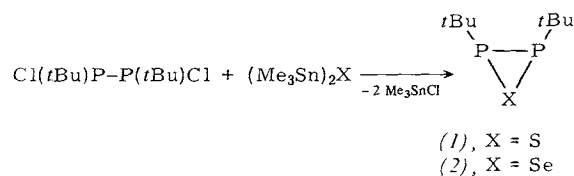


trahydrofuran (THF)); an enrichment compared to the main products $(t\text{BuPS})_3$ ^[3a] and $[t\text{BuP(S)S}]_2$ ^[3b] could not be achieved, however, by varying the reaction parameters. All the more surprising was the finding that (1) is obtainable in 36% yield (99% purity) by high-vacuum distillation after removal of the solvent and thermolysis of the product mixture at 130°C. The formation is apparently achieved by ring contraction of higher-membered phosphorus-sulfur heterocycles.

Larger amounts of (1) could be detected ³¹P-NMR spectroscopically in the reaction of sulfur dichloride with 1,2-di-*tert*-butyldiphosphane^[4] (1:1, boiling toluene) or with the diphosphasilirane $(t\text{BuP})_2\text{SiPh}_1$ ^[1b] (1:1:1, boiling dioxane).

A particularly suitable preparative approach is the [2 + 1]-cyclocondensation of 1,2-di-*tert*-butyl-1,2-dichlorodiphosphane^[5] with bis(trimethylstannyl) sulfide^[6] (1:1,



boiling THF). With bis(trimethylstannyl) selenide^[7], the 2,3-di-*tert*-butyl-1,2,3-selenadiphosphirane (2) is obtained. The four-membered ring compounds $(t\text{BuP})_4$ and $(t\text{BuP})_3\text{X}$ as well as the five-membered heterocycle with an exocyclic chalcogen atom $(t\text{BuPX})_3$ are formed as by-products; in the case of (2) the five-membered ring compound $(t\text{BuP})_4\text{Se}$ is also formed. The product pattern depends on the concentration of the reactants, the reaction time and the quantities used; under suitable conditions the proportion of (1) or (2) is about 60 mol-%. The compounds can be isolated by high-vacuum distillation, in the case of (2) with subsequent low-temperature crystallization.

(1) and (2) are, respectively, pale and bright yellow, viscous, evil-smelling liquids which are stable for weeks at -30°C when not exposed to air and light. They readily dissolve in organic solvents, but the solutions—above all, of (2)—are less stable. The composition of (1) and (2) is confirmed by correct elemental analyses (C, H, P, S, and Se, respectively) as well as mass spectra with high relative intensity of the M^+ ions [(1): $m/z = 208$ (100%); (2): 256 (88%)]. The constitution follows from the ³¹P{¹H}-NMR spectra, which in each case show a singlet in the characteristic high-field region for phosphorus three-membered ring compounds^[8] [(1): $\delta = -91.5$ (THF, 301 K); (2): $\delta = -76.9$, $J(\text{P}^{77}\text{Se}) = 135.2$ Hz (pentane, 213 K)]. The downfield shift of (2) in comparison to (1) is ascribed to the larger P—Se bond length and the resultant widening of the P—P—Se angles. The high-field position of the respective singlets in the ¹H{³¹P}-NMR spectra is also typical for substituents on the three-membered ring [(1): $\delta = 0.94$ (benzene, 298 K); (2): 0.97 (benzene, 300 K)]. The configuration cannot be deduced from the NMR spectra; but *tert*-butyl groups should be *trans*-oriented as in other P_2X compounds^[1b,c,e,9].

Compared to analogous phosphorus three-membered ring compounds, (2) and, in particular, (1) are astonishingly stable towards heat and towards polar solvents such as THF. This high kinetic stability is apparently caused by the steric shielding of the *tert*-butyl substituents and by the free electron pairs on the heteroatoms.

Procedure

(1): 1,2-Di-*tert*-butyl-1,2-dichlorodiphosphane (14.1 g, 57.1 mmol) and bis(trimethylstannyl) sulfide (20.6 g, 57.3

mmol) in 300 mL THF are allowed to react to completion at the boiling temperature with stirring (about 187 h, ³¹P-NMR monitoring). After removal of the solvent trimethyltin chloride is condensed at 0.45 torr and maximum bath-temperature of 35°C over a 10 cm Vigreux column fitted with an air-cooled bridge into a receiver cooled with liquid nitrogen. Distillation of the residue over a Zincke apparatus at 0.15 torr and bath-temperature of 70–75°C yields 5.1 g (43%) of (1), b.p. 45–46°C/0.15 torr, which solidifies to a colorless solid at -78°C; purity >99% (³¹P-NMR).

(2): A mixture of 1,2-di-*tert*-butyl-1,2-dichlorodiphosphane (6.4 g, 25.9 mmol) and bis(trimethylstannyl) selenide (10.47 g, 25.8 mmol) in 120 mL THF is heated under reflux for about 36 h. Since the amount of (2) passes through a maximum, ³¹P-NMR control is frequently necessary. After removal of solvent and trimethyltin chloride as in (1) the orange-yellow, liquid residue is distilled at 5×10^{-4} torr at a bath-temperature of 110°C through a Zincke apparatus, fitted with a 5 cm extension, into a receiver cooled to -78°C; yield 2.85 g (43%), b.p. 57–58°C/ 5×10^{-4} torr, purity 97% (rest $(t\text{BuP})_3\text{S}$, ³¹P-NMR). Dissolution in *n*-pentane (5 mL) and cooling to -78°C yields, after 3 d, 2.19 g (33%) of almost colorless crystals, which after removal of the mother liquor are washed with 2 mL of cold pentane; purity 100%.

Received: July 31, 1981 [Z 943 IE]
German version: Angew. Chem. 93, 1087 (1981)

CAS Registry numbers:

(1), 79898-83-2; (2), 79898-84-2; bis(trimethylstannyl) sulfide, 1070-91-3; bis(trimethylstannyl) selenide, 7262-34-2; 1,2-di-*tert*-butyl-1,2-dichlorodiphosphane, 79898-85-4

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A Ternary Crown Ether "Supercomplex": X-Ray Structure Analysis of the 1:1:1 Adduct of Dibenzo[18]-Crown-6, Potassium Iodide, and Thiourea^[**]

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X-ray structural analyses have made a decisive contribution^[1b] to the investigation of the complexing properties of

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[**] Structures of Polyether Complexes, Part 18.—Part 17: R. Hilgenfeld, W. Saenger, Z. Naturforsch. B36, 242 (1981).

cyclic crown ethers and their open-chain analogues towards metal ions^[1a]. Oligoethers also form inclusion complexes with ionic or neutral guest molecules^[2a], and are therefore considered, *inter alia*, as simple enzyme models^[2b]. According to X-ray crystallographic findings the interactions between host and guest in such adducts can mainly be ascribed to N—H...O or C—H...O hydrogen bonding^[3].

In 1971, *Pedersen* obtained crystalline ternary complexes between crown ether, metal salt, and thiourea in the molar ratio 1:1:1, 2:1:1, 1:1:4, and 1:1:6^[4] on reaction of some metal-salt complexes of benzo-[15]-crown-5 and benzo-[18]-crown-6 with thiourea (in methanol). Such "super complexes" are potential models for transition states of reactions assisted by crown ethers, *e.g.* nucleophilic substitutions in which stereospecificity has been observed^[5]. The existence of loose adducts, in which the crown ether cation complex as well as substrate and anion participate would afford an explanation for this effect. Since no information on the structures of the ternary adducts was available, we decided to determine the structure of the 1:1:1-complex of dibenzo-[18]-crown-6, potassium iodide and thiourea^[6].

The crystal structure is found to be polymeric (Fig. 1). The potassium ion is situated at the center of the crown ether cavity and is in contact with all six ether oxygen atoms with K⁺...O distances between 2.71 and 2.80 Å; the sevenfold coordination is completed by the iodide ion (K⁺...I⁻ 3.57 Å) to give a hexagonal pyramid. This part of the complex is similar to that in the 1:1 adduct of dibenzo-[18]-crown-6 with KI, the crystals of which are found to contain two independent complex molecules^[7]: in one, the apical K⁺ coordination site is occupied by a water molecule, in the second (as in the present case), it is occupied by the I⁻ anion.

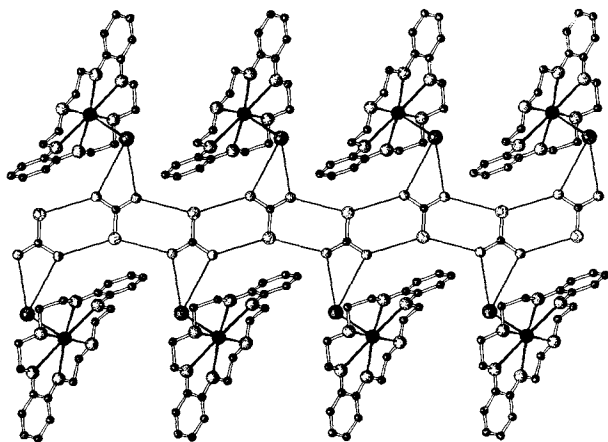


Fig. 1. Polymeric structure of the 1:1:1 complex of dibenzo-[18]-crown-6, potassium iodide, and thiourea (hydrogen atoms not shown). Hydrogen bonds are indicated by thin lines. Atomic spheres symbolize, with increasing radius, C, N, O, S, and I; the K⁺ ions are shown in black. We thank Dr. E. Keller, Freiburg (Germany), for the computer plot program SCHAKAL.

The thiourea neither participates in the complexation of the metal ion, nor has it any contact with the polyether ligand; instead, it forms polymeric chains coupled by hydrogen bonds which run through the crystal structure in the direction of the *c*-axis. One hydrogen atom of each amino group is in contact with the sulfur atom of the neighboring (symmetry generated) thiourea molecule (N...S 3.43(1) and 3.49(1) Å), while the other participates in N—H...I⁻ hydrogen bonding. The two H-bonds of this

latter type formed by each thiourea molecule are of different strength with lengths of 3.55(1) and 3.85(1) Å; the respective I—N—C angles are 110.3(8) and 95.7(7)°. The hydrogen atoms of the thiourea molecule could not be determined with certainty from the difference Fourier synthesis.

The anion plays an important role as hydrogen bond acceptor and as a link between crown-ether complex and thiourea chains. It is therefore of interest to investigate whether anions other than the readily polarizable I⁻ ion form such complexes. *Pedersen* has also obtained ternary complexes with SCN⁻^[4], which is as soft as I⁻. On the other hand, we were unable to prepare the corresponding adduct with the hard F⁻ ion; this is also explainable in terms of the high KF lattice energy, which prevents formation of a crystalline crown-ether complex. Presumably the "supercomplexes" are formed only with sufficiently soft anions.

Received: May 4, 1981 [Z 930 1E]
German version: *Angew. Chem.* 98, 1082 (1981)

CAS Registry number:
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A New Route to 6a-Carbacyclins— Synthesis of a Stable, Biologically Potent Prostacyclin Analogue^[**]

By Werner Skuballa and Helmut Vorbrüggen^[*]

Dedicated to Professor Ferdinand Bohlmann on the occasion of his 60th birthday

The therapeutic use of prostacyclin (PGI₂) (1), a potent vasodilator and inhibitor of blood-platelet aggregation, is

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