$[Au(C_6F_5)_3(PPh_2H)]$: A Precursor for the Synthesis of Gold(III) Phosphide Complexes**

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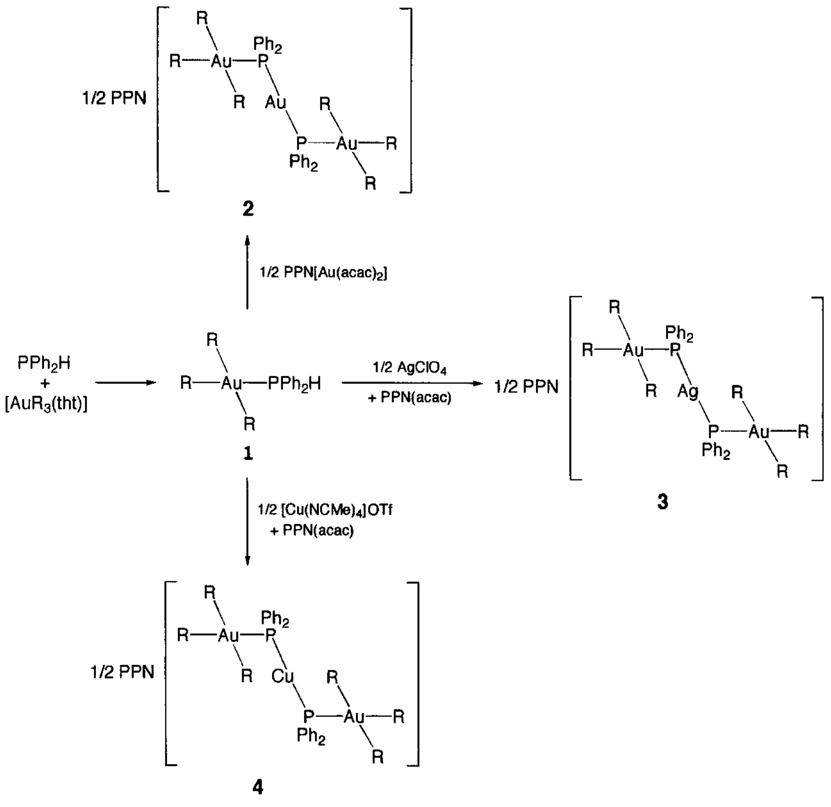
Although a rich and fascinating chemistry of phosphido-bridged transition metal complexes has recently been developed for metals of Groups 9 and 10,[1] the corresponding gold chemistry has experienced little progress since Puddephatt and Thompson prepared $[AuPPh_2]_n$ in 1976;[2] only a few Au^I species containing PR_2H[3] or PR_2^- ligands[2–4] are known. The chemistry of Au^{III} is even more poorly represented, and only the dinuclear complex $[Au_2Me_4(\mu\text{-}PPh_2)_2]$ has been reported.[2] Attempts to prepare Au^{III} complexes with PPh_2H have led only to reduction of the Au^{III} centers.[3a]

We have succeeded in synthesizing a diphenylphosphanylgold(III) complex by exploiting the stabilizing effect of pentafluorophenyl groups. The starting material $[Au(C_6F_5)_3(tht)]$ (tht = tetrahydrothiophene) was treated with PPh_2H, giving $[Au(C_6F_5)_3(PPh_2H)]$ (**1**, Scheme 1). This is the first Au^{III} derivative containing a secondary phosphane.



Scheme 1. Synthesis of phosphane and phosphide derivatives.

Further reaction of **1** with suitable coinage metal species should furnish hitherto unknown phosphido-bridged Au^{III}–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 $PPN[Au(acac)_2]$[5] ($PPN = [N(PPh_3)_2]^+$, acac = $CH(COCH_3)_2$) with such a solution (1:2) afforded the first mixed Au^{III}–M phosphido-bridged complex, $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Au]$ (**2**), which can be easily isolated as a solid in high yield. It behaves as a 1:1 electrolyte in acetone; its ^1H NMR spectrum displays only signals from the aromatic protons.

We wished to synthesize a set of isostructural complexes containing Au^I, Ag^I, or Cu^I centers, whose crystal structures would allow a comparison of the covalent radii of these three metals, a subject of recent discussion.[6] Reaction of **1** with $AgClO_4$ or $[Cu(NCMe)_4]TfO$ ($TfO = CF_3SO_3$) in the presence of PPN(acac) led to $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2M]$ (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**[7] are isotypic and thus allow a comparison of metal–ligand bond lengths (Figure 1).[6a] The M^I atom lies on an inversion center, so its

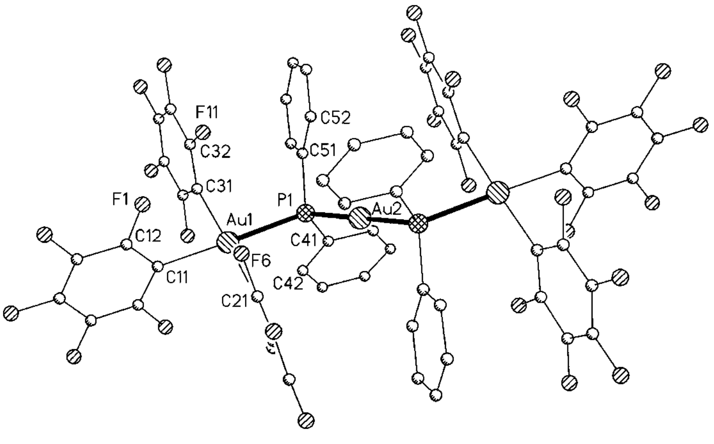


Figure 1. Structure of the inversion-symmetric anion of **2** in the crystal (the radii are arbitrary). Only the asymmetric unit is numbered. Complex **3** is isostructural; the central gold atom is replaced by silver.

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environment is exactly linear. The bond lengths and angles are almost identical in both structures (Table 1) except for the M^I-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 $[(Mes_3P)_2M]BF_4$ (M = Au, Ag).[6a] The Au^I-P bond distance in **2** is similar to those observed in PPN[Mn(CO)$_4${(μ-PPh$_2$)Au(C$_6$F$_5$)}$_2$] (2.313(2) and 2.322(1) Å),[4b] but slightly shorter than those in [{Mn(CO)$_4$(μ-PPh$_2$)$_2$Au}$_2$] (2.332(3)–2.341(3) Å).[4b] The Au^{III} centers display the expected planar coordination, and the $Au^{III}-C$ bond lengths of 2.052(5)–2.078(5) Å are similar to those in other tris(pentafluorophenyl)gold(III) derivatives.[8] The $Au^{III}-P$ bond length of 2.365(2) Å is closely similar to that in NBu$_4$-[{Au(C$_6$F$_5$)$_3$(Ph$_2$PCHPPh$_2$)}$_2$Au] (2.367(2) Å).[8a]

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

	2 (M = Au)	**3** (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)

Experimental Section

1: To a solution of [Au(C$_6$F$_5$)$_3$(tht)] (0.236 g, 0.3 mmol) in diethyl ether was added PPh$_2$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%). ^{31}P NMR (300 MHz, CDCl$_3$, 25 °C, 83% H$_3$PO$_4$): $\delta = -8.4$ (s, PPh$_2$H); ^{1}H NMR: $\delta = 7.57-7.43$ (m, 10H; Ph), ≈6.8 (d, ^1J(H,P) ≈ 440 Hz, 1H; PPh$_2$H).

2: To a freshly prepared solution of **1** (0.2 mmol) in dichloromethane was added PPN[Au(acac)$_2$] (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%). ^{31}P NMR: $\delta = 30.9$ (s, PPh$_2$), 21.1 (s, PPN); ^{1}H NMR: $\delta = 7.60-7.17$ (m, Ph).

3: AgClO$_4$ (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$_4$) was removed by filtration, the solution was concentrated, and hexane was added to precipitate **3** as a white solid (0.159 g, 66%). ^{31}P NMR: $\delta = 21.1$ (s, PPN), 4.5 (dd, ^1J(P,^{109}Ag) = 512.5, ^1J(P,^{107}Ag) = 446.3 Hz; PPh$_2$); ^{1}H NMR: $\delta = 7.63-7.14$ (m, Ph).

4: [Cu(NCMe)$_4$]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 precipitate PPNClO$_4$, 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%). ^{31}P NMR: $\delta = 21.1$ (s, PPN), -7.0 (s, PPh$_2$); ^{1}H NMR: $\delta = 7.61-7.09$ (m, Ph).

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[7] Structure analysis of **2**: C$_{96}$H$_{50}$Au$_3$F$_{30}$NP$_4$, rectangular block 0.25 × 0.22 × 0.20 mm^3, monoclinic, *C2/c*, $a = 28.174(3)$, $b = 11.0751(9)$, $c = 30.202(3)$ Å, $\beta = 113.757(8)°$, $V = 8625.5(14)$ Å^3, $Z = 4$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 5.28$ mm^{-1}, $\rho_{calcd} = 1.927$ Mg m^{-3}, $T = -100$ °C. Of 9917 reflections collected to $2\theta = 50°$, 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^2 (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; $S = 0.79$, $\Delta\rho$ 0.89 e Å^{-3}. Structure analysis of **3**: C$_{96}$H$_{50}$AgAu$_2$F$_{30}$NP$_4$, prism 0.5 × 0.4 × 0.4 mm^3, monoclinic, C2/c, $a = 28.145(3)$, $b = 11.064(1)$, $c = 30.316(4)$ Å, $\beta = 114.08(8)°$, $V = 8619(2)$ Å^3, $Z = 4$, $\mu = 3.81$ mm^{-1}, $\rho_{calcd} = 1.860$ Mg m^{-3}, $T = -100$ °C. Of 10198 reflections collected to $2\theta = 50°$, 7514 were unique; transmissions of 0.57–0.76. Final values: $wR2 = 0.055$, $R1 = 0.033$; $S = 0.85$, $\Delta\rho$ 1.00 e Å^{-3}. 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 CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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