TABLE II

ELECTRONIC SPECTRAL DATA[a]

Compound	λ_{max}, cm^{-1}	ϵ	Compound	λ_{max}, cm^{-1}	ϵ
$Co(M)_3(ClO_4)_2$	18,382	20	$Ni(E)_3(ClO_4)_2$	23,256	16
$Ni(M)_3(ClO_4)_2$	23,419	14		12,195	5
	12,500	5		7,246	4
	7,299	3	$Cu(E)_3(ClO_4)_2$	10,870	27
$Cu(M)_3(ClO_4)_2$	10,870	24	$Co(P)_3(ClO_4)_2$	18,939	21
$Co(E)_3(ClO_4)_2$	18,315	25	$Ni(P)_3(ClO_4)_2$	23,256	20
				12,195	6
				7,220	3
			$Cu(P)_3(ClO_4)_2$	10,870	41

[a] In nitromethane.

complexes, the magnetic moments are at the high end of the range expected for spin-free octahedral complexes [4.7–5.2 BM for Co(II), 2.9–3.4 BM for Ni(II), 1.7–2.2 BM for Cu(II)].

The P–O frequency decreased by about 10–40 cm^{-1} in the complexes, indicating coordination through the phosphoryl donor site. This is expected since X-ray diffraction studies[9] have shown that the coordination sites in octamethylpyrophosphoramide (OMPA) are the phosphoryl oxygen atoms rather than the dimethylamino nitrogen atoms.

Acknowledgments.—Portions of this research were supported by NIH-GM-15451-03. The Varian XL-100-15 spectrometer and the Faraday magnetic apparatus were purchased through Vanderbilt's "Centers of Excellence" award under the Science Development Program sponsored by the National Science Foundation and Vanderbilt University.

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Facile Syntheses of Germanium Dibromide, Hexabromodigermane, and Tribromomethyltribromogermane

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Previously reported syntheses of germanium dibromide are the reactions of hydrogen bromide gas with germanium[1] and aqueous hydrogen bromide with germanium(II) hydroxide.[2] The first method produces a mixture of tribromogermane and germanium tetrabromide. Upon vacuum distillation, the tribromogermane decomposes into hydrogen bromide and germanium dibromide. Tribromogermane is also believed to be an intermediate in the second method.[2] Thus, the dibromide prepared by either method may contain traces of protonic impurities, and we sought a preparation which would eliminate these contaminants.

Germanium dichloride has been prepared from germanium and germanium tetrachloride,[3] and we now report a similar route to the dibromide utilizing germanium and either bromine or germanium tetrabromide. During the investigation, several new insertion reactions of germanium dibromide were also discovered.

Experimental Section

Germanium powder was obtained from the Eagle Pitcher Corp., Quapaw, Okla. Raman spectra were obtained on a Spex Ramalog laser unit with the Spex 1401 monochromator. The excitation wavelength was the 4880-Å line of Ar^+. Precession photographs of $GeBr_2$ were obtained using Cu Kα radiation. A piece of thin nickel foil was placed on the layer line screen to filter the white radiation. Standard Schlenk-tube techniques[4] were used to maintain inert atmospheres. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Germanium Dibromide.—Germanium powder was sprinkled onto glass wool loosely packed in a vertical Vycor tube (18-mm o.d.) wound with a heating element and covered with asbestos tape (Figure 1). The tube was packed by alternately adding thin layers of glass wool and germanium (*ca.* 0.1 g per layer). It is important that the metal be dispersed throughout the volume of the tube as evenly as possible. Bromine (twice the theoretical amount for $GeBr_2$) was placed in A (Figure 1), the

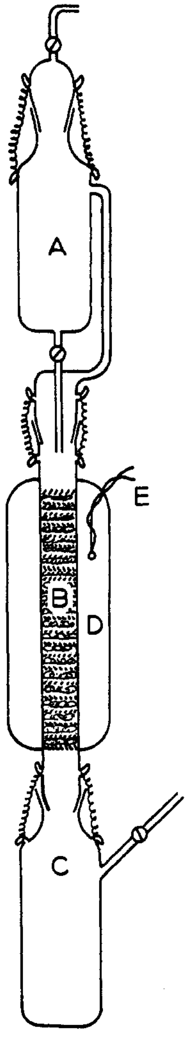

Figure 1.—Apparatus for the synthesis of germanium dibromide: A, constant-pressure dropping funnel; B, germanium powder dispersed on Pyrex wool; C, Schlenk tube; D, heating elements and insulation; E, thermocouple leads.

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[1] F. M. Brewer and L. M. Dennis, *J. Phys. Chem.*, **31**, 1526 (1927).

[2] T. K. Gar and V. F. Mironov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 855 (1965).

[3] L. M. Dennis, W. R. Orndorff, and D. L. Tabern, *J. Phys. Chem.*, **30**, 1050 (1926).

[4] D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1968.

stopcock at C was connected to an oil bubbler, and the whole apparatus was flushed with nitrogen while the tube was heated to 450°. An ice bath was then placed around receiver C and the nitrogen stream was discontinued. Bromine was added dropwise (*ca.* 2 drops/sec) and the rate was adjusted occasionally to maintain a slight positive pressure in the receiver (as indicated by the bubbler). A white mist emerged from the heated tube, followed by drops of yellow, oily liquid which solidified on cooling. The addition of bromine was stopped when the first traces of bromine vapor emerged from the reactor tube. The nitrogen flow was restored and the apparatus was allowed to cool. The oil bubbler at C was replaced by a source of nitrogen and tube C was then removed. The contents of the receiver were dissolved in freshly opened anhydrous ether which had been deoxygenated by a stream of nitrogen. Filtration[4] gave a small amount of subbromide (see below) and a clear yellow solution. The ether was stripped off at reduced pressure and the residue heated to 90° in a water bath. Distillation of the tetrabromide at 0.5 mm into a 0° trap left pale, cream-colored crystals of $GeBr_2$. *Anal.* Calcd for $GeBr_2$: Ge, 31.24; Br, 68.76. Found: Ge, 31.24; Br, 68.71.

Pure germanium dibromide was also obtained by passing recovered germanium tetrabromide over germanium under identical conditions.

Hexabromodigermane.—An 8.0-ml (0.064-mol) amount of germanium tetrabromide, 3.0 g (0.013 mol) of germanium dibromide, and 15 ml of toluene were heated to reflux under nitrogen. In 5 min, the dibromide dissolved to give a clear, colorless solution. Upon cooling to room temperature, the solution deposited a crop of white needles ($GeBr_2$). After filtration, the solvent and most of the tetrabromide were pumped off under high vacuum. Fifty milliliters of petroleum ether (bp 30–60°) was added and the solution was cooled to −60°. White crystals (2.0 g, 25%) slowly deposited. *Anal.* Calcd for Ge_2Br_6: Ge, 23.25; Br, 76.75. Found: Ge, 22.89; Br, 76.44.

Tribromomethyltribromogermane.—This compound was produced in 30% yield from $GeBr_2$ and CBr_4 using the procedure described above for the preparation of hexabromodigermane. *Anal.* Calcd for $GeCBr_6$: Ge, 12.87; Br, 85.00. Found: Ge, 12.46; Br, 84.72.

Germanium Subbromide.—A sample of germanium dibromide was suspended in refluxing toluene (nitrogen atmosphere) for 20 hr. The mixture was filtered while hot to give a brown solid. The toluene was distilled from the filtrate leaving a residue of germanium tetrabromide. *Anal.* Found: Ge, 48.01; Br, 46.00.

Results and Discussion

Germanium powder reacts at a moderately fast rate with germanium tetrabromide at 300–600° to give germanium dibromide. The tetrabromide may be prepared *in situ* by adding bromine to germanium in a flow reactor (Figure 1). Germanium tetrabromide is formed in the head of the tube and is then reduced to the dibromide by the metal lower in the column. As the germanium is consumed and the effective length of the column decreases, the ratio of dibromide to tetrabromide in the effluent decreases. Thus, a low cross section to length ratio is desirable for the reaction tube. Under our conditions, approximately 10–20% of the germanium remained unreacted when the proportion of dibromide in the effluent was so low that further addition of bromine or germanium tetrabromide was unwarranted. The unreacted germanium is readily recycled, as is the tetrabromide which is recovered from the effluent. Higher temperatures give a higher conversion to dibromide, but above about 500° the product is badly discolored by the presence of a subbromide (see below).

In a typical run, bromine was added to 18 g of germanium at 350° to give 22 g (38% conversion[5]) of germanium dibromide and 38 g (39%) of the tetrabromide. Passing 150 g of tetrabromide through the tube packed with 20 g of germanium at 400° gave 65 g (51%) of dibromide. The germanium dibromide is purified by dissolving the contents of the receiver in ether, filtering the resulting solution, and distilling off the ether and tetrabromide at low pressures. A red oil, which appears to be a complex between germanium dibromide, tetrabromide, and ether, often appears during the purification step. Upon heating under vacuum, the complex dissociates and deposits pure germanium dibromide.

When prepared in the manner described here, germanium dibromide has a pale cream color and melts at 143–144° (rapid heating) *in vacuo*. Crystals grown by slowly decomposing Ge_2Br_6 (see below) are monoclinic, $P2_1/c$, $a = 11.3$, $b = 9.07$, $c = 6.76$ Å, $\beta = 102°$, $Z = 4$. At 295°, the molten dibromide rapidly deposits a germanium mirror *via* the disproportionation

$$2GeBr_2 \xrightarrow{295°} Ge + GeBr_4 \quad (1)$$

Heating the dibromide in the presence of a nonpolar solvent causes the disproportionation to occur at a lower temperature to give germanium subbromides. The color of a suspension of germanium dibromide in refluxing toluene rapidly deepens from white to red-orange and to chocolate brown. The brown material had a Ge:Br ratio of 1:0.85 (see eq 2). The sub-

$$GeBr_2 \xrightarrow[\text{toluene}]{110°} GeBr_{0.85} + GeBr_4 \quad (2)$$

bromide is insoluble in all common solvents and liberates bromide on contact with water to form a tan solid. Schwartz and Baronetzky[6] have described a similar series of brown subchlorides, $GeCl_x$ ($0.75 \leq x \leq 1.0$).

During the purification step in which germanium tetrabromide is distilled away from the dibromide, it was observed that some dibromide was transported to cooler portions of the apparatus. Since germanium dibromide is not appreciably volatile up to its decomposition point, it was obvious that a volatile compound was decomposing to give the dibromide. It was shown that the dibromide inserts into the Ge–Br bond of the tetrabromide to give hexabromodigermane in a reversible reaction

$$GeBr_2 + GeBr_4 \rightleftarrows Br_3Ge\text{–}GeBr_3 \quad (3)$$

Hexabromodigermane is a white, air-sensitive solid which melts at 103–106° when the evacuated capillary is placed in an oil bath initially at 95°. Slow heating from room temperature causes the reverse of reaction 3 to occur near 85°. Solutions of the hexabromide are unstable at room temperature and slowly deposit large, single crystals of germanium dibromide. Raman-active fundamentals are observed at 315, 196, and 78 cm^{-1} (all A_{1g}) and 339, 111, and 68 cm^{-1} (all E_g). Ir bands appear at 327 and 247 cm^{-1}. The six Raman modes and the noncoincidence with the ir bands establish a D_{3d} (staggered) conformation for Ge_2Br_6 in the solid.

The only other hexahalodigermane reported to date is Ge_2Cl_6, prepared in small quantities from $GeCl_4$ in a glow discharge.[7,8] An insertion of $GeBr_2$ into the Ge–

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(5) The per cent conversions are based on the amount of germanium placed in the reactor.

(6) R. Schwartz and E. Baronetzky, *Z. Anorg. Allg. Chem.*, **275**, 1 (1954).

(7) D. F. Shriver and W. L. Jolly, *J. Amer. Chem. Soc.*, **80**, 6692 (1958).

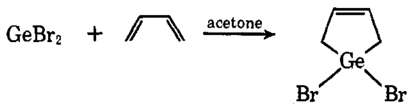
(8) W. L. Jolly, C. B. Lindahl, and R. W. Kopp, *Inorg. Chem.*, **1**, 958 (1962).

Cl bond of germanium tetrachloride, followed by halogen exchange with excess tetrachloride, would be a desirable route to large quantities of hexachlorodigermane. However, under conditions employed for the preparation of Ge_2Br_6, the dibromide failed to react with germanium tetrachloride. Germanium dibromide also did not react with the methylbromogermanes, $(CH_3)_nGeBr_{4-n}$. The dibromide does react with carbon tetrabromide, however, to form tribromomethyltribromogermane (I)

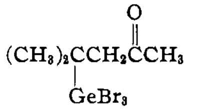
$$GeBr_2 + CBr_4 \longrightarrow \underset{\text{I}}{Br_3C\text{–}GeBr_3} \tag{4}$$

Compound I is a white, air-stable solid which melts with decomposition at 230°. Raman-active fundamentals are observed at 739, 657, 334, 325, 236, 169, 160, 120, 82, and 62 cm^{-1}. Preliminary normal-coordinate calculations by Professor R. C. Taylor of this department indicate that the expected eleventh fundamental (asymmetric $GeBr_3$ rock), which should appear near 30 cm^{-1}, is buried under the excitation line.

The absence of protonic impurities in $GeBr_2$ noticeably improves the yields of "carbenoid" products when allowed to react with unsaturated compounds.[9] We have consistently obtained yields of 1,1-dibromo-1-germacylcyclopentene-3 (II) as high as 81% using $GeBr_2$ prepared as described above in eq 5. In contrast, Gar and Mironov[2] reported the formation of a considerable amount of polymer and only a 28% yield of II using $GeBr_2$ prepared from the hydroxide and hydrobromic acid. Instead of polymer formation, we observed a small amount of 4-methyl-4-tribromogermylpentane-2-one (III) (τ 7.30, 7.83, 8.47; area ratio 2:3:6; mp 63–64°; ν_{CO}, 1670 cm^{-1}) from the reaction of $GeBr_2$ with the acetone solvent.[10]



II (5)



$$(CH_3)_2\underset{\displaystyle GeBr_3}{\underset{|}{C}}CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3$$

III

The facile synthesis of germanium dibromide reported here should aid investigations of the interesting reactions of divalent germanium.

Acknowledgment.—This work was supported by Grant 4853-AC3 from the Petroleum Research Fund, administered by the American Chemical Society. The Raman spectrometer was purchased with the help of the National Science Foundation, Grant GP-87419.

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[9] O. M. Nefedov and M. N. Manakov, *Angew. Chem., Int. Ed. Engl.*, **5**, 1021 (1966).

[10] S. P. Kolesnikov, B. L. Perl'mutter, and O. M. Nefedov, *Dokl. Akad. Nauk SSSR*, **180**, 112 (1968), have reported the corresponding trichlorogermyl ketone (III).

Correspondence

The Character of the Metal Atoms in Platinum–Tin Cluster Compounds

Sir:

The oxidation states of metal atoms in cluster compounds are often not apparent from inspection of the molecular formulas. There has been much discussion about the oxidation state of tin in the clusters formed by interaction of platinum chlorides with stannous chloride. Many spectral techniques including ^{119}Sn Mössbauer spectra[1-3] (nuclear γ-resonance) and far-infrared spectra[4] have been used to diagnose the electronic character of the metal atoms. Despite some conflicting results,[1,2] it appears that coordination of an $SnCl_3^-$ ion to a metal atom forms a covalent bond and the tin becomes formally tetravalent, just as in $SnCl_4$.

The question of oxidation state is even more acute in compounds based on the trigonal bipyramidal Pt_3Sn cluster.[5,6] Chemical evidence[5] suggested that the platinum atoms in this unit were *formally* zerovalent in both $[Pt_3Sn_8Cl_{20}]^{4-}$ and (1,5-cyclooctadiene)$_3Pt_3Sn_2Cl_6$. This formulation gave a plausible oxidation state of 2+ for tin in the ionic compound but resulted in a nonintegral oxidation state in the olefin complex.

TABLE I
X-RAY PHOTOELECTRON SPECTRA OF PLATINUM AND TIN COMPLEXES

Compound[d]	Binding Energy[a,c] $Pt\,4f_{7/2}$	$Sn\,3d_{5/2}$
$[(C_2H_5)_4N]_4[Pt_3Sn_8Cl_{20}]$	72.9	487.3[b]
$(C_8H_{12})_3Pt_3Sn_2Cl_6\cdot CH_3NO_2$	73.2	487.3
$[(C_2H_5)_4N]_3[Pt(SnCl_3)_5]$	73.2	487.1[b]
$[(C_2H_5)_4N]_2[SnCl_6]$	...	486.3
$[(C_2H_5)_4N][SnCl_3]$	...	485.7

[a] Electron volts, calibrated to a C_{1s} binding energy of 285.0 eV to compensate for charging effects. [b] The signals due to the two types of tin environments in the complex were not resolved. However, the peak widths in these two compounds were significantly greater than the 2.05 eV peak width observed for mononuclear tin compounds. [c] Spectra were determined on a Varian IEE-15 spectrometer with an Al source; estimated error ±0.1 eV. [d] Complexes were prepared as described in ref 5 and 12.

The new tool of X-ray photoelectron spectroscopy, which has shown a good correlation between electron binding energy and oxidation state in mononuclear platinum complexes,[7,8] has now been applied to this problem. The tin $3d_{5/2}$ binding energies (Table I) are

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[1] D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, **8**, 1771 (1969).

[2] V. I. Baranovskii, V. P. Sergeev, and B. E. Dzevitskii, *Dokl. Phys. Chem.*, **184**, 55 (1969).

[3] G. V. Novikov, V. A. Trukhtanov, A. P. Krushch, A. E. Shilov, and V. I. Gol'danski, *Dokl. Akad. Nauk SSSR*, **189**, 1294 (1969).

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[5] R. V. Lindsey, G. W. Parshall, and U. G. Stolberg, *ibid.*, **5**, 109 (1966).

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[7] C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, **93**, 1904 (1971); D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Commun.*, 602 (1971).

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