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Synthesis and Molecular Structure of Five-Coordinated Phenyl-Substituted Anionic Germanium(IV) Complexes. Influence of the Central Atom on Geometry[1,2]

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A series of pentacoordinated phenyl-substituted anionic germanates, **1–4**, were synthesized from phenylgermanium trichloride and a catechol or thiocatechol ligand in the presence of a base: $[(C_6H_4O_2)_2GePh][Et_4N]$ (**1**); $[(C_6H_4O_2)_2GePh][Et_3NH]\cdot{}^1/_6CH_3CN$ (**2**); $[(C_6Cl_4O_2)_2GePh][Et_4N]$ (**3**); $[(C_6H_4OS)_2GePh][Ph_4As]$ (**4**). The ethanedithiolato derivative $[(C_2H_4S_2)_2GePh][Et_4N]$ (**5**) also was synthesized. The X-ray structure of **1** is midway between a trigonal bipyramid and rectangular pyramid while **2** and **3** are more nearly rectangular pyramidal. Hydrogen bonding influences the structure of **2**. Electron withdrawal by the ring chlorine atoms rationalizes the structural displacement found for **3**. Comparisons with related structures of phenyl-substituted pentacoordinated derivatives of silicon, phosphorus, arsenic, and antimony show an increasing ease of solid-state distortion toward the rectangular pyramid as the electronegativity of the central atom is decreased: Ge > Si in group 4 (14) and Sb > As > P in group 5 (15). **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.096$ (3) Å, $b = 22.724$ (6) Å, $c = 10.985$ (1) Å, $\beta = 102.65$ (2)°, and $Z = 4$. **2** crystallizes in the trigonal space group $R\bar{3}$ with $a_H = 23.666$ (7) Å, $c_H = 21.967$ (4) Å, and $Z = 18$. **3** crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.591$ (2) Å, $b = 20.979$ (6) Å, $c = 17.367$ (3) Å, $\beta = 90.29$ (2)°, and $Z = 4$. The final conventional unweighted residuals were 0.033 (**1**), 0.059 (**2**), and 0.048 (**3**).

Introduction

As the accompanying paper[2] reveals, five-coordinated germanium(IV) complexes form a series of structures showing progressive distortions from a trigonal bipyramid (TBP) to a square- or rectangular-pyramidal geometry (RP) along the Berry coordinate[4] analogous to that found for phosphoranes,[5-7] arsoranes,[8] and five-coordinated silicon[9,10] compounds. For all of these elements,[2,6,9-16] as well as the lesser studied pentacoordinated complexes of tin,[17,18] a requirement for the formation of the square-pyramidal geometry is the presence of two unsaturated five-membered rings with like atoms in any one ring directly attached to the central atom.[19]

Other factors also influence the particular geometry formed.[6,7,16] Among these are ring-substituent effects,[5,9,13,19,20] ring strain,[19,21] the nature of the acyclic ligand in the case of spirocyclic derivatives,[22,23] and steric factors.[12,23-25] For five-coordinated anionic main-group 4 (14)[38] complexes, hydrogen bonding[9,10,12,13,23] and lattice effects[2,15] assume a role in influencing geometry for these nonrigid entities. While none of these factors by themselves have proved as important as the first cited criterion for stabilizing a square pyramid, their general structural trend is known for silicon, phosphorus, and arsenic acting as central atoms.

The previous paper[2] centered on the structural influence of varying the spirocyclic ring system while keeping the cation and the acyclic ligand the same, i.e., use of Et_4N^+ and the methyl group, respectively, in a series of anionic five-coordinated germanates. In this paper, we investigate a related series of newly synthesized phenyl-substituted five-coordinated anionic germanium complexes, $[(C_6H_4O_2)_2GePh][Et_4N]$ (**1**), $[(C_6H_4O_2)_2GePh][Et_3NH]\cdot{}^1/_6CH_3CN$ (**2**), and $[(C_6Cl_4O_2)_2GePh][Et_4N]$ (**3**), which allows a structural determination of the effects of hydrogen bonding and electron-withdrawing ring substituents on distortion.

Experimental Section

Proton NMR spectra were recorded on a Varian A-60 spectrometer and are referenced vs. tetramethylsilane. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD-4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at an ambient temperature at 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[18] Suitable precautions were taken when benzene was employed as a solvent in some of the reactions. All reactions were carried out in well-ventilated hoods.

Syntheses. Triethylammonium Bis(1,2-benzenediolato)phenylgermanate(IV), $[(C_6H_4O_2)_2GePh][Et_3NH]$ (2). Phenylgermanium trichloride (0.381 g, 1.49 mmol) was stirred in 30 mL of benzene under nitrogen. Catechol (0.328 g, 2.98 mmol) and triethylamine (0.602 g, 5.95 mmol) were dissolved in 30 mL of benzene and placed in a dropping funnel. Slow, dropwise addition caused little change. The solution was refluxed for 1.5 h, and a white solid settled out upon cooling. Chloroform (30 mL) was mixed in and the solution extracted with water. After separating, the organic solvents were evaporated to yield a light-colored oil that subsequently crystallized. It was dissolved in acetonitrile and recrystallized by adding ether and cooling. The product was washed with water and dried under vacuum; mp 210 °C dec (yield 0.516 g, 74.2%). ^1H NMR (CD_3CN/Me_4Si) (ppm): 7.6 (br, 2 H, ortho protons of GePh); 7.3 (br, 3 H, meta and para protons of GePh); 6.68 (m, 8 H, aromatic protons of catecholate groups); 3.1 (q, 6 H, CH_2 protons of Et_3NH^+);

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(1) Pentacoordinated Molecules. 64.

(2) Part 63: Holmes, R. R.; Day, R. O.; Sau, A. C.; Holmes, J. M. *Inorg. Chem.*, preceding paper in this issue.

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1.2 (t, 9 H, CH_3 protons of Et_3NH^+). Anal. Calcd for $C_{24}H_{29}O_4NGe$: C, 61.61; H, 6.25; N, 2.99. Found: C, 61.29; H, 6.39; N, 3.03.

Tetraethylammonium Bis(1,2-benzenediolato)phenylgermanate(IV), $[(C_6H_4O_2)_2GePh][Et_4N]$ (1). To a solution of **2** (0.359 g, 0.768 mmol) in acetonitrile (20 mL) was added tetraethylammonium chloride (0.127 g, 0.769 mmol). The resulting mixture was stirred at room temperature to obtain a clear solution. Evaporation of solvent from the solution afforded a crystalline residue which was washed with water to dissolve the triethylammonium chloride liberated in the reaction. The water-insoluble solid was filtered off under suction, dried under oil-pump vacuum, and dissolved in a minimum volume of boiling acetonitrile. When the solution was cooled to room temperature, crystals (greenish tint) of tetraethylammonium bis(1,2-benzenediolato)phenylgermanate(IV) (**1**), deposited; mp 203–204 °C (yield 0.33 g, 86.6%). ^1H NMR data (CD_3CN/Me_4Si) (ppm): 7.65 (m, 2 H, ortho protons of GePh); 7.35 (m, 3 H, meta and para protons of GePh); 6.6 (m, 8 H, aromatic protons of catecholate groups); 3.05 (q, 8 H, CH_2 protons of Et_4N^+); 1.1 (m, 12 H, CH_3 protons of Et_4N^+). Anal. Calcd for $C_{26}H_{33}NO_4Ge$: C, 62.93; H, 6.73; N, 2.82. Found: C, 62.8; H, 6.82; N, 2.82.

Tetraethylammonium Bis(3,4,5,6-tetrachloro-1,2-benzenediolato)phenylgermanate(IV), $[(C_6Cl_4O_2)_2GePh][Et_4N]$ (3). To a solution of phenylgermanium trichloride (0.48 g, 1.87 mmol) in benzene (75 mL) were added the adduct of triphenylphosphine oxide and tetrachlorocatechol, $Ph_3P{=}O{\cdot}C_6Cl_4(OH)_2$[26] (1.97 g, 3.74 mmol), and triethylamine (0.756 g, 7.48 mmol). When the reaction mixture was stirred at room temperature, a flocculent precipitate formed and the solution turned brown. The resulting reaction mixture was stirred at room temperature for 15 min and then heated under reflux for 1 h. The reaction mixture was cooled to room temperature and filtered to remove the precipitate of $Et_3NH^+Cl^-$. Evaporation of solvent from the filtrate gave a semisolid residue, which was dissolved in acetonitrile (20 mL). Tetraethylammonium chloride (0.4 g, 2.4 mmol) was added to this solution, and the mixture was stirred for 10 min to bring about exchange of the cation from $[(C_6Cl_4O_2)_2GePh][Et_3NH]$ by Et_4N^+. Acetonitrile was evaporated in a rotary evaporator, and the solid residue was treated with water to dissolve the metathetically formed triethylammonium chloride. The insoluble white precipitate, containing $[(C_6Cl_4O_2)_2GePh][Et_4N]$ and $Ph_3P{=}O$, was filtered off under suction and dried in vacuo. The dried solid was treated with benzene (20 mL) at room temperature, and the mixture was stirred magnetically to dissolve $Ph_3P{=}O$. The germanium complex, **3**, which remained insoluble in benzene, was filtered off under suction, washed with hexane (10 mL), dried, and dissolved in a minimum volume of boiling acetonitrile. The solution was filtered hot. When the solution cooled to room temperature, crystals (having a yellow tint) of tetraethylammonium bis(3,4,5,6-tetrachloro-1,2-benzenediolato)phenylgermanate(IV), $[(C_6Cl_4O_2)_2GePh][Et_4N]$ (**3**), deposited; mp >250 °C (yield 1.37 g, 95%). ^1H NMR (Me_2SO-d_6/Me_4Si) (ppm): 7.55 (m, 5 H, aromatic protons of GePh): 3.23 (8 H, q, CH_2 protons of Et_4N^+): 1.15 (m, 12 H, CH_3 protons of Et_4N^+).

Tetraphenylarsonium Bis(1-hydroxybenzene-2-thiolato)phenylgermanate(IV), $[(C_6H_4OS)_2GePh][Ph_4As]$ (4). Phenylgermanium trichloride (0.391 g, 1.53 mmol) was dissolved in 30 mL of benzene under nitrogen. Mercaptophenol (0.389 g, 3.08 mmol) and triethylamine (0.618 g, 6.11 mmol) were dissolved in 20 mL of benzene and added dropwise to the germanium compound. A white solid formed immediately, and the solution was refluxed for 2 h. Tetraphenylarsonium chloride (0.652 g, 1.56 mmol) was added to the mixture and refluxing continued for 2 h. Both solution and solid turned light brown. The solid was filtered off and washed with water, leaving a smaller quantity of brown solid. This was dissolved in acetonitrile and recrystallized by adding ether. Another recrystallization from acetonitrile produced two crops of **4** as a light brown solid, one by evaporation of solvent and the second by addition of ether and cooling; mp 128–132 °C (yield 0.397 g, 32%). Anal. Calcd for $C_{42}H_{35}O_3S_2GeAs$ (with one water molecule): C, 6.31; H, 4.41. Found: C, 6.29; H, 4.47.

Tetraethylammonium Bis(ethane-1,2-dithiolato)phenylgermanate(IV), $[(C_2H_4S_2)_2GePh][Et_4N]$ (5). Disodium ethanedithiolate was prepared by mixing sodium with ethanedithiol in ether. A 0.5-g (3.6-mmol) sample was added over $^1/_2$ h to phenylgermanium trichloride (0.468 g, 1.83 mmol) in 75 mL of benzene under nitrogen. The mixture was refluxed for 1 h, and then tetraethylammonium chloride (0.310 g, 1.87 mmol) was added. A dispersed white solid formed, and after 5 h of refluxing, it clumped into a ball. The solid was filtered off and treated with 5 mL of dry acetonitrile to remove any trapped product. The liquid was added to the benzene solution and the solvent evaporated to yield an oil. It could not be crystallized out by dissolving in acetonitrile and adding ether, but it did form a white solid when treated with pure ether. The solid was collected and dissolved in hot acetonitrile, and the solution was filtered. The first solid to form upon cooling was extremely hygroscopic. Addition of ether with cooling produced **5** as a white solid, which was collected and dried under vacuum; mp 102–105 °C (yield 0.433 g, 51%). ^1H NMR (CD_3CN/Me_2SO) (ppm): 7.8 (m, 2 H, ortho protons of GePh); 7.25 (m, 3 H, meta and para protons of GePh); 3.15 (q, 8 H, CH_2 protons of Et_4N^+); 3.0 (s, 8 H, CH_2 protons of ethanedithiolate ring); 1.15 (t of t, 12 H, CH_3 protons of Et_4N^+). Anal. Calcd for $C_{18}H_{33}NS_4Ge$: C, 46.56; H, 7.16; N, 3.02. Found: C, 46.79; H, 7.42; N, 3.08.

Crystallography. All crystals were mounted in thin-walled glass capillaries that were sealed as a precaution against moisture sensitivity.

X-ray Crystallographic Studies for $[(C_6H_4O_2)_2GePh][Et_4N]$ (1). A colorless crystal (0.30 × 0.33 × 0.35 mm), which was cut from a polycrystalline mass, was used for the X-ray study.

Crystal Data for $C_{26}H_{33}O_4NGe$ (1): uniquely determined monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ (C_{2h}^5-No. 14)[27]), a = 10.096 (3) Å, b = 22.724 (6) Å, c = 10.985 (1) Å, β = 102.65 (2)°, Z = 4, $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 1.353 mm^{-1}. A total of 4305 independent reflections ($+h,+k,\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 50°$. No corrections were made for absorption. The structure was solved by using standard Patterson and difference Fourier techniques and was refined by using full-matrix least squares.[28] The 32 independent non-hydrogen atoms were refined anisotropically. Coordinates for the 12 independent methyl hydrogen atoms were obtained from a difference Fourier synthesis, and these were included in the refinement as fixed isotropic scatterers. Coordinates for the remaining 21 independent hydrogen atoms (included as isotropic scatterers) were calculated and updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The final agreement factors[29] were R = 0.033 and R_w = 0.044 for the 3213 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for $[(C_6H_4O_2)_2GePh][Et_3NH]{\cdot}{}^1/_6CH_3CN$ (2). Experimental and computational techniques were the same as described for **1** unless otherwise noted. Crystals of **2** are colorless with a gray-blue cast. A nearly cubic crystal (0.30 × 0.39 × 0.39 mm) cut from a larger crystal was used for the X-ray study.

Crystal Data for $C_{24}H_{29}O_4NGe{\cdot}{}^1/_6C_2H_3N$ (2): trigonal space group $R\bar{3}$ (C_{3i}^2-No. 148),[30] hexagonal setting, a_H = 23.666 (7) Å, c_H = 21.967 (4) Å, Z = 18, $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 1.401 mm^{-1}. A total of 3185 independent reflections ($+h,-k,+l$) were measured for $2° \leq 2\theta \leq 45°$. The 30 independent non-hydrogen atoms comprising the cation and the anion were refined anisotropically. All methyl hydrogen atoms were omitted from the refinement. The remaining 20 independent hydrogen atoms were included in the refinement as described for **1** (N–H bond length = 0.90 Å). The acetonitrile of solvation is disordered about a $\bar{3}$ site in such a way that it was not possible to resolve two positions for the central carbon atom (C), and this atom (isotropic) was constrained to lie on the inversion center. The independent terminal atom (CN, constrained to lie on the 3-fold axis) was treated as an isotropic scatterer with scattering factors that were taken as the average of those for carbon and nitrogen. The final agreement factors[29] were R = 0.059 and R_w = 0.073 for the 2114 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for $[(C_6Cl_4O_2)_2GePh][Et_4N]$ (3). Experimental and computational techniques were the same as described for **1** unless otherwise noted. Crystals of **3** are boomerang-shaped and colorless, but appear tan in bulk. The crystal used for the X-ray study was cut to dimensions of 0.23 × 0.23 × 0.29 mm.

Crystal Data for $C_{26}H_{25}O_4NCl_8Ge$ (3): uniquely determined monoclinic space group $P2_1/n$,[27] a = 8.591 (2) Å, b = 20.979 (6) Å, c 17.367 (3) Å, β = 90.29 (2)°, Z = 4, $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 1.748 mm^{-1}. A total of 5477 independent reflections were measured. The structure was solved by using initial coordinates for non-hydrogen atoms taken from the isomorphous, isostructural Si analogue,[9] but with $z = 1 - z$. The 40 independent non-hydrogen atoms were refined anisotropically. Methyl hydrogen atoms were omitted from the refinement. The 13 remaining independent hydrogen atoms were treated as for **1**. The final agreement factors were R = 0.048 and R_w = 0.065 for the 3828 reflections having $I \geq 2\sigma_I$.

Results

The atom-labeling scheme for **1** is given in the ORTEP plot of Figure 1, while atomic coordinates are given in Table I. The

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(29) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

(30) Reference 27, p 252.

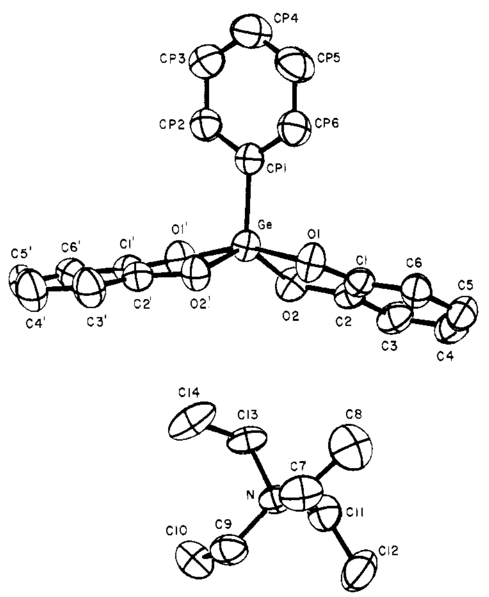

Figure 1. ORTEP plot of [$(C_6H_4O_2)_2$GePh][Et_4N] (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

Table I. Atomic Coordinates in Crystalline [PhGe$(O_2C_6H_4)_2$][NEt_4] (**1**)[a]

atom type[b]	10^4x	10^4y	10^4z
Ge	2454.6 (3)	1509.0 (2)	405.6 (3)
O1	1179 (2)	2068 (1)	−432 (2)
O1′	3631 (2)	1109 (1)	1711 (2)
O2	3632 (2)	2136 (1)	807 (2)
O2′	1053 (2)	1216 (1)	1057 (2)
C1	1787 (3)	2591 (1)	−528 (3)
C2	3131 (3)	2633 (1)	165 (3)
C3	3851 (4)	3150 (2)	194 (4)
C4	3225 (5)	3632 (2)	−506 (4)
C5	1919 (5)	3585 (2)	−1202 (4)
C6	1181 (4)	3064 (2)	−1224 (4)
C1′	2917 (4)	736 (1)	2289 (3)
C2′	1511 (4)	795 (2)	1933 (3)
C3′	672 (4)	442 (2)	2456 (4)
C4′	1259 (5)	24 (2)	3337 (4)
C5′	2641 (5)	−33 (2)	3696 (4)
C6′	3493 (4)	327 (2)	3190 (3)
CP1	2674 (3)	1043 (1)	−1013 (3)
CP2	3446 (4)	532 (2)	−853 (3)
CP3	3553 (4)	181 (2)	−1852 (4)
CP4	2896 (5)	338 (2)	−3036 (4)
CP5	2132 (5)	843 (2)	−3224 (4)
CP6	2020 (4)	1200 (2)	−2225 (4)
N	2152 (3)	3187 (1)	4103 (3)
C7	740 (4)	3302 (2)	3321 (4)
C8	666 (5)	3425 (2)	1966 (5)
C9	2004 (4)	3103 (2)	5440 (4)
C10	3304 (5)	2935 (2)	6357 (4)
C11	3126 (4)	3690 (2)	4016 (4)
C12	2711 (5)	4281 (2)	4437 (5)
C13	2769 (4)	2645 (2)	3648 (4)
C14	2026 (5)	2076 (2)	3747 (5)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

corresponding data for **2** and **3** are given in Figure 2 and Table II and in Figure 3 and Table III, respectively. Important bond lengths and angles are given in Table IV for **1** and **2** and in Table V for **3**. Thermal parameters, hydrogen atom parameters, and additional bond lengths and angles for all three compounds are provided as supplementary material.

Discussion

Basic Structures. All three anionic spirocyclic germanates, **1**–**3**, have a pseudo-2-fold axis coincident with the Ge–C bond. To facilitate examination of this pseudosymmetry, atoms of the bidentate ligands have been labeled so that primed ones go into the unprimed ones by this pseudo-2-fold axis.

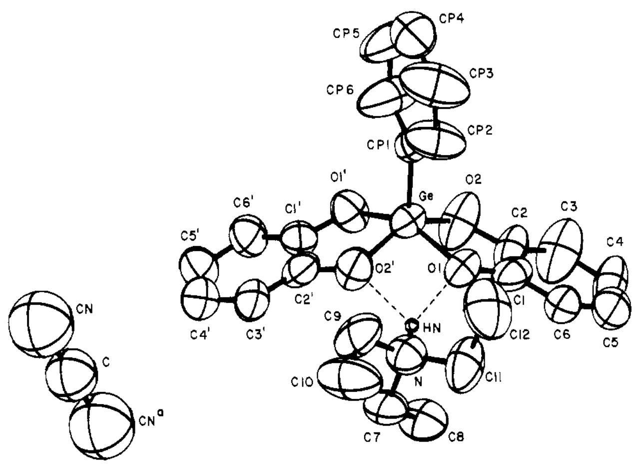

Figure 2. ORTEP plot of [$(C_6H_4O_2)_2$GePh][Et_3NH]$\cdot{}^1/_6CH_3CN$ (**2**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms except for HN are omitted for purposes of clarity. The symmetry-related CN^a shown is related by $^2/_3 - x$, $1^1/_3 - y$, $^1/_3 - z$. Hydrogen bonds are indicated by dashed lines.

Table II. Atomic Coordinates in Crystalline [$(C_6H_4O_2)_2$GePh][Et_3NH]$\cdot{}^1/_6CH_3CN$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
Ge	2324.6 (4)	2575.7 (4)	2132.0 (3)
O1	1500 (2)	1907 (2)	1888 (2)
O2	2652 (3)	2333 (3)	1491 (2)
O1′	3042 (2)	3404 (2)	2024 (3)
O2′	1862 (2)	3005 (2)	2311 (2)
C1	1550 (4)	1555 (4)	1436 (4)
C2	2157 (5)	1777 (4)	1215 (3)
C3	2310 (5)	1470 (5)	733 (4)
C4	1761 (6)	908 (4)	464 (4)
C5	1140 (5)	682 (4)	691 (4)
C6	1030 (4)	1003 (4)	1168 (4)
C1′	2899 (4)	3877 (4)	2159 (3)
C2′	2257 (4)	3664 (4)	2319 (3)
C3′	2055 (4)	4108 (4)	2457 (4)
C4′	2527 (5)	4785 (5)	2422 (5)
C5′	3161 (5)	4990 (4)	2257 (4)
C6′	3372 (4)	4541 (4)	2125 (4)
CP1	2505 (3)	2271 (3)	2886 (3)
CP2	2029 (5)	1784 (5)	3202 (4)
CP3	2166 (6)	1595 (6)	3764 (6)
CP4	2784 (6)	1866 (5)	3985 (4)
CP5	3253 (6)	2338 (6)	3661 (6)
CP6	3112 (5)	2548 (6)	3113 (5)
N	394 (3)	2190 (3)	2168 (3)
C7	367 (5)	2604 (4)	1685 (4)
C8	612 (4)	2496 (5)	1068 (4)
C9	332 (5)	2462 (5)	2788 (4)
C10	−349 (6)	2367 (7)	2909 (5)
C11	−112 (5)	1480 (4)	2081 (5)
C12	−38 (6)	1059 (5)	2549 (5)
C	3333[c]	6667[c]	1667[c]
CN[d]	3333[c]	6667[c]	2502 (13)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] Fixed. [d] Average of C and N scattering factors were used.

The geometry about the Ge atom for all three compounds lies on the coordinate connecting a trigonal bipyramid (TBP) with the phenyl group equatorially positioned to a rectangular pyramid (RP) having four basal oxygen atoms and an apical phenyl group. By the dihedral angle method of assessing displacement,[5,31,32] **1** is displaced 50.5% (51.9% by using unit vectors) from the TBP

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(31) Reference 7, p 34 ff.

(32) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

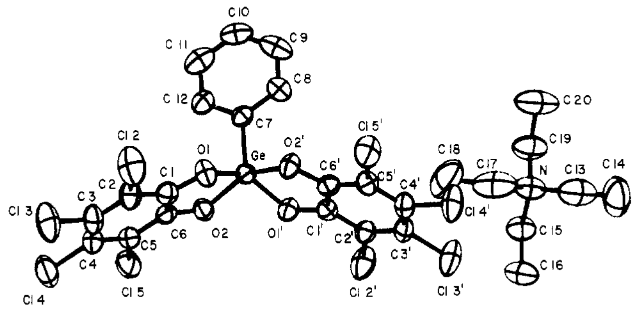

Figure 3. ORTEP plot of [$(Cl_4C_6O_2)_2$GePh][Et_4N] (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

Table III. Atomic Coordinates in Crystalline [$(Cl_4C_6O_2)_2$GePh][Et_4N] (**3**)[a]

atom type[b]	10^4x	10^4y	10^4z
Ge	2659.2 (7)	2319.9 (3)	7513.2 (4)
O1	2949 (5)	1690 (2)	8253 (2)
O2	3600 (5)	1747 (2)	6827 (2)
O1′	3697 (5)	2954 (2)	6945 (2)
O2′	2788 (5)	2893 (2)	8336 (2)
Cl2	3148 (3)	550 (1)	9302 (1)
Cl3	4737 (3)	−626 (1)	8508 (1)
Cl4	5695 (3)	−536 (1)	6776 (1)
Cl5	5052 (2)	715 (1)	5852 (1)
Cl2′	5274 (2)	4061 (1)	6159 (1)
Cl3′	5640 (3)	5242 (1)	7241 (1)
Cl4′	4478 (3)	5173 (1)	8942 (1)
Cl5′	2852 (3)	3928 (1)	9530 (1)
C1	3511 (7)	1150 (3)	7952 (4)
C2	3733 (8)	588 (3)	8345 (4)
C3	4414 (9)	68 (3)	7989 (4)
C4	4839 (8)	106 (3)	7224 (4)
C5	4557 (7)	668 (3)	6807 (4)
C6	3895 (6)	1181 (3)	7165 (4)
C1′	3914 (6)	3486 (3)	7357 (3)
C2′	4602 (7)	4038 (3)	7090 (4)
C3′	4762 (7)	4558 (3)	7577 (4)
C4′	4243 (8)	4527 (3)	8329 (4)
C5′	3545 (7)	3979 (3)	8598 (4)
C6′	3393 (7)	3455 (3)	8124 (3)
C7	485 (6)	2313 (3)	7228 (3)
C8	−421 (8)	2848 (3)	7320 (4)
C9	−2002 (8)	2839 (4)	7117 (4)
C10	−2645 (8)	2295 (4)	6834 (4)
C11	−1741 (9)	1757 (4)	6731 (5)
C12	−162 (8)	1776 (3)	6934 (4)
N	−2757 (6)	2292 (3)	9651 (3)
C13	−3126 (9)	2937 (5)	9247 (5)
C14	−3067 (12)	3535 (5)	9747 (8)
C15	−3903 (8)	2186 (4)	10311 (4)
C16	−5592 (9)	2158 (4)	10080 (5)
C17	−2885 (10)	1739 (5)	9073 (5)
C18	−2499 (14)	1074 (5)	9400 (7)
C19	−1150 (8)	2325 (4)	10023 (5)
C20	191 (10)	2407 (6)	9458 (6)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for [$(C_6H_4O_2)_2$GePh][Et_4N] (**1**) and [$(C_6H_4O_2)_2$GePh][Et_3NH]·$^1/_6CH_3CN$ (**2**)[a]

	1	**2**
Ge–O1[b]	1.897 (2)	1.874 (5)[c]
Ge–O1′	1.883 (2)	1.858 (5)[c]
Ge–O2	1.847 (2)	1.832 (5)[d]
Ge–O2′	1.845 (2)	1.870 (5)[d]
Ge–CP1	1.936 (3)	1.937 (7)
O1–Ge–O1′	160.1 (1)	150.5 (2)
O2–Ge–O2′	134.0 (1)	141.8 (3)
CP1–Ge–O2	115.7 (1)	109.5 (3)
CP1–Ge–O2′	110.3 (1)	108.7 (3)
O1–Ge–CP1	99.3 (1)	105.1 (3)
O1–Ge–O2	86.1 (1)	86.5 (2)
O1–Ge–O2′	86.2 (1)	82.8 (2)
O1′–Ge–CP1	100.7 (1)	104.3 (3)
O1′–Ge–O2	85.7 (1)	85.8 (2)
O1′–Ge–O2′	86.6 (1)	85.9 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 1 and 2. [c] Axial. [d] Equatorial.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for [$(Cl_4C_6O_2)_2$GePh][Et_4N] (**3**)[a]

Ge–O2	1.879 (4)[c]	Ge–O1′	1.884 (4)[d]
Ge–O2′	1.870 (4)[c]	Ge–C7	1.930 (6)
Ge–O1	1.859 (4)[d]		
O1–Ge–O1′	143.3 (2)	O1–Ge–C7	107.4 (2)
O2–Ge–O2′	150.7 (2)	O2′–Ge–C7	104.7 (2)
O1–Ge–O2′	85.5 (2)	O1′–Ge–C7	109.3 (2)
O1–Ge–O2	85.8 (2)	O2–Ge–O1′	85.0 (2)
O2′–Ge–O1′	85.4 (2)	O2–Ge–C7	104.6 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Axial. [d] Equatorial.

Table VI. Structural Displacement of Phenyl-Substituted Anionic Five-Coordinated Compounds of Main Groups 4 (14) and 5 (15)

compd	%(TBP → RP)[a]	ref
[$(C_6H_4O_2)_2$SiPh][Me_4N] (**6**)	29.5	33
[$(C_6H_4O_2)_2$SiPh][Et_3NH] (**7**)	59.4	10
[$(C_6H_4O_2)_2$GePh][Et_4N] (**1**)	51.8	this work
[$(C_6H_4O_2)_2$GePh][Et_3NH] (**2**)	82.2	this work
[$(C_6H_4O_2)_2$PPh] (**8**)	74.9	36
[$(C_6H_4O_2)_2$AsPh] (**9**)	97.0	11
[$(C_6Cl_4O_2)_2$SiPh][Et_4N] (**10**)	89.8	9
[$(C_6Cl_4O_2)_2$GePh][Et_4N] (**3**)	85.2	this work
[$(C_6Cl_4O_2)_2$PPh] (**11**)	94	20
[$(C_6Cl_4O_2)(C_6H_4O_2)$PPh] (**12**)	94	20
[$(C_6Cl_4O_2)(C_6H_4O_2)$SbPh] (**13**)[b]	72.6 (av) 88.9 (av)	37
[(t-$Bu_2C_6H_2O_2)_2$SiPh][Et_3NH] (**14**)	29.0	10

[a] Based on unit bond distances. [b] Two independent molecules.

toward the RP. For **2** and **3** these values are 80.7% (82.2%) and 84.2% (85.2%), respectively.

The catecholate derivatives, **1** and **2**, have the same anion, but in **2** there is a bifurcated hydrogen bond between the amino hydrogen atom, HN, of the cation and O1 and O2′ of the anion (HN···O1 = 2.231 Å, HN···O2′ = 2.305 Å). It is of interest to compare the effects of the hydrogen bonds on the Ge–O bond lengths.

In **1**, residual TBP character is seen in the longer lengths of the Ge–O_{ax} bonds (1.890 Å average) relative to the Ge–O_{eq} bonds (1.846 Å average). The Ge–O bonds in **2** would be expected to be more nearly equal due to the further displacement toward the RP compared to **1**, but with the axial bonds still longer than the equatorial bonds. In this case, however, the Ge–O bonds to oxygen atoms involved in the hydrogen bonding are elongated relative to the other two (see Table IV).

In comparison of **1** (no hydrogen bonding) with **2** (hydrogen bonding to O atoms), it is seen that **2** is displaced further toward the RP (~30%). A similar trend is seen in the analogous Si compounds [$(C_6H_4O_2)_2$SiPh][Me_4N] (**6**)[33] and [$(C_6H_4O_2)_2$SiPh][Et_3NH] (**7**).[10] The former silicon analogue with no hydrogen bonding is displaced 29.5% (unit vectors) from the TBP toward the RP, while the latter silicon analogue containing hydrogen bonding similar to the germanium derivative, **2**, is displaced 59.4% (unit vectors), again a difference of about 30% (Table VI). The shift toward a more RP structure as a result of hydrogen bonding in five-coordinated silicon compounds[9,12] has been noted to be associated with expected removal of electron

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density from the affected Si–O bonds.[10] A similar situation apparently applies here.

The five-coordinated anionic phenylgermanates represent new substances. Their synthesis was accomplished by following the reaction used in obtaining analogous methylgermanates reported in the accompanying paper[2] and represents the first comprehensive study of phenyl-containing pentacoordinated germanates. These substances are among the most stable five-coordinated germanates. The derivatives **1**–**3** all maintain their integrity in contact with water. However, in forming **4**, it was necessary to change the cation from Et_3NH^+ to Ph_4As^+ to achieve hydrolytic stability. It was unfortunate that neither the mixed-ligand derivative **4** nor **5**, containing a saturated thio ring system, was amenable to X-ray analysis. The latter would have provided an example of the influence of structural effects due to ring saturation. So far, all X-ray structures of anionic five-coordinated germanates encompass only unsaturated rings.[16]

Comparisons with Related Main-Group 4 (14) and 5 (15) Element Compounds. Table VI lists phenyl-substituted five-coordinated spirocyclic derivatives of main-group 4 (14) and 5 (15) elements and their structural displacement from the TBP toward the RP.

It is seen that the heavier element in each main group resides in a more RP structure when the ligand environment is the same, i.e., comparing germanate, **1**, with silicate, **6**, and arsorane, **9**, with phosphorane, **8**. This trend has been observed more generally with main group 5 (15) five-coordinated compounds,[6,7] i.e., that the displacement toward the RP structure follows the order Sb > As > P for like ligands. The latter displacement in the group 4 (14) series[34,35] has been discussed in terms of the relaxation of bond electron pair repulsions associated with less electronegative central atoms, a factor that favors the relatively higher energy RP.

Comparison of the structural displacements of the phenyl derivatives containing the tetrachlorocatecholate ligand (**3**, **10**–**13**) in Table VI shows a leveling effect. They all are nearly RP, ranging from a displacement of 85.2% for the germanium derivative, **3**, to 94% for the phosphoranes, **11** and **12**. Apparently, the electron-withdrawing effect associated with the presence of multiple ring chlorine atoms sufficiently reduces central atom–ligand bond electron pair repulsions to allow a near-RP structure in each case.

The most TBP structure listed, the silicate, **14**, exhibits hydrogen bonding between the Si–O bonds and the Et_3NH^+ group, a factor favoring the RP.[9,10,12,23] However, it is felt that the presence of the electron-donating[9,10] and steric properties[10] of the *tert*-butyl groups residing on the ring, both factors conducive to the formation of a TBP, is causative in leading to its structural form.[10]

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Registry No. **1**, 99901-34-5; **2**, 99901-36-7; **3**, 99901-38-9; **4**, 99901-40-3; **5**, 99901-42-5; $PhGeCl_3$, 1074-29-9; $[Et_4N]Cl$, 56-34-8; $Ph_3P{=}O{\cdot}C_6Cl_4(OH)_2$, 22400-36-8; $[Ph_4As]Cl$, 507-28-8; disodium ethanedithiolate, 23851-16-3.

Supplementary Material Available: Listings for **1**–**3**, respectively, of anisotropic thermal parameters (Tables S1–S3), hydrogen atom parameters (Tables S4–S6), additional bond lengths and angles (Tables S7–S9), and observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Synthesis and Characterization of Pd(II) and Pt(II) Complexes of Me_3MCH_2SeR (M = Si, Ge; R = Me, Ph) and Crystal Structures of *trans*-$(Me_3SiCH_2SeMe)_2PdCl_2$ and *trans*-$(Me_3GeCH_2SeMe)_2PtCl_2$

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Six complexes of the general formula $(Me_3MCH_2SeR)_2M'Cl_2$ (M = Si, Ge; R = Me, Ph; M′ = Pd, Pt) have been prepared. Spectroscopic results suggest that the complexes have trans geometry, which is confirmed by the single-crystal X-ray structure determination of two of them. The crystals of $(Me_3SiCH_2SeMe)_2PdCl_2$ (**1**) are orthorhombic, *Pbca*, with $a = 6.492$ (4) Å, $b = 11.438$ (7) Å, $c = 27.247$ (15) Å, $Z = 4$, and $R = 0.0249$. The crystals of $(Me_3GeCH_2SeMe)_2PtCl_2$ (**2**) are also orthorhombic, *Pbca*, with $a = 6.451$ (1) Å, $b = 11.543$ (2) Å, $c = 27.457$ (5) Å, $Z = 4$, and $R = 0.0431$. Compounds **1** and **2** are isostructural, and the configuration around selenium is pyramidal while around palladium or platinum it is square-planar. In solution, the molecules display pyramidal inversion at selenium.

Introduction

The neopentyl groups Me_3MCH_2 (M = C, Si, Ge, Sn) have been used as ligands in transition-metal complexes.[1] Their reactivities toward iodide and ethoxide ions,[2] their electronic effects in organometallic sulfides,[3] and their group VA (group 15[38]) compounds have been investigated.[4] Many palladium(II) and platinum(II) complexes have been prepared for the primary purpose of studying the pyramidal inversion at sulfur or selenium by dynamic NMR spectroscopy.[5-7] Recently, this work has been extended to include complexes of selenium carbonyls.[8-10] In a previous paper[11] we described the synthesis and characterization

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