and the absolute configuration at phosphorus was determined as follows.

Since *tert*-butyl phosphate is a poor substrate for alkaline phosphatase from *E. coli* and for human prostatic acid phosphatase (the stereochemical course of each of which is known[12,13]), we used wheat germ acid phosphatase to catalyze the stereospecific transfer of the phospho group to (*S*)-butane-1,3-diol,[4] and the configuration at phosphorus was then determined by analysis[4,14] of the purified 3-[^{16}O,^{17}O,^{18}O]phospho-(*S*)-butane-1,3-diol product. The resulting ^{31}P NMR spectrum (Figure 1A) demonstrated that *the phospho group had largely racemized.* That is, the stereochemically informative resonances (the middle two peaks of each quartet) are almost equal in intensity (see Table I).   Control experiments showed that (a) the substrate phenyl phosphate was indeed chiral and had not racemized significantly during the course of the reaction (Figure 1B),[15] (b) the product *tert*-butyl phosphate did not racemize under the reaction conditions,[16] and (c) the wheat germ phosphatase catalyzes the phospho group transer with complete retention at phosphorus.[16] It is therefore clear that the phospho group racemizes in the course of its transfer from phenyl phosphate to *tert*-butyl alcohol.[18]

At first sight, this result provides the most direct confirmation of the proposal of Ramirez that the formation of *tert*-butyl phosphate is diagnostic of the intermediacy of free monomeric metaphosphate. That is, the phenyl phosphate decomposes dissociatively to yield the free monomeric metaphosphate ion, PO$_3^-$, which, in the absence of an unhindered nucleophile, has a long enough half-life to lose all stereochemical memory before capture by *tert*-butyl alcohol. It is possible, however, that the phospho group is transferred to solvent acetonitrile and that a sequence of rapid phospho group transfers among acetonitrile molecules is only terminated by the irreversible capture by *tert*-butyl alcohol. This interpretation, involving the generation of a highly reactive metaphosphate–acetonitrile adduct, follows the suggestion of Satterthwaite and Westheimer[19] that metaphosphate might form a complex with (or at least be specifically solvated by) such solvents as dioxane and acetonitrile. While it may prove possible to distinguish between the above possibilities by the use of hydrocarbon solvent and to evaluate the reality of truly liberated monomeric metaphosphate, the present experiments provide the first stereochemical evidence for a metaphosphate species (either free or solvent-associated) as an intermediate in the solution reactions of phosphoric monoesters.

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(15) Stereochemical analysis[4,14] of the unreacted phenyl [^{16}O,^{17}O,^{18}O]phosphate recovered from the reaction mixture showed the configuration was 81 ± 6% *R*.

(16) *tert*-Butyl (*S*)-[^{16}O,^{17}O,^{18}O]phosphate was synthesized by a modification of our general route.[17] This chiral sample was then subjected to the conditions of the solvolysis reaction[10] and reisolated, and the phospho group was transferred to (*S*)-butane-1,3-diol using the wheat germ phosphatase. Stereochemical analysis[4,14] of the configuration at phosphorus in the 3-[^{16}O,^{17}O,^{18}O]phospho-(*S*)-butane-1,3-diol product showed the configuration was 84 ± 6% *S*. We may note in passing that, as expected, the wheat germ acid phosphatase proceeds with overall retention at phosphorus.

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(18) Inspection of Figure 1A and Table I suggests a small degree of *retention* at phosphorus. If real, this could arise from the transfer of the phospho group to acetonitrile, followed by its occasional immediate capture by *tert*-butyl alcohol, each of these steps, predictably,[4] going with inversion. Just as with S$_N$ reactions at carbon centers in solution, incomplete racemization does not eliminate carbonium ion mechanisms. The necessary distinction can, however, be made by the use of solvents that have no solvating lone pairs.

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Synthesis and Properties of Doped μ-Oxo(tetrabenzoporphyrinato)germanium(IV)[†]

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During the past several years great progress has been made in the field of conducting organic materials based on polymeric cofacially assembled bridged macrocycles. Thus, compounds of the type [PcML]$_n$ (Pc = phthalocyaninato) with M = Si, Ge, Al, Ga and L =, e.g., O, F, S, NCN,[1–5] as well as M = transition metals like Fe, Ru, Co, Rh, Cr, Mn and L = organic bridging ligands capable of conjugation, e.g., pyrazine (pyz), tetrazine (tz), diisocyanobenzene (dib) or the cyanide ion, have been prepared.[6–14] All of them show comparatively high conductivities up to 1 Ω^{-1} cm^{-1} after doping with electron acceptors. Several of the polymeric macrocyclic metal compounds containing a transition metal exhibit similarly high conductivities, even without external doping. With regard to the electronic transport properties, the conductivities observed reach a broad spectrum, ranging from "synthetic metals" to wide gap semiconductors.

We have recently reported[15,16] on the use of tetrabenzoporphyrine (TBPH$_2$), structurally related to phthalocyanine, in polymers of the type [TBPML]$_n$, with M = Fe, L = pyz, dib, M = Co, L = CN$^-$. These have similar electrical conductivities as the corresponding [PcML]$_n$ compounds.

To our knowledge, the polymers [TBPMO]$_n$ (M = Si, Ge), which should be similar to the well-studied [PcMO]$_n$ (M = Si, Ge) polymers, have not yet been described. We report here on the synthesis and the electrical conductivities of doped and undoped [TBPGeO]$_n$. According to SCF calculations,[17] the TBP radical cation generated by oxidative doping has a larger bandwidth for the free electron, i.e., a greater electron mobility in comparison to phthalocyanine. On the other hand, the conclusion was drawn that Pc and TBP should behave analogously with regard to their charge carrier properties, since the MO mainly responsible for the conduction band possesses nodes at the four aza-bridged positions in phthalocyanine.[18]

[TBPGeO]$_n$ (**5**) was synthesized as shown in scheme I: The tetrabenzoporphyrinato system was prepared as the best available zinc derivative TBPZn (**1**).[19] Demetalation of TBPZn (**1**) to

[†] Presented in part at the 188th ACS Meeting in Philadelphia, Aug 1984.

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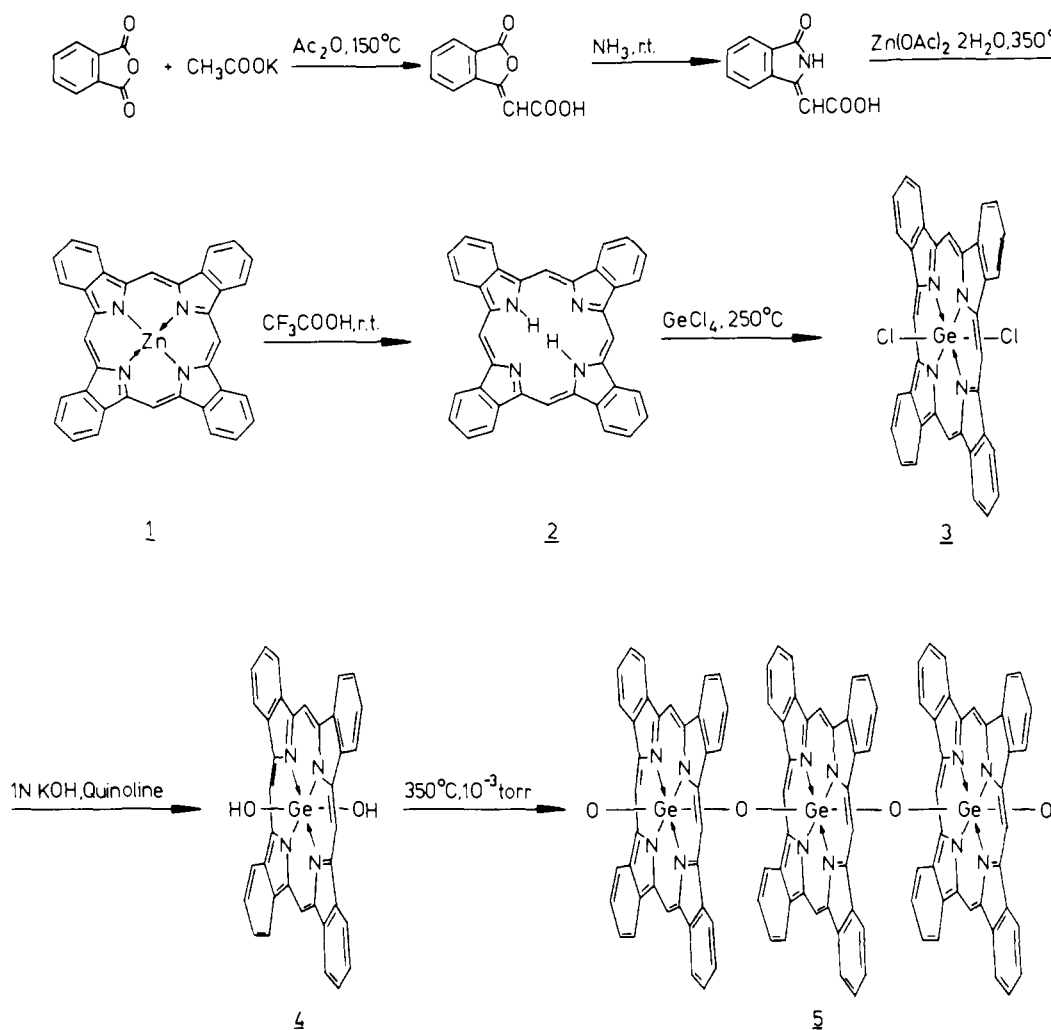(14) Hanack, M.; Münz, X. *Synth. Met.* **1985,** *10,* 357.

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Scheme I

1   2   3

4   5

TBPH$_2$ (**2**) was accomplished with trifluoroacetic acid in chloroform.[20]   TBPH$_2$ (**2**) was converted to TBPGeCl$_2$ (**3**) by a modification of the reported[21] procedure by reacting **2** with GeCl$_4$ in refluxing quinoline. TBPGe(OH)$_2$ (**4**) was obtained from **3** by hydrolysis in quinoline containing 1 N KOH (2:1). Thermal dehydration of **4** at 350 °C (10^{-3} torr) gave the polymer **5** in an overall yield of 47% based on TBPZn. The intermediate products **3** and **4** were characterized by mass spectra, infrared spectra, and elemental analyses. The characteristic Ge–Cl stretching frequencies for **3** are found at 321 and 332 cm^{-1}. The dihydroxide **4** shows three characteristic Ge–OH frequencies at 3600, 966, and 644 cm^{-1}. The disappearance of the three Ge–OH frequencies in [TBPGeO]$_n$ (**5**) in comparison with TBPGe(OH)$_2$ (**4**) as well as the appearance of a broad band at 925 cm^{-1} assigned to the Ge–O–Ge unit in **5** are characteristic for the polymer **5**. Moreover the decrease of the number of C–H out of plane vibrations from three (758, 741, and 704 cm^{-1}) to two (742, 693 cm^{-1}) is also found as in the case of [PcGeO]$_n$.[1] The expected[22] hypsochromic shift in the UV/vis spectra for the Soret band from 433 nm by 28 to 405 nm, and for the Q band by 13 nm to 623 nm, for the polymer **5** as against the monomer **4**, is also seen.

X-ray powder diffractometer measurements show that [TBPGeO]$_n$ (**5**) is microcrystalline and isostructural with

Table I. Electrical Conductivities of Polycrystalline Samples of [(TBPGeO)I$_y$]$_n$ in Comparison with [(PcGeO)I$_y$]$_n$[a]

	[(TBPGeO)I$_y$]$_n$[b]		[(PcGeO)I$_y$]$_n$
y	σ, Ω^{-1} cm^{-1}	E_a, eV	σ, Ω^{-1} cm^{-1}
0.0	1 × 10^{-6}		2 × 10^{-10}
0.1			3 × 10^{-6}
0.2	2 × 10^{-4}		
0.3			2 × 10^{-3}
0.4	5 × 10^{-3}		
0.6	3 × 10^{-2}		2 × 10^{-2}
0.75	5 × 10^{-2}	0.07[b]	
1.1	3 × 10^{-2}		1 × 10^{-1}

[a] Determined by the four-probe van der Pauw method, at 1 kbar.
[b] The temperature-dependence of the conductivity between 125 and 250 K obeys the equation

$$\sigma = \sigma_0 e^{-E_a/kT}$$

[PcGeO]$_n$, where the metal–macrocycle is stacked in the direction of the c axis ($P4/m$, $a = 13.27$ Å, $c = 3.53$ Å) and the rings are eclipsed in the structural arrangement. On the basis of this structure, an interring distance of 3.46 Å is calculated for [TBPGeO]$_n$ (**5**).

[TBPGeO]$_n$ **5** shows an electrical conductivity of 1 × 10^{-6} Ω^{-1} cm^{-1} (see Table I), which is 4 orders of magnitude greater than [PcGeO]$_n$. As expected the conductivity increases strongly by doping **5** with iodine.[10] The compounds obtained (see Table I) have the stoichiometry [(TBPGeO)I$_y$]$_n$. A maximum value of $\sigma = 5 \times 10^{-2}$ Ω^{-1} cm^{-1} is reached with $y = 0.75$. The doped compounds are air-stable and split off iodine with decomposition on heating in a stream of nitrogen at 170 °C (760 torr). Incre-

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mental doping of **5** up to *y* = 1.1 does not lead to a further increase in conductivity. Doping stochiometries exceeding *y* = 1.1 could not be achieved; these doped polymers are not stable and loose iodine already at room temperature. π-radical cations are formed by the oxidation of the metal macrocycle stack **5** by iodine, which is proved by a symmetric ESR signal (*g* = 2.0030). The iodine is thereby reduced to I_3^-. The characteristic totally symmetric scattering pattern (ν = 103 cm^{-1}) of I_3^- in $[(TBPGeO)I_y]_n$ is oberved in the resonance Raman spectrum (exciting wavelength 482.5 nm) accompanied by an overtone. The peaks due to I_5^- and I_2 are not detected.

The present study of doped and undoped $[TBPGeO]_n$ (**5**) indicates that **5** in comparison with $[PcGeO]_n$ can be equally well used in constructing conducting cofacially assembled macrocyclic bridged polymers.

We have not yet succeeded in preparing the corresponding siloxane $[TBPSiO]_n$, for which a shorter interring distance and consequently a higher conductivity after doping are expected.

First Observation by ^{39}K NMR of K$^-$ in Solution and in Crystalline Potassides

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The first salt of an alkali-metal anion (alkalide) was synthesized more than a decade ago.[1,2] This was followed by alkali-metal NMR studies of Na$^-$, Rb$^-$, and Cs$^-$ in solution[3-9] and of Na$^-$ and Cs$^-$ in crystalline alkalides.[10-12] All attempts to observe K$^-$ by ^{39}K NMR were, however, unsuccessful.[4,8,13] We now report the first NMR observation of K$^-$ both in solution and in crystalline potassides. This provides *direct* proof of the existence of K$^-$ in solids, as suggested by optical spectra of thin films.[14-16]

A Bruker WH 180 multinuclear spectrometer operating at a field strength of 4.227 T was used to record the ^{39}K spectra

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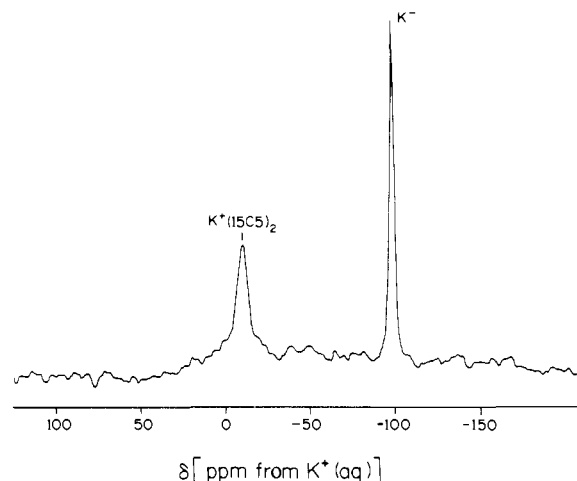

Figure 1. ^{39}K NMR spectrum of K$^+$(15crown5)$_2$·K$^-$ in dimethyl ether (0.06 M) at 220 K, 20 400 acquisitions with 10-Hz exponential broadening.

(frequency = 8.40 MHz). Dimethyl ether (Me$_2$O) was distilled into an evacuated 10-mm NMR tube that contained a weighed amount of crystalline K$^+$(15-crown-5)$_2$·K$^-$. The tube was then flame-sealed under vacuum. Polycrystalline samples for static and magic angle sample spinning (MAS) ^{39}K NMR studies were loaded while cold into axial Doty rotors under a dry nitrogen atmosphere.

The spectrum of a 0.06 M solution of K$^+$(15-crown-5)$_2$·K$^-$ in Me$_2$O is shown in Figure 1. The peaks at −9.9 and −99.3 ppm are assigned to K$^+$(15-crown-5)$_2$ and K$^-$, respectively. The measured chemical shift of the gaseous potassium atom is −101 ± 5 ppm[17] and the anion is expected to be 2 ppm more diamagnetic at −103 ± 5 ppm.[18] The negligible solubility of potassium in Me$_2$O rules out the presence of uncomplexed potassium. The narrower line width of the K$^-$ peak (20 Hz) compared with that of K$^+$(15-crown-5)$_2$ (50 Hz) reflects the more spherical environment of K$^-$.

The prevous failure to observe K$^-$ in solution[4,8,13] may result from the equilibrium

$$K^- \rightleftharpoons K^+ + 2e^-(solv)$$
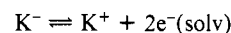
since K$^-$ is more dissociated than Na$^-$, Rb$^-$, or Cs$^-$.[19,20] Rapid equilibration to give paramagnetic solvated electrons (or intermediate species such as K·) would substantially broaden the K$^-$ NMR peak. The low donicity of Me$_2$O shifts the equilibrium to the left, thus permitting observation of K$^-$.

The static ^{39}K NMR spectrum without ^1H decoupling and the decoupled static and MAS spectra of polycrystalline K$^+$(15-crown-5)$_2$·K$^-$ are shown in Figure 2. Only the single peak of K$^-$ at −105 ppm is observed. The full widths at half-height are 300, 175, and 40 Hz, respectively. The residual width of the central transition ($m = ^1/_2$, $m = -^1/_2$) upon spinning and ^1H decoupling gives a *maximum* quadrupolar coupling constant, e^2qQ/h, of about 0.1 MHz.[21]

The absence of the cation NMR peak in solid K$^+$(15-crown-5)$_2$·K$^-$ indicates that e^2qQ/h for K$^+$ in the complex must be greater than 0.5 MHz since we could have detected a signal of line width ≤1000 Hz. Since Na$^+$ cryptand[2.2.2] has a quadrupolar coupling constant of 1.2 MHz,[22] a value greater than 0.5 MHz in the present case is not unexpected.

The MAS-NMR data for several potassides and simple K$^+$ salts are given in Table I. All potassides show only the K$^-$ peak whose

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