The Gold–Germanium Bond in Co-ordination Compounds of the Type $(Ph_3P)_nAuGeCl_3$ with $n = 1, 2$ or 3

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The first co-ordination compounds with gold–germanium bonds of the general formula $(Ph_3P)_nAuGeCl_3$ ($n = 1$–3) have been synthesized in high yields by the insertion of $GeCl_2$ (from its 1,4-dioxane complex) into the corresponding AuCl complexes, and structurally characterized.

Compounds with well-defined gold–germanium bonds are still exceptionally rare. Only three papers in the mid-1960s made the few initial contributions to organogermanium–gold chemistry.[1–3] However, since contacts between gold-based electrical conductors and germanium-based semiconductors are almost ubiquitous in modern electrical and electronic devices, more detailed knowledge of the characteristics of gold–germanium bonding at atomic and molecular levels is becoming increasingly important. We have therefore investigated a few simple bimetallic gold–germanium systems, focussing mainly on the structural chemistry of such species.

The easiest synthetic approach to compounds with gold–germanium bonds is the insertion of germylene-type species GeX_2 into a gold–halogen bond, thereby following analogous examples with tin(II) reagents.[4–7] Thus the reaction of $[AuCl(PPh_3)]$ with $[GeCl_2(diox)]$ (diox = 1,4-dioxane) in tetrahydrofuran (thf) gives high yields of the 1:1 addition compound $(Ph_3P)AuGeCl_3$ **1** [equation (1)]. Its composition has been confirmed by elemental analysis, chemical ionization mass spectrometry ($m/z = 638$, M^+, correct isotope pattern) and NMR spectroscopy.†

Analogous reactions in the presence of 1 or 2 equivalents of PPh_3 [equations (2) and (3)] lead to $(Ph_3P)_2AuGeCl_3$ **2** and $(Ph_3P)_3AuGeCl_3$ **3**, which have been identified along similar lines.†

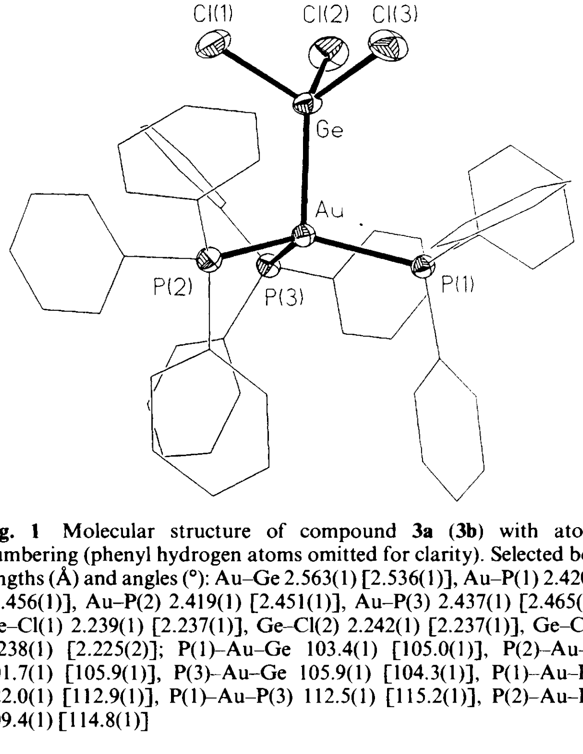

Fig. 1 Molecular structure of compound **3a** (**3b**) with atomic numbering (phenyl hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au–Ge 2.563(1) [2.536(1)], Au–P(1) 2.420(1) [2.456(1)], Au–P(2) 2.419(1) [2.451(1)], Au–P(3) 2.437(1) [2.465(1)], Ge–Cl(1) 2.239(1) [2.237(1)], Ge–Cl(2) 2.242(1) [2.237(1)], Ge–Cl(3) 2.238(1) [2.225(2)]; P(1)–Au–Ge 103.4(1) [105.0(1)], P(2)–Au–Ge 101.7(1) [105.9(1)], P(3)–Au–Ge 105.9(1) [104.3(1)], P(1)–Au–P(2) 122.0(1) [112.9(1)], P(1)–Au–P(3) 112.5(1) [115.2(1)], P(2)–Au–P(3) 109.4(1) [114.8(1)]

$$[AuCl(PPh_3)] + [GeCl_2(diox)] \xrightarrow{-diox} (Ph_3P)AuGeCl_3\ \mathbf{1} \qquad (1)$$

$$+\ PPh_3 \longrightarrow (Ph_3P)_2AuGeCl_3\ \mathbf{2} \qquad (2)$$

$$+\ 2\ PPh_3 \longrightarrow (Ph_3P)_3AuGeCl_3\ \mathbf{3} \qquad (3)$$

Spectroscopic data for complexes **1**–**3** are mutually consistent, indicating that only gradual changes in structure and bonding occur as the number of auxiliary phosphine ligands is increased from one to three. The general solubility properties rule out a fully ionic structure for the complexes.

Compounds **1** and **3** are readily crystallized, but the 1:2 complex **2** undergoes ligand redistribution upon crystallization to give a mixture of crystals of **1** and **3**. Compound **3** crystallizes in two modifications (**3a** and **3b**), which differ only in the

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† Complex **1**: to a solution of $[AuCl(PPh_3)]$ (0.58 g, 1.17 mmol) in thf (20 cm^3) solid $[GeCl_2(diox)]$ (0.27 g, 1.17 mmol) was added at 20 °C and the clear solution heated to reflux for 4 h. Crystallization from chloroform–hexane (1:1) yielded 0.65 g of **1** (87%), m.p. 195 °C (decomp.); $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 41.8 (s); ^1H NMR: δ 7.52 (m) (Found: C, 33.55; H, 2.35; Au, 30.75; Cl, 16.95; Ge, 11.05. $C_{18}H_{15}AuCl_3GeP$ requires C, 33.85; H, 2.35; Au, 30.85; Cl, 16.65; Ge, 11.40%). Complex **3**: to a solution of $[AuCl(PPh_3)]$ (0.21 g, 0.43 mmol) in thf (20 cm^3) solid $[GeCl_2(diox)]$ (0.10 g, 0.43 mmol) and PPh_3 (0.23 g, 0.86 mmol) were added at 20 °C. Crystallization from thf–toluene–hexane (5:1:10) afforded 0.47 g of **3a** (94% yield); decomposition with liberation of PPh_3; m.p. 195 °C (decomp.). (**3b** was obtained from thf–hexane.) $^{31}P-\{^1H\}$ NMR: δ 27.2 (s); ^1H NMR: δ 7.19 (m) and 7.34 (m) (Found: C, 55.75; H, 4.05; Au, 16.65; Cl, 9.40; Ge, 6.05. $C_{54}H_{45}AuCl_3GeP_3$ requires C, 55.80; H, 3.90; Au, 16.95; Cl, 9.15; Ge, 6.25%). Complex **2**: this was prepared as described for **3a**, **3b** using only 0.11 g (0.43 mmol) of PPh_3. All attempts to crystallize **2** resulted in the precipitation of a mixture of crystalline **1** and **3** (total yield 96%); liberation of PPh_3 at 180 °C, m.p. 195 °C (decomp.). $^{31}P-\{^1H\}$ NMR: δ 38.9 (s); ^1H NMR: δ 7.29 (m) and 7.41 (m) (Found: C, 47.90; H, 3.40; Au, 21.60; Cl, 12.15; Ge, 7.95. $C_{36}H_{30}AuCl_3GeP_2$ requires C, 48.00; H, 3.35; Au, 21.85; Cl, 11.80; Ge, 8.05%).

packing; **3a** is monoclinic, space group $P2_1/n$, with $Z = 4$ formula units in the unit cell.‡ The molecule (Fig. 1) features a quasi-tetrahedrally co-ordinated gold atom with a surprisingly large Au–Ge contact of 2.563(1) Å and wide P–Au–P angles, well beyond the tetrahedral standard of 109.5°. Accordingly, all Ge–Au–P angles are smaller than the tetrahedral reference value, indicating a weak Ge–Au co-ordination. More surprisingly, the Cl–Ge–Cl angles are all well below 100° [96.8(1), 98.1(1) and 98.8(1)°], suggesting the presence of a weakly co-ordinating $GeCl_3^-$ anion at a $[Au(PPh_3)_3]^+$ cation that essentially retains its P_3Au planarity. A projection along the Au–Ge axis shows that the conformation of the P_3Au–$GeCl_3$ unit is not staggered, but closer to an eclipsed P/Cl orientation with P–Au–Ge–Cl dihedral angles much smaller than 60°, also indicative of weak Au–Ge bonding. Modification **3b** is also monoclinic, space group $C2/c$, with $Z = 8$ formula units in the unit cell.

Compound **1** crystallizes in the monoclinic space group $C2/c$ with $Z = 8$ formula units in the unit cell.‡ The molecules are aggregated to give centrosymmetrical *dimers* with Au–Au contacts as short as 2.960(1) Å (Fig. 2), which is very close to the Au–Au distance in metallic gold (2.899 Å). The P–Au–Ge molecular axes deviate significantly from linearity [P–Au–Ge 168.3(1)°]. Compared with complex **3** the Au–Ge distance [2.406(1) Å] is much shorter, the Cl–Ge–Cl angles are all greater than 100° [100.6(1), 100.7(1) and 101.5(1)°] and the Ge–Cl distances are shorter. All these data indicate a much stronger Au–Ge bond, which may be taken as a standard for Au–Ge bonding at univalent, two-co-ordinate gold, although the influence of the secondary Au–Au bonding is likely to have a significant effect on the overall bonding situation at the metal atom. The projection along the PAuGe axis reveals an eclipsed Ph/Cl conformation.

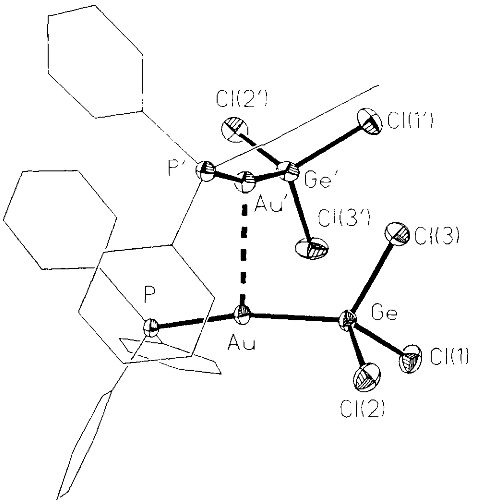

Fig. 2 View of the dimer of molecule **1**, showing the intermolecular Au···Au′ contact [2.960(1) Å] with atomic numbering (phenyl hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au–Ge 2.406(1), Au–P 2.312(1), Ge–Cl(1) 2.178(1), Ge–Cl(2) 2.187(1), Ge–Cl(3) 2.180(1), Ge–Au–P 168.3(1)

Fortunately the structure of the gold–tin complex $(Me_2PhP)_2AuSnCl_3$ has previously been determined.[5] It has a trigonal geometry at the gold centre considerably distorted towards a linear $[P–Au–P]^+$ cation and an unco-ordinated $SnCl_3^-$ anion. A similar structure is proposed for the germanium analogue **2** (in solution).

Compounds **1** and **3** are strongly *luminescent* both in the solid and in solution. The excitation and fluorescence mechanism may be quite different, but is in agreement for both cases with findings for model systems with gold–gold contacts and with trigonal symmetry, respectively.[9,10] Preliminary studies with other phosphine ligands have shown that there is a strong influence of ligand basicity on the luminscence properties of the complex, and future investigations are expected to clarify this point.

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and, through the donation of chemicals, Degussa AG and Heraeus GmbH. The authors are grateful to Mr J. Riede for establishing the X-ray data sets.

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Received 1*st June* 1995; *Communication* 5/03500G

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‡ Crystal data: **1**: $C_{18}H_{15}AuCl_3GeP$, $M_r = 638.21$, monoclinic, $a = 19.272(2)$, $b = 11.000(1)$, $c = 19.572(2)$ Å, $\beta = 104.57(1)°$, crystal dimensions 0.20 × 0.30 × 0.45 mm, space group $C2/c$, $Z = 8$, $U = 4015.7$ Å^3, $D_c = 2.111$ g cm^{-3}, $F(000) = 2400$; Enraf Nonius CAD4 diffractometer, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), $T = -62$ °C. Data were corrected for Lorentz and polarization effects as well as for absorption [empirical, $T_{min} = 0.552$, $T_{max} = 0.998$, μ(Mo-Kα) = 92.7 cm^{-1}]. 5352 Reflections measured [$(\sin\theta/\lambda)_{max} = 0.64$ Å^{-1}], 3816 'observed' [$F_o \geqslant 4\sigma(F_o)$]. Hydrogen atoms were calculated in idealized geometry and included with isotropic contributions [$U_{iso(fix)} = 0.08$ Å^2]. Non-H atoms were refined with anisotropic displacement parameters. 217 Refined parameters, R (R_w) = 0.0228 (0.0255) $\{[\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}, w = 1/\sigma^2(F_o)\}$, $\rho_{final} = +0.83/-0.90$ e Å^{-3}.

3a (**3b**): $C_{54}H_{45}AuCl_3GeP_3$, $M_r = 1162.8$, monoclinic, $a = 13.964(1)$ [19.884(1)], $b = 23.578(1)$ [20.040(1)], $c = 14.870(1)$ [24.193(1)] Å, $\beta = 92.84(1)$ [91.39(1)]°, crystal dimensions 0.25 × 0.25 × 0.40 (0.25 × 0.35 × 0.40) mm, space group $P2_1/n$ ($C2/c$), $Z = 4$ (8), $U = 4889.8$ (9637.5) Å^3, $D_c = 1.579$ (1.603) g cm^{-3}, $F(000) = 2304$ (4608), $T = -68$ °C, $T_{min} = 0.944$ (0.781), $T_{max} = 0.999$ (0.999), μ(Mo-Kα) = 39.9 (39.5) cm^{-1}. 10 128 (9912) Reflections measured [$(\sin\theta/\lambda)_{max} = 0.62$ Å^{-1}], 7707 (7205) 'observed' [$F_o \geqslant 4\sigma(F_o)$]. Hydrogen atoms were calculated in idealized geometry and included with isotropic contributions [$U_{iso(fix)} = 0.08$ Å^2]. Non-H atoms were refined with anisotropic displacement parameters. 559 (559) Refined parameters, R [R_w] = 0.0221 (0.0274) [0.0245 (0.0285)] $\{[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}, w = 1/\sigma^2(F_o)\}$, $\rho_{final} = +0.43/-0.46$ (2.44/−0.80, located at Au atom) e Å^{-3}. The structures were solved by direct methods and refined by full matrix least-squares calculations (SHELXTL-PLUS).[8] Atomic co-ordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See 'Instructions for Authors', *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.