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Intramolecular Interactions between Chalcogen Atoms: Organoseleniums Derived from 1-Bromo-4-*tert*-butyl-2,6-di(formyl)benzene

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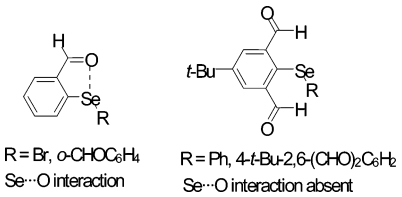

The synthesis and characterization of a series of low-valent organoselenium compounds derived from 1-bromo-4-*tert*-butyl-2,6-di(formyl)benzene (**22**) is described. The synthesis of diselenide **25** was achieved by the lithiation route whereas bis(4-*tert*-butyl-2,6-di(formyl)phenyl) diselenide (**26**) was synthesized by treating **22** with disodium diselenide. A series of monoselenides (**27**, **28**, and **29**) was obtained by facile nucleophilic substitution of bromine in **22**, using the corresponding selenolates as nucleophiles. The halogenation reactions of bis(4-*tert*-butyl-2,6-di(formyl)phenyl) diselenide (**26**) did not afford the corresponding selenenyl halides but resulted in the isolation of an unexpected cyclic selenenate ester **34** as a product. The selenide **32** was synthesized by the treatment of dimethoxymethyl diselenide with trilithiated 2-bromo-5-*tert*-butyl-*N*,*N*′-di(phenyl)-isophthalamide. The existence of potential Se···O intramolecular nonbonding interactions was examined by IR, ^{1}H, and ^{77}Se NMR spectroscopy, X-ray crystallography, and computational studies. The X-ray crystal structures of **26** and **27**, having two ortho formyl groups, reveal the absence of any Se···O interactions. However, the Se···O interactions were observed in the selenenate ester **34** where one of the formyl groups has been utilized for the selenenate ring formation. The crystal structures of **26** and **27** exhibited intermolecular short-range C−H···Se interactions (hydrogen bonding). Although there are four heteroatoms in carbamoyl moieties ortho to selenium capable of forming a five-membered ring on intramolecular coordination, no such intramolecular Se···X (X = N, O) interaction was observed in the crystal structure of **32**. The density functional theory calculations at the B3LYP/6-31G* level predicted that for all the diformyl systems (**47a**−**c**, **48a**−**c**), the anti,anti conformer (when both formyl oxygen atoms point away from the selenium) is more stable. This preference was found to be reversed in the monoformyl-substituted systems (**50a**,**b**, **51a**,**b**), where the syn conformer (when formyl oxygen is near the selenium) is energetically more favorable than the anti conformer.

Introduction

The chemistry of organoselenium derivatives having intramolecular nonbonded Se···X (X = N, O) interactions has attracted considerable current interest. These derivatives afford (a) novel hypervalent, stable organoselenium compounds via intramolecular interaction of selenium with a nearby heteroatom (N, O, S etc.),[1] (b) chiral reagents for asymmetric synthesis,[2] (c) ligands for the isolation of monomeric MOCVD precursors,[3] (d) ligands for achiral and chiral catalysis,[4] and (e) glutathione peroxidase mimics.[5]

Chiral electrophilic selenenylating reagents in asymmetric reactions such as methoxyselenenylation, hydroxyselenenylation, aminoselenenylation, and selenocyclization have been studied extensively over the past few years.[2] A common characteristic of all these reagents described in the literature is the close proximity of the

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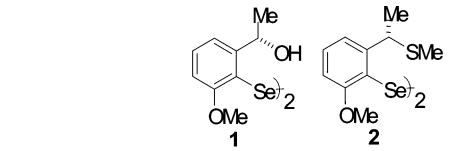
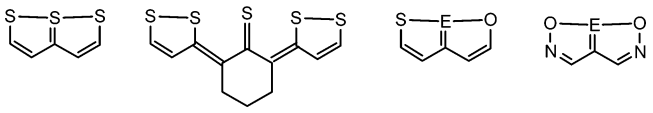
heteroatom (N, O, S) to the selenium. The intramolecular nonbonding interactions between selenium and heteroatom (N, O, S) would force the chiral center to approach the reaction center during the addition of the selenenylating agent to the alkene moiety. This would result in asymmetric induction.[6] It has been recently observed by Tiecco et al.[2j] and Wirth et al.[2k] that better selectivity could be obtained by introducing an additional substituent having heteroatom (O) at the other ortho position to selenium (**1** and **2**). The better efficiency of such reagents further confirmed that the conformational restriction imposed by the interaction of the additional heteroatom is very likely the most important factor responsible for the high facial selectivity. In this way, these interactions play a crucial role in chirality transfer. However, intramolecular interactions in such system have not been studied in detail in solution and the solid state. A notable exception is the single-crystal X-ray structure of compound **1**.[7]



1 **2**



3 **4** **5** **6**

The study of bonding/nonbonding interactions among three adjacent chalcogens appears to have been started by Gleiter et al with the report of thiothiophthene (**3**).[8] Subsequently related structures **4**−**6** were reported where the chalcogen atoms are covalently linked.[8] Recently, Furukawa and co-workers,[1j] in a systematic study, have demonstrated that the arrangements of two or three heavier chalcogen atoms (S, Se, Te) appropriately in juxtaposition tend to develop a repulsive force between the chalcogen atoms in the neutral state.

It is worth noting that the attractive nonbonding interactions between two adjacent chalcogen atoms in which the nucleophile is the lightest chalcogen, oxygen, and the central atoms are the heavier chalcogens, i.e., Se, Te in **7**−**18**, have been extensively studied and proved by X-ray structures, NMR, and theoretical studies.[9] A common interpretation of the interaction of chalcogens with nucleophiles considers donation of electron density from a lone pair on the donor atom into the σ^* (Se−X)) orbital. As the degree of covalency increases, a hypervalent three-center four-electron bond is formed. Detty and co-workers[10] have reported related double bond supported hypervalent heterocycles (**19**−**21**).

In view of the above and our long standing interest in the chemistry of stabilized organochlacogens,[11] we thought to examine the intramolecular interactions in

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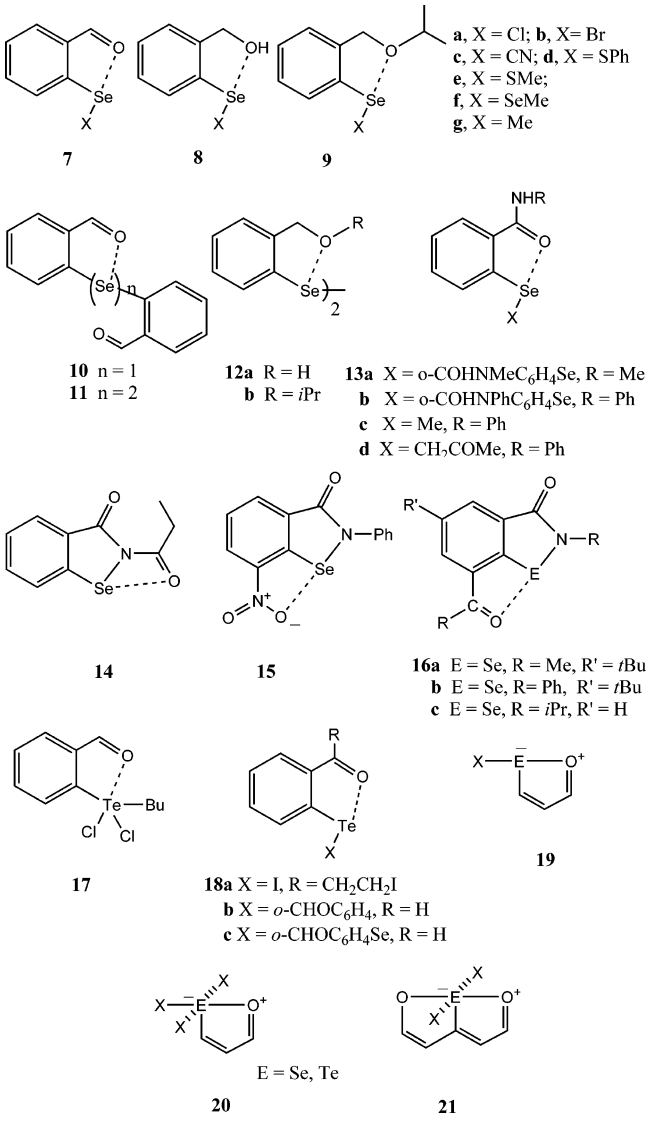
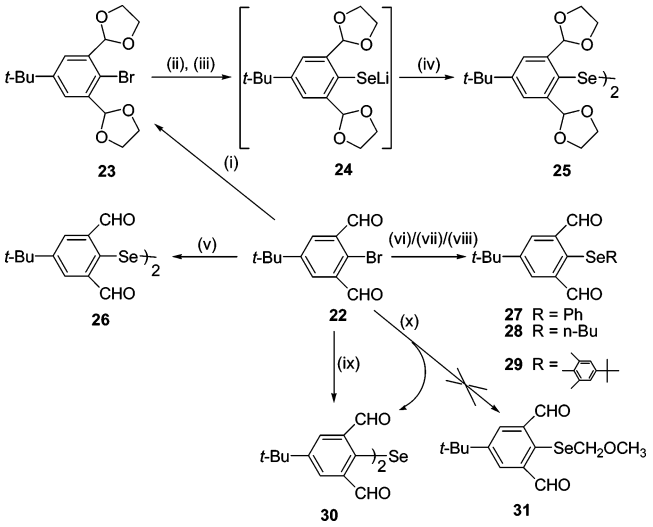


organochalcogens having three appropriately disposed chalcogens of which two terminal chalcogens are oxygen (i.e., compounds with the O, Se, O arrangement). Recently, we have reported an attempted synthesis of organoselenenyl halides with two formyl groups ortho to selenium, which led to the facile isolation of the novel selenenate ester **34**,[12] and also our efforts toward the preparation of diselenides having two ortho amide groups, unexpectedly, afforded novel ebselen derivatives.[9°] In this full paper, we describe the synthesis of a series of organoselenium compounds derived from **22** and related substrates and probe in depth the extent and nature of intramolecular interaction between three chalcogens, i.e., in the O, Se, O system.

SCHEME 1[a]



[a] Reagents and conditions: (i) ethylene glycol, C_6H_6, *p*-toluenesufonic acid, reflux; (ii) *n*-BuLi, Et_2O, rt, 1 h; (iii) Se°, rt, 1 h; (iv) [O]/H_2O; (v) Na_2Se_2, THF, rt, 6 h; (vi) PhSeNa, EtOH, 0 °C→rt, 2 h; (vii) *n*-BuSeNa, EtOH, 0 °C→rt, 2 h; (viii) sodium 2,6-dimethyl-4-*tert*-butylphenyl selenolate, EtOH, 0 °C→rt, 2 h; (ix) Li_2Se, THF, 0 °C→rt,2 h; (x) CH_3OCH_2SeNa, EtOH, 0 °C→rt, 2 h.

Results and Discussion

In the begining, we considered substrate **22** for the synthesis of the desired diselenides **25** and **26**. The precursor **22** was synthesized by oxidation of 1-bromo-4-*tert*-butyl-2,6-di(methyl)benzene with CrO_3 in acetic anhydride.[13] Toward the preparation of **25**, the diselenide **22** was treated with ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid to give **23** as a colorless solid (Scheme 1). The treatment of **23** with *n*-BuLi followed by selenenation and subsequent oxidative workup yielded the desired compound **25** in good yield. Attempted hydrolysis of **25** gave an orange oil that did not solidify and was difficult to purify.

Thereafter, the synthesis of the diselenide **26** was accomplished by the reaction of **22** with disodium diselenide.[14] It is worth mentioning that the carbon bonded to bromine in **22** is so highly prone to nucleophilic

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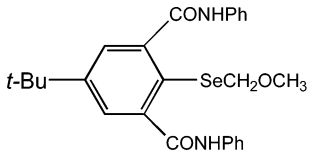
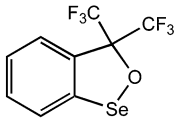
substitution that this reaction proceeds even at 0 °C, whereas the reaction of *o*-chlorobenzaldehyde with disodium diselenide requires the highly polar solvent HMPT and higher temperature to obtain the desired diselenide.[15] The selenides **27**−**29** were prepared by the reaction of **22** with the corresponding selenolates. The symmetrical monoselenide **30** was obtained as a yellow solid by the treatment of **22** with lithium selenide. However, attempts to prepare **31** by the reaction of **22** with sodium methoxymethyl selenolate furnished symmetrical monoselenide **30** in very good yield. The related selenide **32** could be conveniently prepared by the reaction of 2-bromo-5-*tert*-butyl-*N,N′*-di(phenyl)isophthalamide with 3 equiv of *n*-BuLi followed by quenching with bis(methoxymethyl) diselenide.[9o]



32

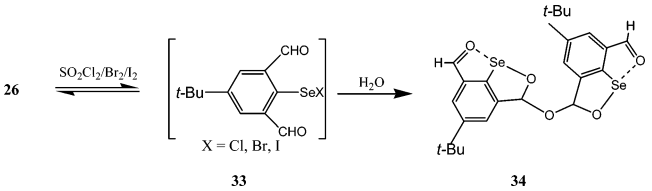


35

Synthesis of the selenenyl halides **33** (RSeCl, RSeBr, RSeI) was approached by the reaction of the diselenide **26** with SO_2Cl_2, Br_2, and I_2, respectively, at ambient conditions (Scheme 2). Interestingly, all the reactions gave the same product whose detailed spectroscopic characterization and X-ray structural elucidation unequivocally revealed it to be the unexpected selenenate ester **34**. There are only a few reports on the isolation of selenenate ester in the literature.[16] The selenenate ester **35** was obtained as a byproduct in the thermolysis of tetracoordinated oxaselenetanes, spiroselenuranes, and selenazetidines.[17] However, the selenenate ester **34** was found to be susceptible to hydrolysis and decomposition. Selenenate ester **34**, in contrast, is stable in air and does not show any decomposition over a year. This extra stability of the selenenate presumably results from the strong Se···O intramolecular interactions (vide infra). As **34** has a Se−O covalent single bond like selenenic acid, it can be considered as a protected form of the unstable selenenic acid. The selenenic acid is a well-known highly reactive intermediate in the catalytic cycle of glutathione peroxidase.[5] Though there are several reports on the synthesis of selenenic acids,[16,18] in the literature, only three of them have been characterized structurally.[19]

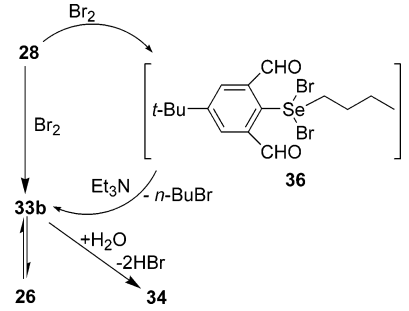
Alternatively, we considered that selenenyl bromide **33b** (X = Br) may be prepared by the reaction of **28** with Br_2-Et_3N via the dibromide **36** since such dibromides are known to undergo elimination of alkyl halides and give

SCHEME 2

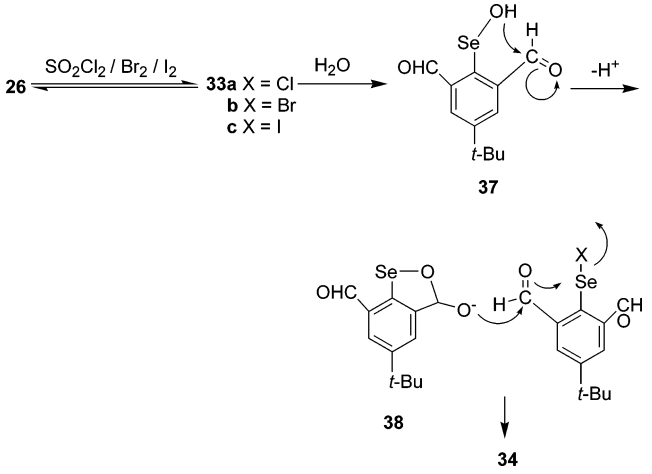


33 **34**

SCHEME 3



SCHEME 4



the corresponding selenenyl bromide (Scheme 3). Generally, the addition of bromine to aryl alkyl selenides affords the tetravalent dibromo species ($ArSeRBr_2$), which undergoes facile elimination of alkyl bromide to give aryl selenenyl bromide.[20] However, the reaction of **28** with Br_2-Et_3N again gave the compound **34** along with **26**.

A possible mechanism of the formation of **34** is shown in Scheme 4. The formation of **34** apparently proceeds through the selenenyl bromide **33b**, which further reacts with water to form selenenic acid **37**.[21] Intramolecular acetal formation in **37** gives the nucleophilic species **38**, which upon reaction with another mole of **33b** finally gives **34**. It is known that simple diorganodiselenides which are not stabilized by intramolecular coordination

(15) Syper, L.; Mlochowski, J. *Tetrahedron* **1988**, *44*, 6119.
(16) (a) Holzle, G.; Jenny, W. *Helv. Chim. Acta* **1958**, *41*, 331. (b) Holzle, G.; Jenny, W. *Helv. Chim. Acta* **1958**, *41*, 593. (c) Jenny, W. *Helv. Chim. Acta* **1958**, *41*, 317. (d) Holzle, G.; Jenny, W. *Helv. Chim. Acta* **1952**, *35*, 1591. (e) Behaghel, O.; Muller, W. *Ber.* **1935**, *68B*, 1540.
(17) (a) Kawashima, T.; Ohno, F.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 10434. (b) Ohno, F.; Kawashima, T.; Okazaki, R. *Chem. Commun.* **1997**, 1671. (c) Kano, N.; Daicho, Y.; Nakanishi, N.; Kawashima, T. *Org. Lett.* **2001**, *3*, 691.
(18) (a) Behaghel, O.; Muller, W. *Ber.* **1934**, *67B*, 105. (b) Jenny, W. *Helv. Chim. Acta* **1952**, *35*, 1429. (c) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 666. (d) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 1037. (e) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 1974. (f) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1956**, *89*, 631.
(19) (a) Saiki, T.; Goto, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2223. (b) Ishii, A.; Matsubayashi, S.; Takahashi, T.; Nakayama, J. *J. Org. Chem.* **1999**, *64*, 1084. (c) Goto, K.; Nagahama, M.; Mizushima, T.; Shimada, K.; Kawashima, T.; Okazaki, R. *Org. Lett.* **2001**, *3*, 3569.
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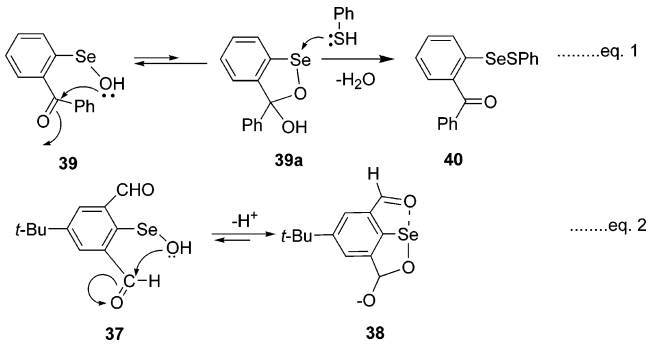
(21) (a) Reich, H. J.; Willis, W. W., Jr.; Wollowitz, S. *Tetrahedron Lett.* **1982**, *23*, 3319. (b) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *Tetrahedron Lett.* **1982**, *23*, 3323.

SCHEME 5



or sterically demanding substituents exist in equilibrium with the corresponding organoselenenyl halides.[22] A similar condition probably prevails in the present case. The above reaction presumably results due to lack of the intramolecular coordination between selenium and oxygen of the −CHO group in solution resulting in unstable selenenyl halide moieties. This is in agreement with the single-crystal X-ray structure of **26** (vide infra), which did not show any intramolecular coordination between selenium and oxygen.

Regarding the acetal formation, it may be mentioned that Kice and co-workers[23] have also proposed a similar mechanism for the formation of selenosulfide **40** from *o*-benzoylbenzeneselenenic acid via the intermediate **39a** (eq 1, Scheme 5). A similar equilibrium between **37** and **38** prevails in the present case, where the additional formyl group stabilizes the structure **38** by intramolecular coordination and drives the equillibrium toward **38** (eq 2, Scheme 5).

In contrast, the treatment of bromine with bis(2-formylphenyl) diselenide having only one formyl group affords the expected 2-formylbenzeneselenenyl bromide as a stable compound.[11] It is clear from the above observations that the second *o*-formyl group and subsequent Se···O intramolecular coordination may be the driving force for the formation of unusual selenenate ester **34**.

Spectroscopic Studies. To further probe the intramolecular interactions detailed spectroscopic studies were undertaken. The carbonyl frequency ($\nu_{C=O}$) in IR spectra of compounds **26**−**30** and **34** appeared in the region 1685−1695 cm^{-1}, which indicated that there was no interaction between selenium and oxygen in the present case.

The ^{1}H NMR spectra of **26**−**30** exhibited only one signal for the formyl protons confirming their equivalence. The selenenate **34** contains two chiral centers and can exist as a meso compound and a *dl* pair. Thus, two sets of signals are expected in the ^{1}H NMR spectrum corresponding to the meso compound and the *dl* pair. The single crystal X-ray structure clearly shows the *dl* pair, which is the major diastereomer. Therefore, for the *dl* pair, the signals at 10.20, 8.00, 7.75, and 6.90 ppm can be assigned respectively to aldehyde, aromatic, aromatic, and acetal protons. In addition, signals were observed at 10.25, 8.10, and 8.80 ppm for the aldehydic and aromatic protons of the meso diastereomer. There is fortuitous magnetic and chemical equivalency for the more remote signals from the "ether" bridge. However, the protons of the acetal group are not equivalent: one projects toward the ether oxygen lone pair and the other projects away. The ratio of two major *tert*-butyl signals (4:1) is also in accordance with the ratio of other proton signals. All attempts including chromatographic separation to purify and separate the diastereoisomers were unsuccessful. Compound **34** is only a diastereomeric mixture that was further confirmed from the reaction of 2 equiv of PhSH with selenenate ester **34** in $CDCl_3$. The ^{1}H NMR spectrum indicated clean formation of the selenenyl sulfide **41** since it exhibited only three singlets corresponding to formyl, *tert*-butyl groups, and aromatic protons, respectively.

The ^{77}Se NMR chemical shifts were found to be quite sensitive to the nature of the substituent groups bonded to the selenium atom. Only single peak is observed for both the diselenides (**25** and **26**). This indicated that both selenium atoms in each diselenide are in the same environment. There is no considerable difference in the chemical shift of the two diselenides (**25** and **26**, 373.6 and 375.9 ppm, respectively). The ^{77}Se NMR chemical shifts are comparable with that of bis(2,5-dimethyl-4-*tert*-butylphenyl)diselenide (369.3 ppm)[5h] in which no coordinating heteroatom is present. The ^{77}Se NMR chemical shift of bis(2-formylphenyl) diselenide (**11**) having one *o*-formyl group is 458.5 ppm, which is much downfield shifted compared to the diselenides **25** and **26**.[11] This can be ascribed to the presence of nonbonding interactions between selenium and oxygen in diselenide **11**. Such interaction is not observed in the crystal structure of **25** and **26** (vide infra). This is in agreement with the fact that the intramolecular Se···N or Se···O interaction results in an apparent downfield shift of the ^{77}Se NMR signals.[24] All monoselenides are relatively upfield shifted compared to the corresponding diselenide. In ^{77}Se NMR spectrum of **34**, the signal obtained at 1401.3 ppm is downfield shifted compared to reported acyclic selenenates **42** (1224 and 1269 ppm).[25] This considerable downfield shift (∼130−180 ppm) is probably due to the presence of nonbonding interaction (Se···O) in **34**. It is interesting to note that in selenenate **35**, a large deshielding (1718 ppm) was observed compared to selenenate **34**. This is presumably due to the strongly electron-withdrawing groups (CF_3) present in the five-membered ring in **35**.[17] However, the ^{77}Se NMR spectrum of **34** shows two additional signals at 1396 and 1408 ppm. The ratio of these signals with the major signal (1401 ppm) is 1:4, which is consistent with the proton NMR where the meso compound and the *dl* pair were observed in the same ratio. The ^{13}C NMR spectrum of **34** exhibits one set of 10 signals as expected for one diastereoisomer. However, with longer acquisition time a larger number of signals were obtained. Out of these, four signals were for carbonyls of aldehyde groups, three signals were for the

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(24) (a) Broschag, M.; Klapötke, T. M. *Compilation of Reported ^{77}Se NMR Chemical Shifts*; Wiley: Chichester, UK, 1996. (b) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1996**, *118*, 8077.

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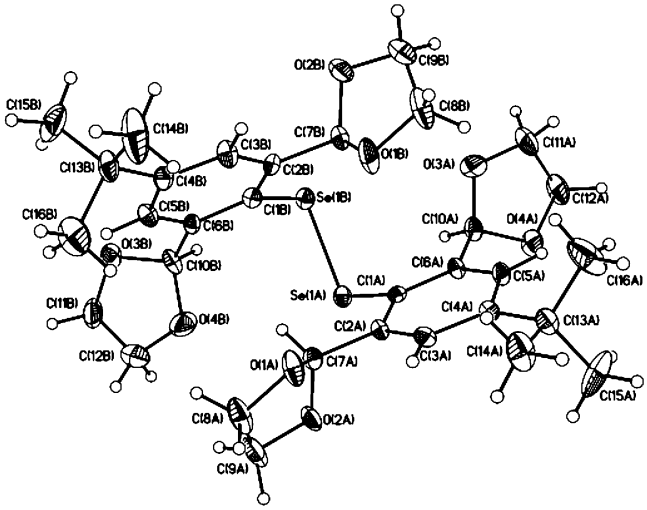


FIGURE 1. ORTEP diagram of compound **25**.

TABLE 1. Important Bond Lengths (Å) and Bond Angles (deg) of Compounds 25

Se(1A)−Se(1B)	2.305(1)	Se(1A)···O(4B)	3.561
Se(1A)−C(1A)	1.899(6)	C(1A)−Se(1A)−Se(1B)	100.5(2)
Se(1B)−C(1B)	1.920(6)	C(1B)−Se(1B)−Se(1A)	100.3(2)
Se(1A)···O(2A)	3.418		

carbon of the acetal, and two sets of two signals were for two carbons of the *tert*-butyl group, whereas thirteen signals for aromatic carbons were obtained.

Mass Spectrometric Studies. Mass spectra were recorded for all compounds to identify the constituents of the products under the mass spectroscopic conditions. The presence of six natural isotopes of Se leads to a highly characteristic group of peaks for selenium-containing fragments. In all compounds the molecular ion peak was observed with considerable intensity. In both diselenides (**25**, **26**), the molecular ion peak was observed as a strong intensity peak and the base peak observed corresponded to the $RSe^{+\bullet}$ fragment (357 and 269, respectively). For diselenide **26**, a peak at 458 represents the corresponding symmetrical monoselenide; however, in the case of diselenide **25**, no such peak was observed for the monoselenide. This can be ascribed to the presence of sterically more hindered five-membered ring present in **25**. The peaks (551, 674) above the molecular ion peak in the mass spectrum of **26** are most probably due to the change in the oxidation state of selenium to IV and attachment of more groups at the selenium center. The base peak in the fragmentation pattern of the mass spectrum of **27** is the molecular ion peak whereas **29** exhibited the molecular ion peak with strong intensity (92%). In the mass spectrum of all monoselenides (**27**−**30**) RSe^+ [R = 4-*t*-Bu-2,6-$(CHO)_2$-C_6H_2Se] is a remarkably intense peak. The molecular ion peak for **28** is of very weak intensity. This observation explains the lability of the alkyl group (*n*-Bu) compared to the aryl group attached at the selenium center.

Crystal Structure of Compound 25. An ORTEP view of compound **25** is shown in Figure 1, and selected bond lengths and bond angles are listed in Table 1. The coordination geometry around each Se is V-shaped with bond angles C(1A)−Se(1A)−Se(1B) and C(1B)−Se(1B)−Se(1A) of 100.5(2)° and 100.3(2)°, respectively. The

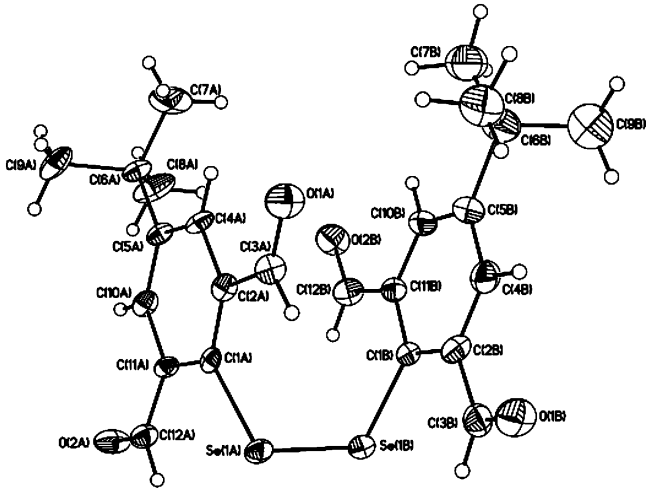
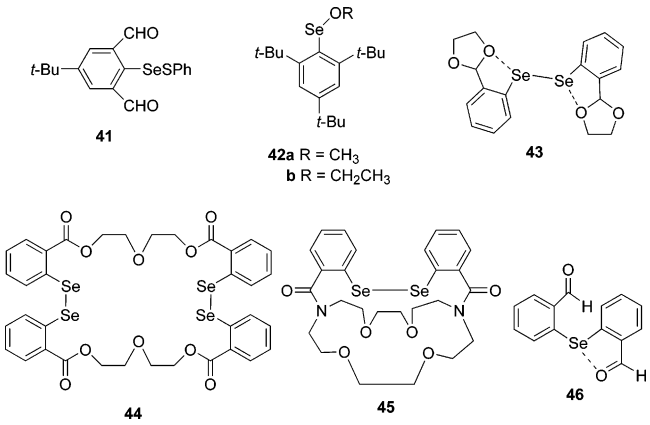


FIGURE 2. ORTEP diagram of compound **26**.

Se−Se distance of 2.305(1) Å relates well to the corresponding distances reported for the related diselenide **43**[5h] [2.318(1) Å], **44** [2.317(3) Å] ,and **45** [2.313(2) Å].[26] The bulky substituents are known to increase the dihedral angle (i.e., 112.1° for $t\text{Bu}_2\text{CHSeSeCH}t\text{Bu}_2$[27] and 82° for PhSeSePh[28]). In contrast, in the present case the C(1A)−Se(1A)−Se(1B)−C(1B) torsion angle is −69.1(3)°.



Interestingly, there is no intramolecular interaction of the oxygen of five-membered rings with the selenium. Only one out of eight oxygens is in proximity of selenium with a distance of 3.418 Å, which is nearly equal to the sum of Se and O van der Waals radii (3.40 Å) but much greater than the value reported for the related compounds **43**, **44**, and **45** (average distances 2.97, 2.68, and 3.29 Å, respectively).[5h,26]

Crystal Structure of Compound 26. An ORTEP view of compound **26** as found in the crystals is depicted in Figure 2, and selected bond lengths and bond angles are listed in Table 2. The unit cell of compound **26** contains eight molecules with two sets of nonsymmetric equivalent molecules. No significant difference between these two molecules was observed. The coordination geometry around each Se is V-shaped with bond angles C(1A)−Se(1A)−Se(1B), C(1B)−Se(1B)−Se(1A), C(1C)−

(26) Tomoda, S.; Iwaoka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 231.
(27) Back, T. G.; Codding, P. W. *Can. J. Chem.* **1983**, *61*, 2749.
(28) Marsh, R. E. *Acta Crystallogr.* **1952**, *5*, 458.

TABLE 2. Important Bond Lengths (Å) and Bond Angles (deg) of Compounds 26

Se(1A)−Se(1B)	2.343(2)	Se(1D)−C(1D)	1.923(9)
Se(1C)−Se(1D)	2.332(2)	C(1A)−Se(1A)−Se(1B)	95.3(3)
Se(1A)−C(1A)	1.937(9)	C(1B)−Se(1B)−Se(1A)	97.4(3)
Se(1B)−C(1B)	1.937(10)	C(1C)−Se(1C)−Se(1D)	98.8(3)
Se(1C)−C(1C)	1.975(11)	C(1D)−Se(1D)−Se(1C)	94.7(3)

Se(1C)−Se(1D), and C(1D)−Se(1D)−Se(1D) of 95.3(3)°, 97.4(3)°, 98.8(3)°, and 94.7(3), respectively. The Se−Se distances of 2.343(2) and 2.332(2) Å relate well to the corresponding distances reported for other diselenides.[5h,26] The C(1A)−Se(1A)−Se(1B)−C(1B) and C(1C)−Se(1C)−Se(1D)−C(1D) torsion angles [66.7(4)° and −71.0(4)°] are smaller as in the structure of **25**. It is interesting to note that there is no intramolecular interaction between oxygen and selenium. The structure shows that all four oxygen atoms of the formyl groups are pointing away from the selenium centers whereas the related monoselenide **46** revealed the strong Se···O interaction (2.806 Å) with one of the oxygen atoms.[8m]

The PLUTON view of the packing diagram (Figure S25 of the Supporting Information) exhibits an interesting aspect of the structure. There exists an intermolecular short-range C−H···Se hydrogen bonding interaction (2.971 Å, 147.9°) that compares well with the reported data [2.98(5) Å, 146°; 3.26(5) Å, 129° for intermolecular[29] and 2.86 Å, 107.0°; 2.92 Å, 101.7° for intramolecular[30] C−H···Se interactions]. Each pair of molecules is held by a C−H···Se interaction. Structures having the C−H···Se hydrogen bonds are very rare, and to the best of our knowledge there are only two reports to date on both intermolecular and intramolecular C−H···Se interaction.[29,30]

To gain better insights on the nonbonded interaction between the selenium and oxygen atoms in **26**, we have performed density functional theory calculations at the B3LYP/6-31G* level.[31] Model diselenides having formyl groups at the ortho positions have been investigated. These are designed to serve as model compounds for experimental structures **25** and **26**. Computed relative energies of three of the most important conformers as given in Figure 3 evidently suggest that an energetically better situation is when hydrogens, instead of oxygens, are syn with respect to the diselenide selenium atom (**47a**). It is also worth noting that the structure with syn,syn arrangement of oxygen atoms is higher in energy by 5.48 kcal/mol. When only one of the formyl oxygens is syn (**47b**), the energy difference is as high as 2.6 kcal/mol compared to **47a**. Relative energies of conformers **47a**−**c** strongly point to the fact that oxygens would prefer not to participate in Se···O nonbonded interactions in bisformyl diselenide systems.

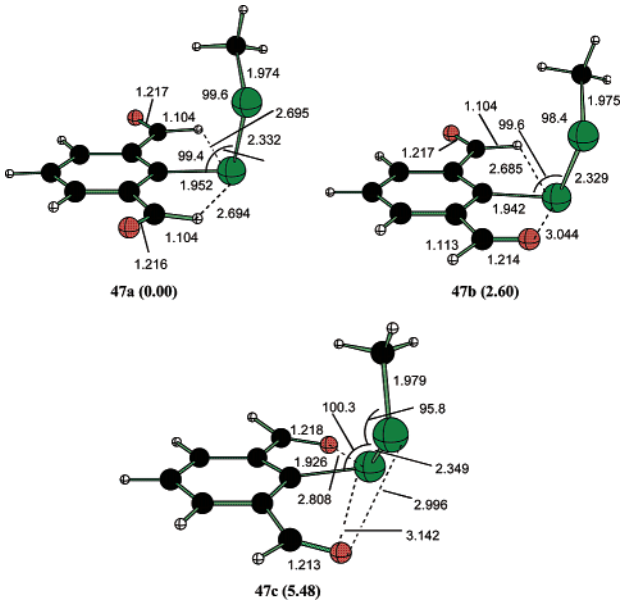


FIGURE 3. The B3LYP/6-31G* optimized geometries (Å and deg) and relative energies (kcal/mol) of bis(formyl) diselenide.

When selenium participates in nonbonding iteraction with ortho substitutes, the ideal situation would be a collinear geometry between the donor atom and the Se−X acceptor bond, which will help maximize the orbital iteraction between the oxygen lone pair with the Se−X σ^* orbital. The B3LYP/6-31G* optimized geometries of **47** reveal that the −Se-Se-Me unit is oriented out of plane, primarily due to the steric effects offered by substituents at both ortho positions. It is interesting to note that in **47c**, both formyl groups are bent out of plane, away from the selenium atom (Figure 3). This can be attributed to the orientation of the selenium lone pair and the repulsive interaction with the formyl oxygens, if the latter occupies a nearly in-plane position. Same discussion also holds good for monoselenide systems (**48a**−**c**) with 2,6-bisformyl substitution (vide infra), where the formyl groups are found out-of-plane in the (syn,syn) orientation.

While the formyl oxygens in bisformyl systems do not exhibit Se···O nonbonded interactions, these turn out to be interesting candidates having intramolecular hydrogen bonding. In both **47a** and **47b**, the distances between formyl hydrogen atoms and selenium is around 2.7 Å. Further, the NBO analysis with the second-order perturbation method reveals that a stabilizing orbital interaction is operating between one of the selenium lone pairs with the C−H σ^* orbital of the formyl group. It is interesting to note that electron delocalization between formyl oxygens and the Se−Se bond is absent in all three compounds (**47a**−**c**) considered here.[32] These predictions are in good agreement with the structural details obtained from our crystal structure studies, where all the oxygens were found to be too far away from selenium atoms highlighting the absence of any Se···O nonbonded interactions in bisformyl dislenides (**25** and **26**).

(29) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Vij, A.; Roy, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 3394.
(30) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 4463.
(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.
(32) Please see the Supporting Information.

TABLE 3. Important Bond Lengths (Å) and Bond Angles (deg) of Compounds 27

Se−C(1)	1.929(2)	C(1)−Se−C(7)	99.1(1)
Se−C(7)	1.919(2)	C(61)−H(61A)···Se(a)	134.3
H(61A)···Se(a)	2.928		

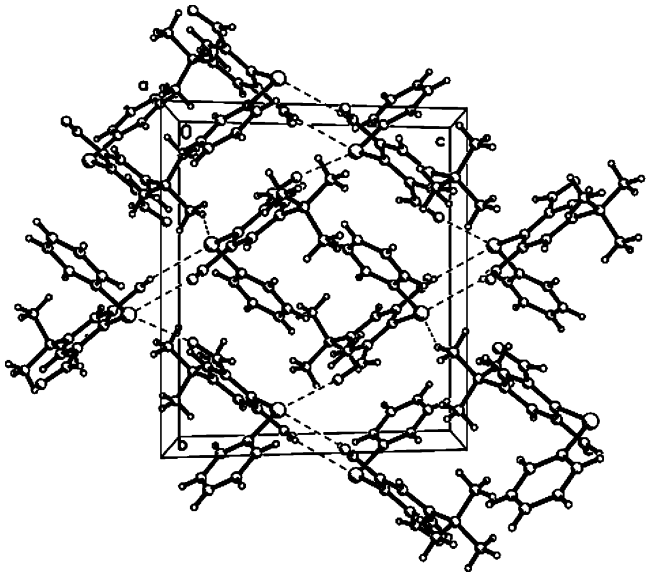


FIGURE 4. Packing diagram of compound **27** showing intermolecular interactions.

Comparison of the optimized structural parameters obtained at the B3LYP/6-31G* level (Figure 3) with those obtained from crystal structure studies (Tables 1 and 2) reveals a fairly close agreement. The fact that the computed structure does not take into account the solid-state packing effects as well as steric factors induced by bulkier substituents could be taken as the reason for the minor deviations in some of the geometrical parameters compared to the real systems.

Crystal Structure of Compound 27. The selected bond lengths and bond angles are listed in Table 3. The ORTEP diagram has been included in the Supporting Information as Figure S28.

The coordination geometry around Se is V-shaped with bond angle C(1)−Se−C(7) of 99.1(1)°, which is comparable to the structure of monoselenide **46** [97.8(1)°].[8m] Similar to **26**, in **27**, both the oxygen atoms of formyl groups are pointing away from the selenium center. However, the structure exhibits intermolecular C−H···Se interaction (2.928 Å, 134.3°). Only one of the formyl protons of the molecule is involved in a C−H···Se intermolecular interaction with the selenium atom of the another molecule and vice versa. Thus each pair of molecules form a centrosymmetric dimer (Figure 4). The corresponding distances and angles for C−H···Se interaction in compound **27** are comparable with those found for compound **26** and the other two reported examples.[29,30]

To explore the conformational and energetic details using computational methods we have considered another set of monoselenides as model systems representing compound **27**. The relative energies computed at the B3LYP/6-31G* level for **48a** (anti,anti), **48b** (syn,anti), and **48c** (syn,syn) and optimized geometries are given in Figure 5. The relative energy preferences follow the same order (**48a**−**c**) as in compound **47**. The NBO analyses on bisformyl systems [(syn,syn) and (syn,anti)] have revealed the absence of any significant delocalization of oxygen lone pair electrons into the Se−C σ^* orbitals, lowering the possibilities of nonbonded interactions through favorable orbital overlap. One of the key geometrical parameters is the Se···H distances in **48a** and **48b** which were found to be around 2.67 Å, highlighting an intramolecular Se···H interaction.

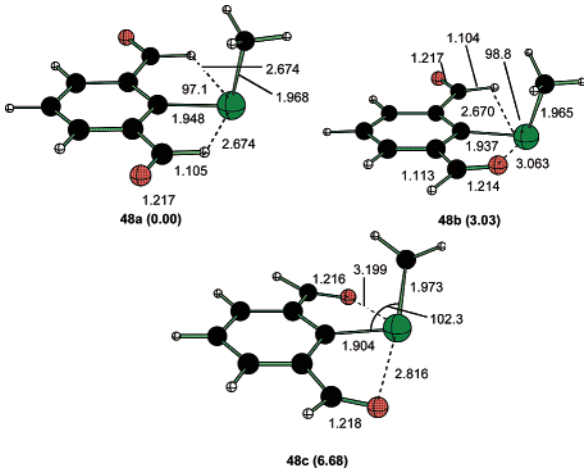


FIGURE 5. The B3LYP/6-31G* optimized geometries (Å and deg) and relative energies (kcal/mol) of bis(formyl) monoselenide.

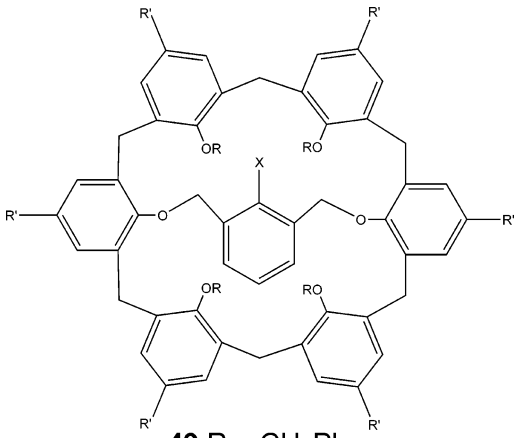
TABLE 4. Important Bond Lengths (Å) and Bond Angles (deg) of Compounds 34

Se(1A)−C(1A)	1.858(2)	Se(1A)−O(1A)	1.855(2)
Se(1B)−C(1B)	1.855(2)	Se(1B)−O(1B)	1.864(2)
Se(1A)···O(1A)	2.604	C(1A)−Se(1A)−O(1A)	86.47(9)
Se(1B)···O(1B)	2.465	C(1B)−Se(1B)−O(1B)	85.80(10)

Crystal Structure of Compound 34. A PLUTON view of compound **34** is shown in Figure S26 of the Supporting Information, and selected bond lengths and bond angles are listed in Table 4. The crystal structure of **34** has been briefly reported elsewhere.[12] Here we present only the salient features of the structure. The crystal structure contains a *dl* pair of diastereomers as two chiral centers are present at the acetal carbons of the five-membered selenenate ring. The Se−O bond lengths [Se(1A)−O(1A), 1.855(2) Å; Se(1B)−O(1B), 1.864(2) Å] are in good agreement with the value of 1.83 Å suggested by Pauling;[33] however, they are comparatively longer than that reported for the selenenic acid **49** [1.763(7) Å],[19a] BmtSeOH (Bmt = 2,6-{[2,6-$(CH_3)_2$-$C_6H_3]_2C_6H_3CH_2\}_2$-5-$C(CH_3)_3C_6H_2$−) [1.808(3) Å][34] and comparable with that of alkaneselenenic acid, Trip-SeOH (triptycene-9-selenenic acid) [1.866(3) and 1.908(5) Å].[35] Interestingly, the distances between selenium and formyl oxygen [Se(1A)···O(1A), 2.604 Å; Se(1B)···O(1B), 2.465 Å] are considerably smaller than the sum of the van der Waals radii (3.4 Å) and slightly greater than that

(33) Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(34) Goto, K.; Nagahama, M.; Mizushima, T.; Shimada, K.; Kawashima, T.; Okazaki, R. *Org. Lett.* **2001**, *3*, 3569.
(35) Ishii, A.; Matsubayashi, S.; Takahashi, T.; Nakayama, J. *J. Org. Chem.* **1999**, *64*, 1084.

observed in *o*-formylphenylselenenyl bromide [2.305(19) Å].[8m] The average Se···O distance (2.534 Å) is considerably shorter than the reported value for selenenic acid **49**,[19a] indicating the presence of strong selenium−oxygen intramolecular nonbonded interaction.



The Se−O and Se···O bonds are trans to each other with the O···Se−O bond angles 160.0° and 158.6°. The Se and O (−CHO) atoms lie in the same plane, i.e., the plane of the five-memered ring formed by Se···O interactions. In contrast with the present case, the crystal structures of **26** and **27**, which have two *o*-formyl groups, do not have any Se···O interactions. The packing diagram of compound **34** revealed the intermolecular hydrogen bonding between the oxygen of the formyl group and one of the hydrogens of the *tert*-butyl group of the other molecule.

There are some intriguing differences in the likely nonbonded interaction between monoformyl and bisformyl aryl systems. Natural Bond Orbital (NBO) analysis on the B3LYP/6-31G* geometries has identified the orbital as well as the electrostatic factors as the key to the nonbonded interaction in these systems.[32] The structural and energetic details of important low-energy conformers of the monoformyl mono- and diselenide systems are summarized in Figure 6 (**50a**,**b**, **51a**,**b**).

Particularly interesting is the reversal of preference of orientation of the formyl oxygens with respect to the selenium from anti to syn. In fact, the anti isomer in both mono- and diselenides was respectively found to be higher in energy by 3.21 and 4.77 kcal/mol compared to the corresponding syn isomer. Additionally, orbital interactions were predicted to be effective in delocalizing oxygen lone pairs into Se−Me σ^* or Se−Se σ^* respectively for mono- and diselenides, in agreement with the findings of Tomoda and others, on similar systems.[1k−o] As per the second-order perturbation analysis with the NBO method, the former interaction was found to be stabilizing by about 6 kcal/mol, while the latter one amounts to 10 kcal/mol. These predictions strongly support the fact that with monoformyl aryl ring systems, Se···O nonbonded interactions are bound to be stronger compared to bisformyl cases. This observation has been borne out by an earlier report from our group (structure **46**) where we found that monoformyl systems (similar to **46**) can participate in Se···O nonbonded interaction, having distances of the order of 2.8 Å.[9m]

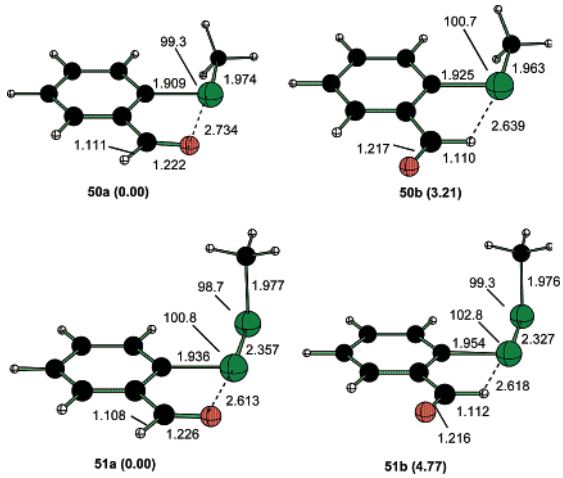


FIGURE 6. The B3LYP/6-31G* optimized geometries (Å and deg) and relative energies (kcal/mol) of monoformyl monoselenide and monoformyl diselenide.

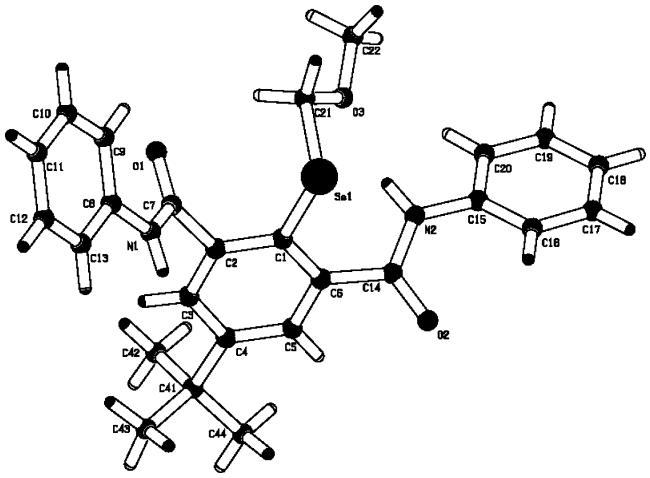


FIGURE 7. PLUTON diagram of compound **32**.

The B3LYP/6-31G* calculations on a number of model compounds reported here point to the fact that orbital as well as electrostatic factors contribute toward the nonbonded interactions between chalcogens.[36,37] While the computed natural charges on oxygen atoms (−0.5) indicate possible electrostatic interaction in monoformyl systems, these were found to be not particularly prominent in bisformyl cases.[38]

Crystal Structure of Compound 32. The synthesis of **32** has been published elsewhere.[9o] Figure 7 is a PLUTON view of compound **32** and selected bond lengths and bond angles are listed in Table 5. The

(36) We have looked at a representative system with the thioformyl group ortho to selenium, having syn orientation. The computed charge on sulfur (+0.02) was found to be much less than that compared to the corresponding oxygen, but the orbital interaction was significantly better having a second order perturbative stabilization energy of the order of 9.53 kcal/mol due to the delocalization of lone pair electrons on sulfur to the Se−Me σ^* orbital.

(37) Landrum, G. A.; Hoffmann R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1887.

(38) Charges are computed by using the natural population analysis on the B3LYP/6-31G* geometries (please see the Supporting Information).

TABLE 5. Important Bond Lengths (Å) and Bond Angles (deg) of Compounds 32

Se(1)−C(1)	1.927(2)	Se(1)···O(2)	4.261
Se(1)−C(21)	1.925(3)	Se(1)···N(1)	3.750
C(1)−Se(1)−C(21)	100.0(1)	Se(1)···N(2)	3.338
Se(1)···O(1)	3.519		

C(1)−Se(1)−C(21) bond angle [100.0(1)°] is comparable with that reported for 2-methylseleno-*N*-phenylbenzamide [99.5(1)°][9i] and 2-acetonylseleno-*N*-phenylbenzamide [101.6(2)°].[9e] The C(1)−Se(1) [1.927(2) Å] and C(21)−Se(1) [1.925(3) Å] distances are comparable with that reported for 2-methylseleno-*N*-phenylbenzamide [1.920(2) and 1.935(3) Å] and 2-acetonylseleno-*N*-phenylbenzamide [1.913(4) and 1.961(4) Å]. In contrast to the structure of **34** [Se···O, 2.604 and 2.465 Å], 2-methylseleno-*N*-phenylbenzamide [Se···O, 2.829 Å],[9i] 2-acetonylseleno-*N*-phenylbenzamide [Se···O, 2.636(4) Å],[9e] *N,N′*-dimethyl-2,2′-diselenodibenzamide [Se···O, 2.849(8) Å], and *N,N′*-diphenyl-2,2′-diselenodibenzamide [Se···O, 2.742(5) Å],[9h] there is no considerable contact between selenium and oxygen or selenium and nitrogen. The Se···O distances [3.519 and 4.261 Å] or Se···N distances [3.338 and 3.750 Å] are larger than the sum of van der Waals radii of these two atoms. Interestingly, bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] telluride and bis-[2-(*N*,*N*-dimethylaminomethyl)phenyl] telluride showed the N···Te···N intramolecular nonbonded interactions in their crystal structures.[39]

Conclusion

Organoselenium derivatives (**26**−**30**) having two formyl groups ortho to selenium have been successfully synthesized. From the present results and previous studies,[9o,12] it is apparent that the organoselnium derivatives with two formyl/carbamoyl groups ortho to selenium differ significantly with respect to the structural features and reactivity compared to the organoselenium derivatives with only one formyl/carbamoyl group ortho to selenium. The halogenation reaction of bis(*o*-formylphenyl) diselenide affords the expected selenenyl halides; in contrast, the halogenation reation (treatment $SOCl_2$, Br_2, or I_2) of diselenide **26** results in the formation of unusual product, i.e., selenenate ester **34**. A similar reactivity of monoselenides **32** having two carbamoyl groups ortho to selenium was observed, which on treatment with an equivalent amount of bromine afforded cyclic seleninamides, i.e., ebselen derivatives.[9o]

The X-ray crystal structures of **26** and **27** having two formyl groups and **32** having two phenylcarbamoyl groups do not show any Se···X (X = O, N) intramolecular interactions, whereas these interactions are present in the crystal structures of related compounds **34**, **44**, **46**, 2-methylseleno-*N*-phenylbenzamide, 2-acetonylseleno-*N*-phenylbenzamide, *N,N′*-dimethyl-2,2′-diselenodibenzamide, and *N,N′*-diphenyl-2,2′-diselenodibenzamide which have only one formyl/carbamoyl group ortho to selenium. Interestingly, the observation of Furukawa et al.[1j] that three chalcogens (S, Se, Te) nearly in juxtaposition develop a repulsive force between them appears to be true for compound **26**, **27**, and **32** which have the lightest terminal chalcogens, i.e., the O, Se, O system. Density functional theory calculations at the B3LYP/6-31G* level are also in agreement with these results and predict that for the monoformyl-substituted systems (**50a**,**b**), the syn conformer (when formyl oxygen is near to selenium) is energetically more favorable than the anti conformer (formyl oxygen pointing away form selenium). This preference is opposite in diformyl systems (**47a**−**c**, **48a**−**c**), where the anti,anti conformer is more stable. The absence of such intramolecular interactions in **26** is probably the driving force for the formation of selenenate ester **34**. The absence of any interactions in **26** destabilizes the intermediate selenenyl halide, which in turn converts into the selenenic acid in the presence of water. The packing of crystals of **26** and **27** exhibited uncommon intermolecular C−H···Se interactions.

Experimental Section

4-*tert*-Butyl-2,6-di(formyl)phenylbromide **22**,[14] di-*n*-butyl diselenide,[40] bis(4-*tert*-butyl-2,6-di(methyl)phenyl) diselenide,[5h] dimethoxymethyl diselenide,[2f] and selenide **32**[9o] were synthesized by literature methods.

2-Bromo-5-*tert*-butylbenzene-1,3-dicarbaldehyde diacetal (23). To a solution of **22** (5.92 g, 20 mmol) in benzene (50 mL) were added ethylene glycol (3.40 mL, 60 mmol) and *p*-toluenesulfonic acid (0.6 g, 3 mmol) and the mixture was refluxed accompanied by water separation by Dean−Stark trap until the completion of the reaction. Excess solvent was removed under vacuum and the residue was treated with water (50 mL); the organic layer was retained. The aqueous layer was extracted with ether (100 mL). The combined organic layer was dried over sodium sulfate and concentrated under vacuum to afford **23** as a white solid (7.77 g, 99%). Mp 82−84 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 2H), 6.16 (s, 2H), 4.12−4.22 (m, 2H), 4.03−4.12 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 31.1, 34.7, 65.3, 102.6, 120.5, 125.6, 136.4, 150.4; ES MS *m/z* (%) 357 (M^+, 7), 313 (70), 269 (100), 213 (18), 142 (25). Anal. Calcd. for $C_{16}H_{21}BrO_4$: C, 53.72; H, 6.05. Found: C, 53.81; H, 5.92.

Bis(4-*tert*-butylbenzene-2,6-dicarbaldehyde diacetal) Diselenide (25). To a solution of compound **23** (0.714 g, 2 mmol) in dry ether (15 mL) taken in a three-necked (50 mL) flask fitted with rubber septum and a nitrogen inlet was added dropwise with stirring a 1.6 M solution of *n*-BuLi (1.25 mL, 2 mmol) at room temperature. The mixture was stirred for 1 h at room temperature. Selenium powder (0.158 g, 2 mmol) was added under a brisk flow of nitrogen. After 1 h of additional stirring at room temperature, the reaction mixture was poured into a 10% solution of $NaHCO_3$ (25 mL) and extracted with chloroform (3 × 20 mL). The combined chloroform layer was dried over sodium sulfate and evaporated under vacuum to give an orange oil. Slow evaporation of benzene/hexane (5:1) solution afforded **25** as an orange solid, which was recrystalized from acetonitrile (0.50 g, 70%). Mp 196−198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 4H), 5.99 (s, 4H), 3.98−4.10 (m, 4H), 3.80−3.93 (m, 4H), 1.34 (s, 18H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 31.2, 34.9, 65.1, 103.4, 124.7, 127.8, 140.9, 152.9; ^{77}Se NMR (500 MHz, $CDCl_3$) δ 373.6; FAB MS *m/z* (%) 713 (M^+, 63), 357 (100), 328 (16), 313 (44), 297 (8), 277 (5), 269 (21), 241 (9); IR (KBr) 2969, 2881, 1470, 1367, 1110 cm^{-1}. Anal. Calcd for $C_{32}H_{42}O_8Se_2$: C, 53.95; H, 5.93. Found: C, 54.24; H, 6.27.

Bis(2,6-diformyl-4-*tert*-butylphenyl) Diselenide (26).[12] Sodium diselenide (8 mmol) was prepared from selenium and sodium in the presence of a catalytic amount of naphthalene in dry THF (25 mL). 2,6-Diformyl-4-*tert*-butyl-1-bromobenzene (1.076 g, 4 mmol) was added to this solution. After being stirred for 4 h at room temperature the reaction mixture was

(39) (a) Apte, S. D.; Singh, H. B.; Butcher, R. J. *J. Chem. Res.* (*S*) **2000**, 160; (*M*) **2000**, 0559. (b) Kaur, R.; Singh, H. B.; Butcher, R. J. *Organometallics* **1995**, *14*, 4755.

TABLE 6. Crystal Data and Structure Refinement for 25, 26, 27, 34, and 32

	25	26	27	34	32
empirical formula	$C_{32}H_{42}O_8Se_2$	$C_{24}H_{26}O_4Se_2$	$C_{18}H_{18}O_2Se$	$C_{24}H_{26}O_5Se_2$	$C_{26}H_{27}N_2O_3Se$
formula wt	712.58	536.37	345.28	352.36	495.46
cryst system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
space group	*P*2(1)2(1)2(1)	*P*2(1)/*c*	*P*2(1)/*c*	$P\bar{1}$	$P\bar{1}$
a (Å)	10.052(4)	13.1015(19)	9.624(3)	8.783(3)	9.7598(7)
b (Å)	13.982(6)	11.423(2)	13.494(4)	8.714(3)	10.5955(9)
c (Å)	22.653(15)	32.125(5)	12.323(4)	14.740(4)	12.6066(12)
α (deg)	90	90	90	88.829(6)	88.969(11)
β (deg)	90	91.448(12)	106.284(5)	81.012(5)	81.747(10)
γ (deg)	90	90	90	81.278(5)	70.167(9)
V (Å^3)	3184(2)	4806.1(14)	1536.2(8)	1101.3(6)	1212.96(19)
Z	4	8	4	4	2
D(calcd) (Mg/m^3)	1.487	1.483	1.493	1.666	1.357
abs coeff (mm^{-1})	2.371	3.103	2.446	3.391	1.577
obsd reflens [$I > 2\sigma$]	22850	11213	11382	5287	19069
final $R(F)$ [$I > 2\sigma(I)$][a]	0.0566	0.0859	0.0261	0.0349	0.0379
$wR(F^2)$ indices [$I > 2\sigma(I)$]	0.1169	0.1772	0.0561	0.0765	0.0787
data/restrains/parameters	7731/0/385	10764/48/618	3761/0/212	5287/0/286	4810/0/293
goodness of fit on F^2	0.852	1.044	0.982	0.923	0.804

[a] Definitions: $R(F_0) = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

poured into water (50 mL) and extracted with $CHCl_3$ (3 × 20 mL). The combined organic layer was dried over sodium sulfate and concentrated under vaccum to leave an orange oil, which solidified by adding hexane to the saturated dichloromethane solution. The orange solid was recrystalized from $CHCl_3$/petroleum ether (1:1) (0.43 g, 40%). Mp 116−118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 10.18 (s, 4H), 8.08 (s, 4H), 1.39 (s, 18H); ^{13}C NMR (500 MHz, $CDCl_3$) *δ* 191.2, 155.4, 137.8, 133.2, 131.5, 35.2, 30.8; ^{77}Se NMR (500 MHz, $CDCl_3$) *δ* 375.8; IR (KBr) 2967, 2877, 1685, 1479, 1367, 1222, 937, 701 cm^{-1}; FAB MS *m/z* (%) 674 (16), 551 (17), 537 (36, M$^+$), 523 (26), 458 (15), 429 (11), 408 (19), 269 (100). Anal. Calcd for $C_{24}H_{26}O_4Se_2$: C, 53.53; H, 4.83. Found: C, 53.83; H, 5.03.

4-*tert*-Butyl-2,6-di(formyl)phenyl Phenyl Selenide (27). To a solution of diphenyl diselenide (0.187 g, 0.6 mmol) in deoxygenated ethanol (10 mL) was added $NaBH_4$ (0.042 g, 1.1 mmol) at 0 °C. The reaction mixture was stirred for 20 min at room temperature. Compound **22** (0.269 g, 1 mmol) was added to the reaction mixture at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 2 h. The solvent was evaporated under vacuum and the residue was dissolved in $CHCl_3$ (10 mL) and washed with water (10 mL) and the water layer was extracted with $CHCl_3$ (2 × 10 mL). The combined chloroform layer was dried over sodium sulfate and concentrated under vacuum to give a yellow solid, which was purified by column chromatography. First the diphenyl diselenide fraction was eluted with petroleum ether (60−80) and then the monoselenide was eluted with ethyl acetate/petroleum ether (60−80) (1:9) (0.33 g, 95%). Mp 120−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 10.70 (s, 2H), 8.23 (s, 2H), 7.22 (s, 5H), 1.39 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) *δ* 30.9, 35.2, 127.4, 129.9, 130.4, 131.5, 132.6, 133.7, 137.9, 153.9, 193.2; ^{77}Se NMR *δ* 237.74; FAB MS *m/z* (%) 346 (M$^+$, 100), 523 (26), 507 (5), 458 (15), 429 (11), 408 (19), 269 (33); IR (KBr) 1678 ($\nu_{C=O}$) cm^{-1}. Anal. Calcd for $C_{18}H_{19}O_2Se$: C, 62.63; H, 5.25. Found: C, 63.10; H, 5.25.

***n*-Butyl 4-*tert*-2,6-Di(formyl)phenyl Selenide (28).** Compound **28** was prepared from compound **22** (0.269 g, 1 mmol) and di-*n*-butyl diselenide (0.163 g, 0.6 mmol) according to the procedure described for **27**. Compound **28** was purified by column chromatography, using petroleum ether as an eluent (0.28 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 10.82 (s, 2H), 8.19 (s, 2H), 2.80 (t, 2H), 1.53−1.63 (m, 2H), 1.31−1.45 (m, 2H), 1.39 (s, 9H), 0.87 (t, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) *δ* 13.4, 22.7, 30.9, 32.1, 32.8, 35.0, 130.9, 134.8, 138.3, 153.0, 193.7; ^{77}Se NMR (300 MHz, $CDCl_3$) *δ* 98.34; ES MS *m/z* (%) 326 (M$^+$, 5), 269 (100), 227 (18), 115 (25); IR (KBr) 1690 ($\nu_{C=O}$) cm^{-1}.

4-*tert*-Butyl-2,6-di(formyl)phenyl 4′-*tert*-Butyl-2′,6′-di(methyl)phenyl Selenide (29). Compound **29** was prepared from compound **22** (0.269 g, 1 mmol) and bis(4-*tert*-butyl-2,6-dimethylphenyl) diselenide (0.240 g, 0.6 mmol) according to the procedure described for **27**. Compound **29** was purified by column chromatography, using petroleum ether (60−80)/ethyl acetate (9:1) as an eluent (0.36 g, 85%). Mp 126−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 10.37 (s, 2H), 8.03 (s, 2H), 7.04 (s, 2H), 2.30 (s, 6H), 1.35 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) *δ* 24.3, 31.0, 31.2, 34.5, 35.0, 126.2, 131.2, 132.0, 137.4, 137.4, 138.6, 140.5, 151.8, 152.4, 191.9; FAB MS *m/z* (%) 430 (M$^+$, 92), 415 (8), 399 (5), 391 (13), 269 (100), 240 (7), 225 (8), 178 (4), 165 (8), 128 (10), 119 (12), 105(8); IR (KBr) 1690 ($\nu_{C=O}$) cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_2Se$: C, 67.14; H, 7.04. Found: C, 66.50; H, 6.79.

Bis(4-*tert*-butyl-2,6-di(formyl)phenyl) Selenide (30). To the stirred solution of Li_2Se [0.5 mmol] (prepared by adding 1 M super hydride ($LiBHEt_3$) solution in THF (10 mL) to selenium powder (0.0395 g) at room temperature in THF) was added compound **22** (0.268 g, 1 mmol) at 0 °C. The reaction mixture was allowed to come to the room temperature and the stirring was continued for an additional 2 h. The reaction mixture was poured into water (20 mL) and extracted with $CHCl_3$ (20 mL). The combined organic layer was dried over sodium sulfate and concentrated to get an orange oil that was purified on silica gel column (1:9 ethyl acetate/petroleum ether). The yellow solid obtained was crystalized from ethyl acetate/petroleum ether (0.12 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 10.23 (s, 4H), 8.01 (s, 4H), 1.35 (s, 18H); ^{13}C NMR (300 MHz, $CDCl_3$) *δ* 30.9, 35.1, 133.4, 136.6, 137.5, 153.4, 190.8; ^{77}Se NMR (300 MHz, $CDCl_3$) *δ* 241; ES MS *m/z* (%) 458 (M$^+$, 36), 429 (68), 413 (32), 269 (28); IR (KBr) 1696 ($\nu_{C=O}$) cm^{-1}. Anal. Calcd for $C_{24}H_{26}O_4Se$: C, 63.03; H, 5.73. Found: C, 62.71; H, 6.04.

Selenenate Ester (34).[12] To a stirred solution of diselenide **26** (0.268 g, 0.5 mmol) in CCl_4 (10 mL) was added Br_2 (0.08 g, 0.5 mmol) in CCl_4 under nitrogen atmosphere. After the mixture was stirred for 1 h, ice−water (10 mL) was added and stirring was continued for additional 10 min. The reaction mixture was extracted with $CHCl_3$ (10 mL), dried over sodium sulfate, and concentrated under vacuum to give an orange oil. Crystalline yellow colored compound was obtained by purification on silica gel column (3:97 acetone/petroleum ether) and crystallization from CH_2Cl_2/petroleum ether (0.184 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$, major isomer) *δ* 10.19 (s, 2H), 7.97 (d, 2H), 7.75 (d, 2H), 6.89 (s, 2H), 1.37 (s, 18H); ^{13}C NMR (300 MHz, $CDCl_3$) *δ* 190.2, 151.4, 143.0 137.6, 130.1, 129.0, 128.6, 102.7, 35.0, 31.6; ^{77}Se NMR (300 MHz, $CDCl_3$) *δ* 1401.3; IR (KBr) 2962, 2874, 1689, 1549, 1221, 930 cm^{-1}; FAB MS *m/z* (%) 553 (23, M$^+$), 537 (43), 524 (30), 508 (60), 479 (32), 422

(70), 404 (24), 269 (97). Anal. Calcd for $C_{24}H_{26}O_5Se_2$: C, 52.2; H, 4.74. Found: C, 51.61; H, 4.50.

Reaction of 22 with Sodium Methoxymethyl Selenolate. A similar procedure was followed as described for the synthesis of **27** with bis(methoxymethyl) diselenide (0.46 g, 3.72 mmol) and compound **22** (1.0 g, 3.72 mmol). The orange oil obtained was purified by column chromatography, using petroleum ether (60−80)/ethyl acetate (9:1) as an eluent, to afford **30** as yellow solid (yield: 0.8 g, 94%).

X-ray Crystallography. The diffraction measurements for compounds **25**, **26**, **27**, and **32** were performed at room temperature and for compound **27** at 93 K with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The structures were solved by direct methods and full-matrix least-squares refinement on F^2 (program SHELXL-97).[41] Hydrogen atoms were localized by geometrical means. A riding model was chosen for refinement. The isotropic thermal parameters of the H atoms were fixed at 1.5 times (CH_3 groups) or 1.2 times U(eq) (Ar−H) of the corresponding C atom. Some details of the refinement are given in Table 6.

Computational Methods. Full geometry optimizations were performed on suitably designed model systems at the B3LYP/6-31G* level of theory.[42] All stationary points were characterized as minima by corresponding Hessian indices. The relative energies are computed based on the bottom-of-the-well energies without inclusion of zero-point corrections. Orbital interactions were analyzed with the Natural Bond Orbital (NBO) method[43] at the B3LYP/6-31G* level. All calculations were performed with the Gaussian98 suite of quantum chemical programs.

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Supporting Information Available: ^{1}H, ^{13}C, and ^{77}Se NMR spectra; optimized geometries, energies, important sections of NBO delocalizations, natural population (charges on atoms) for all the computed structures, and tables for crystallographic data of **25**, **26**, **27**, and **32**, packing diagram for **34**, and a plot of Se···O distances verses ^{77}Se NMR chemical shifts. This material is available free of charge via the Internet at http://pubs.acs.org.

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