Letters to the Editor

Complexes of hypercoordinate germanium with novel five-membered monoanionic (O,O)-chelating ligands based on 2-hydroxycarboxamides*

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Complexes of hypercoordinate germanium with (O,O)- and (S,S)-dianionic, (C,O)-, (O,S)-mono- and dianionic, and (O,N)-monoanionic chelating ligands have been well studied to date.[1] However, only a few germanium complexes containing bidentate (O,O)-monoanionic chelating ligands have been structurally characterized. The examples include six-coordinate acetylacetonate[2a,b] and benzohydroximate[3] trischelate complexes, a six-coordinate bischelate complex with an amygdalic acid fragment as a ligand,[4] and a five-coordinate bischelate complex derived from the hydroxy ketone PhCH(OH)C(=O)Ph.[5]

We found that reactions of germanium polyhalides with 2-trimethylsilyloxycarboxamides can be used as a general route to novel hypercoordinate germanium complexes containing monoanionic (O,O)-chelating ligands. This method can be illustrated with a reaction of trichloro(chloromethyl)germane with *N*,*N*-dimethyl-*O*-trimethylsilylamygdalamide (**1**), which yielded neutral five-coordinate monochelate **2** (Scheme 1).

According to the X-ray diffraction data, the coordination polyhedron of the Ge atom in crystal **2** is a slightly distorted trigonal bipyramid with the carbonyl O atom and one of the Cl atoms in the vertices (Fig. 1, Table 1). It should be noted that the equatorial Ge—Cl bond is somewhat shorter than analogous bonds in five-membered mono-(C,O)-chelate complexes with the fragment $Cl_3Ge—C—Y—C=O$ (Y = C and N).[6] The length of the equatorial Ge—O bond is close to the standard value (1.78 Å) in tetrahedral germanium complexes.[1b] The comprehensive X-ray diffraction data for complex **2** will be published elsewhere.

Five-coordinate complex **2** containing a dichloro(chloromethyl)germyl group is also of interest as a starting reagent for the synthesis of hypercoordinate germa-

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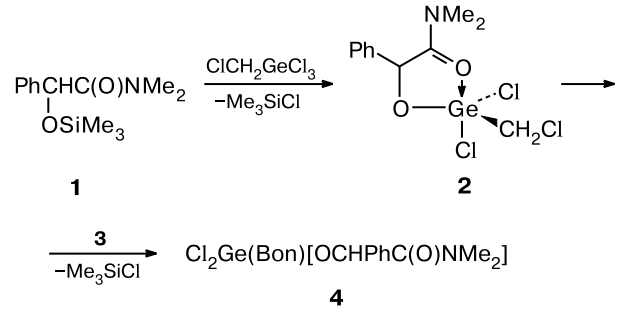
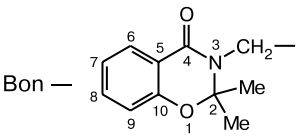
Scheme 1





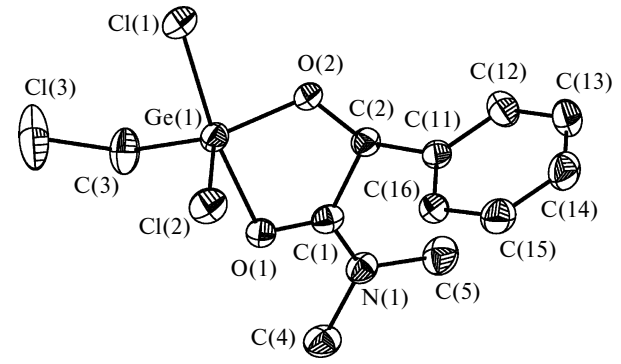


Fig. 1. Crystal structure of $Cl_2(CH_2Cl)GeOCHPhC(O)NMe_2$ (**2**).

Table 1. Selected bond lengths (*d*) and angles (ω) in structure **2**

Bond	*d*/Å	Angle	ω/deg
Ge(1)—O(1)	2.066(2)	O(1)—Ge(1)—O(2)	82.28(8)
Ge(1)—O(2)	1.781(2)	O(1)—Ge(1)—Cl(1)	171.31(6)
Ge(1)—Cl(1)	2.255(1)	Cl(1)—Ge(1)—Cl(2)	95.80(3)
Ge(1)—Cl(2)	2.1184(1)	O(1)—Ge(1)—Cl(2)	89.51(6)
Ge(1)—C(3)	1.956(3)		
Cl(3)—C(3)	1.743(3)		

nium bischelate complexes by reactions with N-trimethylsilyl derivatives of amides and related compounds.[7] For example, the reaction of complex **2** with 2,2-dimethyl-3-trimethylsilylbenzo[2*H*]-1,3-oxazin-4-one (**3**) gave bischelate **4** with two different chelating ligands: the amygdalamide residue and the 2,2-dimethyl-4-oxobenzo[2*H*]-1,3-oxazin-3-ylmethyl (Bon) monoanionic C,O-chelating ligand (see Scheme 1).

The hexacoordination of germanium in complex **4** was confirmed by X-ray diffraction analysis and will be discussed elsewhere.

(O→Ge)-Chelate *N*,*N*-dimethyl-*O*-[dichloro(chloromethyl)germyl]amygdalamide (2). Trichloro(chloromethyl)germane (2.28 g, 0.01 mol) was added to a stirred solution of amide **1** (2.51 g, 0.01 mol) in benzene (9 mL). The reaction mixture was refluxed for 1 h, cooled, and kept at room temperature for 3 days. Then it was concentrated and hexane (4 mL) was added. The crystals that formed were filtered off. Recrystallization from benzene—hexane (4 : 3) gave compound **2** (3.32 g, 89%), m.p. 98—102 °C. Found (%): C, 35.47; H, 3.81, N, 3.69. $C_{11}H_{14}Cl_3GeNO_2$. Calculated (%): C, 35.59; H, 3.88; N, 3.77. IR (Specord IR-75, KBr, CH_2Cl_2), ν/cm^{-1}: 1635 w, 1500 (NCO, Ph). ^{1}H NMR (Varian XL-400, 400.1 MHz, $CDCl_3$), δ: 7.27—7.44 (m, 5 H, Ph); 2.80, 3.20 (both s, 3 H each, NMe_2); 5.63 (s, 1 H, CH); 3.78, 3.83 (both dd, 1 H each, CH_2Cl, $^2J_{H,H}$ = 11.4 Hz).

Bis-(O→Ge)-chelate *N*,*N*-dimethyl-*O*-[dichloro(2,2-dimethyl-4-oxobenzo[2*H*]-1,3-oxazin-3-ylmethyl)germyl]amygdalamide (4). A mixture of amide **2** (0.18 g, 0.0005 mol) and compound **3** (0.13 g, 0.0005 mol) was refluxed in toluene (2 mL) for 10 h and then cooled to room temperature. The solvent and Me_3SiCl were removed in a rotary evaporator. The residue was crystallized by triturating with ether (10 mL). The yield of compound **4** was 0.2 g (80%), m.p. 220—222 °C (benzene—hexane, 14 : 1). Found (%): C, 49.27; H, 4.68; N, 5.37. $C_{21}H_{24}Cl_2GeN_2O_4$. Calculated (%): C, 49.27; H, 4.72; N, 5.47. IR (CH_2Cl_2), ν/cm^{-1}: 1607, 1564, 1500 (NCO, Ar). ^{1}H NMR ($CDCl_3$), δ: 1.78, 1.80 (both s, 3 H each, CMe_2); 2.76, 3.11 (both s, 3 H each, NMe_2), 3.78, 3.83 (both dd, 1 H each, CH_2, $^2J_{H,H}$ = 11.4 Hz); 7.33—7.47 (m, 5 H, Ph); 5.67 (s, 1 H, CH); 7.00 (d, 1 H, H(9), $^3J_{H,H}$ = 7.8 Hz); 7.14 (t, 1 H, H(7), $^3J_{H,H}$ = 7.8 Hz); 7.57 (t, 1 H, H(8), $^3J_{H,H}$ = 7.8 Hz); 7.92 (d, 1 H, H(6), $^3J_{H,H}$ = 7.8 Hz).

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