and formylation of the resultant racemic deformylgeissoschizine (**6b**).[7]

A direct synthesis of (±)-geissoschizine (**6a**) from tetracycle **3** without loss of any nuclear carbon was executed by the following reaction sequence. Reduction of diester **9b** [$(i\text{-Bu})_2AlH$, CH_2Cl_2, −78 °C] yielded (60%) amorphous (±)-3-isogeissoschizine (**10b**) [IR ($CHCl_3$) 3470, 1717, 1662, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50, 1.61 (d, 3, J = 6 Hz, Me of two isomers), 3.13, 3.18 (s, 2, H_2-21 of two isomers), 3.65, 3.71 (s, 3, OMe of two isomers), 5.36, 5.55 (q, 1, J = 6 Hz, H-19 of two isomers), 6.9–7.6 (m, 4, aromatic Hs), 8.00 (s, 1, H-17)], which could be converted (HCl, MeOH, ambient temperature, 18 h) (91%) into amorphous acetal **10c** [IR ($CHCl_3$) 3395, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58, 1.68 (s, 3, Me of two isomers), 3.18 (s, 2, H_2-21), 3.30, 3.35, 3.40, 3.49, 3.58, 3.78 [s, 9, $(OMe)_3$ of two isomers], 4.36 (d, 1, J = 6 Hz, H-17), 5.46, 5.57 (q, 1, J = 6 Hz, H-19 of two isomers), 6.8–7.5 (m, 4, aromatic Hs)]. Carbon-3 epimerization of the latter [$m\text{-}ClC_6H_4CO_3H$, CH_2Cl_2, 0–25 °C, 5 h; $(CF_3CO)_2O$, CH_2Cl_2, −78–0 °C, 4 h; $NaBH_4$, THF, 0 °C, 1 h] yielded (21%) (±)-geissoschizine dimethyl acetal (**6c**) [mp 129–131 °C; IR ($CHCl_3$) 3472, 1733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60, 1.70 (d, 3, J = 6 Hz, Me of two isomers), 3.19 (s, 2, H_2-21), 3.25, 3.31, 3.40, 3.45, 3.58, 3.80 [s, 9, $(OMe)_3$ of two isomers], 5.52, 5.60 (q, 1, J = 6 Hz, H-19 of two isomers), 6.9–7.5 (m, 4, aromatic Hs)], whose partial hydrolysis (4.5 N HCl, acetone, ambient temperature, 24 h) gave (31%) (±)-geissoschizine (**6a**) [mp 186–188 °C (lit.[5] mp 187–189 °C); IR and ^1H and ^{13}C NMR spectra are identical with those of an authentic sample].[8]

Acknowledgment. We are indebted to the U.S. Public Health Service for support of this work, Professor S. Sakai for the gift of a sample of hirsutine, and Drs. R. Goutarel and M. Pais for the present of a geissoschizine specimen.

---

(7) The oxidation–reduction sequence has been reported[5] to produce an 8% (25%, based on actual **10a** utilization) yield of **6b**. This now has been improved to 40% (51%, based on actual **10a** utilization) by the following reaction alteration. Ester **10a** was oxidized ($m\text{-}ClC_6H_4CO_3H$, CH_2Cl_2, 0 °C, 1 h), the N_b-oxide was dehydrated [$(CF_3CO)_2O$, CH_2Cl_2, −78 to 0 °C, 4 h], and the resultant immonium salts were reduced ($NaBH_4$, THF, 0 °C, 1 h).

(8) For previous syntheses of (±)-geissoschizine (**6a**) see ref 5 and B. Hachmeister, D. Thielke, and E. Winterfeldt, *Chem. Ber.*, **109**, 3825 (1976).

Ernest Wenkert,* Yashwant D. Vankar, Jhillu S. Yadav
Department of Chemistry, Rice University
Houston, Texas 77001

Received August 25, 1980

A New Geometrical Form of Germanium. Synthesis and Structure of Tetraethylammonium 2-Chloro-2,2′-spirobis(1,3,2-benzodioxagermole)

Sir:

Although pentacoordinated Ge(IV) species[1] having a trigonal bipyramidal structure have been characterized by X-ray crystallography, no reports are available concerning the structure of a spirocyclic pentacoordinate Ge(IV) compound.

We report herein the preparation and X-ray crystal structure of the first pentacoordinated Ge(IV) compound having a square pyramidal conformation. The compound, tetraethylammonium 2-chloro-2,2′-spirobis(1,3,2-benzodioxagermole) (**2**), mp 223-224 °C, was prepared by the reaction of (**1**)[2,3] with 1 equiv of $Et_4N^+Cl^-$ in methyl cyanide at room temperature (yield 90%). The bromo and fluoro analogues, **3** and **4**, were also prepared. Colorless crystals of **2** suitable for X-ray diffraction analysis were grown from methyl cyanide at 25 °C.

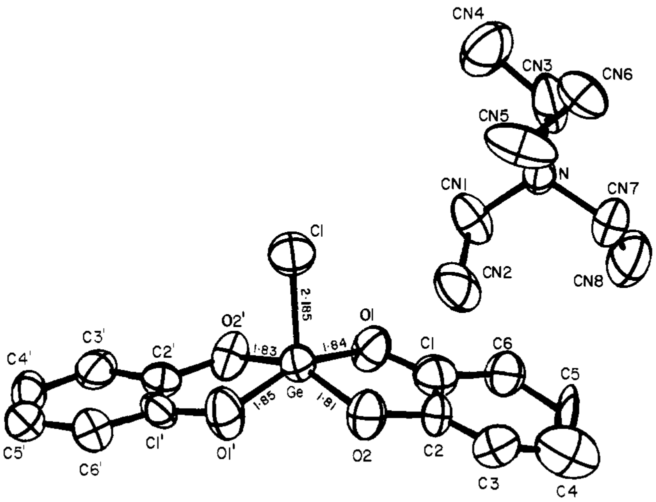
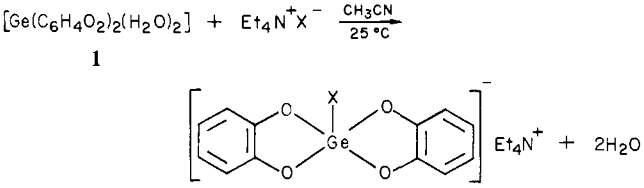


Figure 1. ORTEP plot of $[(C_6H_4O_2)_2GeCl]^-NEt_4^+$ (**2**) with thermal ellipsoids shown at the 50% probability level. Bond lengths: Ge–O1 = 1.842 (11), Ge–O1′ = 1.852 (14), Ge–O2 = 1.811 (12), Ge–O2′ = 1.828 (13), Ge-Cl = 2.185 (4) Å. Bond angles: O1–Ge–O1′ = 157.5 (6)°, O2–Ge–O2′ = 151.6 (6)°, O1–Ge–O2 = 88.0 (4)°, O1′–Ge–O2′ = 87.4 (5)°, O1–Ge–O2′ = 86.5 (6)°, O1′–Ge–O2 = 87.1 (6)°, Cl–Ge–O1 = 102.7 (4)°, Cl–Ge–O2 = 105.3 (5)°, Cl–Ge–O1′ = 99.8 (5)°, Cl–Ge–O2′ = 103.1 (4)°.



1

2, X = Cl, mp 223–224 °C
3, X = Br, mp 210 °C dec
4, X = F, mp 203 °C dec

Crystal Data. $C_{20}H_{28}O_4NClGe$, space group $Pbc2_1$ (alternate setting of $Pca2_1$, C_{2v}^5, No. 29),[4] with a = 12.244 (4), b = 16.366 (5), c = 10.662 (8) Å, and Z = 4. Independent reflections (1986) were measured on an Enraf–Nonius CAD4 automated diffractometer, using graphite monochromated Mo K$\bar{\alpha}$ radiation and the θ–2θ scan mode, to a maximum $2\theta_{MoK\bar{\alpha}}$ of 50°. The structure was solved by using heavy-atom techniques. Anisotropic full-matrix least-squares refinement[5a] based on the 27 independent nonhydrogen atoms led to a conventional unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.059[5b] for the 1428 reflections having $I \geq 2\sigma(I)$.

The molecular geometry of **2** is shown in the ORTEP plot of Figure 1. It is evident, from the bond parameter data given in

---

(1) (a) M. S. Bilton and M. Webster, *J. Chem. Soc., Dalton Trans.*, 722 (1972); (b) L. O. Atovmjan, Ja. Ja. Bleidelis, A. A. Kemme, and R. P. Shibaeva, *J. Struct. Chem.*, **11**, 295 (1970); (c) A. A. Kemme, Ja. Ja. Bleidelis, R. P. Shibaeva, and L. O. Atovmjan, *ibid.*, **14**, 90 (1973); (d) M. Dräger, *Chem. Ber.*, **108**, 1723 (1975); (e) M. Dräger, *Z. Anorg. Allg. Chem.*, **423**, 53 (1976).

(2) G. I. Kurnevich and V. B. Vishnevskii, *J. Appl. Spectros.*, **13**, 1201 (1970).

(3) Compound **1** was prepared by the slow addition (2 h) of a mixture of 2 equiv of catechol and 4 equiv of triethylamine in benzene to 1 equiv of germanium tetrachloride in benzene at room temperature. Evaporation of solvent from the reaction mixture and treatment of the residue with water gave a light-brown flocculent amorphous precipitate. Further purification of the sample of **1** was achieved by dissolving the crude product in a solution of $Et_4N^+Br^-$ in CH_3CN at 25 °C to form $[Ge(C_6H_4O_2)Br]^-Et_4N^+$ (**3**). Hydrolysis of **3** at 25 °C afforded pure **1** (65% yield).

(4) "International Tables for X-ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969, p 115.

(5) (a) The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 4, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Ge, Cl, and O were taken from the same source, pp 149–150; (b) this value is for the configuration having the lowest R_w.

0002-7863/80/1502-7972$01.00/0

the legend, that **2** is near square pyramidal. The four oxygen atoms, which form the base of the square pyramid, are coplanar to within ±0.05 Å, with the Ge atom displaced by 0.40 Å out of this plane toward the Cl atom. Based on the dihedral angle method, as applied to cyclic phosphoranes,[6,7] the geometry about the Ge atom is displaced by 84% (91% using unit vectors) from the trigonal bipyramid toward the square-pyramidal configuration. As is often the case for species which follow the local C_{2v} constraint of the coordinate connecting the trigonal bipyramid to the rectangular pyramid, the molecule has approximate 2-fold symmetry. In this case, the pseudo-2-fold axis is coincident with the Ge–Cl bond. Following the trend observed for cyclic phosphoranes,[6,7] the Ge–O_{ax} bonds are, on the average, 0.03 Å longer than the Ge–O_{eq} bonds.

On the basis of spectroscopic data, the water molecules in **1** are assigned to be coordinated to germanium through oxygen, making germanium hexacoordinated.[2] If this is the case, the formation of **2** from **1** in methyl cyanide and reversing **3** to **1** in aqueous medium[3] reflects the closeness of stabilization energy between a five- and a six-coordinated Ge(IV) species. The recent discovery of the rectangular pyramidal geometry for a pentacoordinated Sn(IV) species[8] and the present square-pyramidal structure for **2** strongly suggest the existence of similar structures for spirocyclic pentacoordinated compounds of silicon(IV).

Acknowledgment. The support of this research by the National Science Foundation is greatly appreciated as is the generous allocation of computing time by the University of Massachusetts Computing Center.

Supplementary Material Available: Atomic coordinates (Table I) and anisotropic thermal parameters (Table II) (4 pages). Ordering information is given on any current masthead page.

---

(6) R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977).
(7) R. R. Holmes, *Acc. Chem. Res.*, **12**, 257 (1979).
(8) A. C. Sau, R. O. Day, and R. R. Holmes, submitted for publication.

Arjun C. Sau, Roberta O. Day, Robert R. Holmes*
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003

Received August 15, 1980

Synthesis and Structural Characterization of Bimetallic Fe-Pt Carbonyl Clusters: Their Relationship with Bimetallic Fe-Pd Carbonyl Clusters

Sir:

Recently we have reported the synthesis and structural characterization of $[Fe_4Pd(CO)_{16}]^{2-}$, $[Fe_4Pt(CO)_{16}]^{2-}$, and $[Fe_6Pd_6(CO)_{24}H]^{3-}$.[1] The dodecanuclear compound has been obtained in very low yields despite efforts to improve its synthesis. Subsequent work on the bimetallic Fe–Pt carbonyl clusters has resulted in the isolation and characterization of new mixed Fe–Pt carbonyl cluster anions, viz., $[Fe_3Pt_3(CO)_{15}]^{2-}$, $[Fe_3Pt_3(CO)_{15}]^-$, and $[Fe_4Pt_6(CO)_{22}]^{2-}$, and has suggested a reasonable mechanism of formation for the dodecanuclear Fe–Pd carbonyl clusters previously reported.[1]

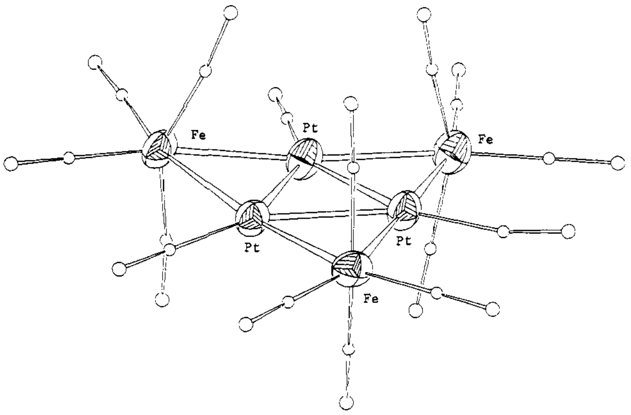


Figure 1. ORTEP view of one of the two independent monoanions found in the unit cell of $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$.

Table I. Average Bond Distances (Å) and Angles (Deg) in the Fe–Pt Bimetallic Carbonyl Clusters[a]

	$[Fe_3Pt_3(CO)_{15}]^{2-}$	$[Fe_3Pt_3(CO)_{15}]^-$	$[Fe_4Pt_6(CO)_{22}]^{2-}$
Pt–Pt	2.750	2.656	2.677[b] 2.790[c]
Fe–Pt	2.596	2.587	2.597[d] 2.540[e]
Pt–C	1.73	1.80	1.78
C–O	1.21	1.19	1.22
Pt–C–O	175.3	173.3	173.9
Fe–C	1.72	1.76	1.72
C–O	1.17	1.16	1.18
Fe–C–O	175.4	173.8	173.1

[a] Typical esd's on single distances follow: Pt–Pt, 0.001; Pt–Fe, 0.004; Pt–C and Fe–C, 0.03; C–O, 0.04 Å. [b] Pt–Pt distances within the two Fe_2Pt_3 units (average of six). [c] Pt–Pt distances between the two Fe_2Pt_3 units (average of four). [d] Fe–Pt distances involving the two outer Pt atoms (average of four). [e] Fe–Pt distances involving the four inner Pt atoms (average of four).

The green $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion (ν_{CO} in CH_3CN at 1995 (s), 1960 (ms), 1930 (sh), and 1905 (m) cm^{-1}) has been obtained both by redox condensation between $[Pt_3(CO)_6]^{2-}$[2] and $Fe(CO)_5$ and by reaction under nitrogen of $[Fe_3(CO)_{11}]^{2-}$[3] with K_2PtCl_4 in a 1:1.5 molar ratio. In acetonitrile at 70 °C the reaction is complete in 3–4 h and follows the apparent stoichiometry in eq 1.

$$2[Fe_3(CO)_{11}]^{2-} + 3Pt^{2+} \rightarrow [Fe_3Pt_3(CO)_{15}]^{2-} + Fe(CO)_5 + 2Fe^{2+} + 2CO \quad (1)$$

Monitoring by IR shows the intermediate formation of $[Fe_4Pt(CO)_{16}]^{2-}$. The $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion may also be obtained by reaction of preformed $[Fe_4Pt(CO)_{16}]^{2-}$ and K_2PtCl_4 in a ca. 1:1 molar ratio.

In the presence of an excess of Pt(II) salts, reaction 1 easily results in the formation of variable amounts of the brown paramagnetic $[Fe_3Pt_3(CO)_{15}]^-$ anion (ν_{CO} in CH_3CN at 2015 (s), 2000 (sh), and 1950 (ms) cm^{-1}; $\mu = 1.6\ \mu_B$[4]).

This last compound has been obtained in almost quantitative yields from preformed $[Fe_3Pt_3(CO)_{15}]^{2-}$ salts by controlled oxidation in dichloromethane or tetrahydrofuran solution with iodine, acids (H_3PO_4 or H_2SO_4), or Cu^+ or Ag^+ salts. The dianion may be reversibly regenerated from the paramagnetic anion by reduction with alkali hydroxides in methanol. As a result, both the $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_3Pt_3(CO)_{15}]^-$ derivatives may be obtained from reaction 1 in very good yields (ca. 70%).

The green $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion is stable in solution under an inert atmosphere, while the paramagnetic $[Fe_3Pt_3(CO)_{15}]^-$ anion slowly decomposes; the decomposition of the latter is greatly accelerated by heating the solution at ca. 80–90 °C for a few hours and affords the decanuclear brown $[Fe_4Pt_6(CO)_{22}]^{2-}$ dianion (ν_{CO} in CH_3CN at 2020 (s), 2010 (s), 1990 (sh), and 1930 (ms) cm^{-1}).

All of these Fe–Pt mixed-metal carbonyl clusters have been isolated in the solid state as trimethylbenzyl- or tetrabutylammonium salts, and their structures have been ascertained by X-ray diffraction.[5,6] The two hexanuclear $[Fe_3Pt_3(CO)_{15}]^{2-}$ and

---

(1) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 3242–4.
(2) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225–31 and references therein.
(3) Yip-Kwai, Lo F.; Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 7691.
(4) By the Gouy method.

0002-7863/80/1502-7973$01.00/0