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Synthesis of Novel Spirocyclic Penta- and Hexacoordinated Germanium(IV) Complexes[1]

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The reactions of $GeCl_4$ with catechol, 3,5-di-*tert*-butylcatechol, and toluene-3,4-dithiol in the presence of triethylamine have been investigated. The spirocyclic derivatives isolated from these reactions are $Ge(C_6H_4O_2)_2{\cdot}2H_2O$ (**5**), $[(Cl)Ge(C_{14}H_{20}O_2)_2][Et_3NH]$ (**14**), and $Ge(C_7H_6S_2)_2$ (**4**). Physical properties and solubility behavior of **4** and **5** suggest a polymeric structure. The complex **14** contains pentacoordinate germanium(IV). This complex reacts with water to form the corresponding hydroxy derivative, $[(OH)Ge(C_{14}H_{20}O_2)_2][Et_3NH]$ (**15**). Reaction of $GeCl_4$ with catechol in triethylamine only and the reaction of **5** with triethylamine give rise to the exclusive formation of a spirocyclic hexacoordinated Ge(IV) complex, $[Ge(C_6H_4O_2)_3][Et_3NH]_2$ (**10**). A metathesis reaction of **10** with $Et_4N^+Cl^-$ leads to the formation of $[Ge(C_6H_4O_2)_3][Et_4N]_2$ (**11**). A similar reaction of **14** with $Et_4N^+Cl^-$ in the presence of water gives $[(OH)Ge(C_{14}H_{20}O_2)_2][Et_4N]$ (**16**). Several novel spirocyclic pentacoordinated Ge(IV) complexes have been prepared by the reaction of **4** and **5** with halide ions and characterized by ^1H NMR spectroscopy. The chemical properties, in particular the hydrolytic behavior of these complexes, are discussed.

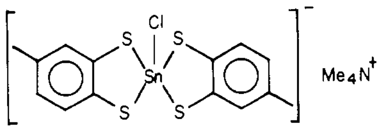
Introduction

A great deal is now known concerning the stability and structure of pentacoordinated phosphorus compounds as a result of extensive theoretical and experimental work carried out in the last 15 years.[2] One is now able to predict the geometry of a given pentacoordinated phosphorus compound with a fair degree of certainty. Stereochemical principles derived from these studies have received wide application in structuring pentacoordinated species postulated in substitution reactions of many phosphorus compounds.[2]

The extent to which these stereochemical principles may be transferred to the pentacoordinated state of other main-group elements is not known in any definitive way.[3] The principal reason for this lack of information apparently centers on the absence of suitable preparative methods leading to a sufficient range of structural types for elements other than phosphorus.

To remedy this situation for group 4A elements, we have begun synthetic and structural studies of pentacoordinate compounds of Si, Ge, Sn,[4] and Pb. Of the few five-coordinated compounds of group 4A examined so far by X-ray diffraction, only the trigonal-bipyramidal geometry has been found.[5-7] Recently, we discovered the first examples of a square-pyramidal geometry for discrete pentacoordinate tin(IV)[8] and germanium(IV)[9] in the complexes **1** and **2**, respectively.

These interesting findings prompted us to search for related derivatives for these elements with the hope of providing a range of structural types similar to that observed for pentacoordinated phosphorus compounds.[1,3,10] Since the latter range of structures was obtained for spirocyclic derivatives, we confined our attention to this class. The synthesis and characterization of some of these compounds for germanium are reported here. Most of the synthetic routes are based on the formation of anionic complexes from bis(*o*-phenylenedioxy)germanium(IV), $Ge(C_6H_4O_2)_2$ (**3**), and bis(toluene-3,4-dithiolato)germanium(IV), $Ge(C_7H_6S_2)_2$ (**4**).



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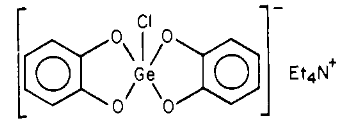

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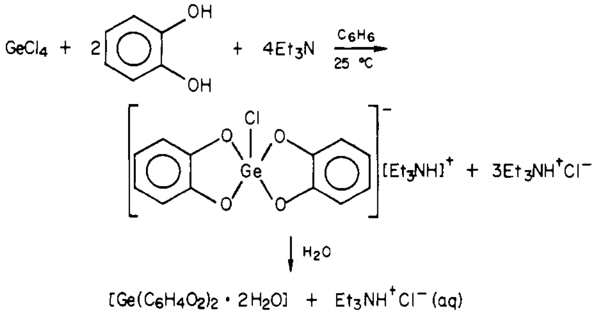
Results and Discussion

Reaction of $GeCl_4$ with Catechol. The reaction of $GeCl_4$ with catechol in benzene is very sluggish even if the reaction mixture is heated. The reaction is found to proceed smoothly if triethylamine is added along with catechol to a solution of $GeCl_4$. Hydrolysis of the resulting curdy white precipitate (containing the triethylammonium chloride adduct of **3** and $Et_3NH^+Cl^-$) yielded an insoluble, amorphous white powder, which analyzes as $C_{12}H_{12}O_6Ge$. The infrared spectrum of this solid is identical with that of the germanium complex $Ge(C_6H_4O_2)_2{\cdot}2H_2O$ (**5**) reported earlier.[11] Compound **5** was originally prepared by Bevillard[12] by the reaction of GeO_2 with catechol in water. He suggested the presence of two molecules of water in the complex from analytical data. We have also been able to demonstrate the presence of two water molecules in **5** from the appearance of a broad band at δ 2.50 when a



5

(1)

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(1) Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, Ga., March 1981; see Abstracts, No. INOR 15.

(2) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*; **1981**, *No. 176*.

(3) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(4) Sau, A. C.; Carpino, L. A.; Holmes, R. R. *J. Organomet. Chem.* **1980**, *197*, 181.

(5) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 6973.

(6) Sheldrick, W. S.; Schomburg, D.; Wolfsberger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 493.

(7) (a) Harrison, P. G. In "Organotin Compounds: New Chemistry and Applications"; Zuckerman, J. J., Ed.; American Chemical Society: Washington, D.C., 1976; ACS Symp. Ser. No. 157, p 258. (b) Van Koten, G.; Noltes, J. G. *Ibid.*, p 275. (c) Roesky, H. W. *Angew. Chem.* **1979**, *91*, 112. (d) Davies, A. G.; Smith, P. J. *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 1. (e) See ref 1 in ref 8.

(8) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1264.

(9) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7972.

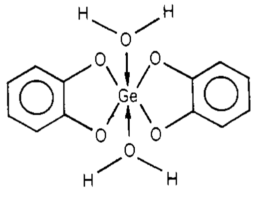
(10) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(11) Kurnevich, G. I.; Vishnevskii, V. B. *J. Appl. Spectrosc.* (*Engl. Transl.*) **1970**, *13*, 1201.

(12) Bevillard, P. *Bull. Soc. Chim. Fr.* **1954**, 304.

1:1 mixture of **5** and $Ph_4P^+Cl^-$ in CD_3CN was examined by ^1H NMR spectroscopy.[13]

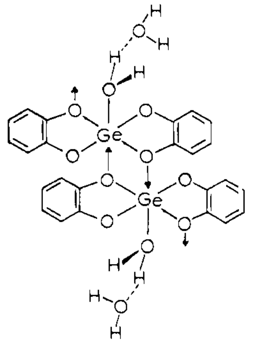
On the basis of infrared spectroscopic data, Kurnevich and Vishnevskii[11] concluded that each of the water molecules in **5** is coordinated to germanium through oxygen and proposed the hexacoordinated structure



This structure, however, does not seem to be compatible with the physical properties of **5**. Its amorphous character, for example, and insolubility in common organic solvents, including polar ones, more likely suggests a polymeric structure.

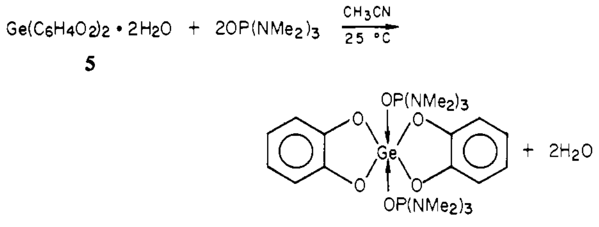
A related crystalline complex is $Ge(C_8H_6O_3)_2 \cdot 4H_2O$ (**6**) isolated[14] from the reaction of GeO_2 with mandelic acid in water. When it is heated to 140 °C, two water molecules are lost. Removal of the remaining two water molecules occurs at 200 °C. An X-ray crystal structure analysis of **6** by Sterling[15] showed that only two of the four water molecules are directly coordinated to the spiro atom, making germanium hexacoordinated. The dehydration pattern[14] of **6** led Sterling[15] to suggest that the weakly bound water molecules are hydrogen bonded to the coordinated water molecules.

Later we discuss the isolation of the triethylammonium hydroxide adduct of bis(3,5-di-*tert*-butylcatecholato)germanium, $[(OH)Ge(dtbc)_2][Et_3NH]$ (**15**). An X-ray study[16] shows the hydroxyl group bonded to the germanium atom with the triethylammonium cation in a position for N–H···O hydrogen bonding. On the basis of the above studies of **6** and **15**, and in keeping with its suspected polymeric nature, we tentatively propose structure **5**, which expresses these findings.



5

Reaction of 5 with Hexamethylphosphoramide, O=P(NMe₂)₃. Compound **5** is reported[17] to react with neutral oxygen donor ligands (e.g., dimethylformamide (DMF) and dimethyl sulfoxide (Me_2SO)) to form hexacoordinated germanium(IV) species. We observed here a similar reaction of **5** with hexamethylphosphoramide (HMPA) to form a hexacoordinated germanium(IV) complex (**7**) (eq 2). The coordination of HMPA ligands to germanium via their oxygen atoms is suggested by analogy with the coordination behavior

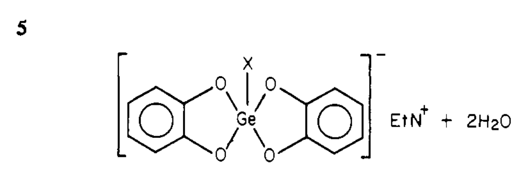


(2)

7

of DMF and Me_2SO ligands toward **5**. The presence of a single N–Me doublet at δ 2.58 in the ^1H NMR spectrum of **7** is also indicative of the presence of both the $OP(NMe_2)_3$ ligands in the same chemical environment. Thus, the presence of octahedrally coordinated germanium is supported but not proven.

Reaction of 5 with Tetraethylammonium Halides, $Et_4N^+X^-$ (X = F, Cl, or Br). Reaction of tetraethylammonium halides, $Et_4N^+X^-$ (X = F, Cl or Br), with **5** resulted in the formation of crystalline compounds, which were characterized by elemental analysis and ^1H NMR spectroscopic data to be 1:1 cationic–anionic complexes (eq 3).



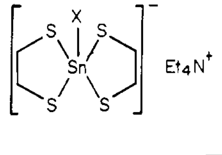
(3)

2, X = Cl
8, X = F
9, X = Br

In the ^1H NMR spectra of complexes **2**, **8**, and **9**, the aromatic protons appear as a symmetric multiplet, which could arise from either an A_2B_2 or $AA'BB'$ spin system constituted by these protons. The most notable feature in the spectra was the appearance of the methyl and methylene signals of Et_4N^+ cation at a higher field compared to those observed in the free tetraethylammonium halides. This upward shift of the tetraethylammonium protons could be attributed to arise from the shielding caused by the ring current of the aromatic ring of the catecholate unit in the anions. Possible reasons for the existence of this ring-current interaction have been discussed.[4]

In the case of **2** and **8**, single-crystal X-ray analysis[9,18] shows germanium is pentacoordinated. Both assume a basic square-pyramidal geometry with the halogen atom oriented in the apical position. The structure of the fluoro derivative **8**[18] is distorted slightly more than the chloro derivative **2**[9] toward the trigonal bipyramid. A similar variation[1,10] was found in the structures of analogous spirophosphoranes.[19] The structures of both **2** and **8** showed the cation positioned above the plane of the aromatic ring in agreement with inferences from solution NMR data cited above. It seems reasonable that some shielding occurs in solution due to the latter effect as the R_4N^+ cation moves in and out of the vicinity of the catecholate rings. We note that no shielding of the cationic protons occurs when the anion lacks an aromatic component, e.g, in

$[Me_3SnX_2]^-R_4N^+$ and



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(13) The apparent insolubility of **5** in organic solvents precluded its ^1H NMR measurements in solution. Reaction of **5** with $Ph_4P^+Cl^-$ in CH_3CN gave rise to the formation of the chloro complex $[(Cl)Ge(C_6H_4O_2)_2]^-Ph_4P^+$, and the water molecules from **5** were released.

(14) Clark, E. R. *Nature (London)* **1959**, *183*, 536.

(15) Sterling, C. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1211.

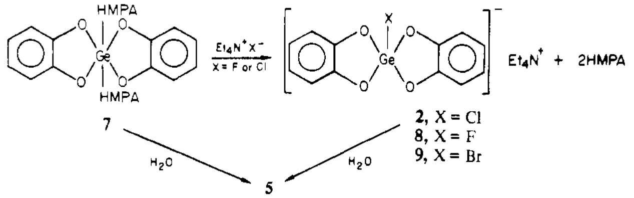
(16) Day, R. O.; Holmes, R. R., unpublished results.

(17) Shagisultanova, G. A.; Kurnevich, G. I.; Vishnevskii, V. B.; Bogdanova, I. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1970**, *15*, 1647.

(18) Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R. *Inorg. Chem.*, in press.

(19) (a) Brown, R. K.; Holmes, R. R. *Inorg. Chem.* **1977**, *16*, 2294. (b) Wunderlich, H.; Mootz, D. *Acta Crystallogr., Sect. B* **1974**, *30*, 935.

Scheme I

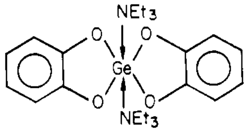


or if steric shielding prevents close proximity of the cation, e.g., in **10**, **14**, and **15**.

Reaction of 7, 2, 8, and 9 with Water. The cationic–anionic five-coordinate complexes **2**, **8**, and **9** and the neutral hexacoordinate complexes $[Ge(C_6H_4O_2)_2 \cdot 2L]$ (L = HMPA (**7**), DMF,[17] or Me_2SO[17]) are stable in a dry nitrogen atmosphere. They are, however, very susceptible to hydrolysis and get converted into the parent hydrated catechol derivative, **5**, in the presence of water (see Scheme I). The hydrolytic stability of the halide complexes (**2**, **8**, and **9**) decreases in the order F > Cl > Br. It is to be pointed out that **7** reacts with chloride and fluoride ions to form the pentacoordinated species **2** and **8** but does not react with bromide ion, to form the bromo derivative, **9**.

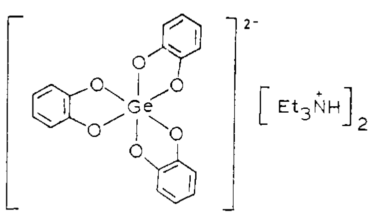
Formation of $[Et_3NH]_2[Ge(C_6H_4O_2)_3]$ (10) from $Ge(C_6H_4O_2)_2 \cdot 2H_2O$ (5). In basic medium (Et_3N in CH_3CN), the hydrated bis(*o*-phenylenedioxy)germanium compound, **5**, dissolved readily at room temperature to form a clear solution. A color change to light green was accompanied by the formation of a gelatinous precipitate, identified as $GeO_2 \cdot 2H_2O$ by its infrared spectrum. From the solution, a water-soluble grayish green crystalline compound, **10**, was isolated in 80% yield. The analytical, infrared, and ^1H NMR data suggested that the compound is the triethylammonium salt of the tris(*o*-phenylenedioxy)germanium(IV) dianion, $[Ge(C_6H_4O_2)_3][Et_3NH]_2$ (**10**).

Yoder and Zuckerman[20] have studied the reaction of $GeCl_4$ with catechol in triethylamine and isolated a solid product (in very low yield), which they characterized as the 1:2 adduct of bis(*o*-phenylenedioxy)germanium(IV) and triethylamine. The following hexacoordinate structure was suggested[20] on the basis of analytical data:



We have reinvestigated this reaction under similar conditions and found that the germanium complex, **10**, is the sole product (see the Experimental Section). The prominent infrared bands reported by Yoder and Zuckerman[20] for their compound were present in the infrared spectrum of **10**. This leads us to believe that the two compounds are the same.

The presence of three catecholate moieties (corresponding to 12 protons) and two Et_3NH^+ cations in **10** was evident from the relative intensities of various groups of signals in its ^1H NMR spectrum. The aromatic proton signals appear as a slightly broadened single peak at δ 6.48. This was in contrast to the observation of an AA′BB′ or A_2B_2 multiplet for the aromatic protons in the penta- and hexacoordinated complexes **2** and **7**–**9**. The triplet appearing at δ 1.2 and a complex multiplet at δ 3.3 (which simplified to a quartet after the sample has undergone a thorough exchange with deuterium oxide) are attributed to arise from the methyl and methylene groups of Et_3NH^+ cations, respectively. From the ^1H NMR spectroscopic data, the spirocyclic hexacoordinated structure **10** is suggested.



10

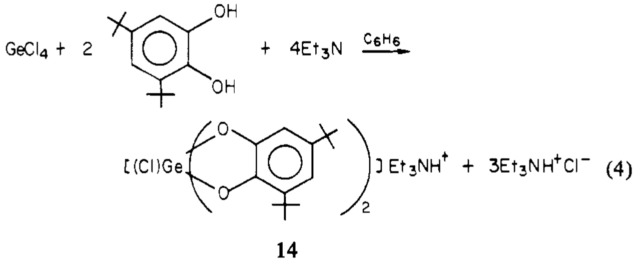
The appearance of a broad band centered at 2550 cm^{-1} (characteristic vibrational frequency[21] of a hydrogen-bonded $\equiv N^+—H$ group) in the infrared spectrum of **10** suggests that the triethylammonium cations are hydrogen bonded to the oxygen atom of the catecholate unit. Further support for this assignment comes from the observation of no upfield shift of the protons of the Et_0NH^+ cations, which indicates that the cations are held away from the shielding zone of the aromatic ring. As anticipated, the ^1H NMR spectrum of the complex $[Ge(C_6H_4O_2)_3][Et_4N]_2$ (**11**), prepared from **10** and $Et_4N^+Cl^-$, showed an upfield shift of the proton resonances of the cation, indicating shielding caused by the aromatic rings of the anion.

An analogy exists between **10** and triethylammonium tris(*o*-phenylenedioxy)phosphate, $[Et_3NH][P(C_6H_4O_2)_3]$, isolated by Allcock.[22] An X-ray analysis[23] showed the presence of a hexacoordinated phosphate anion and the hydrogen bonding between the Et_3NH^+ cation and the oxygen atom of the catecholate unit.

The formation of germanium(IV) dianionic species, similar to **10**, has been postulated in the reaction of GeO_2 with catechol and substituted catechols in basic media.[24] Analogously, the cationic–anionic silicon(IV) complex $[Si(C_6H_4O_2)_3][C_5H_6N]_2$, isolated from the reaction of $SiCl_4$ with catechol in the presence of pyridine, was found to contain a hexacoordinated Si(IV) by X-ray crystallography.[25]

Recently, the synthesis, structure, and properties of the hexacoordinated vanadium(IV) complex $[V(C_6H_4O_2)_3][Et_3NH]_2 \cdot CH_3CN$ have been reported.[26]

Reaction of $GeCl_4$ with 3,5-Di-*tert*-butylcatechol (H_2dtbc). A very slow reaction occurred between $GeCl_4$ and 3,5-di-*tert*-butylcatechol in benzene solution. Addition of a tertiary base (Et_3N, 4 equiv with respect to $GeCl_4$), however, brought about an immediate exothermic reaction. The product, a white crystalline solid, isolated from the reaction was characterized as the triethylammonium chloride adduct of bis(3,5-di-*tert*-butylphenylene-1,2-dioxy)germanium (**14**) (eq 4).



14

The presence of hydrogen bonding between the Et_3NH^+ cation and the chlorine ligand (coordinated to germanium) was evident from the observation of no upward shift of the methyl and methylene signals of Et_3NH^+ cation in the ^1H NMR spectrum of **14**.

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(20) Yoder, C. M. S.; Zuckerman, J. J. *Inorg. Chem.* **1967**, *6*, 163.

(21) Lord, R. C.; Merrifield, R. E. *J. Chem. Phys.* **1953**, *21*, 166.

(22) Allcock, H. R. *J. Am. Chem. Soc.* **1964**, *86*, 2591.

(23) Allcock, H. R.; Bissell, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 3154.

(24) Bevillard, P. *Bull. Soc. Chim. Fr.* **1954**, 296.

(25) Flynn, J. J.; Boer, F. P. *J. Am. Chem. Soc.* **1969**, *91*, 5756.

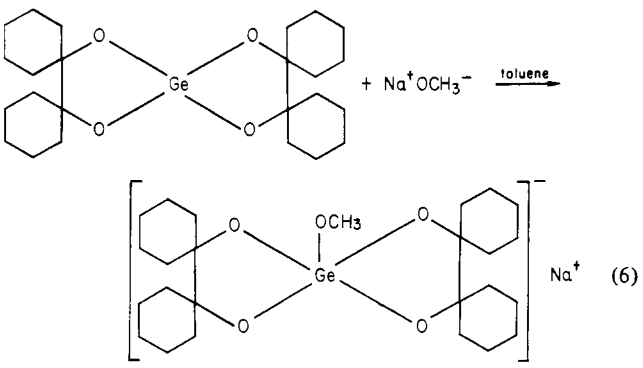
(26) Cooper, S. R.; Hollander, F. J.; Freyberg, D. P.; Raymond, K. N. "Abstracts of Papers", 180th National Meeting of the American Chemical Society, Las Vegas, Nev., Aug 1980; American Chemical Society: Washington, D.C., 1980; INOR 285.

The germanium complex **14** is stable in the solid state in a dry atmosphere. But, in solution containing traces of moisture, it undergoes slow degradation as noted by the gradual change in the solution from colorless to dark green. The sensitivity of **14** toward water was evident from the isolation of a hydroxo derivative **15** when we attempted to recrystallize **14** from a 1:1 mixture of water and acetonitrile. It appears that the germanium undergoes nucleophilic attack by a water molecule to form **15** (eq 5).

$$\underset{\mathbf{14}}{[(Cl)Ge(dtbc)_2][Et_3NH]} + H_2O \rightarrow \underset{\mathbf{15}}{[(OH)Ge(dtbc)_2][Et_3NH]} + HCl \quad (5)$$

The presence of a hydroxyl group in **15** was suggested from the appearance of a broad band centered at 3440 cm^{-1} in its infrared spectrum. The X-ray crystal structure analysis[16] of **15** confirmed the presence of the OH group bonded to germanium. The anion is pentacoordinated having a square-pyramidal configuration with the apical position occupied by the unique hydroxyl group. The distance from the nitrogen atom of the Et_3NH^+ cation to the hydroxyl oxygen is indicative of the presence of a hydrogen bond between the Et_3NH^+ and the hydroxyl oxygen. The infrared ($\equiv N^+H$ vibrational frequency[21]) and ^1H NMR spectroscopic data are in agreement with this result. The tetraethylammonium analogue of **15**, $[(OH)Ge(dtbc)_2][Et_4N]$ (**16**), prepared by a metathesis reaction of **14** with $Et_4N^+Cl^-$ and followed by treatment of the reaction mixture with water, showed the expected upward shift of the methyl and methylene resonances of Et_4N^+ in its ^1H NMR spectrum.

Müller and Heinrich[27] mentioned the formation of a possible pentaoxygermanium(IV) species from the reaction of bis(bicyclohexyl-1,1′-dioxy)germanium(IV) with sodium methoxide in toluene (eq 6).

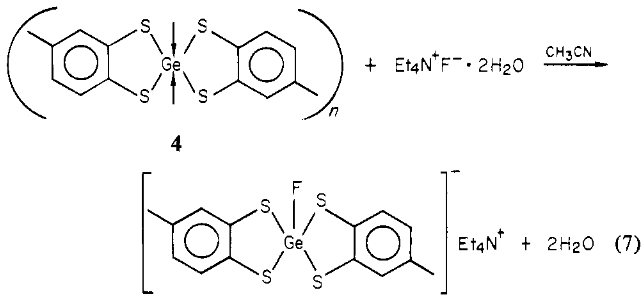


17

The presence of the *tert*-butyl groups in **14**, **15**, and **16** enhances their solubility in less polar organic solvents compared to the unsubstituted catechol derivatives **2**, **8**, and **9**. Steric crowding by the *tert*-butyl groups is suggested by the formation of pentacoordinated germanium in **15** rather than a hexacoordinated derivative analogous to **10**. Construction of a molecular model of the dianion $[Ge(dtbc)_3]^{2-}$ shows this steric crowding.

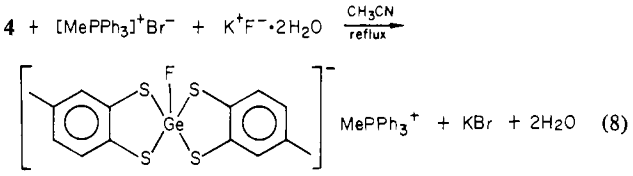
Reaction of $GeCl_4$ with Toluene-3,4-dithiol (H_2tdt). The reaction of $GeCl_4$ with toluene-3,4-dithiol was first studied by Fink,[28,29] who isolated bis(toluene-3,4-dithiolato)germanium(IV) (**4**) in very poor yield from toluene. We carried out the reaction in the presence of triethylamine, under relatively mild conditions, and isolated **4** in excellent yield. Its high melting point and insolubility in common organic solvents suggest a polymeric structure in the solid. This may be somewhat analogous to the polymeric structure of a related tin analogue supported by infrared[30a] and Mössbauer[30b] data.

Reaction of Bis(toluene-3,4-dithiolato)germanium(IV) (4) with Halide Ions. Analogous to the reaction of **5** with halide ions, **4** reacted with $Et_4N^+F^-\cdot 2H_2O$ in acetonitrile solution to give pentacoordinated germanium(IV) in the anionic complex **18** (eq 7). Although **18** is stable in a dry atmosphere, slow decomposition in air was noted by its change from yellow to green after several days. Hydrolytic stability was greatly increased by use of the bulkier cation Ph_3P^+Me. The anionic complex $[(F)Ge(tdt)_2][Ph_3PMe]$ (**19**), prepared according to eq 8, remained intact when suspended in water. Methyltriphenylphosphonium fluoride was generated in situ by the halide exchange reaction of $[Ph_3PMe]^+Br^-$ with $KF\cdot 2H_2O$ in acetonitrile. The generation of "naked" fluoride ion from a mixture of tetraalkylammonium halides and $K^+F^-\cdot 2H_2O$ in a dipolar aprotic solvent and its applications in synthetic chemistry have been documented elsewhere.[31]



4

18



19

^1H NMR data showed that the methyl protons of MeP^+Ph_3 in **19** resonate at a higher field (δ 2.7) than in the free phosphonium salt, $[MePPh_3]^+Br^-$ (δ_{CH_3} = 3.25). However, the phenyl protons of the cation do not show any additional shielding although a change in the line pattern of aromatic signals was discernible in the ^1H NMR spectrum of **19**. An X-ray crystal structure of **19** shows[18] that the geometry around germanium is approximately midway along the Berry distortion coordinate connecting the ideal trigonal bipyramid ($F_{\text{equatorial}}$) to the square pyramid (F_{apical}).

The dissolution of **4** in hot acetonitrile in the presence of $Et_4N^+Cl^-$ to form a light pink clear solution suggested the formation of the chloro analogue of **18**, viz., $[(Cl)Ge(tdt)_2]^-Et_4N^+$ (**20**). However, attempts to isolate the product by cooling the solution to room temperature resulted in the redeposition of the crystals of **4**. This finding is in contrast to the isolation of the crystalline chloro complex **2** from the reaction of **5** with $Et_4N^+Cl^-$. Probably a lower Lewis acidity associated with **4** compared to that with **5** and the tendency of **4** to undergo autocomplexation in the solid state do not allow the stabilization of chloro complex **20**.

As anticipated, the ^{19}F NMR spectra of $[(F)Ge(tdt)_2][Ph_3PMe]$ (**19**) and $[(F)Ge(cat)_2][Et_4N]$ (**8**) show singlets at

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(27) Müller, R.; Heinrich, L. *Chem. Ber.* **1962**, *95*, 2276.

(28) Fink, F. H.; Turner, J. A.; Payne, D. A., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 1571.

(29) Fink, F. H. Ph.D. Dissertation, Tulane University, 1966.

(30) (a) Poller, R. C.; Spillman, J. A. *J. Chem. Soc.* **1966**, 958. (b) Epstein, L. M.; Straub, D. K. *Inorg. Chem.* **1965**, *4*, 1551.

(31) Carpino, L. A.; Sau, A. C. *J. Chem. Soc., Chem. Commun.* **1979**, 514.

Table I. Preparations, Melting Points, and Analytical Data of Spirocyclic Penta- and Hexacoordinated Ge(IV) Complexes[a]

				% found (calcd)			
no.	compd (mp, °C; color)	preparation	recrystn solvent	C	H	N	Cl
7	[(HMPA)$_2$Ge(cat)$_2$] (180–185, greenish)	5 + 2HMPA	C_6H_6:CH_3CN (2:1)	44.51 (44.53)	7.12 (6.85)	13.12 (12.99)	
8	[(F)Ge(cat)$_2$][Et$_4$N] (203–208 dec, gray)	5 or 7 + $Et_4N^+F^-\cdot 2H_2O$	CH_3COCH_3[b]	54.96 (54.84)	6.56 (6.44)	3.24 (3.20)	
2	[(Cl)Ge(cat)$_2$][Et$_4$N] (222–223, gray)	5 or 7 + $Et_4N^+Cl^-$	CH_3CN[b]	52.91 (52.85)	6.04 (6.21)	2.98 (3.08)	
9	[(Br)Ge(cat)$_2$][Et$_4$N] (225–227, brown)	5 + $Et_4N^+Br^-$	CH_3CN	48.25 (48.16)	5.71 (5.66)	2.74 (2.81)	
10	[Ge(cat)$_3$][Et$_3$NH]$_2$ (255 dec, grayish green)	5 + 2Et$_3$N or GeCl$_4$ + 2H$_2$cat + Et$_3$N (excess)	CH_3CN	59.93 (59.94)	7.32 (7.38)	4.72 (4.66)	
11	[Ge(cat)$_3$][Et$_4$N]$_2$ (250 dec, grayish green)	10 + 2$Et_4N^+Cl^-$	CH_3CN:CH_3COCH_3[b] (1:2)	61.87 (62.15)	7.89 (7.97)	4.18 (4.26)	
14	[(Cl)Ge(dtbc)$_2$][Et$_3$NH] (200 dec, colorless)	GeCl$_4$ + 2H$_2$dtbc + 4Et$_3$N	C_6H_6:hexane (1:2)	63.04 (62.74)	8.95 (8.68)	2.07 (2.15)	5.32 (5.42)
15	[(OH)Ge(dtbc)$_2$][Et$_3$NH] (195 dec, colorless)	14 + H_2O	CH_3CN:H_2O (1:1)	64.66 (64.71)	9.00 (9.09)	2.13 (2.21)	0
16	[(OH)Ge(dtbc)$_2$][Et$_4$N] (335 dec, colorless)	14 + $Et_4N^+Cl^-$ + H_2O	CH_3COCH_3[b]	65.76 (65.5)	9.39 (9.31)	2.03 (2.12)	0
18	[(F)Ge(tdt)$_2$][Et$_4$N] (202–203, yellow)	4 + $Et_4N^+F^-\cdot 2H_2O$	CH_3CN	50.01 (49.82)	6.05 (6.09)	2.66 (2.64)	
19	[(F)Ge(tdt)$_2$][Ph$_3$PMe] (110–111, yellow)	4 + $Ph_3PMe^+Br^-$ + $K^+F^-\cdot 2H_2O$	CH_3CN[b]	58.38 (58.50)	4.64 (4.46)		

[a] See text for definitions of abbreviations. [b] Recrystallized from the appropriate solvent at 0 °C.

−118.9 and −140.3 ppm, respectively. Comparison of these data with those of the corresponding spirocyclic tin(IV) compound [(F)Sn(tdt)$_2$][Et$_4$N][32] ($\delta_F = -117.4$) and the spirophosphoranes, FP(cat)$_2$ ($\delta_F = -70.4$[33]) and FP(dtbc) ($\delta_F = -69.5$[34]), shows that there is virtually no change in the ^{19}F chemical shift on changing the spiro atom from Ge to Sn but a significant upward shift of the signal occurs when phosphorus is replaced by germanium. This probably reflects that a Ge–F bond is very similar to a Sn–F bond but differs significantly from a P–F bond as far as the nature of bonding between the central atom and the fluorine atom is concerned. However, additional ^{19}F NMR data for a series of closely related spirocyclic pentacoordinated compounds of main-group elements would be necessary to make a meaningful comparison of this type.

Experimental Section

Proton NMR spectra were recorded with a Varian Model A-60 NMR spectrometer at 60 MHz using 10% (w/v) solutions of the samples in appropriate solvents. Chemical shifts were measured in ppm relative to tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded with a Varian HR-300 spectrometer operating in the CW mode at 282 MHz. The samples were dissolved in acetonitrile, and C_6F_6 was used as the internal standard. The observed chemical shifts are converted to the δ scale, with $CFCl_3$ reference, and shifts upfield from $CFCl_3$ are negative. Infrared spectra of the samples were recorded as KBr pellets on a Beckman IR-10 spectrometer.

Materials. Catechol and 3,5-di-*tert*-butylcatechol (Aldrich) were purified by vacuum sublimation. Tetraethylammonium halides (Eastman Kodak) were dried over P_2O_5 in vacuum before use. Hexamethylphosphoramide (BDH) was stored over calcium chloride and distilled under reduced pressure from calcium hydride. Acetonitrile was dried by distillation over P_2O_5. Triethylamine was distilled over KOH. Germanium tetrachloride (Alfa Ventron) and toluene-3,4-dithiol (Eastman Kodak) were used without further purification.

General Procedure for the Synthesis of Pentacoordinate Ge(IV) Complexes. The spirocyclic derivatives $Ge(C_6H_4O_2)_2\cdot 2H_2O$ (**5**) and $[Ge(C_7H_6S_2)_2]$ (**4**) were treated with an equivalent of the appropriate tetraethylammonium halide in acetonitrile at room temperature in a dry nitrogen atmosphere. Heating of the reaction mixture was necessary to bring about the reaction in the case of the thio derivative **4**. Evaporation of solvent from the reaction mixture gave a crystalline product, which was purified by recrystallization from a suitable solvent or a mixture of solvents. The yields of pure products were 80–85%.

The preparation, melting points, and analytical data of the spirocyclic penta- and hexacoordinated Ge(IV) complexes are given in Table I. The ^1H NMR spectroscopic data of the complexes are presented in Table II. Some typical preparations are described in detail.

Preparation of Bis(*o*-phenylenedioxy)germanium(IV) Dihydrate, $Ge(C_6H_4O_2)_2\cdot 2H_2O$ (5). To a magnetically stirred solution of $GeCl_4$ (4.28 g, 20 mmol) in benzene (50 mL) at room temperature was added dropwise under nitrogen atmosphere a solution of catechol (4.4 g, 40 mmol) and triethylamine (8.08 g, 80 mmol) in benzene (50 mL) over a period of 2 h. Then the reaction mixture was stirred at room temperature for another 1 h. Evaporation of benzene from the reaction mixture afforded a slightly brownish solid dispersed in a gluey mass. This residue was found to be essentially a mixture of $[Et_3NH^+]Cl^-$ and the triethylammonium chloride adduct of bis(*o*-phenylenedioxy)germanium(IV), $[(Cl)Ge(C_6H_4O_2)_2][Et_3NH]$. No attempts were made to isolate the adduct as it was found to be difficultly crystallizable. The residual mixture was treated with water (50 mL) and magnetically stirred to obtain an insoluble white precipitate, which was filtered under suction and dried under oil pump vacuum to obtain **5** (3.2 g, 50%) containing traces of impurities. An analytically pure sample of **5** was obtained as follows: A crude sample of **5** was treated with 1 equiv of $[Et_3NH^+]Cl^-$ or $Et_4N^+Br^-$ in methyl cyanide. When the mixture was stirred, a slightly brownish solution containing some gelatinous precipitate was obtained. The solution was filtered to remove the precipitate. The residue left behind after the evaporation of solvent from the filtrate was hydrolyzed with water to obtain an insoluble white precipitate, which was found to be pure **5**. Anal. Calcd for $C_{12}H_{12}O_6Ge$: C, 44.37; H, 3.72. Found: C, 44.33; H, 3.94. An infrared spectrum of this sample was identical with that of $[Ge(C_6H_4O_2)_2\cdot 2H_2O]$ reported earlier.[11]

Preparation of $[(HMPA)_2Ge(C_6H_4O_2)_2]$ (7). To a suspension of $Ge(C_6H_4O_2)_2\cdot 2H_2O$ (**5**) (0.324 g, 1 mmol) in acetone (15 mL) at room temperature was added hexamethylphosphoramide (0.358 g, 2 mmol). The resulting heterogeneous reaction mixture was heated under reflux for 10 min to obtain a light green solution containing traces of gelatinous precipitate. The solution was cooled to room temperature and filtered. Evaporation of solvent from the filtrate gave a greenish crystalline residue, which was dissolved in methyl cyanide (20 mL), and the solution was treated with $Et_4N^+Br^-$ (0.2 g). The mixture was magnetically stirred to obtain a clear solution. Evaporation of solvent from the mixture gave a crystalline residue, which was treated with benzene (20 mL). The mixture was heated under reflux for 10 min to obtain a colorless solution containing insoluble crystals of

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(32) Sau, A. C.; Holmes, R. R., unpublished results.

(33) Doak, G. O.; Schmutzler, R. *J. Chem. Soc., Chem. Commun.* **1970**, 476.

(34) Eisenhut, M.; Schmutzler, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1452.

Table II. ^{1}H NMR Spectroscopic Data of the Spirocyclic Penta- and Hexacoordinated Ge(IV) Complexes

			chemical shifts (±0.05 ppm)		
no.	compd	solvent	aromatic protons	N–CH_2 or N–CH_3	N–CH_3
7	$[(HMPA)_2Ge(cat)_2]$	$CDCl_3$	6.7^a (m, 8 H)	2.5 (d, 36 H); ^3J(P–N–C–H) = 9 Hz	
8	$[(F)Ge(cat)_2][Et_4N]$	CH_2Cl_2	6.65^a (m, 8 H)	2.80 (q, 8 H)	1.00 (m, 12 H)
2	$[(Cl)Ge(cat)_2][Et_4N]$	CD_3CN	6.80^a (m, 8 H)	3.02 (q, 8 H)	1.10 (m, 12 H)
9	$[(Br)Ge(cat)_2][Et_4N]$	CD_3CN	6.75^a (m, 8 H)	3.15 (q, 8 H)	1.18 (m, 12 H)
10	$[Ge(cat)_3][Et_3NH]_2$	CD_3CN	6.48 (s,^{b} 12 H)	3.3 (m, 12 H)	1.20 (m, 18 H)
11	$[Ge(cat)_3][Et_4N]_2$	CD_3CN	6.32 (s,^{b} 12 H)	3.12 (q, 16 H)	1.12 (m, 24 H)
14	$[(Cl)Ge(dtbc)_2][Et_3NH]^c$	CD_3CN	6.82 (m, 4 H)	3.10 (m, 6 H)	1.20 (t, 9 H)
		CH_2Cl_2	6.82 (m, 4 H)	3.30 (m, 6 H)	1.25 (t, 9 H)
15	$[(OH)Ge(dtbc)_2][Et_3NH]^d$	CH_2Cl_2	6.75 (m, 4 H)	3.11 (m, 6 H)	1.20 (t, 9 H)
16	$[(OH)Ge(dtbc)_2][Et_4N]^e$	CD_3CN	6.75 (m, 4 H)	3.10 (q, 8 H)	1.10 (m, 12 H)
		CH_2Cl_2	6.70 (m, 4 H)	2.82 (q, 8 H)	0.93 (m, 12 H)
18	$[(F)Ge(tdt)_2][Et_4N]^f$	CD_3CN	7.22 (m, 4 H) 6.70 (m, 2 H)	3.10 (q, 8 H)	1.13 (m, 12 H)
19	$[(F)Ge(tdt)_2][MePPh_3]^{g,h}$	CH_2Cl_2	7.2 (m, 4 H) 6.67 (m, 2 H)		

[a] Values are given for the approximate center of the AA′BB′ multiplet. [b] Slightly broadened single peak; the acidic protons of Et_3NH^+ cations could not be located between 0 and 12 ppm. [c] *tert*-Butyl resonances appear as singlets at δ 1.43 and 1.30; the acidic proton of Et_3NH^+ could not be located between 0 and 12 ppm. [d] *tert*-Butyl resonances appear as singlets at δ 1.45 and 1.25; the hydroxyl proton and the acidic proton of the Et_3NH^+ cation were not located between 0 and 10 ppm. [e] *tert*-Butyl resonances appear as singlets at δ 1.40 and 1.30. [f] Methyl protons of the toluene-3,4-dithiolato groups appear as a singlet at δ 2.17. [g] Methyl protons of the toluene-3,4-dithiolato groups appear as a singlet at δ 2.15. [h] Phenyl protons of Ph_3PMe^+ appear as a complex multiplet at δ 7.4–8.18; methyl protons appear as a doublet at δ 2.78; ^2J(P–C–H) = 13 Hz.

$Et_4N^+Br^-$, which adsorbed the greenish impurities. The benzene extract was filtered. Evaporation of solvent from the filtrate gave a solid residue, which was recrystallized for a mixture of benzene and hexane (1:1) to obtain colorless crystals of **7** (yield 0.62 g, 95%).

Preparation of Tetraethylammonium Fluorobis(benzene-1,2-diolato)germanate, $[(F)Ge(C_6H_4O_2)_2][Et_4N]$ (8). To a suspension of $Ge(C_6H_4O_2)_2{\cdot}2H_2O$ (**5**) (0.484 g, 1.5 mmol) in acetonitrile at room temperature was added $Et_4N^+F^-{\cdot}2H_2O$ (0.276 g, 1.5 mmol). When the reaction mixture was stirred, a slightly greenish clear solution formed. Removal of solvent from the mixture in vacuo gave a greenish crystalline residue, which was dried under oil pump vacuum. Recrystallization of the crude product from acetone at 0 °C gave grayish green crystals of **8**.

The complex **8** can also be prepared by the reaction of $[(HMPA)_2Ge(cat)_2]$ (**7**) with 1 equiv of $Et_4N^+F^-{\cdot}2H_2O$ in acetonitrile at room temperature. Selective removal of the hexamethylphosphoramide, liberated in the reaction, by extraction with hot hexane gave the complex **8**.

Complex **2** was prepared by the reaction of $Et_4N^+Cl^-$ with either **5**[9] or **7** and purified by following the same procedure as that described for **8**. No reaction took place between **7** and $Et_4N^+Br^-$ in acetonitrile as was evident by the isolation of the reactants in quantitative yield.

Preparation of Bis(triethylammonium) Tris(*o*-phenylenedioxy)germanium(IV), $[Et_3NH]_2[Ge(cat)_3]$ (10). To a suspension of $Ge(C_6H_4O_2)_2{\cdot}2H_2O$ (**5**) (0.324 g, 1 mmol) in acetonitrile (100 mL) at room temperature was added triethylamine (0.202 g, 2 mmol). When the reaction mixture was stirred, a clear solution was formed immediately. When the reaction mixture was stirred further (after 2–3 min), the clear solution turned green and cloudy and eventually a gelatinous precipitate was thrown out of the solution. The resulting reaction mixture was stirred for another $^1/_2$ h at room temperature. The gelatinous white precipitate (0.04 g) formed was removed by filtration, washed several times with hot acetonitrile, and dried under vacuum. The infrared spectrum of this solid was identical with that of $GeO_2{\cdot}2H_2O$ prepared by the hydrolysis of $GeCl_4$ with water.

Evaporation of solvent from the filtrate of the original reaction mixture gave a grayish green crystalline solid. This was dissolved in hot acetonitrile, and the solution was filtered hot. When the filtrate was cooled to room temperature, crystals of **10** deposited, which were separated by decantation of the mother liquor. Several other crops of crystals of **10** were obtained by gradually stripping off solvent from the mother liquor and cooling the resultant solution to 0 °C.

Reaction of $GeCl_4$ with Catechol in Triethylamine Medium and Formation of $[Et_3NH]_2[Ge(cat)_3]$ (10). Germanium tetrachloride (1.07 g, 5.0 mmol) was added to a vigorously stirred solution of catechol (1.1 g, 10 mmol) in triethylamine (20 mL) at room temperature. An immediate exothermic reaction took place, and a copious white precipitate formed. The resulting reaction mixture was stirred for 1 h. Evaporation of unreacted triethylamine from the reaction mixture in vacuo afforded a brownish white crystalline solid, which was treated with chloroform (50 mL). When the mixture was stirred, a brown solution (due to the dissolution of $[Et_3NH^+]Cl^-$) containing a brownish white insoluble precipitate was obtained. The mixture was filtered under suction. The filtrate was cooled to 0 °C to obtain some brown crystals (0.2 g), which were found to be **10**. The mother liquor left behind was found to contain mainly $[Et_3NH^+]Cl^-$. The residue left behind after treatment of the original reaction mixture with chloroform was treated with acetonitrile (50 mL). The heterogeneous mixture was heated under reflux, and the solution was filtered hot. The insoluble mass was characterized as $GeO_2{\cdot}2H_2O$. The filtrate was cooled to room temperature to obtain grayish green crystals of $[Ge(cat)_3][Et_3NH]_2$ (**10**) (1.92 g).

Preparation of $[Ge(cat)_3][Et_4N]_2$ (11). A mixture of $[Ge(cat)_3][Et_3NH]_2$ (**10**) (0.72 g, 1.2 mmol) and $Et_4N^+Cl^-$ (0.40 g, 2.4 mmol) in acetonitrile (20 mL) was stirred at room temperature for $^1/_2$ h. The reaction mixture turned greenish, and a silky-white crystalline precipitate formed. The precipitate was removed by filtration. When the solvent was stripped from the filtrate in vacuo, a grayish green crystalline solid was obtained. This crude product was dissolved in acetone, and the solution was cooled to 0 °C where pale green lumpy crystals deposited along with colorless crystals of $[Et_3NH^+]Cl^-$. The pale green crystals were separated by handpicking and recrystallized twice from acetone at 0 °C to obtain pure $[Ge(cat)_3][Et_4N]_2$ (**11**).

Both the complexes **10** and **11** were found to be soluble in water.

Reaction of $GeCl_4$ with 3,5-Di-*tert*-butylcatechol and Formation of $[(Cl)Ge(dtbc)_2][Et_3NH]$ (14). To a vigorously stirred solution of $GeCl_4$ (1.29 g, 6 mmol) in benzene (75 mL) at room temperature was added a solution of 3,5-di-*tert*-butylcatechol (2.67 g, 12 mmol) and triethylamine (2.41 g, 24 mmol) in benzene (20 mL) over a period of 0.5 h. An exothermic reaction took place, and a crystalline white precipitate resulted. The reaction mixture was stirred at room temperature for 0.5 h and then heated under reflux for 1 h. The triethylammonium chloride (2.62 g) formed in the reaction was removed by filtration. Evaporation of solvent from the filtrate afforded a brownish white crystalline solid, which was recrystallized twice from a mixture of benzene and hexane (1:1) to obtain colorless needle-shaped crystals of $[(Cl)Ge(dtbc)_2][Et_3NH]$ (**14**). Treatment of **14** with water at room temperature resulted in the formation of the hydroxo derivative $[(OH)Ge(dtbc)_2][Et_3NH]$ (**15**).

Preparation of $[(OH)Ge(C_{14}H_{20}O_2)_2][Et_4N]$ (16). A 1:1 mixture of **14** and $Et_4N^+Cl^-$ in acetonitrile was stirred at room temperature for 0.5 h. The triethylammonium chloride formed due to a metathesis reaction was removed by filtration. Evaporation of solvent from the reaction mixture gave a crystalline residue, which was washed with water to remove traces of $[Et_3NH^+]Cl^-$. The insoluble white solid was filtered under suction and dried under oil-pump vacuum. Recrystallization of this crude product from acetone at 0 °C gave colorless crystals of **16**.

Preparation of Bis(toluene-3,4-dithiolato)germanium(IV) (4). A solution of germanium tetrachloride (0.642 g, 3 mmol) in benzene (10 mL) was added dropwise under vigorous stirring to a solution of toluene-3,4-dithiol (0.94 g, 6 mmol) and triethylamine (1.22 g, 12 mmol) in benzene (50 mL) at room temperature. A curdy white precipitate formed, and the color of the reaction mixture turned yellow. The resulting reaction mixture was heated under reflux for 1 h to obtain a tan solution containing an insoluble white precipitate. Evaporation of solvent from the reaction mixture gave a light purple crystalline residue, which was treated with water (50 mL) to dissolve the triethylammonium chloride byproduct. The water-insoluble crystalline precipitate left behind was filtered under suction and air-dried to obtain an almost pure sample of bis(toluene-3,4-dithiolato)germanium(IV) (**4**) (1.2 g). An analytically pure sample of **4** was prepared as follows: To a suspension of the crude product of **4** in acetonitrile at 81 °C was added tetraethylammonium chloride in small amounts until a clear orange solution was obtained. The solution was filtered hot to remove traces of suspended material. When the solution was cooled to room temperature, needle-shaped crystals of bis(toluene-3,4-dithiolato)germanium(IV) (**4**) were obtained; mp 200–201 °C (lit.[29] mp 195–196 °C). Anal. Calcd for $C_{14}H_{12}S_4Ge$: C, 44.12; H, 3.17. Found: C, 44.21; H, 2.93.

Preparation of Methyltriphenylphosphonium Fluorobis(4-methylbenzene-1,2-dithiolato)germanate, $[Ph_3PMe][(F)Ge(C_7H_6S_2)_2]$ (19). $Ge(tdt)_2$ (**4**) (0.38 g, 1 mmol) and $KF{\cdot}2H_2O$ (0.19 g, 2 mmol) were suspended in a solution of methyltriphenylphosphonium bromide (0.36 g, 1 mmol) in acetonitrile (50 mL). The resulting heterogeneous reaction mixture was heated under reflux for 3 h to obtain a yellow solution. The reaction mixture was cooled to room temperature and filtered to remove the insoluble potassium halide. The filtrate was concentrated (10 mL) and cooled to 0 °C to obtain pale yellow crystals of $[Ph_3PMe][(F)Ge(C_7H_6S_2)_2]$ (**19**).

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Registry No. **2**, 76375-54-7; **4**, 79084-23-4; **5**, 79084-27-8; **7**, 79084-28-9; **8**, 76375-58-1; **9**, 76375-56-9; **10**, 79084-29-0; **11**, 79084-30-3; **14**, 79084-32-5; **15**, 79084-34-7; **16**, 79084-36-9; **18**, 79084-38-1; **19**, 79084-39-2; $GeCl_4$, 10038-98-9.

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Molecular Complex Formation of Tricarbonyl(η^6-[2.2]paracyclophane)chromium and 1,3,5-Trinitrobenzene

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Tricarbonyl(η^6-[2.2]paracyclophane)chromium (([2.2]paracyclophane)$Cr(CO)_3$) forms a charge-transfer complex with 1,3,5-trinitrobenzene (1,3,5-TNB) in 1,2-dichloroethane. The ionization potential of ([2.2]paracyclophane)$Cr(CO)_3$ was determined to be 7.2 eV from the observed intermolecular charge-transfer transition energy. The value was close to those obtained for the usual chromium tricarbonyl complexes with η^6-coordinated benzene derivatives. In solution, the acceptor molecule is more likely to interact directly with the chromium d orbital lobes by sitting beneath the base of the pyramid formed by three metal–carbonyl bonds rather than by stacking on the aromatic ring as in the usual aromatic molecular complexes. This is also supported by the fact that some other chromium–carbonyl complexes without an η^6-coordinated aromatic ring also exhibit spectral evidence of complex formation with 1,3,5-TNB.

(η^6-Arene)tricarbonylchromium ((arene)$Cr(CO)_3$) forms a charge-transfer complex with electron acceptors such as 1,3,5-trinitrobenzene (1,3,5-TNB) and tetracyanoethylene.[1-3] It has been assumed that the bulky acceptor 1,3,5-TNB forms a molecular complex by a charge-transfer interaction of 1,3,5-TNB with the central chromium through the η^6-coordinated benzene ring in a "face-to-face" stack, which has been found in the molecular complexes of 1,3,5-TNB and aromatic compounds.[4] A study by X-ray crystallography of the molecular complex of (η^6-anisole)$Cr(CO)_3$ and 1,3,5-TNB has revealed a structure of "face-to-face" stacking of the benzene rings of coordinated anisole and 1,3,5-TNB. In the crystal, however, a molecule of (anisole)$Cr(CO)_3$ is sandwiched between two 1,3,5-TNB molecules. This implies that 1,3,5-TNB molecules may accept a charge of the chromium dπ orbitals not only through the "face-to-face" stack of the benzene rings but also through a direct interaction with the chromium orbitals extending between three metal–carbonyl bonds. In fact, the distance (4.70 Å) between chromium and the center of the 1,3,5-TNB in contact with carbonyl groups is shorter than the distance (5.14 Å) between chromium and the 1,3,5-TNB located on η^6-coordinated arene (Figure 1). Since the tricarbonylchromium group is electron withdrawing, it confers on the coordinated arene a higher acidity and a higher susceptibility to nucleophilic substitution but a lower susceptibility to electrophilic substitution.[5-9] In fact, a greater dipole moment observed indicates an appreciable migration of the arene π electron into the tricarbonylchromium group.[10] (arene)$Cr(CO)_3$ forms a molecular complex with electron acceptors rather than electron donors. The ionization potential of (arene)$Cr(CO)_3$ can be evaluated from the charge-transfer excitation energy in the molecular complexes with electron

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(1) Huttner, G.; Fischer, E. O.; Fischer, R. D.; Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Organomet. Chem.* **1966**, *6*, 288.

(2) Kobayashi, H.; Kobayashi, M.; Kaizu, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3109.

(3) Kobayashi, H.; Kobayashi, M.; Kaizu, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1222.

(4) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1966**, 822.

(5) Fisher, E. O.; Ofele, L.; Essler, H.; Frohlich, W.; Mortensen, J. P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763.

(6) Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551.

(7) Riemschneider, R.; Becker, O.; Franz, K. *Monatsh. Chem.* **1959**, *90*, 571.

(8) Brown, D. A.; Raju, J. R. *J. Chem. Soc. A* **1966**, 40.

(9) Semmelhack, M. F. "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; p 361.

(10) Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1959**, *92*, 938.