesityl gold(III) compounds both neutral and cationic.

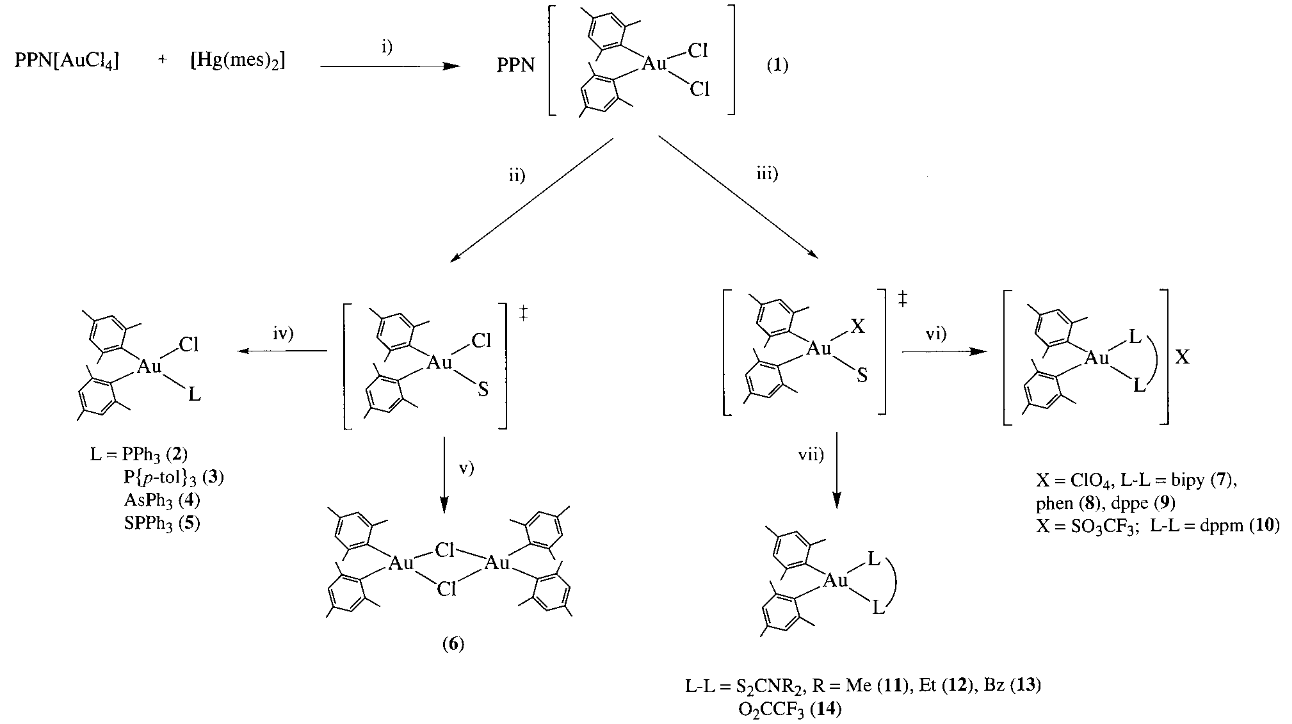
2. Results and discussion

The reaction in refluxing acetone of PPN[AuCl$_4$] with Hg(mes)$_2$ in a molar ratio 1:2 for 10 h leads to the formation of *cis*-PPN[Au(mes)$_2$Cl$_2$] (**1**) together with [Hg(mes)Cl] in high yield (Scheme 1(i)).

Both compounds are easily separated and purified by fractional crystallization. Attempts to substitute more chloride anions by mesityl groups following the method described in Scheme 1(i) failed. This behaviour is similar to what Vicente et al. found for the reaction between HgR_2 (R = *ortho*-nitro aryl groups) and Q[AuCl$_4$] [7,8]. This method only leads to the formation of Q[AuR$_2$Cl$_2$].

Removal of one chloride group from **1** is achieved by reaction of **1** and silver triflate or silver perchlorate in a dichloromethane–OEt$_2$ solution. Neutral complexes are obtained by addition of L = PPh$_3$ (**2**), P{*p*-tol}$_3$ (**3**), AsPh$_3$ (**4**), SPPh$_3$ (**5**) in a 1:1 ratio to solutions of 'Au(mes)$_2$Cl' (Scheme 1(iv)). If no ligand is added to these solutions dimeric [Au(mes)$_2$Cl]$_2$ (**6**) precipitates after subsequent treatment of the filtrate (Scheme 1(v)).

By using two equivalents of silver triflate or silver perchlorate the two chloride anions present in **1** can be removed (Scheme 1(iii)). Proposed [Au(mes)$_2$S(X)] (S = solvent molecule, X = $OClO_3$, OSO_2CF_3) failed to be isolated due to, presumably, their inestability. However, addition of bidentate ligands such as diamines or diphosphines [L–L = bipy, phen, dppe (1,2-bis(diphenylphosphino)ethane), or dppm (1,2-bis-(diphenylphosphino)methane)] stabilises the 'Au-(mes)$_2$SX' species by formation of square-planar cationic complexes of the type [Au(mes)$_2$(L–L)]X (Scheme 1(vi)). Compounds **7** and **8** (with bipy and phen, respectively) had been previously synthesised by



Scheme 1. (i) (1:2) Molar ratio, Δ, acetone, –[Hg(mes)Cl]; (ii) AgX (1:1); –AgCl, –PPNCl; (iii) AgX (1:2), –2AgCl, –PPNCl; (iv) L; (v) *n*-hexane; (vi) L–L; (vii) Q(L–L), –QX.

Table 1
Spectroscopic and conductivity data for compexes **1**–**14**

Complex	^{31}P{^{1}H}-NMR [a]	^{1}H-NMR [a]				ΛM [b]
		o-Me	*p*-Me	*m*-H	Other	
1 *cis*-PPN[Au(mes)$_2$Cl$_2$]	–	2.49 (s)	2.05 (s)	6.49 (s)	–	132
2 *cis*-[Au(mes)$_2$Cl(PPh$_3$)]	27.8 (s)	2.47 (s), 2.07 (s)	2.12 (s), 2.04 (s)	6.65 (d) [c], 6.31 (s)	–	3
3 *cis*-[Au(mes)$_2$Cl(P{*p*-tol}$_3$)]	26.6 (s)	2.47 (s), 2.07 (s)	2.12 (s), 2.04 (s)	6.64 (d) [d], 6.28 (s)	2.35(s) [e]	4
4 *cis*-[Au(mes)$_2$Cl(AsPh$_3$)]	–	2.49 (s), 2.16 (s)	2.13 (s), 2.05 (s)	6.64 (s), 6.34 (s)	–	9
5 *cis*-[Au(mes)$_2$Cl(SPPh$_3$)]	43.9 (s)	2.31 (s), 2.14 (s)	2.53 (s), 2.05 (s)	6.56 (s, br), 6.46 (s)	–	1
6 *cis*-[Au(mes)$_2$Cl]$_2$	–	2.53 (s)	2.13 (s)	6.58 (s)	–	7
7 *cis*-[Au(mes)$_2$(bipy)]ClO$_4$	–	2.32 (s)	2.26 (s)	6.80 (s)	[f]	131
8 *cis*-[Au(mes)$_2$(phen)]ClO$_4$	–	2.37 (s)	2.29 (s)	6.85 (s)	[g]	128
9 *cis*-[Au(mes)$_2$(dppe)]ClO$_4$	45.1 (s)	1.84 (s)	2.13 (s)	6.55 (d) [h]	3.24 (‘d’) [i]	127
10 *cis*-[Au(mes)$_2$(dppm)]TfO	−25.5 (s)	2.05 (s)	2.18 (s)	6.66 (s, br)	5.61 (t) [j]	110
11 *cis*-[Au(mes)$_2$(S$_2$CNMe$_2$)]	–	2.48 (s)	2.15 (s)	6.63 (s)	3.29 (s) [k]	2
12 *cis*-[Au(mes)$_2$(S$_2$CNEt$_2$)]	–	2.49 (s)	2.15 (s)	6.63 (s)	3.68 (q) [l] 1.31 (t) [m]	20
13 *cis*-[Au(mes)$_2$(S$_2$CNBz$_2$)]	–	2.54 (s)	2.16 (s)	6.66 (s)	4.78 (s) [n]	15
14 *cis*-[Au(mes)$_2$(O$_2$CCF$_3$)]	–	2.43 (s)	2.18 (s)	6.63 (s)	–	2

[a] In CDCl$_3$, values in ppm.
[b] In acetone (5×10^{-4} mol l^{-1}).
[c] [$^5J_{P-H}=3.9$ Hz].
[d] [$^5J_{P-H}=3.9$ Hz].
[e] P(*p*-C$_6$H$_4$*CH*$_3$)$_3$.
[f] L = bipy 8.97 (dd) Hd, 8.47 (td) Hc, 7.84 (dd) Hb, 7.72 (td) Ha.
[g] L = phen, 9.05 (H$_2$, H$_9$), 8.35 (H$_5$, H$_6$), 8.23 (H$_7$, H$_4$), 8.09 (H$_3$), 8.07 (H$_8$).
[h] [$^5J_{P-H}=3.7$ Hz].
[i] L = Ph$_2$P–*CH*$_2$*CH*$_2$–PPh$_2$, [$^2J_{P-H}=16.8$ Hz].
[j] L = Ph$_2$P–*CH*$_2$–PPh$_2$, [$^2J_{P-H}=10.8$ Hz].
[k] L = SCN(*CH*$_3$)$_2$.
[l] –*CH*$_2$, [$^3J_{H-H}=10.8$ Hz].
[m] –*CH*$_3$, [$^3J_{H-H}=7.18$ Hz].
[n] –*CH*$_2$–C$_6$H$_5$.

reaction of [AuCl$_2$(L–L)]ClO$_4$ and Mg(mes)Br in a 1:2.5 molar ratio [14].

The filtrates containing ‘Au(mes)$_2$X’ species can be treated with sodium dithiocarbamates (Na[S$_2$CNR$_2$] (R = Me, Et and Bz)) or with [MePPh$_3$]CF$_3$COO to afford neutral complexes [Au(mes)$_2$(L–L)] and salts of the type QX (Q = Na or MePPh$_3$, X = CF$_3$SO$_3$) as side-products (Scheme 1(vii)).

All the gold(III) mesityl products described in this paper are stable in the solid state or in dichloromethane solution at room temperature. They are obtained as white or pale yellow solids. Acetone solutions of **1**, **7**–**10** display conductivities typical of 1:1 electrolytes whereas **2**–**6** and **11**–**14** are non-conducting (Table 1). Compounds **3**–**6**, **8**, **11**–**14** are partly soluble in solvents such as Et$_2$O or *n*-hexane and they are obtained in yields of ca. 50%.

The IR spectra (see Section 3) show absorptions from the mesityl ligand for all the compounds. In the case of anionic or cationic complexes signals that can be assigned to the PPN cation (**1**), anionic ClO$_4$ [25] (**7**–**9**) or TfO [26] (**10**) can be observed. The IR spectra of the starting material *cis*-PPN[Au(mes)$_2$Cl$_2$] (**1**) shows two absorptions at 291 (s) and 278 (s) that can be assigned to two active bands *v* (Au–Cl) (a$_1$, b$_1$) of the *cis*-isomer (C_{2v} symmetry).

Their ^{1}H-NMR spectra (Table 1) are as expected showing three signals due to the mesityl ligand (protons from the *ortho*- and *para*-methyl groups and protons in *meta*). In the case of the complexes [Au(mes)$_2$ClL] (**2**–**5**) signals that belong to two different mesityl groups (in *cis* or *trans* to the entering ligand) can be observed. For the phosphine complexes (**2** and **3**) the assigned signal for *m*-H of one mesityl group is observed as a doublet ($^5J_{P-H}=3.9$ Hz, Table 1) due to the coupling with the phosphine in *trans*. All these data together with the structural determination by means of an X-ray analysis of complex **2** (vide infra) is consistent with the proposal of square-planar complexes **2**–**5** being the *cis* isomers. The signals assigned to the mesityl ligand in the ^{1}H-NMR spectra of the neutral compounds **7**–**14** are very similar to those found for **1**.

The ^{31}P{^{1}H}-NMR of the compounds containing bidentate phosphines (**9** and **10**) shows a singlet but at very different chemical shifts (Table 1). In the case of **9** (L–L = dppe) the signal appears at δ 45.1 ppm (consis-

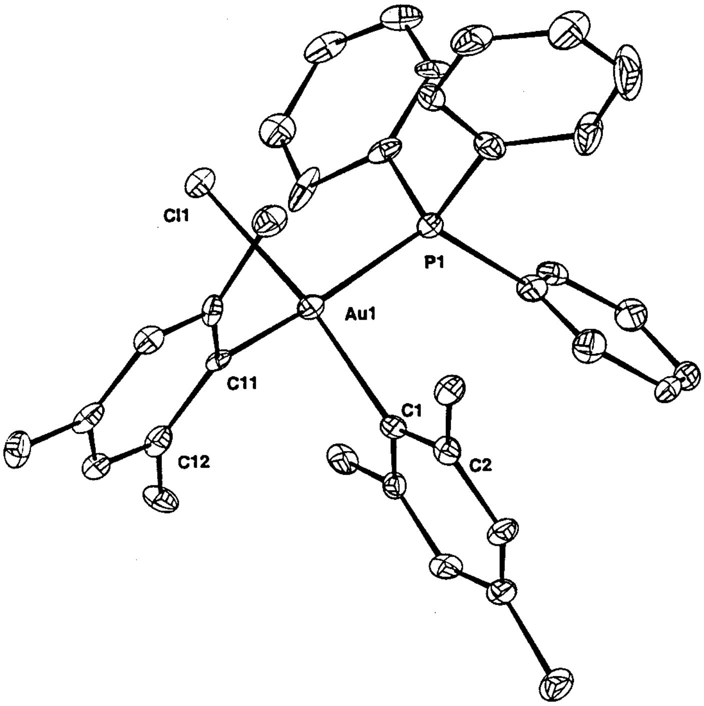


Fig. 1. Molecule of compound **2** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

tent with two phosphorus atoms coordinated to a gold(III) centre). For **10** (L–L = dppm) the resonance is highly shielded (δ −25.5 ppm) and explained on the basis of the constrain imposed on the four-membered phosphorus chelate ring as described for other metallic complexes [27].

In the case of the complexes with bidentate ligands the spectroscopic data indicates a *cis*-configuration and the mass spectra data points to the monomeric nature of these compounds. Furthermore, the crystal structure of **7**, that had been reported earlier, [14] confirmed such a *cis*-configuration. It is noteworthy how, in the case of the complexes with one monodentate ligand (**2**–**6**), the spectroscopic data also indicates such a *cis*-configuration. It seems reasonable to have foreseen a *trans* disposition for the mesityl groups since it would be sterically more favourable. In order to confirm the results in solution, single crystal X-ray diffraction studies of compounds **2** and **6** were carried out.

The molecular structure of **2** is shown in Fig. 1 and selected bond distances and angles are given in Table 2. The gold atom is in an almost square-planar environment with the mesityl ligands in a *cis* disposition. The gold(III)-C_{ipso} distances are 2.062(8) and 2.070(7) Å, a little bit longer than those described for $[Au(mes)_2(bipy)]ClO_4$ (**7**) (2.020(5), 2.029(6) Å) [14], the only gold(III) mesityl complexes to be structurally characterised up to date. These Au–C distances are also slightly longer than those found in the bis(mesityl) complex **6** reported is this article (vide infra). If we compare these Au–C distances to those reported for gold(I)–mesityl complexes there are similar variations. In the case of $[Ag(\mu\text{-dppm})_2\{Au(mes)\}_2]ClO_4$ [13] distances of 2.083(10) and 2.080(9) Å have been reported being shorter than those found in the anionic derivatives $[N(PPh_3)_2][(mes)AuCNAu(mes)]$ (2.035(11) Å) [28] and $[NEt_4][AuCl(mes)]$ (2.018(7) Å) [28]. The *cis*-mesityl groups are disposed perpendicularly to the co-

Table 2
Bond lengths (Å) and angles (°) for **2**

Bond lengths			
Au(1)–C(1)	2.062(8)	Au(1)–C(11)	2.070(7)
Au(1)–Cl(1)	2.381(2)	Au(1)–P(1)	2.423(2)
C(1)–C(2)	1.326(11)	C(1)–C(6)	1.461(11)
C(2)–C(3)	1.390(11)	C(2)–C(02)	1.507(11)
C(3)–C(4)	1.375(11)	C(4)–C(5)	1.376(11)
C(4)–C(04)	1.526(11)	C(5)–C(6)	1.357(11)
C(6)–C(06)	1.516(11)		
P(1)–C(41)	1.828(8)		
Bond angles			
C(1)–Au(1)–C(11)	89.7(3)	C(1)–Au(1)–Cl(1)	172.3(2)
C(11)–Au(1)–Cl(1)	89.1(2)	C(1)–Au(1)–P(1)	92.7(2)
C(11)–Au(1)–P(1)	168.1(2)	Cl(1)–Au(1)–P(1)	90.05(8)
C(2)–C(1)–C(6)	120.2(8)	C(2)–C(1)–Au(1)	125.9(7)
C(6)–C(1)–Au(1)	113.9(6)	C(1)–C(2)–C(3)	120.3(8)
C(1)–C(2)–C(02)	121.7(8)	C(3)–C(2)–C(02)	118.1(7)
C(4)–C(3)–C(2)	121.7(8)	C(3)–C(4)–C(5)	117.4(8)
C(3)–C(4)–C(04)	120.8(8)	C(5)–C(4)–C(04)	121.7(8)
C(6)–C(5)–C(4)	123.6(8)	C(5)–C(6)–C(1)	116.6(8)
C(5)–C(6)–C(06)	120.1(8)	C(1)–C(6)–C(06)	123.2(7)

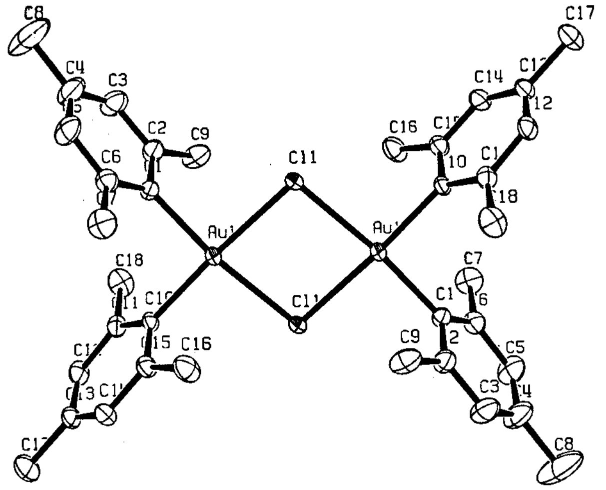


Fig. 2. Molecule of compound **6** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

Table 3
Bond lengths (Å) and angles (°) for **6** [a]

Bond lengths			
Au(1)–C(1)	2.033(3)	Au(1)–C(10)	2.038(3)
Au(1)–Cl(1)	2.4457(8)	Au(1)–Cl(1 ≠ 1)	2.4504(8)
Cl(1)–Au(1 ≠ 1)	2.4504(8)	C(1)–C(2)	1.394(4)
C(1)–C(6)	1.394(4)	C(2)–C(3)	1.399(4)
C(2)–C(9)	1.508(4)	C(3)–C(4)	1.373(5)
C(4)–C(5)	1.394(6)	C(4)–C(8)	1.522(5)
C(5)–C(6)	1.384(4)	C(6)–C(7)	1.505(5)
Bond angles			
C(1)–Au(1)–C(10)	92.73(11)	C(1)–Au(1)–Cl(1)	171.63(9)
C(10)–Au(1)–Cl(1)	92.98(8)	C(1)–Au(1)–Cl(1 ≠ 1)	90.46(8)
C(10)–Au(1)–Cl(1 ≠ 1)	173.15(8)	Cl(1)–Au(1)–Cl(1 ≠ 1)	84.53(2)
Au(1)–Cl(1)–Au(1 ≠ 1)	95.47(2)	C(2)–C(1)–C(6)	121.5(3)
C(2)–C(1)–Au(1)	115.5(2)	C(6)–C(1)–Au(1)	122.7(2)
C(1)–C(2)–C(3)	117.8(3)	C(1)–C(2)–C(9)	124.5(3)
C(3)–C(2)–C(9)	117.7(3)	C(4)–C(3)–C(2)	122.4(3)
C(5)–C(4)–C(8)	121.5(4)	C(6)–C(5)–C(4)	122.3(3)
C(5)–C(6)–C(1)	118.1(3)	C(5)–C(6)–C(7)	118.8(3)
C(1)–C(6)–C(7)	123.1(3)		

[a] Symmetry transformations used to generate equivalent atoms: ≠ 1: $-x+3/2$, $-y+3/2$, $-z+1$.

ordination plane of the gold centre in order to minimise the repulsion between the *ortho*-methyl groups. The Au–Cl distance of 2.381(2) Å and the Au–P distances of 2.423(2) Å are slightly longer than in other examples of gold(III) complexes with bonds to Cl (e.g. 2.337(8) Å in $[Au(C_6F_5)_2Cl(PPh_2CH_2PPh_2)]$) [29] or to PPh_3 ligands (e.g. 2.389(9) Å in $[Au(C_6F_5)_2Cl(PPh_3)]$ [30], 2.314(1) Å in $[Au(S_2C_6H_4)(C_6F_5)PPh_3]$ [31], 2.335(4) Å in $[AuCl_3(PPh_3)]$ [32] and 2.350(6) and 2.347(6)Å (two independent molecules) in $[AuMe_3(PPh_3)]$]) [33]. These elongations of the bonds *trans* to mesityl inditate the strong *trans* influence of this radical.

The crystal structure of dimer **6** is displayed in Fig. 2. Although related compound $[Au(C_6F_5)_2Cl]_2$ has been known for a long time [9] **6** is the only complex of the type $[AuR_2X]_2$ or $[AuRX_2]_2$ (with R = aryl) to have been structurally characterised. However, the crystal structures of $[AuEt_2Br]_2$ [34] and $[AuMeBr_2]_2$ [35] were reported a few decades ago. The molecular structure of **6** is planar and consists of discrete units of two gold atoms (with mesityl ligands in *cis*), each in a square-planar configuration and held by two chlorine atoms. The Au–C_{ipso} distances (2.033(3) and 2.038(3) Å) are shorter than the distances Au–C found for complex **2** and almost identical to those described for $[Au(mes)_2(bipy)]ClO_4$ (**7**) (vide supra). The bond angles around the gold atoms in **6** are all close to 90° and lie between the values of 92.98(8)° for C(10)–Au(1)–Cl(1) and 84.53(2)° for Cl(1)–Au(1)–Cl(1 ≠) (Table 3). These values are comparable to those found in $[AuEt_2Br]_2$ [34] and $[AuMeBr_2]_2$ [35]. The Au–Cl distances of 2.4457(8) and 2.4504(8) Å are slightly longer than observed in **2** as expected for chloro atoms acting as bridges between metallic centres and being *trans* to a mesityl group.

3. Experimental

Instrumentation and general experimental techniques were as described earlier [11]. Proton and $^{31}P\{^1H\}$-NMR and conductivity data are listed in Table 1. All the reactions were performed at room temperature (r.t.) except that of $PPN[AuCl_4]$ with $Hg(mes)_2$. Reactions of **1** with silver salts must be carried out avoiding light exposure until the silver chloride is removed. The starting materials $PPN[AuCl_2]$ [36] and $[Hg(mes)_2]$ [15] were prepared as described previously. $PPN[AuCl_4]$ was prepared by addition of stoichiometric Cl_2 to a solution of $PPN[AuCl_2]$ in dichloromethane. All other reagents were commercially available. *Caution:* perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and all samples handled with great caution.

3.1. Syntheses

3.1.1. cis-$PPN[Au(mes)_2Cl_2]$ (1)

To $PPN[AuCl_4]$ (1.097 g, 1.25 mmol) in acetone (50 ml) was added $[Hg(mes)_2]$ (1.369 g, 3.12 mmol). After heating at reflux for 1.5 h, the yellow mixture became a yellow solution by solubilisation of the organomercury reagent. Heating for a further 4.5 h afforded a colourless solution. The reaction was usually stopped after 10 h of refluxing (when decomposition to metallic gold started to be noticed). The solution was cooled and filtered through Celite. The almost colourless solution was concentrated in vacuo to ca. 5 ml, and Et_2O (20 ml) added to precipitate **1** as a white solid. The analytical sample was purified by recrystallization from dichloromethane–ether. The Et_2O filtrate was concentrated in vacuo to ca. 5 ml, and *n*-hexane (20 ml) added to afford [Hg(mes)Cl] as a white solid. Compound **1** (1.18 g, 92%): Anal. Found: C, 62.85; H, 5.20; N, 2.53. Calc. for $C_{54}H_{52}N_2PCl_2Au$: C, 63.09; H, 5.10; N, 2.73%. FAB MS: M^-, $m/z = 505$, 100%. IR (cm^{-1}, Nujol): ν (mes) = 1588 (w), 855, 845 (m); ν (PPN) = 1299 (vs, br), 1182, 1161 (m), 1113 (s); ν (Au–Cl) = 291, 278 (s).

3.1.2. *cis-[Au(mes)$_2$ClL] (L = PPh$_3$ (**2**), P{p-tol}$_3$ (**3**), AsPh$_3$ (**4**), SPPh$_3$ (**5**))*

To separate solutions of **1** (0.209 g, 0.2 mmol) in dichloromethane (20 ml) solutions of AgOtf (0.051 g, 0.2 mmol) in Et_20 (10 ml) were added. AgCl precipitated instantaneously and was removed by filtration of the reaction mixture through Celite. The resulting colourless solutions were concentrated in vacuo to ca. 5 ml and addition of Et_2O (20 ml) resulted in the precipitation of PPN[TfO] which was removed by filtration. To separate filtrates was added PPh_3 (0.047 g, 0.18 mmol), P{*p*-tol}$_3$ (0.055 g, 0.18 mmol), $AsPh_3$ (0.055 g, 0.18 mmol) or $SPPh_3$ (0.053 g, 0.18 mmol) for the obtention of **2**, **3**, **4** and **5**, respectively. After stirring at r.t. for 20 min. the solutions were concentrated in vacuo to ca. 5 ml and addition of *n*-hexane (20 ml) afforded **2**–**5** as white solids. Crystals of **2** suitable for an X-ray diffraction study were obtained by slowly evaporating a solution in dichloromethane. Compound **2** (0.096 g, 73%): Anal. Found: C, 58.45; H, 4.80. Calc. for $C_{36}H_{37}ClPAu$: C, 58.98; H, 5.09%. FAB MS: [M–Cl], $m/z = 697$, 24%. IR (cm^{-1}, Nujol): ν (mes) = 1586 (w), 855 (s, v br). Compound **3** (0.070 g, 53%): Anal. Found: C, 60.30; H, 5.60. Calc. for $C_{39}H_{43}ClPAu$: C, 60.43; H, 5.59%. FAB MS: [M–Cl], $m/z = 738$, 16%. IR (cm^{-1}, Nujol): ν (mes) = 1598 (w), 863, 849 (m). Compound **4** (0.068 g, 49%): Anal. Found: C, 55.80; H, 4.60. Calc. for $C_{36}H_{37}AsClAu$: C, 55.65; H, 4.80%. FAB MS: [M–Cl], $m/z = 741$, 20%. IR (cm^{-1}, Nujol): ν (mes) = 1582 (m), 855 (s). Compound **5** (0.076 g, 55%): Anal. Found: C, 56.90; H, 4.75; S, 3.80. Calc. for $C_{36}H_{37}ClPSAu$: C, 56.51; H, 4.87; S, 4.20%. FAB MS: [M–Cl], $m/z = 729$, 71%. IR (cm^{-1}, Nujol): ν (mes) = 1586 (m), 847 (s).

3.1.3. *cis-[Au(mes)$_2$Cl]$_2$ (**6**)*

To a solution of **1** (0.209 g, 0.2 mmol) in dichloromethane (20 ml) a solution of AgOtf (0.051 g, 0.2 mmol) in Et_20 (10 ml) was added. The AgCl and PPN[TfO] formed were removed from the solution as in Section 3.1.2. The colourless filtrate in diethyl ether was concentrated in vacuo to ca. 5 ml and addition of *n*-hexane (30 ml) afforded **6** as a pale yellow solid. Crystals of **6** suitable for an X-ray diffraction study were obtained by slowly layering *n*-hexane over a solution of **6** in dichloromethane. Compound **6** (0.048 g, 51%): Anal. Found: C, 46.25; H, 4.40. Calc. for $C_{36}H_{44}Cl_2Au_2$: C, 45.92; H, 4.71%. FAB MS: [M–Au-(mes)], $m/z = 384$, 11%, $[AuCl_2]_2$, $m/z = 538$, 100%. IR (cm^{-1}, Nujol): ν (mes) = 1559 (m), 868 (w), 847 (m).

3.1.4. *cis-[Au(mes)$_2$(L–L)]X (X = ClO$_4$, L–L = bipy (**7**), L–L = phen (**8**), L–L = dppe (**9**) X = SO$_3$CF$_3$, L–L = dppm (**10**))*

To separate solutions of **1** (0.103 g, 0.1 mmol) in dichloromethane (20 ml) solutions of $AgOClO_3$ (0.042 g, 0.2 mmol) to obtain **7**, **8** and **9**, or AgOtf (0.051 g, 0.2 mmol) to obtain **10**, in diethyl ether (10 ml) were added. After removal of AgCl and PPN[X] (X = ClO_4 or TfO) in the way described in Section 3.1.2, to the separate filtrates (containing 'Au(mes)$_2$X') in diethyl ether (20 ml) bipy (0.015 g, 0.1 mmol, **7**), phen (0.020 g, 0.1 mmol, **8**), dppe (0.040 g, 0.1 mmol, **9**) or dppm (0.038 g, 0.1 mmol, **10**) were added. All these compounds (**7**–**10**) precipitated in the media and were separated by filtration as white solids. Compound **7** (0.041 g, 60%): Anal. Found: C, 48.15; H, 4.20; N, 4.30. Calc. for $C_{28}H_{30}N_2ClO_4Au$: C, 48.67; H, 4.38; N, 4.05%. FAB MS: M^+, $m/z = 615$, 96%. IR (cm^{-1}, Nujol): ν (mes) = 1588 (m), 849 (m, br); ν (ClO_4) = 1088 (vs, br), 623 (m). Compound **8** (0.032 g, 44%): Anal. Found: C, 49.90; H, 4.10; N, 3.90. Calc. for $C_{30}H_{32}N_2ClO_4Au$: C, 50.25; H, 4.50; N, 3.90%. FAB MS: M^+, $m/z = 591$, 100%. IR (cm^{-1}, Nujol): ν (mes) = 1569 (w), 868, 849 (m); ν (ClO_4) = 1090 (vs, br), 623 (m). Compound **9** (0.066 g, 71%): Anal. Found: C, 56.10; H, 5.20. Calc. for $C_{44}H_{50}ClO_4P_2Au$: C, 56.39; H, 5.38%. FAB MS: M^+, $m/z = 832$, 39%. IR (cm^{-1}, Nujol): ν (mes) = 1586 (w), 849 (m, br); ν (ClO_4) = 1102 (vs, br), 623 (m). Complex **10** (0.086 g, 88%): Anal. Found: C, 54.15; H, 4.60; S, 3.25. Calc. for $C_{44}H_{48}F_3O_3P_2SAu$: C, 54.32; H, 4.97; N, 3.30%. FAB MS: M^+, $m/z = 819$, 56%. IR (cm^{-1}, Nujol): ν (mes) = 1586 (w), 849 (m, br); ν (TfO) = 1260 (vs, br), 1225 (s), 1156 (s).

3.1.5. *cis-[Au(mes)$_2$(L–L)] (L–L = S$_2$CNR$_2$ (R = Me (**11**), Et (**12**), Bz (**13**)), O$_2$CCF$_3$ (**14**))*

To separate solutions of [Au(mes)$_2$OClO$_3$] (0.1 mmol) obtained by the procedure described in Section 3.1.4, solutions of $Na[S_2CNR_2]_2H_2O$ (R = Me, 0.018 g, 0.1 mmol, **11**; Et, 0.023 g, 0.1 mmol, **12**; Bz, 0.029 g, 0.1 mmol, **13**) in acetone (10 ml) or $[MePPh_3]CF_3COO$ (0.039 g, 0.1 mmol, **14**) in dichloromethane (20 ml) were added. The reaction mixtures were stirred for 40 min (**11**–**13**) or 10 min (**14**) until the dithiocarbamates or acetate solublised. These slightly yellow solutions were filtered through celite in order to remove the $QClO_4$ (Q = Na, **11**–**13**; $MePPh_3$, **14**) formed. Concentration of the resulting filtrates to ca. 5 ml and addition of *n*-hexane (20 ml) gave **11** and **14** as white and **12** and

13 as pale yellow solids. Compound **11** (0.026 g, 46%): Anal. Found: C, 45.10; H, 5.50; N, 2.65; S, 11.30. Calc. for $C_{21}H_{28}NS_2Au$: C, 45.40; H, 5.08; N, 11.55; S, 2.50%. FAB MS: M^+, $m/z = 555$, 90%. IR (cm^{-1}, Nujol): v (mes) = 1545 (m), 849 (s). Compound **12** (0.024 g, 42%): Anal. Found: C, 46.90; H, 5.15; N, 2.45; S, 10.30. Calc. for $C_{23}H_{32}NS_2Au$: C, 47.33; H, 5.53; N, 2.40; S, 10.80%. FAB MS: M^+, $m/z = 583$, 83%. IR (cm^{-1}, Nujol): v (mes) = 1528 (m), 843 (s). Compound **13** (0.037 g, 53%): Anal. Found: C, 55.60; H, 4.90; N, 1.90; S, 8.75. Calc. for $C_{33}H_{36}NS_2Au$: C, 56.00; H, 5.13; N, 1.98; S, 9.05%. FAB MS: M^+, $m/z = 706$, 15%. IR (cm^{-1}, Nujol): v (mes) = 1586 (m), 847 (s). Compound **14** (0.030 g, 55%): Anal. Found: C, 44.15; H, 3.90. Calc. for $C_{20}H_{22}F_3O_2Au$: C, 43.81; H, 4.04%. FAB MS: M^+, $m/z = 548$, 7%. IR (cm^{-1}, Nujol): v (mes) = 1590 (m), 843 (s).

*3.2. Crystal structure determination of compound **2***

3.2.1. Crystal data

Compound **2**: $C_{36}H_{37}AuClP$, $M = 733.04$, monoclinic, space group $P2(1)/n$, $a = 13.216(3)$ Å, $b = 11.159(2)$ Å, $c = 21.229(3)$ Å, $\beta = 104.71(3)°$, $U = 3028.2(10)$ Å^3, $Z = 4$, $D_{calc} = 1.608$ Mg m^{-3}, λ(Mo–K$_\alpha$) = 0.71069 Å, $\mu = 5.023$ mm^{-1}, $F(000) = 1456$, $T = 150(2)$ K.

3.2.2. Data collection and reduction

A yellow prism ca. $0.16 \times 0.14 \times 0.12$ mm^3 was mounted in inert oil on a glass fibre. A total of 10 950 intensities were measured on a Delf Instruments TV area detector diffractometer, θ range for data collection 1.98–25.06°. A Lorentz-polarization type absorption correction was applied using the program DIFABS [37]. Merging equivalents gave 4566 unique reflections (R_{int} 0.0751).

3.2.3. Structure solution and refinement

The structure was solved by PATT instruction of SHELXS 86 [38] and subjected to full-matrix least-squares refinement on F^2 (program SHELXL 93 [39]).The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealised positions. Refinement proceeds to $R = 0.0400$, $wR = 0.092$ and goodness of fit on F^2 0.922 for 358 parameters and six restraints, and $R = 0.0566$, $wR = 0.0924$ for all data. In the final Fourier synthesis the electron density fluctuates in the range 2.619 to -1.330 e Å^{-3}.

*3.3. Crystal structure determination of compound **6***

3.3.1. Crystal data

Compound **2**: $C_{36}H_{44}Au_2Cl_2$, $M = 941.55$, monoclinic, space group $C2/c$, $a = 21.432(2)$ Å, $b = 9.8423(11)$ Å, $c = 16.942(2)$ Å, $\beta = 103.094(3)°$, $U = 3480.7(7)$ Å^3, $Z = 4$, $D_{calc} = 1.797$ Mg m^{-3}, λ(Mo–K$_\alpha$) = 0.71073 Å, $\mu = 8.596$ mm^{-1}, $F(000) = 1808$, $T = 160(2)$ K.

3.3.2. Data collection and reduction

A yellow prism ca. $0.38 \times 0.30 \times 0.16$ mm^3 was mounted in inert oil on a glass fibre. A total of 10 617 intensities were measured on a Siemens SMART CCD diffractometer, θ range for data collection 2.07–28.35°. Reflections were corrected for absorption by a semi-empirical method (ψ-scan) [40]. Merging equivalents gave 3958 unique reflections (R_{int} 0.0340).

3.3.3. Structure solution and refinement

The structure was solved by direct methods and instruction of SHELXS 96 [41] and subjected to full-matrix least-squares refinement on F^2 (program SHELXL 96 [42]).The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealised positions. Refinement proceeds to $R = 0.0209$, $wR = 0.0499$ and goodness of fit on F^2 1.028, and $R = 0.0239$, $wR = 0.0508$ for all data. In the final Fourier synthesis the electron density fluctuates in the range 1.385 to -1.0976 e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 141725 and 141726. 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 www: http://www.ccdc.cam.ac.uk).

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