Terminal Organylchalcogenoethyl- and -propylamines and Their Schiff Base Derivatives

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Abstract: A series of organoselanyl- and organotellanyl-substituted ethyl- and propylamines and their hydrochlorides, as well as 2-(methylsulfanyl)ethylamine have been synthesized. Efficient general synthetic routes have been developed to chalcogen(S, Se, Te)-containing Schiff bases with di- and trimethylene bridges between the nitrogen atom of the imino group and the chalcogen, by condensation of 3-(*tert*-butyl)- and 3-(1-ethylpropyl)-2-hydoxybenzenecarbaldehydes with the amines. The influence of the organylchalcogenyl-group on some spectral characteristics (^{1}H, ^{13}C, ^{77}Se NMR spectroscopy) of both amines and Schiff bases is discussed.

Key words: amines, Schiff bases, condensation, spectroscopy, organometallic reagents

Schiff bases are among the most investigated ligands in coordination chemistry,[1] but interest in them remains high, due partly to the wide range of possibilities for varying the substituents in these ligand systems and also because of their potential applications in homogeneous catalysis. One class of Schiff bases, which has received particular attention, is that of the bidentate salicylaldimines formed by the reaction of *o*-hydroxybenzaldehydes with the corresponding amines. Use of amines which incorporate alkylamino-, hydroxy-, alkoxy-, alkyl- and arylthio groups capable of additional coordination leads to the possibility of an increase in denticity of the ligand in complex formation.[2]

An alternative procedure for the preparation of this type of ligands containing sulfur consists of electrochemical rupture of the disulfide bond of the corresponding bis-2-salicylaldiminoethyl disulfides.[3] Large 24- and 28-membered macrocyclic Schiff bases are also known with selenide and telluride functions linked to the nitrogen atom of the imine bond through polymethylene bridges $(CH_2)_n$ (n = 2,3).[4] Schiff bases bearing a sulfide group connected to the nitrogen atom of the imine function by a dimethylene bridge are formed by condensation of 2-(organosulfanyl)ethylamine, 2-[(2-aminoethyl)thiomethyl]benzimidazole or imidazole, with substituted salicylaldehydes,[5] acetophenone or acetylacetones.[6]

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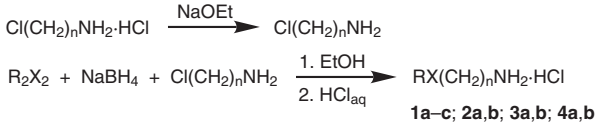
Taking into account the potential of these Schiff bases as tridentate ligands,[1] and at the same time the extremely scarce knowledge about these compounds, which is limited mainly to sulfur-containing derivatives, we have synthesized salicylaldimines bearing sulfide-, selenide- and telluride functions connected to nitrogen by a polymethylene bridge $(CH_2)_n$ (n = 2,3) starting from 3-(*tert*-butyl)- and 3-(1-ethylpropyl)-2-hydroxybenzenecarbaldehydes and a series of 2-(organylselanyl)ethylamines **6**, 2-(organyltellanyl)ethylamines **7**, 3-(organylselanyl)propylamines **8**, and 3-(organyltellanyl)propylamines **9** synthesized by us. For comparison purposes we have also prepared the analogous Schiff bases using 2-(methylsulfanyl)ethylamine **5**.

It should be pointed out that terminal organylchalcogenylalkylamines in themselves are prospective ligands, which has been shown for *N*-{2-(4-methoxyphenyltellanyl)ethyl}morpholine,[7] bis-{2-(*N*-morpholino)ethyl}telluride,[7b] 3-organylselanyl(tellanyl) propylamines,[8] 2-organylselanylethylamine,[9] *N*,*N*-dialkyl(thioalkyl)amines,[10] and hence are interesting per se.

Of the organylchalcogenylalkylamines **5**–**9**, only the sulfur derivatives are well-known.[11] Selenium and tellurium derivatives are represented solely by a few compounds: 2-(methylselanyl)ethylamine hydrochloride (**1a**),[12] 2-(phenylselanyl)ethylamine (**6c**),[13] 3-(phenylselanyl)- and 3-(phenyltellanyl)propylamines **8b** and **9b**, 3-(4-methoxyphenyltellanyl)propylamine,[8] but to date terminal organylselanyl- and tellanylalkylamines remain a poorly studied type of alkylamines. The most general method for their preparation is by nucleophilic substitution of halogen in ω-halogenoalkylamines by organylchalcogenolate anions.[8,11a–c,13] Alternative methods for the preparation of 2-(alkylsulfanyl)ethylamines include substitution of the iodine atom in methyl iodide by the cysteamine anion,[11e–h] substitution of chlorine in chloroethylsulfide by phthalimido anion followed by alkaline hydrolysis of the product,[11i] reduction of 2-methylsulfanylethyl nitrate with hydrogen in the presence of nickel at 50–60 °C and a pressure of 100 atm[11j] or rupture of ethylenimine with thiol.[11c,e] On rupture of ethylenimine with potassium selenosulfate followed by alkaline hydrolysis, selenocysteamine is formed[12a,b] and subsequent treatment with methyl iodide affords 2-(methylselanyl)ethylamine.[12b,c]

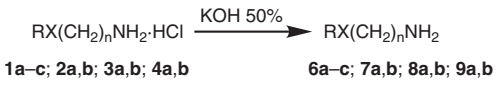
To prepare a series of terminal organylselanyl- and organyltellanylethyl- and propylamines **6–9** we modified the most studied method of nucleophilic substitution of a chlorine atom in ω-chloroalkylamines by chalcogenolate anion.[8,11a–c,13] Treatment of 2-chloroethylamine and 3-chloropropylamine with organylselenolate and organyltellurolate anions generated in situ by treatment of the corresponding diorganyl diselenide and ditelluride with sodium tetrahydroborate in EtOH leads to the corresponding 2-(organylselanyl)ethylamines **6**, 2-(organyltellanyl)ethylamines **7**, 3-(organylselanyl)propylamines **8** and 3-(organyltellanyl)propylamines **9** (Scheme 1). 2-Chloroethylamine and 3-chloropropylamine were generated in turn from the corresponding hydrochlorides by treatment with sodium ethylate and used without separation.



Scheme 1

The synthesized compounds were isolated in good yields (up to 90%) as amine hydrochlorides (**1a–c**; **2a**,**b**; **3a**,**b**; **4a**,**b**) on treatment of the reaction mixtures with concentrated hydrochloric acid (Scheme 1). The method described allows preparation of the pure products **1–4** without additional purification. Unlike free amines **6–9**, their salts **1–4** are more stable on storage and lack any odor.

As individual compounds, amines **6a–c**, **7a**,**b**, **8a**,**b**, **9a**,**b** were prepared by treatment of the salts **1–4** with 50% aqueous solution of KOH (Scheme 2). In contrast to a report that propylamines **8b** and **9b** are crystals,[8] all our compounds **6–9** are liquids. The variance of our data as regards to amines **8b** and **9b** with those reported[8] are probably due to the fact that we had prepared these compounds in metastable form.



1,**6**: X = Se, n = 2, R = Me (**a**), Ph (**b**), Et (**c**)
2,**7**: X = Te, n = 2, R = Me (**a**), Ph (**b**)
3,**8**: X = Se, n = 3. R = Me (**a**), Ph (**b**)
4,**9**: X = Te, n = 3, R = Me (**a**), Ph (**b**)

Scheme 2

It should be pointed out that for both salts and free amines the yields of (phenylchalcogenyl)alkylamines were higher than those of the aliphatic derivatives. A similar comparison can be made for seleno- and telluro-substituted alkylamines and their salts; in the case of selanyl derivatives the yields are higher than for the tellanyl ones.

The structure of 2-(organylselanyl)- **6a–c** and 2-(organyltellanyl)ethyamines **7a**,**b**, 3-(organylselanyl)- **8a**,**b** and 3-(organyltellanyl)propylamines **9a**,**b** and their hydrochlorides **1a–c**, **2a**,**b**, **3a**,**b**, **4a**,**b** was proved by spectral methods (NMR ^{1}H, ^{13}C and ^{77}Se, IR), GC–MS and elemental analysis (experimental section, Tables 1 and 2).

^{1}H NMR spectra of the chalcogeno-substituted alkylamines **6–9** and their salts **1–4** (Table 1) are characterized, apart from singlet signals for the methyl groups in the case of methylchalcogenyl derivatives or aromatic signals in the case of phenylchalcogenyl derivatives, with two distinct triplets of methylene groups in the case of ethylamines **1**, **2**, **6**, **7** and two triplets and a quintuplet for the three methylene groups in the case of propylamines **3**, **4**, **8**, **9**. The NH_2 group of the amine hydrochlorides in D_2O manifests itself as a singlet in the range 4.91–4.59 ppm. The signal for the NH_2 group for free amines appears in the wide range of 1.80–0.85 ppm. Comparison of the spectra for alkylamines **6–9** and hydrochlorides **1–4** with the spectra for the parent 2-chloroethylamine, 3-chloropropylamine and their hydrochlorides indicates that the influence of the organylchalcogenyl group extends only to the adjacent methylene group of the alkyl moiety. The signals for the CH_2X groups (X = Se, Te) are shifted towards higher field compared to those for the CH_2Cl-group of 2-chloroethyl- (3.76 ppm) and 3-chloropropylamines (3.60 ppm). For methylchalcogenylalkylamines the chemical shift of XCH_2-group depends on chalcogen atom and in the case of tellanyl derivatives is shifted to lower field (2.72–2.57 ppm) compared to the selanyl derivatives (2.63–1.98 ppm). For the phenylchalcogenyl derivatives chemical shifts of the XCH_2 group (X = Se, Te) practically do not depend on chalcogen atom and lie in the range of 3.01–2.72 ppm.

In the ^{13}C NMR spectra of the methylchalcogenyl-alkylamines **6–9** (Table 2), the methyl group signal, identified by its characteristic multiplicity (quartet), lies in the range of 4.4–1.5 ppm for the selenium derivatives, while, in the case of tellurium, a very marked shift to higher field (–23.2 to 21.6 ppm) is observed. It is rather hard to assign other signals of aliphatic carbons to specified methylene groups of ethylamines **6** and **7** and propylamines **8** and **9**, but it can be assumed that the signal found in the spectra of all alkylamines **5–9** in the range of 38.9–43.7 ppm corresponds to the CH_2N group and that, as in the ^{1}H spectra, it is not influenced by the organylchalcogenide group.

Lengthening of the methylene chain between the selenium and nitrogen atoms leads to a downfield shift of the selenium signal in the ^{77}Se spectra both for alkylseleno-substituted amines and their salts (Table 2), and for aromatic derivatives.

In the IR spectra, the free amines **5–9** are characterized by two bands for N–H bond valence vibrations at 3367–3348 and 3291–3256 cm^{-1} that shift to the lower frequency region 3020–2926 cm^{-1} in the case of salts **1–4**.

The mass-spectra of the free amines **6–9** are characterized along with the molecular ions, by fragment ions resulting from rupture of C–X (X = Se, Te) and C–N bonds. As a result, these spectra indicate the presence of the ions $[RX]^+$, $[NH_2(CH_2)_n]^+$ (or $[NH_2CH{=}CH]^+$,

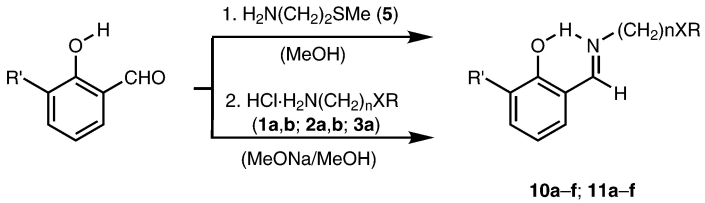
$[NH_2CH{=}CHCH_3]^+$) and $[RX(CH_2)_n]^+$ (or $[RXCH{=}CH]^+$, $[RXCH{=}CHCH_3]^+$) (n = 2, 3). C–C bond scission to form fragments $[RXCH_2]^+$ and $[NH_2CH_3]^+$ is characteristic of ethylamines **6**,**7**. The same C–C bond scission is also found for the propylamines **8**, **9** but with formation of fragments $[RXCH_2CH_2]^+$ (or $[RXCH{=}CH]^+$) and $[NH_2CH_2CH_2]^+$ (or $[NH_2CH{=}CH]^+$). Both selenium- and tellurium-containing amines form the $[Se]^+$ and $[Te]^+$ ions on electron impact. Exceptions are the 2-, 3-(phenylselanyl)alkylamines.

We prepared the organylselanyl- and organyltellanylalkylamines-based Schiff bases by condensation of the corresponding benzaldehydes with free amine (method 1) or amine generated in situ from amine hydrochloride on treatment with sodium methylate in MeOH (method 2) (Scheme 3). The first method was used to synthesize the Schiff bases from 2-(methylsulfanyl)ethylamine **5** prepared from cysteamine according to the known procedure.[11e–h] Yields of the bases reach 99% in this case, in the second method they were 60–97% and, in general, decreased in the order S > Se > Te, being higher for the methylchalcogenyl-derivatives compared to the phenyl ones.

It is known that the Schiff bases prepared from salicylaldehyde and primary amines possess the *E*-configuration due to H-bonding between the hydroxyl and the nitrogen of the imine group.[14] Since the ^{1}H NMR spectral data of the products **10** and **11** (Table 3) are similar to those of reported salicylaldimines,[14] this fact clearly speaks in favor of an *E*-configuration for the Schiff bases **10a–f** and **11a–f**. In the ^{1}H NMR spectra of the compounds **10**, **11**, the hydroxy-group manifests itself as a singlet in the range 14.00–13.77 ppm for *tert*-butyl derivatives, and in the range 13.62–13.41 ppm for 1-ethylpropyl derivatives, being shifted to lower field compared to the starting aldehydes (11.87 and 11.33 ppm respectively). The CH=N group of Schiff bases manifests itself in the range 8.39–8.31 ppm as a broad singlet or doublet with a $^4J_{H\text{-}H}$ splitting constant of 1.22 Hz. The signals for the methylene groups bonded to nitrogen atom of the imine group of bases **10** and **11**, due to the influence of the imine group and the phenol ring occur to lower field (3.87–3.79 ppm in the case of sulfur- and selenium-containing Schiff bases and 3.99–3.95 ppm in the case of tellurium-containing ones) compared to the parent amines **5**–**9** and demonstrate the same splitting pattern with $^4J_{HH}$ 1.22 Hz. The signal of the methyl group on the chalcogen atom and the triplet signal of the methylene group adjacent to the methylsulfanyl, organylselanyl and organyltellanyl groups of bases **10** and **11** are shifted to lower field compared to the starting amine. The presence of an additional methylene in the methylselanylpropyl derivatives of the Schiff bases **10f**, **11f** leads to an up-field shift of the NCH_2 group signal as compared to the ethyl derivatives.

Comparison of the ^{13}C NMR spectra for the parent benzaldehydes and those of the salicylaldimines **10** and **11** (Table 4) prepared from them allows rather simple assignment of observable signals of the carbon atoms to corresponding groups. Thus, the carbon signals in the region of sp^2-hybridized atoms (166.5–165.4 ppm) evidently correspond to the imino group CH=N, the doublet splitting observed in some cases is probably due to residual coupling to the low-field phenolic proton. The signals of the MeX group (X = S, Se, Te) are found in the range of 15.7 to –21.9 ppm and shift from lower to higher field in the order S, Se, Te. A similar tendency is found for the CH_2X group (X = S, Se, Te) which is observed in the wide range of 35.0–4.1 ppm, an up-field shift being observed on going from sulfur (35.0 ppm) to selenium (30.8–25.8 ppm) and tellurium (4.1–9.1 ppm), and also on going from MeX to PhX (X = S, Se) and from the ethyl to propyl derivatives. The methylene group connected to the imino group is strongly deshielded compared to the parent amines. As a result, its signals manifest themselves in the range of 61.3–58.8 ppm with a slight down-field shift observed in the order S, Se, Te. The central methylene group in the propyl derivatives manifests itself at 22.6 ppm.

In conclusion, we have developed a fairly efficient general synthetic route to S-, Se-, Te-containing Schiff bases,



10: R' = $(CH_3)_3C$-; X = S, n = 2, R = Me (**a**); X = Se, n = 2, R = Me (**b**), Ph (**c**); X = Te, n = 2, R = Me (**d**), Ph (**e**); X = Se, n = 3, R = Me (**f**)

11: R' = $(CH_3CH_2)_2CH$-; X = S, n = 2, R = Me (**a**); X = Se, n = 2, R = Me (**b**), Ph (**c**); X = Te, n = 2, R = Me (**d**), Ph (**e**); X = Se, n = 3, R = Me (**f**)

Scheme 3

potential tridentate hemilabile ligands for homogeneous catalysis.[15]

3-(*tert*-Butyl)-2-hydroxybenzenecarbaldehyde and 3-(1-ethylpropyl)-2-hydroxybenzenecarbaldehyde were prepared using a literature procedure.[16] Dimethyl diselenide, diethyl diselenide, diphenyl diselenide, dimethyl ditelluride and diphenyl ditelluride were prepared according to known procedures.[17] 2-(Methylsulfanyl)ethylamine **5** was prepared according to a known procedure.[11f] ^{1}H (400 MHz), ^{13}C (100.6 MHz) and ^{77}Se (76.3 MHz) NMR spectra of amines **5**–**9** and their salts **1**–**4** were recorded in $CDCl_3$ or D_2O (amine hydrochlorides **1**–**4**) on a Bruker DPX-400 spectrometer using hexamethyldisiloxane as internal standard. ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra of Schiff bases **10**, **11** were recorded in $CDCl_3$ on a Bruker AC-300 spectrometer using $CHCl_3$ as internal standard. EI mass spectra were obtained at 70 eV ionization energy on a HP 5971A spectrometer, which was interfaced to a HP-5890 gas chromatograph. IR spectra were recorded on a Bruker IPS 25 spectrometer in KBr (amine hydrochlorides) or neat.

2-(Phenylselanyl)ethylamine Hydrochloride (1b)

$NaBH_4$ was slowly added under an Ar atmosphere to a solution of Ph_2Se_2 (2.00 g, 6.41 mmol) in EtOH (40 mL) and the mixture stirred until discoloring of the solution occurred. 2-Chloroethylamine generated from $Cl(CH_2)_2NH_2{\cdot}HCl$ (1.49 g, 12.82 mmol) and sodium (0.29 g, 12.82 mmol) in EtOH (25 mL) was then added under Ar to a resulting solution of selenolate. This reaction mixture was refluxed for 3 h. On cooling the precipitated NaCl was filtered off, rinsed with EtOH (20 mL) and the combined ethanolic solution was acidified with concd HCl to pH 5 (1 mL) and dried in vacuum to afford $PhSe(CH_2)_2NH_2{\cdot}HCl$ [**1b**, 1.60 g (52.6%)]; mp 115–117 °C (EtOH).

IR (KBr): 2942 (br), 1583, 1503, 1251, 889 cm^{-1}.

Anal. Calcd for $C_8H_{12}NSeCl$: C, 40.10; H, 5.07; N, 5.90. Found: C, 40.61; H, 5.11; N, 5.92.

Ethyl- and propyl amine hydrochlorides **1**–**4** were prepared from the corresponding dichalcogenides by analogous procedures.

2-(Methylselanyl)ethylamine Hydrochloride (1a)

Yield: 29.5%; mp 153–155 °C (EtOH).

IR (KBr): 2980 (br), 1599, 1464, 1478, 1226, 883 cm^{-1}.

Anal. Calcd for $C_3H_{10}NSeCl$: C, 20.65; H, 5.78; N, 8.03. Found: C, 20.40; H, 5.54; N, 7.97.

2-(Ethylselanyl)ethylamine Hydrochloride (1c)

Yield: 98.0%; mp 80–83 °C (EtOH).

IR (KBr): 2969 (br), 1599, 1475, 1461, 1222 cm^{-1}.

Anal. Calcd for $C_4H_{12}SeNCl$: C, 25.48; H, 6.41; N, 7.43. Found: C, 24.87; H, 7.05; N, 8.20.

2-(Methyltellanyl)ethylamine Hydrochloride (2a)

Yield: 84.5%; mp 124–126 °C (decomp.) (EtOH).

IR (KBr): 2963 (br), 1597, 1461, 1228, 889 cm^{-1}.

Table 1 ^{1}H NMR Data for Amine Hydrochlorides $RX(CH_2)_nNH_3^+Cl^-$ **1**–**4** and Amines $RX(CH_2)_nNH_2$ **5**–**9**

Compound	RX	^{1}H NMR data, δ, ppm (multiplicity, $^2J_{HH}$, Hz)				
		R	XCH_2	$-CH_2-$	CH_2N	NH_2
1a	MeSe	1.85 (s)	2.62 (t, 7.08)	–	3.08 (t, 7.01)	4.65 (s)
1b	PhSe	7.16–7.39 (m)	2.95 (t, 6.55)	–	2.98 (t, 6.55)	4.59 (s)
1c	EtSe	1.19 (t, 7.46), 2.47 (q, 7.51)	2.65 (t, 7.08)	–	3.07 (t, 7.23)	4.65 (s)
2a	MeTe	1.79 (s)	2.65 (t, 8.00)	–	3.18 (t, 8.06)	4.62 (s)
2b	PhTe	7.22–7.45 (m)	3.01 (t, 7.84)	–	3.22 (t, 8.22)	4.91 (s)
3a	MeSe	1.88 (s)	2.50 (t, 7.29)	1.90 (m, 7.26)	2.97 (t, 7.51)	4.61 (s)
3b	PhSe	7.28–7.49 (m)	2.92 (t, 7.18)	1.93 (m, 7.42)	3.00 (t, 7.51)	4.67 (s)
4a	MeTe	1.84 (s)	2.57 (t, 7.56)	2.01 (m, 7.51)	2.99 (t, 7.45)	4.67 (s)
4b	PhTe	7.20–7.82 (m)	2.80 (br s)	1.99 (br s)	2.92 (br s)	4.70 (s)
5	MeS	2.08 (s)	2.59 (t, 6.24)	–	2.87 (t, 6.55)	1.56 (s)
6a	MeSe	1.98 (s)	2.63 (t, 6.47)	–	2.92 (t, 6.41)	1.80 (s)
6b	PhSe	7.22–7.48 (m)	2.95 (t, 9.0)	–	2.97 (t, 8.5)	1.58 (s)
6c	EtSe	1.39 (t, 7.61), 2.57 (q, 7.51)	2.66 (t, 7.08)	–	2.90 (t, 6.55)	1.36 (s)
7a	MeTe	1.87 (s)	2.72 (t, 6.85)	–	2.95 (t, 6.85)	1.31 (s)
7b	PhTe	7.16–7.42 (m)	2.95 (t, 4.87)	–	2.99 (t, 5.18)	1.32 (s)
8a	MeSe	1.98 (s)	2.58 (7.32)	1.80 (m, 7.20)	2.78 (t, 6.92)	1.29 (s)
8b	PhSe	7.20–7.46 (m)	2.75 (t, 6.85)	1.79 (m, 7.10)	2.92 (t, 7.34)	1.05 (s)
9a	MeTe	1.88 (s)	2.63 (t, 7.45)	1.85 (m, 7.07)	2.73 (t, 6.91)	1.69 (s)
9b	PhTe	7.16–7.72 (m)	2.72 (t, 6.80)	1.92 (m, 7.07)	2.90 (t, 7.45)	1.14 (s)

Table 2 ^{13}C NMR and ^{77}Se NMR Data for Amine Hydrochlorides $RX(CH_2)_nNH_3^+Cl^-$ **1–4** and Amines $RX(CH_2)_nNH_2$ **5–9**

Compound	RX	^{13}C NMR, δ, ppm (multiplicity, $^3J_{C-H}$, Hz)				^{77}Se NMR
		R	XCH_2	CH_2	CH_2N	δ, ppm
1a[a]	MeSe	4.4 (q, 142)	21.6 (t, 143)	–	39.8 (t, 143)	41.2
1b[a]	PhSe	134.6, 133.0, 131.0, 129.4, 127.8	24.0 (t, 144)	–	39.6 (t, 145)	261.3
1c[a]	EtSe	15.0 (t, 148), 17.4 (q, 128)	18.8 (t, 141)	–	39.4 (t, 145)	154.8
2a[b]	MeTe	–21.6	–2.7	–	41.6	
2b[a]	PhTe	127.1–134.6 (m)	2.9 (t, 138)	–	43.5 (t, 141)	
3a[b]	MeSe	3.5	20.8, 27.1		39.5	62.9
3b[b]	PhSe	132.4, 129.2, 127.2	23.0, 26.9		38.9	281.7
4a[b]	MeTe	–22.2	–2.3	28.9	41.1	
4b[b]	PhTe	138.2, 129.8, 128.5	3.9	29.0	41.0	
5[a]	MeS	14.5 (q, 139)	37.8 (t, 138)	–	39.8 (t, 135)	
6a[b]	MeSe	3.8	30.1	–	41.4	
6b[a]	PhSe	126.1–133.6 (m)	32.5 (t, 141)	–	41.6 (t, 137)	259.2
6c[a]	EtSe	16.6 (t, 141), 15.6 (q, 127)	27.9 (t, 138)	–	41.7 (t, 136)	155.9
7a[b]	MeTe	–23.2	9.3	–	42.8	
7b[a]	PhTe	129.9, 129.5, 128.3, 127.9, 126.8, 126.3	14.6 (t, 142)	–	43.2 (t, 135)	
8a[b]	MeSe	1.5	14.8, 26.4		41.0	77.0
8b[b]	PhSe	132.4, 128.9, 126.6	25.0, 33.8		41.8	292.3[c]
9a[b]	MeTe	–23.3	–1.0	34.4	42.7	
9b[b]	PhTe	138.3, 137.7, 129.2, 128.9, 127.6, 127.3, 112.0	5.2	35.3	43.7	

[a] Without ^{13}C–H decoupling.
[b] With ^{13}C–H decoupling.
[c] Lit.[8]: δ = 306.

Anal. Calcd for $C_3H_{10}TeNCl$: C, 16.15; H, 4.52; N, 6.28. Found: C, 16.04; H, 4.99; N, 6.27.

2-(Phenyltellanyl)ethylamine Hydrochloride (2b)
Yield: 98.6%; mp 79–81 °C (EtOH).

IR (KBr): 3007 (br), 1597, 1572, 1509, 1476, 1204, 730 cm^{-1}.

Anal. Calcd for $C_8H_{12}TeNCl$: C, 33.69; H, 4.24; N, 4.91. Found: C, 33.78; H, 4.00; N, 5.12.

3-(Methylselanyl)propylamine Hydrochloride (3a)
Yield: 46.6%; mp 147–148 °C (EtOH).

IR (KBr): 2926 (br), 1593, 1570, 1520, 1221, 837 cm^{-1}.

Anal. Calcd for $C_4H_{12}SeNCl$: C, 25.48; H, 6.41; N, 7.43. Found: C, 25.30; H, 6.50; N, 7.49.

3-(Phenylselanyl)propylamine Hydrochloride (3b)
Yield: 99.7%; mp 141–143 °C (EtOH).

IR (KBr): 2927 (br), 1613, 1578, 1512, 1228 cm^{-1}.

Anal. Calcd for $C_9H_{14}SeNCl$: C, 43.13; H, 5.63; N, 5.59. Found: C, 42.30; H, 5.74; N, 5.06.

3-(Methyltellanyl)propylamine Hydrochloride (4a)
Yield: 46.4%; mp 85–87 °C (EtOH).

IR (KBr): 3020 (br), 2922, 1618, 1510, 1187, 833 cm^{-1}.

Anal. Calcd for $C_4H_{12}TeNCl$: C, 20.25; H, 5.10; N, 5.91. Found: C, 19.80; H, 4.81; N, 5.84.

3-(Phenyltellanyl)propylamine Hydrochloride (4b)
Yield: 39.9%; mp 81–83 °C (EtOH).

IR (KBr): 2967 (br), 1573, 1505, 1487, 1180, 786 cm^{-1}.

Anal. Calcd for $C_9H_{14}TeNCl$: C, 36.12; H, 4.72; N, 4.68. Found: C, 35.62; H, 4.82; N, 4.71.

2-(Methylsulfanyl)ethylamine (5)
Yield: 43.6%; bp 50–53 °C (25 Torr); n_D^{22} 1.4910.

IR (neat): 3356, 3291, 2916, 1592, 1429, 1273, 860 cm^{-1}.

EI–MS: *m/z* = 91 $[M]^+$, 75 $[MeSCH_2CH_2]^+$, 61 $[MeSCH_2]^+$, 48 $[MeSH]^+$, 45 $[NH_2CH_2CH_3]^+$, 31 $[NH_2CH_3]^+$.

2-(Phenylselanyl)ethylamine (6b)
$PhSe(CH_2)_2NH_2{\cdot}HCl$ (**1b**; 1.55 g, 6.55 mmol) was treated with a 50% aq solution of KOH (10.00 g KOH) and extracted with Et_2O

(3 × 20 mL). The Et_2O extract was dried over $MgSO_4$ for 3 h. Removal of the solvent afforded $PhSe(CH_2)_2NH_2$ [**6b**; 0.59 g (45.0%)] as a yellow liquid; n_D^{22} 1.6131.

IR (neat): 3348, 3256, 2930, 1578, 1477, 1248, 893 cm^{-1}.

EI–MS: *m*/*z* = 201 $[M]^+$, 183 $[PhSeCH{=}CH]^+$, 157 $[PhSe]^+$, 106 $[PhCH_2CH_3]^+$, 77 $[Ph]^+$, 44 $[NH_2CH_2CH_2]^+$, 31 $[NH_2CH_3]^+$.

Free ethylamines **6**, **7** and propylamines **8**, **9** were generated analogously.

2-(Methylselanyl)ethylamine (6a)
Yield: 42.0%; n_D^{20} 1.5863.

IR (neat): 3355, 3283, 2923, 1587, 1424, 1249, 850 cm^{-1}.

EI–MS: *m*/*z* = 139 $[M]^+$, 122 $[MeSeCH{=}CH_2]^+$, 110 $[MeSeMe]^+$, 95 $[MeSe]^+$, 80 $[Se]^+$, 42 $[NH_2CH{=}CH]^+$, 31 $[NH_2CH_3]^+$.

2-(Ethylselanyl)ethylamine (6c)
Yield: 57.9%; n_D^{22} 1.5191.

IR (neat): 3356, 3283, 2922, 1588, 1450, 1231, 846 cm^{-1}.

EI–MS: *m*/*z* = 153 $[M]^+$, 124 $[EtSeCH_3]^+$, 122 $[CH_2{=}CHSeCH_3]^+$, 109 $[EtSe]^+$, 107 $[CH_2{=}CHSe]^+$, 96 $[MeSeH]^+$, 80 $[Se]^+$, 42 $[NH_2CH{=}CH]^+$, 31 $[NH_2CH_3]^+$.

2-(Methyltellanyl)ethylamine (7a)
Yield: 21.3%; n_D^{20} 1.6074.

IR (neat): 3352, 3283, 2921, 1575, 1419, 1219, 832 cm^{-1}.

EI–MS: *m*/*z* = 189 $[M]^+$, 172 $[MeTeCH = CH_2]^+$, 160 $[MeTeMe]^+$, 145 $[MeTe]^+$, 130 $[Te]^+$, 44 $[NH_2CH_2CH_2]^+$, 31 $[NH_2CH_3]^+$.

2-(Phenyltellanyl)ethylamine (7b)
Yield: 24.9%; n_D^{20} 1.6496.

IR (neat): 3364, 3287, 2926, 1596, 1474, 1226, 841 cm^{-1}.

EI–MS: *m*/*z* = 251 $[M]^+$, 222 $[PhTeCH_3]^+$, 207 $[PhTe]^+$, 130 $[Te]^+$, 93 $[PhNH_2]^+$, 77 $[Ph]^+$, 44 $[NH_2CH_2CH_2]^+$, 31 $[NH_2CH_3]^+$.

3-(Methylselanyl)propylamine (8a)
Yield: 18.9%; n_D^{20} 1.6373.

EI–MS: *m*/*z* = 153 $[M]^+$, 138 $[MeSe(CH_2)_2CH_3]^+$, 123 $[MeSeCH_2CH_2]^+$, 109 $[MeSeCH_2]^+$, 95 $[MeSe]^+$, 80 $[Se]^+$, 57 $[NH_2CH{=}CHCH_3]^+$, 42 $[NH_2CH{=}CH]^+$, 31 $[NH_2CH_3]^+$.

Table 3 ^{1}H NMR Data for Schiff Bases **10** and **11**

					^{1}H NMR data, δ, ppm (multiplicity, J_{HH}, Hz)				
Schiff Base	RX	R	C_6H_3	R'	N=CH	NCH_2	CH_2	CH_2X	OH
10a	MeS	2.17 (s)	6.81–7.36 (m)	1.47 (s)	8.39 (t, 1.21)	3.81 (dt, 6.71, 1.22)	–	2.86 (t, 7.02)	13.89 (s)
10b	MeSe	2.04 (s)	6.84–7.34 (m)	1.48 (s)	8.37 (t, 1.22)	3.87 (dt, 6.41, 1.22)	–	2.86 (t, 6.71)	13.91 (s)
10c	PhSe	7.25–7.52 (m)	6.81–7.32 (m)	1.45 (s)	8.30 (t, 1.16)	3.87 (dt, 7.63, 1.22)	–	3.21 (t, 7.02)	13.77 (s)
10d	MeTe	1.94 (s)	6.83–7.33 (m)	1.46 (s)	8.37 (t, 1.24)	3.96 (dt, 7.63, 1.22)	–	2.93 (t, 7.02)	13.88 (s)
10e	PhTe	7.22–7.77 (m)	6.83–7.32 (m)	1.49 (s)	8.31 (s)	3.99 (t, 6.71)	–	3.19 (t, 7.32)	13.81 (s)
10f	MeSe	2.01 (s)	6.83–7.32 (m)	1.46 (s)	8.37 (s)	3.69 (t, 6.41)	2.08 (quint, 6.69)	2.64 (t, 7.32)	14.00 (s)
11a	MeS	2.14 (s)	6.87–7.17 (m)	3.04 (m), 1.68 (m), 0.83 (t, 7.32)	8.37 (t, 1.22)	3.79 (dt, 6.71, 1.22)	–	2.83 (t, 6.71)	13.53 (s)
11b	MeSe	2.01 (s)	6.86–7.17 (m)	3.03 (m), 1.67 (m), 0.80 (t, 7.32)	8.36 (s)	3.86 (t, 7.02)	–	2.84 (t, 7.02)	13.51 (s)
11c	PhSe	7.25–7.53 (m)	6.86–7.18 (m)	3.04 (m), 1.69 (m), 0.84 (t, 7.32)	8.31 (s)	3.87 (t, 7.02)	–	3.21 (t, 7.02)	13.45 (s)
11d	MeTe	1.91 (s)	6.85–7.17 (m)	3.02 (m), 1.66 (m), 0.81 (t, 7.63)	8.36 (t, 1.24)	3.95 (dt, 6.71, 1.24)	–	2.91 (t, 7.02)	13.49 (s)
11e	PhTe	7.20–7.75 (m)	6.86–7.26 (m)	3.03 (m), 1.68 (m), 0.83 (t, 7.32)	8.31 (s)	3.98 (t, 7.32)	–	3.17 (t, 7.32)	13.41 (s)
11f	MeSe	1.99 (s)	6.84–7.15 (m)	3.00 (m), 1.66 (m), 0.81 (t, 7.61)	8.36 (t, 1.22)	3.68 (dt, 6.74, 1.22)	2.06 (quint, 7.32)	2.63 (t, 7.32)	13.62 (s)

3-(Phenylselanyl)propylamine (8b)
Yield: 53.5%; n_D^{18} 1.6371.

IR (neat): 3367, 3290, 2928, 1578, 1477, 1232, 816 cm^{-1}.

EI–MS: *m*/*z* = 215 $[M]^+$, 198 $[PhSeCH{=}CHCH_3]^+$, 183 $[PhSeCH{=}CH]^+$, 157 $[PhSe]^+$, 117 $[PhCH{=}CHCH_2]^+$, 106 $[PhCH_2CH_3]^+$, 91 $[PhCH_2]^+$, 57 $[NH_2CH{=}CHCH_3]^+$, 31 $[NH_2CH_3]^+$.

3-(Methyltellanyl)propylamine (9a)
Yield: 31.0%; n_D^{22} 1.6369.

IR (neat): 3356, 3284, 2922, 1595, 1457, 1205, 832 cm^{-1}.

EI–MS: *m*/*z* = 203 $[M]^+$, 188 $[MeTe(CH_2)_2CH_3]^+$, 171 $[MeTeCH{=}CH]^+$, 145 $[MeTe]^+$, 130 $[Te]^+$, 56 $[NH_2CH{=}CHCH_2]^+$, 42 $[NH_2CH{=}CH]^+$.

3-(Phenyltellanyl)propylamine (9b)
Yield: 37.5%; n_D^{17} 1.6371.

IR (neat): 3362, 3288, 2926, 1573, 1474, 1205, 850 cm^{-1}.

EI–MS: *m*/*z* = 265 $[M]^+$, 235 $[PhTe(CH_2)_2]^+$, 207 $[PhTe]^+$, 130 $[Te]^+$, 77 $[Ph]^+$, 58 $[NH_2(CH_2)_3]^+$, 42 $[NH_2CH{=}CH]^+$.

2-(*tert*-Butyl)-6-{([2-(methylsulfanyl)ethyl]imino)methyl}benzenol (10a)
3-(*tert*-Butyl)-2-hydroxybenzenecarbaldehyde (1.78 g, 10.0 mmol) was added to a solution of $MeS(CH_2)_2NH_2$ (**5**; 0.91 g, 10.0 mmol) in MeOH (10 mL) and the resulting mixture was refluxed for 30 min. After removal of MeOH the residue was diluted with water and extracted with CH_2Cl_2. This extract was dried over Na_2SO_4 for 3 h. Removal of the solvent afforded the product **10a** [2.50 g (99.6%)] as a yellow liquid.

Anal. Calcd for $C_{14}H_{21}NOS$: C, 66.89; H, 8.42; N, 5.57. Found: C, 67.12; H, 8.15; N, 5.27.

2-(*tert*-Butyl)-6-{([2-(methylselanyl)ethyl]imino)methyl}benzenol (10b)
A solution of MeONa, prepared by dissolution of Na (0.12 g, 5.0 mmol) in MeOH (5.22 mL), was added to $MeSe(CH_2)_2NH_2{\cdot}HCl$ (**1a**; 0.88 g, 5.0 mmol). After stirring for 10 min 3-(*tert*-butyl)-2-hydroxybenzenecarbaldehyde (0.89 g, 5.0 mmol) was added to the resulting mixture and refluxed for 30 min. After removal of MeOH, the residue was diluted with water and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 for 3 h. Removal of the solvent afforded the product **10b** [1.42 g (94.7%)] as a yellow liquid.

Anal. Calcd for $C_{14}H_{21}NOSe$: C, 56.37; H, 7.10; N, 4.70. Found: C, 56.65; H, 7.38; N, 4.39.

Schiff bases **10c–f**, **11a–f** were prepared by analogous procedures.

2-(*tert*-Butyl)-6-{([2-(phenylselanyl)ethyl]imino)methyl}benzenol (10c)
Yield: 94.4%.

Table 4 ^{13}C NMR Data for Schiff Bases **10** and **11**

					^{13}C NMR data, δ, ppm			
Schiff Base	RX	R	C_6H_3	R'	N=CH	NCH_2	CH_2	CH_2X
10a	MeS	15.9	160.3, 137.3, 129.6, 129.4, 118.4, 117.8	29.3, 34.7	166.4	58.8	–	35.0
10b	MeSe	4.4	160.3, 137.2, 129.7, 129.4, 118.4, 117.8	29.3, 34.4	166.2	59.6	–	25.8
10c	PhSe	133.0, 129.1, 127.1, 117.9	160.3, 137.4, 129.7, 129.4, 118.5, 117.8	29.3, 34.8	166.4	59.4	–	28.2
10d	MeTe	–21.8	160.3, 137.3, 129.6, 129.4, 118.4, 117.8	29.5, 34.7	165.6	61.3	–	4.1
10e	PhTe	138.6, 129.2, 127.8, 111.0	160.3, 137.3, 129.7, 129.4, 118.4, 117.8	29.3, 34.7	165.8	60.9	–	9.1
10f	MeSe	3.9	160.3, 137.3, 129.5, 129.5, 118.5, 117.7,	29.3, 34.7	165.9	58.8	22.6	30.8
11a	MeS	15.8	159.3, 133.1, 130.3, 128.9, 118.1, 117.9	11.9, 27.6, 40.4	166.2	58.7	–	35.0
11b	MeSe	4.5	159.4, 133.3, 130.5, 128.9, 118.1, 117.9	11.9, 27.6, 40.4	166.0	59.7	–	25.9
11c	PhSe	132.8, 129.4, 127.0	159.3, 133.2, 130.5, 129.1, 118.1, 118.0	12.0, 27.6, 40.5	166.2	59.3	–	28.1
11d	MeTe	–21.9	159.3, 133.2, 130.4, 129.0, 118.1, 118.0	11.9, 27.6, 40.4	165.4	61.3	–	4.2
11e	PhTe	138.6, 129.2, 127.8, 111.1	159.4, 133.2, 130.5, 129.0, 118.2, 118.0,	12.0, 27.6, 40.5	165.6	61.0	–	9.1
11f	MeSe	3.9	159.4, 133.2, 130.3, 128.8, 118.1	11.9, 27.6, 40.4	165.8	58.8	22.6	30.8

Anal. Calcd for $C_{19}H_{23}NOSe$: C, 63.33; H, 6.43; N, 3.89. Found: C, 63.14; H, 6.53; N, 3.59.

2-(*tert*-Butyl)-6-{([2-(methyltellanyl)ethyl]imino)methyl}benzenol (10d)
Yield: 86.2%.

Anal. Calcd for $C_{14}H_{21}NOTe$: C, 48.47; H, 6.10; N, 4.04. Found: C, 48.19; H, 6.32; N, 3.86.

2-(*tert*-Butyl)-6-{([2-(phenyltellanyl)ethyl]imino)methyl}benzenol (10e)
Yield: 82.9%.

Anal. Calcd for $C_{19}H_{23}NOTe$: C, 55.80; H, 5.67; N, 3.42. Found: C, 56.05; H, 5.81; N, 3.20.

2-(*tert*-Butyl)-6-{([2-(methylselanyl)propyl]imino)methyl}benzenol (10f)
Yield: 95.5%.

Anal. Calcd for $C_{15}H_{23}NOSe$: C, 57.69; H, 7.42; N, 4.48. Found: C, 57.91; H, 7.27; N, 4.37.

2-(1-Ethylpropyl)-6-{([2-(methylsulfanyl)ethyl]imino)methyl}benzenol (11a)
Yield: 99.2%.

Anal. Calcd for $C_{15}H_{23}NOS$: C, 67.88; H, 8.73; N, 5.28. Found: C, 67.47; H, 8.65; N, 5.07.

2-(1-Ethylpropyl)-6-{([2-(methylselanyl)ethyl]imino)methyl}benzenol (11b)
Yield: 96.8%.

Anal. Calcd for $C_{15}H_{23}NOSe$: C, 57.69; H, 7.42; N, 4.48. Found: C, 57.83; H, 7.35; N, 4.29.

2-(1-Ethylpropyl)-6-{([2-(phenylselanyl)ethyl]imino)methyl}benzenol (11c)
Yield: 94.1%.

Anal. Calcd for $C_{20}H_{25}NOSe$: C, 64.16; H, 6.73; N, 3.74. Found: C, 64.01; H, 6.89; N, 3.60.

2-(1-Ethylpropyl)-6-{([2-(methyltellanyl)ethyl]imino)methyl}benzenol (11d)
Yield: 88.4%.

Anal. Calcd for $C_{15}H_{23}NOTe$: C, 49.91; H, 6.42; N, 3.88. Found: C, 49.70; H, 6.25; N, 3.64.

2-(1-Ethylpropyl)-6-{([2-(phenyltellanyl)ethyl]imino)methyl}benzenol (11e)
Yield: 63.7%.

Anal. Calcd for $C_{20}H_{25}NOTe$: C, 56.79; H, 5.96; N, 3.31. Found: C, 56.65; H, 5.79; N, 3.19.

2-(1-Ethylpropyl)-6-{([2-(methylselanyl)propyl]imino)methyl}benzenol (11f)
Yield: 94.5%.

Anal. Calcd for $C_{16}H_{25}NOSe$: C, 58.89; H, 7.72; N, 4.29. Found: C, 59.18; H, 7.49; N, 4.46.

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