Coordination Compounds of Coinage Metals with Vinylidenebis(diphenylphosphane) and Its Disulfide and Their Reactivity towards Nucleophiles☆

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Vinylidenebis(diphenylphosphane) reacts with gold(I) or gold(III) compounds to give dinuclear $\{[\{Au(C_6F_5)\}_2\{(PPh_2)_2C{=}CH_2\}]$ or $[Au\{PPh_2C({=}CH_2)Ph_2P\}]_2(ClO_4)_2\}$ or mononuclear complexes $\{[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}]\}$, respectively. The latter reacts with gold(I) or silver(I) compounds to afford dinuclear $\{[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}AuX]$, X = Cl or $C_6F_5\}$ or trinuclear species $\{[\{Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}\}_2M]ClO_4$, M = Au or Ag}. No addition of nucleophiles to the C=C double bond is observed in these complexes, which contain the diphosphane acting as bridging or monodentate ligand. $(SPPh_2)_2C{=}CH_2$ reacts with $AgClO_4$ to give $[Ag\{SPPh_2C({=}CH_2)Ph_2PS\}]_2(ClO_4)_2$ or $[Ag\{PPh_2C({=}CH_2)Ph_2P\}_2]ClO_4$. The crystal structure of $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}Au(C_6F_5)]$ has been established by X-ray crystallography, and confirms the expected square planar and linear geometry for the Au^{III} and Au^{I} centres, respectively.

The coordination chemistry of vinylidenebis(diphenylphosphane) (vdpp) to various transition metals has been studied over the last decade, and complexes such as $[Fe(CO)_3(vdpp)]$,[1] $[M(CO)_4(vdpp)]$ (M = Cr, Mo, W),[2] $[MX_2(vdpp)]$ (M = Pt, X = Me, Cl, I; M = Pd, X = $MeCO_2$, Cl, I),[3] $[PtMe_3I(vdpp)]$,[3a] or $[Pt(vdpp)_2](BF_4)_2$,[4] containing the phosphane as a chelating ligand, are usually obtained.

Before our investigations only two gold derivatives, $[AuCl(vdpp)]_2$ and $[(AuCl)_2(vdpp)]$, which display the ligand acting as a bridge between two gold centres, had been described.[5] We have recently published the synthesis and reactivity of $[Au(C_6F_5)_2Cl\{PPh_2C({=}CH_2)Ph_2P\}]$, which is the first monodentate complex of this phosphane.[6]

The presence of a carbon–carbon double bond in vinylidenebis(diphenylphosphane) has aroused interest in the study of its addition reactions. Thus, it has been shown that the addition of various phosphanes, arsines, alcohols, thiols or amines is only possible in presence of a strong base, such as K*t*BuO,[7] or when the C=C bond is activated through the quaternization of both phosphorus atoms by reaction with MeX (X = I, SOF_3).[5][8]

An alternative method of activating the C=C bond towards species HNu is the coordination of metallic centres to form chelate complexes,[2a][3][4][9] whereby the metal, its oxidation state and its substituents can all have a major influence. The reversible addition of MeOH to the carbon–carbon double bonds in $[AuCl(vdpp)]_2$ is the only reported case in which a facile addition of HNu to a bridging vinylidenebis(diphenylphosphane) unit is described.[5]

In the course of our investigations we have observed that the unprecedented addition of a nucleophile (Nu^-) to the C_β atom of the C=C bond in $[Au(C_6F_5)_2Cl\{PPh_2C({=}CH_2)Ph_2P\}]$[6] or $[Au(C_6F_5)_2\{(SPPh_2)_2C{=}CH_2)\}]ClO_4$[10] gives rise to stable intermediates in Michael-type additions. In all these complexes, the P–C–P fragment of the original phosphane is part of a metallacycle, so the chelation of the ligand seems to favour the nucleophilic attack and the stabilization of these species.

In order to investigate if a similar process could take place with non-chelated complexes, we have synthesized gold and silver derivatives containing vdpp in its less common coordination modes (as monodentate or bridging ligand) and have studied the reactivity of some of them towards nucleophiles Nu^-.

Results and Discussion

Vinylidenebis(diphenylphosphane) (**1**) reacts with the gold(I) species $[Au(tht)_2]ClO_4$ (tht = tetrahydrothiophene) or $[Au(C_6F_5)(tht)]$ in a 1:1 or 1:2 molar ratio, leading to $[Au\{PPh_2C({=}CH_2)Ph_2P\}]_2(ClO_4)_2$ (**2**) or $[\{Au(C_6F_5)\}_2\{(PPh_2)C{=}CH_2\}]$ (**3**), respectively, by displacement of the sulfur donor ligand. Complexes **2** and **3** contain the diphos-

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phane as a bridging ligand, similarly to the gold derivatives of vdpp previously described.[5] They are air- and moisture-stable white solids, soluble in most common organic solvents except diethyl ether (**2**) and hexane (**2** and **3**). Complex **2** behaves as a 1:1 electrolyte, whereas **3** is non-conducting in acetone solutions.

In their $^{31}P\{^1H\}$-NMR spectra a singlet corresponding to the equivalent phosphorus atoms is observed (see Experimental Section). In the ^1H-NMR spectrum of **3** the signal of the CH_2 group appears as a pseudotriplet (AA'XX' system), indicating a similar value for both $J(HP_{cis})$ and $J(HP_{trans})$, whereas the ^1H-NMR spectrum of complex **2** shows a pseudoquintuplet (AA'A''A'''XX'X''X''' system), which could arise from a virtual coupling with the four phosphorus of the ring.

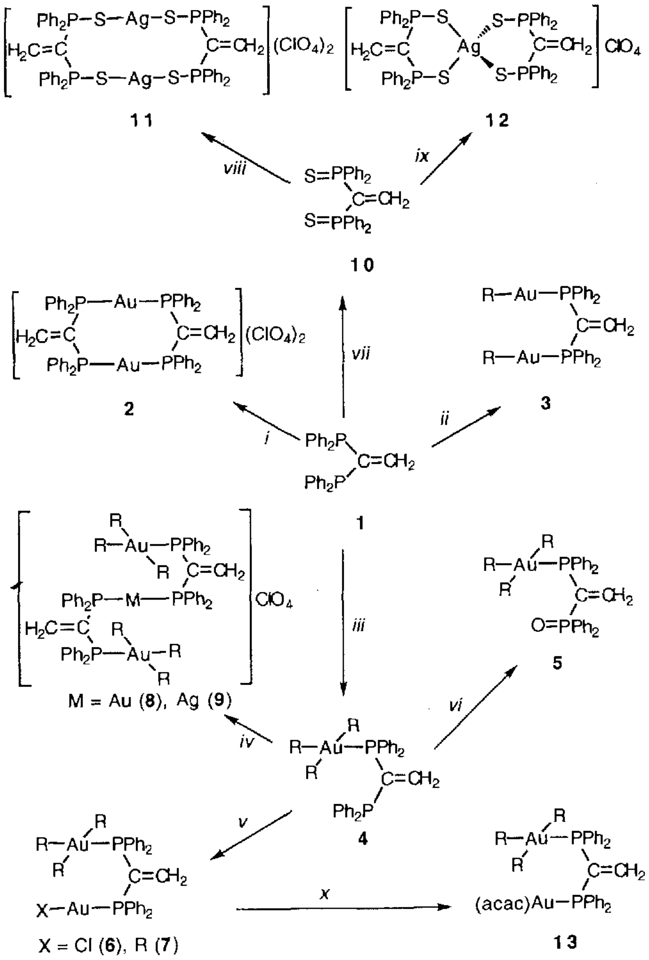
When the gold(III) complex $[Au(C_6F_5)_3(tht)]$ is treated with $(PPh_2)_2C{=}CH_2$ the mononuclear derivative $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}]$ (**4**) is obtained irrespective of the molar ratio of the starting materials. Thus, while with gold(I) the ligand is always bridging, in gold(III) products it is monodenate, as demonstrated by the $^{31}P\{^1H\}$-NMR spectrum of **4**, which displays two doublets at δ = 25.5 and −8.8 [$J(PP)$ = 72.2 Hz], corresponding to the coordinated and the free phosphorus, respectively. Furthermore, in its ^1H-NMR spectrum the resonance of each inequivalent methylenic proton appears as a doublet of doublets, due to the coupling with both inequivalent phosphorus. In its ^{19}F-NMR spectrum the characteristic pattern of $Au(C_6F_5)_3$ groups is observed.[11]

The free phosphorus atom of complex **4** can be oxidized with hydrogen peroxide, leading to $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P{=}O\}]$ (**5**), which features similar properties to those observed for **4**. There are two main differences: the presence of a ν(P=O) stretching band at 1203 cm^{-1} in its IR spectrum and the displacement to lower field of the resonances from the non-coordinated phosphorus (δ = 31.2) and the proton *trans* to it.

In order to prepare complexes in which vinylidenebis(diphenylphosphane) acts as a bridge between gold(III) and a second metallic centre, we treated **4** with equimolecular amounts of $[AuX(tht)]$ to give the neutral dinuclear $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}AuX]$ [X = Cl (**6**), C_6F_5 (**7**)], or with $[Au(tht)_2]ClO_4$ or $AgClO_4$ in a 2:1 molar ratio, to afford the cationic trinuclear derivatives $[\{Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}\}_2M]ClO_4$ [M = Au (**8**), Ag (**9**)] (Scheme 1).

In contrast to the behaviour of gold(I) with vdpp, which always leads to dinuclear complexes with bridging diphosphane, the treatment of its disulfide (**10**) with $AgClO_4$ leads to two different products, $[Ag(S_2vdpp)]_2(ClO_4)_2$ (**11**) or $[Ag(S_2vdpp)_2]ClO_4$ (**12**), depending on the molar ratio of the starting products (see Scheme 1). **11** and **12** are white solids soluble in chlorinated solvents and insoluble in diethyl ether and hexane. They behave as 1:2 or 1:1 electrolytes, respectively.

Scheme 1. R = C_6F_5; i) + $[Au(tht)_2]^+$; ii) + 2 $[Au(C_6F_5)(tht)]$; iii) + $[Au(C_6F_5)_3(tht)]$; iv) + 1/2 $[Au(tht)_2]^+$ or + 1/2 $AgClO_4$; v) + $[AuX(tht)]$; vi) + H_2O_2; vii) + 1/4 S_8; viii) + $AgClO_4$; ix) + 1/2 $AgClO_4$; x) + Tl(acac).



We have recently described the reactivity of $[Au(C_6F_5)_2\{(SPPh_2)_2C{=}CH_2)\}]ClO_4$ and $[Au(C_6F_5)_2Cl\{PPh_2C({=}CH_2)Ph_2P\}]$, where the ligand acts or can potentially act as a chelate after reaction with a nucleophile, giving methanide-type complexes featuring a six- or a four-membered ring, respectively.[6][10] In view of these results, we focussed our interest on the study of the reactions of similar nucleophiles (e.g. acetylacetonate, ethoxide, dithiocarbamates, or cyclopentadienyl) with vdpp derivatives in which such potential ring formation is avoided. When the cationic complex $[Au\{PPh_2C({=}CH_2)Ph_2P\}]_2(ClO_4)_2$ (**2**) is employed signs of reaction are observed, but, unfortunately, we could not isolate any pure compound. Moreover, with neutral complexes such as $[\{Au(C_6F_5)\}_2\{(PPh_2)_2C{=}CH_2\}]$ (**3**) or $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}Au(C_6F_5)]$ (**7**) or with the free ligand, no reaction takes place and the starting materials are recovered. Finally, when chloro derivatives are used, substitution reactions occur instead of nucleophilic additions to the carbon−carbon double bond. This reactions are incomplete with [AuCl(vdpp)] or $[(AuCl)_2(vdpp)]$, while when $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}AuCl]$ (**6**) is treated with equimolecular ammounts of Tl(acac), TlCl precipitates, giving rise to the formation of $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}Au(acac)]$ (**13**).

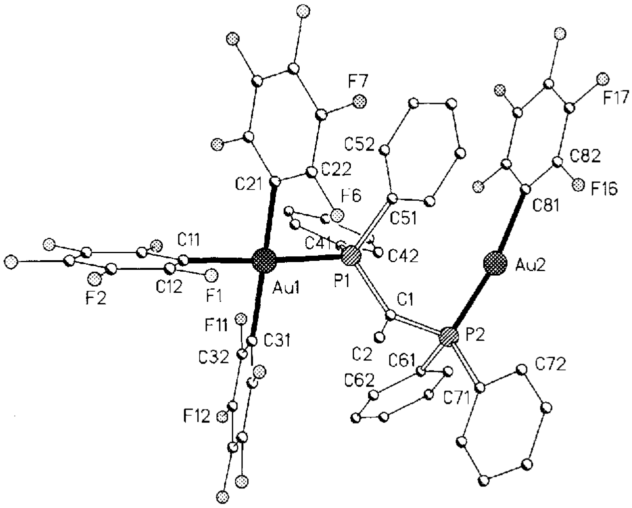
Complex **13** is obtained as a white solid and has been characterized by elemental analysis and the usual spectroscopic techniques. Its IR spectrum shows two broad signals at $\tilde{\nu}$ = 1664 and 1636 cm^{-1}, confirming the presence of the acetylacetonate ligand coordinated through the C^3 carbon atom.[12] Moreover, in its ^1H-NMR spectrum the resonances corresponding to this ligand also appear.

Thus addition of nucleophiles only occurs if complexes with the chelated ligand are used or can be obtained, while with the free phosphane or species containing monodentate or bridging ligands the reaction either does not proceed satisfactorily or only substitution products are isolated.

Crystal Structure Determination of Complex 7

The molecular structure of complex **7** is shown in Figure 1. It crystallizes as an *n*-hexane hemisolvate; the solvent displays crystallographic inversion symmetry.

Figure 1. The structure of compound **7** in the crystal; radii are arbitrary; H atoms and solvent omitted[a]



[a] Selected bond lengths [Å] and angles [°]: Au(1)−C(21) 2.051(6), Au(1)−C(11) 2.059(6), Au(1)−C(31) 2.071(7), Au(1)−P(1) 2.382(2), Au(2)−C(81) 2.054(7), Au(2)−P(2) 2.270(2), P(1)−C(1) 1.825(6), P(2)−C(1) 1.834(6), C(1)−C(2) 1.316(9); C(21)−Au(1)−C(11) 88.1(2), C(21)−Au(1)−C(31) 173.9(2), C(11)−Au(1)−C(31) 87.7(2), C(21)−Au(1)−P(1) 90.5(2), C(11)−Au(1)−P(1) 176.4(2), C(31)−Au(1)−P(1) 94.1(2), C(81)−Au(2)−P(2) 169.0(2), P(1)−C(1)−P(2) 124.8(4).

The molecule of **7** contains two gold atoms with the expected coordination geometries. The gold(III) centre is square planar (maximum deviation from ideal 90 ° angles 4.1 °), whereby Au(1) lies only 0.007(3) Å out of the plane formed by its four bonding partners. The gold(I) centre Au(2) is linear, albeit slightly distorted with C−Au−P 169.0(2) °. The gold atoms are bridged by the diphosphane. There are no interactions between the gold atoms, with an intramolecular distance of 6.157(1) Å and a shortest intermolecular gold(I)−gold(I) distance of 4.268(1) Å. The torsion angles Au(1)−P(1)−C(1)−P(2) and P(1)−C(1)−P(2)−Au(2), which describe the backbone conformation, are 164.30(3) and 42.55(4) °.

The Au−P distances are 2.382(2) Å for the gold(III) and 2.270(2) Å for the gold(I) centre, similar to those found in other (pentafluorophenyl)gold(III) derivatives such as $[\{Au(C_6F_5)_3\{(PPh_2)_2CH\}\}_2Au]$[13] [2.367(2) Å] or -gold(I) species such as $[Au(C_6F_5)(PPh_2CHPPh_2CH_3)]$[14] [2.287(2) Å] or $[Mo(CO)_4\{(PPh_2)_2CHPPh_2\}Au(C_6F_5)]$[15] [2.274(2) Å].

The Au−C bond lengths lie in the range 2.051(6)−2.071(7) Å, with no major difference between gold(III) or gold(I). They also are of the same order to those in related complexes such as $NBu_4[\{Au(C_6F_5)_3\{(PPh_2)_2CH\}\}_2Au]$ [2.057−2.080(8) Å], $[Au(C_6F_5)(PPh_2CHPPh_2CH_3)]$ [2.057(6) Å], or $[Mo(CO)_4\{(PPh_2)_2CHPPh_2\}Au(C_6F_5)]$ [2.051(10) Å].

The longest P−C distances involve the C(1) carbon atom, 1.825(6) and 1.834(6) Å. The C(1)−C(2) bond length is 1.316(9), consistent with the presence of a double bond. The atoms P(1), C(1), C(2), and P(2) are coplanar to within 0.04 Å.

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Experimental Section

General: IR: Range $\tilde{\nu}$ = 4000−200 cm^{-1}, Perkin-Elmer 883, Nujol mulls between polyethylene sheets. − C, H, N, S analysis: Perkin-Elmer 240C microanalyser. − Conductivities: $\Omega^{-1}cm^2mol^{-1}$, ca. 5×10^{-4} M acetone solutions, Jenway 4010 conductimeter. − ^1H, ^{19}F, and ^{31}P NMR: Bruker ARX 300 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). − Mass spectra: VG Autospec, FAB techniques, nitrobenzyl alcohol as matrix. − All experiments were carried out at room temperature. The starting materials $(PPh_2)_2C{=}CH_2$,[16] $(SPPh_2)_2C{=}CH_2$,[17] $[Au(tht)_2]ClO_4$,[18] $[Au(C_6F_5)(tht)]$[19], $[Au(C_6F_5)_3(tht)]$,[20] and $[AuCl(tht)]$[21] were prepared according to the literature.

$[Au\{PPh_2C({=}CH_2)Ph_2P\}]_2(ClO_4)_2$ (**2**): To a dichloromethane solution of ligand **1** (0.079 g, 0.2 mmol) was added $[Au(tht)_2]ClO_4$ (0.095 g, 0.2 mmol). After 1 h of stirring, the solvent was evaporated to ca. 5 ml and diethyl ether was added to give complex **2** as a white solid. Yield 0.137 g (99 %). − $C_{52}H_{44}Au_2Cl_2O_8P_4$ (1385.65): calcd. C 45.05, H 3.2; found C 44.9, H 2.9. − Λ_m: 154. − $^{31}P\{^1H\}$ NMR: δ = 45.3 (s). − ^1H NMR: δ = 6.67 ("q", CH_2, 2 H, *N* = 13.4 Hz). − MS (FAB): *m/z* (%) = 1285 (100) $[M + ClO_4]^+$, 1186 (15) $[M]^+$, 593 (47) $[Au(vdpp)]^+$.

$[\{Au(C_6F_5)\}_2\{(PPh_2)_2C{=}CH_2\}]$ (**3**): To a solution of ligand **1** (0.079 g, 0.2 mmol) in dichloromethane was added $[Au(C_6F_5)(tht)]$ (0.181 g, 0.4 mmol). After stirring the solution for 1 h, the solvent was evaporated to ca. 5 ml and 20 ml of hexane were added to precipitate **3** as a white solid. Yield 0.193 g (86 %). − $C_{38}H_{22}Au_2F_{10}P_2$ (1124.37): calcd. C 40.6, H 2.0; found C 40.7, H 2.35. − Λ_m: 2. − $^{31}P\{^1H\}$ NMR: δ = 41.4 (m). − ^1H NMR: δ = 6.27 ("t", CH_2, 2 H, *N* = 23.7 Hz). − ^{19}F NMR: δ = −116.0 (m, *o*-F, 4 F), −159.1 {t, *p*-F, 2 F [*J*(FF) = 19.9 Hz]}, −163.2 (m, *m*-F, 4 F). − MS (FAB): *m/z* (%) = 1124 (10) $[M]^+$, 957 (100) $[M - C_6F_5]^+$, 593 (32) $[Au(vdpp)]^+$.

$[Au(C_6F_5)_3\{PPh_2C({=}CH_2)Ph_2P\}]$ (**4**): To a solution of **1** (0.079 g, 0.2 mmol) in 20 ml of dichloromethane was added $[Au(C_6F_5)_3(tht)]$ (0.157 g, 0.2 mmol) and the solution was stirred for 1 h. Evaporation of the solvent in vacuo and addition of cold

hexane led to complex **4** as a white solid. Yield 0.184 g (84 %). – $C_{44}H_{22}AuF_{15}P_2$ (1094.42): calcd. C 48.3, H 2.05; found C 48.0, H 2.15. – Λ_m: 1. – $^{31}P\{^1H\}$ NMR: δ = 25.5 {d, $Au^{III}-P-C-P$, 1 P [$^2J(PP)$ = 72.2 Hz]}, –8.8 (d, $Au^{III}-P-C-P$ 1 P). – ^1H NMR: δ = 6.39 {dd, CH_2, 1 H [$^3J(HP_{trans})$ = 26.1, $^3J(HP_{cis})$ = 8.3 Hz]}, 5.90 {dd, CH_2, 1 H [$^3J(HP_{trans})$ = 50.0, $^3J(HP_{cis})$ = 6.0 Hz]}. – ^{19}F NMR: δ = –119.3 (m, *o*-F, 4 F), –157.0 {t, *p*-F, 2 F [$J(FF)$ = 19.9 Hz]}, –160.8 (m, *m*-F, 4 F), –121.8 (m, *o* -F, 2 F), –157.1 {t, *p*-F, 1 F [$J(FF)$ = 20.0 Hz]}, –161.0 (m, *m*-F, 2 F). – MS (FAB): *m/z* (%) = 1095 (7) $[M]^+$, 927 (100) $[M - C_6F_5]^+$, 593 (12) $[Au(vdpp)]^+$.

$[Au(C_6F_5)_3\{PPh_2C(=CH_2)Ph_2P=O\}]$ (**5**): To a solution of **4** (0.219 g, 0.2 mmol) in acetone was added two drops of H_2O_2 (30 % in H_2O). The solution was stirred for 1 h and filtered through a 1-cm layer of anhydrous magnesium sulfate. The solution was concentrated to ca. 5 ml and 20 ml of hexane was added to give complex **5** as a white solid. Yield 0.124 g (56 %). – $C_{44}H_{22}AuF_{15}OP_2$ (1110.56): calcd. C 47.6, H 2.0; found C 47.15, H 1.75. – Λ_m: 10. – $^{31}P\{^1H\}$ NMR: δ = 31.2 {d, $P=O$, 1 P [$^2J(PP)$ = 8.9 Hz]}, 25.6 (m, $Au^{III}-P$, 1 P). – ^1H NMR: δ = 7.50–7.10 [m, Ph + 1 H (CH_2), 21 H], 6.47 {dd, CH_2, 1 H [$^3J(HP_{trans})$ = 48.6, $^3J(HP_{cis})$ = 20.7 Hz]}. – ^{19}F NMR: δ = –119.4 (m, *o*-F, 4 F), –156.8 {t, *p*-F, 2 F [$J(FF)$ = 20.4 Hz]}, –160.6 (m, *m*-F, 4 F), –121.7 (m, *o*-F, 2 F), –156.9 {t, *p*-F, 1 F [$J(FF)$ = 20.8 Hz]}, –160.9 (m, *m*-F, 2 F). – MS (FAB): *m/z* (%) = 942 (33) $[M - C_6F_5]^+$, 776 (20) $[M - 2\ (C_6F_5)]^+$, 609 (100) $[M - 3\ (C_6F_5)]^+$.

$[Au(C_6F_5)_3\{PPh_2C(=CH_2)Ph_2P\}AuCl]$ (**6**): To a dichloromethane solution of **4** (0.219 g, 0.2 mmol) was added [AuCl(tht)] (0.064 g, 0.2 mmol). After 30 min of stirring, the solution was concentrated in vacuo and 20 ml of hexane was added to afford **6** as a white solid. Yield 0.238 g (90 %). – $C_{44}H_{22}Au_2ClF_{15}P_2$ (1326.84): calcd. C 39.85, H 1.65; found C 39.8, H 1.65. – Λ_m: 3. – $^{31}P\{^1H\}$ NMR: δ = 29.1 {d, P-Au^I, 1 P [$^2J(PP)$ = 21.0 Hz]}, 26.8 (m, $Au^{III}-P$, 1 P). – ^1H NMR: δ = 7.79 {dd, CH_2, 1 H [$^3J(HP_{trans})$ = 31.0, $^3J(HP_{cis})$ = 25.9 Hz]}, 6.61 (dd, CH_2, 1 H {$^3J(HP_{trans})$ = 47.9, $^3J(HP_{cis})$ = 18.2 Hz]}. – ^{19}F NMR: δ = –119.9 (m, *o*-F, 4 F), –156.2 {t, *p*-F, 2 F [$J(FF)$ = 19.7 Hz]}, –160.1 (m, *m*-F, 4 F), –121.9 (m, *o*-F, 2 F), –156.5 {t, *p*-F, 1 F [$J(FF)$ = 19.8 Hz]}, –160.7 (m, *m*-F, 2 F). – MS (FAB): *m/z* (%) = 957 (100) $[M - 2\ (C_6F_5), - Cl]^+$, 825 (30) $[M - 3\ (C_6F_5)]^+$, 593 (24) $[Au(vdpp)]^+$.

$[Au(C_6F_5)_3\{PPh_2C(=CH_2)Ph_2P\}Au(C_6F_5)] \cdot 1/2\ C_6H_{14}$ (**7**): A dichloromethane solution of **4** (0.219 g, 0.2 mmol) was treated with $[Au(C_6F_5)(tht)]$ (0.090 g, 0.2 mmol). After 30 min of stirring, the solvent was evaporated to ca. 5 ml and hexane was added to precipitate **7** as a white solid. Yield 0.222 g (74 %). – $C_{53}H_{29}Au_2F_{20}P_2$ (1501.50): calcd. C 42.4, H 1.95; found C 42.35, H 1.65. – Λ_m: 2. – $^{31}P\{^1H\}$ NMR: δ = 40.4 (m, $P-Au^I$, 1 P), 25.7 (m, $Au^{III}-P$, 1 P). – ^1H NMR: δ = 7.65 {"t", CH_2, 1 H [N = 27.2 Hz]}, 6.54 {dd, CH_2, 1 H [$^3J(HP_{trans})$ = 50.0, $^3J(HP_{cis})$ = 16.8 Hz]}. – ^{19}F NMR: δ = –116.5 (m, *o*-F, 2 F), –158.0 {t, *p*-F, 1 F [$J(FF)$ = 20.0 Hz]}, –162.5 (m, *m*-F, 2 F), –119.7 (m, *o*-F, 4 F), –156.3 {t, *p*-F, 2 F [$J(FF)$ = 19.8 Hz]}, –160.3 (m, *m*-F, 4 F), –121.9 (m, *o*-F, 2 F), –156.6 {t, *p*-F, 1 F [$J(FF)$ = 19.9 Hz]}, –160.7 (m, *m*-F, 2 F). – MS (FAB): *m/z* (%) = 1124 (10) $[M - 2\ (C_6F_5)]^+$, 957 (100) $[M - 3\ (C_6F_5)]^+$, 593 (12) $[Au(vdpp)]^+$.

$[\{Au(C_6F_5)_3\{PPh_2C(=CH_2)Ph_2P\}\}_2Au]ClO_4$ (**8**): To a solution of **4** (0.219 g, 0.2 mmol) in 20 ml of dichloromethane was added $[Au(tht)_2]ClO_4$ (0.047 g, 0.1 mmol) and the solution was stirred for 30 min. Evaporation of the solvent to ca. 5 ml and addition of diethyl ether led to the precipitation of **8** as a white solid. Yield 0.186 g (75 %). – $C_{88}H_{44}Au_3ClF_{30}O_4P_4$ (2485.27): calcd. C 42.5, H 1.8; found C 42.35, H 1.9. – Λ_m: 140. – $^{31}P\{^1H\}$ NMR: δ = 49.6 (m, $P-Au^I$, 1 P), 21.7 (m, $Au^{III}-P$, 1 P). – ^1H NMR: δ = 6.15 – 5.80 (m, CH_2, 2 H). – ^{19}F NMR: δ = –118.5 (m, *o*-F, 4 F), –155.1 {t, *p*-F, 2 F [$J(FF)$ = 19.6 Hz]}, –160.4 (m, *m*-F, 4 F) –121.9 (m, *o*-F, 2 F), –155.9 {t, *p*-F, 1 F, [$J(FF)$ = 20.0 Hz]}, –160.4 (m, *m*-F, 2 F). – MS (FAB): *m/z* (%) = 2385 (65) $[M]^+$, 2051 (8) $[M - 2\ (C_6F_5)]^+$, 927 (100) $[Au(C_6F_5)_2(vdpp)]^+$, 593 (12) $[Au(vdpp)]^+$.

$[\{Au(C_6F_5)_3\{PPh_2C(=CH_2)Ph_2P\}\}_2Ag]ClO_4$ (**9**): To a solution of $AgClO_4$ (0.021 g, 0.1 mmol) in 20 ml of diethyl ether was added **4** (0.219 g, 0.2 mmol), whereby a white precipitate was formed. After 1 h of stirring in the dark to complete the precipitation, the solid was filtered off and dried in vacuo. Yield 0.199 g (83 %). – $C_{88}H_{44}AgAu_2ClF_{30}O_4P_4$ (2396.17): calcd. C 44.1, H 1.85; found C 44.5, H 2.05. – Λ_m: 137. – $^{31}P\{^1H\}$ NMR (–50 °C): δ = 20.7 (dm, $P-Ag^I$, 1 P), 21.7 (m, $Au^{III}-P$, 1 P). – ^1H NMR (–50 °C): δ = 5.97–5.83 (m, CH_2, 2 H). – ^{19}F NMR: δ = –118.8 (m, *o*-F, 4 F), –155.8 {t, *p*-F, 2 F [$J(FF)$ = 19.6 Hz]}, –160.5 (m, *m*-F, 4 F), –121.9 (m, *o*-F, 2 F), –156.2 {t, *p*-F, 1 F [$J(FF)$ = 20.0 Hz]}, –160.5 (m, *m*-F, 2 F). – MS (FAB): *m/z* (%) = 2297 (45) $[M]^+$, 927 (100) $[Au(C_6F_5)_2(vdpp)]^+$, 593 (25) $[Au(vdpp)]^+$, 503 (65) $[Ag(vdpp)]^+$.

$[Ag\{SPPh_2C(=CH_2)Ph_2PS\}]_2(ClO_4)_2$ (**11**): To a diethyl ether solution of $AgClO_4$ (0.042 g, 0.2 mmol) was added ligand **10** (0.092 g, 0.2 mmol) and the mixture was stirred for 1 h in the dark. The white solid formed in the reaction was filtered off and dried in vacuo. Yield 0.131 g (98 %). – $C_{52}H_{44}Ag_2Cl_2O_8P_4S_4$ (1335.72): calcd. C 46.75, H 3.3, S 9.6; found C 46.65, H 3.0, S 10.1. – Λ_m: 254. – $^{31}P\{^1H\}$ NMR: δ = 46.5 (s). – ^1H NMR: δ = 6.49 ("t", CH_2, 2 H, N = 33.5 Hz). – MS (FAB): *m/z* (%) = 1235 (15) $[M + ClO_4]^+$, 1136 (10) $[M]^-$, 569 (100) $[Ag(S_2vdpp)]^+$.

$[Ag\{SPPh_2C(=CH_2)Ph_2PS\}_2]ClO_4$ (**12**): To a diethyl ether solution of $AgClO_4$ (0.021 g, 0.1 mmol) was added ligand **10** (0.092 g, 0.2 mmol) and the mixture was stirred for 1 h in the dark.The white solid formed in the reaction was filtered off and dried in vacuo. Yield 0.103 g (91 %). – $C_{52}H_{44}AgClO_4P_4S_4$ (1128.39): calcd. C 55.35, H 3.9, S 11.35; found C 54.9, H 3.5, S 11.2. – Λ_m: 140. – $^{31}P\{^1H\}$ NMR: δ = 44.7 (s). – ^1H NMR: δ = 6.17 ("t", CH_2, 2 H, N = 32.1 Hz). – MS (FAB): *m/z* (%) = 1029 (20) $[M]^+$, 569 (100) $[Ag(S_2vdpp)]^+$.

$[Au(C_6F_5)_3\{PPh_2C(=CH_2)Ph_2P\}Au(acac)]$ (**13**): To a chloroform solution of **6** (0.265 g, 0.2 mmol) was added Tl(acac) (0.061 g, 0.2 mmol) and the mixture was stirred under reflux for 4 h. The TlCl formed was filtered off over celite and the solution was concentrated in vacuo to ca. 5 ml. Addition of hexane led to the precipitation of **13** as a pale yellow solid. Yield 0.153 g (55 %). – $C_{49}H_{29}Au_2F_{15}O_2P_2$ (1390.50): calcd. C 42.3, H 2.1; found C 41.6, H 1.8. – Λ_m: 29. – $^{31}P\{^1H\}$ NMR: δ = 35.4 {d, $P-Au^I$, 1 P [$^2J(PP)$ = 24.5 Hz]}, 25.9 (m, $Au^{III}-P$, 1 P). – ^1H NMR: δ = 7.80 ("t", CH_2, 1 H, N = 25.2 Hz), 6.66 {dd, CH_2, 1 H [$^3J(HP_{trans})$ = 48.0, $^3J(HP_{cis})$ = 17.4 Hz]}, 3.90 {d, CH, 1 H, [$^3J(HP)$ = 11.0 Hz]}, 2.21 (s, CH_3, 6 H). – ^{19}F NMR: δ = –119.8 (m, *o*-F, 4 F), –156.1 {t, *p*-F, 2 F, [$J(FF)$ = 19.8 Hz]}, –160.0 (m, *m*-F, 4 F), –121.9 (m, *o*-F, 2 F), –156.4 {t, *p*-F, 1 F, [$J(FF)$ = 20.3 Hz]}, –160.6 (m, *m*-F, 2 F). – MS (FAB): *m/z* (%) = 1.095 (12) $[M - Au, - (acac)]^+$, 957 (100) $[M - 2\ (C_6F_5), - (acac)]^+$, 889 (25) $[M - 3\ (C_6F_5)]^+$, 593 (75) $[Au(vdpp)]^+$.

Crystal Structure Determination of Complex **7**: Crystals of **7** · 0.5 C_6H_{14} were grown from chloroform/hexane. – Crystal data: $C_{53}H_{29}Au_2F_2OP_2$, M = 1501.63, triclinic, $P\bar{1}$, a = 13.427(2), b = 14.027(2), c = 14.807(2) Å, α = 88.918(14), β = 64.643(10), γ = 76.146(14) °, V = 2435.7(7) Å^3, Z = 2, D_c = 2.047 Mg m^{-3}, $F(000)$ = 1430, μ = 6.2 mm^{-1}, T = –100 °C. – Data collection and reduction: A colourless prism of ca. 0.6 × 0.6 × 0.4 mm was mounted in inert oil on a glass fibre. A total of 8940 intensities were registered using monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å, $2\theta_{max} = 50$ °) on a Siemens P4 diffractometer; 8509 independent reflections ($R_{int} = 0.0259$) were used for all calculations. Cell constants were refined from setting angles of 63 reflections in the range $\theta = 3.8-12.6$ °. An absorption correction based on ψ-scans was applied, with transmission factors 0.619–0.908. – Structure solution and refinement: The structure was solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL-93[21]. H atoms were included using a riding model. The solvent was well-behaved. The final $wR(F^2)$ was 0.0923 for all reflections, with a conventional $R(F)$ of 0.036, for 680 parameters and 685 restraints (to light atom displacement parameters and ring planarity). $S = 1.020$; max $\Delta\rho = 2.073$ eÅ^{-3}. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100447. Copies of the data may be obtained free of charge from: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Telefax: Int. +44 (1223)336033; E-mail: deposit@chemcrys.cam.ac.uk).

☆ Dedicated to Professor *P. Royo* on the occasion of his 60th birthday.

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