

**[Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(PPh<sub>2</sub>H)]: A Precursor for the Synthesis of Gold(III) Phosphide Complexes\*\***

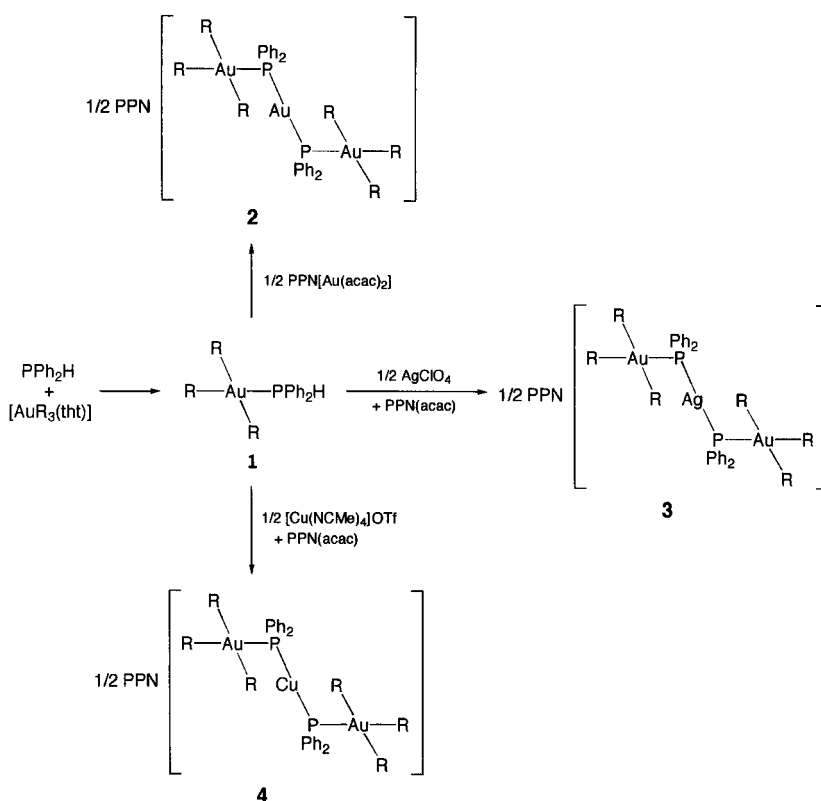
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Although a rich and fascinating chemistry of phosphido-bridged transition metal complexes has recently been developed for metals of Groups 9 and 10,<sup>[1]</sup> the corresponding gold chemistry has experienced little progress since Puddephatt and Thompson prepared [AuPPh<sub>2</sub>]<sub>n</sub> in 1976;<sup>[2]</sup> only a few Au<sup>I</sup> species containing PR<sub>2</sub>H<sup>[3]</sup> or PR<sub>2</sub><sup>-</sup> ligands<sup>[2-4]</sup> are known. The chemistry of Au<sup>III</sup> is even more poorly represented, and only the dinuclear complex [Au<sub>2</sub>Me<sub>4</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>] has been reported.<sup>[2]</sup> Attempts to prepare Au<sup>III</sup> complexes with PPh<sub>2</sub>H have led only to reduction of the Au<sup>III</sup> centers.<sup>[3a]</sup>

We have succeeded in synthesizing a diphenylphosphanylgold(III) complex by exploiting the stabilizing effect of pentafluorophenyl groups. The starting material [Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(tht)] (tht = tetrahydrothiophene) was treated with PPh<sub>2</sub>H, giving [Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(PPh<sub>2</sub>H)] (**1**, Scheme 1). This is the first Au<sup>III</sup> derivative containing a secondary phosphane.

Further reaction of **1** with suitable coinage metal species should furnish hitherto unknown phosphido-bridged Au<sup>III</sup>-M species. As **1** can only be isolated in low yields as an oily material, freshly prepared solutions of **1** were used directly for further reactions. The reaction of PPN[Au(acac)<sub>2</sub>]<sup>[5]</sup> (PPN = [N(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, acac = CH(COCH<sub>3</sub>)<sub>2</sub>) with such a solution (1:2) afforded the first mixed Au<sup>III</sup>-M phosphido-bridged complex, PPN[{Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>Au}] (**2**), which can be easily isolated as a solid in high yield. It behaves as a 1:1 electrolyte in acetone; its <sup>1</sup>H NMR spectrum displays only signals from the aromatic protons.

We wished to synthesize a set of isostructural complexes containing Au<sup>I</sup>, Ag<sup>I</sup>, or Cu<sup>I</sup> centers, whose crystal structures



Scheme 1. Synthesis of phosphane and phosphide derivatives.

would allow a comparison of the covalent radii of these three metals, a subject of recent discussion.<sup>[6]</sup> Reaction of **1** with AgClO<sub>4</sub> or [Cu(NCMe)<sub>4</sub>]TfO (TfO = CF<sub>3</sub>SO<sub>3</sub>) in the presence of PPN(acac) led to PPN[{Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>M}] (M = Ag (**3**), Cu (**4**)). Both are air- and moisture-stable solids whose physical and spectroscopic data are in accordance with the proposed formulation.

Crystals of **2** and **3** suitable for X-ray diffraction studies were obtained from solutions in dichloromethane layered with hexane; unfortunately, we have not been able to obtain good crystals of **4**. Complexes **2** and **3**<sup>[7]</sup> are isotopic and thus allow a comparison of metal-ligand bond lengths (Figure 1).<sup>[6a]</sup> The M<sup>I</sup> atom lies on an inversion center, so its

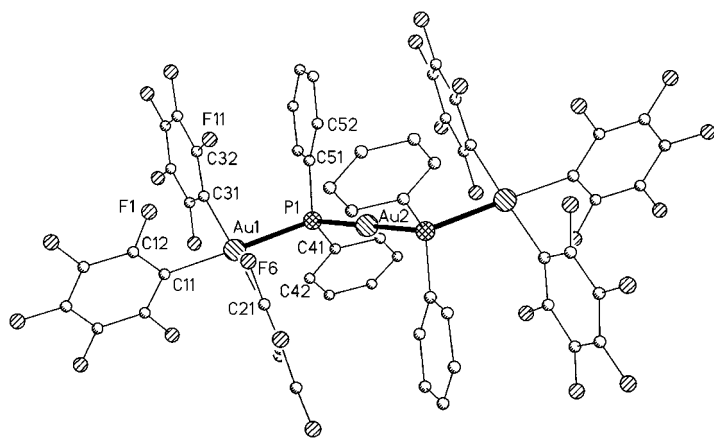


Figure 1. Structure of the inversion-symmetric anion of **2** in the crystal (the radii are arbitrary). Only the asymmetric unit is numbered. Complex **3** is isostructural; the central gold atom is replaced by silver.

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[\*\*] This work was supported by the DGICYT. (PB94-0079), the University of La Rioja (API-98/B09), and the Fonds der Chemischen Industrie.

environment is exactly linear. The bond lengths and angles are almost identical in both structures (Table 1) except for the M<sup>I</sup>–P distance, which is shorter by 0.07 Å in the gold complex. This confirms the results obtained by Schmidbaur et al., who compared the bond lengths in complexes

precipitate PPNClO<sub>4</sub>, which was removed by filtration. The solution was concentrated, and hexane was added to afford **4** as a pale yellow solid (0.121 g, 51 %). <sup>31</sup>P NMR: δ = 21.1 (s, PPN), –7.0 (s, PPh<sub>2</sub>); <sup>1</sup>H NMR: δ = 7.61–7.09 (m, Ph).

Received: June 18, 1998 [Z12007IE]

German version: *Angew. Chem.* **1998**, *110*, 3199–3201

Table 1. Bond lengths [Å] and angles [°] for **2** and **3**.

	<b>2</b> (M = Au)	<b>3</b> (M = Ag)
Au1–C31	2.052(5)	2.052(5)
Au1–C21	2.058(6)	2.068(5)
Au1–C11	2.073(6)	2.078(5)
Au1–P	2.365(2)	2.365(2)
M–P	2.319(2)	2.386(1)
P–C41	1.814(6)	1.804(5)
P–C51	1.818(7)	1.813(5)
C31–Au1–C21	176.4(2)	176.6(2)
C31–Au1–C11	87.6(2)	88.1(2)
C21–Au1–C11	89.5(2)	89.3(2)
C31–Au1–P	92.0(2)	91.9(1)
C21–Au1–P	90.9(2)	90.6(1)
C11–Au1–P	177.7(2)	178.0(1)
P–M–P'	180.0	180.0
C41–P–C51	101.4(3)	101.3(2)
C41–P–Au1	110.6(2)	110.9(2)
C51–P–Au1	110.7(2)	110.8(2)
C41–P–Au1	110.6(2)	110.9(2)
C41–P–M	111.9(2)	113.7(2)
C51–P–M	109.1(2)	108.2(2)
M–P–Au1	112.54(7)	111.48(5)

[(Mes<sub>2</sub>P)<sub>2</sub>M]BF<sub>4</sub> (M = Au, Ag).<sup>[6a]</sup> The Au<sup>I</sup>–P bond distance in **2** is similar to those observed in PPN[Mn(CO)<sub>4</sub>(μ-PPh<sub>2</sub>)Au(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (2.313(2) and 2.322(1) Å),<sup>[4b]</sup> but slightly shorter than those in [(Mn(CO)<sub>4</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>Au)<sub>2</sub>] (2.332(3)–2.341(3) Å).<sup>[4b]</sup> The Au<sup>III</sup> centers display the expected planar coordination, and the Au<sup>III</sup>–C bond lengths of 2.052(5)–2.078(5) Å are similar to those in other tris(pentafluorophenyl)gold(III) derivatives.<sup>[8]</sup> The Au<sup>III</sup>–P bond length of 2.365(2) Å is closely similar to that in NBu<sub>4</sub>-[Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(Ph<sub>2</sub>PCHPh<sub>2</sub>)<sub>2</sub>Au] (2.367(2) Å).<sup>[8a]</sup>

### Experimental Section

**1:** To a solution of [Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(tht)] (0.236 g, 0.3 mmol) in diethyl ether was added PPh<sub>2</sub>H (0.5 mL, 0.3 mmol). After 30 min the solvent was concentrated in vacuo, and cold hexane was added to afford **1** as a white solid (0.098 g, 37 %). <sup>31</sup>P NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, 83 % H<sub>3</sub>PO<sub>4</sub>): δ = –8.4 (s, PPh<sub>2</sub>H); <sup>1</sup>H NMR: δ = 7.57–7.43 (m, 10H; Ph), ≈ 6.8 (d, <sup>1</sup>J(H,P) ≈ 440 Hz, 1H; PPh<sub>2</sub>H).

**2:** To a freshly prepared solution of **1** (0.2 mmol) in dichloromethane was added PPN[Au(acac)<sub>2</sub>] (0.093 g, 0.1 mmol). After the reaction mixture was stirred for 1 h at room temperature, part of the solvent was evaporated, and hexane (20 mL) was added to afford **2** as a white solid (0.225 g, 90 %). <sup>31</sup>P NMR: δ = 30.9 (s, PPh<sub>2</sub>), 21.1 (s, PPN); <sup>1</sup>H NMR: δ = 7.60–7.17 (m, Ph).

**3:** AgClO<sub>4</sub> (0.021 g, 0.1 mmol) and PPN(acac) (0.127 g, 0.2 mmol) were added to a solution of **1** (0.2 mmol) in diethyl ether. After 1 h a white precipitate (PPNClO<sub>4</sub>) was removed by filtration, the solution was concentrated, and hexane was added to precipitate **3** as a white solid (0.159 g, 66 %). <sup>31</sup>P NMR: δ = 21.1 (s, PPN), 4.5 (dd, <sup>1</sup>J(P,<sup>109</sup>Ag) = 512.5, <sup>1</sup>J(P,<sup>107</sup>Ag) = 446.3 Hz; PPh<sub>2</sub>); <sup>1</sup>H NMR: δ = 7.63–7.14 (m, Ph).

**4:** [Cu(NCMe)<sub>2</sub>]TfO (0.038 g, 0.1 mmol) and PPN(acac) (0.127 g, 0.2 mmol) were added to a solution of **1** (0.2 mmol) in dichloromethane. After 1 h the solvent was evaporated, and diethyl ether was added to

**Keywords:** copper • gold • P ligands • silver

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- Structure analysis of **2**: C<sub>96</sub>H<sub>50</sub>Au<sub>3</sub>F<sub>30</sub>NP<sub>4</sub>, rectangular block 0.25 × 0.22 × 0.20 mm<sup>3</sup>, monoclinic, C2/c, a = 28.174(3), b = 11.0751(9), c = 30.202(3) Å, β = 113.757(8)°, V = 8625.5(14) Å<sup>3</sup>, Z = 4, λ(MoKα) = 0.71073 Å, μ = 5.28 mm<sup>-1</sup>, ρ<sub>calcd</sub> = 1.927 Mg m<sup>-3</sup>, T = –100 °C. Of 9917 reflections collected to 2θ = 50°, 7559 were unique and used for all calculations. Absorption corrections were carried out by ψ scans with transmissions of 0.72–0.98. The structure was solved with Patterson methods, and refined anisotropically on F<sup>2</sup> (program SHELXL-93, G. M. Sheldrick, Universität Göttingen) with 580 restraints to U components of light atoms and local ring symmetry. Hydrogen atoms were included with a riding model. Final values: wR2 = 0.051, R1 = 0.036 for 606 parameters; S = 0.79, Δρ = 0.89 e Å<sup>-3</sup>. Structure analysis of **3**: C<sub>96</sub>H<sub>50</sub>AgAu<sub>2</sub>F<sub>30</sub>NP<sub>4</sub>, prism 0.5 × 0.4 × 0.4 mm<sup>3</sup>, monoclinic, C2/c, a = 28.145(3), b = 11.064(1), c = 30.316(4) Å, β = 114.08(8)°, V = 8619(2) Å<sup>3</sup>, Z = 4, μ = 3.81 mm<sup>-1</sup>, ρ<sub>calcd</sub> = 1.860 Mg m<sup>-3</sup>, T = –100 °C. Of 10198 reflections collected to 2θ = 50°, 7514 were unique; transmissions of 0.57–0.76. Final values: wR2 = 0.055, R1 = 0.033; S = 0.85, Δρ = 1.00 e Å<sup>-3</sup>. The structure was solved and refined as for **2**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101732 (**2**) and CCDC-101733 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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