Journal of Organometallic Chemistry, 435 (1992) 235–247
Elsevier Sequoia S.A., Lausanne
JOM 22687

Asymmetrical monocationic or neutral gold(II) complexes: X-ray crystal structure of $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuPPh_3]ClO_4 \cdot 0.5CH_2Cl_2$

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(Received January 15, 1992)

Abstract

The reaction of $[RAu(CH_2PPh_2CH_2)_2AuR]$ ($R = C_6F_5$ or 2,4,6-$C_6F_3H_2$) with $Au(ONO_2)PPh_3$, $[Au(PPh_3)_2]ClO_4$ or $[Au(PPh_3)tht]ClO_4$ (tht = tetrahydrothiophene) leads to neutral $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuONO_2]$ **1** or monocationic derivatives $[RAu(CH_2PPh_2CH_2)_2AuL]ClO_4$ [$R = C_6F_5$, $L = PPh_3$(**2**) or tht(**3**); $R =$ 2,4,6-$C_6F_3H_2$, $L = PPh_3$(**4**) or tht(**5**)]. Complexes **3** and **5** react with anionic or neutral reagents, giving new neutral or monocationic gold(II) compounds. The structure of $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuPPh_3]ClO_4 \cdot 0.5CH_2Cl_2$ (**2**) was determined by single-crystal X-ray diffraction. Crystals are triclinic, space group $P\bar{1}$, $a = 12.468(2)$, $b = 13.493(2)$, $c = 18.283(3)$ Å, $\alpha = 108.13(1)°$, $\beta = 91.09(1)°$, $\gamma = 111.95(1)°$ and $Z = 2$. Final R is 0.0376 for 4906 unique observed reflections. The Au–Au bond length is 2.6612(8) Å.

Introduction

Most reported gold(II) complexes containing the bis(ylide) ligand $(CH_2)_2PR_2^-$ have been synthesized by a binuclear oxidative addition [1–8], giving neutral derivatives. We have recently described [9,10] the synthesis of dicationic gold(II) complexes with the ligand $(CH_2)_2PPh_2^-$ which are stable at room temperature, not only in the solid state but also in solution.

Despite the great stability of these gold(II) complexes, it is noteworthy that only a few reactions, including substitution [11–14], oxidative addition [4,8] or electrophilic reactions [15] have been performed with them, in contrast with the isoelectronic platinum(I) derivatives [16].

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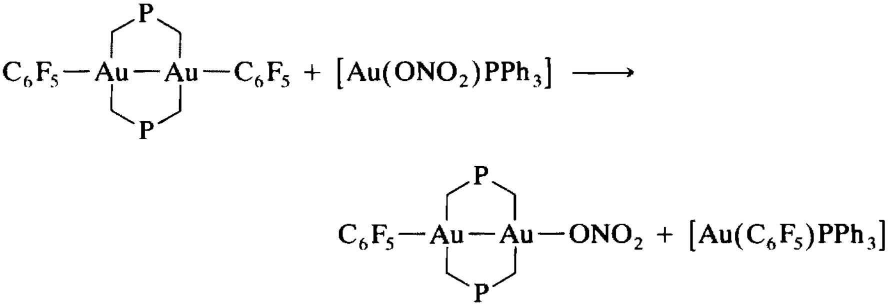
In this paper we describe the reactions of [RAu($CH_2PPh_2CH_2$)$_2$AuR] (R = C_6F_5 [10,12], 2,4,6-$C_6F_3H_2$ [10]) with gold(I) complexes [Au(ONO_2)PPh_3] or [Au(PPh_3)L]ClO_4 [L = tht (tetrahydrothiophene) or PPh_3] to give neutral or monocationic asymmetric gold(II) complexes, by group exchange. It is noteworthy that only three monocationic gold(II) complexes have been reported so far [14], [XAu($CH_2PPh_2CH_2$)$_2$AuCH_2PR_3]X (X = I, R = Ph or Me; X = Br, R = Ph).

The subsequent reaction of these gold(II) complexes with anionic or neutral reagents permits the preparation of novel neutral or monocationic gold(II) derivatives. The molecular structure of [(C_6F_5)Au($CH_2PPh_2CH_2$)$_2$AuPPh_3]ClO_4 was established by X-ray studies.

Results and discussion

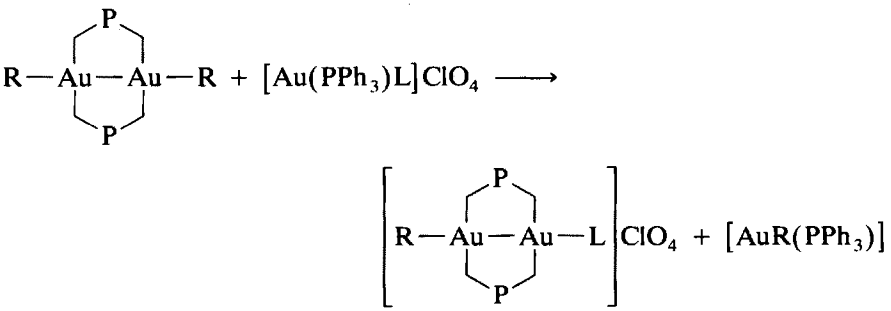
The reaction of [Au(ONO_2)PPh_3] with [(C_6F_5)Au($CH_2PPh_2CH_2$)$_2$Au(C_6F_5)] in dichloromethane (1 : 1 molar ratio) leads to a mixture of [Au(C_6F_5)PPh_3] and the new gold(II) compound **1** (eq. 1). The isolation of complex **1** is easy owing to its low solubility in diethyl ether.



(1)

(**1**)

In a similar way, starting from the same gold(II) complex or from the 2,4,6-$C_6F_3H_2$ analogue and by reacting with the cationic gold(I) derivatives [Au(PPh_3)$_2$]ClO_4 or [Au(PPh_3)(tht)]ClO_4 in 1 : 1 molar ratio, a mixture of [Au(C_6F_5)PPh_3] and complexes **2–5** is obtained:



(2)

R = C_6F_5, L = PPh_3 (**2**) or tht (**3**)

R = 2,4,6-$C_6F_3H_2$, L = PPh_3 (**4**) or tht (**5**)

The different solubility in diethyl ether of gold(II) complexes and the gold(I) derivatives permits their separation.

The formation of monocationic gold(II) complexes may proceed through a monocationic intermediate $[RAu(CH_2PPh_2CH_2)_2Au]^+$; species of this type have been proposed by Fackler and Murray [17] for the group exchange in other gold(II) derivatives. The gold(I) complex must play two roles. First, it must remove the polyfluorophenyl group to form $[AuR(PPh_3)]$; secondly, it must provide the ligands ONO_2, PPh_3 or tht, which move to the vacant coordination site.

The tht in complexes **3** and **5** can be displaced by a variety of ligands. Complex **3** reacts with an excess of salts MX (X = Cl or SCN; M = Na or K) in a mixture of dichloromethane–water to give the asymmetric neutral complexes $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuX]$ [X = Cl(**6**) or SCN(**7**)]. The trifluorophenyl derivative **5** reacts in a similar way with NaCl to give $[(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2AuCl]$ (**8**).

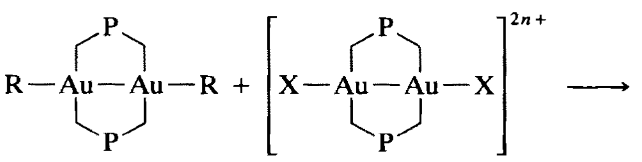
We have recently shown [10] that chloride derivatives of gold(II) can react with silver salts or silver complexes, giving rise to new gold(II) complexes by abstraction of chloride. In a similar way, complex **6** reacts with $AgNO_3$, $Ag(CH_3COO)$ or silver complexes $[Ag(OClO_3)L]$ (L = tht or PPh_3) in 1:1 molar ratio, to give complexes **1–3** or the new acetato-derivative $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(OOCCH_3)]$ (**9**). Complex **8** reacts analogously with $[Ag(OClO_3)L]$ to yield complexes **4** and **5**.

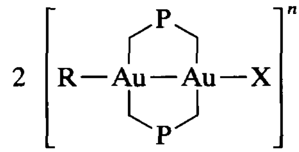
A less clean reaction occurs with complex **6** and $AgC_6F_3H_2$ (1:1 molar ratio); in the reaction mixture, three different components can be detected by spectroscopic methods ($^{31}P\{^1H\}$ and ^{19}F NMR). They cannot be separated because of their similar solubilities. Two of the complexes are the symmetrical derivatives $[RAu(CH_2PPh_2CH_2)_2AuR]$ (R = C_6F_5 and 2,4,6-$C_6F_3H_2$), but a third group of signals belongs to the asymmetric complex $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_3H_2)]$ (**10**).

Neutral reagents react with **3** and **5** 1:1 molar ratio to replace the tht, giving rise to novel monocationic gold(II) derivatives $[RAu(CH_2PPh_2CH_2)_2AuL]ClO_4$ [R = C_6F_5, L = PPh_3(**3**), $P(C_6H_4Me\text{-}4)_3$(**11**), $AsPh_3$(**12**), py(**13**); R = 2,4,6-$C_6F_3H_2$, L = PPh_3(**5**)]. The reaction of complex **3** with a freshly prepared tetrahydrofuran solution of CH_2PPh_3 (1:1 molar ratio) gives a mixture of several components, which can be partially separated in a mixture of methanol–diethyl ether. The most soluble and insoluble fractions are $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ and $[(Ph_3PCH_2)Au(CH_2PPh_2CH_2)_2Au(CH_2PPh_3)](ClO_4)_2$ (**14**) respectively.

Complex **14** can be synthesized in better yield (88%) by reaction between $[(tht)Au(CH_2PPh_2CH_2)_2Au(tht)](ClO_4)_2$ and a freshly prepared solution of CH_2PPh_3 in THF.

Some of these asymmetric complexes can be obtained from an equimolecular mixture of the corresponding symmetrical gold(II) derivatives (eq. 3) in dichloromethane:





(3)

$R = C_6F_5$	$X = Cl$	$n = 0$	**(6)**
	$X = \text{tht}$	$n = 1$	**(3)**
$R = C_6F_3H_2$	$X = Cl$	$n = 0$	**(8)**
	$X = \text{tht}$	$n = 1$	**(5)**

The phosphine complexes **2** and **4**, cannot be prepared by this route, as no reaction occurs.

The complexes **1–9** and **11–14** are air- and moisture-stable yellow (**1**, **6–9**, **12**, **13**), orange (**2–5**, **11**) or red (**14**) solids. They are soluble in chlorinated solvents such as dichloromethane and chloroform, but complexes **6**, **8**, **10** and **14** are only slighly soluble in acetone. In diethyl ether all the complexes are insoluble, except **6** and **8** which are slightly soluble. Acetone solutions of complexes **2–14** show conductivities in agreement with their formulation. Solutions of neutral complexes **6–9** are non-conducting. In contrast, an acetone solution of complex **1** has a conductivity of 71 Ω^{-1} cm^2 mol^{-1}; this value is due to partial displacement of ONO_2 ligand by acetone. Solutions of **2–5** and **11–13** show conductivities between 90 and 110 Ω^{-1} cm^2 mol^{-1}, characteristic of 1:1 electrolytes and an acetone solution of **14** has a conductivity of 167 Ω^{-1} cm^2 mol^{-1}, as expected for 1:2 electrolyte.

The mass spectra (FAB, nitrobenzyl alcohol as matrix) show a parent ion at $m/e = 1022$ (**6**), 1249 (**2**) and 1213 (**4**), but for complexes **3** and **13** the highest m/e is at 987, corresponding to the fragment $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au]^+$. This ion at 987 is the highest m/e ion, or the most intense in all the mass spectra, even in the mass spectrum of $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ which has a weak parent ion at 1154. This is a very stable ion and could be involved in the formation of these asymmetrical complexes (eqs. 1 and 2).

Table 1 shows the IR band corresponding to $\nu(Au{-}C_{\text{ylide}})$ [8,18] around 565 cm^{-1}. Complexes **14**, with another $Au{-}C_{\text{ylide}}$ bond also has a shoulder in this region. The IR spectra of all pentafluorophenyl complexes show bands at approximately 960 cm^{-1} and 800 cm^{-1} owing to the C_6F_5 group [19], whilst the trifluorophenyl derivatives [20] show absorptions at approximately 990 and 840 cm^{-1}. Ionic perchlorate is confirmed here by bands at approximately 1100(s,br) and 620 cm^{-1} [21].

The nitrate derivative **1** shows $\nu(NO)$ bands at 1445(vs) and 1280(vs) cm^{-1}. The difference, 165 cm^{-1}, is consistent with monodentate coordination [22,10]. Other absorptions of this group are obscured by other ligand bands.

Complexes **6** and **8** have weak $\nu(AuCl)$ bands at 230 and 247 cm^{-1} [23]; these absorptions are at lower frequencies than in $[ClAu(CH_2PPh_2CH_2)_2AuCl]$, in accordance with the suggestion that the "structural *trans* effect" is transmitted through the gold–gold bond [1,7].

The thiocyanate group in **7** seems to be bound through sulphur [24] because $\nu(C{\equiv}N)$ appears at lower frequencies (2055 cm^{-1}) than in the symmetrical *S*-bonded

Table 1

Analytical data for products

Complex	Yield (%)	Analysis (%) [a]			NMR [b]			ν(Au–C_{ylide}) (cm^{-1})
		C	H	N	^{31}P		(^1H)	
					$\delta(PPh_2)[^3J(P-P)]$ [c]	$\delta(PPh_3)$	$\delta(CH_2)$ [N] [c]	
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(ONO_2)]$ **(1)**	84	38.9 (38.9)	2.8 (2.7)	1.65 (1.35)	35.54(s)	-	1.45("d")[9.9], 1.81("d")[12]	570
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(PPh_3)]ClO_4$ **(2)**	85	46.15 (46.3)	3.1 (3.2)		44.7(d)[54.5]	23.01(m)	1.51("t")[10.7] [d], 1.60("d")[10.7]	567
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(tht)]ClO_4$ **(3)**	90	39.3 (38.9)	3.1 (3.1)		37.89(s)	-	1.48("d")[10.6], 1.8("d")[12.9]	568
$[(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au(PPh_3)]ClO_4$ **(4)**	85	47.2 (47.55)	3.4 (3.45)		44.09(d)[59.1]	23.67(m)	1.50("t")[10.6] [d], 1.61("d")[9.4]	571
$[(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au(tht)]ClO_4$ **(5)**	85	40.35 (40.05)	4.05 (3.35)		35.54(s)	-	1.44("d")[9.8], 1.79("d")[12.6]	570
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuCl]$ **(6)**	78	39.65 (39.9)	2.75 (2.75)		39.12(s)	-	1.50("d")[10.2], 1.87("d")[12.2]	568
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuSCN]$ **(7)**	75	40.55 (40.2)	3.02 (2.7)	1.7 (1.35)	39.94(s)	-	1.53("d")[10.1], 1.72("d")[11.5]	567
$[(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2AuCl]$ **(8)**	75	41.15 (41.4)	3.25 (3.05)		38.54(s)	-	1.48("d")[9.3], 1.88("d")[10.4]	575
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(OOCCH_3)]$ **(9)**	75	41.5 (41.3)	3.4 (3.0)		38.55(s)	-	1.77("d")[10.4], 2.22("d")[10.2]	567
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_3H_2)]$ **(10)**	-	-	-		42.98(s)	-	-	-
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuP(4\text{-}MePh)_3]ClO_4$ **(11)**	85	45.2 (44.9)	3.65 (3.55)		44.7(d)[54]	22.18(m)	1.5("t")[10.6] [d], 1.62("d")[10]	562
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(AsPh_3)]ClO_4$ **(12)**	77	45.1 (44.85)	3.35 (3.1)		42.62(s)	-	1.61("d")[9.6], 1.73("d")[12.8]	566
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Aupy]ClO_4$ **(13)**	85	39.75 (40.15)	3.05 (2.85)	0.9 (1.2)	38.3(s)	-	1.57("d")[9.6], 1.68("d")[12.1]	572
$[(Ph_3PCH_2)Au(CH_2)_2PPh_2]_2(ClO_4)_2$ **(14)**	88	50.2 (50.45)	4.25 (4.0)		44.66(s)	30.08(s)	2.98("d")[13.4], 0.97("d")[11.2]	568

[a] Calculated values are given in parentheses. [b] In $CDCl_3$, values in ppm; other data are in the experimental section. [c] Values of *J* and *N* in hertz. [d] *N* is the splitting between two consecutive lines.

derivative [NCSAu$(CH_2PPh_2CH_2)_2$AuSCN] (2090 cm^{-1}), and the internal standard ratio [25] is 0.6.

Complex **9** has two acetate bands at 1596(s) and 1370(s,br) cm^{-1} assignable to $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ respectively. The difference between them, $\Delta\nu = 226$ cm^{-1}, is higher than in ionic derivatives ($\Delta\nu \approx 165$ cm^{-1}), confirming that the acetato-group is monodentate [26].

The ^1H NMR spectra in the methylene region of complexes **1–14** show two groups of signals, as expected. The assignment is not unambiguous, except in the case of **2**, **4** and **11**, which contain a phosphine. Here the protons of the methylene group bonded to the Au–PPh_3 fragment appear as pseudo-triplets, rather than pseudo-doublets in the rest of the complexes. In complex **14** it is possible to assign the doublet at 2.98 ppm to methylene protons of the CH_2PPh_3 owing to their intensity. Consequently the pseudo-doublet at 0.97 ppm must correspond to the methylene protons of the ylide ligand $CH_2PPh_2CH_2^-$.

Their $^{31}P\{^1H\}$ NMR spectra show signals between 35.45 and 44.77 ppm from the phosphorus atom in the PPh_2 group. This is usually a singlet, but is a doublet for **2**, **4** and **11** because of the coupling with phosphine ligand. The high values of 54.2 (**2**), 59.1 (**4**) and 54.0 Hz (**11**) for ^3J(P–P) two phosphorus atoms in a *cis*-position are noteworthy. ^3J(P–P) in gold(III) complexes containing a phosphine and a ylide ligand is zero [27] in *cis*-derivatives (*cis*-$[Au(C_6F_5)_2(CH_2PPh_3)(PPh_3)]ClO_4$ or *cis*-$[Au(C_6F_5)_2(CH_2PPh_2Me)(PPh_3)]ClO_4$), and also in *trans*-$[Au(C_6F_5)_2(CH_2PPh_3)(PPh_3)]ClO_4$. The resonances of the phosphorus atom of the phosphines appear as multiplets at 23.01 (**2**), 23.67 (**4**) and 22.18 ppm (**11**) because of the coupling with the phosphorus atom of PPh_2 groups and with the fluorine atoms of polyfluorophenyl groups. Complex **14** has a signal at 30.08(s) ppm assignable to CH_2PPh_3 group.

The $^{31}P\{^1H\}$ NMR spectra of complexes **3**, **5**, **6** and **8** show no fluxionality down to −50°C.

The ^{19}F NMR spectra show three groups of signals in all the pentafluorophenyl complexes, as expected for one C_6F_5 group. Complexes **4**, **5** and **8** show two multiplets (2:1 ratio) as expected for 2,4,6-$C_6F_3H_2$ derivatives.

The X-ray structure determination of complex $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuPPh_3]ClO_4 \cdot 0.5\ CH_2Cl_2$ (**2**) confirms the novel binuclear gold(II) structure, with square-planar coordination for the metal atoms and, as usual, the Au–Au bond lying across the eight-membered ring. An Ortep drawing of the complex cation is shown in Fig. 1 and important bond distances and angles are given in Table 2. The Au–Au bond length is 2.6612(8) Å, which lies between the 2.579(3) Å for the dicationic triphenylphosphine complex [10] $[Ph_3PAu(CH_2PPh_2CH_2)_2AuPPh_3]^{2+}$ and 2.675(1) Å for $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ [12]. Usually, the Au^{II}–X bond lengths trans to a metal–metal bond are longer than Au^{III}–X bonds, but in this case the Au^{II}–C_6F_5 bond length is 2.078(12) Å, which is comparable with the Au^{III}–C_6F_5 bond (typical values 2.050–2.075 Å) [28] and identical with the Au^{II}–C_6F_5 bond in $[(C_6F_5)ClAu(PPh_2NHPPh_2)AuCl(C_6F_5)]$ [29] (2.064(6) Å) (the C_6F_5 group is not trans to the Au–Au bond), but shorter than in the symmetrical derivative $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ (average Au–C_6F_5 bond 2.1508(10) Å). The Au–PPh_3 bond length is 2.443(3) Å, longer than in $[Ph_3PAu(CH_2PPh_2CH_2)_2AuPPh_3]^{2+}$ (2.365(6) and 2.384(6) Å).

The shortening of the Au–C_6F_5 length and the lengthening of the Au–PPh_3

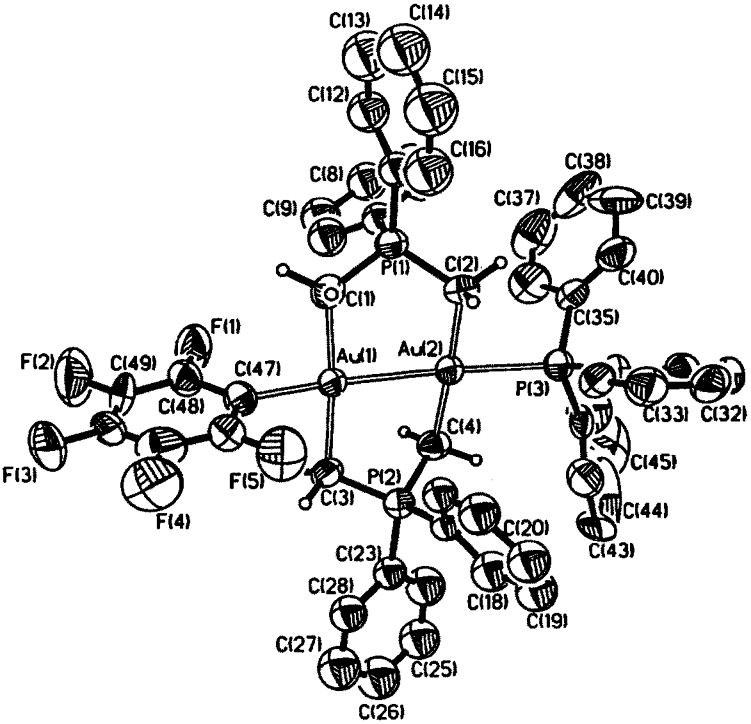


Fig. 1. Molecular structure of complex $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(PPh_3)]^+$ (2), with the labelling scheme.

bond in 2, compared with the symmetrical PPh_3 or C_6F_5 derivatives, may reflect how the *trans* influence or the "structural *trans* effect" of C_6F_5 and PPh_3 groups seems to be transmitted through the Au^{II}-Au^{II} bond. Murray and Fackler [7] showed that the different groups attached to gold(II) atoms in $[XAu(CH_2PPh_2CH_2)_2AuX]$ species do not much affect metal-metal bond length but have more influence on Au-X distances. There are no significant differences between the Au-CH_2 bond lengths compared with the symmetrical complexes above mentioned.

Experimental

Instrumentation and general experimental techniques were as described earlier [30], with the exception of the mass spectra which were obtained with a VG Autospec using a cesium FAB with nitrobenzyl alcohol as matrix. All the reactions were performed at room temperature. Complex $[Au(PPh_3)_2]ClO_4$ was synthesized by adding $[Ag(OClO_3)PPh_3]$ (0.470 g, 1 mmol) to a dichloromethane solution (40 cm^3) of $[AuCl(PPh_3)]$ (0.495 g, 1 mmol). After 1 h, the precipitated AgCl was filtered off and the solution reduced to 5 cm^3. Addition of diethyl ether (30 cm^3) gave white crystals of $[Au(PPh_3)_2]ClO_4$.

Table 2

Selected bond lengths (Å) and angles (deg) for the complex $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(PPh_3)]$-$(ClO_4)\cdot 0.5\ CH_2Cl_2$ (**2**)

Au(1)–Au(2)	2.6612(8)		
Au(1)–C(1)	2.098(12)	Au(2)–C(2)	2.085(13)
Au(1)–C(3)	2.103(12)	Au(2)–C(4)	2.119(14)
Au(1)–C(47)	2.078(12)	Au(2)–P(3)	2.443(3)
P(1)–C(1)	1.748(14)	P(2)–C(3)	1.765(10)
P(1)–C(2)	1.760(10)	P(2)–C(4)	1.772(13)
P(1)–C(5)	1.792(14)	P(2)–C(17)	1.793(14)
P(1)–C(11)	1.823(14)	P(2)–C(23)	1.802(14)
C(47)–C(48)	1.383(18)	C(48)–F(1)	1.336(19)
C(47)–C(52)	1.358(22)	C(49)–F(2)	1.329(18)
C(48)–C(49)	1.394(21)	C(50)–F(3)	1.345(20)
C(49)–C(50)	1.340(29)	C(51)–F(4)	1.340(22)
C(50)–C(51)	1.371(25)	C(52)–F(5)	1.380(17)
C(51)–C(52)	1.347(23)		
Au(2)–Au(1)–C(1)	93.5(4)	Au(1)–Au(2)–C(2)	89.5(3)
Au(2)–Au(1)–C(3)	93.2(3)	Au(1)–Au(2)–C(4)	88.5(3)
Au(2)–Au(1)–C(47)	174.6(4)	Au(1)–Au(2)–P(3)	172.7(1)
C(1)–Au(1)–C(3)	173.1(5)	C(2)–Au(2)–C(4)	176.4(5)
C(1)–Au(1)–C(47)	88.5(5)	C(2)–Au(2)–P(3)	89.2(3)
C(3)–Au(1)–C(47)	84.8(5)	C(4)–Au(2)–P(3)	93.3(4)
Au(1)–C(1)–P(1)	113.1(7)	Au(1)–C(3)–P(2)	112.1(6)
Au(2)–C(2)–P(1)	110.9(6)	Au(2)–C(4)–P(2)	106.6(6)
C(1)–P(1)–C(2)	106.4(6)	C(3)–P(2)–C(4)	104.7(6)
Au(1)–C(47)–C(48)	123.2(10)	C(49)–C(50)–F(3)	120.5(16)
Au(1)–C(47)–C(52)	122.4(10)	C(51)–C(50)–F(3)	120.3(17)
C(48)–C(47)–C(52)	114.5(12)	C(49)–C(50)–C(51)	119.3(17)
C(47)–C(48)–F(1)	119.6(12)	C(50)–C(51)–F(4)	119.9(16)
C(49)–C(48)–F(1)	118.8(13)	C(52)–C(51)–F(4)	121.4(16)
C(47)–C(48)–C(49)	121.4(15)	C(50)–C(51)–C(52)	118.7(17)
C(48)–C(49)–F(2)	118.9(15)	C(51)–C(52)–F(5)	116.5(14)
C(50)–C(49)–F(2)	120.5(15)	C(47)–C(52)–F(5)	118.0(13)
C(48)–C(49)–C(50)	120.5(14)	C(51)–C(52)–C(47)	125.5(15)

$[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuONO_2]$ *(1)*

To a solution of $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ [10,12] (0.1155 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Au(ONO_2)PPh_3]$ [22] (0.0521 g, 0.1 mmol) and the mixture was stirred for 30 min. The solution was evaporated to *ca.* 5 cm^3; addition of diethyl ether (20 cm^3) led to the precipitation of the complex **1**. The complex $[Au(C_6F_5)PPh_3]$, also formed, is soluble in diethyl ether. NMR (see Table 1): ^1H, δ 7.56–7.38 (m, 20H, Ph), ^{19}F, δ −123.82 (m, 2F, *o*-F), −158.46 (t, 1F, *p*-F), and −161.32 (m, 2F, *m*-F).

$[RAu(CH_2PPh_2CH_2)_2AuL]ClO_4$ [R = C_6F_5, L = PPh_3 (**2**) or tht (**3**); R = 2,4,6-$C_6F_3H_2$, L = PPh_3 (**4**) or tht (**5**)]

(a) To a solution of $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ [10,12] (0.1155 g, 0.1 mmol) or $[(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au(C_6F_3H_2)]$ [10] (0.1083 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Au(PPh_3)L]ClO_4$ L=PPh_3 (0.0821 g, 0.1 mmol) or L = tht [31] (0.0641 g, 0.1 mmol), and the mixture was stirred for 30 min.

The solution was evaporated to *ca.* 5 cm^3; addition of diethyl ether (20 cm^3) led to the precipitation of the complexes **2**–**5**. Complex [Au(C_6F_5)PPh_3], also formed, is soluble in diethyl ether.

(b) To a solution of [RAu($CH_2PPh_2CH_2$)$_2$AuCl] (R = C_6F_5 (**6**) or 2,4,6-$C_6F_3H_2$ (**8**), see below) [0.1 mmol, 0.1023 g (**6**), 0.0987 g (**8**)] in dichloromethane (20 cm^3) was added [Ag($OClO_3$)PPh_3] [32] (0.0470 g, 0.1 mmol) or [Ag($OClO_3$)tht] [10] (0.0295 g, 0.1 mmol) and the mixture was stirred for 2 h. The AgCl was filtered off and the solution was evaporated to *ca.* 5 cm^3; addition of hexane (20 cm^3) gave complexes **2**–**5**.

(c) To a solution of [(tht)Au($CH_2PPh_2CH_2$)$_2$Au(tht)](ClO_4)$_2$ [10] (0.1196 g, 0.1 mmol) in dichloromethane (20 cm^3) was added [RAu($CH_2PPh_2CH_2$)$_2$AuR] [10,12] (R = C_6F_5, 2,4,6-$C_6F_3H_2$) (0.1 mmol, 0.1155 g or 0.1083 g respectively). The mixture was stirred for 15 min. Concentration of the solution to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to the precipitation of complexes **3** and **5**. NMR (see Table 1): **2**, ^{1}H, δ 7.62–7.12 (m, 35H, Ph), ^{19}F, δ −122.12 (m, 2F, *o*-F), −158.61 (t, 1F, *p*-F) and −160.66 (m, 2F, *m* − F); **3**, ^{1}H, δ 7.58–7.4 (m, 20H, Ph), 3.11 (m, 4H, SCH_2), 2.04 (m, 4H, CH_2), ^{19}F, δ −123.44 (m, 2F, *o*-F), −158.05 (t, 1F, *p*-F) and −160.97 (m, 2F, *m*-F); **4**, ^{19}F, δ −92.42 (m, 2F, *o*-F) and −114.72 (m, 1F, *p*-F); **5**, ^{1}H, δ 7.60–7.36 (m, 20H, Ph), 6.54 (m, 2H, $C_6F_3H_2$), 3.07 (m, 4H, SCH_2), 2.01 (m, 4H, CH_2), ^{19}F, δ −93.41 (m, 2F, *o*-F) and −113.62 (m, 1F, *p*-F).

[RAu($CH_2PPh_2CH_2$)$_2$AuX] [R = C_6F_5, X = Cl (6) or SCN (7); R = 2,4,6-$C_6F_3H_2$ or X = Cl (8)]

(a) To a solution of complex **3** (0.1175 g, 0.1 mmol) or **5** (0.1139 g, 0.1 mmol) in dichloromethane (20 cm^3) was added a solution of NaCl (0.0175 g, 0.3 mmol) or KSCN (0.0292 g, 0.3 mmol) in water (10 cm^3) and the mixture was stirred for 15 min. The dichloromethane layer was removed using a separating funnel and dried with anhydrous magnesium sulphate (1–2 g). The filtered solution was evaporated to *ca.* 5 cm^3 and addition of hexane (20 cm^3) led to the precipitation of complexes **6**–**8**.

(b) To a solution of [ClAu($CH_2PPh_2CH_2$)$_2$AuCl] [1] (0.0891 g, 0.1 mmol) in dichloromethane (20 cm^3) was added [RAu($CH_2PPh_2CH_2$)$_2$AuR] (R = C_6F_5 or 2,4,6-$C_6F_3H_2$) (0.1 mmol, 0.1155 g or 0.1083 g, respectively). The mixture was stirred for 15 min. Concentration of the solution to *ca.* 5 cm^3 and addition of hexane (20 cm^3) led to the precipitation of complexes **6** and **8**. NMR (see Table 1): **6**, ^{1}H, δ 7.62–7.31 (m, 20H, Ph), ^{19}F, δ −123.18 (m, 2F, *o*-F), −159.29 (t, 1F, *p*-F) and −161.64 (m, 2F, *m*-F); **7**, ^{1}H, δ 7.54–7.37 (m, 20H, Ph), ^{19}F, δ −122.82 (m, 2F, *o*-F), −159.15 (t, 1F, *p*-F) and −161.37 (m, 2F, *m*-F); **8**, ^{1}H, δ 7.58–7.31 (m, 20H, Ph), 6.52 (m, 2H, $C_6F_3H_2$), ^{19}F, δ −93.04 (m, 2F, *o*-F) and −115.41 (t, 1F, *p*-F).

[(C_6F_5)Au($CH_2PPh_2CH_2$)$_2$AuX] [X = CH_3COO (9), 2,4,6-$C_6F_3H_2$ (10)]

To a solution of complex **6** (0.1123 g, 0.1 mmol) in dichloromethane (40 cm^3) was added $AgCH_3COO$ (0.0167 g, 0.1 mmol). The mixture was stirred for 10 h. The precipitated AgCl was filtered off and washed with dichloromethane (3 × 5 cm^3). Concentration of filtrate and washings to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to the precipitation of complex **9**. To a solution of complex **6** (0.1123 g, 0.1 mmol) in dichloromethane (20 cm^3) was added a solution of

$Ag(2,4,6\text{-}C_6F_3H_2)$ [33] (0.11 mmol) in diethyl ether (20 cm^3). The mixture was stirred for 2 h. The precipitated AgCl was filtered off and washed with dichloromethane (3 × 5 cm^3). Concentration of the filtrate and washings to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to the precipitation of a mixture of the symmetrical derivatives, $[RAu(CH_2PPh_2CH_2)_2AuR]$ ($R = C_6F_5$ or $C_6F_3H_2$), and complex **10**. NMR (see Table 1): **9**, ^1H, δ 7.63–7.24 (m, 20H, Ph), 2.09 (s, 3H, Me), ^{19}F, δ −123.31 (m, 2F, *o*-F), −159.69 (t, 1F, *p*-F) and −161.95 (m, 2F, *m*-F); **10**, ^{19}F, δ −120.69 (m, 2F, *o*-F), −161.32 (t, 1F, *p*-F), −161.80 (m, 2F, *m*-F) $[C_6F_5]$, and −91.35 (m, 2F, *o*-F), −117.72 (m, 1F, *p*-F) $[C_6F_3H_2]$.

$[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuL]ClO_4$ [$L = PPh_3$(2), $P(4\text{-}MePh)_3$(11), $AsPh_3$(12), or py(13)]

To a solution of complex **3** (0.1175 g, 0.1 mmol) in dichloromethane (20 cm^3) was added PPh_3 (0.0262 g, 0.1 mmol), $P(4\text{-}MePh)_3$ (0.0304 g, 0.1 mmol), $AsPh_3$ (0.0306 g, 0.1 mmol), or py (1 cm^3 of a solution 0.1 mol dm^{-3} in hexane). The mixture was stirred for 15 min. Concentration of the solution to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to the precipitation of complexes **2**, **11–13**.

$[(Ph_3PCH_2)Au(CH_2PPh_2CH_2)_2Au(CH_2PPh_3)](ClO_4)_2$ (14)

To a solution of $[(tht)Au(CH_2PPh_2CH_2)_2Au(tht)](ClO_4)_2$ [10] (0.1196 g, 0.1 mmol) in dichloromethane (20 cm^3) was added a solution of free ylide in THF (20 cm^3, containing 0.25 mmol of CH_2PPh_3). The mixture was stirred for 30 min. Concentration of the solution to *ca.* 5 cm^3 and addition of THF (20 cm^3) led to the precipitation of complex **14**, which was washed with methanol–THF (25–75%). NMR (see Table 1): **11**, ^1H, δ 7.41–7.03 (m, 32H, Ph), 2.44 (s, 9H, Me), ^{19}F, δ −122.05 (m, 2F, *o*-F), −158.75 (t, 1F, *p*-F) and -160.68 (m, 2F, *m*-F); **12**, ^1H, δ 7.64–7.18 (m, 35H, Ph), ^{19}F, δ −122.44 (m, 2F, *o*-F), −158.21 (t, 1F, *p*-F) and −160.67 (m, 2F, *m*-F); **13**, ^1H, δ 8.35–7.46 (m, 25H, Ph and py), ^{19}F, δ −123.28 (m, 2F, *o*-F), −158.36 (t, 1F, *p*-F) and −161.17 (m, 2F, *m*-F); **14**, ^1H, δ 7.65–7.30 (m, 50H, Ph).

X-Ray structure determination of compound 2: Crystal data

$C_{52}H_{43}Au_2ClF_5O_4P_3 \cdot 0.5\ CH_2Cl_2$, $M = 1391.67$, triclinic, space group $P\bar{1}$, $a = 12.468(2)$, $b = 13.493(2)$, $c = 18.283(3)$ Å, $\alpha = 108.13(1)$, $\beta = 91.09(1)$, $\gamma = 111.95(1)°$, $U = 2679.0(8)$ Å^3, $Z = 2$, $D_c = 1.725$ Mg m^{-3}, $F(000) = 1346$, λ(Mo-K_α) = 0.71069 Å, $\mu = 5.71$ mm^{-1}, $T = 20°C$.

Data collection and reduction

A Siemens AED-2 diffractometer with monochromated Mo-K_α radiation was used. An orange prismatic block 0.129 × 0.188 × 0.412 mm^3 was mounted on a glass fibre. 7414 intensities were registered to $2\theta_{max} = 45°$. Averaging equivalents gave 7023 unique reflections, of which 4906 with $F > 5\sigma(F)$ were used for all calculations (program SHELX76). Cell constants were refined from setting angles of 56 reflections in the range 2θ 20°–35°. A numerical absorption correction based on morphological indexed faces of the crystal was applied (minimum and maximum transmission factor 0.2076 and 0.3192).

Table 3

Fractional atomic coordinates ($\times 10^4$; $\times 10^5$ for gold atoms) for the non-hydrogen atoms for the complex $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(PPh_3)](ClO_4)\cdot 0.5CH_2Cl_2$ (2)

Atom	*x*	*y*	*z*
Au(1)	16856(4)	263(4)	13026(3)
Au(2)	14237(4)	12289(4)	26956(3)
P(1)	−124(3)	−1419(3)	2189(2)
P(2)	3241(3)	2718(3)	1907(2)
P(3)	1417(3)	2333(3)	4037(2)
C(1)	700(11)	−1540(10)	1428(7)
C(2)	805(10)	−244(9)	2985(7)
C(3)	2748(10)	1486(9)	1066(7)
C(4)	1970(10)	2671(10)	2339(7)
C(5)	−1411(10)	−1221(9)	1946(7)
C(6)	−2150(12)	−1148(11)	2480(8)
C(7)	−3169(13)	−1007(12)	2312(9)
C(8)	−3446(13)	−931(11)	1631(9)
C(9)	−2734(14)	−1026(13)	1073(9)
C(10)	−1697(13)	−1137(12)	1237(8)
C(11)	−636(11)	−2744(10)	2396(7)
C(12)	−1739(12)	−3594(11)	2106(9)
C(13)	−2015(16)	−4609(14)	2247(12)
C(14)	−1288(18)	−4776(14)	2700(11)
C(15)	−252(17)	−3947(15)	2984(12)
C(16)	114(14)	−2922(13)	2848(10)
C(17)	4346(10)	2734(9)	2558(6)
C(18)	5161(12)	3766(12)	3055(8)
C(19)	5975(14)	3816(12)	3595(8)
C(20)	6020(13)	2814(13)	3618(8)
C(21)	5232(12)	1802(11)	3097(9)
C(22)	4396(10)	1755(10)	2587(7)
C(23)	3956(10)	3977(10)	1661(7)
C(24)	3840(13)	4997(11)	2020(8)
C(25)	4434(17)	5957(13)	1847(10)
C(26)	5123(16)	5895(13)	1292(11)
C(27)	5276(13)	4922(14)	922(9)
C(28)	4673(12)	3941(11)	1119(9)
C(29)	2352(9)	2252(10)	4766(7)
C(30)	2439(11)	2864(10)	5579(7)
C(31)	3174(12)	2838(12)	6115(8)
C(32)	3817(13)	2188(13)	5876(9)
C(33)	3773(12)	1606(11)	5112(9)
C(34)	3029(10)	1646(10)	4539(8)
C(35)	−68(10)	1851(10)	4269(8)
C(36)	−933(13)	1763(13)	3717(10)
C(37)	−2070(15)	1387(16)	3818(13)
C(38)	−2383(15)	1068(15)	4447(15)
C(39)	−1580(15)	1077(13)	4957(11)
C(40)	−400(12)	1484(12)	4871(9)
C(41)	1901(13)	3855(9)	4250(7)
C(42)	3075(16)	4452(12)	4248(8)
C(43)	3460(20)	5619(16)	4311(9)
C(44)	2637(35)	6104(24)	4388(15)
C(45)	1578(30)	5534(22)	4459(16)
C(46)	1169(17)	4412(13)	4335(9)
C(47)	2054(10)	−859(10)	257(7)

Table 3 (continued)

Atom	x	y	z
C(48)	1298(12)	−1331(12)	−439(8)
C(49)	1616(16)	−1839(12)	−1139(8)
C(50)	2648(15)	−1934(12)	−1150(10)
C(51)	3392(14)	−1523(13)	−464(11)
C(52)	3075(12)	−1002(11)	199(8)
F(1)	277(7)	−1221(8)	−453(5)
F(2)	878(10)	−2229(10)	−1795(5)
F(3)	2953(9)	−2428(8)	−1826(6)
F(4)	4425(8)	−1616(8)	−465(7)
F(5)	3855(7)	−598(8)	874(5)
Cl(1)	−6352(3)	−1380(3)	3186(3)
O(1)	−6791(17)	−2441(17)	3176(11)
O(2)	−7026(15)	764(15)	3337(10)
O(3)	−5211(20)	−799(18)	3490(12)
O(4)	−6288(29)	−1429(27)	2358(19)
C(53)	1369(29)	5597(19)	1009(15)
Cl(2)	1025(14)	4163(13)	793(10)
Cl(3)	2016(14)	5992(13)	264(10)

Structure solution and refinement

The structure was solved by Patterson and extended by difference syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at their calculated positions and introduced in the final structure factor calculation. A dichloromethane solvent molecule was also included in the refinement to account for the remaining peaks in the difference Fourier map; its occupancy factor was fixed to 0.5. The final R value was 0.0376, with R_w 0.0390. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with g 0.000608; 597 parameters; maximum $\Delta/\sigma < 0.014$, maximum $\Delta\rho$ 1.34 e Å^{-3}. Final atomic coordinates are given in Table 3, with derived bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen-atom coordinates, thermal parameters and remaining bond lengths and angles. A list of observed and calculated structure factors is available from the author.

Acknowledgments

We thank the Dirección General de Investigación Científica y Técnica (no. PB88-0075).

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