

# Generation and Mesolytic Dynamics of Organoselenane and Selenosilane Radical Ions: Development of Mechanistically Interesting and Synthetically Useful Chemistry<sup>†</sup>

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**ABSTRACT**

PET oxidation of PhSe–SePh and R–CH<sub>2</sub>–Se–R' generates an electrophilic selenium and carbocationic species, respectively. Similarly, one-electron reductive activations of R–CH<sub>2</sub>–Se–R' and R<sub>3</sub>–Si–SePh produces alkyl and alkyl silyl radicals, respectively. The possible structure of the reactive electrophilic selenium species is discussed and the fragmentation of –C–Se]<sup>++</sup> is found to be nucleophilic-assisted. These mechanistically interesting studies have been shown to be useful in initiating various synthetic reactions.

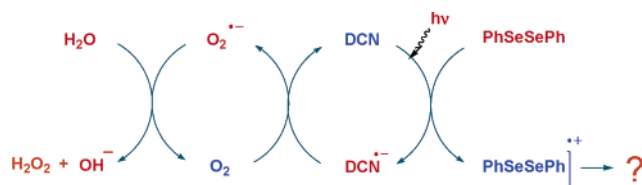
**Introduction**

Addition or removal of an electron determines the chemical fate of the molecular entities to a large extent, although at the primary stage bonds are neither broken nor formed. Photoexcitation, which renders well-defined redox potential differences between two interacting species, has emerged an increasingly useful tool in initiating electron-exchange processes and generating radical ions from neutral substrates.<sup>1–5</sup> The concept of photoinduced electron transfer (PET) processes in generating radical ions has grown rapidly in the recent past, and sufficiently vast literature has accumulated on the chemical dynamics and reactivity profiles of these short-lived odd-electron species, which has also led to the development of several new and novel synthetically useful chemical reactions.<sup>6–8</sup> Product formation in these transformations is often governed by the mesolysis<sup>9</sup> of the initially formed radical ions into charged or neutral species or both.

The exchange of electron follows free-energy gap law,<sup>10</sup> and under thermodynamically favorable PET reactions

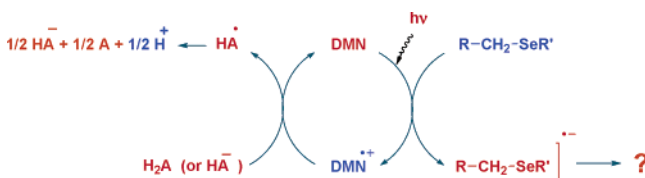
Ganesh Pandey was born in Varanasi, India, on July 5, 1954. After obtaining his Ph.D. from Banaras Hindu University (under the direction of K. N. Mehrotra) in 1980, he proceeded to Purdue University for a postdoctoral study in the group of H. A. Morrison. On returning, he first joined IICT, Hyderabad, in 1984 and later moved to NCL, Pune. His research interest includes development of newer synthetic strategies through PET processes and natural products synthesis.

Smita R. Gadre was born and raised in Pune. She studied organic chemistry from University of Pune and completed her Ph.D. in 1994 while working in NCL under the supervision of Dr. Rajappa. Immediately afterward, she joined the group of Dr. Pandey and has been contributing toward the development of new synthetic methodology and total synthesis.



DCN = 1,4 Dicyanonaphthalene

**FIGURE 1.** PET reaction cycle to initiate PET oxidation of organoselenanes.



DMN = 1,5 - dimethoxynaphthalene

H<sub>2</sub>A = Ascorbic acidHA<sup>-</sup> = Ascorbate ion

**FIGURE 2.** PET reaction cycle to initiate PET reduction of organoselenane and selenosilanes.

( $\Delta G_{\text{et}} < 0$ ), the radical ions are formed either as a contact ion pair (CIP) or as a solvent-separated ion pair (SSIP).<sup>11</sup> The reactivity profile of these intermediates is highly solvent-dependent. The SSIPs are more stable than CIPs in polar solvents ( $\epsilon > 7$ ), and in these solvents, the highly solvated radical ions can separate to form free radical ion pairs (FRIP).<sup>12</sup> Often, the efficiency of PET processes is limited by the rapid back electron transfer (BET) and the main challenge in designing an efficient reaction lies in circumventing this energy-wasting process so as to optimize the amount of useful chemistry that can be ensued. Several of the strategies that have been utilized toward this end include the facilitation of solvent cage escape to provide increased yields of FRIP from which BET efficiencies are greatly diminished.<sup>2,7,11,13–18</sup>

As a fundamental curiosity, we got interested in exploring the chemical dynamics and synthetic potentials of PhSe–SePh]<sup>++</sup>, R–CH<sub>2</sub>–Se–R']<sup>++</sup>, R–CH<sub>2</sub>–SeR']<sup>•+</sup>, and R<sub>3</sub>–Si–SePh]<sup>-•</sup> and innovated new and improved PET reaction cycles (Figures 1 and 2, respectively) to provide increased FRIP yields of these species. Our endeavors in developing these improved PET cycles, employing multicomponent “electron relay” system in aqueous solvents, may have partly been guided by the strategies developed to mimic photosynthesis.<sup>19,20</sup> We chronicle in this Account the emergence of conceptually new and synthetically interesting chemistry from our study in this area.

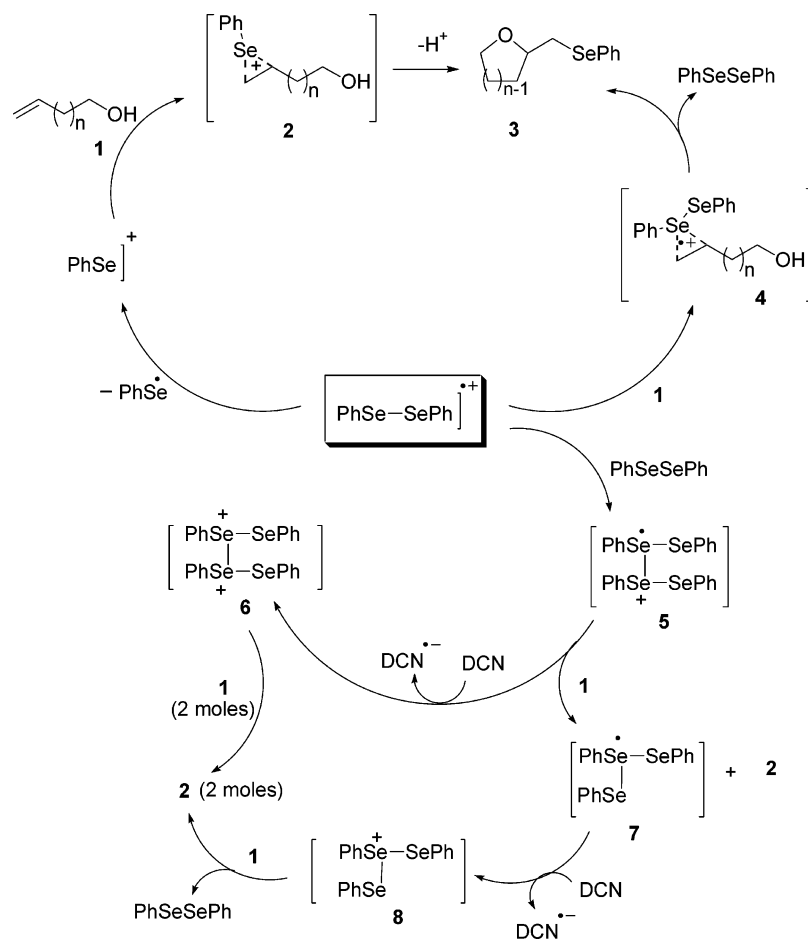
## PET Activation of PhSe–SePh to an Electrophilic Selenium Species: Selenoetherification Reactions.

PET oxidation of PhSe–SePh to PhSe–SePh]<sup>++</sup> is achieved through the photosystem as shown in Figure 1, employing

<sup>†</sup> Dedicated to Prof. G. Mehta on the occasion of his 61st birthday.

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Scheme 1. PET-Generated Electrophilic Selenium Species and Selenoetherification reaction



1,4-dicyanonaphthalene (DCN) as a light-harvesting electron acceptor<sup>21</sup> in aqueous acetonitrile. Dissolved oxygen in the solvent is found to be sufficient to regenerate DCN through the cycle as shown in Figure 1. The excited-state interactions between the <sup>1</sup>DCN\* and PhSe–SePh pair via electron-transfer processes is established<sup>22,23</sup> by estimating some important photophysical parameters such as the diffusion-controlled fluorescence quenching rate constant ( $1.83 \pm 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ;  $K_{\text{diff}} = 2.30 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) of DCN by PhSe–SePh and the exergonic value for free energy change associated with the electron transfer ( $\Delta G_{\text{et}} = -14.75 \text{ kcal mol}^{-1}$ ) processes. Other possible competing pathways for DCN fluorescence quenching, either by ground-state molecular association or by exothermic singlet energy transfer from the <sup>1</sup>DCN\* or by heavy-atom-induced intersystem crossing,<sup>24</sup> are also ruled out with the aid of appropriate experiments.

In the absence of any suitable spectroscopic techniques available to us for probing the fate of PhSe–SePh]<sup>•+</sup>, we resorted to a synthetic strategy of trapping electrophilic selenium species for selenoetherification reaction. PET activation of PhSe–SePh in the presence of **1** through the photosystem as depicted in Figure 1 produced **3** in good yield suggesting the involvement of an electrophilic selenium species in this reaction.<sup>22,23</sup> Involvement of various possible electrophilic selenium species in initiating the formation of **3** along with their mechanistic pathways and reactive intermediates is summarized in Scheme 1.

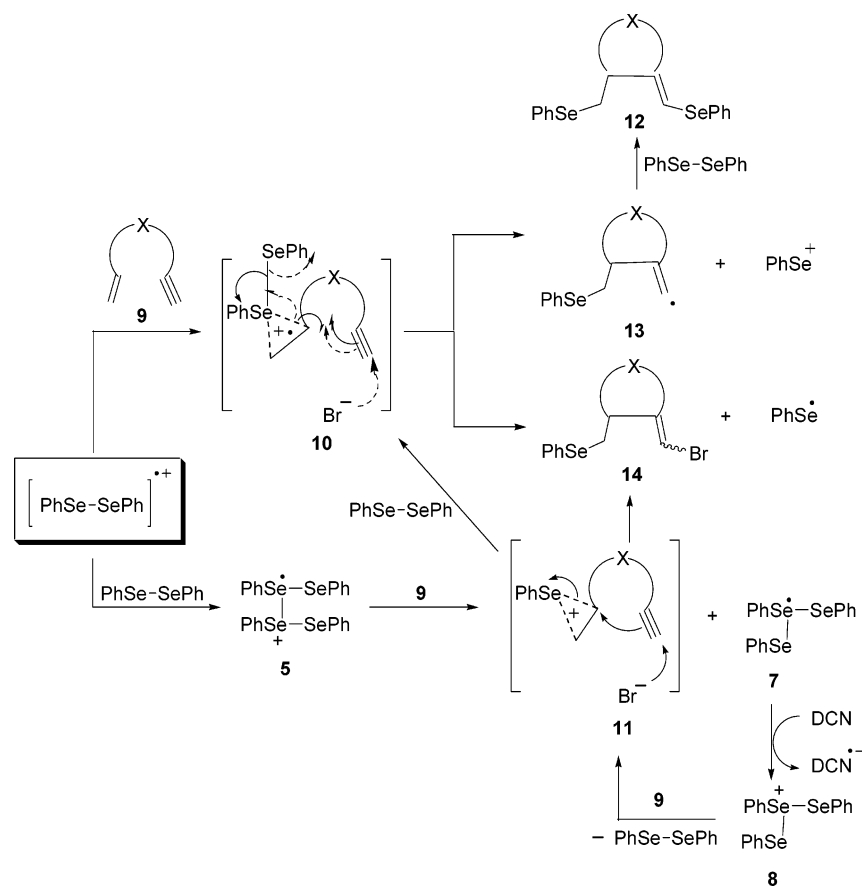
Although we do not have any support in favor of or against any one of these proposed intermediates, the reaction through distonic radical cation **5** appears more convincing because of the reported<sup>25</sup> dimeric structure of organoselenium radical cation. Comparison of the identical rate constant values ( $K_{\text{etr}} = 107.04 \pm 10.62$ ), obtained through the double reciprocal plot of  $\Phi_{\text{dissapp}}$  vs [PhSe–SePh]<sup>-1</sup> ( $\Phi^{-1}$  vs  $[Q^{-1}]$ ), and fluorescence quenching rate constant ( $K_{\text{qfr}} = 183.20 \pm 6.02$ ) suggests a common electron transfer (ET) mechanism<sup>22,23</sup> for both photophysical and photochemical processes between DCN–PhSe–SePh pairs.

Selenoetherification of a number of unsaturated alcohols in fairly good yields (60–72%) established the generality and the synthetic utility of this reaction. Electrophilic selenium intermediates are excellent initiators for the ring closure reaction of unsaturated substrates with proximate nucleophiles and several reagents/approaches are known<sup>26</sup> for the generation of this (PhSe<sup>+</sup>) species. However, the present strategy of in situ activation of PhSe–SePh to an electrophilic species is conceptually new and environmentally benign.

## Electrophilic Selenium-Mediated Enyne Cyclization: A New Carbocyclization Strategy

To explore further the utility of the PET-generated electrophilic selenium species, we envisaged a unique carbocyclization strategy by attempting the cyclization of

Scheme 2. PET-Generated Electrophilic Selenium Species in Enyne Cyclizations



enyne **9** (Scheme 2). It was visualized that the PET-generated electrophilic selenium species, which is devoid of the counteranion, will selectively react with the olefinic part of **9** owing to marked differences in the nucleophilicity between an olefin and acetylene<sup>27</sup> and would produce either intermediate **10** or intermediate **11** depending upon the structure of electrophilic selenium species. Intramolecular cyclization of these intermediates by an acetylenic moiety could produce either radical cyclized product **12** or ionic product **14** or both by following the mechanistic pathways as suggested in Scheme 2.

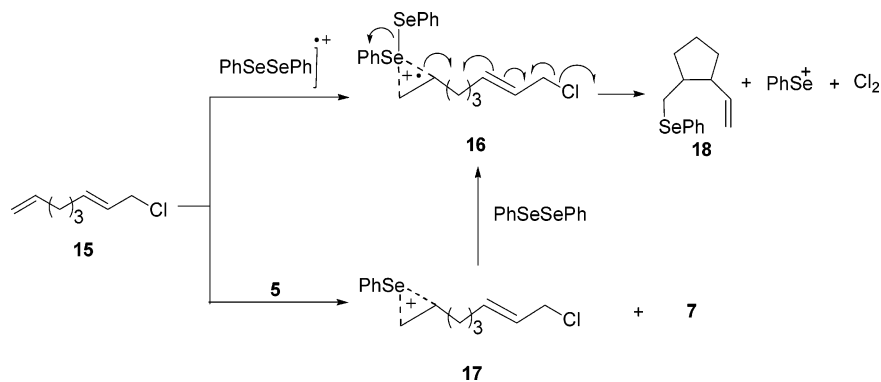
Indeed, the cyclization of **9**, utilizing PET-generated electrophilic selenium intermediate in the presence of *n*-tetrabutylammonium bromide (in the presence of strong nucleophilic environment, polarization of the acetylene bond occurs leading to nucleophilic reactions<sup>28</sup>), produced both compounds **12** (minor) and **14** (major) (Scheme 2).<sup>29,30</sup> The possibility of the formation of **12** by  $\text{PhSe}^\bullet$  mediation, via addition to either the olefin or the acetylene, followed by subsequent radical cyclization reaction, is ruled out because the addition of  $\text{PhSe}^\bullet$  to an olefin is reversible<sup>31,32</sup> and that to the acetylenes occurs only under some special experimental conditions.<sup>33</sup> The suggested involvement of intermediate **10**, formed either by the reaction of  $[\text{PhSe-SePh}]^{2+}$  or by that of **11** (Scheme 2), in the formation of **12** is supported by studying<sup>30</sup> the cyclization of 1-chloro-2,7-octadiene (**15**), which provided **18** through the radical chain initiation as shown in Scheme 3.

The above enyne cyclization strategy is conceptually new and is found to have additional advantages due to the addition of the multifunctional appendages in the product, amenable for further synthetic manipulations. The enyne cyclization is usually known to be performed by transition metal catalyses.<sup>34,35</sup> Generality and the synthetic usefulness of this strategy are established by studying a number of examples.<sup>30</sup>

### Diastereoselective Oxselenylation Reaction: Synthesis of $\alpha,\alpha'$ -*trans*-Dialkyl Cyclic Ethers.

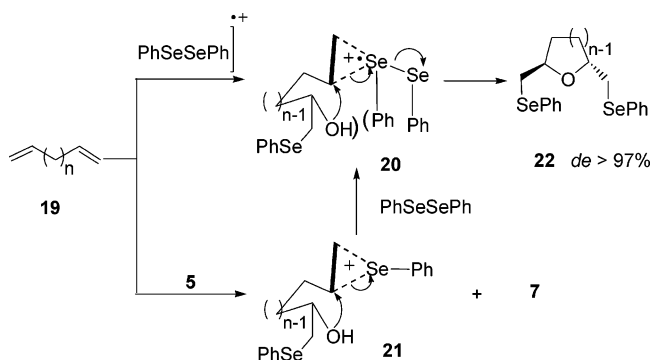
Another synthetic potential of PET-promoted in situ generated electrophilic selenium species was visualized in effecting *trans*-selective oxselenylation of 1,*n*-diolefins (**19**, Scheme 4) due to the anticipated *syn*-addition of the hydroxyl moiety from the expected transition state structures **20** (Scheme 4). It may be important to highlight here that oxselenylation of **19**, employing classical electrophilic selenium reagents ( $\text{PhSeCl}$  or  $\text{PhSeCN-CuCl}_2$ ), is reported<sup>36</sup> to be nonselective and produces an equal mixture of both *cis* and *trans*  $\alpha,\alpha'$ -dialkyl cyclic ethers. To our delight, when **19** was subjected to the PET-promoted oxselenylation reaction, it produced *trans*- $\alpha,\alpha'$ -dialkyl cyclic ethers **22** in very high diastereoselectivity (de > 97%)<sup>37</sup> (Scheme 4). The synthetic merit of this strategy is suggested by constructing various *trans*- $\alpha,\alpha'$ -dialkyl tetrahydrofurans, tetrahydropyrans, and oxepanes<sup>37</sup>—

Scheme 3. Electrophilic Selenium-Mediated Cyclization of 1-Chloro-2,7-octadiene

Table 1. Photophysical Constants to Establish PET Processes between  $^1\text{DCN}^*$ –**23a–d** Pairs

selenides <b>23</b> <sup>a</sup>		$K_{\text{qf}}^b$ ( $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ )	$K_{\text{qet}}^c$ ( $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ )	$E_{1/2}^{\text{oxid}}$ (eV)	$\Delta G_{\text{et}}^e$ (kcal mol <sup>-1</sup> )	$\Phi_{\text{disap}}^f$	$\Phi_{\text{lim}}^{f,g}$	
R	R'							
<b>a</b>	CH <sub>3</sub>	Ph	$1.92 \pm 0.07$	$1.59 \pm 0.05$	1.35	-18.90	$0.012 \pm 0.001$	$0.054 \pm 0.002$
<b>b</b>	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	Ph	$0.44 \pm 0.03$	$0.26 \pm 0.02$	1.62	-12.66	$0.021 \pm 0.002$	$0.172 \pm 0.007$
<b>c</b>	Ph	PhCH <sub>2</sub>	$0.54 \pm 0.02$	$0.54 \pm 0.04$	1.60	-13.08	$0.023 \pm 0.002$	$0.121 \pm 0.005$
<b>d</b>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	$0.47 \pm 0.04$	$0.59 \pm 0.04$	1.65	-11.99	$0.015 \pm 0.001$	$0.141 \pm 0.006$

<sup>a</sup> Errors are standard deviations from the average. <sup>b</sup> From fluorescence quenching Stern–Volmer plot. <sup>c</sup> From reciprocal plot;  $(\Phi_{\text{disap}})^{-1}$  vs  $[\mathbf{a-d}]^{-1}$ . <sup>d</sup> Referred to saturated calomel electrode (SCE) using tetraethylammonium perchlorate as electrolyte in dry acetonitrile. <sup>e</sup>  $\Delta G_{\text{et}}$  expressed in kcal/mol (calculated employing Weller equation<sup>4</sup> ( $\Delta G_{\text{et}} = E_{1/2}^{\text{oxid}} - E_{1/2}^{\text{red}} - E_{0,0}$ ); reduction half-wave potential ( $E_{1/2}^{\text{red}}$ ) for DCN is -1.28 eV, and  $E_{0,0} = 3.45$  eV (ref 3a)). <sup>f</sup> Light intensity evaluated by uranyl oxalate actinometry. <sup>g</sup> At infinite donor concentration; measured from the plot of  $(\Phi_{\text{disap}})^{-1}$  vs  $[\mathbf{23a-d}]^{-1}$ .

Scheme 4. Diastereoselective Oxyselelylation of 1,*n*-diolefins

unique structural features present in the large number of biologically active polyether antibiotics.<sup>38</sup>

### Mesolysis of $\text{R-CH}_2\text{-Se-R'}^{\bullet+}$ to a Carbocationic Species: Deselenylation as well as One-Pot Selenylation and Deselenylation Strategy

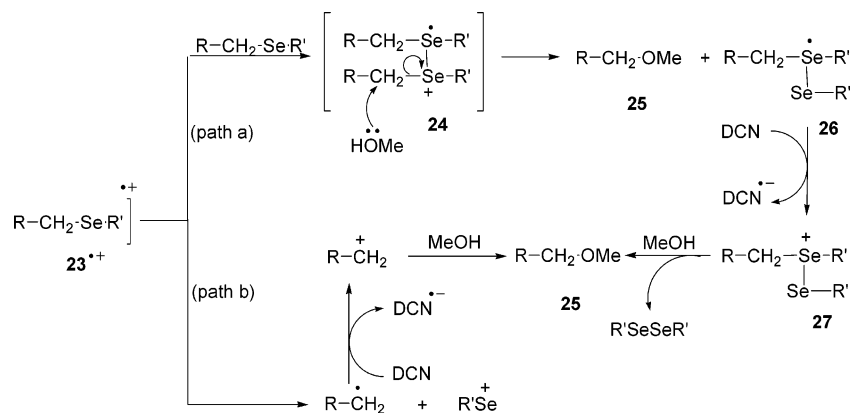
Subsequently, we turned our attention toward exploring the mesolytic dynamics of  $\text{R-CH}_2\text{-Se-R'}^{\bullet+}$ , generated by utilizing the same photosystem as shown in Figure 1. The PET phenomena between  $^1\text{DCN}^*$  and various carbon–selenium bond compounds (**23a–d**) are established<sup>39</sup> by estimating some important photophysical parameters as depicted in Table 1. Based on the detailed spectroscopic studies, the electron-transfer mechanism between these pairs is suggested to involve charge transfer (CT) stabilized exciplex.

The chemical fate of  $\text{R-CH}_2\text{-Se-R'}^{\bullet+}$  is examined by PET activation of **23** in aqueous methanol, which produced corresponding methoxy ethers **25** along with the

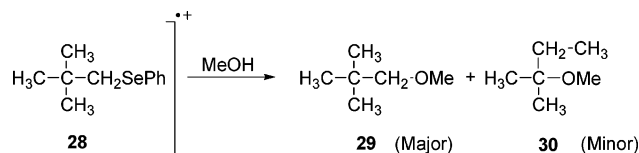
$\text{R'Se-SeR'}$ . The formation of **25** is analogously (cf. Scheme 1) rationalized by considering path a as shown in Scheme 5. Alternative path b for the formation of **25** is ruled out as our attempt to trap  $\text{R'Se}^+$  for the selenoetherification reaction failed.<sup>40</sup> Further, support for the mechanism for the formation of **25** through path a is supported by studying the mesolysis of neopentyl phenylselenide radical cation (**28<sup>•+</sup>**) owing to the well-known fact that if free neopentyl carbocation is formed, it would lead to rearranged product.<sup>41</sup> Indeed, the mesolysis of **28<sup>•+</sup>** produced un-rearranged ether **29** as the major product (Scheme 6) indicating that the cleavage does not involve free carbocationic species. Therefore, it is concluded that in this reaction the formation of **23<sup>•+</sup>** is associated with its collapse to distonic radical cation **24**, which fragments with the assistance of methanol in the solvent cage before the rearrangement can take place. It may be important to mention that the mesolysis of  $\text{R-CH}_2\text{-Se-R'}^{\bullet+}$  producing carbocationic species is in sharp contrast to the fragmentation pattern observed from the radical cations of group 14 organometallics ( $\text{-C-MR}_3$ ; M = Pb, Sn, Ge, Si)<sup>42</sup> where cleavage occurs with the loss of  $\text{-MR}_3^+$  leading to the generation of the carbon-centered radical.

The synthetic potential of this fundamental study is demonstrated for efficient deselenylation reaction, an important step after synthetic manipulations using organoselenium reagents,<sup>43</sup> of organoselenium substrates (e.g., **31** → **32**)<sup>39,40</sup> (Scheme 7). Subsequently, Furuta et al. also utilized<sup>44</sup> this strategy for the synthesis of O-glycosides **33** (Scheme 8) by the PET activation of selenoglycosides **34** in the presence of various alcohols.

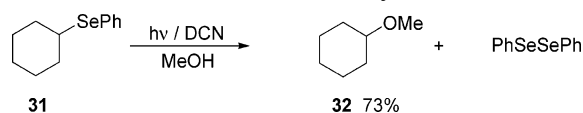
At this stage, we also hypothesized that if the chemistries of  $\text{PhSe-SePh}^{\bullet+}$  (selenoetherification reaction), as

Scheme 5. PET Generation and Chemistry of  $R-CH_2-Se-R']^{\bullet+}$ 

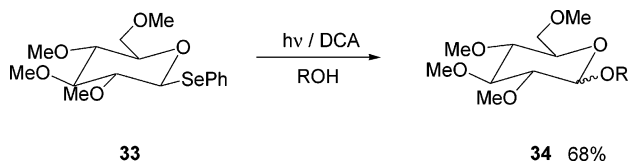
Scheme 6. Mesolysis of Neopentyl Phenylselenium Radical Cation



Scheme 7. PET-Promoted Deselenylation Reaction



Scheme 8. PET Activation of Selenoglycosides in Various Alcohols

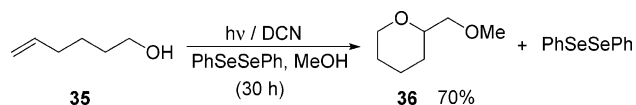


well as the  $-C-Se-]^{+\bullet}$  (carbocation equivalent), are combined together, for example, by irradiating DCN in the presence of  $PhSe-SePh$  and the substrates of type **35** for little longer duration, an interesting synthetic strategy of initiating one-pot selenylation–deselenylation approach for the synthesis of cyclic ethers may emerge. To our utmost pleasure, when a mixture containing  $PhSe-SePh$ , DCN, and **35** is activated through the photosystem as shown in Figure 1, cyclic ether **36** is obtained in good yields (Scheme 9)<sup>39,40</sup> essentially without utilizing any consumable reagents. The generality of this environmentally benign strategy of initiating one-pot selenylation–deselenylation reaction is established by studying a number of examples.<sup>40</sup>

## Cross-Coupling of Organoselenium and Organosilicon Compounds: A New $-C-C-$ Bond Formation Strategy

In an effort to provide further support to the hypothesis of nucleophilic assistance during the dissociation of  $-C-Se-]^{+\bullet}$  and to explore its synthetic potentials, we visualized a cross-coupling reaction between alkylphenylselenide ( $S_N1$  inactive) and silylenol ethers for developing a new  $-C-C-$  bond formation strategy. It may be mentioned that the cross-coupling between silylenol ethers and alkyl

Scheme 9. One-Pot Selenylation–Deselenylation Reaction



halides catalyzed by Lewis acids is limited only to  $S_N1$ -active alkyl halides (benzyl and allylic halides)<sup>45</sup> and analogous coupling with nonactivated primary or secondary alkyl halides has been reported to be rather difficult.<sup>46</sup> In this context, we attempted the PET-promoted cross-coupling of alkyl phenylselenide (**37**) with silylenol ether (**38**), which produced **39** in 60–70% yield<sup>37b,47</sup> (Scheme 10). The failure of compounds **37vi,vii** in undergoing the cross-coupling reaction is attributed to the strong stabilization of the corresponding radical cation by the arene ring. The selective PET activation of **37** in the presence of **38** is attributed to the difference in the magnitude of  $\Delta G_{et}$  values for the formation of **37**<sup>•+</sup> ( $-13.0 \text{ kcal mol}^{-1}$ ) and **38**<sup>•+</sup> ( $-10.8 \text{ kcal mol}^{-1}$ )<sup>37b,47</sup> because selectivity in the radical ion generation from a mixture of potential electron donors is known to depend on the magnitude of  $\Delta G_{et}$  values associated with the electron-transfer processes.<sup>11b,48</sup> An intramolecular version of this cross-coupling reaction is also developed for the carbocyclization reaction (Scheme 11, **40**  $\rightarrow$  **41**).<sup>37b,47</sup>

## Mesolysis of $R-CH_2-Se-R']^{\bullet-}$ to Alkyl Radicals: Unimolecular Group Transfer Radical Reactions.

From the above discussion, it is firmly established that the mesolysis of  $-C-Se-]^{+\bullet}$  produces carbocationic species, which is opposite of the cleavage pattern reported from the radical cations of group 14 organometallics.<sup>42</sup> Therefore, we got interested in exploring the consequences of one-electron reductive PET activations of  $-C-Se-$  bond compounds to their corresponding  $-C-Se-]^{-\bullet}$ . Toward this goal, a photosystem (Figure 2) consisting of 1,5-dimethoxynaphthalene (DMN) as light-absorbing electron donor<sup>49</sup> and ascorbic acid as a sacrificial electron donor is designed to generate  $R-CH_2-Se-R']^{-\bullet}$  from the organoselenides **23a–e**. The  $E_{1/2}^{red}$  values ( $-0.29$  to  $-1.0 \text{ eV}$ ) of **23a–e** from our earlier cyclic voltammetry (CV) studies,<sup>39,40</sup> and the reported<sup>50</sup> values of  $E_{1/2}^{oxid}$  and excita-

Scheme 10. PET-Promoted Cross-Coupling Reaction

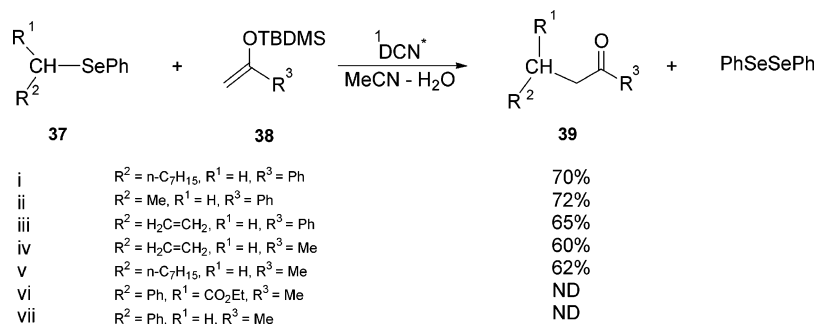
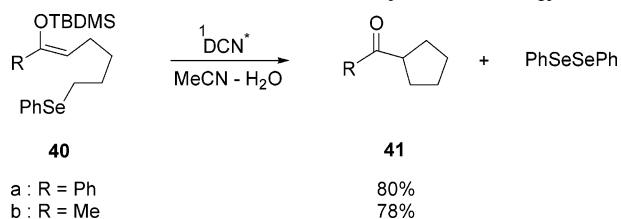


Table 2. Photophysical Constants to Establish PET Processes between DMN\*–23a–e Pairs

Selenides 23		$K_{\text{qf}}^{a,b}$	$K_{\text{qET}}^c$	$E_{1/2}^{\text{red } d}$	$\Delta G_{\text{ET}}^e$	$\Phi_{\text{disap}}^f$	$\Phi_{\text{im}}^g$	
R	R'	( $\times 10^{10}$ $\text{M}^{-1}\text{S}^{-1}$ )	( $\times 10^{10}$ $\text{M}^{-1}\text{S}^{-1}$ )	(eV)	(kcal M <sup>-1</sup> )			
a	CH <sub>3</sub>	Ph	0.368 ± 0.001	0.361 ± 0.003	-0.70	-42.14	0.026 ± 0.004	0.083 ± 0.002
b	n-C <sub>7</sub> H <sub>15</sub>	Ph	0.303 ± 0.005	0.288 ± 0.002	-0.80	-39.83	0.023 ± 0.006	0.068 ± 0.005
c	Ph	CH <sub>2</sub> Ph	0.611 ± 0.002	0.623 ± 0.005	-0.60	-44.45	0.080 ± 0.003	0.128 ± 0.007
d	n-C <sub>3</sub> H <sub>7</sub>	n-C <sub>4</sub> H <sub>9</sub>	0.184 ± 0.003	0.211 ± 0.004	-1.00	-35.22	0.013 ± 0.007	0.049 ± 0.003
e		Ph	0.822 ± 0.005	0.782 ± 0.007	-0.29	-51.60	0.095 ± 0.004	0.130 ± 0.005

<sup>a</sup> Errors are standard deviations from the average. <sup>b</sup> From fluorescence quenching Stern–Volmer plot. <sup>c</sup> From the double reciprocal plot;  $(\Phi_{\text{disap}})^{-1}$  vs  $[\mathbf{a-e}]^{-1}$ . <sup>d</sup> Referred to saturated calomel electrode (SCE) using tetraethylammonium perchlorate as supporting electrolyte in dry acetonitrile. <sup>e</sup> Oxidation half-wave potential ( $E_{1/2}^{\text{oxid}}$ ) for DMN is 1.28 eV, and  $E_{0,0} = 3.81$  eV (ref 45). <sup>f</sup> Light intensity evaluated by uranyl oxalate actinometry. <sup>g</sup> At infinite donor concentration; measured from the plot of  $(\Phi_{\text{disap}})^{-1}$  vs  $[\mathbf{23a-e}]^{-1}$ .

Scheme 11. PET-Promoted Carbocyclization Strategy

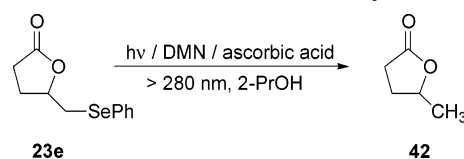


tion energy ( $E_{0,0}$ ) of DMN) helped us to design this photosystem.

The thermodynamic feasibility of electron transfer from excited DMN to the organoselenium substrates **23a–e** is established<sup>51,52</sup> by estimating usual physical parameters as shown in Table 2. These observations along with the detailed excitation as well as absorption spectral studies of DMN in the presence of **23a–e** suggested that the ET mechanism involves a CT-stabilized exciplex. The ET feasibility from ascorbic acid to DMN<sup>+</sup> is also established by estimating negative  $\Delta G_{\text{et}}$  ( $-4.51$  kcal mol<sup>-1</sup>) value.<sup>51,52</sup> The electron-donating ability of ascorbate ion and its transformation to dehydroascorbic acid, and proton has precedent in the literature.<sup>53</sup>

The PET activation of **23e** in *i*-PrOH at a preparative scale, through the photosystem as shown in Figure 2,

Scheme 12. PET-Initiated Reductive Deselenylation Reaction



produced deselenylated product **42** (83% yield, Scheme 12) and PhSe–SePh.

The formation of **42** is explained by considering the cleavage of **23e**<sup>•-</sup> following path a because the reaction in deuterated *i*-propanol (*i*-PrOD) failed to produce<sup>52</sup> deuterium-labeled **42**. (Scheme 13).

The efficient mesolysis of  $\text{R-CH}_2\text{-SePh}^{\bullet-}$  into  $\text{R-CH}_2^{\bullet}$  and PhSe–SePh, an excellent radical trapping agent,<sup>54</sup> provided a unique opportunity to develop this study for initiating the phenylselenenyl groups transfer radical reactions (unimolecular group transfer, UMGT) as shown in Figure 3. Furthermore, the merit of this strategy is shown in overcoming the limitations of radical initiations using tin hydride reagents.<sup>55</sup> Generality of UMGT radical reaction concept is also established by studying a number of substrates (yield, 71–80%).<sup>51,52</sup>

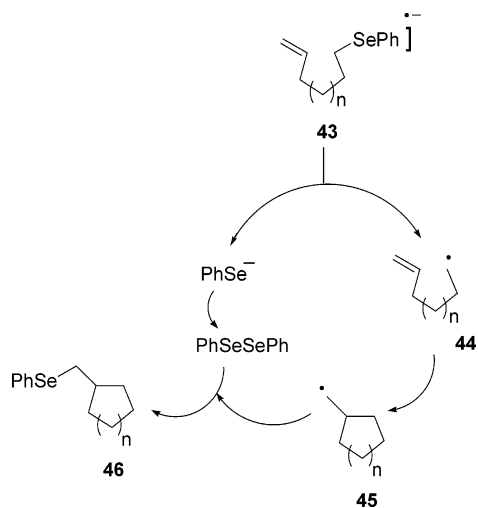


FIGURE 3. PET-initiated unimolecular group transfer radical reaction.

### Scheme 13. Proposed Mesolytic Pathways for Organoselenium Radical Anions

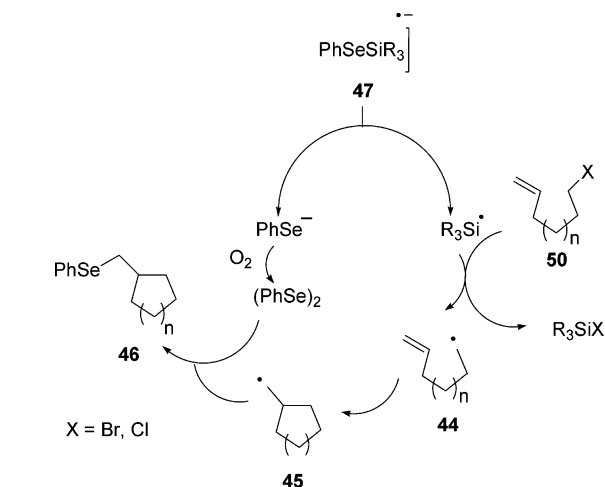
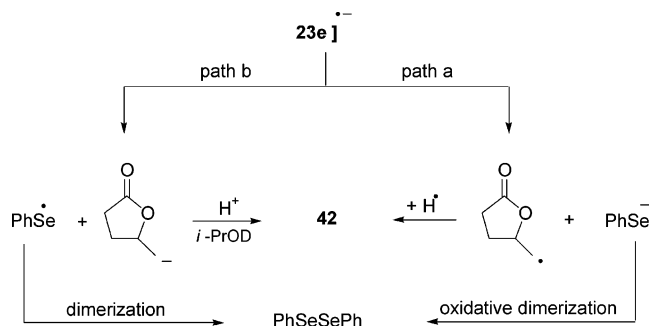
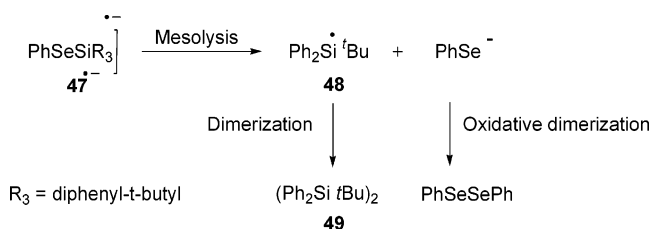


FIGURE 4. PET generation of alkylsilyl radical and initiation of bimolecular group transfer radical reactions.

### Scheme 14. Generation of Alkylsilyl Radical by the Mesolysis of $\text{PhSeSiR}_3\text{]}^{\bullet-}$



$R_3 = \text{diphenyl-}t\text{-butyl}$

## Mesolytic Activation of $\text{PhSe-SiR}_3\text{]}^{\bullet-}$ to an Alkylsilyl Radical: Bimolecular Group Transfer Radical Reactions

Carbon and silicon elements are isoelectronic, and often the chemistry of silicon compounds is correlated analogously to corresponding carbon compounds;<sup>56</sup> however, certain important differences<sup>57</sup> between the silicon and carbon atom make this analogy only formal. Therefore, it was thought interesting and important to explore the mesolytic dynamics of  $\text{R}_3\text{Si-SePh}]^{\bullet-}$ . In this context, *tert*-butyldiphenyl(phenylseleno)silane (**47**) was selected as the substrate because of its stability in aqueous solvents. Compound **47** is easily synthesized by the nucleophilic displacement of chloride ion of *tert*-butyldiphenylsilyl chloride by the phenylselenide anion.<sup>58</sup> For reductive activation of **47**, we employed the same photosystem as shown in Figure 2 except utilizing 9,10-dimethoxyanthracene (DMA) in place of DMN because of its longer wavelength (405 nm) absorption property. Thermodynamic feasibility of PET phenomena between DMA and **47** is established in the usual manner, as discussed above for organoselenium compounds, by estimating exergonic  $\Delta G_{\text{et}}$  value ( $-43.46 \text{ kcal mol}^{-1}$ ) for the radical ion formation steady-state and time-resolved fluorescence quenching studies.<sup>59,60</sup> In this particular study, transient species related to the formation of  $\text{DMA}^{\bullet+}$  as well as to  $\text{47}^{\bullet-}$  are also characterized by picosecond and nanosecond laser flash photolysis experiments.<sup>60</sup>

PET activation ( $\lambda_{\text{exc}} = 405 \text{ nm}$ ) of **47** in acetonitrile produced **49** and  $\text{PhSe-SePh}$  as the only two observable products.<sup>59,60</sup> Mechanistically, the formation of these products are rationalized by implicating the mesolysis of the  $\text{47}^{\bullet-}$  (Scheme 14) into  $\text{R}_3\text{Si}^{\bullet}$  and  $\text{PhSe}^-$  followed by their efficient dimerizations.

Since this study clearly demonstrates that  $\text{PhSe-SiR}_3$  could be utilized as an in situ source of alkyl silyl radical, more halophilic than alkyl (aryl) tin radical,<sup>61</sup> and  $\text{PhSe-SePh}$  by the PET activation, a new concept is derived<sup>59,60</sup> for initiating the bimolecular group transfer radical reactions as shown in Figure 4. The reaction is shown to be general and high-yielding (70–81%). A comparative study suggests that initiation of radical reaction by this strategy is 4–5 times faster than the one developed earlier<sup>52</sup> (Figure 3).

## Development of Catalytic Group Transfer Radical Reactions

Due to growing demand to reduce the amount of toxic wastes and byproducts arising out of the chemical reactions,<sup>62</sup> increasing emphasis is laid on the invention and development of a catalytic and environmentally compatible strategy for initiating radical-based chemistry owing to its ever increasing popularity among synthetic chemists.<sup>63–65</sup> Considering the significantly higher rate constant ( $9.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) for the reaction of  $\text{R}_3\text{Si}^{\bullet}$  with alkyl phenylselenides<sup>66</sup> and fast oxidative dimerization of  $\text{PhSe}^-$  to  $\text{PhSe-SePh}$ , a catalytic strategy for phenylselenyl

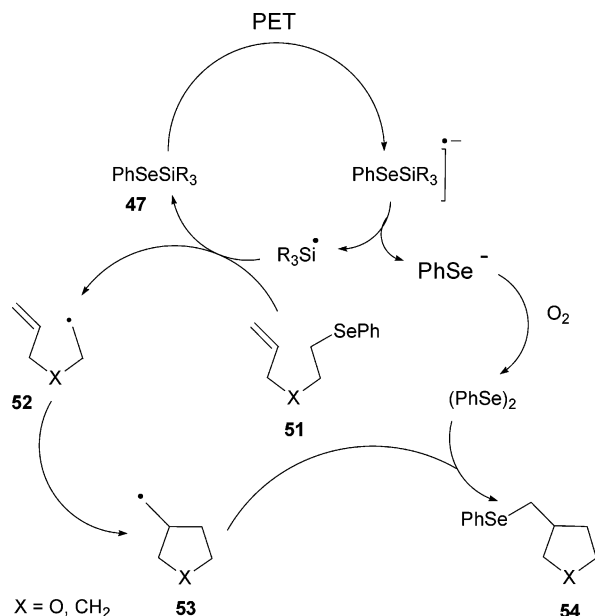


FIGURE 5. Catalytic group transfer radical reactions.

group transfer based radical reaction is developed<sup>67</sup> from a precursor of type **51** through a cycle as shown in Figure 5.

The significant difference between the  $\Delta G_{et}$  values for the formation of **47**<sup>-</sup> ( $-43.46 \text{ kcal mol}^{-1}$ ) and **51**<sup>-</sup> ( $-39.83 \text{ kcal mol}^{-1}$ ) is attributed for the selectivity of **47**<sup>-</sup> generation when a mixture of **47** and **51** is activated.<sup>67</sup> Optimization study suggested a 10:1 mole ratio of substrate (**51**) to catalyst (**47**) for optimum performance.<sup>67</sup>

## Intermolecular Addition and Tandem Radical Reactions

Intermolecular radical additions, though a powerful tool in organic synthesis, have difficulty in their implementation using tin-based radical initiators due to competing bimolecular radical reactions (hydrostannylation), premature termination of adduct radical, and telomerization/polymerization.<sup>68</sup> Since both polymerization and premature termination of the adduct radical can be avoided utilizing the reaction protocol as illustrated in Figure 6, an interesting bimolecular group transfer intermolecular radical reaction (yield, 55–60%) is developed.<sup>67</sup>

Further extension of this strategy is evaluated in initiating a tandem radical cyclization reaction. Ring construction by annulation of two or more olefins through tandem radical reactions has been explored well, and in all these reactions, 5-hexenyl radicals cyclize preferentially in the exo mode to give rise to five-membered carbocyclic rings.<sup>69</sup> Since silicon atom  $\alpha$ , as well as  $\beta$ , to the radical center is known<sup>70</sup> to influence the regioselectivity of cyclizations, we envisaged that a tandem annulation reaction between olefins **60** and **61** may produce endo-cyclized product **64** (reverse of the normal radical cyclization regioselectivity) involving the route as shown in Figure 7. True to our expectation, PET activation of a mixture of olefins **60** and **61** in the presence of **47** produced **64** in 61% yield.<sup>67</sup> This observed reversal of

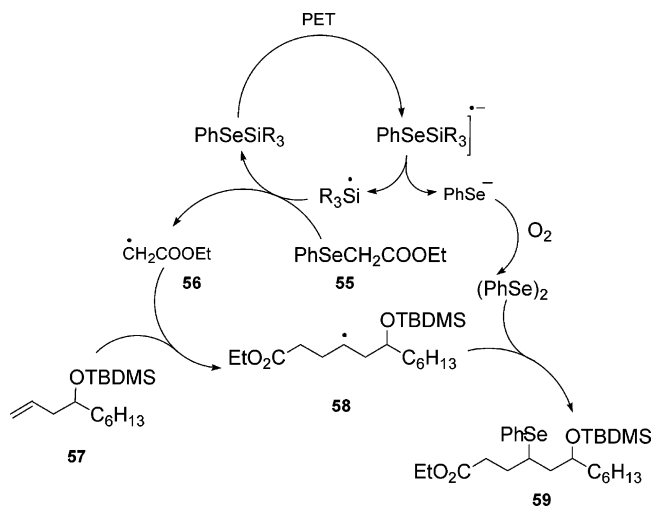


FIGURE 6. Catalytic intermolecular group transfer radical addition reaction.

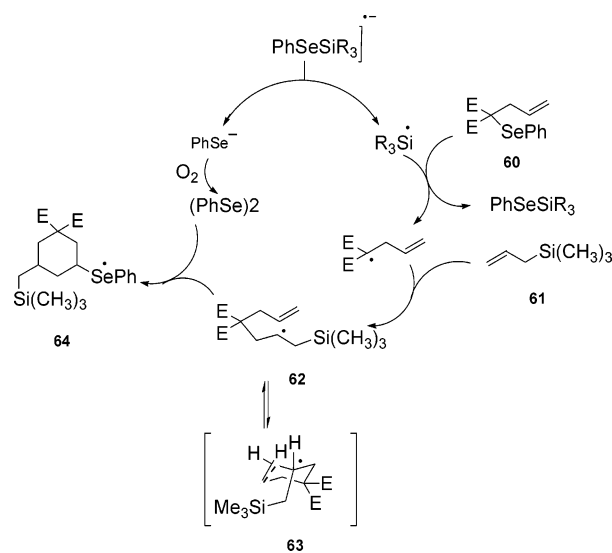


FIGURE 7. Strategy for endo-trig cyclization in radical reactions.

regioselectivity in the formation of **64** is explained by invoking seemingly less dipolar transition state structure **63**, because the silicon atom  $\beta$  to the radical center is postulated<sup>70</sup> to enhance the fractional negative charge at the radical center of the intermediate **62**. Furthermore, greater  $-\text{C}-\text{Si}-$  bond length (25% larger than  $-\text{C}-\text{C}-$ ) is also implicated to participate in the reversal of the regioselectivity because it would make an easier approach of the radical center from the  $-\text{CH}_2-$  end of the double bond.<sup>70b</sup>

## Conclusions

The results presented in this Account demonstrate the development of conceptually new chemistry utilizing organoselenanes and selenosilanes. The study is mechanistically interesting and synthetically useful. The strategy of in situ PET activation of  $\text{PhSe}-\text{SePh}$  to an electrophilic selenium species is not only important for the selenoetherification reaction but also shown to be useful for the enyne cyclization and stereoselective oxyseleenylation reactions as well. PET oxidative activation of organoselen-



nium compounds to carbocationic equivalents allows the utility of these compounds as carbocation precursors in addition to their well-known utility as anionic and radical equivalents. The one-pot selenylation–deselenylation strategy for the synthesis of cyclic ethers adheres very well to the emerging concept of atom economy in organic synthesis. Design of the photosystem for reductive activation of organoselenium compounds to generate carbon-centered radical and the development of the unimolecular group transfer radical reaction is conceptually new. This strategy also overcomes the inherent limitations of initiating radical reactions utilizing tin-based reagents. Similarly, the activation of  $R_3Si-SePh$  to the corresponding  $R_3Si-SePh]^{\cdot-}$  and its mesolysis to generate  $R_3Si^{\cdot}$  is unprecedented. The unique application of in situ PET activation of  $R_3Si-SePh$  has been demonstrated in the development of various radical-based reactions. Future exploitation of these chemistries is expected to add newer dimensions in organic synthesis.

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