PREPARATION AND MULTI-NUCLEAR NMR STUDY OF NEW BENZODICHALCOGENAPHOSPHOLES

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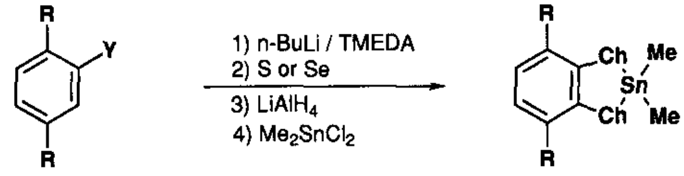
Abstract - Benzene fused 5-membered dichalcogenaheterocycles containing sulfur, selenium, and phosphorus, 2-phenyl-1,3,2-benzodichalcogenaphospholes (**4**), were newly prepared by the reactions of corresponding 2,2-dimethyl-1,3,2-benzodichalcogenastannoles (**3**) with dichlorophenylphosphine in excellent yields. The structure of these new 5-membered heterocycles containing tin, phosphorus, sulfur, and selenium was characterized by multi-nuclear nmr experiments.

Interest in the design of new 5-membered ring systems containing mixed group 14, 15, and 16 elements has led us to explore the synthesis of new benzene fused dichalcogenastannoles and dichalcogenaphospholes. Among such heterocycles, however, those with phosphorus bound to third- or fourth-low chalcogeniums, i.e., sulfur, selenium, have received little attention due to their synthetic limitations. While benzene fused 5-membered frameworks in which phosphorus has two oxygen ligands have been exclusively studied,[1] there have been a few reports of 5-membered phospholes containing sulfur[2] or selenium.[3] Recently, we reported a new efficient method for the synthesis of benzotrichalcogenoles containing sulfur and selenium atoms.[4] As a further advance of our research on the preparation and reactions of new stable benzene fused 5-membered frameworks, we wish to report here the convenient synthesis of benzodichalcogenaphospholes containing different kinds of heteroatoms in the ring and the characterization of the structure by multi-nuclear nmr technique.

A typical synthetic procedure of the 2,2-dimethyl-1,3,2-benzodichalcogenastannoles (**3a-i**) is as follows (Scheme 1). Thiophenol (5.1 ml, 50 mmol) in cyclohexane (20 ml) was slowly added dropwise to a mixture of 1.60 M n-BuLi (68.8 ml, 110 mmol; n-hexane solution) and TMEDA (16.6 ml, 110 mmol) in cyclohexane (50 ml) at 0 °C under an N_2 atmosphere. The reaction mixture was stirred for 30 min at 0 °C and for 24 h at room temperature. Selenium powder (4.3 g, 55 mmol) was slowly added to the mixture at 0 °C. After having been stirred for 8 h at room temperature the solvent was removed under reduced pressure. The residue was dissolved in anhydrous THF (90 ml) and treated with $LiAlH_4$ (2.5 g, 66 mmol) at 70 °C for 1 h. After treatment with ice-water (100 ml) the mixture was treated with dimethyltin dichloride (12.1 g, 55 mmol) in H_2O (20 ml) and stirred for 30 min at room temperature. The whole mixture was extracted with CH_2Cl_2 (3 x 50 ml), the extract was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, $CCl_4/CHCl_3=1/1$) to give 2,2-dimethyl-1,3,2-benzothiaselenastannole (**3b**) in 99% yield.[5]

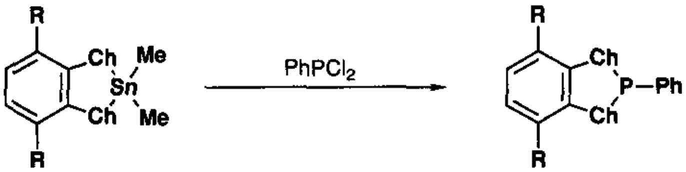


1a	Y=SH	R=H
b	SH	^{i}Pr
c	SH	OMe
2a	$SeSiMe_3$	H
b	$SeSiMe_3$	^{i}Pr
c	$SeSiMe_3$	OMe

3a	Ch=S,S	R=H	90%
b	S,Se	H	99%
c	Se,Se	H	92%
d	S,S,	^{i}Pr	70%
e	S,Se	^{i}Pr	70%
f	Se,Se	^{i}Pr	64%
g	S,S	OMe	45%
h	S,Se	OMe	49%
i	Se,Se	OMe	31%

Scheme 1

A typical procedure for introduction of phosphorus atom at 2-position is as follows (Scheme 2). To a stirred solution of stannole (**3b**) (336 mg, 1.0 mmol) in benzene (5 ml) was added dichlorophenylphosphine (0.14 ml, 1.0 mmol) under an N_2 atmosphere at 0 °C. After having been stirred for 15 min at room temperature, the mixture was treated with water and extracted with benzene (3 x 10 ml). The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, CCl_4) to give 2-phenyl-1,3,2-benzothiaselenaphosphole (**4b**) in 97% yield. Phospholes (**4a-i**) were characterized by physical and spectroscopic means.[6]



3a-i

4a	Ch=S,S	R=H	99%
b	S,Se	H	97%
c	Se,Se	H	98%
d	S,S,	^{i}Pr	99%
e	S,Se	^{i}Pr	92%
f	Se,Se	^{i}Pr	99%
g	S,S	OMe	90%
h	S,Se	OMe	92%
i	Se,Se	OMe	94%

Scheme 2

Tin has two, selenium has one, and phosphorus has one nmr-active spin 1/2 nuclei of relatively high natural abundance; ^{117}Sn, ^{119}Sn, ^{77}Se, and ^{31}P. Therefore, the ^{119}Sn, ^{77}Se and ^{31}P nmr spectra provided good information about the new 5-membered frameworks of dichalcogenastannoles (**3**) and dichalcogenaphospholes (**4**) (Table 1 and 2). The ^{77}Se nmr spectra of **3b,c,e,f,h,i** showed the signals with ^{119}Sn and ^{117}Sn satellites, which were in accordance with the existence of selenium atom or atoms neighboring with a tin atom in the ring. The ^{119}Sn nmr spectra of **3b,c,e,f,h,i** also showed ^{77}Se satellites. The ^{77}Se nmr spectra of **4b,c,e,f,h,i** showed the doublet signals and indicate that each 5-membered ring has a selenium atom or atoms neighboring with a phosphorus atom. The ^{31}P nmr spectra of **4b,c,e,f,h,i** showed the signals with ^{77}Se satellites. These multi-nuclear nmr data clearly indicate that the tin-selenium bonding in **3** and the phosphorus-selenium bonding in **4** are present in their 5-membered ring and also provide the good structural information of their sulfur analogues, stannoles (**3a,d,g**) and phospholes (**4a,d,g**).

Table 1. Multi-nuclear Nmr Data for Stannoles

Compd	^{119}Sn a) δ	^{77}Se b) δ	$^{1}J_{^{119}Sn-^{77}Se}$ (Hz)
3a	180.2	-	-
3b	137.6	57.9	1108
3c	87.5	109.9	1077
3d c)	174.3	-	-
3e c)	121.4	27.2	1139
3f c)	62.9	83.2	1110
3g	202.2	-	-
3h	147.3	21.7	1093
3i	90.7	72.0	1064

a) Relative to neat Me$_4$Sn b) Relative to neat Me$_2$Se
c) Ref. 4-c

Table 2. Multi-nuclear Nmr Data for Phospholes

Compd	^{31}P a) δ	^{77}Se b) δ	$^{1}J_{^{31}P-^{77}Se}$ (Hz)
4a	41.7	-	-
4b	30.0	460.1	254
4c	16.4	483.5	255
4d	32.4	-	-
4e	17.5	439.4	256
4f	-0.1	468.3	257
4g	40.9	-	-
4h	26.1	447.5	236
4i	9.0	469.0	238

a) Relative to H$_3$PO$_4$ b) Relative to neat Me$_2$Se

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4. (a) S. Ogawa, N. Yomoji, S. Chida, and R. Sato, *Chem. Lett.*, 1994, 507; (b) S. Ogawa, T. Kikuchi, S. Niizuma, and R. Sato, *J. Chem. Soc., Chem. Commun.*, 1994, 1593; (c) S. Ogawa, T. Kikuchi, A. Sasaki, S. Chida, and R. Sato, *Tetrahedron Lett.*, 1994, **35**, 5469.
5. Stannoles (**3a**-**i**) were characterized by physical and spectroscopic means. Full data will be reported in a future paper.
6. **4a**: Colorless crystals; mp 60.0-62.0 °C; ^{1}H nmr (400 MHz, CDCl$_3$) δ 7.06 (dd, J=5.8, 2.6 Hz, 2H, ArH), 7.24-7.27 (m, 3H, PhH), 7.46 (dd, J=5.8, 2.6 Hz, 2H, ArH), 7.51-7.56 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, CDCl$_3$) δ 125.6 (d), 126.1 (s), 128.4 (d), 129.7 (d), 129.9 (s), 138.3 (s),

139.7 (d); ms (m/z) 248 (M$^+$); Anal. Calcd for $C_{12}H_9PS_2$: C, 58.04; H, 3.65. Found: C, 57.89; H, 3.55. **4b**: Pale yellow crystals; mp 52.0-53.0 °C; ^{1}H nmr (400 MHz, $CDCl_3$) δ 7.03 (ddd, J=7.7, 7.4, 1.3 Hz, 1H, ArH), 7.10 (ddd, J=7.7, 7.4, 1.3 Hz, 1H, ArH), 7.22-7.25 (m, 3H, PhH), 7.48 (dd, J=7.7, 1.3 Hz, 2H, ArH), 7.53-7.58 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 126.1 (d), 126.2 (s), 126.3 (s), 126.7 (d), 128.4 (d), 129.8 (s), 130.1 (d), 136.1 (d), 139.3 (d), 140.9 (s); ms (m/z) 296 (M$^+$); Anal. Calcd for $C_{12}H_9PSSe$: C, 48.83; H, 3.07. Found: C, 48.68; H, 3.06. **4c**: Yellow crystals; mp 47.0-48.0 °C; ^{1}H nmr (400 MHz, $CDCl_3$) δ 7.09 (dd, J=5.8, 2.7 Hz, 2H, ArH), 7.23-7.25 (m, 3H, PhH), 7.49 (dd, J=5.8, 2.7 Hz, 2H, ArH), 7.58-7.62 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 126.3 (s), 128.0 (d), 128.4 (d), 129.8 (s), 130.7 (d), 138.9 (d), 139.1 (d); ms (m/z) 344 (M$^+$); Anal. Calcd for $C_{12}H_9PSe_2$: C, 42.13; H, 2.65. Found: C, 42.19; H, 2.87. **4d**: Colorless oil; ^{1}H nmr (400 MHz, $CDCl_3$) δ 1.22 (d, J=6.8 Hz, 6H ,Me), 1.24 (d, J=6.8 Hz, 6H, Me), 3.18 (sept., J=6.8 Hz, 1H, CH), 3.19 (sept., J=6.8 Hz, 1H, CH), 7.01 (s, 2H, ArH), 7.22-7.24 (m, 3H, PhH), 7.50-7.54 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 22.7 (s), 22.9 (s), 34.9 (s), 123.4 (s), 128.2 (d), 129.5 (d), 129.6 (s), 137.4 (s), 140.4 (d), 143.8 (d); ms (m/z) 332 (M$^+$); Anal. Calcd for $C_{18}H_{21}PS_2$: C, 65.02; H, 6.37. Found: C, 64.85; H, 6.49. **4e**: Pale yellow oil; ^{1}H nmr (400 MHz, $CDCl_3$) δ 1.23 (d, J=6.8 Hz, 3H, Me), 1.23 (d, J=6.8 Hz, 3H, Me), 1.24 (d, J=6.8 Hz, 3H, Me), 1.25 (d, J=6.8 Hz, 3H, Me), 2.97 (sept., J=6.8 Hz, 0.5H, CH), 2.98 (sept., J=6.8 Hz, 0.5H, CH), 3.28 (sept., J=6.8 Hz, 0.5H, CH), 3.29 (sept., J=6.8 Hz, 0.5H, CH), 7.03 (d, J=7.9 Hz, 1H, ArH), 7.09 (d, J=7.9 Hz, 1H, ArH), 7.21-7.24 (m, 3H, PhH), 7.52-7.57 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 22.8 (s), 23.0 (s), 23.0 (s), 23.0 (s), 35.2 (s), 38.0 (s), 123.5 (s), 124.0 (s), 128.2 (d), 129.6 (s), 130.0 (d), 137.1 (s), 139.6 (s), 140.0 (d), 144.7 (d), 145.5 (d); ms (m/z) 380 (M$^+$); Anal. Calcd for $C_{18}H_{21}PSSe$: C, 56.99; H, 5.58. Found: C, 57.04; H, 5.68. **4f**: Pale yellow oil; ^{1}H nmr (400 MHz, $CDCl_3$) δ 1.24 (d, J=6.8 Hz, 6H ,Me), 1.25 (d, J=6.8 Hz, 6H, Me), 3.07 (sept., J=6.8 Hz, 1H, CH), 3.08 (sept., J=6.8 Hz, 1H, CH), 7.10 (s, 2H, ArH), 7.21-7.24 (m, 3H, PhH), 7.57-7.61 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 23.1 (s), 23.2 (s), 38.3 (s), 124.0 (s), 128.3 (d), 129.6 (s), 130.6 (d), 139.5 (d), 139.6 (s), 146.4 (d); ms (m/z) 428 (M$^+$); Anal. Calcd for $C_{18}H_{21}PSe_2$: C, 50.72; H, 4.97. Found: C, 50.84; H, 5.05. **4g**: Colorless crystals; mp 141.5-143.0 °C; ^{1}H nmr (400 MHz, $CDCl_3$) δ 3.81 (s, 6H, OMe), 6.59 (s, 2H, ArH), 7.24-7.26 (m, 3H, PhH), 7.52-7.56 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 56.4 (s), 109.2 (s), 128.4 (d), 128.6 (s), 129.6 (d), 129.7 (s), 140.1 (d), 151.0 (d); ms (m/z) 308 (M$^+$); Anal. Calcd for $C_{14}H_{13}O_2PS_2$: C, 54.53; H, 4.25. Found: C, 54.30; H, 4.15. **4h**: Pale yellow crystals; mp 145.0-146.0 °C; ^{1}H nmr (400 MHz, $CDCl_3$) δ 3.79 (s, 3H, OMe), 3.83 (s, 3H, OMe), 6.58 (d, J=8.6 Hz, 1H, ArH), 6.66 (d, J=8.6 Hz, 1H, ArH), 7.23-7.27 (m, 3H, PhH), 7.54-7.59 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 56.3 (s), 56.5 (s), 108.8 (s), 109.8 (s), 126.8 (d), 128.4 (d), 129.6 (s), 130.0 (d), 131.0 (s), 139.9 (d), 151.7 (d), 151.9 (d); ms (m/z) 356 (M$^+$); Anal. Calcd for $C_{14}H_{13}O_2PSSe$: C, 47.33; H, 3.69. Found: C, 47.20; H, 3.53. **4i**: Pale yellow crystals; mp 152.5-153.5 °C; ^{1}H nmr (400 MHz, $CDCl_3$) δ 3.79 (s, 6H ,OMe), 6.63 (s, 2H, ArH), 7.20-7.27 (m, 3H, PhH), 7.58-7.63 (m, 2H, PhH); ^{13}C{^{1}H} nmr (100 MHz, $CDCl_3$) δ 56.4 (s), 109.3 (s), 128.4 (d), 129.4 (s), 129.6 (s), 130.7 (d), 139.7 (d), 152.6 (d); ms (m/z) 404 (M$^+$); Anal. Calcd for $C_{14}H_{13}O_2PSe_2$: C, 41.81; H, 3.26. Found: C, 41.61; H, 3.32.

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