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Bis- and tris-(trichlorogermyl)gold(I) anions in their salts with cyclic dications $[Au_2(Ph_2PCH_2PPh_2)_2]^{2+}$ and $[Au_2(Ph_2PCH_2CH_2PPh_2)_2]^{2+}$

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Insertion of $GeCl_2$ into the Au–Cl bonds of $[(AuCl)_2(dppm)]$ or $[(AuCl)_2(dppe)]$ (dppm = $Ph_2PCH_2PPh_2$ and dppe = $Ph_2PCH_2CH_2PPh_2$) leads to the formation of bis(trichlorogermyl) complexes $[Au_2(dppm/e)_2]^{2+}[Au(GeCl_3)_2]_2^{-}$, of which the dppm complex undergoes slow decomposition in solution to give $[Au_2(dppm)_2][Au(GeCl_3)_3]$, where the gold atom of the dianion is co-ordinated solely to three germanium atoms.

Until recently the molecular chemistry of compounds with Au–Ge bonds[1,2] was limited to a few isolated examples, and structural data were not available. A new synthetic approach to this family of compounds *via* the insertion of germylene units into Au–Cl bonds is now giving ready access to gold(I) complexes with germyl ligands with a variety of co-ordination numbers and geometries.[3–5] This synthetic method was adopted from gold–tin chemistry, where it was first applied very successfully in a number of preparations.[6–8] As a continuation of our studies in this area we have recently extended the synthetic and structural investigations to complexes of the difunctional, potentially bridging or chelating phosphine ligands bis(diphenylphosphino)-methane and -ethane [dppm and dppe, respectively]. The dinuclear chlorogold(I) complexes of these ligands are known compounds[9,10] which have been widely used as synthons in the co-ordination chemistry of univalent gold. Their structures have been established by X-ray diffraction methods (**1**, **2**)[9,11] and are prototypes of intra- and inter-molecular auriophilic[12] (Au···Au) interactions, respectively. It is important to note that no ionic, isomeric forms other than the molecular structures **1** and **2** were detected in any of the previous studies.

Treatment of $[(AuCl)_2(dppm)]$ **1** or $[(AuCl)_2(dppe)]$ **2** with 2 equivalents of $[GeCl_2(diox)]$ (diox = 1,4-dioxane) in chloroform at ambient temperature gives a yellow slurry from which almost quantitative yields of the bis(trichlorogermyl) complexes (**3**, **4**) can be isolated by filtration [equation (1)].†

$$\underset{\mathbf{1},\mathbf{2}}{[(\mathrm{AuCl})_2(\mathrm{dppm/e})]} + 2\,[\mathrm{GeCl_2(diox)}] \longrightarrow \underset{\mathbf{3},\mathbf{4}}{[\mathrm{Au_2(dppm/e)_2}][\mathrm{Au(GeCl_3)_2}]_2} + 2\,\mathrm{diox} \qquad (1)$$

The dppe complex **4** is only sparingly soluble in acetonitrile and insoluble in chloroform or tetrahydrofuran. The solid, its slurries and the dilute solutions in MeCN are stable to air and moisture. Polycrystalline samples decompose at 245 °C. The ^1H and ^{31}P-$\{^1H\}$ NMR spectra of CD_3CN solutions (25 °C) show broad, poorly resolved CH_2 (δ_H 2.38) and Ph resonances (δ_H 7.70) and a singlet at δ_P 38.0, respectively. The mass spectra [field desorption (FD), cations] indicate the presence of species $[Au_2(dppe)_2]^{2+}$ and $[Au_2Cl(dppe)_2]^{+}$ as the parent ions, together with $[Au(dppe)_2]^{+}$ and $[AuCl(dppe)_2]^{+}$.

These experimental results suggest an ionic structure composed of the complexes $[Au_2(dppe)_2]^{2+}$ and 2 $[Au(GeCl_3)_2]^{-}$, but there is no final proof for this assumption, since no single crystals of **4** could be grown, and solubility of it in standard solvents is too low for further, more detailed solution studies.

The yellow dppm complex **3** is also stable as a solid and decomposes at 202 °C. It is more soluble in acetonitrile and chloroform than **4**, and therefore the results of the spectroscopic studies in these solvents are more meaningful, although slow decomposition ensues after a few hours at 25 °C. The NMR shifts† of **3** are very similar to those found for other compounds containing the dication $[Au_2(dppm)_2]^{2+}$.[14] The field desorption mass spectrum (cations) of **3** has this dication as the parent ion.

These data, together with the microanalysis results, are again in good agreement with an ionic structure $[Au_2(dppm)_2][Au(GeCl_3)_2]_2^{-}$ **3**, but the poor crystal quality of all solid samples prevented a corroboration by an X-ray diffraction study. However, when solutions of compound **3** in CD_3CN were left standing at ambient temperature (in a tightly closed NMR tube) for several weeks, a small number of colourless crystals separated, which were amenable to a single-crystal X-ray investigation. This study showed that the original compound had slowly been transformed into a different salt (**5**) with the same dication, but associated with the novel tris(trichlorogermyl)gold(I) dianion, $[Au_2(dppm)_2][Au(GeCl_3)_3]$ [equation (2)].

$$\underset{\mathbf{3}}{[\mathrm{Au_2(dppm)_2}][\mathrm{Au(GeCl_3)_2}]_2} \longrightarrow \underset{\mathbf{5}}{[\mathrm{Au_2(dppm)_2}][\mathrm{Au(GeCl_3)_3}]} + \text{‘}\mathrm{AuGeCl_3}\text{’} \qquad (2)$$

Crystals of compound **5** are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell.‡ The lattice is composed of cyclic dications $[Au_2(dppm)_2]^{2+}$ with the eight-membered ring in a boat conformation (Fig. 1). As in other compounds containing this type of dication,[14,17,18] there is a short transannular Au···Au contact [Au(1)–Au(2) 2.9736(4) Å] and the angles P(1)–Au(1)–P(3) and P(2)–Au(2)–P(4) deviate significantly

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† Compound **3**: a slurry of **1** (0.28 g, 0.33 mmol) in chloroform (10 cm^3) was treated with small portions of $[GeCl_2(diox)]$[13] (0.15 g, 0.66 mmol) at 20 °C with stirring. Compound **1** slowly dissolves and a yellow solution is formed, from which the product **3** is precipitated after 2 h by addition of hexane (10 cm^3); yield 0.33 g (88%), m.p. 202 °C (decomp.). ^1H NMR (CD_3CN, 25 °C): δ 4.22 (t, $^2J_{HP}$ = 6.5 Hz, 2 H, CH_2), 7.57 (m, 20 H, Ph). ^{31}P-$\{^1H\}$ NMR (CD_3CN, 25 °C): δ 35.3 (s). Mass spectrum: *m/z* 581 {100%, $[Au_2(dppm)_2]^{2+}$} (Found: C, 26.7; H, 2.05; Cl, 18.35. $C_{25}H_{22}Au_2Cl_6Ge_2P_2$ (1136.28) requires C, 26.45; H, 1.95; Cl, 18.70%). Compound **4**: as described for **3**, $[(AuCl)_2(dppe)]$ **2** (0.24 g, 0.28 mmol) is treated with $[GeCl_2(diox)]$ (0.13 g, 0.56 mmol) to yield 0.31 g (96%) of **4**, m.p. 245 °C (decomp.). ^1H NMR (CD_3CN, 25 °C): δ 2.38 (br s, 4 H, CH_2), 7.70 (m, 20 H, Ph). ^{31}P-$\{^1H\}$ NMR (CD_3CN, 25 °C): δ 38.0 (s). Mass spectrum: *m/z* 1226 {12, $[Au_2Cl(dppe)_2]$}, 1029 {100 $[AuCl(dppe)_2]^{+}$}, 994.62 {62, $[Au(dppe)_2]^{+}$}, 595 {14% $[Au_2(dppe)_2]^{2+}$}. Compound **5**: colourless block-like crystals of **5** formed at the wall of a tightly closed NMR tube after keeping solutions of compound **3** in CD_3CN at 20 °C for several weeks. The estimated yield is less than 10%. By-products left in solution could not be identified.

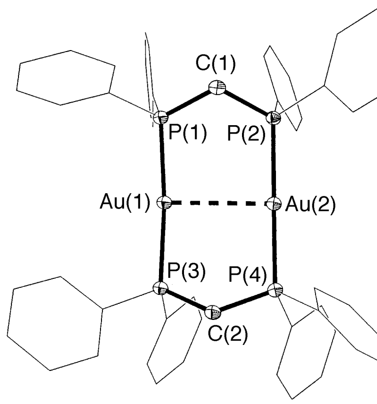

Fig. 1 Structure of the dication $[Au_2(dppm)_2]^{2+}$ in compound **5** with atomic numbering (ORTEP,[16] 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au(1)–Au(2) 2.9736(4), Au(1)–P(1) 2.295(1), Au(1)–P(3) 2.302(1), Au(2)–P(2) 2.329(1), Au(2)–P(4) 2.321(1); P(1)–Au(1)–P(3) 172.50(5), P(2)–Au(2)–P(4) 175.45(4)

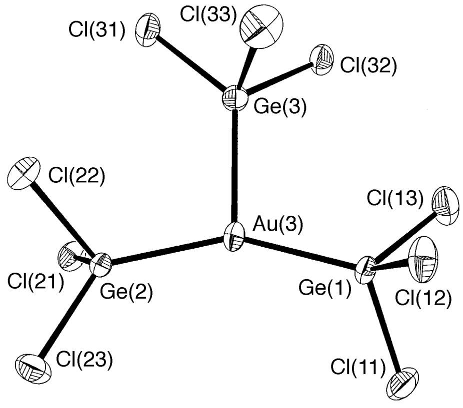

Fig. 2 Structure of the dianion $[Au(GeCl_3)_3]^{2-}$ in compound **5** with atomic numbering (ORTEP,[16] 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Au(3)–Ge(1) 2.4150(6), Au(3)–Ge(2) 2.4284(6), Au(3)–Ge(3) 2.5351(7); Ge(1)–Au(3)–Ge(2) 153.12(2), Ge(1)–Au(3)–Ge(3) 104.97(2), Ge(2)–Au(3)–Ge(3) 101.72(2)

from 180° owing to this interaction [172.50(5) and 175.45(4)°, respectively]. There are sub van der Waals contacts of gold atoms Au(1) and Au(2) with the chlorine atoms of the counter ion, but this is not unusual, and there are many parallels for such interionic contacts in other gold complexes of dppm.[17–19]

The dianions $[Au(GeCl_3)_3]^{2-}$ have three-co-ordinate gold atoms in a planar geometry between a T- and a Y-shaped pattern (Fig. 2). The gold co-ordination is homoleptic in that the metal atom Au(3) is solely bound to germanium atoms, but the three Au–Ge distances and Ge–Au–Ge angles each fall in two categories such that the $AuGe_3$ unit approaches local C_{2v} symmetry: Au(3)–Ge(1) 2.4150(6), Au(3)–Ge(2) 2.4284(6), Au(3)–Ge(3) 2.5351(7) Å; Ge(1)–Au(3)–Ge(2) 153.12(2), Ge(1)–Au(3)–Ge(3) 104.97(2), Ge(2)–Au(3)–Ge(3) 101.72(2)°. The structure of the dianion may thus be taken as derived from a quasi-linear $[Au(GeCl_3)_2]^-$ anion which has undergone distortion owing to the approach of a third $[GeCl_3]^-$ anion perpendicular to the original principal axis [Ge(1)–Au(3)–Ge(2)]. The structural result also lends support to the formula (**3**) proposed for the anionic component of the precursor compound.

The nine Ge–Cl bond lengths are within the range 2.184(2) [for Ge(2)–Cl(23)] to 2.273(1) Å [Ge(3)–Cl(32)], but there is no obvious reason for this spread of the values, and interionic contacts may play a decisive role. This is probably also true for the nine Cl–Ge–Cl angles in the range 96.67(5)–100.47(6)°, which are generally much smaller than the tetrahedral standard. This is in agreement with all data presently available for Au–$GeCl_3$ complexes.[3–5]

The dianion in compound **5** is a unique example of a species in which gold(I) accommodates three anionic groups with a Group 14 element as the donor atom. Organogold chemistry has no precedent for this, and analogous silicon, tin or lead compounds are also unknown. Except for some ill characterized polycyano complexes present in cyanide-rich aqueous solutions there appears to be no other case with gold(I) as the central atom in an anion with a negative charge higher than −1.

All gold–germanium compounds reported recently in the literature are strongly photoluminescent.[3–5] Complexes **3**–**5** are no exception and strong visible emission is observed upon UV irradiation of the polycrystalline solids. The theory of the luminescence of this type of compounds is not sufficiently developed, and a more detailed study will be necessary to trace the origin and the mechanism of the optical phenomena.

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References

1 F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 1962, 2658.
2 F. Glockling and M. D. Wilbey, *J. Chem. Soc. A*, 1968, 2168.
3 A. Bauer, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1995, 2919.
4 A. Bauer and H. Schmidbaur, *J. Am. Chem. Soc.*, 1996, **118**, 2919.
5 A. Bauer, Ph.D. Thesis, Technical University of Munich, 1996.
6 J. A. Dilts and M. P. Johnson, *Inorg. Chem.*, 1966, **5**, 2079.
7 W. Clegg, *Acta Crystallogr., Sect. B*, 1978, **34**, 278.
8 D. M. Mingos, H. R. Powell and T. L. Stolberg, *Transition Met. Chem.*, 1992, **17**, 334.
9 H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama and G. Huttner, *Chem. Ber.*, 1977, **110**, 1748.
10 F. Cariati, L. Naldini, G. Simonetta and L. Malatesta, *Inorg. Chim. Acta*, 1967, **1**, 315.
11 P. A. Bates and J. M. Waters, *Inorg. Chim. Acta*, 1985, **98**, 125.
12 H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11; *Chem. Soc. Rev.*, 1996, 391.
13 N. A. Viktorov, T. K. Gar and V. A. Mironov, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1985, **55**, 1079.
14 M. N. I. Khan, C. King, D. D. Heinrich, J. P. Fackler, jun. and L. C. Porter, *Inorg. Chem.*, 1989, **28**, 2150.
15 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
16 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
17 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751.
18 H. Schmidbaur, T. Pollok, R. Herr, F. E. Wagner, R. Bau, J. Riede and G. Müller, *Organometallics*, 1986, **5**, 566.
19 J.-C. Wang and L.-K. Liu, *Acta Crystallogr., Sect. C*, 1994, **50**, 704.

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‡ Crystal data_for **5**. $C_{50}H_{44}Au_3Cl_9Ge_3P_4$, $M_r = 1896.45$, monoclinic, space group $P1$ (no. 2), $a = 11.458(1)$, $b = 11.564(1)$, $c = 22.395(3)$ Å, $\alpha = 93.55(1)$, $\beta = 95.03(1)$, $\gamma = 102.01(1)°$, $U = 2881.4(5)$ Å^3, crystal dimensions 0.18 × 0.20 × 0.40 mm, $Z = 2$, $D_c = 2.186$ g cm^{-3}, $F(000) = 1780$, $T = -74$ °C, Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Data were corrected for Lorentz and polarization effects as well as for absorption [empirical, $T_{min} = 0.7526$, $T_{max} = 0.9997$, μ(Mo-Kα) = 97.16 cm^{-1}]. 9872 Reflections measured, 9871 unique reflections from which 9864 reflections were used for refinement. Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated in idealized geometry and their thermal parameters were tied to the adjacent carbon atom by a factor of 1.5. 622 Refined parameters, $wR2$ [used reflections] = 0.0543, $R1$ [$F_o \geqslant 4\sigma(F_o)$, 8832 reflections] = 0.0247 $\{wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{\frac{1}{2}}$, $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $w = q/2\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$; $a = 0.0247$, $b = 4.9355\}$, $\rho_{final} = +1.17, -1.17$ e Å^{-3} [located at the heavier atoms]. The structure was solved by direct methods and refined by full-matrix least-squares calculations (SHELXTL 93[15]). Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instuctions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/454.