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(Diphenylphosphine)-, (Diphenylphosphido)-, and (Diphenylphosphinito)gold(I) Complexes. Crystal Structure of $[(PPh_3)_2N][Au\{P(O)Ph_2\}_2]$

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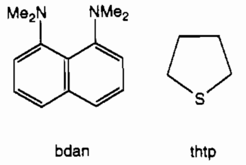
$[AuX(thtp)]$ (thtp = tetrahydrothiophene) reacts with PPh_2H 1:1 to give $[AuX(PPh_2H)]$ (X = Cl (**1**) or Br (**2**)) or 1:2, in the presence of excess of $NaClO_4{\cdot}H_2O$, to give $[Au(PPh_2H)_2]ClO_4$ (**3**). A new high yield synthesis of the polymer $[AuPPh_2]_n$ is reported by addition of concentrated aqueous ammonia to the solution obtained from a 1:1 mixture of $[AuCl(thtp)]$ and PPh_2H in dichloromethane. $Q[AuX_2]$ reacts with $[AuPPh_2]_n$ (1:1) to give $Q[(AuX)_2(\mu\text{-}PPh_2)]$ ($Q = (PPh_3)_2N$ = bis(triphenylphosphoranyliden)ammonium, X = Cl (**4a**), Br (**5a**), I (**6**); $Q = Bu_4N$, X = Br (**5b**)). $[AuCl(thtp)]$ reacts with PPh_2H and Proton Sponge (bdan = 1,8-bis(dimethylamino)naphthalene) (2:1:1) to give $[Hbdan][(AuCl)_2(\mu\text{-}PPh_2)]$ (**4b**). $[(PPh_3)_2N][Au(acac)_2]$ (Hacac = acetylacetone) reacts with PPh_2H (1:2) to give, after air oxidation, $[(PPh_3)_2N][Au\{P(O)Ph_2\}_2]$ (**7**). The crystal structure of **7** was determined at 178 °K ($C_{60}H_{50}AuNO_2P_4$, monoclinic, $C2/c$, $a = 17.299(5)$, $b = 12.487(4)$, $c = 22.863(9)$ Å, $\beta = 91.47(3)°$; $Z = 4$). **7** shows exactly linear coordination at the gold atom, which lies on a center of symmetry. The P—Au bond length (2.324(2) Å) is significantly greater than in $Bu_4N[(AuBr)_2(\mu\text{-}PPh_2)]$ and the P=O bond distance (1.499(4) Å) is similar to typical values for phosphine oxides.

Introduction

Very few gold(I) complexes with secondary phosphines or phosphides as ligands are known. The associated controversies and synthetic difficulties make this a challenging subject in gold chemistry. Thus, a preliminary communication[1] reported the synthesis and X-ray crystal structure of $Bu_4N[(AuBr)_2(\mu\text{-}PPh_2)]$ and difficulties in isolating $[AuCl(PPh_2H)]$. The corresponding full paper[2] confirmed that $[AuCl(PPh_2H)]$ and $[Au(PPh_2H)_n]^+$ (n = 2–4) could be detected but not isolated and that attempts to repeat the preparation of $[(AuBr)_2(\mu\text{-}PPh_2)]^-$ were unsuccessful. In addition, the authors expressed some doubts about the preparation of the complex $[AuCl(PBu^t{}_2H)]$ by Schmidbaur.[3] However, he immediately reported the synthesis of $[AuCl(PR_2H)]$ (R = 2,4,6-trimethylphenyl, 2-methylphenyl, Bu^t, and cyclohexyl) and the crystal structures of two of them (R = 2-methylphenyl, Bu^t).[4] Polymers of formula $[AuPR_2]_n$ (R = aryl or alkyl groups) have also been reported, but their true nature is still uncertain.[2,5] We describe in this paper simple methods to prepare all the previously nonisolated PPh_2H and PPh_2^- gold(I) complexes mentioned above and also an easy preparation of $[AuPPh_2]_n$. As far as we are aware no $P(O)R_2^-$ (phosphinito-*P* complexes) gold complexes have been reported.[6] In this paper we describe the synthesis and X-ray crystal structure of the first (phosphinito)-gold(I) complex.

Chart I



Experimental Section

The IR, the Au analyses, conductance measurements, and melting point determinations were carried out as described elsewhere.[7] Some NMR spectra were recorded on a Varian Unity-300. Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ and conductivity measurements in acetone. Chemical shifts are in ppm and referred to TMS [^1H and $^{13}C\{^1H\}$] or H_3PO_4 [$^{31}P\{^1H\}$]. C, H, and N analyses were carried out with a Carlo Erba EA 1108. $[AuCl(thtp)]$ [8] (thtp = tetrahydrothiophene, see Chart I) and $[(PPh_3)_2N][Au(acac)_2]$[9] ($(PPh_3)_2N$ = bis(triphenylphosphoranylidene)ammonium, Hacac = acetylacetone) were prepared as reported. Proton Sponge (bdan, see Chart I) and $[(PPh_3)_2N]Cl$ were from commercial sources (Aldrich) and used without further purification.

$[(PPh_3)_2N][AuCl_2]$ was prepared by reacting $[AuCl(thtp)]$ (1.115 g, 3.47 mmol) with $[(PPh_3)_2N]Cl$ (1.997 g, 3.47 mmol) in 10 cm^3 of dichloromethane. After 45 min at room temperature the solution was concentrated (2 cm^3) and diethyl ether (20 cm^3) added to give crystalline $[(PPh_3)_2N][AuCl_2]$ (2.68 g, 96%). Anal. Calcd for $C_{36}H_{30}AuCl_2NP_2$: C, 53.62; H, 3.75; N, 1.74. Found: C, 53.91; H, 4.05; N, 1.93. Mp 210 °C. ν(AuCl) 350 cm^{-1} (vs).

$[AuX(PPh_2H)]$ (X = Cl (1), Br (2)). To a suspension of $[AuCl(thtp)]$ (368 mg, 1.15 mmol) in dichloromethane (2 cm^3) was added PPh_2H (0.2 cm^3, 1.15 mmol) under nitrogen. The resulting solution was stirred for 15 min and *n*-hexane (30 cm^3) added to precipitate a solid which was washed repeatedly with *n*-hexane (3 × 20 cm^3) to remove tetrahydrothiophene and then recrystallized from diethyl ether/*n*-hexane to give

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1 (325 mg, 68%). Anal. Calcd for $C_{12}H_{11}AuClP$: C, 34.43; H, 2.65; Au, 47.05. Found: C, 34.63; H, 2.39; Au, 46.25. Mp 102 °C. Λ_M = 2 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (3 × 10^{-4} mol·L^{-1}). ν(PH) 2.335 (w) cm^{-1}. ν(AuCl) 320 cm^{-1}. ^{1}H NMR: 7.00 (d, 1H, $HPPh_2$, $^1J_{PH}$ = 389 Hz), 6.90–7.76 (m, 10H, Ph) ppm. $^{31}P\{^1H\}$: 1.5 (s) ppm.

Starting from [AuBr(thtp)] (188 mg, 0.51 mmol), and following the above procedure, **2** can be obtained (160 mg, 67% yield). Mp 112 °C. Λ_M = 0 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (9 × 10^{-4} mol·L^{-1}). NMR and IR data are identical to those reported.[2]

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great caution.

$[Au(PPh_2H)_2]ClO_4$ (3). To a suspension of [AuCl(thtp)] (460 mg, 1.43 mmol) in acetone (5 cm^3) $NaClO_4\cdot 2H_2O$ (220 mg, 1.57 mmol) and PPh_2H (0.5 cm^3, 2.87 mmol) were successively added under nitrogen giving a solution from which a new precipitate appeared within a few minutes. The suspension was stirred for 30 min, the solvent evaporated to dryness, and the residue extracted with dichloromethane and filtered through anhydrous $MgSO_4$. The solution was concentrated (2 cm^3), diethyl ether (15 cm^3) added, and the white solid obtained recrystallized from dichloromethane/Et_2O to give **3** (785 mg, 82%). Anal. Calcd for $C_{24}H_{22}AuClO_4P_2$: C, 43.10; H, 3.31; Au, 29.45. Found: C, 42.93; H, 3.53; Au, 28.47. Mp 79 °C. Λ_M = 103 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (4 × 10^{-4} mol·L^{-1}). ν(PH) 2335 cm^{-1}. ^{1}H NMR: 7.45 (d, 2H, PPh_2H, $^1J_{PH}$ = 408 Hz), 7.20–7.62 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$: 10.46 (s) ppm.

A New Synthesis of $[AuPPh_2]_n$. To a solution of [AuCl(thtp)] (921 mg, 2.87 mmol) in dichloromethane (10 mL), PPh_2H (0.5 mL, 2.87 mmol) was added under a nitrogen atmosphere. The resulting solution was stirred at room temperature for 30 min and then aqueous ammonia (0.2 mL, 3.14 mmol) was added. The resulting suspension was filtered off and the residue washed with water (2 × 5 mL), acetone (5 mL), and diethyl ether (5 mL) to give $[AuPPh_2]_n$ (890 mg, 81%) as a pale yellow solid. Anal. Calcd for $C_{12}H_{10}AuP$: C, 37.71; H, 2.64; Au, 51.54. Found: C, 37.89; H, 2.82; Au, 51.21. Mp 265 °C (dec).

$[(PPh_3)_2N][(AuX)_2(\mu\text{-}PPh_2)]$ (X = Cl (4a), Br (5a), I (6)). To a solution of $[(PPh_3)_2N][AuCl_2]$ (123 mg, 0.152 mmol) in dichloromethane (20 mL) $[AuPPh_2]_n$ (58.2 mg, 0.152 mL) was added. This polymer immediately dissolved and the resulting solution was stirred at room temperature for 12 h. It was filtered over Celite, the solvent evaporated (1 mL) and diethyl ether (20 mL) added to precipitate **4a** as a white solid, which was recrystallized from acetone/diethyl ether (152 mg, 84%). Following the same procedure **5a** and **6** were obtained from the corresponding $[(PPh_3)_2N][AuX_2]$ complexes. In these cases the reactions are slower and take some 4 h to dissolve $[AuPPh_2]_n$. **4a**: Anal. Calcd for $C_{48}H_{40}Au_2Cl_2NP_3$: C, 48.50; H, 3.39; N: 1.18; Au, 33.14. Found: C, 48.27; H, 3.87; N: 1.26; Au, 32.88. Mp 189 °C. Λ_M = 92 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (3 × 10^{-4} mol·L^{-1}). ν(AuCl) 313 cm^{-1}. ^{1}H NMR: 7.1–7.8 (m, PPh_2 + $(PPh_3)_2N$) ppm. $^{31}P\{^1H\}$: 16.58 (s, PPh_2), 19.76 (s, $(PPh_3)_2N$) ppm. **5a** (78% yield). Anal. Calcd for $C_{48}H_{40}Au_2Br_2NP_3$: C, 45.13; H, 3.16; N: 1.10; Au, 30.83. Found: C, 45.23; H, 3.46; N: 1.17; Au, 31.43. Mp 174 (dec) °C. Λ_M = 85 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (3 × 10^{-4} mol·L^{-1}). ν(AuBr) 225, 214 cm^{-1}. ^{1}H NMR: 7.1–7.8 (m, PPh_2 + $(PPh_3)_2N$) ppm. $^{31}P\{^1H\}$: 25.98 (s, PPh_2), 20.93 (s, $(PPh_3)_2N$) ppm. **6** (58% yield). Anal. Calcd for $C_{48}H_{40}Au_2I_2NP_3$: C, 42.03; H, 2.94; N, 1.02; Au, 28.72. Found: C, 42.03; H, 3.14; N, 1.06; Au, 30.00. Mp 182 °C (dec). Λ_M = 79 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (2 × 10^{-4} mol·L^{-1}). ^{1}H NMR: 7.2–7.9 (m, PPh_2 + $(PPh_3)_2N$) ppm. $^{31}P\{^1H\}$: 40.31 (s, PPh_2), 20.96 (s, $(PPh_3)_2N$) ppm.

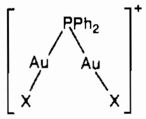
[Hbdan][$(AuCl)_2(\mu\text{-}PPh_2)$] (4b). To a suspension of [AuCl(thtp)] (370 mg, 1.152 mmol) in acetone (10 mL), PPh_2H (0.1 mL, 0.576 mmol) and 1,8-bis(dimethylamino)naphthalene (bdan) (123.4 mg, 0.576 mmol) were successively added under a nitrogen atmosphere. The resulting solution was stirred at room temperature for 1 h, the solvent evaporated under vacuum (2 mL), and diethyl ether (20 mL) added to precipitate crude **4b** as a white solid. It was washed with diethyl ether (2 × 15 mL) to remove tetrahydrothiophene and then treated with a mixture of acetone (2 mL) and diethyl ether (3 mL) and filtered and the filtrate collected over diethyl ether (20 mL) which precipitates pure **4b** (390 mg, 78%). The small amount of substance that remained insoluble in the acetone/diethyl ether mixture (5 mg) was identified as $(AuPPh_2)_n$. From the mother liquor after the precipitation of crude **4b** an additional crop of $(AuPPh_2)_n$ (15 mg) was obtained after evaporation to dryness and stirring the residue with diethyl ether (10 mL). Anal. Calcd for $C_{26}H_{29}Au_2Cl_2N_2P$: C, 36.09; H, 3.38; N, 3.24; Au, 45.52. Found: C, 36.09; H, 3.58; N, 3.23; Au, 45.20. Mp 168 °C. Λ_M = 105 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (7 × 10^{-4} mol·L^{-1}). ν(AuCl) 315 cm^{-1}. ^{1}H NMR: 3.326 (s, 3H, Me), 3.334 (s, 3H, Me), 7.2–7.9 (m, 16H, Hbdan + PPh_2), 11.56 (br s, 1H, Hbdan) ppm. $^{31}P\{^1H\}$: 16.2 (s) ppm.

Table I. Crystallographic Data for $[(PPh_3)_2N][Au\{P(O)Ph_2\}_2]$ (7)

formula	$C_{60}H_{50}AuNO_2P_4$	*Z*	4
M	1137.9	D_x, Mg m^{-3}	1.531
space group	monoclinic, *C*2/*c*	λ(Mo Kα), pm	71.073
a, Å	17.299(5)	μ, mm^{-1}	3.2
b, Å	12.487(4)	*F*(000)	2288
c, Å	22.863(9)	*T*, K	178
β, deg	91.47(3)	*R*, R_w[a]	0.035, 0.036
U, $Å^3$	4937		

[a] The *R* values are defined as $R = \sum|(F_o - F_c)|/\sum(F_o)$ and $R_w = [\sum\{w(F_o - F_c)^2\}/\{\sum(wF_o^2\}]^{1/2}$.

$Bu_4N[(AuBr)_2(\mu\text{-}PPh_2)]$ (5b). To a suspension of $[AuPPh_2]_n$ (120 mg, 0.31 mmol) in dichloromethane (10 mL) $Bu_4N[AuBr_2]$ (188 mg, 0.31 mmol) was added and the resulting suspension stirred at room temperature for 14 h. The resulting solution was filtered over $MgSO_4$, the filtrate concentrated under vacuum (1 mL), and diethyl ether (20 mL) added to precipitate **5b** as a white solid which was recrystallized from dichloromethane/diethyl ether (246 mg, 81%). Anal. Calcd for $C_{28}H_{46}Au_2Br_2NP$: C, 34.27; H, 4.72; N: 1.43; Au, 40.14. Found: C, 34.30; H, 5.35; N, 1.50; Au, 39.97. Mp 112 °C (dec). Λ_M = 94 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (4 × 10^{-4} mol·L^{-1}). ν(AuBr) 227, 209 cm^{-1}. ^{1}H NMR: 0.98 (t, 12H, Me, $^3J_{HH}$ = 6.9 Hz), 1.44, 1.71, 3.27 (m, 8H, CH_2), 7.2–7.8 (m, 10H, PPh_2) ppm. $^{31}P\{^1H\}$: 25.20 (s, PPh_2) ppm.


X = Cl (**4**), Br (**5**), I (**6**)

$[Ph_2(O)P-Au-P(O)Ph_2]^+$

7

$[(PPh_3)_2N][Au\{P(O)Ph_2\}_2]$ (7). To a solution of PPh_2H (0.1 mL, 0.574 mmol) in diethyl ether (15 mL) $[(PPh_3)_2N][Au(acac)_2]$ (268.3 mg, 0.29 mmol) was added under a N_2 atmosphere. The resulting suspension, initially white, becomes deep yellow for a while and slowly turns to pale yellow. After 2 h of stirring, the suspension was filtered off in the air and the solid washed with diethyl ether (2 × 10 mL) and air-dried to give a solid which was recrystallized from methylene chloride/diethyl ether to give **7** as a white solid (205 mg, 65%). Anal. Calcd for $C_{60}H_{50}AuNO_2P_4$: C, 63.33; H, 4.43; N, 1.23; Au, 17.31. Found: C, 62.91; H, 4.58; N, 1.29; Au, 16.85. Mp 218 °C (dec). Λ_M = 110 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (2 × 10^{-4} mol·L^{-1}). ^{1}H NMR: 7–8 (m, PPh_2O + $(PPh_3)_2N$) ppm. $^{31}P\{^1H\}$: 20.70 (s, $(PPh_3)_2N$), 97.19 (s, PPh_2O) ppm.

X-ray Structure Determination of Compound 7. Data Collection and Reduction. A colorless prism 0.5 × 0.4 × 0.3 mm, obtained by slow diffusion of *n*-hexane into a solution of **7** in dichloromethane, was used to collect 4605 intensities on a Siemens R3 diffractometer ($2\theta_{max}$ 50°, 4349 unique, 3078 > $4\sigma(F)$, R_{int} 0.015). The orientation matrix was refined from setting angles of 50 reflections in the 2θ range 20–22°. An absorption correction based on ψ-scans was applied, with transmission factors 0.65–0.93.

Structure Solution and Refinement. The program system "Siemens SHELXTL PLUS" was employed. The structure was solved by the heavy-atom method and refined anisotropically on *F*. H atoms were included using a riding model. The final *R* for 309 parameters was 0.035, with *wR* 0.036. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00015F^2$; *S* = 1.5; max Δ/σ = 0.001; max $\Delta\rho$ = 1.4 e $Å^{-3}$. Tables I, II, and III give crystallographic data, selected bond lengths and angles and, final atomic coordinates, respectively.

Results

Synthesis of Complexes. Addition of PPh_2H to a dichloromethane suspension of [AuX(thtp)] (thtp = tetrahydrothiophene) (1:1) gives a solution from which the complex $[AuCl(PPh_2H)]$ (**1**) or the already reported[2] $[AuBr(PPh_2H)]$ (**2**) can be isolated (see Scheme I). Recrystallization from diethyl ether/*n*-hexane allows the isolation of complex **1** in a pure state. If the reaction time is extended beyond 30 min, a mixture of **1** and $[AuPPh_2]_n$ is obtained. We also obtained complex **1** as one of the products from $[AuCl_3(thtp)]$ and PPh_2H (1:1). Complex **1** is stable in

Table II. Selected Bond Lengths (Å) and Angles (deg) for $[(PPh_3)_2N][Au\{P(O)Ph_2\}_2]$ (7)[a]

Au–P(1)	2.324(2)	P(1)–O	1.499(4)
P(1)–C(11)	1.827(5)	P(1)–C(21)	1.844(5)
P(2)–N	1.575(2)	P(2)–C(31)	1.805(5)
P(2)–C(41)	1.800(5)	P(2)–C(51)	1.798(5)
P(1)–Au–P(1i)	180.0	Au–P(1)–O	118.6(2)
Au–P(1)–C(11)	112.0(2)	O–P(1)–C(11)	108.7(2)
Au–P(1)–C(21)	106.0(2)	O–P(1)–C(21)	109.6(2)
C(11)–P(1)–C(21)	100.4(2)	N–P(2)–C(31)	110.3(2)
N–P(2)–C(41)	107.6(2)	C(31)–P(2)–C(41)	110.6(2)
N–P(2)–C(51)	114.9(3)	C(31)–P(2)–C(51)	106.0(2)
C(41)–P(2)–C(51)	107.3(2)	P(2)–N–P(2ii)	142.0(4)

[a] Symmetry operators: (i) $1-x, 1-y, 1-z$; (ii) $1-x, y, 1.5-z$. P(2) is the phosphorus atom of the cation $(PPh_3)_2N$.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^4) for Compound 7

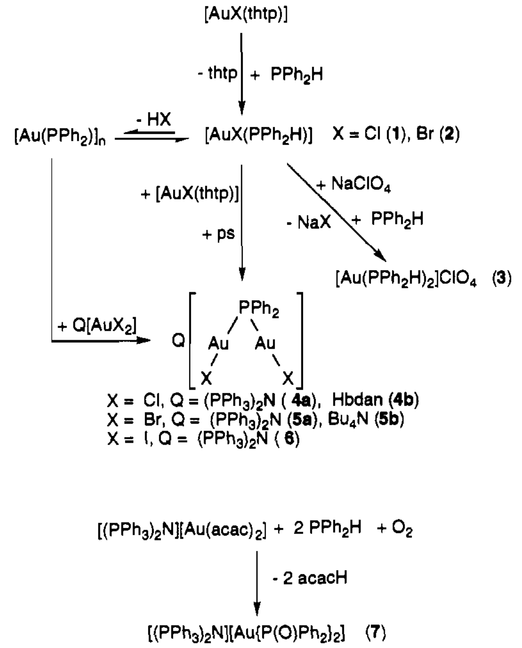
	x	*y*	*z*	*U*(eq)[a]
Au	5000	5000	5000	392(1)
P(1)	5113.5(8)	6417.7(12)	5655.3(6)	325(5)
O	4395(2)	6846(3)	5924(2)	397(13)
C(11)	5655(3)	7537(4)	5353(2)	289(17)
C(12)	6226(4)	7417(5)	4945(2)	445(22)
C(13)	6638(4)	8271(6)	4742(3)	494(24)
C(14)	6480(4)	9285(6)	4943(3)	500(25)
C(15)	5912(4)	9439(5)	5348(3)	485(24)
C(16)	5505(3)	8556(5)	5547(3)	436(22)
C(21)	5797(3)	5968(4)	6237(2)	310(18)
C(22)	5666(3)	6225(4)	6814(2)	337(18)
C(23)	6164(3)	5864(4)	7247(3)	399(20)
C(24)	6787(3)	5247(4)	7117(3)	427(22)
C(25)	6929(3)	4995(5)	6547(3)	399(18)
C(26)	6436(3)	5348(4)	6107(3)	389(20)
P(2)	5861.2(7)	2177.6(10)	7512.7(6)	220(4)
N	5000	2588(5)	7500	260(19)
C(31)	6267(3)	2288(4)	6795(2)	250(16)
C(32)	5773(3)	2494(4)	6320(2)	332(18)
C(33)	6059(4)	2525(5)	5764(3)	463(23)
C(34)	6826(4)	2338(5)	5680(3)	463(23)
C(35)	7330(3)	2150(5)	6140(3)	406(21)
C(36)	7042(3)	2128(4)	6705(2)	324(18)
C(41)	6399(3)	2984(4)	8034(2)	229(16)
C(42)	7147(3)	2708(4)	8220(2)	285(17)
C(43)	7547(3)	3361(4)	8611(2)	340(20)
C(44)	7210(3)	4278(4)	8812(2)	344(19)
C(45)	6465(3)	4560(4)	8637(2)	327(18)
C(46)	6068(3)	3908(4)	8247(2)	262(17)
C(51)	5985(3)	803(4)	7728(2)	251(17)
C(52)	6016(3)	−6(5)	7311(2)	320(15)
C(53)	6037(3)	−1073(5)	7484(3)	376(22)
C(54)	6027(3)	−1329(5)	8067(3)	427(22)
C(55)	6009(3)	−545(6)	8482(3)	380(22)
C(56)	5977(3)	534(5)	8315(3)	338(19)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

solution for only a few minutes, because it is converted rapidly into a mixture of **1** and $[Au(PPh_2)]_n$ that is very insoluble. In the solid state, complex **1** is also rather unstable and IR spectra (see below) or elemental analysis carried out on stored samples indicate that $[Au(PPh_2)]_n$ is also present. However, it can be melted without apparent decomposition at 102 °C.

Because the decomposition process that affords $[Au(PPh_2)]_n$ from **1** seems to be an equilibrium (see Scheme I), the reaction between [AuCl(thtp)] and PPh_2H is not a good synthesis of $[Au(PPh_2)]_n$ unless a base is added. This polymer has been synthesized by four different methods, namely by reacting PPh_2H with $[AuMe(PMe_2Ph)]$ or with $[AuCl(PPh_3)]$ in pyridine or with AuCN[2] or by electrochemical oxidation of gold in the presence of PPh_2H.[10] We report here that addition of concentrated aqueous ammonia to the solution obtained from a 1:1 mixture of [AuCl(thtp)] and PPh_2H in dichloromethane gives a high yield (81%) of $[Au(PPh_2)]_n$ which we consider a more convenient synthesis than those above. It is also safer than the method using AuCN, which produces HCN.[2] Alternatively, we have also obtained it by reacting **1** with Tl(acac) (1:1) or $[(PPh_3)_2N][Au(acac)_2]$ [9] with PPh_2H (1:1). The reaction of [AuBr(thtp)] with PPh_2H (1:1) gives a better yield of the complex $[AuBr(PPh_2H)]$ (**2**) than that reported[2] by reacting $[Bu_4N][AuBr_2]$ with PPh_2H.

Scheme I



We have shown[11] that $[Au(acac)(PPh_3)]$ reacts with species containing one acidic proton to produce Hacac and the corresponding gold(I) complexes. The same idea was applied here in an attempt to prepare $[Au(PPh_2)(PPh_3)]$ from PPh_2H and $[Au(acac)(PPh_3)]$ (1:1, 2.5 h, Et_2O, room temperature). However, $[Au(PPh_2)]_n$ was obtained instead. Probably, the expected complex $[Au(PPh_2)(PPh_3)]$, behaving as a ligand, replaces PPh_3 from another molecule giving $[Au(PPh_2)]_n$.

By reacting [AuCl(thtp)] with PPh_2H in 1:2 molar ratio in the presence of an excess of $NaClO_4 \cdot H_2O$, the complex $[Au(PPh_2H)_2]ClO_4$ (**3**) can be isolated.

$Q[AuX_2]$ reacts with $[AuPPh_2]_n$ (1:1) to give $Q[(AuX)_2(\mu\text{-}PPh_2)]$ ($Q = (PPh_3)_2N$, X = Cl (**4a**), Br (**5a**), I (**6**); $Q = Bu_4N$, X = Br (**5b**)). In the case of X = Cl, the reaction is immediate, as shown by the rapid dissolution of the very insoluble $[Au(PPh_2)]_n$ reagent. When X = Br or I, the suspension remains for about 4 h and the reaction is accompanied by the formation of some metallic gold. The anionic complex present in complex **4a** can also be obtained by reacting [AuCl(thtp)] with PPh_2H and Proton Sponge (1,8-bis(dimethylamino)naphthalene = bdan, see Chart I) (2:1:1) to give $[Hbdan][(AuCl)_2(\mu\text{-}PPh_2)]$ (**4b**). In this reaction the order of addition of reagents is important. If Proton Sponge is added first to [AuCl(thtp)], immediate reduction to metallic gold occurs.

$[(PPh_3)_2N][Au(acac)_2]$[9] reacts with PPh_2H (1:2) to give, on exposure to air, the phosphinito complex $[(PPh_3)_2N][Au\{P(O)Ph_2\}_2]$ (**7**).

Structure of Complexes. NMR data for complexes **1** and **3** are similar to those reported previously for these complexes while those of complex **2** are the same. Differences of 2–3 ppm in the $\delta[^{31}P\{^1H\}]$ and of 10–20 Hz in $^1J(H\text{-}P)$ could be due to the

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(10) Annan, T. A.; Kumar, R.; Tuck, D. G. *J. Chem. Soc., Chem. Commun.* **1988**, 447.

(11) See, for example, Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Chem. Commun.*, **1991**, 1730, and references therein.

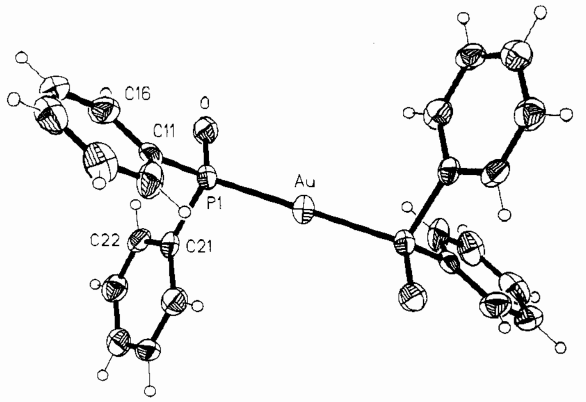


Figure 1. Thermal ellipsoid plot of the anion of compound **7**. Ellipsoids correspond to 50% probability levels. H atom radii are arbitrary. The numbering of the asymmetric unit is indicated.

influence of the other components of the mixture in which **1** and **3** were previously obtained.[2] The value of $\delta[^{31}P\{^1H\}]$ NMR found for complex **5b** (25.20 ppm) is quite different from that reported[2] (0.8 ppm) and is discussed below.

Molar conductivities in acetone are according to the proposed formulas. An IR spectrum of complex **1** can easily be distinguished from that of $[AuPPh_2]_n$ and also from mixtures of both compounds. Bands at 1102, 890, 850, 652, and 320 [ν(AuCl)] cm^{-1} are typical of complex **1** and that at 480 cm^{-1} of $[AuPPh_2]_n$. The band assignable to the ν(PH) mode in complexes **1**–**3** is a weak and broad band appearing at *ca.* 2330 cm^{-1}.

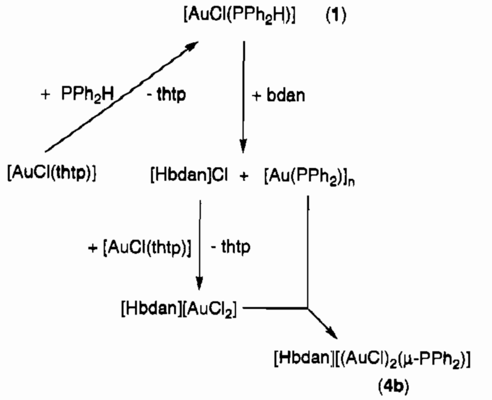
The crystal structure of complex **7** (see Figure 1) shows exactly linear coordination at the gold atom, which lies on a center of symmetry (see Table II). The P–Au bond length (2.324(2) Å) is similar to those found in complexes $[(PPh_3)_2N][Mn(CO)_4\{PPh_2(AuC_6F_5)\}_2]$ (2.313(2), 2.322(1) Å) and $[\{Mn(CO)_4(\mu\text{-}PPh_2)_2\}_2Au_2]$ (2.332(3)–2.341(3) Å),[12] but significantly greater than in $Bu_4N[(AuBr)_2(\mu\text{-}PPh_2)]$[1] (2.243(3) Å). Au–P bonds *trans* to halogens are typically *ca.* 0.1 Å shorter than those to P or C donors.[13] The P=O bond distance (1.499(4) Å) is similar to typical values for phosphine oxides (mean value 1.489(10) Å).[14] The nitrogen atom of the $(PPh_3)_2N$ cation lies on a 2-fold axis.

Discussion

Previous reports on (diphenylphosphine)gold(I) derivatives had given us the impression that very few such complexes could be prepared. Thus, **1** or the cation $[Au(PPh_2H)_2]^+$ present in **3** could only be obtained mixed with $[Au(PPh_2)]_n$ or with $[AuBr(PPh_2H)]$ and $[Au(PPh_2H)_n]^+$ (n = 3, 4), respectively.[2] In addition, complex **5b** was serendipitously obtained only in one experiment and could not be reproduced. Although its crystal structure was solved and $\delta[^{31}P\{^1H\}]$ given, no melting point, conductivity or IR spectral data were reported.[2] The only isolable new complexes were the very stable complex **2**[2] and $[AuCl(PR_2H)]$, in which R is *ortho*-substituted aryl or bulky alkyl groups[4]

The synthesis of **1** was first attempted by addition of ethanol solutions of PPh_2H to aqueous solutions of [AuCl(thiodiglycol)].[2] It is quite likely that water acted against complex **1** as a base giving $[Au(PPh_2)]_n$. We have solved this problem by reacting a similar gold(I) complex, [AuCl(thtp)], with PPh_2H in dichloromethane. Complex **1** is unstable and decomposes easily to the polymer $[Au(PPh_2)]_n$. The use of a different gold(I) complex ([AuCl(CO)]) in diethyl ether also gives complexes $[AuCl(PR_2H)]$.[4]

Scheme II



The reaction of [AuCl(thiodiglycol)] with PPh_2H in 1:2 molar ratio was reported to give $[Au(PPh_2)]_n$.[2] The authors assume intermediate formation of complex **1** which should be deprotonated by PPh_2H to give $[AuCl(PPh_2)]PPh_2H_2$ which, as a ligand, could attack complex **1** to give $[Au(PPh_2)]_n$.[2] The similar reaction between [AuCl(thtp)] with PPh_2H (1:2 molar ratio) probably gives $[Au(PPh_2H)_2]Cl$ which, in the presence of $NaClO_4 \cdot H_2O$, gives **3**. The cation $[Au(PPh_2H)_2]^+$ has been detected in solutions containing PPh_2H and $Bu_4N[AuBr_2]$ in P:Au ratios in the 1.5–3 range. However, attempts to isolate this complex were unsuccessful because other species such as $[AuBr(PPh_2H)]$ and $[Au(PPh_2H)_n]^+$ (n = 3, 4) were present.[2]

It has been suggested[2] that $[Au(PPh_2)]_n$ consists of a chain of the type $[L\{Au(\mu\text{-}PPh_2)\}_{n-1}(AuPPh_2)]$ where L is the deprotonating agent used in its preparation (see above). We also agree with this possibility, because its color depends on the nature of L and on the Au:L ratio. Thus, when it is obtained by decomposition of **1** (see Scheme I) or by reacting **1** with Tl(acac) (1:1) or $[Au(acac)_2]^-$ with PPh_2H (1:1), it is an off-white solid, whereas when it is obtained by reacting **1** with an excess of NH_3, it precipitates as a pale or deep yellow solid depending on the excess of NH_3. Analytical data and infrared spectra of these yellow solids are the same as the off-white $[Au(PPh_2)]_n$. In addition, reaction of $[Au(PPh_2)]_n$ with excess of PPh_3 gives also yellow solids.

We have designed two different methods to prepare complexes $[(AuX)_2(\mu\text{-}PPh_2)]^-$. The former involves the reaction between the polymer $[Au(PPh_2)]_n$ and $[AuX_2]^-$. When X = Cl the reaction seems to be very fast, because the precipitate of $[Au(PPh_2)]_n$ disappears almost immediately after addition of $[(PPh_3)_2N][AuCl_2]$. When X = Br or I dissolution takes approximately 4 h. We assume that the terminal $AuPPh_2$ end of $[L\{Au(\mu\text{-}PPh_2)\}_{n-1}(AuPPh_2)]$ displaces one X ligand of $[AuX_2]^-$ to give $[L\{Au(\mu\text{-}PPh_2)\}_n(AuX)]$ and X^-. This anion splits the chain to give $[(AuX)_2(\mu\text{-}PPh_2)]^-$ and the shorter polymer $[L\{Au(\mu\text{-}PPh_2)\}_{n-2}(AuPPh_2)]$. We have tried to prove that chloride anion is able to split the polymer by itself; however, reaction between the polymer and $[(PPh_3)_2N]Cl$ does not take place.

The second method of preparing complexes $[(AuX)_2(\mu\text{-}PPh_2)]^-$ uses [AuCl(thtp)], PPh_2H, and Proton Sponge in the molar ratios 2:1:1 to give complex **4b**. This reaction presumably occurs with the intermediate formation of **1** (see Scheme II), which reacts with Proton Sponge to displace the above mentioned acid–base equilibrium (see Scheme I) to generate $[Au(PPh_2)]_n$ and [Hbdan]Cl. This salt reacts with [AuCl(thtp)] displacing tetrahydrothiophene to give $Hbdan[AuCl_2]$ and, finally, $[Au(PPh_2)]_n$ reacts in the same way as with the other $[AuCl_2]^-$ salts to give **4b**.

According to the above results we assume that the serendipitous synthesis of **5b** from PPh_2H and $Me_4N[AuBr_2]$[2] was due to a chance deficiency of PPh_2H, giving a mixture of $[AuBr_2]^-$ and $[AuBr(PPh_2H)]$. The last complex should decompose slowly to

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(12) Carriedo, G. A.; Riera, V.; Rodríguez, M. L.; Jones, P. G.; Lautner, J. *J. Chem. Soc., Dalton Trans.* **1989**, 639.

(13) Jones, P. G. *Gold Bull.* **1981**, *14*, 102.

(14) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.

give $[Au(PPh_2)]_n$ (and HBr) which should react with $[AuBr_2]^-$ to give **5b**. We have confirmed this hypothesis by reacting PPh_2H and $Me_4N[AuBr_2]$ (1:2) in dichloromethane. After 2 h the volatiles (HBr and dichloromethane) were removed and the residue dissolved in CD_2Cl_2. The $^{31}P\{^1H\}$ NMR spectrum of this solution shows the presence of $[AuBr(PPh_2H)]$ (1.64 ppm) and $[Au(PPh_2)]_n$ (90.68 ppm)[2] (aproximately 3:1). After 2 days, a third resonance appears (25.56 ppm) showing the presence of **5b** ($[Au(PPh_2)]_n$:**5b** approximately 10:1) the concentration of which is approximately doubled after 2 more days. This study also supports our value of $\delta[^{31}P\{^1H\}]$ (25.20 ppm) for complex **5b** instead of the reported (0.8 ppm)[2] which could correspond to $[AuBr(PPh_2H)]$ (1.99 ppm when pure). Isolated single crystals of **5b** were characterized by the known cell constants.[1] Values of $\delta[^{31}P\{^1H\}]$ increase in the sequence Cl (16) < Br (25) < I (40) and are similar to those found in Mn(I)/Au(I) complexes containing diphenylphosphido bridges (range 11–59 ppm).[12]

The reaction between $[(PPh_3)_2N][Au(acac)_2]$ and PPh_2H (1:2) gives first a yellow precipitate that slowly turns pale yellow. Many attempts to isolate the yellow complex, probably $[(PPh_3)_2N][Au(PPh_2)_2]$, were fruitless even under nitrogen. When the pale yellow solid was isolated, recrystallization finally gave the white solid **7**. We suspected that the complex was not $[(PPh_3)_2N][Au(PPh_2)_2]$, in spite of the acceptable elemental analyses, because it does not behave as a phosphorus donor ligand; thus, it does not react with $N_3CH_2CO_2Et$, H_2O_2, or S_8. The true nature of complex **7** was only ascertained by the solution of its crystal structure.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.