Silyl and Germyl Derivatives of Selenophenol and Related Species

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The silyl and germyl derivatives of selenophenol, $SiH_3(SePh)$, $GeH_3(SePh)$, and $SiH_2(SePh)_2$, and the methylated analogues $MMe_nH_{3-n}(SePh)$ (M = Si, n = 2 or 3; M = Ge, n = 1—3; M = Sn, n = 3) have been prepared and characterized. The comparative synthetic routes include reactions of halides with lithium benzeneselenolate, lithium tetra(phenylseleno)aluminate, and trimethyl(phenylseleno)silane, and also of selenophenol with bisgermylcarbodi-imides. The spectroscopic properties of these species are reported and discussed. The seleno-boranes, $B(SePh)_3$ and $B(SeMe)_3$, -phosphine, $P(SePh)_3$, and -arsine, $As(SePh)_3$, are formed by reactions of the corresponding chlorides with $SiMe_3(SePh)$ and $SiMe_3(SeMe)$. Reduction of $B(SePh)_3$ by trimethylsilane is quantitative but a similar reaction with monosilane does not occur.

WE recently reported the characterization of some simple silyl and germyl derivatives of methaneselenol, *e.g.* $SiH_3(SeMe)$ and $GeH_3(SeMe)$.[1, 2] Their spectroscopic and physical properties confirm that they are the simple monomeric selenium analogues of the well known methoxy- and methylthio-silanes [3-5] and -germanes.[3, 6-8] The corresponding hydridic arene phenols and thiophenols have been prepared [9] but reports of Group 4 derivatives of selenophenol † are limited to fully substituted silicon [10] and tin species.[11, 12] In the present study the formation of the hydrides $SiH_3(SePh)$, $GeH_3(SePh)$, and $SiH_2(SePh)_2$ and their methylated analogues is described using comparative routes derived from the earlier work.

RESULTS AND DISCUSSION

Alkali-metal organochalcogenolates, *e.g.* Na(SMe), have been used successfully in the preparation of many silyl and germyl derivatives.[1-3, 7-9, 13] The utility of the lithium selenolate, Li(SeMe), appears to be limited to non-hydridic systems [1] because it catalyzes the disproportionation of bromosilane.[2]

We found that the arene analogue, lithium benzeneselenolate, Li(SePh), was obtained in moderate yield from the reaction (1) of elemental selenium with phenyllithium or, more satisfactorily, from the deprotonation (2) of selenophenol by methyl-lithium. Route (2) becomes more attractive depending on the commercial

$$\tfrac{1}{8}\,Se_8 + LiPh \xrightarrow{thf} Li(SePh) \qquad (1)$$

$$PhSeH + LiMe \xrightarrow{OEt_2} Li(SePh) + MeH \qquad (2)$$

availability of selenophenol. The selenolate produced moderate yields of phenylselenosilanes with hydridic as well as non-hydridic halogenosilanes [equations (3) and (4)]. With Li(SeMe) [2] and MgBr(SePh) [13] disproportionation products predominate.

$$SiBrH_3 + Li(SePh) \xrightarrow{OEt_2} SiH_3(SePh) + LiBr \qquad (3)$$

$$SiMe_3Cl + Li(SePh) \longrightarrow SiMe_3(SePh) + LiCl \qquad (4)$$

The use of selenophenol as a source of the SePh moiety is further exemplified by its rapid reaction (5) with lithium tetrahydridoaluminate to form the complex lithium tetra(phenylseleno)aluminate. The latter compound underwent facile exchange [equation (6)] with halogenosilanes in an analogous fashion to the related phosphino-[14] and arsino-aluminates.[15] Competing disproportionation does not appear to accompany the reaction, but the idealized stoicheiometry (5) is only achieved with pure $Li[AlH_4]$. The acidity of the protic species is probably

$$Li[AlH_4] + 4PhSeH \longrightarrow Li[Al(SePh)_4] + 4H_2 \qquad (5)$$

$$Li[Al(SePh)_4] + 4SiMe_2ClH \longrightarrow 4SiMe_2H(SePh) + LiCl + AlCl_3 \qquad (6)$$

as important as or even more important than steric factors in governing the ease of substitution in these aluminates. Reactions similar to (3), (4), and (6) also occur with halogeno-germanes [1, 2, 14, 15] and -stannanes,[16] but the ease of preparation of $SiMe_3(SePh)$ in (4) and the general applicability of metathetical reactions lead to more efficient syntheses of the germanes. Rapid, and virtually quantitative, exchange occurred (7) when $SiMe_3(SePh)$ and the fluorogermane were mixed at room temperature.

$$SiMe_3(SePh) + GeFH_3 \longrightarrow GeH_3(SePh) + SiMe_3F \qquad (7)$$

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† Also known as benzeneselenol and phenylselenol; see D. L. Klayman and W. H. H. Gunther, ' Organic Selenium Compounds: Their Chemistry and Biology,' Wiley, New York, 1973, p. 77.

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A fourth comparative route arises from the known susceptibility of Si–N,[3,17] Ge–N,[18,19] and Sn–N [18,20] bonds to attack by protic reagents. In germane chemistry the instability of hydridic Ge–N species [21] has limited this approach, with the notable exception of the germyl carbodi-imides.[22,23] In recent work we have found that the latter species are generally reactive towards a wide range of weakly acidic chalcogenols.[23] The comparative reaction (8) with selenophenol proceeded readily under mild conditions to give high yields of phenylselenogermane and dicyanodiamide. A similar reaction did not occur with silylcarbodi-imide.

$$(GeH_3N{:})_2C + 2PhSeH \longrightarrow 2GeH_3(SePh) + \tfrac{1}{2}(H_2NCN)_2 \quad (8)$$

The dehydrohalogenation of organosubstituted silicon, germanium, and tin halides with chalcogenols and amine bases has had wide application.[3] A similar reaction of the hydride iodosilane, trimethylamine, and methanol or methanethiol has led to $SiH_3(OMe)$ [4] and $SiH_3(SMe)$.[5] We found that the reaction of bromosilane with selenophenol in the presence of NMe_3 does not lead to the isolation of $SiH_3(SePh)$. The intractible material that results was tentatively identified as $[NMe_3H]Br$ and $SiH_n(SePh)_{4-n}$, which may be complexed with NMe_3. This was supported by the observation that the phenylselenosilanes readily formed 1 : 1 adducts with NMe_3 in a similar fashion to the halogenosilanes.[24]

We have shown that the Si–Se bond is quite reactive to a wide range of chloro-phosphines and -arsines,[25] in contrast to the reported inertness of the Sn–Se linkage.[12] Similar reactions in the present study [equation (9);

$$MCl_3 + 3SiMe_3(SePh) \longrightarrow M(SePh)_3 + 3SiMe_3Cl \quad (9)$$

M = P, As, or B] led to the isolation of tris(phenylseleno)-phosphine and -arsine. We found no evidence for an Arbusov-type [26] rearrangement occurring in these species as reported for some related thio- and seleno-phosphines.[27]

The comparative reactions (9) of boron trichloride with $SiMe_3(SeMe)$ and $SiMe_3(SePh)$ gave $SiMe_3Cl$ quantitatively and high yields of the selenoboranes, $B(SeMe)_3$ and $B(SePh)_3$, which have been reported in lower yield from the reaction of boron trihalides with selenols or organoselenolates.[28] Boron trihalides are efficient halogenating agents for silanes [29] and germanes.[30] The utility of chalcoboranes as direct chalcogenating agents has not been demonstrated. Tris(phenylseleno)borane was quantitatively reduced by trimethylsilane to diborane under somewhat forcing conditions (10), although a similar reaction with monosilane could not be duplicated. The selenophenols did not form adducts with diborane.

$$2B(SePh)_3 + 6SiMe_3H \longrightarrow 6SiMe_3(SePh) + B_2H_6 \quad (10)$$

Protolytic cleavage of the Si–Se bond in these species by HBr, H_2O, and MeOH proceeded in an analogous fashion to that in the methylselenosilanes [1,2] to give the corresponding bromosilane, siloxane, and methoxysilane, respectively.

^1H *N.M.R. Spectra.*—The parameters for the selenophenols are given in Table 1. The chemical shifts and coupling constants are similar to those of the related silyl and germyl selenides [1,2,31] and provide confirmation of the molecular species. The α-proton shifts along the series $MH_3(EPh)$ (M = C, Si, or Ge; E = O, S, or Se) show typical trends reflecting the electronegativity of the chalcogenide: *viz.* $\delta(CH_3EPh)$ 3.57(O), 2.32(S), and 2.17(Se) p.p.m.; $\delta(SiH_3EPh)$ 4.77(O), 4.39(S), and 4.22(Se) p.p.m.; $\delta(GeH_3EPh)$ 5.44(O), 4.71(S), and 4.35(Se) p.p.m.[9] The aromatic resonances were resolved into two envelopes, the low-field set being attributable to *meta*- and the high-field set to *ortho*- and *para*-protons. There was negligible difference between the *ortho*- and *para*-proton shift in the silanes and germanes suggesting similar $(p-d)\pi$ interactions with selenium, unlike the corresponding phenols.[9] However, the observation of the two envelopes in the selenophenols differs from the single envelope of the thiophenols where negligible sulphur–aromatic ring interaction was proposed.[9] This suggests that factors other than differences in electronegativity govern these shifts. Satellites were observed due to proton coupling with the magnetic isotope of selenium (^{77}Se, $I = \tfrac{1}{2}$, 7.58%) so that under these conditions there is no exchange of silyl or germyl groups.

Raman Spectra.—The observed frequencies for PhSeH, $MH_3(SePh)$ (M = C, Si, or Ge), and $MMe_3(SePh)$ (M = Si or Ge) are given in Tables 2 and 3. The assignments were made assuming unhindered rotation about the Se–Ph bond, as has been determined for the Ge–Ph bond in

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TABLE 1

The ^1H n.m.r. parameters [a] of the phenylseleno-silanes and -germanes and related species

Compound	δ(Me)	δ(MH′)	δ(Ph) [b]		*J*(HH′)	*J*(CH)	*J*(SeH)	*J*(SiH)
			o, *p*	*m*	(*vic*)		(*gem*)	
$CH'_3(SePh)$ [c]		2.17	7.11			142.2	11.3(3)	
$SiH'_3(SePh)$		4.22	7.08	7.46			16.8(0)	237.3
$SiH'_2(SePh)_2$		5.26	7.25	7.49			20.6(4)	298 [d]
$SiMe_2H'(SePh)$ [e]	0.36	4.75	7.12	7.48	3.45	123.0	*f*	210.3
$SiMe_3(SePh)$ [c,g]	0.34		7.29	7.53		123.3		
$GeH'_3(SePh)$		4.35	7.12	7.46			14.2(5)	
$GeMeH'_2(SePh)$	0.57	4.67	7.14	7.44	3.56	132.6	*f*	
$GeMe_2H'(SePh)$	0.52	4.91	7.12	7.47	3.14	132.1	*f*	
$GeMe_3(SePh)$ [c]	0.52		7.28	7.55		131.7		
$SnMe_3(SePh)$ [c,h]	0.42		7.27	7.57		134.9		

[a] The spectra were recorded at ambient temperature in C_6H_{12} solution (*ca.* 5% v/v). Chemical shifts (±0.02 p.p.m.) are in p.p.m. to low field of tetramethylsilane. Coupling constants are ±0.05 Hz (HH′) or ±0.1 Hz (^{13}CH, ^{29}SiH). [b] Most intense lines in complex envelope. [c] In CCl_4 solution (5% v/v). [d] Estimated from high-field satellite. [e] *J*(SeH)(*vic*) 3.8(1), *J*(SiH)(*gem*) 7.71 Hz. [f] Not observed. [g] *J*(SeH)(*vic*) 3.7(2), *J*(SiH)(*gem*) 7.14 Hz. [h] *J*(SnH)(*gem*) 58.56 (^{119}Sn), 55.86 (^{117}Sn) Hz.

TABLE 2

Raman spectra (cm^{-1}) of the selenophenols (liquids) [a]

PhSeH	MeSePh	$SiH_3(SePh)$	$GeH_3(SePh)$	Assignment [b] (M = C, Si, or Ge)
2 303s, p				ν(SeH)
	3 011w, dp	*ca.* 2 190 (sh), dp	2 095 (sh), dp	$\nu(MH_3)$
	2 933m, p	2 174vs, p	2 073vs, p	
1 076m, p	1 075s, p	1 071wm, p	1 070m, p	X-sens (*q*)
	1 425w, dp	936w, dp	861wm, dp	$\delta(MH_3)$
	1 274w, p	917w, dp	796wm	
		885 (sh), p		
794m, p				δ(SeH)
669m, p	673wm, p	669wm, p	668wm, p	X-sens. (*r*)
	907vw	598w, dp	546w, dp	$\rho(MH_3)$
450vw	467vw	*ca.* 480vw	*ca.* 460vw	X-sens. (*y*)
	595s, p	394vs, p	285vs, p	ν(MSe)
305m, p	310m, p	305m, p	*ca.* 304m, p	X-sens. (*t*)
238w, dp	*c*	*c*	*c*	X-sens. (*u*)
	280wm, p	250wm, p	230m, p	δ(CSeM)
174m, dp	190 (sh)	193wm, dp	188m, dp	X-sens. (*x*)

[a] w = Weak, m = medium, s = strong, v = very, sh = shoulder, p = polarized, dp = depolarized. Lines attributable to the substituent-insensitive phenyl modes were observed at: ν(CH) 3 060m, p (*z*); ν(CC) 1 578m, dp (*k*), 1 475vw (*m*), 1 439vw (*n*), 1 330vw (*o*); β(CH) 1 180w, p (*a*), 1 156w, dp (*c*), 1 022m, p (*b*); ring 999vs, p (*p*); γ(CH) 905vw (*i*), 838vw (*g*), 738vw (*f*); α(CCC) 615w, dp (*s*); ϕ(CC) 404vvw (*w*); combinations 3 150w, p (2*k*), 1 612 (*s* + *p*), 1 380 (2*v*), 1 284w, p (*p* + 285?). [b] Italic letters in parentheses denote *Whiffen* notation for monosubstituted benzenes.[35] [c] Line may be obscured by δ(CSeM).

several phenylgermanes.[32] The effective symmetry of the ring is then C_{2v} which has 30 associated vibrations. These may be classified according to Herzberg's notation.[33] The 24 substituent-insensitive vibrations may be satisfactorily correlated with the corresponding degenerate modes in benzene [34] so a detailed discussion is inappropriate. The six substituent-sensitive modes (X-sens. in Tables 2 and 3) were assigned by comparison with the spectra of monosubstituted benzenes [35] and related molecules.[31,36] Vibrations attributable to the MH_3 and MMe_3 groups were observed in regions similar to other seleno-methanes, -silanes, and -germanes.[1,2,31,37]

TABLE 3

Raman spectra (cm^{-1}) of the series $MMe_3(SePh)$ (M = Si,Ge, or Sn)

$SiMe_3(SePh)$	$GeMe_3(SePh)$	$SnMe_3(SePh)$	Tentative assignment [a]
2 960m, dp	2 977m, dp	2 993w, dp	$\nu(CH_3)$ asym.
2 893vs, p	2 905s, p	2 918m, p	sym.
1 410vw, dp	1 407vw, dp	1 430vw, dp	$\delta(CH_3)$ asym.
1 260w, p	1 240wm, p	1 196m, p	sym.
1 072m, p	1 068m, p	1 072m, p	X-sens. (*q*)
840w	824vw, p	781vw	$\rho(CH_3)$
750w, br	739vw, p	745vw	
670wm, p	665wm, p	670w, p	X-sens. (*r*)
695w, dp	604m, dp	535m, dp	ν(MC) asym.
626ms, p	563vs, p	512vs, p	sym.
450vvw	461vvw	467vvw	X-sens. (*y*)
367s, p	268vs, p	236s, p [b]	ν(MSe)
308m, p	302wm, p	309wm, p	X-sens. (*t*)
ca. 250 (sh), p	224m, p [b]	187s, p [c]	δ(CSeM)
235m, dp [b]			$\delta_{asym}(MC_3)$
207m, p [c]	183s, p [c]	152s, dp	$\delta_{sym}(MC_3)$
166m, dp	138ms, dp	124s, dp	$\rho(MC_3)$

[a] See footnote to Table 2. [b] Envelope may contain X-sens.-(*u*). [c] Envelope may contain X-sens.(*x*).

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The spectra are consistent with the local C_{3v} symmetry expected for the MH_3 groups. The observation of lines attributable to skeletal deformation, *viz.* δ(Ph–Se–M) at 280 (C), 250 (Si), and 230 cm^{-1} (Ge), confirmed that the heavy-atom skeletons are bent at the central atom like the bis(silyl)- and bis(germyl)-selenides.[31,37,38] However, coupling of the skeletal modes of the side chain with the X-sensitive phenyl modes *t*, *u*, and *x*, which occur below *ca.* 400 cm^{-1}, may make assignments to normal modes in this region artificial.

EXPERIMENTAL

The apparatus and associated spectroscopic techniques were as described previously.[23] The silyl and germyl starting materials were prepared by standard methods.[23,30,39,40] Other materials were of commercial origin. The germyl and silyl groups in the selenophenols were analyzed by reaction with hydrogen bromide.[9]

Preparation of Silyl Derivatives of Selenophenol via *Lithium Benzeneselenolate.*—(a) *Preparation of lithium benzeneselenolate.* Powdered selenium (0.8027 g, 10.17 mmol) and phenyllithium (*ca.* 20 mmol) were allowed to react in tetrahydrofuran (thf) (20 cm^3) as described for Li(SeMe).[1] The solvents were removed *in vacuo* after 18 h leaving a mustard-coloured crystalline material (*ca.* 1.92 g). Bands attributable to the SePh moiety were observed at 3 050, 1 569, 1 069, 1 021, 1 000vs, 668, 617, and 310 cm^{-1} in the Raman spectrum. Treatment of the crude Li(SePh) with HBr did not give PhSeH. The volatile products contained $SeEt_{2-n}Ph_n$, Se_2Ph_2, OEt_2, and thf.

(b) *Preparation of trimethyl(phenylseleno)silane.* Treatment of crude Li(SePh) (*ca.* 1.6 g) with chloro(trimethyl)silane (*ca.* 15 mmol) at 25 °C gave a vigorous exothermic reaction during which the mixture became white. The volatile material was fractionated using baths at −23 and −196 °C. The latter trap retained unchanged $SiMe_3Cl$ (4.6 mmol) and trace amounts of $O(SiMe_3)_2$ with OEt_2 and thf, while the former trap contained $Se(SiMe_3)_2$ and $SiMe_3Ph$ (1 : 1.8, total *ca.* 3.0 mmol) all identified in the n.m.r. spectra. The involatile liquid remaining in the reaction vessel was transferred with heating (*ca.* 60 °C) to a side arm and shown to be $SiMe_3(SePh)$ (5.8 mmol, 70%; vapour pressure at 25 °C, <1 Torr;* *m/e* 226—232, $P^+=[C_9H_{14}SiSe]^+$). (An involatile residue contained some selenium as Se_2Ph_2.) Cleavage of $SiMe_3(SePh)$ with HBr gave $SiBrMe_3$ (91%) [41,42] and PhSeH (97%). Protolysis of $SiMe_3(SePh)$ with water and MeOH gave $O(SiMe_3)_2$ (98%) and $SiMe_3(OMe)$ (97%). No reaction occurred with H_2S.

(c) *Preparation of phenylselenosilane.* Treatment of crude Li(SePh) (*ca.* 0.3 g) with $SiBrH_3$ (*ca.* 1 mmol) in OEt_2 gave $SiH_3(SePh)$ (*ca.* 5%) with $Se(SiH_3)_2$ (*ca.* 20%) and Se_2Ph_2. Lithium benzeneselenolate was synthesized alternatively from the reaction of PhSeH (1.94 mmol) with LiMe (*ca.* 2.5 mmol). After 15 min at 25 °C methane liberation (total *ca.* 1.8 mmol) was judged to be complete, leaving a crystalline material soluble in OEt_2. After degassing the mixture, bromosilane (3.0 mmol) was condensed into the ampoule. A white precipitate was formed immediately. After 15 min at 25 °C the volatile material was fractionated using baths at −23, −95, and −196 °C. The first trap contained $SiH_3(SePh)$ (0.85 mmol; vapour pressure at 20 °C, *ca.* 1 Torr; *m/e* 184—190, $P^+=[C_6H_8SiSe]^+$), the second OEt_2, and the following trap a mixture of $SiBrH_3$ (*ca.* 0.9 mmol), $SiMeH_3$ (*ca.* 0.2 mmol), and SiH_4 (trace), all identified by n.m.r. spectra. [The involatile residue was soluble in OEt_2 and gave ^1H n.m.r. resonances (4.2—5.5 p.p.m.) indicative of $SiH_n(SeSiH_3)_{4-n}$.] Cleavage of $SiH_3(SePh)$ (0.25 mmol) with HBr gave $SiBrH_3$ (88%) [31,41] and PhSeH (80%). The compound $SiH_3(SePh)$ did not react with B_2H_6.

Preparation of Phenylselenosilanes via *Lithium Tetra(phenylseleno)aluminate.*—(a) *Preparation of lithium tetra(phenylseleno)aluminate.* Recrystallized $Li[AlH_4]$ (*ca.* 2.5 mmol) was introduced into an ampoule (50 cm^3) containing anhydrous OEt_2 (*ca.* 1.5 cm^3). The ampoule was cooled to −196 °C, evacuated, and PhSeH (10.94 mmol) added. On warming slowly to 25 °C a vigorous reaction ensued and the mixture was then stirred for 30 min. Non-condensible gas (total *ca.* 10 mmol) was pumped off with the ampoule cooled to −196 °C. The solvent was removed leaving a flocculent white material which evolved OEt_2 slowly at 50 °C. After continuous pumping at 50 °C, $Li[Al(SePh)_4]$ was obtained as a colourless, oily, semicrystalline material (1.6419 g). The aluminate did not give H_2 on hydrolysis, was insoluble in C_6H_{12}, C_6H_6, and CCl_4, formed a complex with OEt_2, and became yellow when exposed to air or heat. Strong Raman lines were observed at 3 057, 1 576, 1 071, 1 020, 1 001vs, 669, 617, 307, 282, 249, 197, and 166 cm^{-1}; the ^1H proton shift was 7.09 p.p.m. The combining ratio $Li[Al(SePh)_4]$: MeI giving SeMePh was 1 : 3.8.

(b) *Reactions of* $Li[Al(SePh)_4]$ *with halogenosilanes.* Typically, $SiMe_2ClH$ (12.2 mmol) was distilled into an ampoule containing a slurry of $Li[Al(SePh)_4]$ (*ca.* 2.5 mmol) in OEt_2 and held at −196 °C. The mixture was brought to 25 °C and allowed to react (15 min) with occasional shaking. The volatile species were OEt_2, unchanged $SiMe_2ClH$ (2.1 mmol), and trace amounts of $O(SiMe_2H)_2$ and PhSeH. The liquid in the ampoule was $SiMe_2H(SePh)$ (9.79 mmol, 95% ; *m/e* 211—218, $P^+=[C_8H_nSiSe]^+$). Raman lines attributable to the silyl group were at: 2 966 and 2 902p $\nu(CH_3)$; 2 143p ν(SiH); 1 410 and 1 260p $\delta(CH_3)$; 700 and 662p ν(SiC); 765, and 616 δ(SiH); 380 cm^{-1} ν(SiSe). Treatment of $SiMe_2H(SePh)$ with HBr gave $SiBrMe_2H$ (94%), PhSeH, and trace amounts of Se_2Ph_2. Hydrolysis of $SiMe_2H(SePh)$ gave $O(SiMe_2H)_2$ (95%).

By a similar procedure $SiBr_2H_2$ (1.19 mmol) was condensed on to a slurry of the aluminate (2.36 mmol) in OEt_2 (2 cm^3). The mixture was held at −78 °C (15 min) and then brought to 25 °C; SiH_4 and PhSeH in trace amounts were the only volatile species. The colourless residue in the ampoule was extracted with C_6H_{12} to give $SiH_2(SePh)_2$ (*ca.* 0.6 mmol; *m/e* 338—348, $P^+=[C_{12}H_nSiSe_2]^+$; m.p. *ca.* 20 °C). Disproportionation to $Si(SePh)_4$, Se_2Ph_2, and PhSeH occurred during subsequent distillations. Features in the i.r. (C_6H_{12}) and (Raman) spectra assignable to the SiH_2Se group were at 2 176s [2 180(sh),dp] $\nu_{asym}(SiH)$; 2 153s (2 156s,p) $\nu_{sym}(SiH)$; 918m, 885m, and 790vs (900m and 711w) $\delta(SiH_2)$; 429s (428m,dp) $\nu_{asym}(SiSe_2)$; (347s,p) $\nu_{sym}(SiSe_2)$;

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* 1 Torr = (101 325/760) Pa.

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[110(sh)] cm^{-1} δ(SiSe$_2$). Other lines were assigned to the SePh moiety.

Preparation of Germyl Derivatives of Selenophenol.—(a) *Reactions of* SiMe$_3$(SePh) *with halogenogermanes.* Fluorogermane (1.16 mmol) and SiMe$_3$(SePh) (0.48 mmol) were allowed to react in an ampoule (10 cm^3) at 25 °C (15 min). The products were fractionated using baths at -23 and -196 °C. The former bath retained pure GeH$_3$(SePh) [0.44 mmol, 90%; vapour pressure at 20 °C, <1 Torr; *m/e* 226—238 (P^+)] (Found: Ge, as GeH$_3$Br, 29.7; Calc. for C$_6$H$_8$GeSe: 31.35%); the latter bath contained a mixture of SiMe$_3$F (*ca.* 0.4 mmol) [42,43] and unchanged GeFH$_3$ (*ca.* 0.7 mmol).[44] In similar experiments GeMeH$_2$(SePh) (89%), GeMe$_2$H(SePh) (92%), and GeMe$_3$(SePh) (91%) were obtained from SiMe$_3$(SePh) and the corresponding fluorides. Raman lines attributable [45] to the germyl groups were assigned as follows: GeMeH$_2$(SePh) 2 988 and 2 917p ν(CH$_3$), 2 064p ν(GeH), 1 440 and 1 243p δ(CH$_3$), 865, 688, and 473 δ(GeH$_2$), 850 ρ(CH$_3$), 602p ν(GeC), 283vs,p ν(GeSe), 152 δ(CGeSe); GeMe$_2$H(SePh) 2 985 and 2 912p ν(CH$_3$), 2 047p ν(GeH), 1 437 and 1 242p δ(CH$_3$), 657 and 630 δ(GeH), 612 and 584p ν(GeC), 277p ν(GeSe), 195p cm^{-1} δ(C$_2$Ge). Cleavage of SiMe$_3$(SePh) (0.47 mmol) also occurred with the tin(IV) species SnMe$_3$Cl (1.49 mmol) leading to the known [11] derivative SnMe$_3$(SePh) (0.43 mmol, 91%). Using GeMeCl$_3$ (0.58 mmol) in OEt$_2$ (1 cm^3) with excess of SiMe$_3$(SePh) (1.8 mmol) the trisubstituted species GeMe(SePh)$_3$ [0.56 mmol, 97%; δ(Me) 1.9 p.p.m.] was isolated as an immobile yellow oil. Raman lines arising from the GeMeSe$_3$ moiety were observed at 2 997w and 2 917wm,p ν(CH$_3$), 1 382vw and 1 228w,p δ(CH$_3$), 843vw,p ρ(CH$_3$), 593wm,p ν(GeC), 292(sh) and 261vs,p ν(GeSe$_3$), 230s,p, 157w, 117(sh), and 84s cm^{-1}.

(b) *Reaction of selenophenol with bisgermylcarbodi-imide.* The compounds (GeH$_3$N:)$_2$C (0.96 mmol) and PhSeH (1.70 mmol) were allowed to react in an ampoule (10 cm^3) at 25 °C (15 min). The volatile material was fractionated using baths at -23, -78, and -196 °C. The first trap contained GeH$_3$(SePh) (1.53 mmol, 90%), the second unchanged (GeH$_3$N:)$_2$C (*ca.* 0.2 mmol),[22] and the following trap trace amounts of GeH$_4$, identified in the i.r. spectrum.[46] Yellow material remaining in the ampoule was dicyanodiamide with trace amounts of diphenyl diselenide.

Reactions of SiMe$_3$(SePh) *with Boron, Phosphorus, and Arsenic Trichloride.*—The trichloride (*ca.* 0.5 mmol) and an excess of SiMe$_3$(SePh) were allowed to react in an ampoule fitted with a 5-mm n.m.r. tube. The reactants were shaken and warmed to *ca.* 60 °C. In each case SiMe$_3$Cl was recovered quantitatively. The excess of SiMe$_3$(SePh) was removed *in vacuo* at *ca.* 50 °C and the involatile selenide was sealed in the n.m.r. tube.

Typically, BCl$_3$ (0.43 mmol) and SiMe$_3$(SePh) (1.50 mmol) gave B(SePh)$_3$ [0.39 mmol, 90%; soluble in C$_6$H$_6$, C$_6$H$_{12}$, and CCl$_4$; m.p. *ca.* 150 °C; δ(Ph) 7.28 and 7.46 p.p.m., 10% v/v in C$_6$H$_{12}$] as a colourless solid which rapidly became yellow on exposure to air. X-Sensitive lines in the Raman spectrum were assigned at 1 072m (*q*), 670m (*r*), 469w (*y*), 308s (*t*), 264s [ν_{sym}(BSe$_3$)], 238(sh) (*u*), 220s, and 192m cm^{-1} (*x*).

Similarly, BCl$_3$ (0.47 mmol) and SiMe$_3$(SeMe) (1.63 mmol) gave a pale yellow liquid, B(SeMe)$_3$ [0.45 mmol, 95%; m.p. *ca.* 10 °C; δ(Me) 2.20 p.p.m., *J*(SeCH) 9.4, *J*(CH) 146.6 Hz, 10% v/v in CCl$_4$]. By comparison with data for the thioboranes [47] the i.r. in CCl$_4$ and (Raman) spectra of B(SeMe)$_3$ were assigned as follows: 3 017w (3 009m,dp), 2 989w [2 986(sh)], and 2 939s (2 932vs,p) ν(CH$_3$); 1 425vs (1 421w,dp) and 1 279vs (1 271w,p) δ(CH$_3$); 922s and 899m (928vw) ρ(CH$_3$); 832vs and 815(sh) ν_{asym}(BSe$_3$); 589w (588vs,p) ν(CSe); (373w,p) δ(BSe$_3$); (259vs,p) ν_{sym}(BSe$_3$); (219m,dp and 197m,p) δ(CSeB); [130w,dp and 92(sh) cm^{-1}] δ(BSe$_3$).

The corresponding reactions of PCl$_3$ or AsCl$_3$ with SiMe$_3$(SePh) gave P(SePh)$_3$ [56%; m.p. 150 °C (decomp.); δ(Ph) 7.19 and 7.46 p.p.m. in C$_6$H$_{12}$] and As(SePh)$_3$ [83%; δ(Ph) 7.21 and 7.48 p.p.m.] respectively. Both compounds were sparingly soluble in C$_6$H$_{12}$, CCl$_4$, or CS$_2$. Typical SePh-X-sensitive lines were observed in the i.r. and Raman spectra of both species, together with features attributable to skeletal modes at 405 [ν_{sym}(PSe$_3$)], 119 [δ(PSe$_3$)], 260 [ν_{sym}(AsSe$_3$)], and *ca.* 90 cm^{-1} [δ(AsSe$_3$)].

Reaction of B(SePh)$_3$ *with Silanes.*—The compounds SiMe$_3$H (*ca.* 3 mmol) and B(SePh)$_3$ (0.55 mmol) were allowed to react at 60 °C in a thick-walled ampoule (5 cm^3). After 1 h the volatile material was fractionated using traps at -23, -126, and -196 °C. Trace amounts of non-condensible gas were formed. The ampoule and the first trap contained SiMe$_3$(SePh) (total 1.82 mmol, 96%), the second trap SiMe$_3$H (*ca.* 1.1 mmol), and the following trap B$_2$H$_6$ (0.2 mmol). A similar reaction with SiH$_4$ at 25° gave only trace amounts of SiH$_3$(SePh) after 2 h.

Reaction of NMe$_3$·SiBrH$_3$ *with Selenophenol.*—The adduct NMe$_3$·SiBrH$_3$ (0.55 mmol) was prepared from SiBrH$_3$ and NMe$_3$ in equimolar proportions.[24] After degassing the material at 0°C PhSeH (0.72 mmol) was condensed into the reaction ampoule and the mixture was maintained at 0 °C for 1 h. The volatile material contained small amounts of PhSeH and NMe$_3$ and an intractable solid remained in the ampoule. The n.m.r. spectrum of the solid (MeCN solution) showed several resonances in the ranges 4.2—5.9, 2.0—3.3, and *ca.* 7.4 p.p.m. of variable intensity. The Raman spectrum showed lines attributable to SePh, SiH$_3$, and NMe$_3$ moieties. In control experiments pure samples of the selenosilanes formed 1 : 1 solid adducts with NMe$_3$. Their spectroscopic properties resembled those of the material formed from NMe$_3$·SiBrH$_3$ and PhSeH but do not show the series of resonances in the 4.2—5.9 p.p.m. region. These lines are assumed to arise from NMe$_3$·SiH$_3$(SePh) together with condensed species SiH$_n$(SePh)$_{4-n}$ adducted to an unknown degree with NMe$_3$. Such condensation reactions are well known for disiloxane and disilyl sulphide in the presence of Lewis bases.[48]

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