Isolation of a Cyclic Intermediate in the Reaction of a Phosphorus Ylide with Elemental Sulfur: Synthesis, Structure, and Reactivity of a 1,2σ^5-Thiaphosphirane

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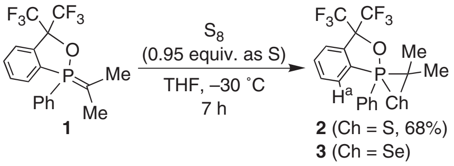
The reaction of a phosphorus ylide with elemental sulfur gave a pentacoordinate thiaphosphirane, which was characterized by X-ray crystallographic analysis, and it was allowed to react with elemental sulfur resulting in a thiophosphinate.

Phosphorus ylides, which are useful reagents for organic synthesis,[1] have been known to react with elemental sulfur resulting in thiocarbonyl compounds and phosphine sulfides.[2] A betaine that is formed by addition of sulfur to an ylidic carbon is postulated as an intermediate in the reaction.[2c] There has been, however, no report on the isolation of an intermediate during the course of the reaction of phosphorus ylides with elemental sulfur. On the other hand, we have recently reported the synthesis of a pentacoordinate selenaphosphirane by the reaction of a phosphorus ylide bearing the Martin ligand, which is an effective bidentate ligand for stabilization of hypervalent compounds,[3] with elemental selenium.[4] A similar three-membered heterocyclic intermediate is expected to be formed in the reaction of a phosphorus ylide with elemental sulfur. In addition, there have been limited examples of three-membered ring compounds bearing a pentacoordinate phosphorus atom,[5] although extensive studies have been carried out on three-membered ring compounds bearing a tri- or tetracoordinate phosphorus atom.[6,7] In this paper, we report the synthesis of a pentacoordinate thiaphosphirane by the reaction of the phosphorus ylide bearing the Martin ligand with elemental sulfur, its structure and reactivity.

Treatment of ylide **1** bearing the Martin ligand (170 mg, 0.43 mmol) with 0.95 equiv. of elemental sulfur (13 mg, 0.41 mmol) in THF at −30 °C for 7 h resulted in a 68% yield of thiaphosphirane **2** as colorless crystals after recrystallization from hexane (Scheme 1).[8] Thiaphosphirane **2** is air-sensitive but thermally stable. No decomposition was observed, upon heating in C_6D_6 at 60 °C for 3 h under an argon atmosphere.



Scheme 1.

A single crystal of **2** was obtained by recrystallization from hexane at −30 °C under an argon atmosphere and the molecular structure of **2** was clearly determined by X-ray crystallographic analysis (Figure 1).[9] Thiaphosphirane **2** has an oxygen and a sulfur atom at the apical positions and three carbon atoms at the equatorial positions. The O1–P1–S1 angle [155.60(7)°] and the O1–P1–C1 angle [102.41(11)°] are quite different from those of TBP structure (180 and 90°, respectively). The C1–S1 bond length [1.868(3) Å] roughly agrees with the sum of the corresponding covalent radii (1.81 Å).[10] The P–S bond length [2.2553(13) Å] of **2** is significantly longer than that of tricoordinate thiaphosphirane (2.113 Å),[7e] tetracoordinate thiaphosphiranes (2.049 Å, 2.101 Å),[7a,c] and the sum of the corresponding covalent radii (2.14 Å).[10] The elongation of the P–S bond of **2** is a typical feature of an apical bond in a TBP structure, which is composed of a 3 centered 4-electron bond. The P1–C1–S1 angle [76.50(11)°] and the C1–P1–S1 angle [53.63(10)°] are significantly less than those of a tetrahedral structure (109.5°) and a TBP structure (90°), respectively. These structural features clearly suggest that **2** has the P–S–C three-membered ring with a pentacoordinate phosphorus atom. This is the first example of crystallographically characterized 1,2σ^5-thiaphosphirane.

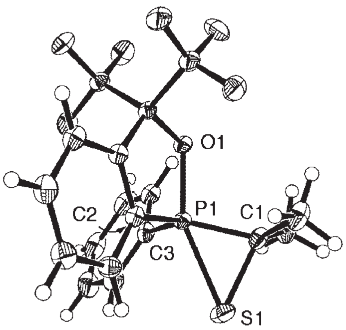


Figure 1. ORTEP drawing of **2** with thermal ellipsoid plot (50% probability). Selected bond lengths [Å] and bond angles [°]: P1–S1 2.2553(13), P1–C1 1.773(3), C1–S1 1.868(3), P1–O1 1.723(2), P1–C2 1.805(3), P1–C3 1.810(3), O1–P1–S1 155.60(7), P1–C1–S1 76.50(11), C1–P1–S1 53.63(10), P1–S1–C1 49.86(9), O1–P1–C1 102.41(11).

In the ^{1}H NMR spectrum of **2** in THF-d_8, the *ortho* proton of the Martin ligand (H^a) shifted to downfield (δ_H 8.73) compared to that of **1** (δ_H 7.53), which is a typical feature of hypervalent compounds bearing the Martin ligand with TBP structure.[11] The downfield shift is attributable to magnetic deshielding by the polar apical P–S bond.[12] In the ^{31}P NMR spectrum of **2** in THF-d_8, the signal of **2** was observed at δ_P −48.8, which lies in the typical region of pentacoordinate phosphorus compounds bearing the Martin ligand,[13] while that of the pentacoordinate thiaphosphiranes reported by Abdou et al. was observed in a much lower field (δ_P −6.2, −8.4).[5c,14] Table 1 shows the selected NMR data of **2** in several solvents together with the acceptor number of the solvents.[15] The ^{31}P NMR chemical shifts of **2** in various solvents correlate with the acceptor numbers of the solvents. The ^{31}P NMR spectra of thiaphosphirane **2** showed weak solvent-dependence compared with selenaphosphirane **3**.[4] The downfield shift of the ^{31}P NMR signal of **2** along with an increase of the acceptor number indicates that the positive charge on the phosphorus atom increases as the acceptor number in-

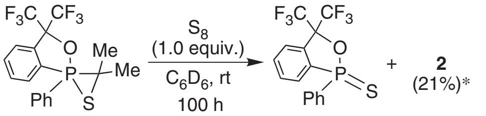
Table 1. Selected NMR data of **2** in various solvents and acceptor numbers of the solvents

Solvent	Acceptor Number	$\delta_{\rm P}$	$\delta_{\rm H}$a
THF-d_8	8.0	−48.8	8.73
C_6D_6	8.2	−48.5	8.63
CD_3CN	18.9	−44.7	8.72
CD_2Cl_2	20.4	−43.8	8.72
$CDCl_3$	23.1	−40.4	8.76

creases. The correlation suggests an interaction in solution between the negatively charged sulfur and the solvents. As the acceptor number increases, the interaction becomes stronger, such that the degree of polarization of the P–S bond increases, which leads to deshielding of the phosphorus nucleus.

To elucidate whether thiaphosphirane **2** affords thiophosphinate **4** or not, the reaction of **2** with 1 equiv. of elemental sulfur in C_6D_6 at room temperature was carried out, resulting in a 72% yield of **4** together with unreacted **2**. (Scheme 2) Thiophosphinate **4** was also formed by the reaction of phosphorus ylide **1** with 2 equiv. of elemental sulfur at −30 °C in 31% yield. Products including the dimethylmethylene unit were a complex mixture, which could not be characterized. These results suggest that a pentacoordinate thiaphosphirane can be presented as an intermediate during the reaction of phosphorus ylides with elemental sulfur.

Treatment of **2** with 1 equiv of triphenylphosphine in C_6D_6 at room temperature and 60 °C resulted in no reaction; neither the expected triphenylphosphine sulfide nor ylide **1** was detected. The reaction of **2** with 1.6 equiv. of tributylphosphine at room temperature exhibited the same result. Such inertness of **2** toward phosphines is in contrast to the ready desulfurization of tri- and tetracoordinate thiaphosphiranes with phosphines to yield the corresponding phosphaalkene derivatives and phosphine sulfides.[7a–c] Thiaphosphirane **2** is an interesting example of a dicoordinate sulfur-containing three-membered ring compound resistant to desulfurization by phosphines.[16]



2 4 (72%)* *estimated by ^{19}F NMR

Scheme 2.

In summary, we have successfully achieved the synthesis of the pentacoordinate thiaphosphirane **2** by the reaction of a phosphorus ylide with elemental sulfur, and elucidated its three-membered ring structure with a polarized P–S bond. The formation of the three-membered ring compound provides a good contrast to a previously proposed mechanism for a similar reaction that gave the corresponding phosphine sulfide and thioketone via the betaines.

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8 Satisfactory spectral data were obtained.

9 Crystallographic data of **2**: $C_{18}H_{15}F_6OPS$, fw 424.33, monoclinic, $a = 14.149(8)$, $b = 8.637(5)$, $c = 15.561(9)$ Å, $\beta = 107.976(7)°$, $V = 1808.9(17)$ Å^3, $T = 120(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.332\,\text{mm}^{-1}$, $D_{\rm calcd} = 1.558$ g cm^{-3}, $R_1 = 0.0598$ ($I > 2.00\sigma(I)$), $wR_2 = 0.1234$ (all data), GOF = 1.194. CCDC-237445.

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