Chelate Ring Size Effect on the Reactivity of [2-(2-Phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]lithium and Se···N Interactions in Low-Valent Organoselenium Compounds: Facile Isolation of Diorganotriselenide

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Received April 16, 2004

The reaction of [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]lithium (**13**), containing a six-membered oxazine ring, with elemental selenium gave lithium aryldiselenolate (**14**) as the major reaction intermediate along with other polyselenolates (**15** and **16**), whereas [2-(4,4-dimethyl-2-phenyloxazolinyl]lithium (**21**), containing a five-membered oxazoline ring, on reaction with selenium gave only lithium arlyselenolate **22** under similar conditions. The unusual selenation reaction of aryllithium **13** has been studied by ES-MS spectrometry. The oxidative workup of in situ-generated lithium arylpolyselenolates (**14**−**16**) afforded a mixture of diorganopolyselenides (**10**, **11**, **17**, and **18**), from which diorganotriselenide **11** was obtained as the major product, whereas lithium arylselenolate **22** gave only diselenide **6** on oxidation. Equimolar reactions of diorganotriselenide **11** with sulfuryl chloride and benzenethiol give the novel selenium halide [RSeSeCl (**24**)] and seleniumselenenyl sulfide (**28**), respectively. However, the reaction of triselenide **11** with an excess amount of halogenating reagents afforded selenenyl halides [RSeX; X = Cl (**25**), Br (**26**), I (**27**)]. The reaction of lithium arylpolyselenolates (**14**−**16**) with benzyl chloride gave a mixture of diselenide (**10**), unsymmetrical diselenide (**31**), benzyl selenide (**32**), and dibenzyl diselenide (**33**). The reaction of **14**−**16** with α,α′-dibromo-*ortho*-xylene gave the 10-membered diselenocine (**34**) and **26**. GPx-like activities of diselenide **10** and triselenide **11** have been evaluated by using both benzenethiol and coupled reductase assay methods. Triselenide **11** shows much better GPx-like activity than diselenide **10**. Crystal structures of organoselenium compounds (**11**, **25**−**27**, **29**, **32**, and **34**) were determined by single X-ray crystallography to study the ring size effect of the oxazine ring on Se···N intramolecular interactions.

Introduction

Glutathione peroxidase (GPx) is a selenoenzyme, which is well known for its antioxidant function.[1] This selenoenzyme catalyzes the reduction of various harmful peroxides produced in the biological system and protects the cell from oxidative stress. A variety of organoselenium compounds have been reported as GPx mimics. The premier examples are diorganodiselenides,[2,3] heterocycles containing Se−N (**1**−**3**)[4] and Se−O (**4**)[5] bonds, and selenosubtilisin.[6] The tellurium analogues (ditellurides, tellurides)[7−9] have also shown good GPx mimietic properties. Recently our group has reported

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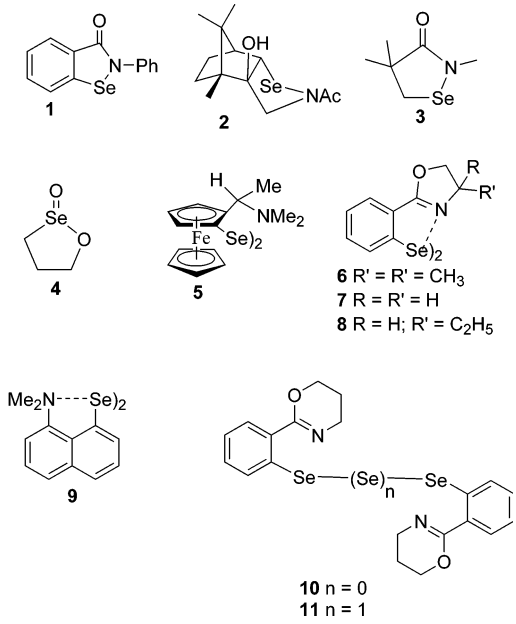
10.1021/om049722f CCC: $27.50
Publication on Web 07/28/2004

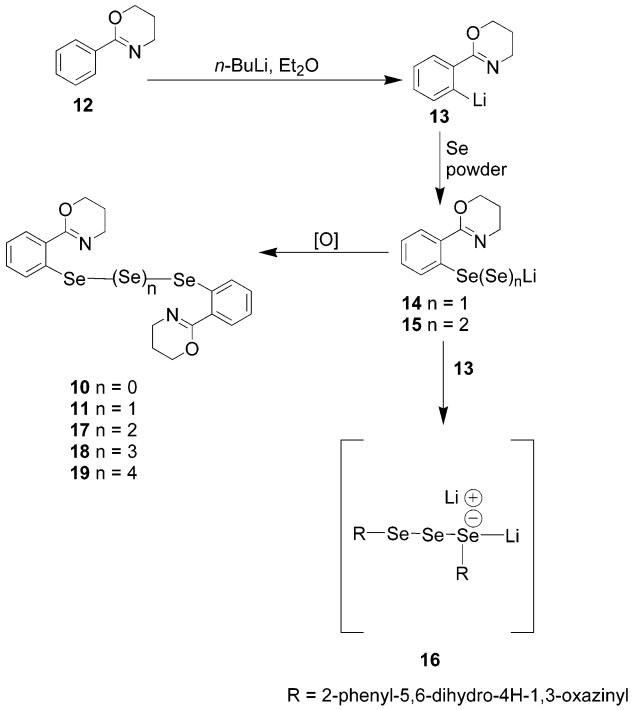
Chart 1. Glutathione Peroxidase Mimics



that diselenide **5**, having a ferrocene-bearing tert-amino group in close proximity of selenium, acts as an excellent GPx mimic, whereas diselenides **6**−**9**, which have strong Se···N (amino/imino groups) interactions, show low GPx-like activity (Chart 1).[2b,7] In an attempt to fine-tune the Se···N interactions to enhance the GPx activity, when we attempted to prepare diselenide **10** (where the sp^2 N donor atom was part of a six-membered oxazine ring instead of a five-membered oxazoline ring),[2b,7] unexpectedly we obtained the corresponding novel diorganotriselenide **11**.

Diorganotriselenides are rare,[10] and to the best of our knowledge, only one example of a structurally characterized diorganotriselenide is reported.[10a] This triselenide was stabilized by incorporating a sterically bulky thiophenetriptycyl group. Triselenide diamide ($R_2N-SeSeSe-NR_2$)[10b] was reported in 1977, and there are also a few reports where the diorganotriselenides were not fully characterized.[10c−g] Here we report the synthesis, GPx activity, and structural characterization of diorganotriselenide **11**, which is stabilized by intramolecular Se···N coordination. Furthermore a detailed study of the interesting selenation reaction of

Scheme 1. Synthesis of Triselenide 11



[2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]lithium (**13**) is described.

Results and Discussion

Synthesis. The substrate 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**12**) was synthesized by following the literature method with minor modifications.[11] The synthesis of diselenide **10** was attempted by the established *ortho*-lithiation route. Addition of *n*-BuLi to a THF solution of 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**12**) produced a red-colored solution. Thereafter, the selenium addition and oxidative workup gave only di-*n*-butyl diselenide. Since attempts to prepare **10** in THF were unsuccessful, we decided to synthesize the desired diselenide **10** by using ether as the solvent. Addition of *n*-BuLi to **12** in ether gave a brown-colored lithiated compound (**13**), which on treatment with selenium powder gave lithium aryldiselenolate (**14**) along with lithium aryltriselenolate (**15**) and dilithium diaryltriselenolate (**16**) (Scheme 1) (vide infra).

The oxidative workup of lithium arylpolyselenolates (**14**−**16**) gave a yellow-colored solid, which turned out to be a mixture of di-, tri-, tetra-, and pentaselenides (**10**, **11**, **17**, and **18**) (vide infra). Purification of the yellow solid afforded the triselenide **11** as the major product. Generally, bulky ligands such as dithiophenetriptycyl,[10a] tri(trimethylsilyl)methyl,[10c] and 2,5-di[2,5-di(2,5-dimethylphenyl)tolyl]-4-*tert*-butylphenyl[10e] have been used to isolate triselenides or tetraselenides. In this case the triselenide **11** has been stabilized by an intramolecular Se···N coordination. To compare the selenation reaction of 2-phenyloxazine (**12**) with 4,4-dimethyl-2-phenyloxazoline (**20**), the synthesis of previously studied lithium arylselenolate (**22**)[2b] was carried out under identical conditions. No formation of lithium

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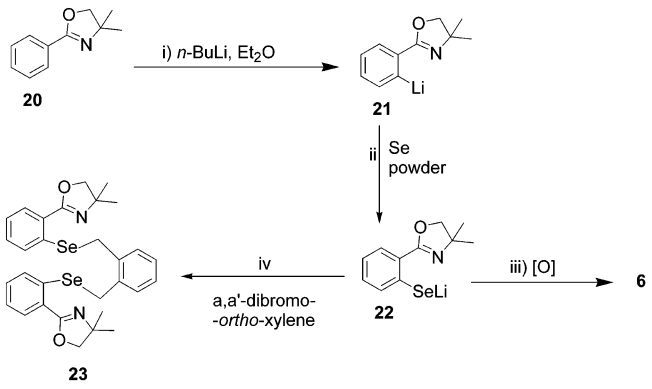
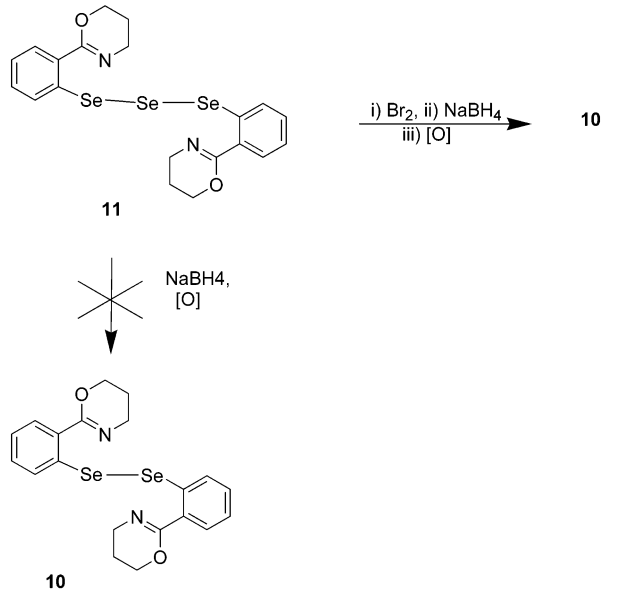
Scheme 2. Synthesis of Lithium Aryselenolate 21, Diselenide 6, and 23[a]



[a] Reagents and conditions: (i) *n*-BuLi, Et_2O, 0 °C; (ii) Se powder; (iii) oxygen; (iv) α,α′-dibromo-*ortho*-xylene.

Scheme 3. Synthesis of Diselenide 10 from Triselenide 11



arylpolyselenolates was observed in the case of **21**. Similarly oxidative workup of **22** gave only the diselenide **6** (Scheme 2) (based on ES-MS). It is worth mentioning that other related ligands, (*R*)-4-ethyl-4-hydro-2-phenyloxazoline,[2b] and 2-phenyl-2-oxazoline[7] containing five-membered oxazolines also gave the expected diselenides (**7** and **8**) as the major product.

Conversion of triselenide **11** to diselenide **10** was first approached by direct reduction. Reduction of triselenide **11** with $NaBH_4$, followed by oxidation with oxygen, again gave **11**. Alternatively, diselenide **10** was obtained as a colorless powder by bromination of the triselenide, followed by reduction with $NaBH_4$ and reoxidation (Scheme 3). Our attempts to grow single crystals of **10** using hexane/Et_2O were unsuccessful, and use of hexane/CH_2Cl_2 led to facile isolation of the selenenyl chloride **25**. The selenenyl chloride presumably results from the oxidation of **10** with CH_2Cl_2.

The synthesis of the as yet unknown [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]seleniumselenenyl halides (RSeSeX) was our next objective (Scheme 4). The 1:1 molar reaction of triselenide **11** with sulfuryl chloride in CH_2Cl_2 gave a homogeneous red-colored solution, which was a mixture of RSeSeCl (**24**), RSeCl (**25**), and RSeSeR (**10**) (based on ES-MS). RSeSeCl (**24**) was stable for a few hours in solution, and after that red amorphous selenium separated out, which indicates the dissociation of RSeSeCl (**24**). When the reaction of triselenide **11** with Br_2 and I_2 was carried out, formation of RSeSeBr and RSeSeI was not observed. The reaction of triselenide **11** with an excess amount of appropriate halogenating reagents gave the corresponding selenenyl halides (**25**−**27**) in excellent yields with the concomitant release of the red amorphous selenium.

The equimolar reaction of triselenide **11** with benzenethiol gave a mixture of seleniumselenenyl sulfide **28** and selenenyl sulfide **29** (vide infra). The isolation of seleniumselenenyl sulfide **28** was unsuccessful. The reaction of **11** with an excess of benzenethiol gave the selenenyl sulfide **29** in good yield. Similarly the synthesis of selenenyl sulfide **30** was achieved. A few selenenyl sulfides are known, and most of them are found to be unstable.[12,13] These selenenyl sulfides undergo disproportionation reaction to give diselenides (R−Se−Se−R) and disulfides (R′−S−S−R′). Selenenyl sulfide, 2-$NO_2C_6H_4SeSCH_2Ph$, disproportionates in solution to give an equilibrium mixture containing the diselenide (2-$NO_2C_6H_4Se)_2$ and the disulfide $(PhCH_2S)_2$.[12] Recently Back et al.[5] also reported that 3-hydroxypropylbenzyl selenenyl sulfide gradually disproportionated to bis(3-hydroxypropyl) diselenide and dibenzyl disulfide.[5b] du Mont et al. have reported some structurally characterized selenenyl sulfides, which are stabilized by a sterically bulky tris(trimethylsilyl)methyl group[13a] or intramolecular Se···N interactions.[13b]

The reaction of benzyl chloride with the reaction mixture containing lithium arypolyselenolates (**14**−**16**) led to the formation of a mixture of products, [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]benzyl diselenide (**31**), selenide **32**, diselenide **10**, and dibenzyl diselenide **33** (Scheme 5) (based on ES-MS). However, the benzylic compound **32** was isolated as the major product. The formation of a mixture of **10** and **33** may be due to poor stability of unsymmetrical diselenide **31**. Krief et al.[14] have reported the reaction of lithium *n*-butyldiselenolate with *sec*-butyl bromide and obtained a mixture of *n*-butyl-*s*-butyl diselenide, di-*n*-butyl diselenide, and di-*sec*-butyl diselenide. Thus formation of **10**, **31**, and **33** is consistent with the above report. The formation of [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]benzyl triselenide ($RSeSeSeCH_2Ph$) was not observed. The reaction of lithium arylpolyselenolates (**14**−**16**) with α,α′-dibromo-*ortho*-xylene did not yield the expected benzylic compound like **23** but gave the selenenyl bromide **26** and the known 10-membered diselenocine **34**.[15]

The above reaction was repeated several times to check its reproducibility. The synthesis of **34** has

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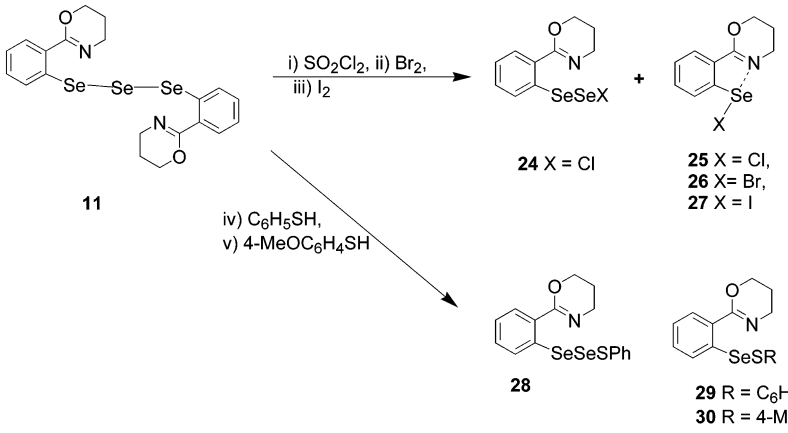
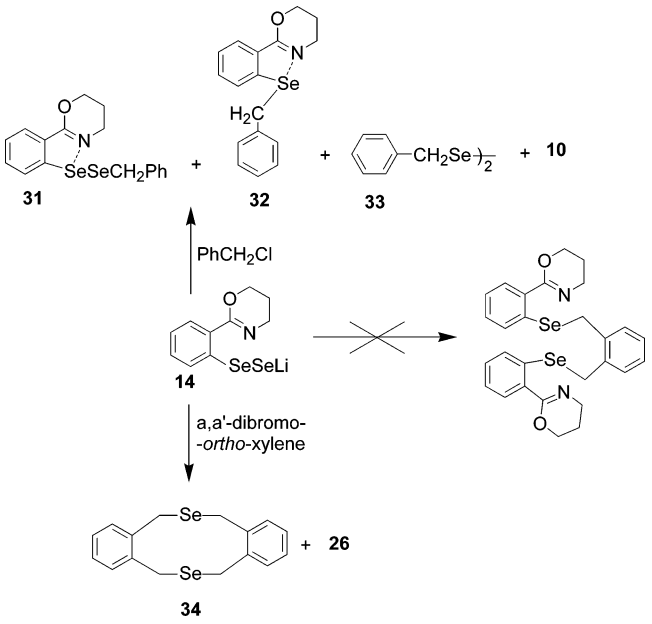
Scheme 4. Synthesis of Selenenyl Halides 24−27 and Sulfides 28−30



Scheme 5. Synthesis of Benzylic Compounds 32, $RSeSeCH_2Ph$ (31), Dibenzyl Diselenide (33), and 10-Membered Diselenocine (34)[a]



[a] Reagents and conditions: (i) $C_6H_5CH_2Cl$, 0 °C; (ii) α,α′-dibromo-*ortho*-xylene.

Scheme 6. Proposed Mechanism for the Formation of 10-Membered Diselenocine (34) and Selenenyl Bromide (26) from 14

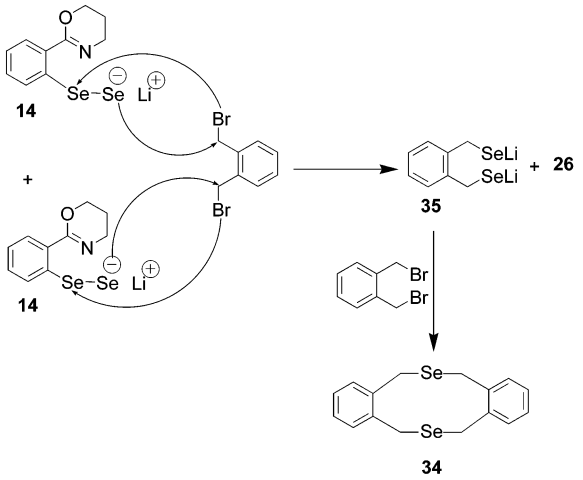


Table 1. ^1H and ^{77}Se NMR Chemical Shifts of Organoselenium Compounds 10−34

compound	C−*CH_2*−C	N−CH_2− and O−CH_2-	^{77}Se chemical shift
10	2.05	3.75, 4.40	482
11	2.12	3.66, 4.42	330, 625
12	1.65	3.45, 4.12	
25	2.36	4.08, 4.68	934
26	2.35	4.06, 4.68	899
27	2.32	4.02, 4.63	889
29	2.05	3.73, 4.39	625
30	2.07	3.74, 4.36	660
32	1.95	3.62, 4.32	362
34			373

previously been reported by a two-step procedure where α,α′-dibromo-*ortho*-xylene was first converted to 1,2-bis(selenocynatomethyl)benzene by reaction with KSeCN. Then reaction of 1,2-bis(selenocynatomethyl)benzene with α,α′-dibromo-*ortho*-xylene and $NaBH_4$ finally gave the 10-membered diselenocine **34** under high dilution conditions.[15a] Here, the synthesis of **34** has unexpectedly been achieved in one pot. The unexpected formation of **26** and **34** can be rationalized by the formation of ArSeSeLi (**14**) in solution. Nucleophilic attack of Br^- on the selenium (Ar−*Se*−SeLi) leads to **35** and selenenyl bromide **26**. The reaction of **35** with α,α′-dibromo-*ortho*-xylene would then probably lead to the formation of the 10-membered diselenocine **34** (Scheme 6). Interestingly, lithium arylselenolate **22**, based on 4,4-dimethyl-2-phenyloxazoline, gave the expected dibenzylic product (**23**) (Scheme 2).[16]

Spectroscopic Behavior. The ^1H NMR chemical shifts for **12** and its selenium derivatives are listed in Table 1. In solution, the Se···N interaction is considerable, as the methylene protons in **10**, **11**, **25**−**27**, **29**, **30**, and **32** are shifted downfield (0.17−0.71 ppm) compared to the free ligand (**12**).

The ^{77}Se NMR spectrum of the crude product (oxidized lithium arylpolyselenolates) shows five signals, at 345, 468, 546, 640, and 674 ppm, respectively. Interpretation of the ^{77}Se NMR spectrum is difficult and requires more work. However, these signals may be due to the presence of diorganopolyselenides (**10**, **11**, and **17**), which were further characterized by ES-MS (vide infra). The ^{77}Se NMR spectrum of the pure triselenide **11** shows two signals, at 330 and 625 ppm, due to C−*Se*− and Se−*Se*−Se, respectively. The ^{77}Se chemical

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shifts are well separated in this case. This is in contrast to the reported corresponding values for bis[tris(trimethylsilyl)methyl] triselenide (560, 651 ppm)[10c] and dithiophenetriptycyl triselenide (549, 558 ppm).[10a] The significant separation of ^{77}Se chemical shifts in **11** may be due to the strong intramolecular Se···N nonbonded interaction. The ^{77}Se chemical shift of isolated **10** is 482 ppm. The selenenyl halides show the ^{77}Se chemical shifts at 934 (RSeCl, **25**) 899 (RSeBr, **26**), and 889 (RSeI, **27**) ppm, respectively. The ^{77}Se NMR chemical shift values for **29** and **30** (625 and 660 ppm) are shifted upfield compared to selenenyl halides (**25**−**27**). The ^{77}Se NMR spectra of **29** and **30** do not show any signal due to formation of diselenide **10**, which indicates the stability of these selenenyl sulfides in solution. In contrast to selenenyl halides (**25**−**27**), benzylic compound **32** resonates upfield (362 ppm). Diselenocine **34** shows a signal at 373 ppm in the ^{77}Se NMR. The ^{77}Se chemical shift of **34** is in close agreement with the reported eight-membered diselenocine (378 ppm).[17]

It is interesting to compare the ^{77}Se chemical shift values of the compounds derived from **12** with corresponding analogues derived from the related ligand 4,4-dimethyl-2-phenyloxazoline (**20**)[16] and (*R*)-4-ethyl-4-hydro-2-penyloxazoline.[18] Generally, the ^{77}Se chemical shifts of selenium compounds derived from **12** appear downfield compared with analogous compounds derived from 4,4-dimethyl-2-phenyloxazoline and (*R*)-4-ethyl-4-hydro-2-penyloxazoline. For example, the chemical shifts of RSeCl (**25**) (934 ppm), RSeBr (**26**) (899 ppm), and RSeI (**27**) (889 ppm) are more downfield than R′SeCl (856 ppm), R′SeBr (849 ppm), and R′SeI (762 ppm) derived from 4,4-dimethyl-2-phenyloxazoline and similarly more downfield than the R″SeBr (877 ppm) and R″SeI (769 ppm) derived from (*R*)-4-ethyl-4-hydro-2-phenyloxazoline. Similarly the ^{77}Se NMR signals for selenenyl sulfides are also shifted downfield than the selenenyl sulfides (576 and 612 ppm)[2b,13b] based on 4,4-dimethyl-2-phenyloxazoline.

ES-MS Studies. The electrospray mass spectra of organoselenium compounds gave distinct molecular ion peaks with characteristic isotopic patterns (illustrated for **10**, **11**, **14**, **15, 17**, **18**, and **24**−**34** in Figure S10-48 in the Supporting Information). The ES-MS of the in situ-generated lithium arylpolyselenolates shows the presence of lithium aryldiselenolate **14** as the major product. In addition to the molecular ion peak of **14** (*m*/*z* 327), the molecular ion peaks for lithium aryltriselenolate **15** (*m*/*z* 405) and polyselenides [di-, tetra-, and hexaselenides (**10**, **17**, and **19**)] (*m*/*z* 481, 633, 792) and a peak at 573 were also observed. The molecular ion peak at 573 is probably due to the formation of dilithium diarylseleniumselenolate **16**. The formation of **16** may be due to the reaction of lithium aryltriselenolate **15** with unreacted aryllithium **13**. Krief et al.[14] have also reported that lithium *n*-butlydiselenolate reacted with *n*-BuLi to produce dilithium di-*n*-butylselenium selenolate (*n*-$Bu_2SeSeLi_2$). The ES-MS of the crude product obtained by oxidizing lithium arylpolyselenolates shows molecular ion peaks for di-, tri-, tetra-, and pentaselenides (**10**, **11**, **17**, and **18**). However, diselenide **10**, triselenide **11**, and tetraselenide **17** were the major products (based on their relative ratio in the mass spectrum). It is difficult to account for the formation of polyselenides **10**, **11**, and **17**−**19** with certainty because formation of the mixture of polyselenides is also possible under mass spectroscopic conditions. On the other hand ES-MS of the reaction mixture of in situ-generated lithium [2-(4,4-methyl-2-phenyloxazolinyl)]selenolate (**22**) and its oxidative workup did not give the molecular ion peaks for the corresponding lithium arylpolyselenolates and polyselenides (Scheme 2).

The ES-MS of pure **10**, **11**, and **25**−**34** were recorded separately and are included in the Experimental Section. All compounds show expected molecular ion peaks. In all the cases (except **34**) peaks observed at $m/z = 239$ can be assigned to the RSe^+ fragments.

Table 2. Glutathione Peroxidase-like Activity of 1, 11, and 10 as Determined by Benzenethiol Assay and the Coupled Reductase Assay

	thiol assay	coupled reductase assay	
compound	v_0,[a] μM min^{-1}	v_0,[b] (M min^{-1}) × 10^{-5}	activity[c]
1		1.42	0.98[3a]
10	33 ± 2	0.89	0.63
11	(4.0 ± 0.2) × 10^2	3.22	2.30

[a] Standard deviations are shown in parentheses. [b] Moles of NADPH utilized per minute. [c] μmoles of NADPH utilized per minute per μmole.

Glutathione Peroxidase-like Activity. Glutathione peroxidase (GPx)-like activities of **10** and **11** were determined by both the coupled reductase assay[3a] and the benzenethiol assay[3b] methods. In the coupled reductase assay the GPx activity was measured by a coupled enzyme system containing glutathione reductase (1 unit), GSH (1 mM), NADPH (0.25 mM), catalysts (2 μM), and H_2O_2 (0.5 mM). The reduction of H_2O_2 by GSH was carried out in the presence of catalysts Ebselen (**1**),[3a] **10**, and **11**. The decrease in NADPH monitored spectrophotometrically at 340 nm is a measure of GPx activity. In the thiol assay, benzenethiol was used as a glutathione equivalent. The initial rates for the reduction of H_2O_2 (3.75 mM), in the presence of catalyst (0.1 mM) and PhSH (1 mM), were determined in the methanol medium at 305 nm due to the formation of diphenyl disulfide.

Although it is not easy to rationalize all the data from the benzenethiol and the coupled reductase assay (Table 2) due to different parameters such as pH, solvent, and thiol structure in the two assays, it is clear that triselenide **11** shows glutathione peroxidase-like activity in both assays. Triselenide **11** is 12 and 3 times more efficient as a catalyst than the diselenide analogue (**10**) and Wilson's catalyst [bis{2-(*N*,*N*-dimethylbenzylamine)} diselenide] according to the thiol assay.[7] Triselenide **11** shows 3.6- and 2.3-fold higher activity than the diselenide **10** and Ebselen (**1**),[3a] respectively, in the coupled reductase assay (Figure 1). Concerning the mechanism of the thiol peroxidase activity of diselenides, it is well known that selenol (RSeH) and selenenyl sulfide (RSeSR′) are key intermediates in the catalytic cycle.[2,3] The high catalytic activity of triselenide **11**, probably indicates a totally different mechanism. To know the mechanism and the reactive intermediates for triselenide **11** involved in thiol peroxidase reaction, we set out to use ES-MS spectrometry as

(17) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 4463.
(18) Mugesh, G.; Singh, H. B.; Butcher, R. J. *Tetrahedron Asymmetry* **1999**, *10*, 237.

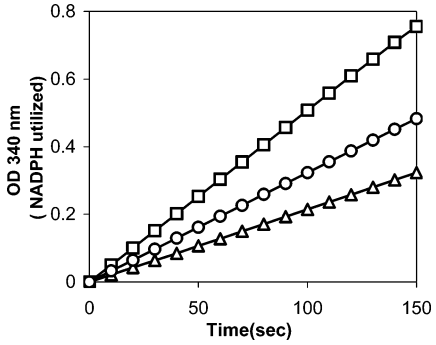

Figure 1. Compound-catalyzed reduction of H_2O_2 by GSH: ○ (**1**), △ (**10**), and □ (**11**). The catalytic reaction contains GSH (1 mM), glutathione reductase (1 unit), NADPH (0.25 mM), and 2 μM catalyst (pH 7.0 at 25 °C).

Table 3. Significant Bond Lengths (Å) and Angles (deg) for 11

Se(1)···N(1A)	2.562(18)	N(1A)···Se(1)−Se	171.6(4)
Se(1)···N(1B)	2.569(14)	N(1B)···Se(1)−Se	174.8(3)
Se(1)−Se	2.3555(11)	Se(1)−Se−Se(1)#	102.04(6)
Se(1)−C(1)	1.936(5)	Se(1)#1−Se−Se(1)−C(1)	86.44(19)
C(1)−Se(1)−Se	102.2(2)		

recently described by Detty et al.[8e] to identify the reaction intermediates of thiol peroxidase reaction. The 1:1 molar reaction of **11** with PhSH indicated the formation of the novel seleniumselenenyl sulfide **28** (*m*/*z* 429) and selenenyl sulfide **29** (*m*/*z* 350). The formation of selenenyl sulfide **29** was also confirmed by its independent synthesis (vide supra). No molecular ion peaks were observed for RSeSeH and RSeH even after the addition of an excess of PhSH to **11**. When an equimolar amount of H_2O_2 was added immediately after the addition of PhSH to **11**, the spectrum did not show molecular ion peaks for RSeSeOH and RSeOH. However, with an excess amount of H_2O_2, the molecular ion peak for the overoxidized seleninic acid ($RSeO_2H$) was observed. On the basis of these experiments it is suggested that triselenide **11** gets rapidly converted to seleniumselenenyl sulfide **28** and selenenyl sulfide **29** when treated with benzenethiol. Intermediates RSeSeSPh (**28**) and RSeSPh (**29**) are probably stabilized by the strong Se···N interaction between selenium and nitrogen. The strong Se···N intramolecular interaction in selenenyl sulfide **29** is also confirmed by single X-ray crystallography (vide infra). Selenenyl sulfides (**28** and **29**) then react readily with H_2O_2 to produce the seleniumselenenic (RseSeOH) and selenenic (RSeOH) acid, which in turn react with PhSH to again produce selenenyl sulfides (**28** and **29**). However, molecular ion peaks for RSeSeOH and RSeOH were not observed, probably because of their high reactivity. The catalytic cycle is thus completely different from the catalytic cycle of GPx.

Crystallographic Studies: Crystal Structure of 11. Figure 2 shows the molecular geometry and the crystallographic numbering scheme. Selected bond lengths and angles are listed in Table 3. Compound **11** crystallizes as a *cis* rotamer with a torsion angle of 86.44(19)°. The molecule resides on a crystallographic 2-fold axis passing through the central selenium atom. The geometry around the central selenium is 'V' shaped with an angle of 102.04(6)°. The Se−Se and Se−C bond lengths are 2.3555(11) and 1.936(5) Å, respectively.

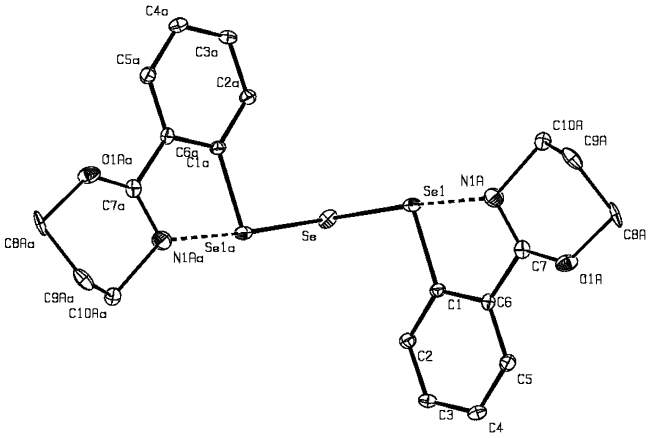

Figure 2. Molecular structure of **11** (hydrogen atoms are removed for clarity).

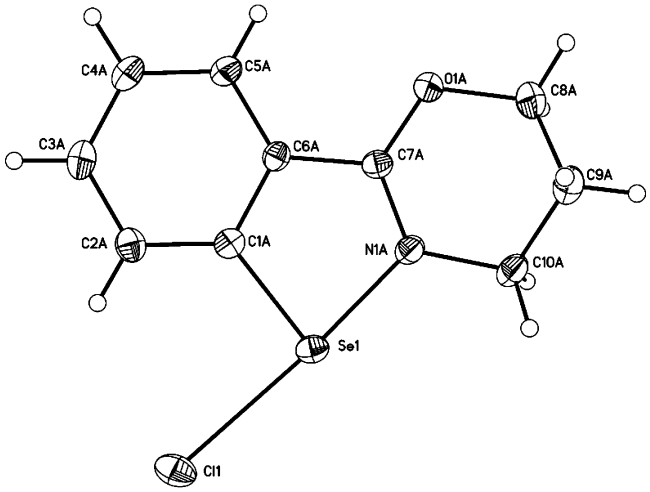

Figure 3. Molecular structure of **25**.

These distances are comparable with the corresponding mean values reported for dithiophenetriptycyl triselenide [2.316(2) and 1.851(9) Å].[10a] Of particular interest in the structure is the intramolecular interaction between selenium and nitrogen.

The atomic distances of Se(1)···N(1A) and Se(1)···N(1B) are 2.562(18) and 2.569(14) Å, respectively. These distances are significantly shorter than the sum of their van der Waals radii (3.5 Å).[19] These distances are also shorter than the Se···N distances of related reported diselenide **6** (2.705, 2.891 Å)[2a] and diselenide **8** (2.780, 2.798 Å).[2a] The N(1A)···Se(1)−Se# angle is 171.6(4)°.

Crystal Structure of 25. An ORTEP view of compound **25** is shown in Figure 3. Significant bond lengths and angles are summarized in Table 4. There are two molecules in the asymmetric unit, as each molecule is chiral and represents one enantiomer. The geometry around the selenium is 'T' shaped with selenium bonded to carbon, nitrogen, and chlorine. The intramolecular interaction Se···N distance [1.964(3) and 1.975(3) Å] is one of the shortest reported. This bond length is significantly shorter than the reported Se···N distances in intramolecularly coordinated selenenyl chlorides [2.052(5)−2.191(8) Å].[16,20−22]

(19) Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(20) Iwaoka, M.; Tomoda, S. *J. Org. Chem.* **1995**, *60*, 5299.
(21) Panda, A.; Mugesh, G.; Singh, H. B.; Butcher, R. J. *Organometallics* **1999**, *18*, 1986.

Table 4. Significant Bond Lengths (Å) and Angles (deg) for 25−27 and 29

	25 (X = Cl)	**26** (X = Br)
Se(1)···N(1A)	1.964(3)	1.970(5)
Se(2)···N(1B)	1.975(3)	1.980(5)
Se(1)−X(1)	2.5730(11)	2.7299(10)
Se(2)−X(2)	2.5547(12)	2.7164(11)
Se(1)−C(1A)	1.892(3)	1.892(6)
Se(2)−C(1B)	1.893(3)	1.898(6)
N(1A)···Se(1)−X(1)	176.02(8)	177.29(14)
N(1B)···Se(2)−X(2)	176.46(9)	177.75(15)
Se(1)···Se(2)	4.0017(6)	4.0481
	27 (X = I)	**29** (X = SPh)
Se···N	1.971(3)	2.458(2)
Se−X	2.9825(6)	2.2495(6)
Se−C(1)	1.896(3)	1.9374(19)
N···Se−X	179.66(10)	176.36(4)
C(1)−Se−X	97.24(11)	100.36(6)
C(1)−Se−S−C(11)		−90.45(9)

The Se−Cl bond lengths [2.5730(11) and 2.5547(12) Å] are more elongated than those reported for similar compounds.[16,18,21] The packing diagram of **25** shows weak Se···Se intermolecular contacts between two asymmetric molecules. The Se···Se intermolecular distance is 4.0017(6) Å, which is close to the sum of its van der Waals radii (4.0 Å).[19] It is interesting to note here that compound **25** does not show any Se···Cl intermolecular interaction, as related reported compounds show this interaction.[16,21]

Crystal Structure of 26. Compound **26** is isostructural with **25**. Bond lengths and angles are listed in Table 4. The intermolecular N···Se separations are 1.970(5) and 1.980(5) Å. The N···Se distances are similar to the chloro derivative **25**. These distances are shorter than those reported for related selenenyl bromides, derived from 4,4-dimethyl-2-phenyloxazoline (2.063(3) Å) and (*R*)-4-ethyl-4-hydro-2-phenyloxazoline [2.050(9) Å].[16,18] The intermolecular Se···Se distance [4.1852(9) Å] between two asymmetric molecules is longer than in the chloro derivative **25**.

Crystal Structure of 27. Compound **27** is isostructural with **25** and **26**. Compounds containing a Se−I bond are rare, and until recently only one compound was structurally characterized by du Mont et al. by using a sterically demanding 2,4,6-tri-*tert*-butylphenyl ligand.[23] Our group has been able to stabilize organoselenenyl iodides by using the intramolecular Se···N interaction approach. The isolation of **26** is inconsistent with our earlier reports.[16,18,21] The Se···N distance (1.971(3) Å) is significantly shorter than those reported for related selenenyl iodides [2.242−2.984 Å].[16,18,21] The N···Se−I alignment is linear [179.66(10)°]. The packing of compound **27** does not show any Se···Se intermolecular contact, as the shortest distance between the two seleniums is 7.210 Å.

Crystal Structure of 29. An ORTEP view of **29** is shown in Figure 4. The significant bond lengths and angles are listed in Table 4. The Se···N intramolecular distance in **29** (2.458(2) Å) is longer than that observed for selenenyl halides (**25**−**27**). The Se···N distance in **29** is significantly shorter than corresponding distances for reported organylselenenyl sulfides [2.617(2)−2.590(2) Å].[13b] The Se−S distance is 2.2495(6) Å, which is similar to the reported distances for selenenyl sulfides [2.22176(6)−2.2416(6) Å] based on 4,4-dimethyl-2-phenyloxazoline.[13b] The C(1)−Se−S angle is 100.36(6)°, which is well within the range of reported corresponding angles (100−104°).[13b]

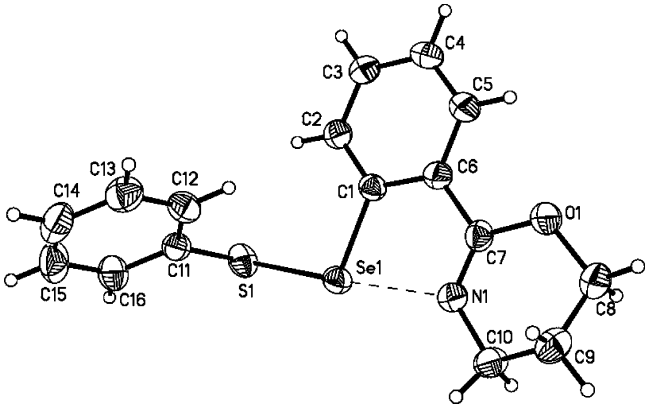

Figure 4. Molecular structure of **29**.

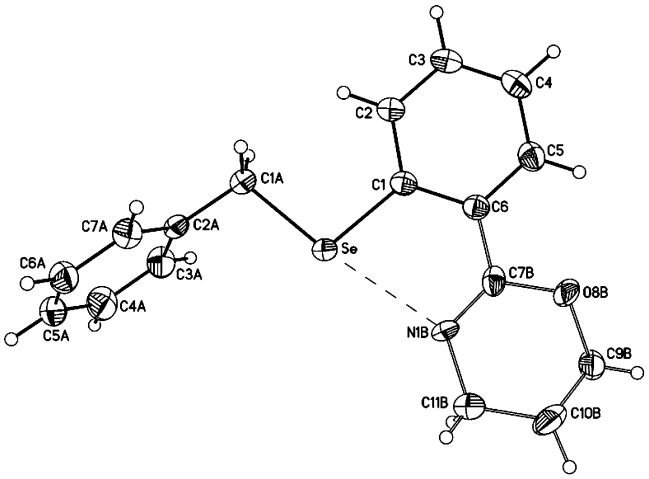

Figure 5. Molecular structure of **32**.

Table 5. Significant Bond Lengths (Å) and Angles (deg) for 32 and 34

	32		
Se···N(1A)	2.777(16)	Se−C(1)	1.909(3)
Se···N(1B)	2.686(9)	Se−C(1A)	1.975(3)
N(1B)···Se−C(1A)	173.0(3)	C(1)−Se−C(1A)	100.16(13)
N(1A)···Se−C(1A)	173.8(4)		
	34		
Se−C(7)	1.942(5)	Se−C(8)	1.973(5)
C(7)−Se−C(8)	99.8(2)	C(7)−Se−C(8)−C(6)#1	−56.5(5)
C(8)−Se−C(7)−C(1)	−82.2(4)	C(6)−C(1)−C(7)−Se	145.4(4)

Crystal Structure of 32. An ORTEP diagram is given Figure 5. The bond lengths and angles are given in Table 5. The Se−C bond lengths [Se−C(1) = 1.909(3) Å, Se−C(1A) = 1.975(3) Å] in **32** are within the range of corresponding values reported for related derivatives.[16a] The Se···N distances [Se···N(1A) = 2.777(16) Å; Se···N(1B) = 2.686(9) Å] are shorter than the corresponding value reported for [2-(4,4-dimethyl-2-oxazolinyl)phenyl]-benzyl selenide (2.798(3) Å).[16a] The Se···N distance in **32** is longer than those in the halo derivatives **25**−**27** and triselenide **11**.

(22) Fujihara, H.; Mima, H.; Ikemori, M.; Furukawa, N. *J. Am. Chem. Soc.* **1991**, *113*, 6337.

(23) (a) du Mont, W.-W.; Kubiniok, S.; Peters, K.; Schnering, H. V. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 780. (b) du Mont, W.-W.; Martens, A.; Ponl, S.; Saak, W. *Inorg. Chem.* **1990**, *29*, 4847.

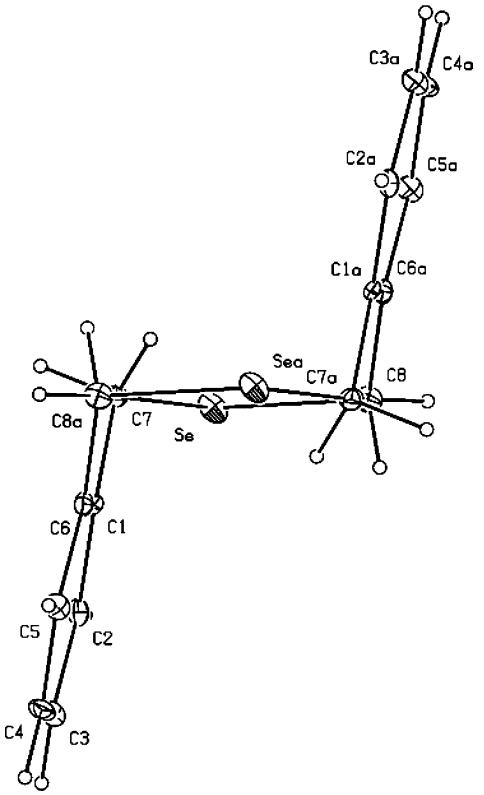

Figure 6. Molecular structure of **34**.

Crystal Structure of 34.[15b] The crystal structure of **34** has been reported previously by Fukazawa et al.[15b] to study the conformational property in the solid state. However, no molecular parameters were given. Here we describe the salient features of **34**. The molecular structure of **34** is shown in Figure 6. The bond lengths and angles are listed in Table 5. An interesting feature of the compound is that it crystallizes in chair form (Figure 6). The geometry around the selenium atom is 'V' shaped with a $CH_2-Se-CH_2$ angle of 99.8(2)°. Each selenium is bonded to two carbons [Se−C(7) = 1.942(5) Å, Se−C(8) = 1.973(5) Å]. The Se−C distances are similar to that reported for the eight-membered diselenocine.[17]

Conclusion

In conclusion, a comparison of the structure and reactivity of intramolecularly coordinated low-valent organoselenium compounds derived from 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**12**), 4,4-dimethyl-2-phenyloxazoline, and (*R*)-4-ethyl-4-hydro-2-phenyloxazoline has been made. The reactivity of **12** is quite different from 2-phenyloxazolines containing a five-membered oxazoline ring. The noticeable differences in the reactivities are as follows. (i) Reaction of lithiated product **13** with selenium powder afforded a mixture of lithium arylpolyselenolates (**14**−**16**), whereas 4,4-dimethyl-2-phenyloxazoline gives only the lithium arylselenolate (RSe^- Li^+) under similar conditions. (ii) The strength of Se···N intramolecular interactions in 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**12**)-based selenium compounds is stronger than those derived from 4,4-dimethyl-2-phenyloxazoline and (*R*)-4-ethyl-4-hydro-2-phenyloxazoline. Furthermore we have presented some evidence for the existence of a novel selenium halide, RSeSeCl (**24**), 2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)phenyl seleniumselenenyl sulfide (**28**), and an unsymmetrical diselenide (RSeSeR′) (**31**). The isolation of triselenide **11** indicates that it is possible to synthesize the unstable organoselenium compounds by using the intramolecular coordination approach.[24]

The novel triselenide is a better catalyst in the reduction of hydrogen peroxide compared to the diselenide analogue in both benzenethiol and coupled reductase assays. Thus triselenides can be used equally or more effective as commonly studied diselenides and heterocycles containing Se−N and recently studied Se−O bonds.

Experimental Section

General Procedures. All reactions were carried out in oven-dried glassware under a nitrogen atmosphere using standard vacuum-line techniques. Solvents were purified by standard procedures[25] and were freshly distilled prior to use. Melting points are not corrected and were recorded on a Buchi-SMP-20. ^1H and ^{13}C and ^{77}Se NMR spectra were recorded at 300, 75.42, and 57.22 MHz in $CDCl_3$ on a Varian VXR 300S spectrophotometer. Chemical shifts are reported in parts per million (ppm) relative to $SiMe_4$ as internal (^1H and ^{13}C) and Me_2Se (^{77}Se) as external standard. Elemental analyses were determined with a Carlo-Erba model 1106 elemental analyzer. IR spectra were recorded on a Bio-Rad FT-IR spectrophotometer model FTS165 with KBr pellets or liquid film. Electrospray mass spectra (ES-MS) were performed at room temperature on a Q-Tof micro (YA-105) mass spectrometer. Mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using a dichloromethane (otherwise mentioned separately) mobile phase. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μL min^{-1}. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 200 and 20 mL min^{-1}, respectively. Pressure in the mass analyzer region was usually about 4×10^{-5} mbar. GC−MS analyses was obtained on a Hewlett-Packard-1800 system equipped with a capillary column using an electron ionization detector. Column chromatography was performed with silica gel (60−120 mesh). All reported yields are isolated yields unless specified otherwise.

Synthesis of 2-Phenyl-5,6-dihydro-4*H*-1,3-oxazine (12).[11] To a stirred solution of benzonitrile (51.56 mL, 0.5 mol) were added 1,3-propanolamine (57 mL, 0.75 mol) and anhydrous $ZnCl_2$ (1.7 g, 0.0125 mol) simultaneously, and the reaction mixture was refluxed under N_2 overnight. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (250 mL), and washed with water several times. The organic layer was dried over Na_2SO_4 and the solvent evaporated to give a yellow oil. This oil was purified by vacuum distillation to give a colorless liquid, **12**. Yield: 71.6 g, 89%. GC retention time (free base) = 8.201 min. ^1H NMR (300 MHz, $CDCl_3$): δ 1.65(m, 2H); 3.45(t, 2H); 4.12(t, 2H); 7.35(m, 3H); 7.91(m, 2H). IR (neat, cm^{-1}): 3056, 2940, 2897, 2860, 1656, 1486, 1450, 1354, 1274,1137, 936, 792. GC−MS: *m*/*z* 161 (M^+).

Preparation of Bis[2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)] Triselenide (11). A stirred solution of 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**12**) (1.61 g, 10 mmol) in dry ether (150 mL) was treated with a 1.6 M solution of *n*-BuLi in hexane (6.8 mL, 11 mmol) under N_2 at −5 °C. On stirring the reaction mixture for 30 min at this temperature, a brown-colored product was obtained. Selenium powder (0.8 g, 10 mmol) was

(24) Mugesh, G.; Singh, H. B. *Acc. Chem. Res.* **2002**, *35*, 226.
(25) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, 1980.

added to this mixture under a brisk flow of N_2 gas, and the stirring was continued for an additional 6 h at room temperature; after that O_2 passed into the reaction mixture at a moderate rate for 5 h. The reaction residue was extracted with dry ether (30 × 5 mL) and dried over Na_2SO_4. The filtrate was concentrated to give a yellow oil. The triselenide **11** was crystallized from dry hexane/ether (1:1) as the major product. The yellow-colored crystals were obtained by cooling the solution at −30 °C. Yield: 0.74 g, 53%. Mp: 168−170 °C. Anal. Calcd for $C_{20}H_{20}N_2O_2Se_3$: C 43.12, H 3.62, N 5.02. Found: C 43.24, H 3.96, N 4.76. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12(m, 4H), 3.66(m, 4H), 4.42(m, 4H), 7.22−7.52(m, 4H) 7.81−8.56(m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.96, 40.97, 65.27, 125.32, 127.08, 127.71, 130.45, 130.74, 155.54. IR (KBr, cm^{-1}): 3067, 2936, 2857, 1618, 1622, 1542,1448, 758. UV/vis (CH_3-OH): λ_{max} (ϵ) 286.0, 320.0 nm (2550 mol^{-1} dm^3 cm^{-1}). ES-MS: *m*/*z* 559 (M^+).

Preparation of Bis[2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)] Diselenide (10). To a solution of triselenide **11** (0.56 g, 1 mmol) in CCl_4 was added a solution of bromine (0.24 g, 1.5 mmol) in CCl_4 at 0 °C. The addition was carried out over a period of 30 min and then allowed to come to room temperature. The solution was concentrated to give a yellow oily precipitate. In a two-necked 50 mL flask was placed the yellow oil, and $NaBH_4$ in methanol was added at 0 °C. The mixture became a homogeneous solution. Standard workup gave a yellow oil (**10**), which was purified by column chromatography on silica gel with hexane/ethyl acetate (7:3) as eluent. The product was crystallized from dichloromethane/hexane (1:1) as a white solid, **10**. Yield: 0.36 g, 75%. Mp: 136−137 °C. Anal. Calcd for $C_{20}H_{20}N_2O_2Se_2$: C, 50.24; H, 4.22; N, 5.85; Found: C, 49.24, H, 3.98, N, 6.32. ^{1}H NMR (300 MHz, $CDCl_3$): 2.05(m, 4H), 3.75(t, 4H), 4.40(t, 4H), 7.16−7.19(m, 4H) 7.75−7.79(m, 2H), 7.83−7.86(m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): 22.25, 41.67, 65.36, 125.26, 127.65, 130.39, 130.68, 132.14, 132.75, 155.40. IR (KBr, cm^{-1}): 3065, 2934, 2855, 1618, 1539, 1446, 755. ES-MS: *m*/*z* 481 (M^+).

Synthesis of [2-(2-Phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]-benzyl Selenide (32). A stirred solution of 2-phenyloxazine **12** (1.61 g, 10 mmol) in dry ether (100 mL) was treated with a 1.6 M solution of *n*-BuLi in hexane (6.8 mL, 11 mmol) under N_2 at 0 °C. On stirring for 30 min at this temperature, a brown-colored product (**13**) was obtained. Selenium powder (0.78 g, 10 mmol) was added to this mixture under a brisk flow of N_2 gas, and the stirring was continued for an additional 4 h at room temperature. To the resulting reaction mixture was added dropwise at 0 °C a solution of benzyl chloride (0.5 mL, 5 mmol) in 15 mL of dry ether. The stirring was continued for 2 h at 0 °C, and then the reaction mixture was allowed to attain room temperature. The resulting mixture was washed with water, and the aqueous layer was extracted thrice with ether. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated to give a yellow oil. Yellow crystals of the desired product were obtained by the addition of hexane and ether (3:5). Yield: 1.19 g, 35%. Mp: 137−139 °C. Anal. Calcd for $C_{17}H_{17}NOSe$: C 61.84, H 5.19, N 4.24. Found: C 62.02, H 5.14, N 4.14. ^{1}H NMR (300 MHz, $CDCl_3$): 1.95(m, 2H), 3.62(t, 2H), 4.02(s, 2H). 4.32(t, 3H), 7.17−7.48(m, 7H), 7.74−7.77(m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): 21.99, 31.22, 41.75, 65.18, 124.60, 126.73, 128.08, 128.46, 128.59, 129.37, 130.17, 132.54, 136.17, 137.54, 155.36. IR (KBr, cm^{-1}): 3062, 2966, 2927, 2895, 1648, 1462, 1353, 1264, 1149, 1097, 765. ES-MS: *m*/*z* 332 (M^+).

Synthesis of Diselenocine 34.[15a] To a solution of **12** (1.61 g, 10 mmol) in dry ether (100 mL) was added a solution of *n*-BuLi (6.8 mL, 11 mmol, 1.6 M solution in hexane) via syringe under N_2 at 0 °C. This was stirred for 30 min at this temperature to give the lithiated compound (**13**). Se powder (0.8 g, 10 mmol) was added under a brisk flow of N_2 gas. After 5 h stirring at 0 °C, 1.3 g (5 mmol) of α,α′-dibromo-*ortho*-xylene in THF (10 mL) was added dropwise, and stirring was continued for an additional 1 h at 0 °C followed by 3 h at room temperature. The resulting mixture was washed with water, dried, and evaporated to give a yellow liquid. A white solid was obtained by adding a hexane and dichloromethane (2:1) mixture. Column chromatography using SiO_2 (60−120 mess) and dichloromethane and methanol (2:1) of the white solid provided two fractions: (i) the first fraction that eluted using dichloromethane gave white-colored pellets. Yield: 0.27 g, 30%. Mp: 116−118 °C (lit. mp 120−122 °C).[15a] Anal. Calcd for $C_{16}H_{16}Se_2$: C 52.50, H 4.40. Found: C 52.86, H 4.62. ^{1}H NMR (300 MHz, $CDCl_3$): 3.62(s, 8H); 7.08−7.36(m, 4H); 7.42−7.54(m, 2H), 7.62(d, 2H). ES-MS: *m*/*z* 368 (M^+).

Synthesis of [2-(2-Phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)-selenenyl] Bromide (26). Method A. The second fraction isolated during the purification of **34** gave white-colored needles of **26**. Yield: 2.16 g, 56%. Mp: 223−226 °C. Anal. Calcd for $C_{10}H_{10}NOSeBr$: C 37.66, H 3.16, N 4.39. Found: C 38.12, H 3.59, N 5.18. ^{1}H NMR (300 MHz, $CDCl_3$): 2.36(m, 2H); 4.06(t, 2H), 4.68(t, 2H), 7.42(t, 1H); 7.62(t, 1H); 7.78(d, 1H); 8.82(d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): 21.68, 41.95, 41.50, 67.00, 124.76, 125.62, 126.30, 129.55, 132.50, 159.43. IR (KBr, cm^{-1}): 3068, 2927, 2857, 1718, 1622, 1283, 1123, 720. ES-MS: *m*/*z* 319 (M^+).

Method B. To a solution of triselenide **11** (0.28 g, 0.5 mmol) in CCl_4 (25 mL) was added a solution of bromine (0.32 g, 2 mmol) in CCl_4 at 0 °C. The addition was carried out over a period of 30 min and then allowed to come to room temperature. The solution was concentrated to give a yellow oil, **26**. Purification by flash chromatography using dichloromethane/ethyl acetate (9:1) followed by recrystallization from CH_2Cl_2 provided 0.3 g, 94% of **26** as white needles.

Synthesis of [2-(2-Phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]-selenenyl Chloride (25). The treatment of triselenide **11** (0.28 g, 0.5 mmol) in CCl_4 with a solution of SO_2Cl_2 (0.268 g, 2 mmol) in 20 mL of CCl_4 at 0 °C gave a white precipitate after 1 h. The mixture was evaporated completely under vacuum to give the desired product (**25**). Purification by flash chromatography using CH_2Cl_2/ethyl acetate (10:1) afforded pure **25**. White-colored pellets were obtained after recrystallization from dichloromethane/methanol (3:1). Yield: 0.25 g, 91%. Mp: 193−195 °C. Anal. Calcd for $C_{10}H_{10}NOSeCl$: C, 43.76; H, 3.66; N, 5.09. Found: C, 44.03, H, 3.77, N, 4.65. ^{1}H NMR (300 MHz, $CDCl_3$): 2.35(m, 2H), 4.06(t, 2H), 4.72(t, 2H), 7.24−7.58(m, 2H), 7.72(d, 2H), 8.65(d, 1H). IR (KBr, cm^{-1}): 3065, 2934, 2855, 1618, 1539, 1446, 755. ES-MS: *m*/*z* 275 (M^+).

Synthesis of [2-(2-Phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]-selenenyl Iodide (27). The procedure followed for the preparation of **27** was the same as that used for the preparation of compound **26** except the addition of I_2/CCl_4 was carried out for 3 h at room temperature. The compound was recrystallized from a chloroform/methanol (4:1) mixture to give yellow crystals. Yield: 0.3 g, 82%. Mp: 247−249 °C. Anal. Calcd for $C_{10}H_{10}NOSeI$: C, 32.83; H, 2.75; N, 3.82. Found: C, 32.39, H, 2.64, N, 3.42. ^{1}H NMR (300 MHz, $CDCl_3$): 2.32(m, 4H), 4.02(t, 4H), 4.63(t, 2H), 7.42−7.62(m, 2H) 7.76(dd, 1H), 7.78(d, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): 21.69, 41.84, 66.90, 125.74, 128.23, 130.10, 132.81, 133.05, 133.33, 158.78. IR (KBr, cm^{-1}): 3065, 2934, 2855, 1618, 1539, 1446, 755. ES-MS: *m*/*z* 366 (M^+).

Synthesis of [2-(2-Phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]-selenenyl Phenylsulfide (29). To a stirred solution of triselenide **11** (0.56 g, 1 mmol) in anhydrous CH_2Cl_2 (10 mL) was added benzenethiol (0.44 g, 4 mmol) at room temperature. After addition of benzenethiol, the color of the reaction mixture changed to orange-red. The reaction mixture was stirred for an additional 5 h. The solvent was removed under vacuum. The residue was washed with hexane and purified by column chromatography using hexane and ethyl acetate (3:1) to afford **29** as a white-colored compound. Yield: 0.6 g, 86%. Mp: 110−112 °C. Anal. Calcd for $C_{16}H_{15}NOSSe$: C, 55.19; H, 4.33, N, 4.02, S, 9.20. Found: C, 54.87; H, 4.02, N, 4.23, S, 8.92. ^{1}H

Table 6. Crystal Data and Structure Refinement for 11, 25, and 26

	11	25	26
empirical formula	$C_{20}H_{20}N_2O_2Se_3$	$C_{10}H_{10}ClNOSe$	$C_{20}H_{20}Br_2N_2O_2Se_2$
fw	557.26	274.60	638.12
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$	$P2_1/c$
a (Å)	13.847(3)	7.7682(9)	7.8729(4)
b (Å)	12.576(3)	14.3617(10)	14.4935(7)
c (Å)	12.486(3)	18.5991(10)	18.7790(9)
β (deg)	106.40(3)	97.288(7)	97.4610(10)
V (Å^3)	2085.9(7)	2058.2(3)	2124.65(18)
Z	4	8	4
D(calcd) (Mg/m^3)	1.775	1.772	1.995
abs coeff (mm^{-1})	5.307	3.872	7.261
obsd reflns [$I > 2\sigma$]	2467	15 939	16 702
final $R(F)$ [$I > 2\sigma(I)$][a]	0.0429	0.0438	0.0734
$wR(F^2)$ indices [$I > 2\sigma(I)$]	0.0902	0.0882	0.1109
no. of data/restraints/params	2372/12/176	5256/0/254	5401/0/254
goodness of fit on F^2	0.959	1.129	1.353

[a] Definitions: $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

Table 7. Crystal Data and Structure Refinement for 27, 29, 32, and 34

	27	29	32	34
empirical formula	$C_{10}H_{10}I_{0.5}NOSe_{0.5}$	$C_{16}H_{15}NOSSe$	$C_{20}H_{20}N_2OSe$	$C_{32}H_{32}Se_4$
fw	263.12	348.31	383.34	732.42
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	7.8141(10)	13.6779(11)	12.4922(5)	8.2196(7)
b (Å)	16.109(2)	7.6783(4)	12.9919(10)	4.8868(4)
c (Å)	9.1770(12)	15.2080(11)	9.5241(5)	16.9818(4)
β (deg)	103.302(3)	112.554(8)	104.128(3)	98.559(3)
V (Å^3)	1124.2(3)	1475.03(18)	1498.98(15)	674.52(10)
Z	4	4	4	1
D(calcd) (Mg/m^3)	1.555	1.568	1.699	1.803
abs coeff (mm^{-1})	3.058	2.681	3.459	5.460
obsd reflns [$I > 2\sigma$]	8764	20363	2138	3135
final $R(F)$ [$I > 2\sigma(I)$][a]	0.0330	0.0256	0.0299	0.0619
$wR(F^2)$ indices [$I > 2\sigma(I)$]	0.0796	0.0596	0.0836	0.0757
no. of data/restraints/params	2845/0/128	3123/0/181	2037/12/237	1245/0/91
goodness of fit on F^2	1.063	0.911	1.080	1.137

[a] Definitions: $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

NMR (300 MHz, $CDCl_3$): 2.05(q, 2H), 3.73(t, 2H), 4.39(t, 2H), 7.06−7.17(m, 7H) 7.82(d, 1H), 8.24(d, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): 22.14, 29.92, 41.03, 65.51, 125.60, 127.12, 127.46, 128.63, 129.08, 130.76, 136.94, 138.05. IR (KBr, cm^{-1}): 3067, 2936, 2857, 1618, 1622, 1542,1448, 758. ES-MS: *m*/*z* 348 (M^+).

Synthesis of [2-(2-Phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]-selenenyl (4-Methoxyphenyl)sulfide (30). Selenenyl sulfide **30** was similarly prepared at 1 mmol stoichiometry from triselenide **11** and benzene 4-methoxybenzenethiol. Selenenyl sulfide **30** was obtained as a yellow oil after purification by column chromatography by using hexane/ethyl acetate (4:1). Yield: 0.45 g, 60%. ^{1}H NMR (300 MHz, $CDCl_3$): 2.07(q, 2H), 3.74(t, 2H), 3.72(s, 3H), 4.36(t, 2H), 6.51−6.82(m, 4H), 7.28−7.44(m, 2H) 7.81(d, 1H), 8.38(d, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): 21.94, 40.86, 50.878, 55.34, 65.36, 114.42, 114.65, 125.42, 127.28, 127.59, 129.23, 130.67, 131.74, 132.69, 136.64, 158.48. IR (KBr, cm^{-1}): 3067, 2936, 2857, 1618, 1622, 1542, 1448, 758. ES-MS: *m*/*z* 377 (M^+).

X-ray Crystallography. The diffraction measurements for compounds **11**, **25**−**27**, **32**, and **34** were performed on a Bruker SMART diffractometer with graphite-monochromated Mo/Kα radiation (λ = 0.7170 Å), and for compound **29** diffraction measurements were performed in a STOE (Darmstadt, Germany) IPDS imaging plate single-crystal diffractometer. The structures were determined by heavy-atom routine using SHELXS-86[26] and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogens with fixed isotropic thermal parameters of 0.07 Å^2 by means of the SHELEXL-97 program.[27] Hydrogens were partially located from difference electron-density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources. Some details of the structure and refinement are given in Tables 6 and 7.

Acknowledgment. This work was supported by the Department of Science and Technology, New Delhi (DST grant to H.B.S.), and Council of Scientific and Industrial Research (CSIR), Government of India, New Delhi (Senior Research Fellowship to S.K.).

Supporting Information Available: Details of kinetic measurements, ES-MS, ^{77}Se NMR spectra, additional figures, and tables giving crystal data, details of structure determination, molecular structures for selenenyl halides (**26** and **27**), final atomic coordinates for compounds **11** (CCDC No. 225495), **25**−**27** (CCDC No. 225494, 225493, and 225492), **29** (CCDC No. 225491), **32** (CCDC No. 225490), and **34** (CCDC No. 225489). This material is available free of charge via the Internet at http://pubs.acs.org.

OM049722F

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