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Synthesis and Structure of the First 1,2σ^5-Selenaphosphirane

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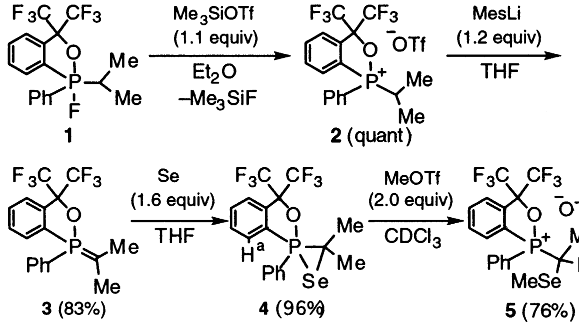
Received March 6, 2002

Three-membered-ring compounds containing phosphorus have been studied for four decades both experimentally and theoretically in view of their interesting structural features and high strain energies.[1] Many examples bearing a tri- and tetracoordinate phosphorus atom, such as phosphiranes, as well as those containing another heteroatom in the ring were synthesized, and their structures and properties were established.[2] In contrast, there are only limited reports on three-membered-ring compounds bearing a phosphorus atom with a coordination number higher than four.[3,4] Although some σ^5(P)-phosphirenes bearing a C−C double bond in the ring were synthesized and some of them were crystallographically characterized,[3c] only a few compounds bearing a pentacoordinate phosphorus atom located in the saturated three-membered ring have been reported to date. Furthermore, no X-ray crystal structure is available for these saturated ring compounds. In this communication, we report the synthesis of the first selenaphosphirane involving a pentacoordinate phosphorus atom by taking advantage of the stabilizing effect of the Martin ligand, together with its structure in solid and solution state.[5]

Heterolytic cleavage of the P−F bond of fluorophosphorane **1** bearing the Martin ligand with 1.1 equiv of trimethylsilyl triflate in ether at room temperature gave the corresponding phosphonium triflate **2** quantitatively.[6] Deprotonation of **2** with 1.2 equiv of 2,4,6-trimethylphenyllithium (MesLi) in THF at −72 °C provided phosphorus ylide **3** in 83% yield. Treatment of **3** with 1.6 equiv of elemental selenium in THF at room temperature successfully afforded selenaphosphirane **4** as a colorless solid in 96% yield (Scheme 1).[7,8] The selenaphosphirane **4** is highly moisture-sensitive. It is purified by recrystallization from hexane in an argon atmosphere. The molecular structure of **4** was established by X-ray crystallographic analysis (Figure 1), and it was found that **4** has a highly distorted trigonal bipyramidal (TBP) structure with an oxygen and a selenium atom at the apical positions and three carbon atoms at the equatorial positions, respectively.[9] The O1−P1−Se1 angle (155.82(6)°) and the O1−P1−C1 angle (102.61(10)°) are far from those of a TBP structure (%TBP → SP: 56).[10] Judging from the value of %TBP character, **4** exhibits an intermediate structure between TBP and square pyramidal. The C1−Se1 bond length (1.998(2) Å) roughly agreed with the sum of the corresponding covalent bond radii (1.94 Å).[11] The P−Se bond length (2.4540(10) Å) is much shorter than the sum of van der Waals radii of phosphorus and selenium (3.9 Å), which apparently indicates the interaction between the phosphorus and selenium atoms of **4** in the crystalline state. Although the P−Se bond length is longer than the sum of the covalent bond radii (2.27 Å), such an elongation is a typical feature of the apical bond of hypervalent compounds. The P1−C1−Se1 angle (81.13(10)°) is significantly reduced from the bond angle of a tetrahedral structure (109.5°), and the C1−P1−Se1 angle (53.53(8)°) apparently deviates from a TBP structure (90°), respectively. These structural features clearly suggest the formation of the P−C−Se three-membered-ring structure of **4**. This is the first example of an X-ray structural analysis not only of a selenaphosphirane but also of a saturated three-membered-ring compound involving a pentacoordinate phosphorus atom.

Scheme 1



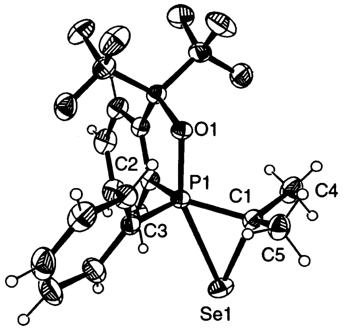


Figure 1. ORTEP drawing of **4** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and bond angles (deg): P(1)−Se(1) 2.4540(10), P1−O(1) 1.706(2), P(1)−C(1) 1.767(2), P(1)−C(2) 1.806(2), P(1)−C(3) 1.803(2), C(1)−Se(1) 1.998(2), O(1)−P(1)-Se(1) 155.82(6), O(1)−P(1)-C(1) 102.61(10), O(1)−P(1)-C(2) 90.26(9), O(1)−P(1)-C(3) 97.65(9), C(1)−P(1)-Se(1) 53.53(8), P(1)−C(1)-Se(1) 81.13(10), C(1)−Se(1)-P(1) 45.35(7).

In the solid-state ^{31}P{^{1}H} NMR spectrum, the selenaphosphirane **4** showed a singlet at δ_P −26.1, the value of which is in the range of the ^{31}P NMR chemical shifts of typical pentacoordinate phosphorus compounds. This result also proves the pentacoordinate state of the phosphorus atom of **4** in the solid state. In the C_6D_6 solution, the signal of **4** in the ^{31}P{^{1}H} NMR spectrum was observed at δ_P −26.6 as a singlet, which is almost the same value as that in the solid state, suggesting the pentacoordinate state of the phosphorus atom of **4** to persist also in C_6D_6. In the ^{77}Se{^{1}H} NMR spectrum (C_6D_6), **4** showed a singlet at δ_{Se} 147.5, which differs from that of a selenaphosphirane bearing a tricoordinate phosphorus atom (δ_{Se} −130.4).[2f] Although the coupling constant between the

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10.1021/ja026107z CCC: $22.00

Table 1. NMR Spectral Data of **4** in Several Solvents and Acceptor Number of the Solvents

solvent	δ_P	δ_{Se}	δ_{H^a}	acceptor number
C_6D_6	−26.6	147.5	8.97	8.2
CD_3CN	−20.2	144.3	9.04	18.9
CD_2Cl_2	−19.3	138.3	9.08	20.4
$CDCl_3$	−13.6	129.9	9.11	23.1

phosphorus and the selenium nuclei was observed in the cases of 1,2σ^3-selenaphosphiranes,[2d,f,l] **4** showed no coupling between these two nuclei. The reason for the absence of the coupling of **4** is unclear at present. In the ^{1}H NMR spectrum (C_6D_6), the *ortho* proton of the Martin ligand (H^a) showed a high downfield shift (δ_{H^a} 8.97), which is a typical feature of the compounds bearing the Martin ligand with TBP and pseudo-TBP structures. It has been already reported that the downfield shift of H^a is attributed to magnetic deshielding by a polar apical bond.[12] Therefore, the downfield shift of H^a of **4** suggests that **4** has a polar P−Se bond and that the selenium atom seems to be close to the C−H^a bond.

In the solution state, the selenaphosphirane **4** showed an interesting behavior depending on the solvent. The results are summarized in Table 1, together with acceptor numbers of the solvents. Since the ^{31}P resonances of **4** in these solvents still appeared at high field, the phosphorus atom of **4** should retain the pentacoordinate state in these solvents.[13] A rough correlation was found between the acceptor numbers of the solvents and the ^{31}P and ^{77}Se NMR shifts of **4**.[14] The larger the acceptor number becomes, the lower field the signal of **4** appeared in the ^{31}P NMR spectrum and the higher field the signal of **4** in the ^{77}Se NMR spectrum, respectively. Moreover, the signal of H^a is shifted to lower field in the ^{1}H NMR spectra as the acceptor number increases. These results show that the negative charge on the selenium atom and the positive charge on the phosphorus atom increase with increasing acceptor number of the solvent, that is, the polarization of the P−Se bond depends on the acceptor number of the solvent. Considering the rough correlation of the acceptor number of the solvents with the chemical shifts of **4** and its significance as an indicator of the electrophilic property of the solvent, an interaction between the negatively charged selenium atom of **4** and the solvent should exist in the solution state.

Treatment of **4** with 2 equiv of methyl triflate in $CDCl_3$ gave the highly air-sensitive α-(methylseleno)alkyl phosphonium triflate **5** in 76% yield. The formation of **5** was reasonably explained by the electrophilic attack of methyl triflate on the negatively charged selenium atom of **4** and the subsequent dissociation of the P−Se bond, reflecting the polarized character of the P−Se bond.

In summary, we have succeeded in the isolation of the first stable 1,2σ^5-selenaphosphirane, **4**, and elucidated its three-membered-ring structure with a polarized P−Se bond. Further studies on its reactivity are in progress.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We are grateful to Dr. T. Sasaki of the University of Tokyo for technical assistance in the solid-state NMR studies and for helpful comments. We also thank Central Glass, Tosoh Finechem Corporation, and Shin-etsu Chemical Co., Ltd. for gifts of organofluorine compounds, alkyllithiums, and organosilicon compounds, respectively.

Supporting Information Available: Details of experimental procedures of all compounds (PDF) and data for X-ray crystallographic analysis of **4** (CIF). This material is available free of charge via the Internet at http//:www.acs.org.

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(7) **4**: colorless crystals, mp 94.1−96.2 °C (dec); ^{1}H NMR (500 MHz, C_6D_6) δ 1.78 (d, $^3J_{PH} = 6.3$ Hz, 3H), 1.86 (d, $^3J_{PH} = 7.4$ Hz, 3H), 6.95−7.10 (m, 5H), 7.33 (brt, 1H), 8.07−8.12 (m, 2H), 8.97 (dd, $^3J_{PH} = 13.2$ Hz, $^3J_{HH} = 7.8$ Hz, 1H); ^{13}C{^{1}H}NMR (126 MHz, C_6D_6) δ 14.0 (d, $^1J_{PC} =$ 93 Hz, P*C*Se), 28.65 (s), 28.73 (s), 122.4 (q, $^1J_{FC} = 288$ Hz), 122.7 (q, $^1J_{FC} = 287$ Hz), 124.6 (d, $^3J_{PC} = 15$ Hz), 127.5 (d, $^3J_{PC} = 15$ Hz), 131.2 (d, $^4J_{PC} = 3$ Hz), 131.5 (d, $^3J_{PC} = 14$ Hz), 134.7 (d, $^4J_{PC} = 3$ Hz), 134.9 (d, $^2J_{PC} = 11$ Hz), 136.0 (d, $^2J_{PC} = 20$ Hz), 139.1 (d, $^2J_{PC} = 8$ Hz), three signals due to quaternary carbons were not observed; ^{19}F NMR (254 MHz, C_6D_6) δ −74.3 (q, $^4J_{FF} = 9.1$ Hz, 3F), −74.9 (q, $^4J_{FF} = 9.1$ Hz, 3F); ^{31}P{^{1}H} NMR (109 MHz, C_6D_6) δ −26.6 (s); ^{77}Se{^{1}H} NMR (95 MHz, C_6D_6) δ 147.5 (s); LRMS (EI): *m*/*z* 472 (M$^+$). Anal. Calcd for $C_{18}H_{15}F_6OPSe$: C, 45.88; H, 3.21. Found: C, 45.26; H, 4.00.

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(9) Crystallographic data for **4**: $C_{18}H_{15}F_6OPSe$, FW = 471.24, $T = 173$ K, monoclinic, $P2_1/n$, $a = 14.306(2)$, $b = 8.6454(8)$, and $c = 16.0518(13)$ Å, $\beta = 109.0760(9)°$, $V = 1876.3(3)$ Å^3, $Z = 4$, $D_{calc} = 1.668$ g cm^{-3}. The final cycle of full-matrix least squares refinement was based on all 3796 observed reflections and 304 variable parameters and converged at R1 = 0.033 ($I > 2.00\sigma(I)$) and wR2 = 0.080 (all data) with GOF = 1.13.

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JA026107Z