

Different coordination modes of the 1,1,1-tris(diphenylphosphinomethyl)ethane ligand in gold(I) and gold(III) complexes

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Abstract

The synthesis of pentafluorophenyl mono- or poly-nuclear gold(I) and/or gold(III) complexes with the tridentate ligand $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ (tdppme) are described in different coordination modes not represented thus far. The reaction of the free phosphine with gold(I) or gold(III) derivatives in different molar ratios gives $\{[\text{Au}(\text{C}_6\text{F}_5)]_3(\mu_3\text{-}\eta^3\text{-tdppme})\}$, $\{[\text{Au}(\text{C}_6\text{F}_5)]_2(\mu\text{-}\eta^2\text{-tdppmeO})\}$, $[\text{Au}(\text{C}_6\text{F}_5)_2(\eta^1\text{-tdppme})]$ or $[\text{Au}(\text{C}_6\text{F}_5)_2(\eta^2\text{-tdppme})]\text{Cl}$. The mononuclear derivatives further react with gold(I) or gold(III) species giving rise to di- or tri-nuclear complexes which contain the triphosphine acting as a $\mu_3\text{-}\eta^3$, $\mu\text{-}\eta^2$, $\mu\text{-}\eta^3$ or η^2 ligand.

Keywords: Gold(I); Gold(III); 1,1,1-tris(diphenylphosphinomethyl)ethane complexes; Syntheses; Di- and tri-nuclear complexes; ³¹P NMR spectra

1. Introduction

Although in recent years the chemistry of diphosphines, as bis(diphenylphosphino)methane [1,2] or its methanide $(\text{PPh}_2)_2\text{CH}^-$ [3], has received a great deal of attention, and some examples of gold derivatives have been prepared [3–7], the chemistry of triphosphines is less developed. Thus, only a few complexes containing the ligand $(\text{PPh}_2)_3\text{CH}$ or $(\text{PPh}_2)_3\text{C}^-$ have been synthesized [8]. Some transition-metal complexes with $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ (tdppme) have been prepared, but in most of them the phosphine is acting as a tridentate-chelating ligand (Fig. 1(A)), as in $[\text{RuH}(\text{BH}_4)(\eta^3\text{-tdppme})]$, $[\text{RuH}_2(\text{AsPh}_3)(\eta^3\text{-tdppme})]$ [9] or $[\text{Ru}(\text{MeCN})_3(\eta^3\text{-tdppme})]^{2+}$ [10] and in the carbonyl derivatives $\text{fac-}[\text{Mn}(\text{CO})_3(\eta^3\text{-tdppme})]^+$ [11] or $\text{fac-}[\text{Mo}(\text{CO})_3(\eta^3\text{-tdppme})]$ [12]. The same coordination mode appears in the heteropolynuclear clusters $[(\eta^3\text{-tdppme})\text{MH}_3(\text{AuL})_n]^{n+}$ ($\text{M} = \text{Rh}, \text{Ir}; n = 1, 2$), $[(\eta^3\text{-tdppme})\text{MH}_2(\text{AuL})_3]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$), $[(\eta^3\text{-tdppme})\text{-RuH}_3(\text{AuL})_n]^{(n-1)+}$ ($n = 1, 2, 3$) or $[(\eta^3\text{-tdppme})$

$\text{RuH}_2(\text{AuL})_3]^+$ ($\text{L} = \text{PR}_3$ or AsR_3) [9,13,14], which contain Au–Rh, –Ir or –Ru bonds supported by bridging hydrides.

A few transition-metal complexes in which the triphosphine acts as bidentate-chelating (Fig. 1(B)) have been prepared: $\text{fac-}[\text{Mn}(\text{CO})_3\text{Br}(\eta^2\text{-tdppme})]$ [15] or $[\text{M}(\text{CO})_4(\eta^2\text{-tdppme})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [16], and there is only one example of its coordination as a tridentate-bridging ligand (Fig. 1(C)) [17], in which the phosphine bridges three chlorogold(I) fragments.

In this paper we describe the synthesis of mono-, di- or tri-nuclear gold(I) and/or gold(III) compounds con-

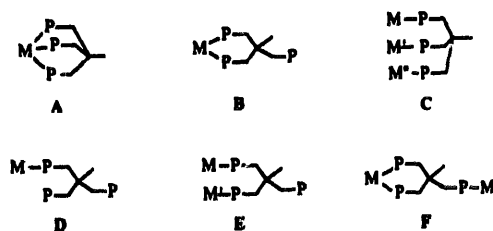


Fig. 1. Different coordination modes of the 1,1,1-tris(diphenylphosphinomethyl)ethane ligand.

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taining $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ in different coordination modes, some of which are unprecedented (Figs. 1(D)–1(F)).

2. Results and discussion

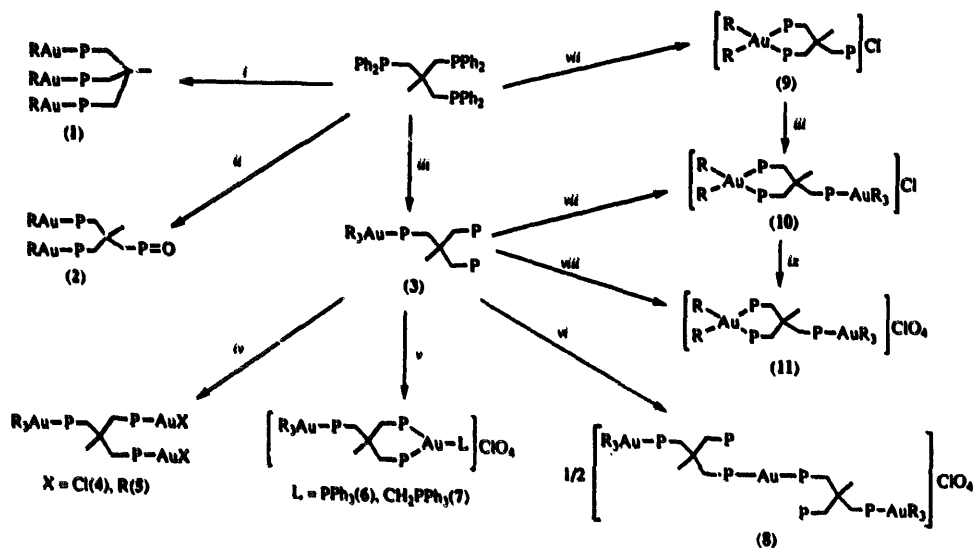
The reaction of $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ with $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (1:3) (tht = tetrahydrothiophene) in dichloromethane leads to the synthesis of the trinuclear complex $[\{\text{Au}(\text{C}_6\text{F}_5)\}_3\{(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3\}]$ (1) (Scheme 1, reaction (i)). The same reaction in a different molar ratio (1:2) (Scheme 1, reaction (ii)) produces the displacement of the S-donor ligands for two phosphorus atoms, and the free phosphorus is oxidized by atmospheric oxygen, leading to the dinuclear complex $[\{\text{Au}(\text{C}_6\text{F}_5)\}_2\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\text{O}\}]$ (2). All our trials to obtain the unoxidized phosphine derivative by using a nitrogen atmosphere and deoxygenated solvents were unsuccessful. Similarly, we could not prepare a gold(I) compound with the triphosphine as a monodentate ligand. Similar behaviour was previously observed by us in the reaction of $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ with bidentate phosphines [18].

Although it is not possible to prepare a monodentate derivative with gold(I), when a similar reaction is carried out with $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ and $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ in a molar ratio 1:1, the first monodentate compound described with this ligand, $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\}]$ (3) is obtained and no oxidation of the phosphine is observed. A similar result was described for the reaction of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ and $\text{PPh}_2\text{CH}_2\text{PPh}_2$ [18].

Complexes 1–3 are white solids, air- and moisture-stable at room temperature and non-conducting in ace-

tone solutions. They are very soluble in chlorinated solvents, acetone and diethyl ether, and partially soluble in hexane (this could explain the low yields obtained). Moreover, the solubility of complex 3 in hexane is so high that it is necessary to evaporate the solvent to dryness to obtain the solid. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 1 shows one multiplet and in the spectra of 2 and 3 there are two resonances with different intensities. In no case was P–P coupling observed between the phosphorus of the triphosphine. The signals corresponding to the phosphorus trans to C_6F_5 always appear as multiplets because of their coupling with the fluorine atoms. In their ^{19}F NMR spectra there are three resonances due to only one type of pentafluorophenyl group bonded to gold(I) (1, 2) or the characteristic pattern of $\text{Au}(\text{C}_6\text{F}_5)_3$ groups (3) [18]. The ^1H NMR spectrum of 1 shows a singlet for the methyl protons and a doublet for the three methylene groups. In contrast, the ^1H spectra of 2 and 3 show two different types of methylene proton, which appear as a doublet (2H) and an ABX system (4H), where X is a phosphorus atom. The mass spectra (FAB +) of 1 and 2 contain the parent ion at $m/z = 1716$ (1, 17%) or 1368 (2, 12%); in both of them the base peak corresponds to the fragment $[\text{M}-\text{C}_6\text{F}_5]^+$. In the mass spectrum of 3 the parent ion appears protonated at $m/z = 1323$ (4%) and peaks due to the fragments $[\text{M}-(\text{C}_6\text{F}_5)_n]^+$ ($n = 1, 2, 3$) can also be observed.

The tetrahydrothiophene ligand in gold(I) complexes can be easily displaced by the free phosphorus atoms of $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\}]$ (3). Thus, its reaction with $[\text{AuCl}(\text{tht})]$ or $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (1:2) results in the formation of the trinuclear gold(I)–gold(III) derivatives $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\}_2(\text{AuX})_2]$ ($\text{X} = \text{Cl}$ (4), C_6F_5 (5)), in which



Scheme 1. $\text{R} = \text{C}_6\text{F}_5$; (i) $3[\text{AuR}(\text{tht})]$; (ii) $2[\text{AuR}(\text{tht})]$; (iii) $[\text{AuR}_3(\text{tht})]$; (iv) $2[\text{AuX}(\text{tht})]$; (v) $[\text{AuL}(\text{tht})]\text{ClO}_4$; (vi) $1/2[\text{Au}(\text{tht})_2]\text{ClO}_4$; (vii) $1/2[\text{AuR}_2(\mu\text{-Cl})_2]$; (viii) $[\text{AuR}_2(\text{OEt})_2]\text{ClO}_4$; (ix) $\text{NaClO}_4 \cdot \text{H}_2\text{O}$.

the phosphine acts as a $\mu_3\text{-}\eta^3$ ligand and bridges different metallic fragments.

Complex **3** can also react with equimolar quantities of $[\text{AuL}(\text{tht})]\text{ClO}_4$ ($\text{L} = \text{PPh}_3, \text{CH}_2\text{PPh}_3$) to obtain $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2\}\text{AuL}]\text{ClO}_4$ ($\text{L} = \text{PPh}_3$ (**6**), CH_2PPh_3 (**7**)), which contain $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ in a new coordination mode ($\mu\text{-}\eta^3$) not represented to date. These two complexes are three-coordinated gold(I) derivatives, which is not the most commonly observed geometry for this centre, although some three- and four-coordinated gold(I) species have been described.

The reaction of **3** with $[\text{Au}(\text{tht})_2]\text{ClO}_4$ (2:1) leads to the trinuclear derivative $[\{\text{Au}(\text{C}_6\text{F}_5)_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2\}\}_2\text{Au}]\text{ClO}_4$ (**8**), in which a gold(I) centre bridges two molecules of **3**.

Complexes **4–8** are white air-stable solids, soluble in dichloromethane, chloroform and acetone, and partially soluble in diethyl ether and hexane (which causes their low yields). **4** and **5** are non-conducting in acetone solutions, and **6–8** behave as 1:1 electrolytes. The IR spectra of these compounds show the characteristic vibrations of tris(pentafluorophenyl)gold(III) groups [18], and in the spectra of **6–8** bands at 1100 (s, br) and 620 (m) cm^{-1} , due to the ClO_4^- anion [19] appear. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4** and **5** show two signals with different intensities, due to the phosphorus bonded to gold(I) (2P) or gold(III) (1P). A new resonance appears in the spectra of **6** and **7**, corresponding to the L ligands. In the spectrum of complex **6**, where $\text{L} = \text{PPh}_3$, the three-coordinated geometry of the gold(I) centre is easily proved, because of the presence of a doublet (28.1 ppm) and a triplet (45.3 ppm, $^2J(\text{P-P}) = 121.3$ Hz) for the different types of phosphorus bonded to gold(I). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** at room temperature shows a multiplet for the P–Au(III) atoms and a broad signal (ca. -7 ppm) due to the P–Au(I) atoms; however, on cooling to 223 K this signal splits into two multiplets centred at -11.4 and -3.1 ppm, which looks like an AA'BB' system, similar to those found for related systems $\text{Au}_3(\text{dppm})_2$ [20]. These spectra are consistent with a fluxional equilibrium at room temperature, which makes the phosphorus close to the gold(I) centre equivalent (Fig. 2).

The ^{19}F NMR spectra for **4–8** show the characteristic pattern for an $\text{Au}(\text{C}_6\text{F}_5)_3$ fragment, and in complex **5** there are three more groups of signals for the two equivalent C_6F_5 groups bonded to gold(I). Their ^1H NMR spectra show three resonances assigned to the CH_3 (s), Au(III)-P-CH_2 (d) and Au(I)-P-CH_2 (m) protons. For complex **7**, an additional doublet arising at the ylide ligand appears at 1.54 ppm ($^2J(\text{H-P}) = 8.9$ Hz).

In all the mass spectra (FAB +) the cation fragment ion appears at $m/z = 1751$ (**4**, 17%), 2050 (**5**, 23%), 1781 (**6**, 75%), 1795 (**7**, 20%) and 2841 (**8**, 52%). They

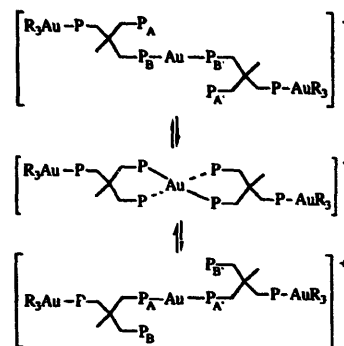


Fig. 2. Fluxional behaviour of complex **8** in solution.

also present the peak due to the loss of an $\text{Au}(\text{C}_6\text{F}_5)_3$ group and those corresponding to the fragments $[\text{Au}(\text{tdppme})]^+$ and $[\text{Au}_2(\text{C}_6\text{F}_5)(\text{tdppme})]^+$ at $m/z = 821$ and 1185 respectively.

Taking into account that the reaction of $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ with $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ gives the monodentate complex **3**, we tried to prepare a similar monodentate derivative through the reaction of $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ and $[\text{Au}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2]_2$ (2:1). Surprisingly, this reaction produces not only the rupture of the Au–Cl–Au bridges, but also the displacement of the chloride by one phosphorus, leading to $[\text{Au}(\text{C}_6\text{F}_5)_2\{\text{PPh}_2\text{CH}_2\}_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2]\text{Cl}$ (**9**). It is necessary to work under nitrogen atmosphere, because in otherwise a partial oxidation of the free phosphorus takes place.

The free phosphorus can also displace tetrahydrothiophene from $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ to give the new dinuclear complex $[\text{Au}(\text{C}_6\text{F}_5)_2\{\text{PPh}_2\text{CH}_2\}_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2]\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}$ (**10**). The same cation with perchlorate (**11**) instead of chloride can be obtained by the reaction of **10** with an excess of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. Complexes **10** and **11** can also be synthesized from $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2\}]$ (**3**) and $[\text{Au}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2]_2$ or $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{OEt})_2]\text{ClO}_4$ in molar ratios of 2:1 or 1:1 respectively (see Scheme 1).

Complexes **9–11** were obtained as white solids. **9** is air-sensitive, but **10** and **11** are air-stable at room temperature. All of them behave as 1:1 electrolytes in acetone solutions and their IR spectra show the presence of C_6F_5 groups bonded to gold(III) centres. In the IR spectrum of **11** the characteristic vibrations of the ClO_4^- anion also appear. The ^{19}F NMR spectrum of **9** contains five groups of signals with similar intensity, which means that the free rotation around the Au– C_6F_5 bonds is not possible. The ^{19}F NMR spectra of **10** and **11** are more complicated, because of the presence of two more types of pentafluorophenyl ring with relative intensities 2:1. Moreover, some resonances are superposed, which makes their assignment more difficult.

The mass spectra of **9–11** show, as in the rest of the complexes, the $[\text{M-X}]^+$ ($\text{X} = \text{Cl}$ or ClO_4) ion at $m/z = 1155$ (**9**, 60%), 1853 (**10**, 100%) and 1853 (**11**, 52%).

The spectrum of **9** also shows peaks due to the loss of one or two pentafluorophenyl groups at $m/z = 988$ or 821 respectively; also, the spectra of **10** and **11** show peaks at $m/z = 1519$, 1185 and 821 due to the ions $[\text{Au}_2(\text{C}_6\text{F}_5)_3(\text{tdppme})]^+$, $[\text{Au}_2(\text{C}_6\text{F}_5)(\text{tdppme})]^+$ and $[\text{Au}(\text{tdppme})]^+$ respectively.

3. Experimental

Instrumentation and general experimental techniques were described previously [21]. The NMR spectra were recorded on Bruker ARX 300 in CDCl_3 . Chemical shifts are cited relative to SiMe_4 (^1H), $85\% \text{H}_3\text{PO}_4$ (external ^{31}P) and CFCl_3 (external ^{19}F). Mass spectra were recorded on a VG Autospec, FAB technique, using 3-nitrobenzylalcohol as matrix. All the reactions were performed in air (except for complex **9**) and at room temperature. $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ was purchased from Strem. The yields, melting points, elemental analyses and conductivities for the new complexes are listed in Table 1 and the NMR data in Table 2.

3.1. $[\{\text{Au}(\text{C}_6\text{F}_5)_3\}_3\{(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3\}]$ (**1**)

To a solution of $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ (0.062 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ [22] (0.136 g, 0.3 mmol) and the mixture was stirred for 30 min. Concentration of the solution to ca. 5 cm^3 and addition of hexane (15 cm^3) led to the precipitation of **1** as a white solid. Yield: 44%.

NMR: ^{19}F , $\delta -115.2$ (m, 6F, *o*-F), -158.5 (t, 3F, *p*-F) ($J(\text{Fp}-\text{Fm}) = 19.8 \text{ Hz}$) and -162.4 (m, 6F, *m*-F).

3.2. $[\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\text{O}\}]$ (**2**)

To a dichloromethane solution (20 cm^3) of $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ (0.094 g, 0.15 mmol) was added $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ [22] (0.136 g, 0.3 mmol). After 1 h stirring at room temperature the solution was evaporated to ca. 5 cm^3 . Addition of hexane (15 cm^3) gave complex **2** as a white solid. Yield: 64%. NMR: ^{19}F , $\delta -115.6$ (m, 4F, *o*-F), -158.5 (t, 2F, *p*-F) ($J(\text{Fp}-\text{Fm}) = 19.6 \text{ Hz}$) and -162.4 (m, 4F, *m*-F).

3.3. $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2\}]$ (**3**)

To a solution of $(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3$ (0.125 g, 0.2 mmol) in dichloromethane (20 cm^3) was added $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ [22] (0.157 g, 0.2 mmol) and the mixture was stirred for 30 min. Evaporation of the solvent to dryness gave complex **3** as a white solid. Yield: 92%. NMR: ^{19}F , $\delta -119.8$ (m, 4F, *o*-F), -156.7 (t, 2F, *p*-F) ($J(\text{Fp}-\text{Fm}) = 19.8 \text{ Hz}$), -160.1 (m, 4F, *m*-F), -121.3 (m, 2F, *o*-F), -157.3 (t, 1F, *p*-F) ($J(\text{Fp}-\text{Fm}) = 20.0 \text{ Hz}$) and -161.2 (m, 2F, *m*-F).

3.4. $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2)(\text{AuX})_2\}]$ ($X = \text{Cl}$ (**4**), C_6F_5 (**5**))

To a solution of **3** (0.132 g, 0.1 mmol) in 20 cm^3 of dichloromethane was added $[\text{AuCl}(\text{tht})]$ [22] (0.064 g,

Table 1
Analytical data of complexes

Complex	Yield %	Analysis (%) ^a		M.p. (°C)	Λ_m^b
		C	H		
1 $[\{\text{Au}(\text{C}_6\text{F}_5)_3\}_3\{(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3\}]$	44	41.6 (41.3)	2.45 (2.3)	95 ^c	31
2 $[\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\text{O}\}]$	64	46.55 (46.55)	2.7 (2.85)	95 ^c	4
3 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2\}]$	92	53.0 (53.55)	3.25 (2.95)	65	6
4 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2)(\text{AuCl})_2\}]$	81	39.7 (39.65)	2.3 (2.2)	150	7
5 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2)(\text{Au}(\text{C}_6\text{F}_5)_2)\}]$	39	42.0 (41.6)	2.0 (1.9)	125	10
6 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2)(\text{Au}(\text{PPh}_3))\text{ClO}_4\}]$	42	49.15 (49.15)	2.85 (2.9)	140 ^c	129
7 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2)(\text{Au}(\text{CH}_2\text{PPh}_3))\text{ClO}_4\}]$	63	49.3 (49.45)	2.55 (2.95)	105	135
8 $[\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2\{(\text{PPh}_2\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2)\}_2\text{Au}\text{ClO}_4\}]$	57	48.4 (48.15)	2.35 (2.65)	168	137
9 $[\text{Au}(\text{C}_6\text{F}_5)_2\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\text{Cl}\}]$	90	53.4 (53.45)	3.5 (3.3)	130	70
10 $[\text{Au}(\text{C}_6\text{F}_5)_2\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}\}]$	84	45.2 (45.15)	2.15 (2.1)	120 ^c	75
11 $[\text{Au}(\text{C}_6\text{F}_5)_2\{(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2\text{Au}(\text{C}_6\text{F}_5)_3\text{ClO}_4\}]$	86	43.35 (43.65)	2.15 (2.0)	140	80

^a Calculated values are given in parentheses. ^b In acetone, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^c With decomposition.

Table 2
NMR data of complexes

Complex	$^{31}\text{P}\{^1\text{H}\}(\delta)$			$^1\text{H}(\delta)$			
	P-Au(I)	P	P-AuR ₃	P-AuR ₂	CH ₃	M-P-CH ₂	2CH ₂ -P
$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2)_3\text{CCH}_3](1)$	24.0(m)				1.15(s)	3.29(d)	
$[\text{Au}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{CH}_2)_2\text{CCH}_3\text{CH}_2\text{PPh}_2\text{O}](2)$	25.4(m)	26.9(s)			0.98(s)	2.95(d)	3.53(ABX)
$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](3)$		-26.3(s)	6.2(m)		0.83(s)	2.86(d)	2.21(ABX)
$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](4)$	16.2(s)		0.6(m)		1.32(s)	3.02(d)	$[\text{J}(\text{AB})13.9]$ 3.05(m)
$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](5)$	22.7(m)		0.0(m)		1.46(s)	$[\text{J}(\text{HP})11.3]$	3.27(m)
$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](6)$	28.1(d)	45.3(t)	0.6(m)		0.91(s)	2.44(d)	2.90(m)
$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](7)$	$[\text{J}(\text{PP})121.3]$ 22.6(s)	31.6(s)	1.2(m)		0.81(s)	2.83(d)	2.20(ABX)
$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2)_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](8)$	-7.2(AA'BB')		-0.5(m) ^b		0.85(s)	2.82(d)	$[\text{J}(\text{AB})13.0]$ 2.19(m)
$[\text{Au}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](9)$		-29.7(s)		5.0(m)	0.45(s)	$[\text{J}(\text{HP})11.2]$ 2.45(m)	3.62(m) 4.58(m)
$[\text{Au}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](10)$			-0.6(m)	3.5(m)	0.81(s)	3.15(d)	2.24(m)
$[\text{Au}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{CH}_2)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2](11)$			-1.3(m)	3.3(m)	0.88(s)	$[\text{J}(\text{HP})11.5]$ 3.50(d)	3.72(m) 2.31(m) 3.86(m)

Values in ppm; values of J in hertz. ^a The ^1H NMR of complex 7 also shows a doublet at 1.54(d) [$^2\text{J}(\text{HP})8.9$], due to the ylide ligand. ^b Registered at 223 K.

0.2 mmol) or $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ [22] (0.090 g, 0.2 mmol). After stirring for 2 h the solution was evaporated to ca. 5 cm³. Addition of hexane (20 cm³) led to the precipitation of the white solids 4 (yield: 81%) or 5 (yield: 39%). NMR: 4, ¹⁹F, δ -119.5 (m, 4F, *o*-F), -155.0 (t, 2F, *p*-F) ($J(\text{Fp-Fm}) = 19.8$ Hz), -159.1 (m, 4F, *m*-F), -121.7 (m, 2F, *o*-F), -156.3 (t, 1F, *p*-F) ($J(\text{Fp-Fm}) = 19.9$ Hz) and -160.7 (m, 2F, *m*-F); 5, ¹⁹F, δ -119.5 (m, 4F, *o*-F), -155.5 (t, 2F, *p*-F) ($J(\text{Fp-Fm}) = 19.3$ Hz), -159.3 (m, 4F, *m*-F), -121.6 (m, 2F, *o*-F), -156.3 (t, 1F, *p*-F) ($J(\text{Fp-Fm}) = 20.0$ Hz), -160.6 (m, 2F, *m*-F), -115.0 (m, 4F, *o*-F), -159.0 (t, 2F, *p*-F) ($J(\text{Fp-Fm}) = 20.1$ Hz) and -162.6 (m, 4F, *m*-F).

3.5. $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2\}\text{AuL}]\text{ClO}_4$ (L = PPh_3 (6), CH_2PPh_3 (7))

To a solution of 3 (0.132 g, 0.1 mmol) in 20 cm³ of dichloromethane was added $[\text{Au}(\text{PPh}_3)(\text{tht})]\text{ClO}_4$ [23] (0.065 g, 0.1 mmol) or $[\text{Au}(\text{CH}_2\text{PPh}_3)(\text{tht})]\text{ClO}_4$ [24] (0.066 g, 0.1 mmol) and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 cm³ and addition of hexane (20 cm³) gave the white solids 6 (yield: 42%) or 7 (yield: 63%). NMR: 6, ¹⁹F, δ -119.4 (m, 4F, *o*-F), -155.9 (t, 2F, *p*-F) ($J(\text{Fp-Fm}) = 19.9$ Hz), -159.8 (m, 4F, *m*-F), -121.5 (m, 2F, *o*-F), -157.1 (t, 1F, *p*-F) ($J(\text{Fp-Fm}) = 20.0$ Hz) and -161.1 (m, 2F, *m*-F); 7, ¹⁹F, δ -119.4 (m, 4F, *o*-F), -156.1 (t, 2F, *p*-F) ($J(\text{Fp-Fm}) = 19.5$ Hz), -159.7 (m, 4F, *m*-F), -121.5 (m, 2F, *o*-F), -156.8 (t, 1F, *p*-F) ($J(\text{Fp-Fm}) = 19.8$ Hz) and -160.9 (m, 2F, *m*-F).

3.6. $\{[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2\}]\}_2\text{AuClO}_4$ (8)

To a solution of 3 (0.264 g, 0.2 mmol) in dichloromethane (20 cm³) was added $[\text{Au}(\text{tht})_2]\text{ClO}_4$ [23] (0.047 g, 0.1 mmol). After stirring for 30 min the solution was concentrated to ca. 5 cm³. Addition of hexane led to the precipitation of 8 as a white solid. Yield: 57%. NMR: ¹⁹F, δ -119.5 (m, 8F, *o*-F), -156.0 (t, 4F, *p*-F) ($J(\text{Fp-Fm}) = 20.0$ Hz), -159.9 (m, 8F, *m*-F), -121.4 (m, 4F, *o*-F), -157.0 (t, 2F, *p*-F) ($J(\text{Fp-Fm}) = 20.0$ Hz) and -161.2 (m, 4F, *m*-F).

3.7. $[\text{Au}(\text{C}_6\text{F}_5)_2\{\text{PPh}_2\text{CH}_2\}_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2]\text{Cl}$ (9)

To an anhydrous deoxygenated dichloromethane solution (20 cm³) of $(\text{PPh}_2\text{CH}_2)_2\text{CCH}_3$ (0.125 g, 0.2 mmol) and under nitrogen atmosphere was added $[\text{Au}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2]$ [25] (0.113 g, 0.1 mmol). The mixture was stirred for 1 h. Concentration of the solution to ca. 5 cm³ and addition of diethyl ether (20 cm³) gave complex 9 as a white solid. Yield: 90%. NMR: ¹⁹F, δ

-116.7 (m, 2F, *o*-F), -118.8 (m, 2F, *o*-F), -156.1 ("t", 2F, *p*-F) ($N(\text{Fp-Fm}) = 19.8$ Hz), -158.9 (m, 2F, *m*-F) and -160.1 (m, 2F, *m*-F).

3.8. $[\text{Au}(\text{C}_6\text{F}_5)_2\{\text{PPh}_2\text{CH}_2\}_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2]\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}$ (10)

(a) To a solution of 9 (0.119 g, 0.1 mmol) in dichloromethane (20 cm³) was added $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ [22] (0.079 g, 0.1 mmol). After stirring for 30 min the solvent was evaporated to ca. 5 cm³. Addition of hexane (20 cm³) led to the precipitation of complex 10 as a white solid. Yield: 84%.

(b) To a dichloromethane solution (20 cm³) of 3 (0.264 g, 0.2 mmol) was added $[\text{Au}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2]$ [25] (0.113 g, 0.1 mmol). The mixture was stirred for 1 h. Concentration of the solvent to ca. 5 cm³ and addition of hexane (20 cm³) gave complex 10 as a white solid. Yield: 64%. NMR: ¹⁹F, δ -116.5 (m, 2F, *o*-F), -121.9 (m, 2F, *o*-F), -155.2 ("t", 2F, *p*-F), -157.5 (m, 2F, *m*-F), -160.1 (m, 2F, *m*-F), -119.8 (m, 4F, *o*-F), -155.3 (t, 2F, *p*-F), -159.5 (m, 4F, *m*-F), -121.9 (m, 2F, *o*-F), -156.6 (t, 1F, *p*-F) ($J(\text{Fp-Fm}) = 18.9$ Hz) and -160.8 (m, 2F, *m*-F).

3.9. $[\text{Au}(\text{C}_6\text{F}_5)_2\{\text{PPh}_2\text{CH}_2\}_2\text{C}(\text{CH}_3)\text{CH}_2\text{PPh}_2]\text{Au}(\text{C}_6\text{F}_5)_3\text{ClO}_4$ (11)

(a) To a freshly prepared solution of $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{OEt})_2]\text{ClO}_4$ in diethyl ether [26] (0.1 mmol) was added complex 3 (0.132 g, 0.1 mmol) and the mixture was stirred for 2 h. Concentration of the solution to ca. 5 cm³ and addition of hexane (20 cm³) gave 11 as a white solid. Yield: 80%.

(b) To a solution of 10 (0.189 g, 0.1 mmol) in dichloromethane (20 cm³) was added an excess of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. After stirring for 2 h, the resulting mixture was filtered through a 1 cm layer of Celite and washed with dichloromethane (3 × 5 cm³). Concentration of the filtrate to ca. 5 cm³ and addition of hexane (20 cm³) gave 11 as a white solid. Yield: 86%. NMR: ¹⁹F, δ -115.7 (m, 2F, *o*-F), -121.9 (m, 2F, *o*-F), -154.8 ("t", 2F, *p*-F) ($N(\text{Fp-Fm}) = 20.0$ Hz), -157.1 (m, 2F, *m*-F), -159.9 (m, 2F, *m*-F), -119.9 (m, 4F, *o*-F), -154.9 (t, 2F, *p*-F) ($J(\text{Fp-Fm}) = 20.7$ Hz), -159.2 (m, 4F, *m*-F), -121.9 (m, 2F, *o*-F), -156.5 (t, 1F, *p*-F) ($J(\text{Fp-Fm}) = 19.9$ Hz) and -160.7 (m, 2F, *m*-F).

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