Synthesis of Complexes $[\mathrm{Au(PPh_3)L}]^+$ (L = Primary, Secondary or Tertiary Amine). Crystal Structure of $[\mathrm{Au(PPh_3)(NMe_3)}][\mathrm{ClO_4}]\cdot\mathrm{CH_2Cl_2}$†

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The 1:1 reaction of $[\mathrm{Au(acac)(PPh_3)}]$ (Hacac = acetylacetone) with ammonium salts [HL]X (X = $\mathrm{CF_3SO_3}$, L = 2-nitroaniline, 4-methoxyaniline, $\mathrm{NHPh_2}$ or $\mathrm{NHEt_2}$; X = $\mathrm{ClO_4}$, L = $\mathrm{NMe_3}$) in diethyl ether gave complexes $[\mathrm{Au(PPh_3)L}]\mathrm{X}$ and acetylacetone. The crystal structure of $[\mathrm{Au(PPh_3)(NMe_3)}][\mathrm{ClO_4}]$ was determined; orthorhombic, space group $P2_12_12_1$, $a = 9.498(2)$, $b = 10.322(2)$, $c = 26.154(4)$ Å, $wR(F^2)$ 0.091. The gold atom is linearly co-ordinated to both ligands [Au–P 2.231(2), Au–N 2.108(7) Å, P–Au–N 179.3(2)°] and no intermolecular Au $\cdots$ Au contacts exist.

Gold(I) complexes with neutral N-donor ligands are much less common than those with P-donor ligands because of the soft acid nature of the metal centre. For instance, $[\mathrm{AuX(ER_3)}]$ and $[\mathrm{Au(ER_3)_2}]^+$ complexes with E = P are known for a wide range of X and R groups,[1] whereas, as far as we are aware, only one complex of each type with E = N has been reported, namely the rather unstable [AuCl(pip)] (pip = piperidine) and $[\mathrm{Au(pip)_2}]^+$.[2] Therefore, mixed complexes $[\mathrm{Au(PR_3)(NR'_3)}]^+$ might be expected to be of intermediate stability. However, only a few such complexes have been described with full experimental or spectroscopic details.[3] Only one of them $[\mathrm{Au(PPh_3)(qncd)}]\mathrm{BF_4}$ (qncd = quinuclidine)[3d] has been characterized by X-ray diffraction methods. These complexes are prepared (usually in low yields) by the reaction of $[\mathrm{AuX(PR_3)}]$ with the corresponding amine, where X is $\mathrm{ClO_4}^-$, $\mathrm{BF_4}^-$ or $\mathrm{NO_3}^-$. We report in this paper a method to prepare some related mixed-ligand complexes and the crystal structure of one of them.

Results and Discussion

By reacting $[\mathrm{Au(acac)(PPh_3)}]$ (Hacac = acetylacetone) with ammonium salts $[\mathrm{NHRR'_2}]\mathrm{X}$ (1:1), the cationic complexes $[\mathrm{Au(PPh_3)(NRR'_2)}]\mathrm{X}$ (X = $\mathrm{ClO_4}$, R = R′ = Me **1**; X = $\mathrm{CF_3SO_3}$, R = H, R′ = Et **2**; R = H, R′ = Ph **3**; R = $\mathrm{C_6H_4NO_2}$-2, R′ = H **4**; R = $\mathrm{C_6H_4OMe}$-4, R′ = H **5**) can be isolated [equation (1)]. Except for **4**, all complexes were obtained in high yield (78–95%).

$$[\mathrm{Au(acac)(PPh_3)}] + [\mathrm{NHRR'_2}]\mathrm{X} \longrightarrow \mathrm{Hacac} + [\mathrm{Au(PPh_3)(NRR'_2)}]\mathrm{X} \qquad (1)$$

The result of these reactions depends on the nature of the solvent. Thus, acetone could only be used in the case of the synthesis of the tertiary amine complex **1**, while a mixture of complexes is obtained for primary and secondary amines. We assume that complexes **2**–**5**, behaving as ammonium salts, react rapidly in acetone with $[\mathrm{Au(acac)(PPh_3)}]$ to give gold(I) complexes with bridging amido or imido ligands [equations (2)–(4)].

$$[\mathrm{Au(acac)(PPh_3)}] + [\mathrm{Au(PPh_3)(NHR'_2)}]\mathrm{X} \longrightarrow \mathrm{Hacac} + [\mathrm{(AuPPh_3)_2(\mu\text{-}NR'_2)}]\mathrm{X} \qquad (2)$$

$$[\mathrm{Au(acac)(PPh_3)}] + [\mathrm{Au(PPh_3)(NH_2R)}]\mathrm{X} \longrightarrow \mathrm{Hacac} + [\mathrm{(AuPPh_3)_2(\mu\text{-}NHR)}]\mathrm{X} \qquad (3)$$

$$[\mathrm{Au(acac)(PPh_3)}] + [\mathrm{(AuPPh_3)_2(\mu\text{-}NHR)}]\mathrm{X} \longrightarrow \mathrm{Hacac} + [\mathrm{(AuPPh_3)_3(\mu_3\text{-}NR)}]\mathrm{X} \qquad (4)$$

Examples of these aurioammonium salts, *i.e.* one diaurioammonium salt $[\mathrm{(AuPPh_3)_2(\mu\text{-}NHC_6H_4NO_2\text{-}4)}]\mathrm{BF_4}$,[4] and several triaurioammonium salts $[\mathrm{(AuPPh_3)_3(\mu_3\text{-}NR)}]\mathrm{BF_4}$ (R = alkyl or aryl) have been described.[4,5] The tendency of gold(I) to establish weak intramolecular Au $\cdots$ Au bonding interactions (aurophilicity)[6] in these di- or tri-nuclear complexes is probably the reason why they are much more stable than complexes **1**–**5**, which slowly decompose in the solid state and in solution. This is also likely to be the reason for the formation of the very stable $[\mathrm{(AuPPh_3)_4(\mu_4\text{-}N)}]\mathrm{BF_4}$[7] and the hypervalent $[\mathrm{(AuPPh_3)_5(\mu_5\text{-}N)}]\mathrm{BF_4}$[8] complexes. Although this stabilizing aurophilicity can also lead to intermolecular Au $\cdots$ Au interactions,[6] these were not observed in the only previously reported crystal structure of a monoaurioammonium salt $[\mathrm{Au(PPh_3)(qncd)}]\mathrm{BF_4}$,[3d] or in complex **1** (see below).

The success of reactions leading to complexes **2**–**4** relied on the use of diethyl ether because of the solubility of the ammonium trifluoromethanesulfonates and $[\mathrm{Au(acac)(PPh_3)}]$ and the insolubility of the resulting complexes in this solvent. Probably, the rapid precipitation of complexes **2**–**4** allows the corresponding reactions to be performed without special precautions against atmospheric moisture and prevents reactions (2)–(4). In those reported methods where reaction conditions were indicated,[3b–d] a dinitrogen atmosphere was used. Careful precautions to eliminate all traces of moisture from the reactants proved to be vital for the generation of $[\mathrm{Au(PPh_3)(qncd)}]\mathrm{BF_4}$.[3d] In the presence of water, the reaction between quinuclidine and $[\mathrm{Au(PPh_3)}]\mathrm{BF_4}$ gives quinuclidinium and $[\mathrm{(AuPPh_3)_3O}]^+$ salts.[3d]

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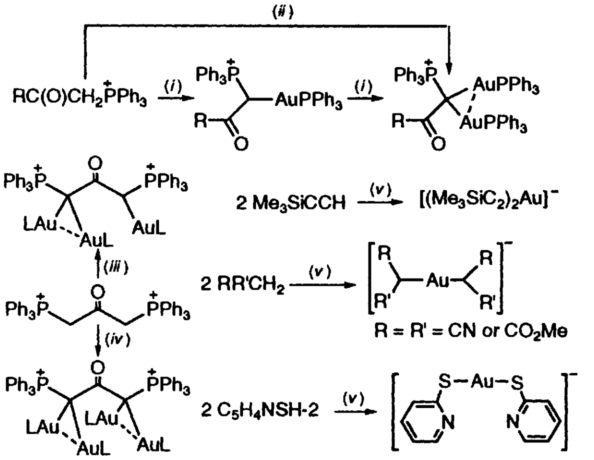
† Gold(I) Complexes with N-Donor Ligands. Part 1.

Supplementary data available: Full details have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 401358.



Scheme 1 (*i*) +[Au(acac)(PPh$_3$)] − Hacac; (*ii*) + 2[Au(acac)(PPh$_3$)] − 2 Hacac; (*iii*) +3[Au(acac)L] (L = PPh$_3$) − 3 Hacac; (*iv*) +4 [Au(acac)L] (L = PMe$_2$Ph) − 4 Hacac; (*v*) + [Au(acac)$_2$]$^-$ − 2 Hacac

This is a new example of the utility of acetylacetonatogold(I) complexes as starting materials for the synthesis of gold(I) complexes (see Scheme 1).[9] We have previously used [Au(acac)(PPh$_3$)] to prepare mono-, di-, tri- and tetra-nuclear gold(I) complexes. More recently Laguna and co-workers[10] have also found interesting synthetic applications for [Au(acac)(PPh$_3$)].

All complexes behave in solution as 1 : 1 electrolytes.[11] The IR spectra of complexes **2**, **4** and **5** show ν(NH) in the region 3214–3092 cm^{-1}. For complex **3**, ν(NH) could not be assigned because only very weak bands in this region were observed.

Structure of Complex **1**.—The structure of complex **1** (see Fig. 1 and Table 1) consists of the cation [Au(PPh$_3$)(NMe$_3$)]$^+$, a perchlorate anion and a dichloromethane molecule. In the cation the gold atom is linearly co-ordinated [P–Au–N 179.3(2)°]. The Au–N and Au–P bond distances [2.108(7) and 2.231(2) Å, respectively] are similar to those in the complex [Au(PPh$_3$)(qncd)]BF$_4$ [3d] [2.11(1) and 2.240(4) Å, respectively]. The cationic nature of **1** and the large PPh$_3$ groups are probably responsible for the absence of Au ··· Au contacts.

Experimental

The IR, C, H and N analyses, conductance measurements and melting point determinations were carried out as described elsewhere.[9] The NMR spectra were recorded in CDCl$_3$ on a Varian Unity 300 spectrometer and conductivity measurements were carried out in acetone. Chemical shifts are referred to SiMe$_4$ (^{1}H and ^{13}C) or external H$_3$PO$_4$ (^{31}P). The following reagents were commercially available: CF$_3$SO$_3$H, NH$_2$(C$_6$H$_4$OMe-4) (Merck), [NHMe$_3$]Cl (Fluka), NHEt$_2$, NH$_2$(C$_6$H$_4$NO$_2$-2) (Aldrich), NHPh$_2$ (Probus). The compound [Au(acac)(PPh$_3$)] was prepared following a literature method.[12]

Syntheses.—[NHMe$_3$][ClO$_4$]. To a solution of [NHMe$_3$]Cl (1 g, 10.46 mmol) in acetone (20 cm^3) was added NaClO$_4$·H$_2$O (1.47 g, 10.46 mmol) and the suspension stirred for 30 min. It was then filtered through Celite, the resulting solution concentrated (2 cm^3) and diethyl ether (20 cm^3) added to precipitate [NHMe$_3$][ClO$_4$] (1.33 g, 92%) as a white solid which was washed with diethyl ether (2 × 5 cm^3) and air dried. M.p. 234 °C (Found: C, 22.65; H, 6.50; N, 8.55. Calc. for C$_3$H$_{10}$ClNO$_4$: C, 22.60; H, 6.30; N, 8.80%). Λ_M = 146 Ω^{-1} cm^2 mol^{-1} (1.35 × 10^{-3} mol dm^{-3}). NMR: ^{1}H, δ 3.12 (s, 9 H, Me), 4.16 (br, 1 H, NH). IR: ν(NH) 3128 cm^{-1}.

[NH$_2$Et$_2$][CF$_3$SO$_3$]. To a solution of NHEt$_2$ (98%, 1 cm^3, 9.47 mmol) in diethyl ether (20 cm^3) HO$_3$SCF$_3$ (Merck, 0.83 cm^3, 9.47 mmol) was added dropwise. A white solid precipitated immediately which was washed with diethyl ether (2 × 5 cm^3), filtered off and air dried (381 mg, 18%). M.p. 121 °C (Found: C, 27.35; H, 5.75; N, 6.45; S, 14.60. Calc. for C$_5$H$_{12}$F$_3$NO$_3$S: C, 26.90; H, 5.40; N, 6.25; S, 14.35%). Λ_M = 85 Ω^{-1} cm^2 mol^{-1} (7.2 × 10^{-4} mol dm^{-3}). NMR: ^{1}H, δ 1.35 (t, 6 H, Me), 3.23 (m, 4 H, CH$_2$), 7.69 (m br, 2 H, NH). IR: ν(NH) 3156, 3054 cm^{-1}.

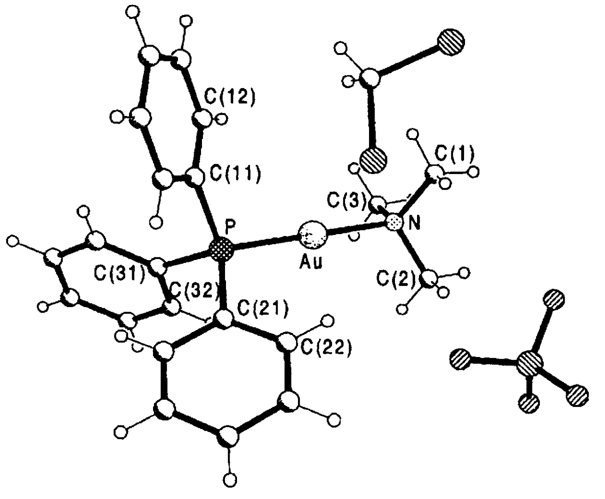


Fig. 1 The structure of complex **1**

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Au–N	2.108(7)	Au–P	2.231(2)
P–C(21)	1.804(10)	P–C(11)	1.804(9)
P–C(31)	1.807(9)	N–C(2)	1.472(12)
N–C(3)	1.482(11)	N–C(1)	1.487(10)
N–Au–P	179.3(2)	C(21)–P–C(11)	107.9(4)
C(21)–P–C(31)	104.5(4)	C(11)–P–C(31)	105.7(4)
C(21)–P–Au	113.0(3)	C(11)–P–Au	112.6(3)
C(31)–P–Au	112.5(3)	C(2)–N–C(3)	108.6(7)
C(2)–N–C(1)	109.1(8)	C(3)–N–C(1)	109.5(8)
C(2)–N–Au	109.3(6)	C(3)–N–Au	110.2(6)
C(1)–N–Au	110.1(5)		

[NH$_2$Ph$_2$][CF$_3$SO$_3$]. Similarly, [NH$_2$Ph$_2$][CF$_3$SO$_3$] (350 mg, 18%) was obtained from NHPh$_2$ (1 g, 5.91 mmol) in diethyl ether (10 cm^3) and CF$_3$SO$_3$H (0.8 cm^3, 9.1 mmol). M.p. 135 °C (Found: C, 49.50; H, 3.90; N, 4.55; S, 9.50. Calc. for C$_{13}$H$_{12}$F$_3$NO$_3$S: C, 48.90; H, 3.80; N, 4.40; S, 10.05%). Λ_M = 106 Ω^{-1} cm^2 mol^{-1} (5.0 × 10^{-4} mol dm^{-3}). ^{1}H NMR: δ 7.39–7.87 (m, Ph). IR: ν(NH) 3184 cm^{-1}.

[NH$_3$(C$_6$H$_4$NO$_2$-2)][CF$_3$SO$_3$]. Similarly, [NH$_3$(C$_6$H$_4$NO$_2$-2)][CF$_3$SO$_3$] (650 mg, 63%) was obtained from a solution of NH$_2$(C$_6$H$_4$NO$_2$-2) (98%, 500 mg, 3.55 mmol) in diethyl ether (20 cm^3) and HO$_3$SCF$_3$ (0.5 cm^3, 5.7 mmol). M.p. 148 °C (Found: C, 29.70; H, 2.50; N, 10.00; S, 10.75. Calc. for C$_7$H$_7$F$_3$N$_2$O$_5$S: C, 29.15; H, 2.45; N, 9.70; S, 11.10%). Λ_M = 94 Ω^{-1} cm^2 mol^{-1} (6.9 × 10^{-4} mol dm^{-3}). NMR: ^{1}H, δ 7.96 (m, 2 H), 8.06 (m, 1 H), 8.43 (m, 1 H). The ^{1}H NMR spectrum shows the presence of a small amount of 2-nitroaniline in equilibrium with the ammoniun salt. IR: ν(NH) 3119 cm^{-1}.

[NH$_3$(C$_6$H$_4$OMe-4)][CF$_3$SO$_3$]. Similarly, [NH$_3$(C$_6$H$_4$OMe-4)][CF$_3$SO$_3$] (820 mg, 92%) was obtained from a solution of NH$_2$(C$_6$H$_4$OMe-4) (400 mg, 3.25 mmol) in diethyl ether (15 cm^3) and CF$_3$SO$_3$H (0.3 cm^3, 3.25 mmol). M.p. 232 °C (Found: C, 35.35; H, 3.80; N, 5.20; S, 11.65. Calc. for C$_8$H$_{10}$F$_3$NO$_4$S: C, 35.15; H, 3.70; N, 5.15; S, 11.75%). Λ_M = 115 Ω^{-1} cm^2 mol^{-1} (7.32 × 10^{-4} mol dm^{-3}). ^{1}H NMR: δ 3.87 (s, 3 H, OMe), 7.11, 7.16, 7.47, 7.52 (AA'BB' system). IR: ν(NH) 3073 cm^{-1}.

[Au(PPh$_3$)(NMe$_3$)][ClO$_4$] **1**. To a suspension of [Au-

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Au	3 598.1(4)	2 878.9(3)	4 273.69(12)
P	3 367(2)	4 766(2)	3 866.7(8)
N	3 836(8)	1 089(7)	4 652(3)
C(1)	3 771(12)	8(7)	4 277(4)
C(2)	5 209(10)	1 060(10)	4 913(4)
C(3)	2 712(10)	923(10)	5 040(4)
C(11)	2 398(10)	4 619(9)	3 276(3)
C(12)	1 223(10)	3 836(9)	3 267(3)
C(13)	432(10)	3 718(11)	2 832(4)
C(14)	807(12)	4 364(12)	2 397(4)
C(15)	2 004(11)	5 147(11)	2 395(4)
C(16)	2 779(12)	5 285(10)	2 837(4)
C(21)	5 033(10)	5 526(10)	3 725(3)
C(22)	6 255(10)	4 772(10)	3 697(3)
C(23)	7 512(11)	5 382(11)	3 586(4)
C(24)	7 599(11)	6 686(10)	3 488(4)
C(25)	6 392(11)	7 409(10)	3 507(3)
C(26)	5 120(10)	6 856(10)	3 631(3)
C(31)	2 428(9)	5 956(8)	4 242(4)
C(32)	2 767(10)	6 051(10)	4 761(3)
C(33)	2 114(10)	6 959(10)	5 064(3)
C(34)	1 096(9)	7 758(10)	4 868(3)
C(35)	743(9)	7 660(8)	4 352(3)
C(36)	1 394(10)	6 766(8)	4 036(3)
Cl(1)	9 038(2)	1 041(2)	3 994.0(8)
O(1)	9 301(10)	1 170(8)	4 530(3)
O(2)	8 381(9)	2 179(8)	3 801(3)
O(3)	8 171(9)	−66(8)	3 917(3)
O(4)	10 339(9)	854(9)	3 735(3)
C(4)	2 971(15)	908(14)	2 885(5)
Cl(2)	3 249(4)	−755(4)	2 826(2)
Cl(3)	4 535(5)	1 742(4)	2 994(2)

(acac)(PPh_3)] (500 mg, 0.89 mmol) in degassed acetone (10 cm^3), [$NHMe_3$][ClO_4] (143 mg, 0.89 mmol) was added and the reaction mixture stirred under a nitrogen atmosphere in an ice–water bath for 1.5 h. The resulting solution was concentrated (2 cm^3) and diethyl ether (20 cm^3) added to precipitate **1** (523 mg, 95%) as a white solid which was recrystallized twice from dichloromethane–diethyl ether. M.p. 178 °C (decomp.) (Found: C, 40.70; H, 4.20; Au, 31.55; N, 2.20. Calc. for $C_{21}H_{24}AuClNO_4P$: C, 40.80; H, 4.00; Au, 31.90; N, 2.25%). $\Lambda_M = 90\ \Omega^{-1}\ cm^2\ mol^{-1}$ (3.24×10^{-4} mol dm^{-3}). NMR: ^1H, δ 2.97 (s, 9 H, Me), 7.4–6.1 (m, 15 H, Ph); ^{31}P, δ 30.42 (s); ^{13}C, δ 134.5 (d, $^3J_{PC}$ 13), 133.1 (s), 130.0 (d, $^2J_{PC}$ 12), 127.1 (d, $^1J_{PC}$ 64 Hz), 52.7 (s, Me).

[Au(PPh_3)($NHEt_2$)][CF_3SO_3] **2**. To a suspension of [Au(acac)(PPh_3)] (179.5 mg, 0.32 mmol) in diethyl ether (15 cm^3) was added [NH_2Et_2][CF_3SO_3] (71.7 mg, 0.32 mmol). Immediate reaction was observed with formation of an oil which converted into a powder upon stirring in diethyl ether for 1 h. It was filtered off, washed with diethyl ether (10 cm^3) and recrystallized from acetone–diethyl ether to give **2** (191 mg, 87%). M.p. 124 °C (Found: C, 40.00; H, 3.70; Au, 29.00; N, 1.95; S, 4.60. Calc. for $C_{23}H_{26}AuF_3NO_3PS$: C, 40.55; H, 3.85; Au, 29.0; N, 2.05; S, 4.70%). $\Lambda_M = 101\ \Omega^{-1}\ cm^2\ mol^{-1}$ (2.96×10^{-4} mol dm^{-3}). NMR: ^1H, δ 1.48 (t, 6 H, Me, $^3J_{HH}$ = 7 Hz), 3.2 (m, 4 H, CH_2), 7.4–7.6 (m, 15 H, Ph); ^{31}P, δ 30.89 (s). IR: ν(NH) 3149 cm^{-1}.

[Au(PPh_3)($NHPh_2$)][CF_3SO_3] **3**. To a suspension of [Au(acac)(PPh_3)] (60 mg, 0.11 mmol) in diethyl ether (10 cm^3), [NH_2Ph_2][CF_3SO_3] (40 mg, 0.11 mmol) was added. The resulting solution gave, on stirring, a suspension which was filtered after 1 h. The cream solid was washed with diethyl ether (5 cm^3) and recrystallized from dichloromethane–diethyl ether to give **3** (67 mg, 78%) as a white solid. M.p. 137 °C (decomp.) (Found: C, 47.60; H, 3.35; Au, 26.10; N, 1.80; S, 4.45. Calc. for $C_{31}H_{26}AuF_3NO_3PS$: C, 47.90; H, 3.35; Au, 25.35; N, 1.80; S, 4.10%). $\Lambda_M = 110\ \Omega^{-1}\ cm^2\ mol^{-1}$ (9.25×10^{-5} mol dm^{-3}). NMR: ^1H, δ 7.0–7.8 (m, 25 H, Ph), 8.84 (s br, 1 H, NH); ^{31}P, δ 28.89 (s).

[Au(PPh_3){$NH_2(C_6H_4NO_2$-2)}][CF_3SO_3] **4**. To a solution of [$NH_3(C_6H_4NO_2$-2)][CF_3SO_3] (81.6 mg, 0.28 mmol) in diethyl ether (15 cm^3) was added [Au(acac)(PPh_3)] (158 mg, 0.28 mmol). The resulting suspension was stirred for 3 h and filtered to give **4** (68 mg, 32%) which was washed with diethyl ether (10 cm^3) and air dried. M.p. 150 °C (decomp.) (Found: C, 40.45; H, 2.60; Au, 25.70; N, 3.35; S, 4.35. Calc. for $C_{25}H_{21}AuF_3N_2O_5PS$: C, 40.25; H, 2.85; Au, 26.40; N, 3.75; S, 4.30%). $\Lambda_M = 99\ \Omega^{-1}\ cm^2\ mol^{-1}$ (2.84×10^{-4} mol dm^{-3}). NMR: ^1H, δ 7.02 ('t', 1 H, $NH_2C_6\mathit{H}_4NO_2$-2), 7.4–7.7 (m, 15 H, PPh_3 + 2 H, $NH_2C_6\mathit{H}_4NO_2$-2), 8.17 ('d', 1 H, $NH_2C_6\mathit{H}_4$-NO_2-2); ^{31}P, δ 28.99 (s). IR: ν(NH) 3214 cm^{-1}.

[Au(PPh_3){$NH_2(C_6H_4OMe$-4)}][CF_3SO_3] **5**. To a suspension of [Au(acac)(PPh_3)] (174 mg, 0.31 mmol) in diethyl ether (20 cm^3) was added [$NH_3(C_6H_4OMe$-4)][CF_3SO_3] (105 mg, 0.31 mmol). Immediate reaction was observed with formation of an oily solid which converted into a powder upon stirring in diethyl ether for 1 h. It was filtered off, washed with diethyl ether (5 cm^3) and air dried to give **5** (189 mg, 83%). M.p. 131 °C (decomp.) (Found: C, 42.25; H, 3.05; Au, 27.50; N, 1.85; S, 4.40. Calc. for $C_{26}H_{24}AuF_3NO_4PS$: C, 42.70; H, 3.30; Au, 26.95; N, 1.85; S, 4.40%). $\Lambda_M = 52\ \Omega^{-1}\ cm^2\ mol^{-1}$ (4.65×10^{-4} mol dm^{-3}). NMR: ^1H, δ 3.71 (s, 3 H, Me), 6.73, 6.76, 7.24, 7.27 (AA′BB′, 4 H), 7.4–7.6 (m, 15 H, PPh_3); ^{31}P, δ 31.07 (s). IR: ν(NH) 3173, 3092 cm^{-1}.

Crystal Structure Determination of Compound **1**.—*Crystal data*. $C_{22}H_{26}AuCl_3NO_4P$, orthorhombic, space group $P2_12_12_1$, $a = 9.498(2)$, $b = 10.322(2)$, $c = 26.154(4)$ Å, $U = 2564.1$ Å, $Z = 4$, $D_c = 1.820$ Mg m^{-3}, $F(000) = 1368$, λ(Mo-Kα) = 0.710 73 Å, $\mu = 6.1\ mm^{-1}$, $T = -130$ °C. A colourless prism *ca.* 0.5 × 0.2 × 0.15 mm was mounted on a glass fibre in inert oil and transferred to the cold-gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low temperature attachment). A total of 6114 reflections were collected to 2θ 55°, of which 5288 were independent (R_{int} 0.0359) after an absorption correction based on ψ scans (transmissions of 0.56–0.99). Cell constants were refined from ± ω values of 74 reflections in the range 2θ 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined on F^2 (ref. 13). Hydrogen atoms were included using a riding model or as rigid methyl groups. The absolute structure was determined by the *x* parameter −0.022(11).[14] The final $wR(F^2)$ was 0.091 for all reflections, with a conventional $R(F)$ of 0.043, for 292 parameters and 192 restraints; $S = 1.05$, max. Δ/σ 0.002, max. Δρ 0.75 e $Å^{-3}$. Selected bond lengths and angles are given in Table 1 and final atomic coordinates in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

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References

1 R. J. Puddephatt, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 861 and refs. therein.

2 J. J. Guy, P. G. Jones, M. J. Mays and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1977, 8.

3 (*a*) E. G. Perevalova, K. I. Grandberg, V. P. Dyadchenko and T. V. Baukova, *J. Organomet. Chem.*, 1981, **217**, 403; (*b*) E. M. Kinsch and D. W. Stephan, *Inorg. Chim. Acta*, 1984, **91**, 263; (*c*) J. F. Vollano, D. H. Picker and J. A. Statler, *Inorg. Chim. Acta*, 1989, **155**, 31; (*d*)

A. Grohmann, J. Riede and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1992, **47**, 1255.

4 E. G. Perevalova, K. I. Grandberg, E. I. Smyslova, L. G. Kuz'mina, V. I. Korsunskii and D. N. Kravtsov, *Metalborg. Khim.* (*Engl. Transl.*), 1989, **2**, 523.

5 V. Ramamoorthy and P. R. Sharp, *Inorg. Chem.*, 1990, **29**, 3336; A. Grohmann, J. Riede and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1991, 783; A. Kolb, P. Bissinger and H. Schmidbaur, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1580; A. Grohmann and H. Schmidbaur, *Inorg. Chem.*, 1992, **31**, 3378.

6 P. G. Jones, *Gold Bull.*, 1981, **14**, 102, 159; 1983, **16**, 114; 1986, **19**, 46; H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11; P. Pyykkö and J. P. Desclaux, *Acc. Chem. Res.*, 1979, **12**, 276; P. Pyykkö, *Chem. Rev.*, 1988, **88**, 563 and refs. therein.

7 Yu. L. Slovokhotov and Yu. T. Struchkov, *J. Organomet. Chem.*, 1984, **277**, 143; E. Zeler, H. Beruda, A. Kolb, P. Bissinger, J. Riede and H. Schmidbaur, *Nature* (*London*), 1991, **352**, 141.

8 A. Grohmann, J. Riede and H. Schmidbaur, *Nature* (*London*), 1990, **345**, 140.

9 J. Vicente, M. T. Chicote, J. A. Cayuelas, J. Fernandez-Baeza, P. G. Jones, G. M. Sheldrick and P. Espinet, *J. Chem. Soc., Dalton Trans.*, 1985, 1163; J. Vicente, M. T. Chicote, I. Saura-Llamas, J. Turpin and J. Fernandez-Baeza, *J. Organomet. Chem.*, 1987, **333**, 129; J. Vicente, M. T. Chicote, I. Saura-Llamas, P. G. Jones, K. Meyer-Bäse and C. F. Erdbrügger, *Organometallics*, 1988, **7**, 997; J. Vicente, M. T. Chicote and I. Saura-Llamas, *J. Chem. Soc., Dalton Trans.*, 1990, 1941; J. Vicente, M. T. Chicote, M. C. Lagunas and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1991, 2579; J. Vicente, M. T. Chicote, M. C. Lagunas and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1991, 1730; J. Vicente, M. T. Chicote and M. C. Lagunas, *Inorg. Chem.*, 1993, **32**, 3748; J. Vicente, M. T. Chicote, P. González-Herrero and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1994, 3183; J. Vicente, M. T. Chicote, P. González-Herrero, P. G. Jones and B. Ahrens, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1852.

10 M. C. Gimeno, A. Laguna, M. Laguna, F. Sanmartin and P. G. Jones, *Organometallics*, 1993, **12**, 3984; 1994, **13**, 1538; E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna and J. M. Lopez de Luzuriaga, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 87 and refs. therein.

11 W. J. Geary, *Coord. Chem. Rev.*, 1981, **7**, 81.

12 D. Gibson, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, 1970, 367.

13 G. M. Sheldrick, SHELXL 93, Program for refining crystal structures, *J. Appl. Crystallogr.*, in the press.

14 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

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