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 $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuPPh_3]ClO_4 \cdot 0.5CH_2Cl_2$

Antonio Laguna, Mariano Laguna, Josefina Jiménez, Fernando J. Lahoz and Elena Olmos

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza – C.S.I.C., 50009 Zaragoza (Spain)

(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].

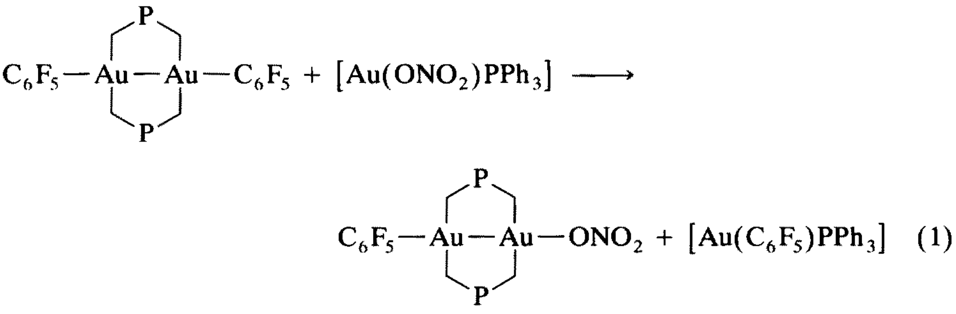
Correspondence to: Professor A. Laguna, Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza – C.S.I.C., 50009 Zaragoza, Spain.

In this paper we describe the reactions of $[RAu(CH_2PPh_2CH_2)_2AuR]$ ($R = C_6F_5$ [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], $[XAu(CH_2PPh_2CH_2)_2AuCH_2PR_3]X$ (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 $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuPPh_3]ClO_4$ was established by X-ray studies.

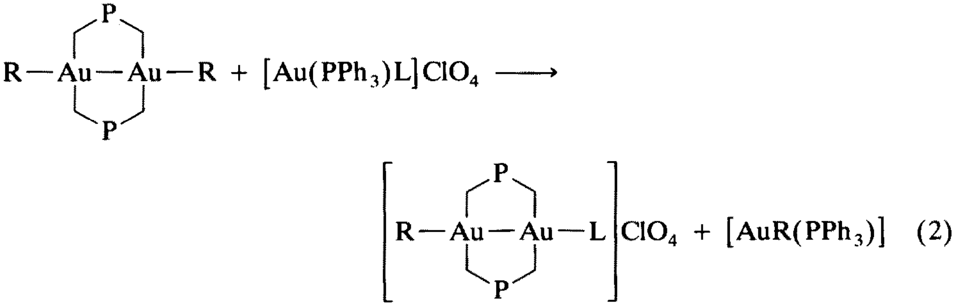
Results and discussion

The reaction of $[Au(ONO_2)PPh_3]$ with $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ 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)

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:



$R = C_6F_5$, $L = PPh_3$ (**2**) or tht (**3**)
$R = 2,4,6\text{-}C_6F_3H_2$, $L = PPh_3$ (**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**).

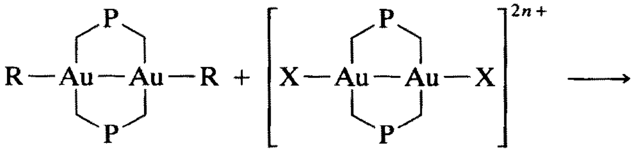
We have recently shown [10] that chloride derivatives of gold(II) can react with silver salts or silver complexes, giving rise to new gold(II) complexes by abstraction of chloride. In a similar way, complex **6** reacts with $AgNO_3$, $Ag(CH_3COO)$ or silver complexes $[Ag(OClO_3)L]$ (L = tht or PPh_3) 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**.

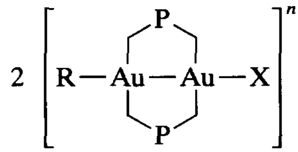
A less clean reaction occurs with complex **6** and $AgC_6F_3H_2$ (1 : 1 molar ratio); in the reaction mixture, three different components can be detected by spectroscopic methods ($^{31}P\{^1H\}$ and ^{19}F NMR). They cannot be separated because of their similar solubilities. Two of the complexes are 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)**
	$X = tht$	$n = 1$	**(3)**
$R = C_6F_3H_2$	$X = Cl$	$n = 0$	**(8)**
	$X = tht$	$n = 1$	**(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 $\nu(Au{-}C_{ylide})$ [8,18] around 565 cm^{-1}. Complexes **14**, with another $Au{-}C_{ylide}$ 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 ν(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 ν(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]			$\nu(Au-C_{ylide})$ (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 ν_{asym}(COO) and ν_{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_2-PPh_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($CH_2PPh_2CH_2$)$_2$ $AuPPh_3$]ClO_4 · 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($CH_2PPh_2CH_2$)$_2$$AuPPh_3$]$^{2+}$ and 2.675(1) Å for [(C_6F_5)Au($CH_2PPh_2CH_2$)$_2$Au(C_6F_5)] [12]. Usually, the Au^{II}–X bond lengths trans to a metal–metal bond are longer than Au^{III}–X bonds, but in this case the Au^{II}–C_6F_5 bond length is 2.078(12) Å, which is comparable with the Au^{III}–C_6F_5 bond (typical values 2.050–2.075 Å) [28] and identical with the Au^{II}–C_6F_5 bond in [(C_6F_5)ClAu(PPh_2NHPPh_2)AuCl(C_6F_5)] [29] (2.064(6) Å) (the C_6F_5 group is not trans to the Au–Au bond), but shorter than in the symmetrical derivative [(C_6F_5)Au($CH_2PPh_2CH_2$)$_2$Au(C_6F_5)] (average Au–C_6F_5 bond 2.1508(10) Å). The Au–PPh_3 bond length is 2.443(3) Å, longer than in [Ph_3PAu ($CH_2PPh_2CH_2$)$_2$$AuPPh_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

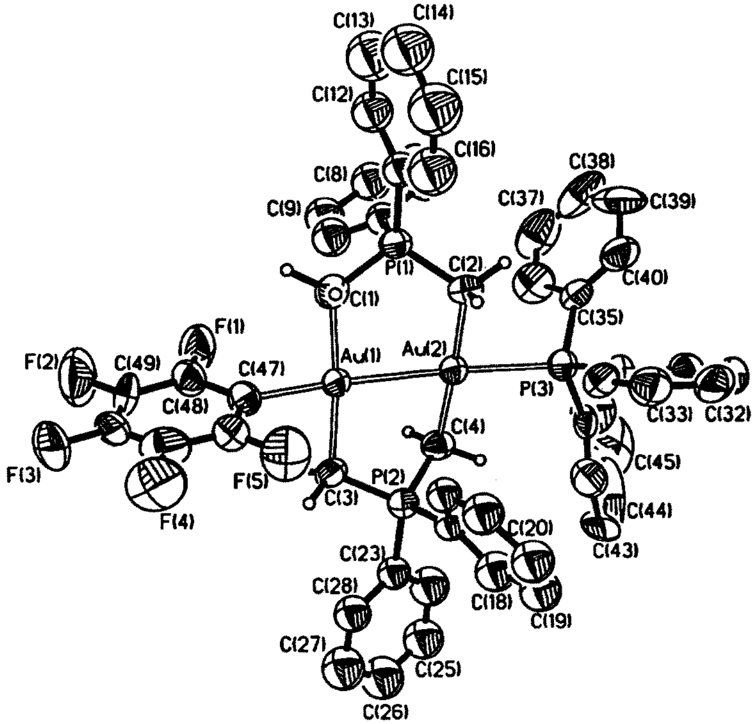


Fig. 1. Molecular structure of complex $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(PPh_3)]^+$ (**2**), with the labelling scheme.

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 $0.129 \times 0.188 \times 0.412$ 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).

References

1 J.D. Basil, H.H. Murray, J.P. Fackler, jr., J. Tocher, A.M. Mazany, B. Trzcinska-Bancroft, H. Knachel, D. Dudis, T.J. Delord and D. Marler, J. Am. Chem. Soc., 107 (1985) 6908.

2 H. Schmidbaur, Acc. Chem. Res., 8 (1975) 62.

3 H. Schmidbaur, Angew. Chem., Int. Ed. Engl., 15 (1976) 728.

4 H. Schmidbaur, J.R. Mandl, A. Frank and G. Huttner, Chem. Ber., 109 (1976) 466.

5 H.H. Murray, J.P. Fackler, jr., A.M. Mazany, L.C. Porter, J. Shain and L.R. Falvello, Inorg. Chim. Acta, 114 (1986) 171.

6 H.H. Murray, A.M. Mazany and J.P. Fackler, jr., Organometallics, 4 (1985) 154.

7 H.H. Murray, J.P. Fackler, jr., and B. Trzcinska-Bancroft, Organometallics, 4 (1985) 1633.

8 H. Schmidbaur and R. Franke, Inorg. Chim. Acta, 13 (1975) 85.

9 R. Usón, A. Laguna, M. Laguna, J. Jiménez and P.G. Jones, Angew. Chem., Int. Ed. Engl., 30 (1991) 198.

10 R. Usón, A. Laguna, M. Laguna, J. Jiménez and P.G. Jones, J. Chem. Soc., Dalton Trans., (1991) 1361.

11 J.P. Fackler and L.C. Porter, J. Am. Chem. Soc., 108 (1986) 2750.

12 H.H. Murray, J.P. Fackler, jr., L.C. Porter, P.A. Briggs, M.A. Guerra and R.J. Lagow, Inorg. Chem., 26 (1987) 357.

13 D.D. Heinrich and J.P. Fackler, jr., J. Chem. Soc., Chem. Commun., (1987) 1260.

14 H. Schmidbaur, C. Hartmann, G. Reber and G. Müller, Angew. Chem., Int. Ed. Engl., 26 (1987) 1146.

15 H.C. Knachel, D.S. Dudis and J.P. Fackler, jr., Organometallics, 3 (1984) 1312.

16 R.J. Puddephatt, Chem. Soc. Rev., (1983) 99.

17 J.P. Fackler, jr., and H.H. Murray, Organometallics, 3 (1984) 821.

18 H. Schmidbaur and R. Franke, Angew. Chem., 108 (1975) 1321.

19 R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and J.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 285.

20 R. Usón, A. Laguna, J. García and M. Laguna, Inorg. Chim. Acta, 37 (1979) 201.

21 B.J. Hathaway and A.E. Underhill, J. Chem. Soc., (1961) 3091.

22 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986, p. 254; 4th edn. R. Usón, A. Laguna and J. Buil, J. Organomet. Chem., 85 (1975) 403.

23 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, Chem. Ber., 110 (1977) 2751 and 2758; H. Schmidbaur, F.E. Wagner and A. Wohlleben-Hammer, Chem. Ber., 112 (1979) 496; H. Schmidbaur and P. Jandik, Inorg. Chim. Acta, 74 (1983) 97.

24 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986, p. 283, 4th edn.

25 R.A. Bailey, F.W. Michelson and W.N. Mills, J. Inorg. Nucl. Chem., 33 (1971) 3206.

26 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986, p. 231, 4th edn.

27 A. Laguna, M. Laguna and M. Palacios, unpublished results.

28 R. Usón, A. Laguna, M. Laguna, I. Lázaro, P.G. Jones and C. Fittschen, J. Chem. Soc., Dalton Trans., (1988) 2323; R. Usón, A. Laguna, M. Laguna, M.N. Fraile, P.G. Jones and C.F. Erdbrügger, J. Chem. Soc., Dalton Trans., (1989) 73; R. Usón, A. Laguna, M. Laguna, M.L. Castilla, P.G. Jones and C. Fittschen, J. Chem. Soc., Dalton Trans., (1987) 3017.

29 R. Usón, A. Laguna, M. Laguna, M.N. Fraile, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1986) 291.

30 R. Usón, A. Laguna, M. Laguna, J. Jiménez and M.E. Durana, Inorg. Chim. Acta, 168 (1990) 89.

31 R. Usón, A. Laguna, M. Laguna, J. Jiménez, M.P. Gómez, A. Sainz and P.G. Jones, J. Chem. Soc., Dalton Trans., (1990) 3457.

32 F.A. Cotton, L.R. Falvello, R. Usón, J. Forniés, M. Tomás, J.M. Casas and I. Ara, Inorg. Chem., 26 (1987) 1366.

33 R. Usón, A. Laguna, E.J. Fernández, A. Mendía and P.G. Jones, J. Organomet. Chem., 350 (1988) 129.