

149 Hz. In the case of **2g** the coupling constant changed to 578.8 Hz in D₂O from 610.4 Hz in CDCl₃ (Run 7).

The X-ray molecular structure analysis of the potassium 18-crown-6 selenothiophosphinic acid salt **2e** was carried out.⁹ Although the quality of the crystal was not high and the position of sulfur and selenium atoms was disordered, the structure of **2e** could be refined. The molecular structure of **2e** is shown in Figure 1 along with selected bond lengths and angles. The salt **2e** adopts a monomeric structure. The K atom resides in the center of the 18-crown-6 ether and is coordinated by the sulfur and selenium atoms.

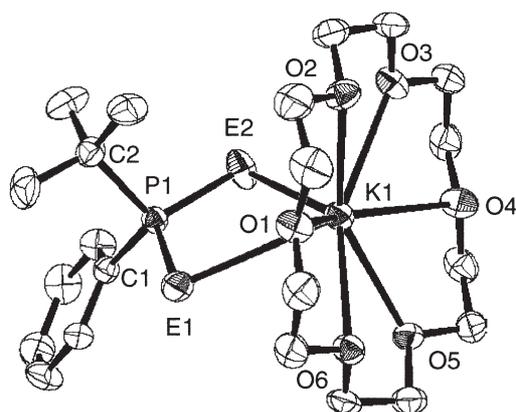
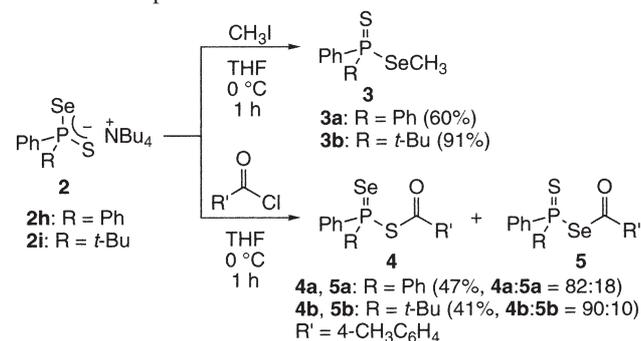


Figure 1. ORTEP drawing of **2e** with thermal ellipsoid plots (50% probability). Hydrogen atoms were omitted for clarity. The atoms E1 and E2 represent selenium or sulfur atom. Selected interatomic distance (Å) and bond angles (deg): P1–E1 2.082(1), P1–E2 2.113(1), P1–C1 1.841(4), P1–C2 1.873(4), E1···K 3.319(1), E2···K 3.4753(9), O···K (ave.) 2.891; E1–P1–E2 117.26(5), E1–P1–C1 109.5(1), E1–P1–C2 106.8(1), E2–P1–C1 107.6(1), E2–P1–C2 109.3(1), C1–P1–C2 105.8(2), P1–E1–K1 90.60(4), P1–E2–K1 85.90(3), E1–K1–E2 63.58(2).

The reactivity of selenothiophosphinates **2** was elucidated (Scheme 2). The reaction of **2h** and **2i** with methyl iodide selectively took place at the selenium atoms of **2h** and **2i** to give *Se*-methyl selenothiophosphinates **3** in high yields within 1 h. In contrast, acylation of the salts **2h** and **2i** preferentially proceeded at the sulfur atom to give mainly the products **4** along with a small amount of the product **5**.¹⁰



Scheme 2. Reaction of ammonium salts **2** with CH₃I and 4-CH₃C₆H₄COCl.

In summary, we successfully synthesized and characterized selenothiophosphinic acid salts. Further studies on their applications as new metal ligands and as key precursors of selenothiophosphinic acids are in progress.

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References and Notes

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- Typical experimental procedure for the synthesis of selenothiophosphinic acid salts: To a suspension of KF (0.116 g, 2.00 mmol) and 18-crown-6 ether (0.264 g, 1.00 mmol) in THF (5 mL) was added a solution of **1d** (0.377 g, 1.00 mmol) in THF (5 mL) at room temperature under Ar atmosphere. The mixture was stirred under reflux in THF for 1.5 h. After the addition of CH₂Cl₂ (20 mL), the insoluble parts were removed by filtration, and the solvent was evaporated under reduced pressure (20 °C, 120 Pa). To the residue was added Et₂O (5 mL), and it was stirred for 10 min. The resulting precipitates were collected by filtration to give 0.544 g (94%) of **2e** as a colorless solid. mp 202–204 °C (dec); ¹H NMR (CDCl₃): δ 1.21 (d, ³J_{H-P} = 17.1 Hz, 9H, CH₃), 3.60 (s, 24H, OCH₂), 7.26–7.48 (m, 3H, Ar), 8.39–8.44 (m, 2H, Ar); ¹³C NMR (CDCl₃): δ 25.4 (d, ²J_{C-P} = 3.3 Hz, CH₃), 37.8 (d, ¹J_{C-P} = 44.7 Hz, CCH₃), 70.0 (OCH₂), 126.1 (d, ³J_{C-P} = 11.6 Hz, Ar), 128.6 (Ar), 133.7 (d, ²J_{C-P} = 9.9 Hz, Ar), 138.4 (d, ¹J_{C-P} = 56.2 Hz, Ar); ³¹P NMR (CDCl₃): δ 74.8 (¹J_{P-Se} = 607.4 Hz); ⁷⁷Se NMR (CDCl₃): δ -128.4 (d, ¹J_{Se-P} = 607.4 Hz); Anal. Calcd for C₂₂H₃₈KO₆PSSe: C, 45.59; H, 6.61. Found: C, 45.31, H, 6.56.
- Representative spectroscopic data of **1** measured in CDCl₃: **1a**: ³¹P NMR δ 54.0, ⁷⁷Se NMR δ -217.9, ¹J_{P-Se} = 774.2 Hz; **1b**: ³¹P NMR δ 50.9, ⁷⁷Se NMR δ -209.7, ¹J_{P-Se} = 763.7 Hz; **1c**: ³¹P NMR δ 76.0, ⁷⁷Se NMR δ -354.4, ¹J_{P-Se} = 766.7 Hz; **1d**: ³¹P NMR δ 86.1, ⁷⁷Se NMR δ -311.5, ¹J_{P-Se} = 762.2 Hz.
- Crystallographic data for **2e**: C₂₂H₃₈KO₆PSSe, fw = 579.63, monoclinic, space group *P2₁/n*, *a* = 10.650(4), *b* = 16.682(6), *c* = 15.479(6) Å, β = 91.973(5)°, *V* = 2748(1) Å³, *Z* = 4, *D*_{calcd} = 1.401 g cm⁻³, *T* = 193 K, *R* = 0.102, *R_w* = 0.141, 6293 reflections (*I* > 3σ(*I*)). The selenium or sulfur atom appeared at the position [E(1)] or at the position [E(2)] shown in Figure 1. The occupancy of the selenium atom is 0.37 in [E(1)] and 0.63 in [E(2)], respectively, and the reverse results are obtained for the sulfur atom.
- The starting salts **2** were also recovered, but the reaction at higher temperatures did not necessarily gave the products in better yields mainly because of the decomposition of the products formed.