SYNTHESIS, PROPERTY, AND X-RAY CRYSTAL STRUCTURE OF NEW DIBENZOPHOSPHASELENOCINES

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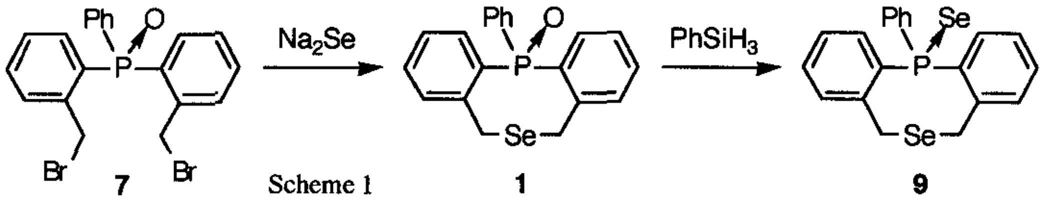
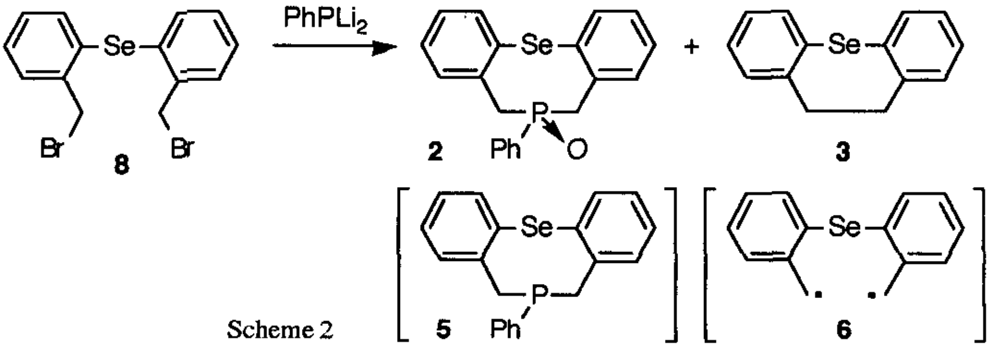
Abstract — New phosphorus-selenium heterocycles, dibenzophosphaselenocines (**1** and **2**), have been prepared. The structure of the dibenzophosphaselenocines was determined by multinuclear nmr spectroscopy and X-ray diffraction analysis.

There has been considerable interest in the transannular interaction or bond formation (e.g., dication formation) between heteroatoms in medium-sized heterocyclic compounds containing nitrogen and/or sulfur atoms.[1,2] In contrast, such interactions and the properties of heterocycles involving selenium or two different heteroatoms are not well explored. This paper presents the first synthesis, property, and crystal structure of new dibenzophosphaselenocines (**1** and **2**). The conformational work of phosphorus-heterocycles has been conducted with rings containing O-P-O unit, since these are generally easier to synthesize. However, little is known about the property of phosphorus-heterocycles containing CH_2-P-CH_2 unit.

New phosphorus-selenium heterocycles (**1**) and (**2**) were synthesized as follows. Bis-bromide (**7**) (1.00 g, 2.16 mmol) in CH_2Cl_2 (500 ml)-EtOH (500 ml) was treated with Na_2Se (297 mg, 2.38 mmol) in EtOH (10 ml) using a high dilution technique under an Ar atmosphere at room temperature. The whole mixture was stirred at room temperature for 24 h. After work-up, the crude products were purified by preparative liquid chromatography to give 12-phenyl-*5H,7H*-dibenzo[*c,f*][1,5]phosphaselenocine 12-oxide (**1**) (81%) (Scheme 1).[3]



Scheme 1



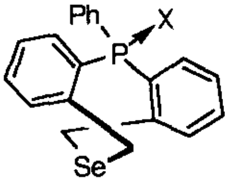
Scheme 2

Solutions of bis(2-bromomethyl)phenyl selenide (**8**) (2.00 g, 4.77 mmol) in anhydrous THF (100 ml) and $PhPLi_2$ (4.77 mmol) in anhydrous THF (100 ml) were added separately and simultaneously over 60 min to a stirred solution of anhydrous THF (400 ml) under an Ar stream. The mixture was stirred at room temperature for 18 h, after which it was worked up. The crude products were purified by silica gel column chromatography (eluent, $CHCl_3$-MeOH) to afford 6-phenyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]phosphaselenocine 6-oxide (**2**) (2%) and 5,6-dihydrodibenzo[*b*,*f*]selenepin (**3**) (75%) (Scheme 2).[4] The selenepin (**3**) could be produced by the radical coupling of the benzylic carbon radical (**6**) generated *via* an electron transfer pathway of the phosphonium anion toward the bis-bromide (**8**). The phosphine oxide (**2**) would be obtained during the work-up of the reaction mixture, since the phosphine (**5**) was formed on treatment of phosphine oxide (**2**) with $PhSiH_3$.

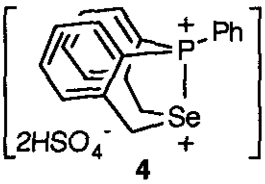
The conformers of **1** and **2** can be assigned by the ^{1}H-nmr spectral data for benzylic methylene protons of the eight-membered ring.[5] The ^{1}H-nmr spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic protons as two types of AB quartet peaks at δ 3.60, 3.70 (J = 12.5 Hz) and 3.86, 4.11 (J = 12.7 Hz), which are assigned to a twist-boat form (**1a**) (*vide infra*).

When the phosphine oxide (**1**) was dissolved in concentrated D_2SO_4 (98%) at room temperature, the conformation of **1** in $CDCl_3$ was changed completely to the boat-boat form, dication (**4**) in D_2SO_4, as shown by ^{1}H-nmr spectroscopy, i.e., the benzylic methylene protons appear at δ 4.91, 5.13 (ABq, J = 15.5 Hz). The ^{77}Se-chemical shift of **4** in D_2SO_4 is δ 387.8. While, the ^{31}P-nmr spectrum of **4** in

D_2SO_4 shows a remarkable downfield shift to δ 104.9 from δ 26.0 for **1** in $CDCl_3$. More significant spectroscopic evidence for the formation of **4** was obtained in the both ^{31}P and ^{77}Se-nmr spectra; the proton-decoupled ^{31}P and ^{77}Se-nmr spectra of **4** exhibit the ^{31}P-^{77}Se coupling ($J_{P\text{-}Se}$ = 252 Hz). This observation indicates the occurrence of transannular bond formation between phosphorus and selenium atoms. The phosphine oxide (**1**) was recovered quantitatively after hydrolysis of **4**.



X = O : **1a**
X = Se : **9a**



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Interestingly, treatment of **1** with $PhSiH_3$ (3 equiv) in toluene under reflux gave the phosphane-selenide (**9**) (17%) (Scheme 1).[6] The X-ray analysis of **9** reveals the twist-boat form (**9a**) (Figure 1).[7] Meanwhile, the donor-acceptor complex (**10**) of the phosphine oxide **2** and $SbCl_5$ shows the boat-chair form as evidenced from the X-ray crystal data (Figure 2).[8,9]

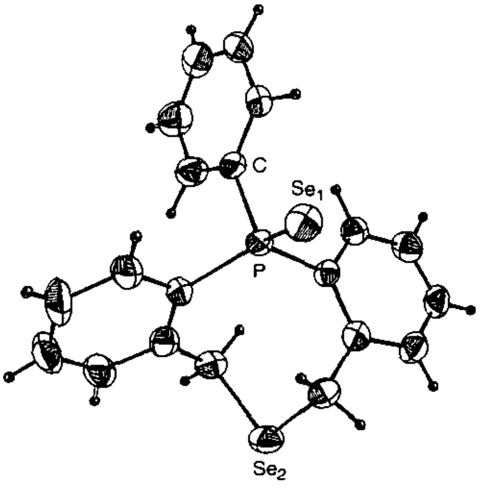

Figure 1. Crystal Structure of **9**.

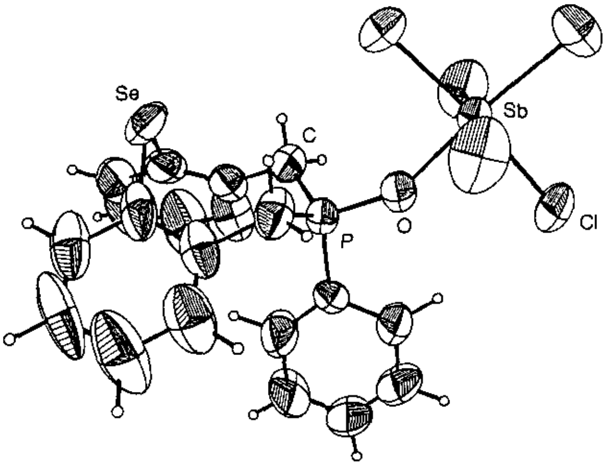

Figure 2. X-Ray Structure of **10**.

ACKNOWLEDGMENT

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3. **1**: mp 200 °C, FT-ir (KBr) 1185 cm^{-1}; ^1H-nmr ($CDCl_3$) δ 3.60, 3.70 (ABq, J = 12.5 Hz, 2H. CH_2), 3.86, 4.11 (ABq, J = 12.7 Hz, 2H, CH_2), 7.14-7.49 (m, 10H, ArH), 7.65-7.73 (m, 2H, ArH), 8.10-8.13 (m, 1H, ArH); ^{31}P-nmr ($CDCl_3$) δ 26.0 (relative to H_3PO_4); ^{77}Se-nmr ($CDCl_3$) δ 445 (relative to Me_2Se); ms (m/z) 384 (M^+). Anal. Calcd for $C_{20}H_{17}OPSe$: C, 62.67; H, 4.47. Found: C, 62.97; H, 4.40.

4. **2**: mp 225 °C; FT-ir (KBr) 1184 cm^{-1}; ^1H-nmr ($CDCl_3$) δ 3.00-4.80 (m, 4H, CH_2), 7.11-7.82 (m, 13H, ArH); ^{13}C-nmr ($CDCl_3$) δ 42.0, 127.66, 127.69, 129.0, 130.4, 131.5, 131.54, 132.1, 133.0, 135.9; ^{31}P-nmr ($CDCl_3$) δ 27.2; ^{77}Se-nmr ($CDCl_3$) δ 355; Exact mass calcd for $C_{20}H_{17}OPSe$: 384.0182. found: 384.0215. **3**: mp 50-52 °C; ^1H-nmr ($CDCl_3$) δ 3.19 (s, 4H, CH_2), 6.93-7.10 (m, 6H, ArH), 7.46-7.49 (m, 2H, ArH); ^{13}C-nmr ($CDCl_3$) δ 34.4, 126.1, 127.4, 130.3, 130.4, 131.9, 143.1; ^{77}Se-nmr ($CDCl_3$) δ 354.5; ms (m/z) 260 (M^+).

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6. **9**: mp 282 °C; ^1H-nmr ($CDCl_3$) δ 3.74 (s, 2H, CH_2), 3.98, 4.43 (ABq, J = 12.5 Hz, 2H, CH_2), 6.77-6.85 (m, 1H, ArH), 7.06-7.12 (m, 1H, ArH), 7.28-7.34 (m, 2H, ArH), 7.42-7.48 (m, 6H, ArH), 7.84-7.93 (m, 2H, ArH), 8.36-8.45 (m, 1H, ArH); ^{13}C-nmr ($CDCl_3$) δ 24.1, 24.6, 126.7, 127.6, 128.6, 129.6, 130.5, 131.2, 131.5, 131.9, 132.0, 132.5, 132.54, 133.0, 135.1, 135.5, 140.2, 140.9; ^{31}P-nmr ($CDCl_3$) δ 31.6 ($J_{P\text{-}Se}$ = 714 Hz); ^{77}Se-nmr ($CDCl_3$) δ -143.9 ($J_{P\text{-}Se}$ = 714 Hz), 441.3. Anal. Calcd for $C_{20}H_{17}PSe_2$: C, 53.83; H, 3.84. Found: C, 53.87; H, 3.78.

7. (a) Crystal data for **9**: $C_{20}H_{17}PSe_2$, monoclinic, space group P21/C, a = 11.698(1), b = 10.232(1), c = 15.042(1) Å, β = 96.82(1)°, V = 1787.5 $Å^3$, Z = 4, D = 1.66 g/cm^3, R = 0.045. (b) Selected bond lengths (Å): P-Se(1) 2.114(1), P-Se(2) 4.2449(5).

8. **10**: mp 215-218 °C (decomp.); ^1H-nmr ($CDCl_3$) δ 3.99, 5.63 (ABq, J = 14.5 Hz, 4H. CH_2), 6.45-6.52 (m, 2H, ArH), 6.75-6.77 (m, 2H, ArH), 7.17-7.30 (m, 6H, ArH), 7.50-7.55 (m, 1H, ArH), 8.02-8.05 (m, 2H, ArH); ^{31}P-nmr ($CDCl_3$) δ 50.5; ^{77}Se-nmr ($CDCl_3$) δ 363.4. Anal. Calcd for $C_{20}H_{17}OCl_5PSbSe$: C, 35.21; H, 2.51. Found: C, 35.16; H, 2.45.

9. (a) Crystal data for **10**: $C_{20}H_{17}OCl_5PSbSe$, orthorhombic, space group Pnma, a = 11.207(1), b = 11.165(3), c = 19.925(2) Å, V = 2493.1 $Å^3$, Z = 4, D = 1.82 g/cm^3, R = 0.053. (b) Selected bond lengths (Å): P-O 1.53(1), O-Sb 1.998(9), P-Se 3.8156.

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