

### 511. Triphenylgermyl Complexes of Copper, Silver, and Gold.

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Triphenylgermyl-lithium,  $\text{Ph}_3\text{GeLi}$ , and the tertiary phosphine halide derivatives,  $\text{R}_3\text{PMX}$ , of copper(I), silver(I), and gold(I) form complexes of the type  $\text{Ph}_3\text{Ge}\cdot\text{M}(\text{PR}_3)_n$ . The stability is greatest for gold(I) and least for copper(I). The Ge-M bond is readily cleaved by 1,2-dibromethane giving mainly ethylene,  $\text{Ph}_3\text{GeBr}$  and  $\text{R}_3\text{PMBR}$ . Phenyl-lithium also cleaves the Ge-Au bond in  $\text{Ph}_3\text{Ge}\cdot\text{Au}, \text{PPh}_3$ , forming  $\text{PhAuPPh}_3$  and the salt  $\text{Li}[(\text{Ph}_3\text{Ge})_2\text{Au}], 4\text{Et}_2\text{O}$ , which is readily converted into the stable tetra-ethylammonium salt,  $\text{Et}_4\text{N}[(\text{Ph}_3\text{Ge})_2\text{Au}]$ .

ORGANOGERMANIUM compounds in which the germanium atom is also bonded to a non-transition metal have been known for a number of years. Examples include  $\text{Ph}_3\text{Ge}\cdot\text{SiPh}_3$ ,<sup>1</sup>  $\text{Ph}_3\text{Ge}\cdot\text{SnPh}_3$ ,<sup>2</sup>  $(\text{Ph}_3\text{Ge})_3\text{B}^3$ , and  $\text{Me}_4\text{N}[\text{Ph}_3\text{Ge}\cdot\text{BPh}_3]$ .<sup>4</sup> We have succeeded in preparing compounds in which triphenylgermyl groups are bonded to copper(I), silver(I), and gold(I), where the Group IB metal is also co-ordinated to a tertiary phosphine. The formation of these compounds involves the interaction of triphenylgermyl-lithium and a tertiary phosphine-metal halide complex in an inert solvent:



where M = Cu(I), Ag(I), or Au(I), and  $n = 1$  for Au and 1 or 3 for Cu and Ag.

The stability of these complexes is greatest for gold and least for copper. Thus the gold compound,  $\text{Ph}_3\text{Ge}\cdot\text{AuPPh}_3$ , is stable to air and water; it separates from benzene with one molecule of solvent, or from acetone in the unsolvated form. Both the copper and the silver analogue are susceptible to hydrolysis and oxidation at room temperature, especially when in solution. There is a striking difference in stability depending on the structure of the phosphine ligand. The gold-triphenylphosphine complex is considerably more stable than the monomeric trimethylphosphine derivative,  $\text{Ph}_3\text{Ge}\cdot\text{AuPMe}_3$ . Diethylphenylphosphinemonoiodosilver gave a complex of such low stability that it deposited silver on attempted purification from benzene. Triphenylphosphinemonoiodosilver also gave a highly insoluble and rather unstable compound with triphenylgermyl-lithium, but the addition of an excess of triphenylphosphine or the use of tris(triphenylphosphine)monoiodosilver,  $(\text{Ph}_3\text{P})_3\text{AgI}$ , produced the complex,  $\text{Ph}_3\text{Ge}\cdot\text{Ag}(\text{PPh}_3)_3$  which is isolable, but unstable in dry air. Similarly triphenylphosphinemonochlorocopper(I) gave a highly

<sup>1</sup> Gilman and Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 4675.

<sup>2</sup> Gilman and Gerow, *J. Amer. Chem. Soc.*, 1956, **78**, 5823.

<sup>3</sup> Smith and Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 1418.

<sup>4</sup> Seyferth, Raab, and Grim, *J. Org. Chem.*, 1961, **26**, 3034.

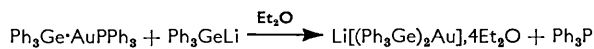
insoluble complex which fumed on exposure to air, but with an excess of triphenylphosphine the complex,  $\text{Ph}_3\text{Ge}\cdot\text{Cu}(\text{PPh}_3)_3$  was obtained in low yield and with some difficulty.

The low solubility of some of these compounds in benzene led us to attempt molecular-weight determinations in 1,2-dibromethane, but for each of the complexes described a rapid, though not quantitative, reaction occurred in which the 1,2-dibromethane behaved as a mild brominating agent, cleaving the metal-metal bond with simultaneous formation of ethylene:



Ethyl bromide and *o*-dichlorobenzene failed to react under similar conditions.

It was expected that phenyl-lithium would also cleave the germanium-gold bond in  $\text{Ph}_3\text{Ge}\cdot\text{AuPPh}_3$ , forming triphenylgermyl-lithium and triphenylphosphinemonophenyl-gold(I). However, in ether solution an insoluble and unstable white solid was produced which deposited gold on storage. This compound contained ether but no triphenylphosphine, and an equimolar ratio of gold to lithium. The limited analyses possible were compatible with the formulation:  $\text{Li}[(\text{Ph}_3\text{Ge})_2\text{Au}]_4\text{Et}_2\text{O}$ . Addition of tetraethylammonium iodide gave the well crystalline and stable salt,  $\text{Et}_4\text{N}[(\text{Ph}_3\text{Ge})_2\text{Au}]$ , which was very soluble in acetone and relatively insoluble in ethanol. Hydrolysis of the original lithium salt,  $\text{Li}[(\text{Ph}_3\text{Ge})_2\text{Au}]_4\text{Et}_2\text{O}$ , gave gold, lithium hydroxide, and hexaphenyldigermene, whilst the mother-liquors from the preparation yielded triphenylphosphinemonophenyl-gold(I),  $\text{Ph}_3\text{PAuPh}$ . Addition of benzyl chloride to the mother-liquors failed to produce benzyltriphenylgermane; hence the solution did not contain appreciable quantities of triphenylgermyl-lithium. It seems likely that this reaction involves first cleavage of the germanium-gold bond by addition of phenyl-lithium:  $\text{Ph}_3\text{Ge}\cdot\text{AuPPh}_3 + \text{PhLi} \longrightarrow \text{Ph}_3\text{GeLi} + \text{PhAuPPh}_3$ ; followed by rapid addition of triphenylgermyl-lithium to the original compound with displacement of the triphenylphosphine:



When triphenylgermyl-lithium in ethylene glycol dimethyl ether was added to the preformed germanium-gold complex a somewhat more stable salt was precipitated. Analytical data were difficult to obtain owing to contamination with lithium methoxide formed in the preparation of the triphenylgermyl-lithium, but the structure,  $\text{Li}[(\text{Ph}_3\text{Ge})_2\text{Au}]_4\text{C}_4\text{H}_{10}\text{O}_2$ , analogous to the diethyl ether solvate, is probable since addition of tetraethylammonium iodide again gave the stable unsolvated salt,  $\text{Et}_4\text{N}[(\text{Ph}_3\text{Ge})_2\text{Au}]$ .

#### EXPERIMENTAL

M.p.s are corrected. Reactions on sensitive compounds were carried out in an atmosphere of dry oxygen-free nitrogen.

*Triphenylphosphinemonochlorocopper(I)*.—Triphenylphosphine (18.5 g.) and copper(I) chloride (7 g.) were refluxed in benzene (300 c.c.) for 12 hr.; *triphenylphosphinemonochlorocopper(I)*, m. p. 194—203°, separated (Found: C, 60.0; H, 4.4.  $\text{C}_{18}\text{H}_{15}\text{ClCuP}$  requires C, 59.8; H, 4.2%).

*Triphenylphosphinemonoiodosilver(I) and Tris(triphenylphosphine)monoiodosilver(I)*.—Silver iodide (7.03 g.) in saturated potassium iodide solution was added to triphenylphosphine (7.85 g.) in acetone (150 c.c.). The *monophosphine complex* (14 g.), which was precipitated immediately, was insoluble in all solvents; it had m. p. 298—307° [Found: C, 44.4; H, 3.5; AgI (by sublimation of the phosphine), 46.3.  $\text{C}_{18}\text{H}_{15}\text{AgIP}$  requires C, 43.5; H, 3.0; AgI, 47.2%]. The *trisphosphine complex*, m. p. 169—170°, was obtained by crystallisation of this material from acetone containing an excess of triphenylphosphine (Found: C, 64.2; H, 4.9; AgI, 23.5.  $\text{C}_{54}\text{H}_{45}\text{AgIP}_3$  requires C, 63.5; H, 4.4; AgI, 23.0%).

*Triphenylgermyl-lithium*.—Solutions of triphenylgermyl-lithium in ethylene glycol dimethyl ether were prepared by the cleavage of either hexaphenyldigermene<sup>5</sup> (6.0 g., 0.01 mole) or tetraphenylgermane<sup>1</sup> (3.7 g., 0.0098 mole) with lithium shot (1.0 g.). In both cases we assumed a 60% yield of triphenylgermyl-lithium.

<sup>5</sup> Gülman and Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 5509, 5740.

*Triphenylgermyltriphenylphosphinegold*(I),  $\text{Ph}_3\text{Ge}\cdot\text{AuPPh}_3$ .—To a stirred suspension of triphenylphosphinemonochlorogold(I) (6.0 g., 0.012 mole) in ethylene glycol dimethyl ether (75 c.c.) was added dropwise triphenylgermyl-lithium (0.012 mole) in the same solvent (40 c.c.). A dense pale brown solid separated and, after 30 min., the mixture was hydrolysed and the crude *triphenylgermyltriphenylphosphinegold*(I) separated. This crystallised from benzene as colourless plates containing 1 mol. of solvent, with m. p.  $185^\circ$  (complete decomp.) [Found: C, 60.8; H, 4.7; Au, 23.2; Ge, 9.0;  $\text{C}_6\text{H}_6$  (loss at  $110^\circ$  *in vacuo*), 9.4.  $\text{C}_{42}\text{H}_{36}\text{AuGeP}$  (*i.e.*,  $\text{Ph}_3\text{Ge}\cdot\text{AuPPh}_3\cdot\text{C}_6\text{H}_6$ ) requires C, 59.9; H, 4.3; Au, 23.4; Ge, 8.6;  $\text{C}_6\text{H}_6$ , 9.3%]. Crystallisation from acetone gave the unsolvated compound (Found: C, 56.9; H, 4.5; Au, 25.6.  $\text{C}_{36}\text{H}_{30}\text{AuGeP}$  requires C, 56.7; H, 4.0; Au, 25.8%).

*Triphenylgermyl-trimethylphosphinegold*(I),  $\text{Ph}_3\text{Ge}\cdot\text{AuPMe}_3$ .—This compound was prepared from trimethylphosphinemonochlorogold(I) (3.1 g., 0.01 mole) as described above. It formed colourless needles from acetone (nitrogen atmosphere) which decomposed without melting at  $125$ – $130^\circ$  [Found: C, 44.7; H, 4.1; Au, 33.3%; *M* (freezing benzene), 614.  $\text{C}_{21}\text{H}_{24}\text{AuGeP}$  requires C, 43.7; H, 4.2; Au, 34.2%; *M*, 577].

*Triphenylgermyltris(triphenylphosphine)silver*(I),  $\text{Ph}_3\text{Ge}\cdot\text{Ag}(\text{PPh}_3)_3$ .—To a stirred suspension of triphenylphosphinemoniodosilver (5.0 g., 0.01 mole) and triphenylphosphine (5.24 g., 0.02 mole) in ethylene glycol dimethyl ether (100 c.c.) was added triphenylgermyl-lithium (0.01 mole) in the same solvent (40 c.c.). The resulting heavy brown solid was filtered under nitrogen and extracted at room temperature with ethylene glycol dimethyl ether (500 c.c.) in which it was almost completely soluble. Evaporation of the solvent to half volume (under a vacuum at room temperature) followed by cooling to  $-30^\circ$  gave *triphenylgermyltris(triphenylphosphine)silver*(I) as very pale green crystals, m. p.  $167$ – $170^\circ$  (decomp.), containing two molecules of solvent of crystallisation [Found: C, 69.3; H, 4.9; Ag, 7.8;  $\text{Ph}_3\text{P}$ , 57.7;  $\text{C}_4\text{H}_{10}\text{O}_2$ , 13.6.  $\text{C}_{80}\text{H}_{80}\text{AgGeO}_4\text{P}_3$ , *i.e.*,  $\text{Ph}_3\text{Ge}\cdot\text{Ag}(\text{PPh}_3)_3\cdot 2\text{C}_4\text{H}_{10}\text{O}_2$ , requires C, 69.7; H, 5.8; Ag, 7.8;  $\text{Ph}_3\text{P}$ , 56.6;  $\text{C}_4\text{H}_{10}\text{O}_2$ , 13.1%]. The solvent was removed at  $120^\circ$  *in vacuo* and estimated as gas with infrared characterisation.

In a similar experiment without the addition of an excess of triphenylphosphine a pale brown powder (5.7 g.) was isolated which was insoluble in common solvents and decomposed rapidly to silver on exposure to the atmosphere. This material, presumably  $\text{Ph}_3\text{Ge}\cdot\text{AgPPh}_3$  dissolved in a solution of triphenylphosphine in ethylene glycol dimethyl ether to yield the same trisphosphine compound, m. p.  $165$ – $170^\circ$ .

*Triphenylgermyltris(triphenylphosphine)copper*(I),  $\text{Ph}_3\text{Ge}\cdot\text{Cu}(\text{PPh}_3)_3$ .—This compound was obtained from triphenylphosphinemonochlorocopper(I) (3.61 g., 0.01 mole), triphenylphosphine (5.24 g., 0.02 mole), and triphenylgermyl-lithium (0.01 mole) in ethylene glycol dimethyl ether (100 c.c.). Crystallisation from the same solvent gave triphenylgermyltris(triphenylphosphine)-copper(I), decomp.  $130^\circ$ , slightly contaminated with lithium chloride (Found: C, 71.5; H, 5.4; Cu, 5.4. Calc. for  $\text{C}_{72}\text{H}_{60}\text{CuGeP}_3$ : C, 74.9; H, 5.2; Cu, 5.5%). In the absence of an excess of triphenylphosphine a dark grey solid (6.3 g.; decomp.  $168^\circ$ ), presumably  $\text{Ph}_3\text{Ge}\cdot\text{CuPPh}_3$ , was obtained which fumed in air and was insoluble in organic solvents. Addition of an excess of triphenylphosphine gave the trisphosphine complex in small yield.

*Reactions with 1,2-Dibromethane.*—(a) 1,2-Dibromethane (20 c.c.) was added to triphenylgermyltriphenylphosphinegold(I) (0.318 g.) in a slow stream of nitrogen. The emergent gases were passed through two traps, the first at  $-78^\circ$  and the second at liquid-air temperature. After 30 min. the contents of the liquid-air trap were purified by fractional condensation and the ethylene measured (7.1 N-c.c., 75%; infrared identification). The clear ethylene bromide solution was evaporated and the colourless residue extracted with hot ethanol, giving *triphenylphosphinemonobromogold*(I) (0.13 g.), m. p.  $253$ – $254^\circ$  (decomp.) (Found: C, 39.5; H, 3.1; Au, 36.8.  $\text{C}_{18}\text{H}_{15}\text{AuBrP}$  requires C, 40.1; H, 2.8; Au, 36.6%). The ethanol filtrate from the above was evaporated and the residue sublimed ( $100^\circ/10^{-3}$  mm.), giving bromotriphenylgermane, m. p. and mixed m. p.  $134$ – $136^\circ$ .

(b) Triphenylgermyltrimethylphosphinegold(I) (0.260 g.) similarly gave ethylene (5.5 N-c.c., 51%), trimethylphosphinemonobromogold(I), m. p.  $214^\circ$  (decomp.) (Found: Au, 55.2. Calc. for  $\text{C}_3\text{H}_9\text{AuBrP}$ : Au, 55.8%), and bromotriphenylgermane.

(c) Triphenylgermyltris(triphenylphosphine)silver(I) (0.672 g.) in a similar reaction gave ethylene (12.6 N-c.c., 65%). The white residue, on extraction with light petroleum (b. p.  $40$ – $60^\circ$ ), gave bromotriphenylgermane, m. p.  $134$ – $136^\circ$ . The part insoluble in petroleum crystallised from acetone, giving colourless needles of *bis(triphenylphosphine)monobromosilver*,

$(\text{Ph}_3\text{P})_2\text{AgBr}$ , which begins to lose triphenylphosphine at  $179^\circ$  with partial melting (Found: C, 60.5; H, 3.4.  $\text{C}_{36}\text{H}_{30}\text{AgBrP}_2$  requires C, 60.7; H, 4.2%).

(d) Triphenylgermyltris(triphenylphosphine)copper(I) in a similar experiment gave a 30% yield of ethylene, and the grey sticky residue was extracted with methanol. The methanol-insoluble part gave colourless *tris(triphenylphosphine)bis(monobromocopper)*,  $(\text{Ph}_3\text{P})_3\text{Cu}_2\text{Br}_2$ , m. p. 236—237° (from propan-1-ol) (Found: C, 59.5; H, 4.7; Cu, 12.1.  $\text{C}_{54}\text{H}_{45}\text{Br}_2\text{Cu}_2\text{P}_3$  requires C, 60.4; H, 4.2; Cu, 11.8%). The fraction soluble in methanol gave some triphenylphosphine by sublimation and bis(triphenylgermanium) oxide, m. p. 184—185° (from light petroleum) (Found: C, 69.4; H, 5.5. Calc. for  $\text{C}_{36}\text{H}_{30}\text{Ge}_2\text{O}$ : C, 69.3; H, 4.8%). The oxide was probably formed by hydrolysis of bromotriphenylgermane in the working-up process.

*Triphenylgermyltriphenylphosphinegold(I) and Phenyl-lithium.*—Phenyl-lithium (3.38 mmoles) in ether was added dropwise to a suspension of triphenylgermyltriphenylphosphinegold(I) (2.1 g., 2.75 mmoles) in ether (50 c.c.). After 1 hr. the pink precipitate (1.2 g.) was collected under nitrogen and washed with ether. This unstable compound was hydrolysed readily to lithium hydroxide, gold, and hexaphenyldigermane, m. p.  $340^\circ$ ; its infrared spectrum indicated the presence of ether and the absence of triphenylphosphine {Found: Au, 17.3; Li (as LiOH), 0.62.  $\text{C}_{52}\text{H}_{70}\text{AuGe}_2\text{LiO}_4$ , i.e.,  $\text{Li}[(\text{Ph}_3\text{Ge})_2\text{Au}]_4\text{Et}_2\text{O}$ , requires Au, 17.8; Li, 0.63%}. An ethanol solution of this *ether complex* (0.4 g.) was added to solid tetraethylammonium iodide (0.2 g.) and the pale yellow product, *tetraethylammonium bis(triphenylgermyl)aurate(I)*, was purified by crystallisation from warm acetone as pale yellow plates (0.3 g.) {Found: C, 56.7; H, 5.6; Au, 20.8; Ge, 15.6.  $\text{C}_{44}\text{H}_{50}\text{AuGe}_2\text{N}$ , i.e.,  $\text{Et}_4\text{N}[(\text{Ph}_3\text{Ge})_2\text{Au}]$ , requires C, 5.67; H, 5.4; Au, 21.1; Ge, 15.5%}. Tetraethylammonium bis(triphenylgermyl)aurate(I) is insoluble in water. It darkens rapidly above  $150^\circ$  and melts with decomposition at  $195$ — $200^\circ$ .

The ethereal filtrate from the original reaction was treated with benzyl chloride (0.36 g.). Extraction of the oily residue with propanol gave triphenylphosphinemonophenylgold(I) (0.4 g., 29%), m. p.  $152^\circ$  (decomp.) (Found: Au, 36.0. Calc. for  $\text{C}_{24}\text{H}_{20}\text{AuP}$ : Au, 36.7%). No benzyltriphenylgermane was isolated.

*Triphenylgermyltriphenylphosphinegold(I) and Triphenylgermyl-lithium.*—Triphenylgermyl-lithium (1.5 mmoles) in ethylene glycol dimethyl ether (5 c.c.) was added with stirring to a solution of triphenylgermyltriphenylphosphinegold(I) (1.45 mmoles) in ethylene glycol dimethyl ether (100 c.c.). The white solid which separated rapidly was filtered off and dried *in vacuo* (1.3 g.). This *complex*, probably  $\text{Li}[(\text{Ph}_3\text{Ge})_2\text{Au}](\text{C}_4\text{H}_{10}\text{O}_2)_4$ , was rather more stable than the diethyl ether analogue but still decomposed slowly in air. The presence of the glycol ether and the absence of triphenylphosphine were established from the infrared spectrum. The excess of lithium in the solid is probably due to lithium methoxide formed in the preparation of triphenylgermyl-lithium (Found: Au, 16.5; Ge, 11.7; Li, 1.0.  $\text{C}_{52}\text{H}_{70}\text{AuGe}_2\text{LiO}_8$  requires Au, 16.8; Ge, 12.4; Li, 0.6%). The filtrate from this reaction gave, by sublimation, triphenylphosphine (0.311 g., 82%).

The crude glycol ether solvate, on treatment with tetraethylammonium iodide, yielded tetraethylammonium bis(triphenylgermyl)aurate(I) identical with the product isolated in the preceding experiment (Found: Au, 20.7; Ge, 15.2%).

*Analytical Procedures.*— $\text{Et}_4\text{N}[(\text{Ph}_3\text{Ge})_2\text{Au}]$ . Nitric-sulphuric acid breakdown gave gold and germanium dioxide. Heating with aqua regia gave gold by removal of germanium tetrachloride.

*Gold.* Gold was determined by boiling with aqua regia and precipitation as metal by hydrazine.

*Germanium in the presence of gold and phosphorus.* Decomposition with concentrated sulphuric acid preceded dilution and collection of the gold. Germanium was then precipitated as the sulphide and converted into the oxide.<sup>6</sup>

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<sup>6</sup> Johnson and Dennis, *J. Amer. Chem. Soc.*, 1925, **47**, 790.