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*J. Org. Chem.*, **Just Accepted Manuscript** • Publication Date (Web): 22 May 2017

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# Seleniranium ions undergo $\pi$ -ligand exchange via an associative mechanism in the gas phase

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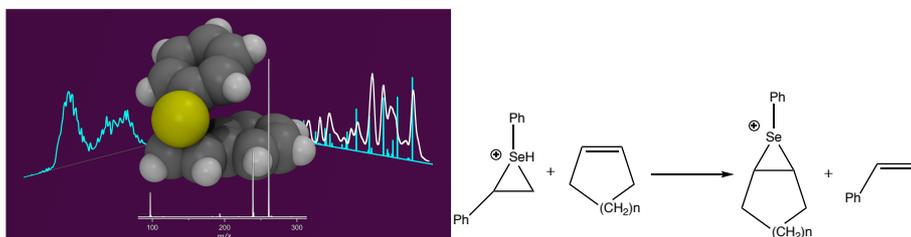
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## Graphical Abstract.

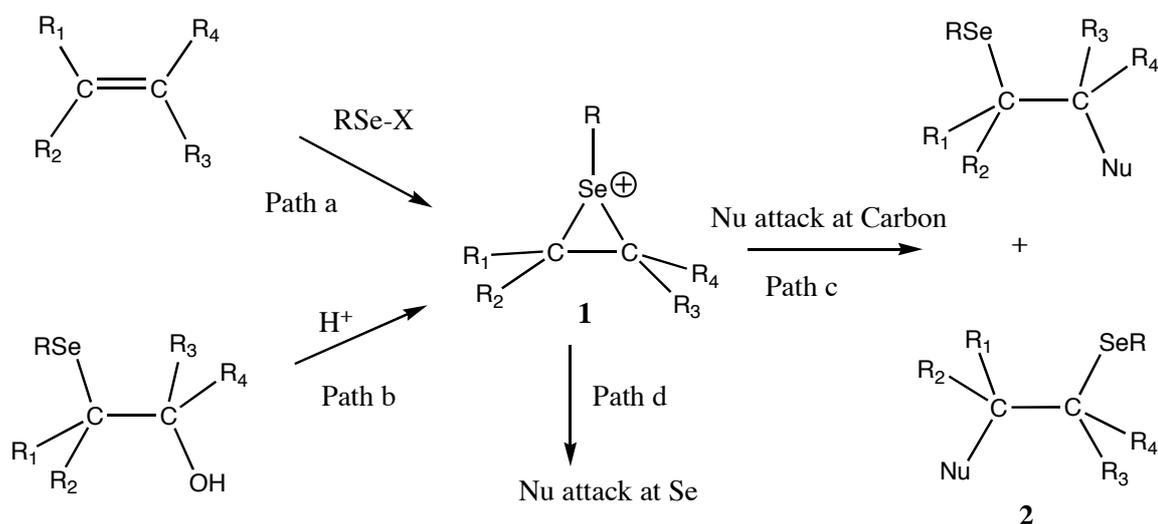


**Abstract:**

Collision-induced dissociation mass spectrometry of the ammonium ions **4a** and **4b** results in the formation of the seleniranium ion **5**, the structure and purity of which was verified using gas phase infra-red spectroscopy coupled to mass spectrometry, and gas phase ion-mobility measurements. Ion-molecule reactions between the ion **5** ( $m/z = 261$ ) and cyclopentene, cyclohexene, cycloheptene and cyclooctene, resulted in the formation of the seleniranium ions **7** ( $m/z = 225$ ), **6** ( $m/z = 239$ ), **8** ( $m/z = 253$ ), and **9** ( $m/z = 267$ ) respectively. Further reaction of seleniranium **6** with cyclopentene resulted in further  $\pi$ -ligand exchange giving seleniranium ion **7**, confirming that direct  $\pi$ -ligand exchange between seleniranium ion **5** and cycloalkenes occurs in the gas phase. Pseudo first order kinetics established relative reaction efficiencies for  $\pi$ -ligand exchange for cyclopentene, cyclohexene, cycloheptene and cyclooctene as 0.20, 0.07, 0.43, and 4.32 respectively. DFT calculations at the M06/6-31+G(d) level of theory provide the following insights into the mechanism of the  $\pi$ -ligand exchange reactions; the cycloalkene forms a complex with the seleniranium ion **5** with binding energies of 57 and 62 kJ/mol for cyclopentene and cyclohexene respectively with transition states for  $\pi$ -ligand exchange having barriers of 17.8 and 19.3 kJ/mol for cyclopentene and cyclohexene respectively.

## Introduction:

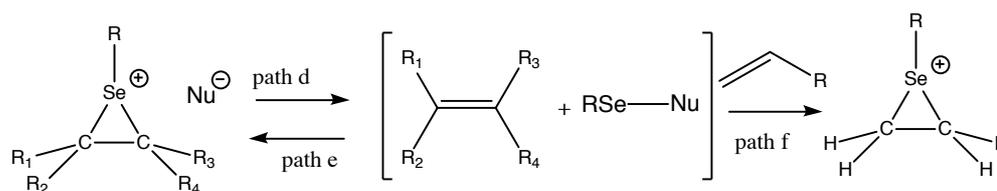
Seleniranium ions, which have the general structure **1**, are important reactive intermediates that are involved in a wide range of transformations in organic synthesis.<sup>1-14</sup> These intermediates may be formed by addition of an electrophilic selenium reagent to an alkene precursor (Scheme 1, path a) or alternatively by a neighbouring group pathway involving water loss from  $\beta$ -seleno-substituted alcohols upon acid treatment (Scheme 1, path b).



**Scheme 1.** Pathways for formation and possible reactions of seleniranium ions **1**.

Seleniranium ions have been shown to undergo two types of reaction: (i) Attack by a variety of nucleophiles (C, O, N) at carbon (Scheme 1, path c) yielding products of the type **2**, which are themselves useful synthetic intermediates; and (ii) Nucleophilic attack at the selenium atom of the seleniranium ion yielding an alkene and an active selenium electrophile (Scheme 1, path d). This latter process, which is elaborated in Scheme 2, results in  $\pi$ -decomplexation. This step is reversible, and subsequent

recomplexation results in reformation of the seleniranium ion **1** (Scheme 2, path e). Evidence for this process is provided by the observation of crossover products when seleniranium ions are generated in the presence of a second alkene (Scheme 2 path f) and provides a rationale for the low configurational stability of chiral seleniranium ions under certain conditions.<sup>15</sup>



**Scheme 2.** Recomplexation-decomplexation pathways

$\pi$ -Decomplexation-recomplexation can be suppressed by employing sterically hindered substituents on the selenium atom,<sup>16,17</sup> which disfavours nucleophilic attack at the selenium, or electron deficient aryl substituents such as 2-pyridyl and *o*-nitrophenyl substituents which appear to enhance nucleophilic attack at carbon.<sup>18,19</sup> Although the formal olefin-to-olefin  $\text{RSe}^+$  transfer shown in scheme 2 occurs with nucleophilic assistance and involves the electrophilic selenium reagent ( $\text{RSe-Nu}$ ) Denmark *et al.* have provided strong evidence for direct olefin to olefin transfer by generating seleniranium ions in the presence of the relatively non-nucleophilic counterion  $\text{SbF}_6^-$  in the non-nucleophilic solvent  $\text{CD}_2\text{Cl}_2$  and have demonstrated that formal transfer of  $\text{RSe}^+$  to a second added olefin occurred rapidly at  $-70^\circ\text{C}$ .<sup>20</sup> The facile nature of the  $\text{RSe}^+$  transfer and insights gained from DFT calculations<sup>21</sup> were suggestive of direct transfer of  $\text{RSe}^+$  from one olefin to another in an associative process, rather than a dissociative process involving  $\text{RSe}^+ \text{SbF}_6^-$  as intermediate. An elegant study on olefin-olefin transfer that utilized enantiomerically enriched

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3 thiiranium ions ruled out participation by nucleophilic solvent or impurities in the  
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5 thiiranium ion transfer.<sup>22</sup>  
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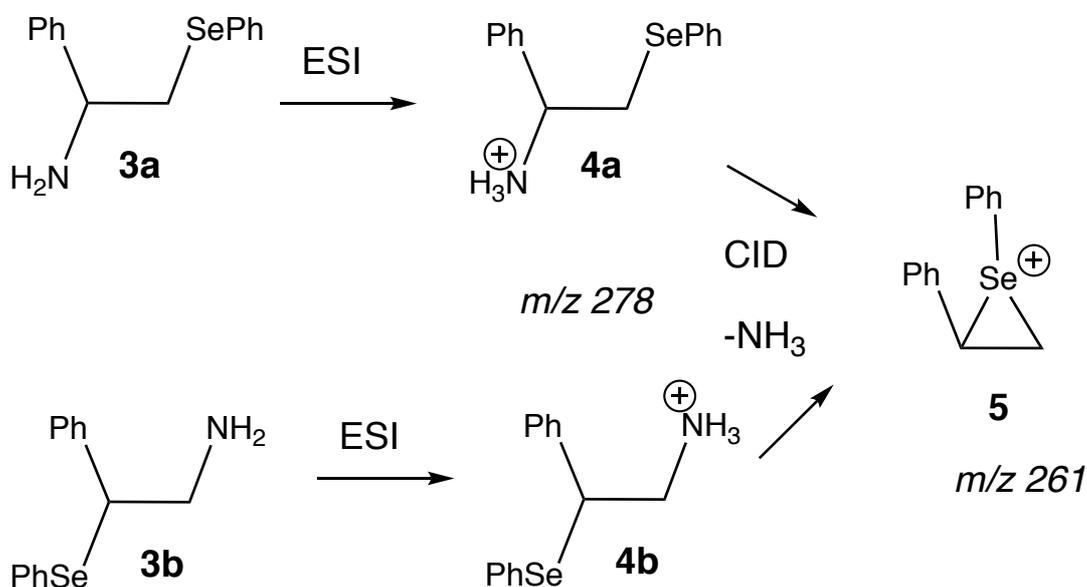
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11 Mass spectrometry in combination with theoretical calculations has proven to  
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13 be a powerful method for elucidating the intrinsic reactivity of charged species in the  
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15 gas phase away from the potential complications arising from the presence of solvent  
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17 and counterions.<sup>23,24,25</sup> In addition, the use of gas-phase infra-red spectroscopy coupled  
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19 to mass spectrometry,<sup>26</sup> has proven its worth by experimentally confirming the  
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21 theoretically predicted structures of ionic species involved in gas-phase reactions.<sup>27</sup>  
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23 Here, multistage mass spectrometry experiments on a modified LTQ-FT high  
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25 resolution mass spectrometer,<sup>28,29</sup> infrared spectroscopy integrated with mass  
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27 spectrometry, ion mobility spectrometry<sup>30</sup> and theoretical calculations, are used to  
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29 investigate the gas-phase structure of seleniranium ions and to probe the mechanism of  
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31 olefin-to-olefin RSe<sup>+</sup> transfer in the gas phase, away from the possible complications  
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33 of solvent, counterions, and impurities, in order to determine the transfer mechanisms  
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35 involved.  
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#### 43 **Results and discussion:**

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46 The  $\beta$ -selenylamine **3a** [C<sub>14</sub>H<sub>15</sub>NSe] (*cf* Scheme 3) or the regioisomer **3b** in  
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48 acetonitrile at a concentration *ca* 0.1 mM, were introduced into the mass spectrometer  
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50 via electrospray ionisation. These solutions generated, amongst others, ions at *m/z* 278  
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52 consistent with formation of the ammonium ions **4a** or **4b** as confirmed via isotope  
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54 distribution and accurate mass measurement (Supplementary Figure S1). These ions  
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56 were then isolated in a further stage of mass spectrometry (MS<sup>2</sup>) and subjected to low-  
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58 energy collision-induced dissociation (CID) with the helium bath gas. Loss of  
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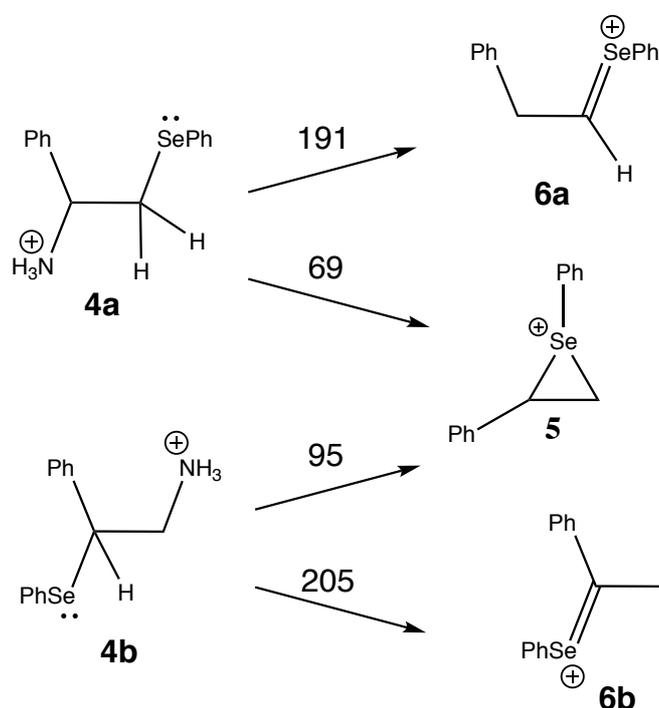
ammonia resulted in clean conversion to an ion at  $m/z$  261 which was assigned as the seleniranium ion **5** (Scheme 3, Supplementary Figure S2), the ions ( $m/z$  261) obtained from **4a** and **4b** had identical fragmentation patterns under similar CID voltages. This ion, in turn, was mass selected in a further stage of mass spectrometry ( $MS^3$ ) and allowed to undergo near thermal (room temperature) ion-molecule reactions<sup>31</sup> with cyclopentene, cyclohexene, cycloheptene and cyclooctene as described later.



**Scheme 3.** Electrospray ionisation of the  $\beta$ -selenyl amines **3a/b** and CID of the derived ammonium ions **4a** and **4b**.

Further experiments were undertaken to shed light on the identity of the ion at  $m/z$  261 since in principle, competition between direct displacement of the  $NH_3^+$  leaving group in **4a** and **4b** by the neighbouring selenium nucleophile and hydride migration (as has been suggested to occur in the generation of the corresponding halonium ions),<sup>32</sup> generating ions **6a** and **6b** ( $m/z$  261) (Scheme 4) might plausibly have occurred upon fragmentation of **4a** or **4b** (Scheme 4). However, the low energy nature of the CID in the ion-trap, as well as theoretical calculations at the M06 level of theory suggest against the formation of **6a** and **6b**. Thus, it was shown theoretically that the formation

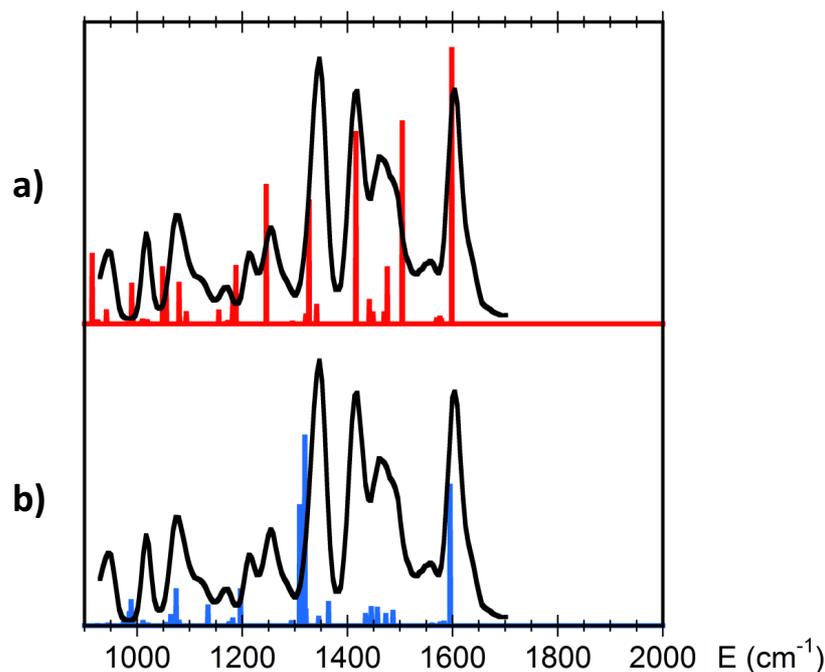
of **5** from **4a** and **4b** proceeds via transition states with respective barrier heights of 69 and 95 kJ/mol (Scheme 4), while formation of **6a** and **6b** from **4a** and **4b** proceeds via transition states with respective barrier heights of 191 and 205 KJ/ mol. In addition, the isomerisation of **5** to **6b** proceeds with a substantial barrier of 135 kJ/mol, whereas the formation of **6a** requires a barrier of 182 kJ/mol. This result is despite the DFT calculations predicting the selenonium isomer **6b** to be *ca.* 20 kJ/mol lower in energy than the seleniranium ion **5**, presumably due to resonance stabilisation.



**Scheme 4.** Alternative unimolecular reaction pathways for ammonium ions **4a** and **4b** upon CID, energies are in kJ/mol.

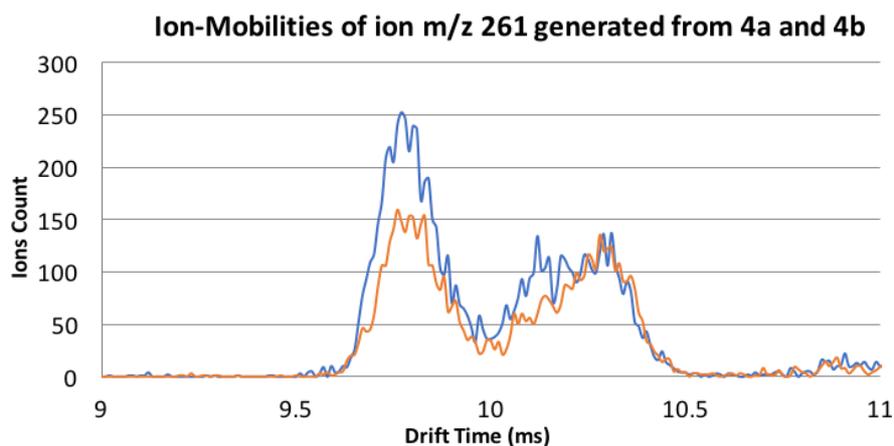
To provide further support for the formation of the proposed seleniranium ion structure **5**, an experiment was conducted where the ions at  $m/z$  261 generated by CID of ion **4a** were mass selected and stored in the cell of a Fourier transform ion cyclotron resonance mass spectrometer, and subjected to infrared radiation.<sup>26</sup> Tuneable mid-infrared radiation produced by the free-electron laser (FEL) of CLIO (Centre Laser Infrarouge d'Orsay) was used to record the spectrum in the 900–1700  $\text{cm}^{-1}$  range.<sup>33</sup>

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4 By monitoring the number of detected ions in both the parent and fragment mass  
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6 channels at each IR wavenumber, which was raised stepwise ( $\sim 5\text{ cm}^{-1}$ ), the IR  
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8 multiple photon dissociation (IRMPD) spectrum was recorded. In Figure 1, the  
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10 experimental IRMPD spectrum (black) is compared to the calculated IR absorption  
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12 spectrum, at the B3LYP/6-311++G(d,p) level of theory, of a seleniranium isomer **5**  
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14 (Fig. 1a, red stick spectrum) and of the second lowest calculated energy structure,  
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16 selenonium isomer, **6a** which could potentially be generated from **4a** (Fig. 1b, blue  
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18 stick spectrum). Overall, there is a good qualitative match between the observed  
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20 IRMPD spectrum of the ion at  $m/z$  261 and that computed for **5**. All the observed  
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22 bands can be assigned (See Supplementary Table S1), and the relative error position  
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24 between the (scaled) predicted band for structure **5** and observed ones is less than 4%.  
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27 Two bands can be considered as diagnostic of the Se- $\pi$ (CH<sub>2</sub>CHPh) structural motif.  
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29 These two bands are observed at  $\sim 950$  and  $1415\text{ cm}^{-1}$  and are characteristic of the out-  
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31 of-plane (wagging) and in-plane (scissoring) motion of the ethylenic  $\pi$ -complex.  
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34 Nevertheless, one cannot exclude the presence of small quantities of either **6a** or **6b**  
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37 based on this spectroscopic data.  
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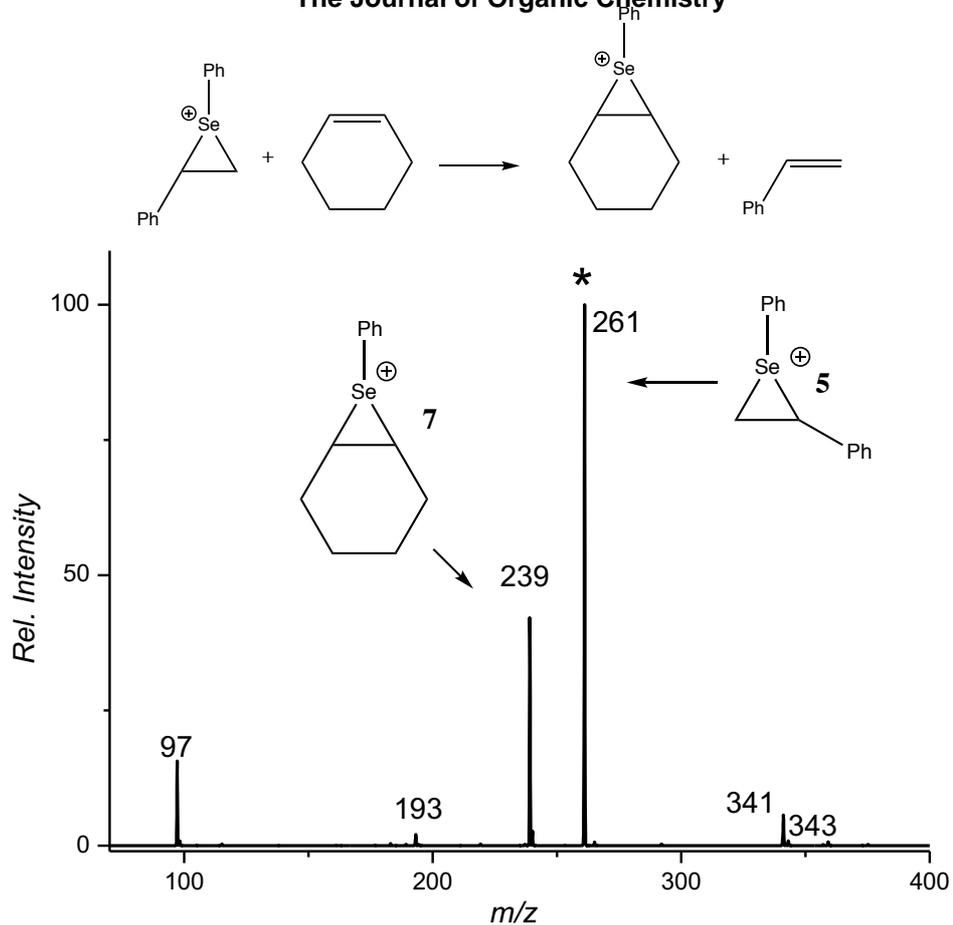
**Figure 1.** Experimental IRMPD spectrum (black) compared to the calculated IR absorption spectrum of: a) a seleniranium isomer **5** generated from **4a** (red stick spectrum) and; b) a selenonium isomer **6a** (blue stick spectrum).

To investigate further the identity and purity of the ion at  $m/z$  261, ions generated by electrospray ionization and subsequent CID of both amines **4a** and **4b** were subjected to ion mobility measurements. The results (Figure 2) clearly show that the  $m/z$  261 ion generated from precursor **4a** has the same mobility as the ion generated from **4b** (peaks at 9.8 ms) and they can be concluded to be identical. Furthermore, there is no evidence for the presence of isomeric ions with the same composition; collision cross sections calculated for the ions **5**, **6a** and **6b** were 147.85, 150.55 and 153.74 Å<sup>2</sup> respectively, suggesting that they should be distinguishable in the mobility spectrometer.<sup>34,35,36</sup> The slower ions in Figure 2 (peaks at 10.3 ms) correspond to CID conversion of **4a/4b** into the seleniranium ion after the ion drift cell but before the mass filter and ion detector.



**Figure 2.** Arrival time distribution of ions at  $m/z$  261 generated by CID of protonated amines **4a** and **4b**. The slower peak represents  $m/z$  261 ions formed after the drift region by CID of  $m/z$  278 ions generated from **4a** and **4b**. The red trace is from ESI of **4a** whereas the blue trace is from ESI of **4b**.

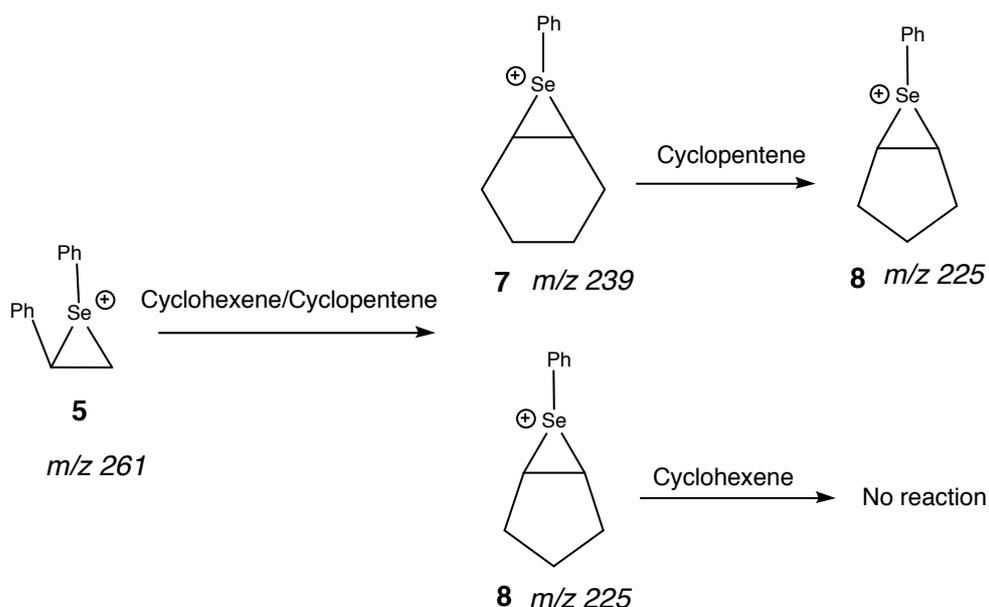
In order to study the gas-phase bimolecular reactivity of **5** and investigate the potential for  $\pi$ -ligand exchange, ion-molecule reactions (IMR) with cyclopentene, cyclohexene (also D10-cyclohexene), cycloheptene and cyclooctene in the ion-trap mass spectrometer were employed.<sup>28</sup> For instance, the seleniranium ion **5** ( $m/z$  261) was isolated and allowed to react with cyclohexene introduced into the ion-trap via the ion-molecule reaction line at a concentration range of *ca.*  $1\text{-}5 \times 10^{10}$  molecules. $\text{cm}^{-3}$ . A slow reaction occurs with loss of intensity of **5** and formation of a product ion at  $m/z$  239 (Figure 3) amongst others. This latter ion is consistent with formation of the seleniranium ion **7** by direct olefin to olefin transfer of the  $\text{PhSe}^+$  moiety. The elemental composition of this ion was further confirmed via its isotope distribution (data not shown) and HRMS (Supplementary Figure S3).



**Figure 3.** Ion-molecule reaction between seleniranium ions **5** and cyclohexene (at a concentration of  $ca\ 10^{11}$  molecules  $cm^{-3}$  for  $t = 10,000$  ms) (the most abundant selenium isotope  $^{80}Se$  was used). The mass selected ion is denoted by an asterisk.

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3 To further confirm that the reaction corresponds to olefin transfer, reaction of seleniranium  
4 ion **5** with the fully deuterated analogue of cyclohexene (d10-cyclohexene, C<sub>6</sub>D<sub>10</sub>) was  
5 studied. A similar reaction was observed where the exchange product formed corresponded to  
6 the corresponding deuterated seleniranium ion d10-**7** at *m/z* 249 (Supplementary Figure S4).  
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8 A related reaction of the seleniranium ion **5** (*m/z* 261) with cyclopentene resulted in the  
9 formation of a product ion at *m/z* 225 corresponding to an exchange with the cyclopentene  
10 and formation of seleniranium ion **8** (*m/z* 225) (Supplementary Figure S5).  
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22 To provide further evidence that the ions (*m/z* 239) and (*m/z* 225), formed upon  
23 treatment of the seleniranium ion **5** with cyclohexene and cyclopentene respectively, were  
24 indeed the seleniranium ions **6** and **7** we examined whether phenylselenyl transfer could  
25 occur, more than once, to different alkenes. To this end, seleniranium ion **5** (*m/z* 261) was  
26 allowed to react in the ion trap mass spectrometer with a *ca.* 1:1 mixture of cyclopentene and  
27 cyclohexene, whereupon ions **7** (*m/z* 239) and **8** (*m/z* 225) were formed (Supplementary  
28 Figure S6). When ion **7** was isolated via a further stage of MS (still in the presence of  
29 cyclohexene and cyclopentene) further transfer of PhSe<sup>+</sup> from seleniranium ion **7** to  
30 cyclopentene occurred, giving rise to seleniranium ion **8** (Scheme 5) (Supplementary Figure  
31 S7). In contrast, isolation of seleniranium ion **8** under the same conditions, did not result in  
32 any conversion into seleniranium ion **7** indicating that while transfer of PhSe<sup>+</sup> from  
33 cyclohexene to cyclopentene occurs readily, the back reaction does not.  
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**Scheme 5.** Reaction of Seleniranium ion **5** with a mixture of cyclohexene and cyclopentene, and further reactions of the formed seleniranium ions with the neutral reagents.

The  $\pi$ -ligand exchange reaction was then investigated by reaction of **5** with cycloheptene and cyclooctene, to probe the effect of the cycloalkane ring size. Both of the larger cycloalkenes reacted with **5** and  $\pi$ -ligand transfer products **9** and **10** were observed at  $m/z$  253 from cycloheptene and  $m/z$  267 from cyclooctene respectively (Supplementary Figures S8 and S9). Pseudo first order kinetics for the reactions observed with all the cycloalkenes studied were determined by measuring the decrease in intensity of the parent ion ( $m/z$  261) over periods of time from 30 ms up to 20 s (Supplementary Figures S10-S13). The results of these kinetics measurements are presented in Table 1. A close inspection of Table 1 shows that the reaction with cyclohexene is the slowest, while that with cyclooctene is the fastest ( $k_{\text{expt}}$  (cyclooctene)  $>$  60  $\times$   $k_{\text{expt}}$  (cyclohexene)). These patterns of reactivity qualitatively follow that observed for other related reactions of cycloalkenes, for example the reaction with dihalocarbenes follows the order cyclohexene  $<$  cycloheptene  $<$  cyclooctene.<sup>37,38</sup> While the intrinsic reactivities of this series of cycloalkenes as determined from their heats of hydrogenation follow the order cyclohexene  $<$  cyclopentene  $<$  cycloheptene  $<$  cyclooctene.<sup>39</sup> In

addition the reaction rates are related to the exothermicities of the overall  $\pi$ -ligand exchange process for each alkene.

**Table 1:** Experimental and theoretical reaction rate constants for the reactions of **5** with cycloalkenes.

Neutral	$k_{\text{expt}}^{[\text{a}][\text{b}]}$	$k_{\text{rel}}$	$\varphi^{[\text{c}]}$	$\Delta E$ (kJ/mol) <sup>[d]</sup>
Cyclopentene	$1.9 \times 10^{-12}$	2.9	0.20	-16.3
Cyclohexene	$6.6 \times 10^{-13}$	1	0.07	-8.6
Cycloheptene	$4.3 \times 10^{-12}$	6.5	0.43	-16.7
Cyclooctene	$4.4 \times 10^{-11}$	66.7	4.32	-30.5

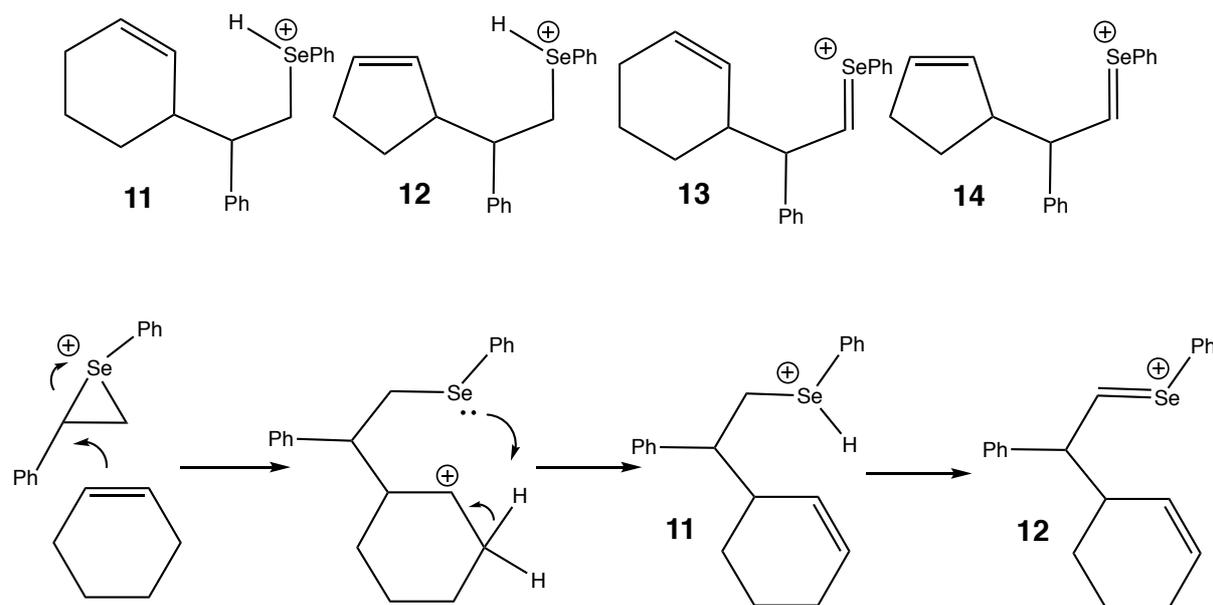
[a] In units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . [b] Experimental rates for consumption of reactant ion at  $m/z$  261. [c] Reaction efficiency ( $\varphi$ ) =  $(k_{\text{expt}}/k_{\text{theor}}) \times 100\%$ . The theoretical ion-molecule collision rate was obtained from average-dipole orientation (ADO) theory, calculated using the Colrate program.<sup>40,41</sup>  $k_{\text{rel}}$  is the relative rate as compared to the slowest reaction (i.e. cyclohexene), [d] exothermicities were calculated at the M06/6-31+G(d) level of theory (see experimental section).

We should note that the ion at  $m/z$  261 and assigned as seleniranium **5** was generated independently from both the amine precursors **4a** and **4b**. We found that for both, the CID spectra and the rate of the  $\pi$ -ligand transfer reactions (e.g.; conversion into the seleniranium ion **7** ( $m/z$  239) upon reaction with cyclohexene) were virtually identical (data not shown) suggesting against any isomeric ion contamination.

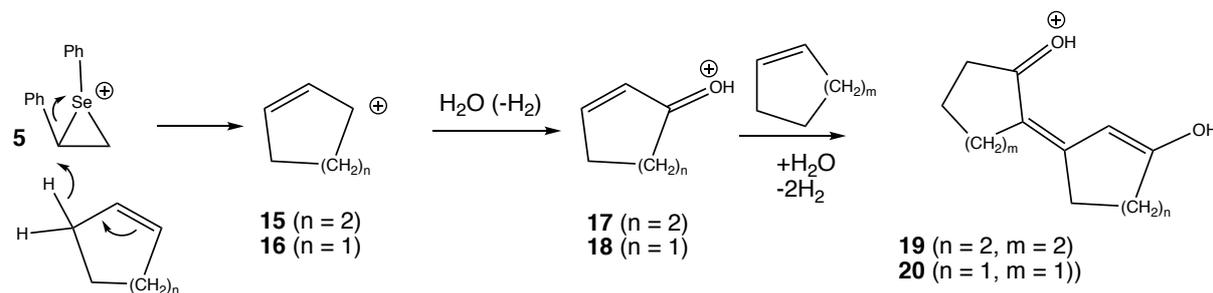
In addition to the selenium transfer products **7** ( $m/z$  239) and **8** ( $m/z$  225) resulting from reaction of the seleniranium ion **5** with cyclohexene and cyclopentene respectively, minor ions at  $m/z$  341 and 343 (in the case of cyclohexene, Fig. 3) and  $m/z$  327 and 329 (in the case of cyclopentene, were also observed (Supplementary Figure S5). These ions have been tentatively assigned to the electrophilic-addition products **11** and **12** and the ions **13** and **14** derived from **11** and **12** by loss of  $\text{H}_2$  (scheme 6). Their elemental compositions were confirmed via HRMS in addition to deuterium isotope labelling experiments (Supplementary

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Figures S4, S5, S8, S9) where loss of HD was observed in the reaction with d10-cyclohexene ( $C_6D_{10}$ ). In this latter reaction, ions at  $m/z$  350 and 353 (*c.f.* ions at  $m/z$  341 and 343 in the reaction with  $C_6H_{10}$ ) were observed corresponding to the electrophilic addition product as well as the ion corresponding to the loss of HD. Another interesting channel was also observed in the reaction with both neutrals where ions at  $m/z$  97 and  $m/z$  193 ( $[C_6, H_9, O]$  and  $[C_{12}, H_{17}, O_2]$  in the case of cyclohexene) and,  $m/z$  83 and  $m/z$  165 ( $[C_5, H_7, O]$  and  $[C_{10}, H_{13}, O_2]$  in the case of cyclopentene) were detected. These ions did not contain selenium as was confirmed by the isotope distribution and their elemental composition confirmed via HRMS (Supplementary Figures S6-9). These ions, whose intensity increases with time, may plausibly have arisen by an initial hydride transfer from the added alkene to the seleniranium ion **5** as well as other derived seleniranium ions formed over time, to give the allylic cations **15** and **16** followed by reaction with adventitious water within the mass spectrometer (Scheme 7), and loss of a hydrogen molecule to give the delocalised cations **17** and **18**. Reaction of **17** and **18** with cyclohexene or cyclopentene respectively, present in the ion trap would plausibly lead to the extensively delocalised cations **19** and **20**. This reaction could conceivably represent an alternative pathway from the same collision complex leading to the electrophilic addition reaction (Scheme 6). Thus cyclohexene reacts with the seleniranium cation via hydride transfer to generate  $[Cyclohexene - H]^+$ . This latter ion quickly reacts with  $H_2O$ , followed by loss of  $H_2$  generating the ion  $[C_6H_8OH]^+$  at  $m/z$  97. This is further supported when comparing the reaction of the d10-cyclohexene where the corresponding ion, at  $m/z$  105 forms, corresponds to  $[C_6D_8OH]^+$ . The larger cycloalkenes (cycloheptene and cyclooctene) exhibited similar products except in the case of cyclooctene where  $m/z$  123 involved the additional loss of  $H_2$  (Supplementary Figures S8-9). Further work involving specifically isotopically labelled substrates will shed more light on these proposed mechanisms.



**Scheme 6:** Proposed Electrophilic addition products and their derived ions. Plausible mechanism for the formation of adduct ion **12**.

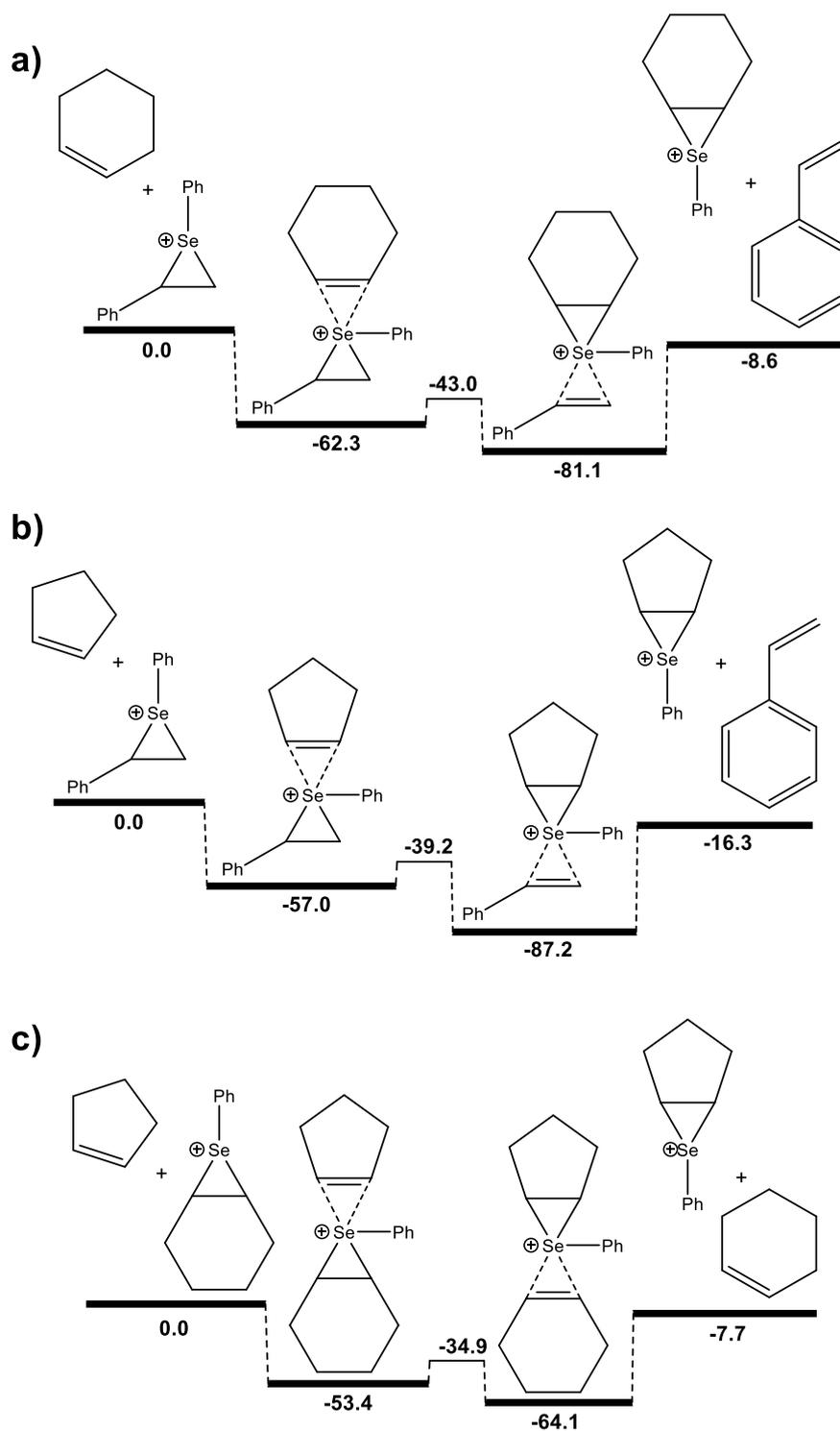


**Scheme 7.** Proposed hydride transfer reaction occurring in competition with electrophilic addition reaction.

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To gain insights into the mechanism of the direct transfer of  $\text{PhSe}^+$  from one alkene to another, theoretical calculations were undertaken. Figure 4 represents potential energy diagrams for the reaction of **5** with (A) cyclohexene and (B) cyclopentene as well as (C) the reaction of **7** with cyclopentene. These diagrams correspond to the three exchange processes observed to take place within the mass spectrometer. The exchange reaction found not to take place – the reaction of cyclohexene with **8** – corresponds to the reverse process in Figure 3(C).

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3 In all cases the approaching/leaving alkene coordinates relatively strongly with the  
4 seleniranium ions, producing adducts with energies *ca.* 60 kJ mol<sup>-1</sup> below the separated  
5 reactants/products. For all three systems, the transition states corresponding to alkene  
6 exchange sit well below the energies of both the reactant and product sets, at about 20 kJ mol<sup>-1</sup>  
7 above the adducts. In the gas phase, ligand exchange is therefore expected to be rapid, with  
8 the reaction products controlled not by the barrier to reaction but by the overall  
9 thermodynamics. Consistent with the experiments reported here, the reaction of **5** with both  
10 cyclohexene and cyclopentene is exothermic to release styrene, with **7** also reacting  
11 exothermically with cyclopentene to liberate cyclohexene. The reaction of **8** with cyclohexene  
12 is endothermic by almost 8 kJ mol<sup>-1</sup> in producing cyclopentene; this process would be  
13 expected to be slow in the gas phase at room temperature, consistent with the experimental  
14 results.  
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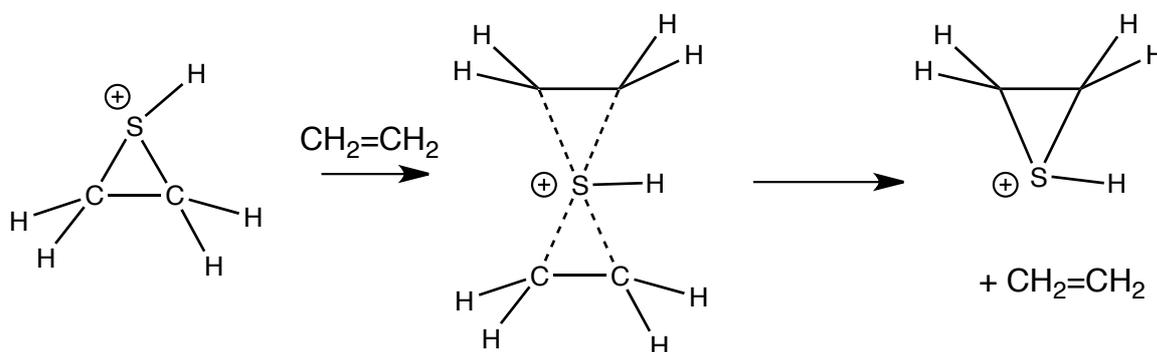


53 **Figure 4:** potential energy diagrams at the M06/6-31+G(d) level of theory for the reaction of:  
54 a) **5** with cyclohexene; b) **5** with cyclopentene and; c) Product of the reaction of **5** with  
55 cyclohexene then addition of cyclopentene. Energies are in kJ.mol<sup>-1</sup>.

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It is worthwhile noting the work of Radom *et al.* who have calculated the barrier to  $\pi$ -ligand exchange for thiranium ions using the identity reaction shown in Scheme 8. They showed that the reaction proceeds via a complex with a binding energy of 25.6 kJ mol<sup>-1</sup> and the transition state lies at 46.6 kJ mol<sup>-1</sup> above this complex.<sup>42</sup>



Scheme 8.  $\pi$ -ligand exchange in the thiranium ion.

### Conclusions

This paper represents, to our knowledge, the first gas-phase experimental study on the mechanisms involved in the  $\pi$ -ligand transfer of PhSe<sup>+</sup> from one alkene ligand to another. These results support the conclusions of Denmark *et al.* from their solution phase experiments.<sup>20</sup> The relative reactivities of a series of cycloalkenes towards  $\pi$ -ligand exchange of the seleniranium ion **5** were determined and found to follow the following order; cyclohexene < cyclopentene < cycloheptene < cyclooctene which is consistent with relative rates of reaction of this series of alkenes towards dihalocarbene reagents, and from heats of hydrogenation.

Both, gas-phase experiments and theoretical modeling have demonstrated that direct selenium ion transfer between a seleniranium ion and an alkene, occurs in the gas phase. This reaction is in competition with electrophilic addition reactions as well as hydride-transfer reactions. Theoretical calculations results show that the transfer reactions are thermodynamically controlled. Experiments and theory have also shown that this transfer is ligand dependant.

### **Experimental Section.**

Cycloalkenes used in this study were used as supplied from Sigma Aldrich chemical company.

#### **Synthesis**

The precursor  $\beta$ -selenyl amine **3a** was prepared by the addition of *in-situ* generated phenylselenium azide to styrene,<sup>43</sup> followed by reduction of the intermediate azide with NaBH<sub>4</sub> in THF/methanol.<sup>44</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.64 (m, 1H), 7.47 (m, 1H), 7.32-7.21 (m, 8H), 4.14 (dd,  $J = 9.3, 4.1$  Hz, 1H), 3.30 (dd,  $J = 12.5, 4.2$  Hz, 1H), 3.09 (dd,  $J = 12.4, 9.3$  Hz), 1.72 (bs, 2H, -NH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  143.6, 132.9, 129.7, 129.1, 128.6, 127.7, 127.1, 126.4, 55.2, 37.5.

The precursor  $\beta$ -selenyl amine **3b** was prepared by free radical azidoselenation of styrene followed by NaBH<sub>4</sub> reduction in THF/methanol by the method of Tingali *et al.*<sup>45</sup> Compound **3b** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.55 (m, 1H), 7.32 (m, 1H), 7.32-7.21 (m, 8H), 4.27 (t,  $J = 7.3$  Hz), 3.27 (m, 1H), 3.19 (dd,  $J = 13.5, 6.2$  Hz, 1H), 1.29 (bs, 2H, -NH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  140.6, 135.0, 128.6, 128.2, 127.6, 127.5, 127.0, 51.6, 46.6.

#### **Mass Spectrometry:**

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3 Ion-molecule reactions (IMR) were performed using a Finnigan hybrid linear quadrupole  
4 (LTQ)-Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer that was  
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6 modified to allow the introduction of neutral reagents, such as volatile alkenes, into the ion  
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8 trap with the helium bath gas. The He pressure in the trap is always maintained at  $\sim 2$  mTorr<sup>28</sup>  
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10 and the trapped ions are at near room temperature.<sup>31</sup> The reagent concentrations  
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12 (cyclopentene; cyclohexene; cycloheptene; cyclooctene) in the ion trap were calculated to lie  
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14 between  $1-5 \times 10^{10}$  molecules.cm<sup>-3</sup> in this work. Ions formed in the linear ion trap resulting  
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16 from ion-molecule reactions and/or CID were transferred to the FT-ICR cell for accurate mass  
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18 measurements. Standard ion isolation and excitation procedures were performed using the  
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20 LTQ-FT-ICR software.  
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27 ESI solutions were introduced into the mass spectrometer using a syringe pump operating  
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29 at  $5 \mu\text{L}\cdot\text{min}^{-1}$  and by applying 3.3–4.8 kV to the ESI capillary relative to the heated capillary  
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31 entrance to the mass spectrometer (250 °C). The sheath gas and lenses were tuned to optimize  
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33 the signal of  $m/z$  261.  
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### 37 ***Theoretical calculations:***

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39 *Ab initio* calculations were performed using the Gaussian 09 software package.<sup>46</sup> Structures  
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41 and energies were obtained at the M06/6-31+G(d) level of theory, using the “ultrafine”  
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43 integration grid. The M06 density functional<sup>47</sup> is a hybrid meta-GGA functional designed for  
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45 use with both metal and non-metal compounds, and is thus applicable to the study of  
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47 organometallic reaction mechanisms. Reported energies are at 298 K and include zero-point  
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49 vibrational energy corrections. Optimized coordinates for all reported structures are provided  
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51 as supporting Information. Ion mobility collision cross sections for **5**, **6a** and **6b** were  
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53 modelled in a modified version of MOBCAL parametrised for N<sub>2</sub> buffer gas using the  
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55 trajectory method. The input charge distributions were calculated using the CHELPG scheme  
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57 from M06/def2-TZVPP densities using the ORCA 4.0 program.<sup>34,35,36</sup>  
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3 For comparison with experimental IRMPD spectra, infrared absorption spectra of the lowest  
4 energy structures were calculated at the B3LYP/6-311++G(d,p) level of theory using the  
5 Gaussian suite of programs.<sup>46</sup> Harmonic frequencies were scaled using a factor of 0.98 which  
6 has been shown to be adequate for simulating IRMPD spectra in the 800-1800 cm<sup>-1</sup> spectral  
7 range.<sup>48</sup>  
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### 18 ***Ion mobility measurements:***

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20 The ion mobility mass spectrometer, which is home built has been described previously.<sup>49,50,51</sup>  
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22 Ions generated by electrospray ionization were introduced through a desolvation capillary into  
23 an ion funnel. An electrostatic gate at the end of the ion funnel was periodically opened (at 20  
24 Hz) to introduce packets of ions into a 0.9 m drift tube filled with N<sub>2</sub> gas at ≈6 torr and with  
25 an electric field of ≈40 V/cm sustained by a series of ring electrodes. At the end of the drift  
26 tube, the ions were collected by a second ion funnel before passing through a 0.3 mm aperture  
27 into a octupole ion guide and then through a 3 mm aperture into a quadrupole mass filter that  
28 was tuned to the mass of the ion of interest. Finally, the ions were sensed by a channeltron ion  
29 detector connected to a multichannel scaler. Arrival time distributions were built up as a  
30 histogram of ion counts versus arrival time.  
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### 43 ***IRMPD spectroscopy:***

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45 Infrared multiple photon dissociation (IRMPD) spectroscopy of mass-selected ions was  
46 performed using a 7 Tesla Fourier transform ion cyclotron resonance (FT-ICR) tandem mass  
47 spectrometer (Bruker Apex IV Qe)<sup>52</sup> coupled to the IR FEL beam line of CLIO.<sup>53</sup>  
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53 Electro sprayed ions were mass-selected and accumulated in a linear hexapole pressurized  
54 with Ar at ~10-3 mbar thus ensuring for thermalization through multiple collisions.<sup>48</sup> Ions are  
55 subsequently pulse-extracted into the ICR cell where they are irradiated with the IR beam  
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3 tuned at a selected wavenumber. The irradiation time was 1 second, which corresponds to 25  
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5 macropulses, i.e.  $\sim 8 \mu\text{s}$  long trains of picopulses.<sup>53</sup>  
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## 10 **Acknowledgement**

11  
12 We thank the Australian Research Council for financial support for financial support  
13 (DP0770565) and an award of a APA to B.H. Financial support from the French FT-ICR  
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15 network (FR3624 CNRS) for conducting the research is gratefully acknowledged.  
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## 22 **Supporting information.**

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24 Mass spectral outputs of all the ion-molecule reactions with observed high-resolution data.  
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26 Gaussian archive entries for all calculated structures and transition states, assignments of the  
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28 vibrational modes for **5**.  
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