

The Trichlorogermanite(II) Anion and its Gold(I) Complexes

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Tetraphenylphosphonium trichlorogermanite(II) (**1**) has been prepared (as a reference compound) from $\text{Ph}_4\text{P}^+ \text{Cl}^-$ and GeCl_2 (dioxane) in tetrahydronaphthalene. Its structure has been determined by single crystal X-ray methods. The lattice contains independent monomeric GeCl_3^- anions (Ge-Cl distances between 2.290 and 2.320 Å, Cl-Ge-Cl angles between 95.33 and 98.27°). Treatment of $(\text{Ph}_3\text{As})\text{AuCl}$ with GeCl_2 (dioxane) affords $(\text{Ph}_3\text{As})\text{AuGeCl}_3$ in high yields as a germylene insertion product (**2**). The complex is a dimer in the crystal with a short Au--Au contact of 2.9415(4) Å and bent As-Au-Ge axes [169.353(13)°]. The GeCl_3 ligand has shorter Ge-Cl bonds [2.175 to 2.183 Å] and wider Cl-Ge-Cl angles than in the free anion [100.9 to 101.9°]. The analogous reaction with $\text{CH}_2(\text{AsPh}_2\text{AuCl})_2$ leads only to a mono-insertion product in the form of a salt with $\{[\text{CH}_2(\text{AsPh}_2)_2\text{Au}]\}_2^{2+}$ dications and two $[\text{ClAuGeCl}_3]^-$ anions (**3**). In the lattice these three ions form a centrosymmetrical tetranuclear unit through short Au--Au contacts. The resulting z-shaped Au--Au--Au--Au chain has distances of 3.0499(6) (twice) and 3.1613(8) Å and angles of 118.833(8)° (twice). The geometry of the GeCl_3 units is similar to that in **2**. $\{(\text{Et}_3\text{N})\text{Au}[\text{P}(o\text{-Tol})_3]\}^+ \text{PF}_6^-$ (**4**) was obtained as a by-product in several reactions with the bulky phosphine and where NEt_3 was used as a base. The crystals contain two crystallographically independent cations with a similar core structure, but different conformations of the substituents. Both the P-Au and the N-Au bonds are elongated owing to steric effects.

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