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Two alternatives for the synthesis of non-cyclic phosphino-methanide derivatives of gold

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Abstract—The reaction of phosphine–phosphonium derivatives, such as $[AuX(PPh_2CH_2PPh_2Me)]ClO_4$ or $[Au(C_6F_5)_3(PPh_2CH_2PPh_2Me)]ClO_4$, or non-cyclic bis(diphenylphosphino)methane-bridging complexes, as $[Au(C_6F_5)_2X(PPh_2CH_2PPh_2)Au(C_6F_5)]$ (X = Cl, C_6F_5) or $[Au(C_6F_5)(PPh_2CH_2PPh_2)Au(C_6F_5)]$, with acetylacetonate derivatives or gold(I) compounds leads to the synthesis of non-cyclic methanide gold complexes of the types $[AuX\{PPh_2C(AuPPh_3)_2PPh_2Me\}]ClO_4$, $[Au(C_6F_5)_2X\{PPh_2CH(AuPPh_3)PPh_2Me\}]ClO_4$, $[Au(C_6F_5)_3\{PPh_2CH–(AuPPh_3)PPh_2\}Au(C_6F_5)]$, $[N(PPh_3)_2][Au(C_6F_5)_3\{PPh_2CH–(AuX)PPh_2\}Au(C_6F_5)]$ or $[N(PPh_3)_2][\{Au(C_6F_5)_3(PPh_2CH_2PPh_2)–Au(C_6F_5)\}_2Au]$. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: gold; bis(diphenylphosphino)methane; methanide; methanediide

INTRODUCTION

The chemistry of diphosphines, mainly of bis(diphenylphosphino)methane has been extensively developed in the past [1]. By deprotonation of the methylenic group an anion that can be described by different resonant forms [2] is obtained and its chemistry has been studied by several laboratories producing results that have been included in a recent revision [3]. We have contributed to this topic with the preparation of a great number of methanide or methanediide gold complexes, as for example the structurally characterized $[AuR_2\{(PPh_2)_2CH(AuR)\}]$, [4] $[AuR_2\{(PPh_2)_2C(AuPPh_3)_2\}]ClO_4$, [5] $[(RAu)HC(PPh_2AuPPh_2)_2CH(AuR)]$ [6], or $[(Ph_3PAu)_2C(PPh_2AuPPh_2)_2C(AuPPh_3)_2](ClO_4)_2$ [7] ($R = C_6F_5$).

However, in these products the diphosphine acts as a chelating or bridging ligand, respectively, and after the deprotonation the only possibility for further coordination is through the methanide carbon atom. Even when the free phosphine is treated with $[Au(acac)(PPh_3)]$ the eight-membered ring methanide $[CH(PPh_2AuPPh_2)_2CH]$, previously prepared by different methods by Schmidbaur [8, 8] and structurally characterized by Mingos, [9] is formed with displacement of triphenylphosphine [10]. The only examples of bridging non-cyclic methanides of gold described to date are obtained from $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)]$ [11] or its calcogenide derivatives [12].

These results show that the formation of cyclic methanides is more likely than the preparation of open ones, probably due to the additional stabilization produced by the delocalization of the electronic density through the ring. This made up our minds to study the possibility of synthesizing non-cyclic gold methanide complexes and to obtain this we used two different strategies. The first one is the use of the phosphino–phosphonium ligand $PPh_2CH_2PPh_2Me^+$ that features a positive charge on the quaternary phosphorus, which increases the acidity of the methylenic protons, and where the formation of cycles is avoided because of the presence of the quaternary phosphorus. The second strategy is the employment of gold complexes, such as $[Au(C_6F_5)_2X(PPh_2CH_2PPh_2)Au(C_6F_5)]$ (X = Cl, C_6F_5) or $[Au(C_6F_5)(PPh_2CH_2PPh_2)Au(C_6F_5)]$, with a saturated coordination sphere for the metal centers, which also prevents the formation of rings.

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This result differs from that previously described in which although the formation of rings is avoided, the coordination was possible through two donor atoms [12].

RESULTS AND DISCUSSION

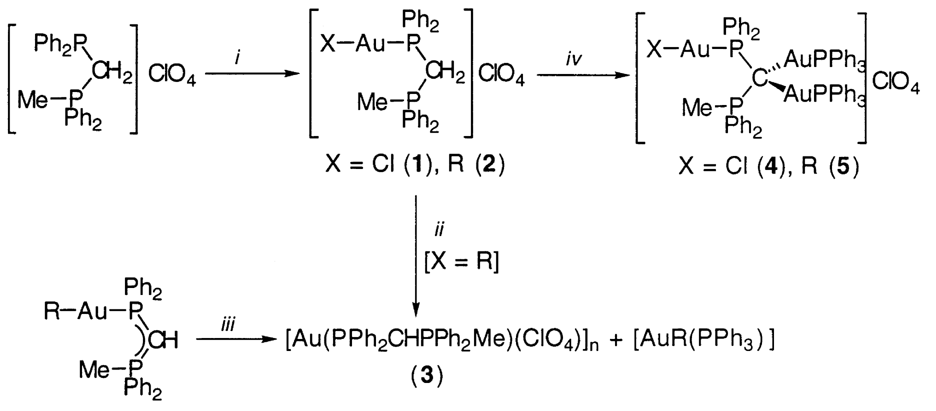
We have mentioned above two different strategies for the synthesis of open phosphino–methanide derivatives. With regard to the use of $PPh_2CH_2PPh_2Me^+$ as ligand we prepared the gold(I) complex $[AuCl(PPh_2CH_2PPh_2Me)]ClO_4$ (**1**) as starting material, by reaction of [AuCl(tht)] (tht = tetrahydrothiophene) with an equimolecular amount of $(PPh_2CH_2PPh_2Me)ClO_4$ (see Scheme 1). Complex **1** is obtained as an air and moisture stable white solid, with similar physical and spectroscopic properties to those observed for the previously described perfluorophenyl derivative **2** [13].

The use of acetylacetonate (acac) complexes has been previously reported in the synthesis of ylide or methanide complexes of gold (Refs. [10, 14, 14] and references therein). When complex **2** is treated with equimolecular amounts of $[Au(acac)(PPh_3)]$ in dichloromethane an initial yellow colour appears, which becomes subsequently discoloured with the simultaneous formation of a white precipitate. After 1 h of reaction the solid is filtered off and $[Au(C_6F_5)(PPh_3)]$ is obtained from the solution. The analytical data for the insoluble product are in accordance with those expected for a complex with an stoichiometry $[Au(PPh_2CHPPh_2Me)]ClO_4$. Its IR spectrum shows two absorptions at 620 (m) and 1100 (vs, br) cm^{-1} [15] due to the perchlorate ion; some bands corresponding to the phosphino–phosphonium ligand at about 500 and 895 cm^{-1}, as well as a band at 586 (m) cm^{-1}, assigned to the ν(Au–C) vibration [16, 16, 16, 16, 17]. Taking these data and its insolubility into account, we propose that a polymeric complex $[Au(PPh_2CHPPh_2Me)(ClO_4)]_n$ (**3**) (probably featuring Au–P and Au–C bonds) is formed, but its low solubility did not allow us to complete its characterization.

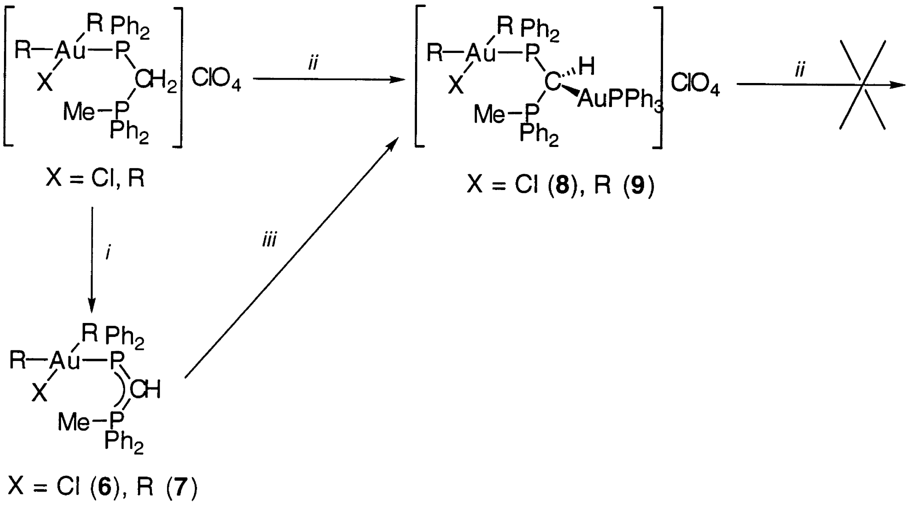
The same result is obtained when the methanide $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ [13] is treated with $[Au(PPh_3)(tht)]ClO_4$, and no sign of formation of $[Au(C_6F_5)\{PPh_2CH(AuPPh_3)PPh_2Me\}]ClO_4$ is observed.

In contrast, when complexes **1** or **2** are treated with $[Au(acac)(PPh_3)]$ in a 1:2 molar ratio, both methylenic protons are substituted by $[AuPPh_3]^+$ groups, affording the trinuclear species $[AuX\{PPh_2C(AuPPh_3)_2PPh_2Me\}]ClO_4$ [X = Cl (**4**), C_6F_5 (**5**)] Scheme 1. Complexes **4** and **5** are air and moisture stable solids, soluble in chlorinated solvents and acetone and non soluble in diethyl ether and hexane. Their analytical and spectroscopic data are in accordance with the proposed formulation, displaying three resonances with relative intensities 2:1:1 in their $^{31}P\{^1H\}$ NMR spectra.

Non-cyclic methanides are also obtained using phosphino–phosphonium derivatives of gold(III). Thus, reaction of $[Au(C_6F_5)_2X(PPh_2CH_2PPh_2Me)]ClO_4$ (X = Cl, C_6F_5) with $[N(PPh_3)_2](acac)$ in dichloromethane affords the previously described species $[Au(C_6F_5)_2X(PPh_2CHPPh_2Me)]$ [X = Cl (**6**), C_6F_5 (**7**)] through an alternative synthetic pathway. Their analytical and spectroscopic data agree with those previously described. [13] Treatment of the same starting products with one equivalent of $[Au(acac)(PPh_3)]$ leads to different results than the related gold(I) compounds and the monosubstituted species $[Au(C_6F_5)_2X\{PPh_2CH(AuPPh_3)PPh_2Me\}]ClO_4$ [X = Cl (**8**), C_6F_5 (**9**)] are now easily isolated (see Scheme 2). Complexes **8** and **9** can also be prepared from the methanide compounds **6** and **7**, respectively, when reacted with the appropriate amounts of $[Au(PPh_3)(tht)]ClO_4$. Also in contrast with the behavior of the gold(I) species, the disubstituted products $[Au(C_6F_5)_2X\{PPh_2C(AuPPh_3)_2PPh_2Me\}]ClO_4$ can not be prepared even when an excess (1:3) of $[Au(acac)(PPh_3)]$ is employed.



Scheme 1. R = C_6F_5; (i) [AuX(tht)]; (ii) $[Au(acac)(PPh_3)]$; (iii) $[Au(PPh_3)(tht)]ClO_4$; (iv) 2 $[Au(acac)(PPh_3)]$.



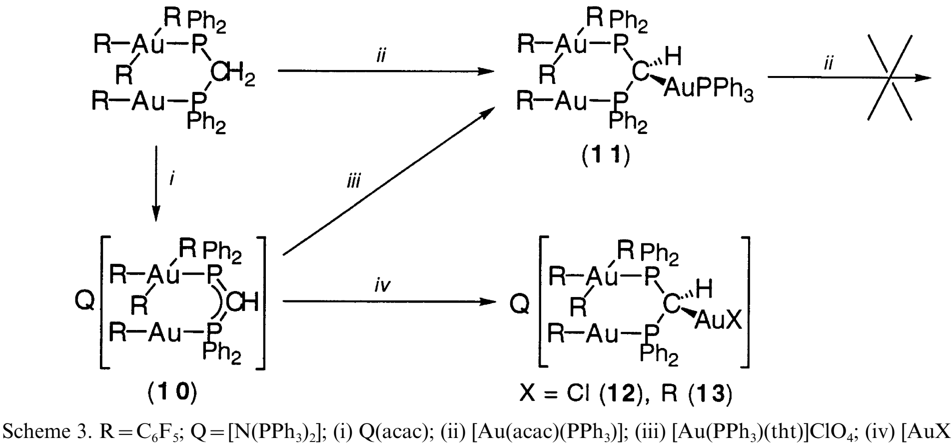
Scheme 2. R = C_6F_5; (i) $[N(PPh_3)_2](acac)$; (ii) $[Au(acac)(PPh_3)]$; (iii) $[Au(PPh_3)(tht)]ClO_4$.

Compounds **8** and **9** are obtained as white, air and moisture stable solids. Their $^{31}P\{^1H\}$ NMR spectra show three resonances with similar relative intensities, in accordance with the substitution of only one methylenic proton. This fact is also confirmed in their ^1H NMR spectra, which display one signal due to the remaining hydrogen atom, as well as a doublet corresponding to the protons of the methyl group. The ^{19}F NMR spectrum is in agreement with the *cis* position of the pentafluorophenyl groups in **8**.

Regarding the second strategy mentioned in Section 1, the use of dinuclear complexes featuring a saturated coordination sphere for the gold atoms, the employment of $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)Au(C_6F_5)]$ [18] leads to the same observations than the gold(III) phosphino–phosphonium species. Thus, the reaction of this dinuclear complex with $[N(PPh_3)_2](acac)$ gives rise to the synthesis of $[N(PPh_3)_2][Au(C_6F_5)_3(PPh_2CHPPh_2)Au(C_6F_5)]$ (**10**), one of the few anionic methanides reported to date (Scheme 3).

Complex **10** is obtained as a yellow air and moisture sensitive oil, which makes its characterization difficult. In its IR spectrum a broad signal located at 1184 (m) cm^{-1}, assigned to the methanide system [3], is present. Its $^{31}P\{^1H\}$ NMR spectrum confirms the presence of the cation, because a sharp singlet at $\delta = 21.7$ ppm appears. It also shows two multiplets with the same intensity, according with the existence of two inequivalent phosphorus of the diphosphino–methanide ligand with a pentafluorophenyl group in *trans* position.

Reaction of **10** with one equivalent of $[Au(PPh_3)(tht)]ClO_4$ or $[AuX(tht)]$ (X = Cl, C_6F_5) leads to the displacement of the sulfur donor ligand and the coordination of the non-saturated methanide carbon to the gold(I) centre affording the trinuclear neutral (**11**) or anionic (**12** and **13**) derivatives, as represented in Scheme 3. Compound **11** can alternatively be synthesized directly from $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)Au(C_6F_5)]$ and $[Au(acac)(PPh_3)]$ in a 1:1 molar ratio.

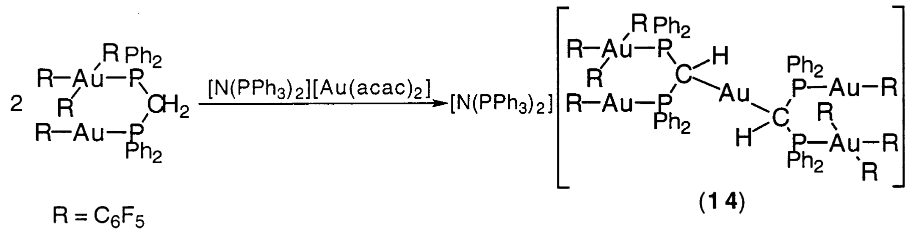


Scheme 3. R = C_6F_5; Q = $[N(PPh_3)_2]$; (i) Q(acac); (ii) $[Au(acac)(PPh_3)]$; (iii) $[Au(PPh_3)(tht)]ClO_4$; (iv) $[AuX(tht)]$.

Besides, as observed for gold(III) derivatives with $PPh_2CH_2PPh_2Me^+$, the use of an excess of $[Au(acac)(PPh_3)]$ does not produce a double deprotonation and the monosubstituted product **11** is formed again.

Complexes **11**, **12** and **13** are obtained as white powders. They are stable in solid state and in solution, except **12**, which rapidly decomposes in solution. They are soluble in most common organic solvents, except in hexane and their analytical and spectroscopic data are in accordance with the proposed formulation (see Section 3).

In order to increase the nuclearity of the products we can use $[N(PPh_3)_2][Au(acac)_2]$, which can at once extract one methylenic proton of two different molecules of $[Au(C_6F_5)_2X(PPh_2CH_2PPh_2)Au(C_6F_5)]$ ($X = Cl, C_6F_5$) and coordinate both methanide units to the gold(I) center, affording the pentanuclear $[N(PPh_3)_2][\{Au(C_6F_5)_3(PPh_2CHPPh_2)Au(C_6F_5)\}_2Au]$ (**14**) (equation 1).



This complex is obtained as a white solid and it is air and moisture stable in solid state, but its stability decreases in solution. Its $^{31}P\{^1H\}$ NMR spectrum is similar to those registered for **10** and **12**, featuring a singlet at $\delta = 21.7$ ppm, corresponding to the cation, and two multiplets due to both types of phosphorus of the methanide unit. In spite of complex **14** having two chiral carbon atoms and thus two pairs of enantiomers which can be present at the same time (RR, SS and RS, SR), the ^{19}F and ^1H NMR spectra show only one set of signals.

Finally, we have studied the behavior of $[Au(C_6F_5)(PPh_2CH_2PPh_2)Au(C_6F_5)]$ [19]. The reaction with one equivalent of $[Au(acac)(PPh_3)]$ gives rise to the substitution of one methylenic hydrogen, affording $[Au(C_6F_5)\{PPh_2CH(AuPPh_3)PPh_2\}Au(C_6F_5)]$ (**15**), while an excess of the acetylacetonate derivative does not lead to further substitutions, recovering always complex **15** (Scheme 4). This is a white stable solid, soluble in common organic solvents, except in hexane. Its $^{31}P\{^1H\}$ NMR spectrum shows two resonances at $\delta = 40.8$ (t) and 36.8 (d) ppm, with a relative intensity 1:2 and in its ^1H NMR spectrum a pseudotriplet of doublets centered at $\delta = 3.9$ ppm, due to the methylinic proton appears.

EXPERIMENTAL

General

NMR spectra were recorded on a Bruker ARX 300 spectrometer in $CDCl_3$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and H_3PO_4 (85%) (^{31}P, external). All experiments were carried out at room temperature and under nitrogen.

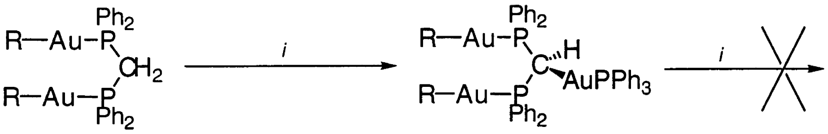
$[AuCl(PPh_2Ch_2PPh_2Me)]ClO_4$ (*1*)

To a dichloromethane solution of [AuCl(tht)] [20] (0.064 g, 0.2 mmol) was added $(PPh_2CH_2PPh_2Me)ClO_4$ (0.098 g, 0.2 mmol). After 30 min of stirring a little amount of precipitate is filtered over celite and the solution was concentrated to *ca.* 5 ml and diethyl ether was added to give complex **1** as a white solid. Yield: 80%. m.p.: 198 (dec). -$C_{26}H_{25}AuCl_2O_4P_2$ (731.30), calcd. C, 42.7; H, 3.45; found C, 42.55; H, 3.3. Λ_m: 115 Ω^{-1} cm^2 mol^{-1}. -$^{31}P\{^1H\}$NMR: δ 22.0 (d, 1P, Au–*P*Ph$_2$), [$^2J(PP^+) = 4.8$ Hz]) and 18.2 (m, 1P, *P*Ph$_2$Me); -^1H NMR δ 4.5 (dd, 2H, C*H*$_2$, [$^2J(HP) = 8.4$, $^2J(HP) = 5.4$ Hz]) and 2.4 (d, 3H, *Me*, [$^2J(HP) = 6.7$ Hz]).

$[Au(PPh_2CHPPh_2Me)]ClO_4$ (*3*)

(a) To a dichloromethane solution of **2** [13] (0.086 g, 0.1 mmol) was added $[Au(acac)(PPh_3)]$ [21] (0.055 g, 0.1 mmol) and the solution initially turned yellow, but after a few minutes it became discoloured with the appearance of **3** as a white solid. The mixture was stirred for 1 h and complex **3** (yield: 87%) was then filtered off and $[Au(C_6F_5)(PPh_3)]$ was isolated from the filtrate.

(b) A dichloromethane solution of $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ [13] (0.076 g, 0.1 mmol) was treated with $[Au(PPh_3)(tht)]ClO_4$ [22] (0.065 g, 0.1 mmol) and a white precipitate appears. After 1 h the precipitation was complete and filtration of the



(15)

Scheme 4. R = C_6F_5; (i) [Au(acac)(PPh_3)].

solid afforded **3** (yield: 82%) while [Au(C_6F_5)(PPh_3)] was recovered from the solution. $C_{26}H_{24}AuClO_4P_2$ (694.84), calcd. C, 44.95; H, 3.5; found C, 44.75; H, 2.9.

[$\mathit{Au}\{PPh_2C(AuPPh_3)_2PPh_2Me\}$]$ClO_4$ [$X = Cl$ (*4*), C_6F_5 (*5*)]

To a solution of **1** (0.073 g, 0.1 mmol) or **2** (0.086 g, 0.1 mmol) in 20 ml of dichloromethane was added [Au(acac)(PPh_3)] (0.110 g, 0.2 mmol) and after 2 h of stirring a little amount of precipitate is filtered over celite. The solvent was then evaporated in a vacuum and 20 ml of diethyl ether was added to give complexes **4** (yield: 70%) or **5** (yield: 85%) as white solids. 4: m.p.: 130 (dec). $C_{62}H_{53}Au_3Cl_2O_4P_4$ (1647.80), calcd. C, 45.2; H, 3.25; found C, 45.25; H, 3.6. Λ_m: 95 Ω^{-1} cm^2 mol^{-1}. -$^{31}P\{^1H\}$ NMR: δ 37.6 (dd, 2P, $P\mathrm{Ph_3}$, [$^3J(PP) = 11$, $^3J(PP^+) = 6.3$ Hz]), 32.5 (t, 1P, Au–$P\mathrm{Ph_2}$) and 22.6 (t, 1P, $P\mathrm{Ph_2Me}$); -^1H NMR: δ 2.3 (d, 3H, Me, [$^2J(HP) = 13.9$ Hz]). 5: m.p.: 142 (dec). -$C_{68}H_{53}Au_3ClF_5O_4P_4$ (1779.37), calcd. C, 45.8; H, 3.0; found C, 45.9; H, 2.95. Λ_m: 104 Ω^{-1} cm^2 mol^{-1}. -$^{31}P\{^1H\}$ NMR: δ 37.6 (m, 2P, $P\mathrm{Ph_3}$), 44.9 (m, 1P, Au–$P\mathrm{Ph_2}$) and 23.7 (m, 1P, $P\mathrm{Ph_2Me}$); ^1H NMR: δ 2.4 (d, 3H, Me, [$^2J(HP) = 7.8$ Hz]); -^{19}F NMR: δ −115.3 (m, 2F, *o*-F), −159.5 (t, 1F, *p*-F, [$^3J(FF) = 19.5$ Hz]) and −162.8 (m, 2F, *m*-F).

[$\mathit{Au}(C_6F_5)_2X(PPh_2CHPPh_2Me)$] [$X = Cl$ (*6*), C_6F_5 (*7*)]

To a solution of [Au(C_6F_5)$_2$X($PPh_2CH_2PPh_2Me$)]ClO_4 [13] [0.106 g (Cl) or 0.119 g (C_6F_5), 0.1 mmol] in dichloromethane was added [N(PPh_3)$_2$](acac) (0.076 g, 0.12 mmol). After 2 h of stirring the solvent was evaporated to dryness in a vacuum and 15 ml of diethyl ether was added to precipitate the [N(PPh_3)$_2$]ClO_4 formed in the reaction, which is removed by filtration over celite. Concentration of the filtrate and addition of hexane led to complexes **6** (yield: 95%) or **7** (yield: 98%) as white solids. Their analytical and spectroscopic data agree with those previously described [13].

[$\mathit{Au}(C_6F_5)_2X\{PPh_2CH(AuPPh_3)PPh_2Me\}$]$ClO_4$ [$X = Cl$ (*8*), C_6F_5 (*9*)]

(a) A dichloromethane solution of [Au(C_6F_5)$_2$X($PPh_2CH_2PPh_2Me$)]ClO_4 [0.106 g (Cl) or 0.119 g (C_6F_5), 0.1 mmol] was treated with [Au(acac)(PPh_3)] (0.055 g, 0.1 mmol). The mixture was stirred for 2 h and the solvent was then evaporated to *ca.* 5 ml. 20 ml of diethyl ether was added to precipitate complexes **8** (yield: 90%) or **9** (yield: 65%) as white solids.

(b) To a solution of [Au(C_6F_5)$_2$X(PPh_2CHPPh_2Me)] [0.096 g (Cl) or 0.110 g (C_6F_5), 0.1 mmol] in 20 ml of dichloromethane was added [Au(PPh_3)(tht)]ClO_4 (0.065 g, 0.1 mmol) and after 30 min of stirring the solution was concentrated in a vacuum. Addition of diethyl ether gave complexes **8** (yield: 83%) or **9** (yield: 62%) as white solids. **8**: m.p.: 95 (dec). -$C_{56}H_{39}Au_2Cl_2F_{10}O_4P_3$ (1523.59), calcd. C, 44.15; H, 2.6; found C, 44.45; H, 2.35. Λ_m: 130 Ω^{-1} cm^2 mol^{-1}. -$^{31}P\{^1H\}$ NMR: δ 39.5 ("t", 1P, $P\mathrm{Ph_3}$, [$^3N = 9.8$ Hz]), 27.4 (dm, 1P, Au–$P\mathrm{Ph_2}$) and 21.3 (dd, 1P, $P\mathrm{Ph_2Me}$, [$^2J(PP^+) = 29$ Hz]); -^1H NMR: δ 5.2 ("td", 1H, CH, [$^2J(HP) = 14.3$, $^3J(HP) = 8.8$ Hz]) and 2.6 (d, 3H, Me,

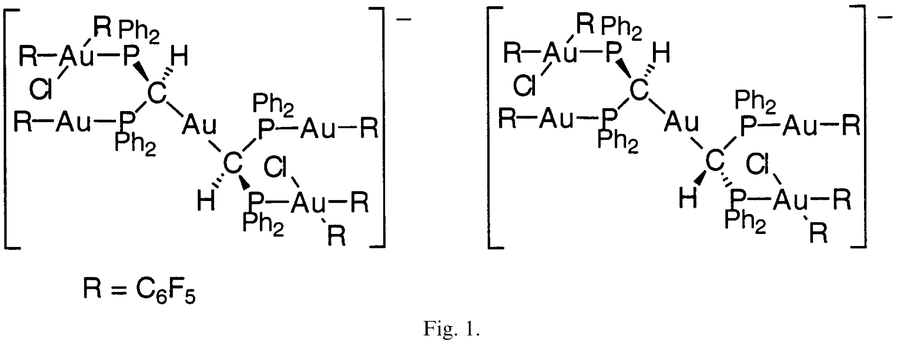


Fig. 1.

[^2J(HP) = 14.1 Hz]); -^{19}F NMR: δ-120.3 (m, 1F, *o*-F), −121.7 (m, 1F, *o*-F), −156.4 (t, 1F, *p*-F, [^3J(FF) = 19.3 Hz]), −159.4 (m, 1F, *m*-F), −160.4 (m, 1F, *m*-F), −121.8 (m, 1F, *o*-F), −122.1 (m, 1F, *o*-F), −156.5 (t, 1F, *p*-F, [^3J(FF) = 19.0 Hz]), −160.6 (m, 1F, *m*-F) and −160.8 (m, 1F, *m*-F). 9: m.p.: 114 (dec). -$C_{62}H_{39}Au_2ClF_{15}O_4P_3$ (1655.15), calcd.: C, 45.0; H, 2.4; found C, 45.5; H, 2.45. Λ_m: 126 Ω^{-1} cm^2 mol^{-1}. -^{31}P{^{1}H} NMR: δ 38.6 (m, 1P, *P*Ph$_3$), 23.4 (m, 1P, Au–*P*Ph$_2$) and 17.4 (m, 1P, *P*Ph$_2$Me); -^{1}H NMR: δ 3.6 (m, 1H, C*H*) and 2.1 (d, 3H, Me, [^2J(HP) = 13.1 Hz]); -^{19}F NMR: δ −119.1 (m, 2F, *o*-F), −155.7 (t, 1F, *p*-F, [^3J(FF) = 19.9 Hz]), −159.6 (m, 2F, *m*-F), −120.7 (m, 2F, *o*-F), −156.5 (t, 1F, *p*-F, [^3J(FF) = 20.3 Hz]) and −160.8 (m, 2F, *m*-F).

*[N(PPh$_3$)$_2$][Au(C$_6$F$_5$)$_3$(PPh$_2$CHPPh$_2$)Au(C$_6$F$_5$)] (**10**)*

To a diethyl ether solution of [Au(C_6F_5)$_3$(PPh$_2$CH$_2$PPh$_2$)Au(C_6F_5)] [18] (0.144 g, 0.1 mmol) was added [N(PPh$_3$)$_2$](acac) (0.076 g, 0.12 mmol) and the solution turned yellow. After 2 h of stirring the excess of [N(PPh$_3$)$_2$](acac) was removed by filtration and the solution was dried in a vacuum giving complex **10** as a yellow oil. -^{31}P{^{1}H} NMR: δ 31.1 (m, 1P, Au(I)–*P*Ph$_2$), 18.5 (m, 1P, Au(III)–*P*Ph$_2$) and 21.7 (s, 2P, [N(*P*Ph$_3$)$_2$]$^+$).

*[Au(C$_6$F$_5$)$_3${PPh$_2$CH(AuPPh$_3$)PPh$_2$}Au(C$_6$F$_5$)] (**11**)*

(a) A dichloromethane solution of [Au(C_6F_5)$_3$(PPh$_2$CH$_2$PPh$_2$)Au(C_6F_5)] (0.144 g, 0.1 mmol) was treated with [Au(acac)(PPh$_3$)] (0.055 g, 0.1 mmol). The mixture was stirred for 2 h and a little amount of solid was filtered over celite. The solvent was then evaporated to *ca.* 5 ml and hexane was added to precipitate complex **11** as a white solid. Yield: 50%.

(b) To a freshly prepared solution of **10** (0.1 mmol) in dichloromethane was added [Au(PPh$_3$)(tht)]ClO$_4$ (0.065 g, 0.1 mmol) and the solution turned rapidly colourless. The solution was stirred for 30 min and the solvent was then dried in a vacuum. Addition of diethyl ether led to the precipitation of the [N(PPh$_3$)$_2$]ClO$_4$ formed in the reaction, which was removed by filtration over celite. Concentration of the filtrate and addition of hexane gave complex **11** as a white solid. Yield: 40%. m.p.: 140 (dec). -$C_{67}H_{36}Au_3F_{20}P_3$ (1904.65) calcd.: C, 42.2; H, 1.9; found C, 41.5; H, 2.0. Λ_m: 10 Ω^{-1} cm^2 mol^{-1}. -^{31}P{^{1}H} NMR: δ 39.2 ("t", 1P, *P*Ph$_3$, [*N* = 9.8 Hz]), 36.8 (m, 1P, Au(I)–*P*Ph$_2$) and 22.3 (m, 1P, Au(III)–*P*Ph$_2$); -^{1}H NMR: δ 3.6 (m, 1H, C*H*); -^{19}F NMR: δ −118.7 (m, 4F, *o*-F), −158.2 (t, 2F, *p*-F, [^3J(FF) = 20.6 Hz]), −161.1 (m, 4F, *m*-F), −121.5 (m, 2F, *o*-F), −157.9 (t, 1F, *p*-F, [^3J(FF) = 20.6 Hz]), −161.8 (m, 2F, *m*-F), −116.1 (m, 2F, *o*-F), −159.2 (t, 1F, *p*-F, [^3J(FF) = 19.3 Hz]) and −163.1 (m, 2F, *m*-F).

*[N(PPh$_3$)$_2$][Au(C$_6$F$_5$)$_3${PPh$_2$Ch(AuX)PPh$_2$}Au(C$_6$F$_5$)] [X = Cl (**12**), C$_6$F$_5$ (**13**)]*

To a freshly prepared solution of **10** (0.1 mmol) in dichloromethane was added [AuCl(tht)] (0.032 g, 0.1 mmol) or [Au(C_6F_5)(tht)] [23] (0.045 g, 0.1 mmol) and the solution turned rapidly colourless. After 30 min of stirring the solvent was evaporated in a vacuum and hexane was added to precipitate complexes **12** (yield: 75%) or **13** (yield: 70%) as white solids. **12**: m.p.: 63 (dec). -$C_{85}H_{51}Au_3ClF_{20}NP_4$ (2216.40), calcd. C, 46.05; H, 2.3; N, 0.6; found C, 45.8; H, 2.35; N, 0.4; **13**: m.p.: 75 (dec). -$C_{91}H_{51}Au_3F_{25}NP_4$ (2347.96), calcd.: C, 46.55; H, 2.2; N, 0.6; found C, 46.6; H, 2.4; N, 0.5. Λ_m: 81 Ω^{-1} cm^2 mol^{-1}. -^{31}P{^{1}H} NMR: δ 39.4 (m, 1P, Au(I)–*P*Ph$_2$), 22.4 (m, 1P, Au(III)–*P*Ph$_2$) and 21.7 (s, 2P, [N(*P*Ph$_3$)$_2$]$^+$); -^{1}H NMR: δ 3.55 ("t", 1H, C*H*, [*N* = 9.4 Hz]); -^{19}F NMR: δ −118.1 (m, 4F, *o*-F), −159.5 (t, 2F, *p*-F, [^3J(FF) = 21.7 Hz]), −162.4 (m, 4F, *m*-F), −120.2 (m, 2F, *o*-F), −159.3 (t, 1F, *p*-F, [^3J(FF) = 20.2 Hz]), −163.5 (m, 2F, *m*-F), −115.2 (m, 2F, *o*-F), −159.9 (t, 1F, *p*-F, [^3J(FF) = 19.5 Hz]), −164.2 (m, 2F, *m*-F), −116.2 (m, 2F, *o*-F), −160.4 (t, 1F, *p*-F, [^3J(FF) = 20.3 Hz]) and −164.7 (m, 2F, *m*-F).

*[N(PPh$_3$)$_2$][{Au(C$_6$F$_5$)$_3$(PPh$_2$CHPPh$_2$)Au(C$_6$F$_5$)}$_2$Au] (**14**)*

A dichloromethane solution of [Au(C_6F_5)$_3$(PPh$_2$CH$_2$PPh$_2$)Au(C_6F_5)] (0.144 g, 0.1 mmol) was treated with [N(PPh$_3$)$_2$][Au(acac)$_2$] [5, 24] (0.032 g, 0.05 mmol) and the solution turned rapidly yellow, which disappeared after 2 h of reaction. A little amount of solid was filtered over celite and the solution was concentrated in a vacuum. 20 ml of hexane was added to precipitate complex **14** as a white solid. Yield: 64%. m.p.: 86. -$C_{134}H_{72}Au_5F_{40}NP_6$ (3626.33), calcd. C, 44.4; H, 2.0; N, 0.4; found C, 44.55; H, 1.85; N, 0.35. Λ_m: 113 Ω^{-1} cm^2 mol^{-1}. -^{31}P{^{1}H} NMR: δ 28.0 (m, 2P, Au(I)–*P*Ph$_2$), 11.3 (m, 2P, Au(III)–*P*Ph$_2$) and 21.7 (s, 2P, [N(*P*Ph$_3$)$_2$]$^+$); -^{1}H NMR: δ 3.54 ("t", 1H, C*H*, [*N* = 9.3 Hz]); -^{19}F NMR: δ −119.1 (m, 8F, *o*-F), −154.3 (t, 4F, *p*-F, [^3J(FF) = 19.3 Hz]), −158.7 (m, 8F, *m*-F), −120.3 (m, 4F, *o*-F), −155.4 (t, 2F, *p*-F, [^3J(FF) = 19.5 Hz]), −159.6 (m, 4F, *m*-F), −114.9 (m, 4F, *o*-F), −156.5 (t, 2F, *p*-F, [^3J(FF) = 20.0 Hz]) and −161.1 (m, 4F, *m*-F).

*[Au(C$_6$F$_5$){PPh$_2$CH(AuPPh$_3$)PPh$_2$}Au(C$_6$F$_5$)] (**15**)*

A dichloromethane solution of [Au(C_6F_5)(PPh$_2$CH$_2$PPh$_2$)Au(C_6F_5)] (0.112 g, 0.1 mmol) was treated with [Au(acac)(PPh$_3$)] (0.055 g, 0.1 mmol). The mixture was stirred for 1 h and a little amount of solid was filtered over celite. The solvent was then evaporated to *ca.* 5 ml and hexane was added to precipitate complex **15** as a white solid. Yield: 68%. m.p.:

130 (dec). -$C_{55}H_{36}Au_3F_{10}P_3$ (1570.61), calcd. C, 42.05; H, 2.3; found C, 41.1; H, 2.7. Λ_m: $4\,\Omega^{-1}\,cm^2\,mol^{-1}$. -$^{31}P\{^1H\}$NMR: δ 40.8 (t, 1P, *P*Ph$_3$, [^3J(PP) = 14.5 Hz]) and 36.8 (d, 2P, Au(I)–*P*Ph$_2$); -^{1}H NMR: δ 3.9 (td, 1H, C*H*, [^2J(HP) = 14.4, ^3J(HP) = 7.1 Hz]); -^{19}F NMR: $\delta - 115.3$ (m, 4F, *o*-F), -160.8 (t, 2F, *p*-F, [^3J(FF) = 19.6 Hz]) and -164.2 (m, 4F, *m*-F).

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