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Face to face activation of phenylselenium boranes with α,β-unsaturated carbonyl substrates: facile synthesis of C-Se bonds

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Activated olefins directly react with phenylselenium boranes, at room temperature, without the need of metal or organocatalytic assistance. A simple mechanism that involves the interaction of the electron pair of carbonyl functional group in α,β-unsaturated ketones and aldehydes, with the empty p orbital of the boron atom, justifies the efficient reaction towards the kinetically and thermodynamically most stable 1,4-addition product. Up to 12 examples of β-(phenylseleno) substituted ketones and aldehydes have been prepared with moderate to high yield. The simplicity and efficiency of this new reactivity generates new strategic platforms towards the C-Se bond formation and opens non existing pathways to create C-heteroatom bonds, as a general tool.

Introduction

There has been recent considerable interest in the generation of organoselenium compounds for their extensive applications in organic synthesis, material science, ligands for transition metals and even as therapeutic agents.[1] Of particular significance is the synthesis of selenium substituted carbonyl compounds which are well known to act as enone β-anion synthons.[2] Routes to these remarkable compounds either suffer from low yields and/or harsh reaction conditions utilizing the sensitive and malodorous selenols. A study by Leonard and Livinghouse showed that novel monomeric selenium boron compounds, derived from dialkylboranes, could be used as a gentle and efficient alternative to the starting selenols.[2c] Unfortunately, reactions with bulky α,β-unsaturated carbonyl compounds gave the corresponding organoselenium products in low yields, presumably due to the steric congestion arising from the bulky borane group. While selenium boron compounds derived from carboranes are well known,[3] the synthetic potential of these simple compounds has not yet been fully realised. As a result, we decided to prepare the analogous compound from pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$) and examine its reactivity with a number of α,β-unsaturated carbonyl compounds.

The selenium boron species PhSeBpin (**1**) was prepared by the room temperature metal catalysed dehydrogenative borylation of the selenol PhSeH and one equivalent of the borane HBpin.[4] Complete conversion of the starting materials to **1** was achieved selectively using 0.02 mol% of $RhCl(PPh_3)_3$. Compound **1** was characterized using a number of physical methods including multinuclear NMR spectroscopy. A peak in the ^{11}B NMR spectra for **1** at 33 ppm is consistent with a three coordinate RBpin group.[5,6] The selenium boron species **1** was also characterized by a single crystal X-ray diffraction study, whereupon the molecular structure is shown in Figure 1. The Se-B distance of 1.950(3) Å is somewhat shortened compared to previous carborane examples, which tend to be greater than 2.0 Å.[3a-e] Complete crystallographic details, including bond distances and angles, are included in the Supporting Information.

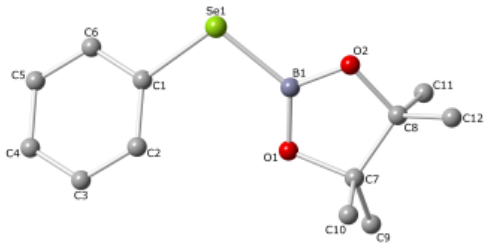


Figure 1. Ball and stick diagram of **1** with hydrogen atoms omitted for clarity. Selected bond distances (Å): Se(1)-C(1) 1.923(3), Se(1)-B(1) 1.950(3), B(1)-O(2) 1.349(4), B(1)-O(1) 1.349(3); Selected bond angles (°): C(1)-Se(1)-B(1) 103.69(12), O(2)-B(1)-O(1) 115.2(2), O(2)-B(1)-Se(1) 118.3(2), O(1)-B(1)-Se(1) 126.5(2), B(1)-O(1)-C(7) 105.9(2), B(1)-O(2)-C(8) 106.9(2).

Quaternization of one boron atom in species containing B-B and B-E bonds (E= elements from group 14) induces the heterolytic cleavage of these stable bonds.[5] The pull-push effect of diboranes,

silanoboranes and aminoboranes when reacted with bases, by forming the corresponding Lewis acid-base adducts [Nu→B(OR)$_2$-B(OR)$_2$],[6] [Nu→B(OR)$_2$-SiMe$_2$Ph][7] and [Nu→B(OR)$_2$-NR'$_2$][8] facilitate the release of a boryl, silyl or amine moiety with enhanced nucleophilic character. However, their reactivity with olefins, even activated olefins such as α,β-unsaturated carbonyl compounds, has always required of the assistance of bases, principally alkoxides ($^-$OMe, $^-$O^{t}Bu) or N-heterocyclic carbenes, to activate the B-B, B-Si or B-N reagent (Figure 2). Therefore, a three element performance was designed.

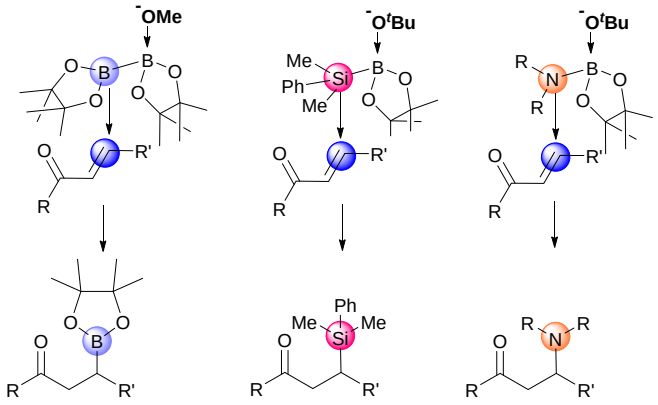
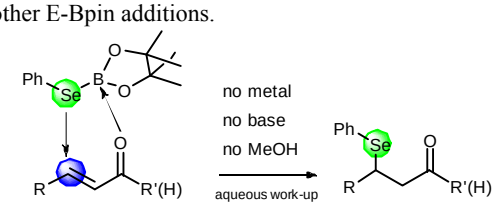


Figure 2. Postulated activation of B-B, B-Si or B-N reagents with alkoxides to facilitate reactivity of boryl, silyl or amine moieties with C=C bonds.

Now, we have found that the simple approach of the substrate α,β-unsaturated carbonyl compounds to the selenium boron species PhSeBpin (**1**), promotes the PhSe transfer from the reagent to the substrate, in a selective manner (Scheme 1). Remarkably, the direct addition does not require the presence of any transition metal complex as catalyst or bases or even co-solvents such as MeOH, unlike other E-Bpin additions.

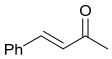
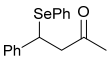
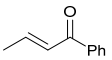
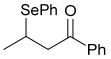
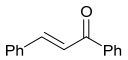
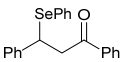
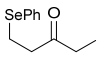
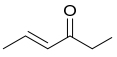
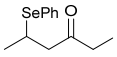
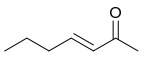
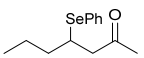
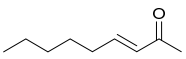
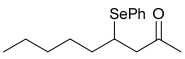
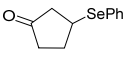
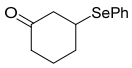
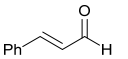
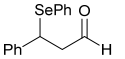
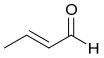
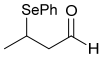
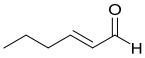
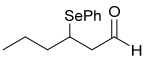


Scheme 1. Hypothetical reactivity of phenylselenium boranes with α,β-unsaturated ketones and aldehydes.

Results and Discussion

With the aim of activating **1** and selectively transferring the PhSe moiety to activated olefins, we first attempted to find the optimal conditions for the conjugate addition of 4-phenyl-3-buten-2-one (**2**). When the reaction was carried out in chloroform, benzene and THF as solvents, at room temperature, low percentages of β-(phenylseleno) substituted ketone was observed (Table 1, entries 1-3). An excess of PhSeBpin reagent (1.5 eq) or higher reaction temperatures (60ºC) did not improve the product formation.

Table 1. Conjugate addition of PhSe moiety to α,β-unsaturated ketones[a]

Entry	Substrate	Product	Solvent	Conv. (%)[b]	I.Y. [%]
1	 **2**	 **3**	$CHCl_3$	27	
2	,,	,,	benzene	30	
3	,,	,,	THF	40	[35]
4[c]	,,	,,	THF	24	
5[d]	,,	,,	THF	29	
6	 **4**	 **5**	THF	69	[49]
7	 **6**	 **7**	THF	67	[60]
8	 **8**	 **9**	THF	99	[54]
9	 **10**	 **11**	THF	94	[37]
10	 **12**	 **13**	THF	78	[70]
11	 **14**	 **15**	THF	65	[31]
12	 **16**	 **17**	THF	65	[44]
13	 **18**	 **19**	THF	93	[65]
14	 **20**	 **21**	THF	41	[39]
15	 **22**	 **23**	THF	99	[68]
16	 **24**	 **25**	THF	53	[50]

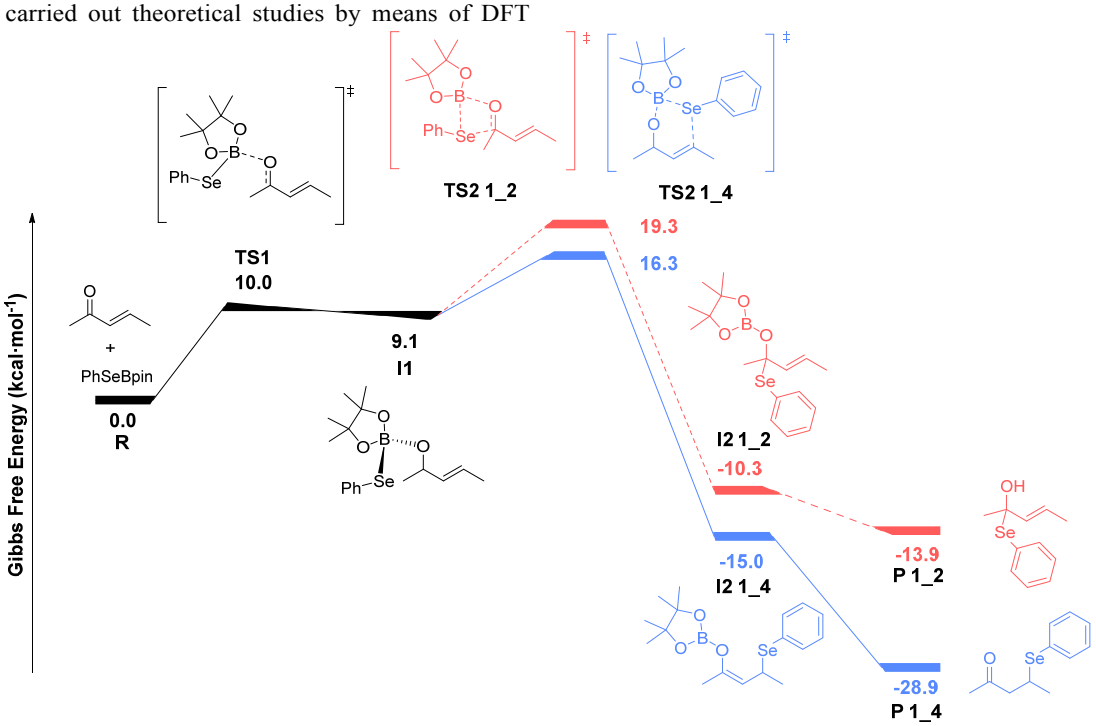
[a]Reaction conditions: substrate (0.10 mmol), PhSeBpin (1.1 eq), THF (2 mL), 25ºC, 16h. [b]Conversion calculated by NMR spectroscopy from an average of two essays. [c] PhSeBpin (1.5 eq), [d]T=60ºC.

The influence of other α,β-unsaturated ketones towards the preparation of β-(phenylseleno) substituted ketones was next examined. As shown in Table 1, the substrate *trans*-1-phenyl-2-buten-1-one (**4**) was more efficiently converted into the corresponding product **5** (Table 1, entry 6) than the analogue 4-phenyl-3-buten-2-one (**2**) (Table 1, entry 3) under the same

reaction conditions. The conjugated Ph substituent to the C=O of the ketone seems to favour the interaction of the lone pair from C=O to Bpin. This hypothesis was also proved in the conjugate addition of PhSe moiety to *trans*-chalcone (**6**) achieving 67% conversion (Table 1, entry 7). More remarkably, the aliphatic ketones 1-penten-2-one (**8**) and 4-hexen-3-one (**10**), which contain an ethyl group bonded to the carbonyl group, were quantitatively transformed into the corresponding β-(phenylseleno) substituted ketones **9** and **11**, up to 99% conversion (Table 1, entries 8-9). For the bulkiest aliphatic ketones 3-hepten-2-one (**12**) and 3-nonen-2-one (**14**), the conversion diminished slightly probably as a consequence of the steric hindrance around the C_β (Table 1, entries 10-11). Interestingly, the cyclic α,β-unsaturated ketones 2-cyclopente-1-one (**16**) and 2-cyclohexen-1-one (**18**) were efficiently transformed into the β-seleno adducts (up to 98% conversion in the case of β-(phenylseleno)-cyclohexanone (**19**)) (Table 1, entries 12-13). It is important because for these cases where the C=O and C=C are in *trans* each other, the lone pair from the oxygen seems to activate the Bpin as well. Next, we turned our attention to explore the β-selenation of α,β-unsaturated aldehydes. In the case of cinnamaldehyde (**20**), the conjugate addition of PhSe was similar to the same reaction on 4-phenyl-3-buten-2-one (**2**), indicating that the functional groups ketone or aldehyde do not provide a significant difference on the C=O interaction with Bpin (Table 1, entries 3 and 14). When the substrate was the aliphatic aldehyde crotonaldehyde (**22**), quantitative transformation into the desired product was observed (99%, Table 1, entry 15), however steric factors on the β-carbon diminished the conjugate addition of PhSe on *trans*-2-hexenal (**24**) (Table 1, entry 16). Unfortunately, when α,β-unsaturated esters were subjected to the same reactivity, the corresponding β-(phenylseleno) substituted ester was not formed.

In order to establish a rational understanding of the reaction outcome we carried out theoretical studies by means of DFT methods including dispersion effects (M06-2X, see Supporting Information) to unravel the mechanism of this new reaction of PhSeBpin (**1**) with α,β-unsaturated carbonyl compounds.

Scheme 2 shows the proposed reaction pathway (Gibbs free energy profile in gas phase) for the reaction of **1** with 3-penten-2-one chosen as model substrate. In the first step, the carbonylic oxygen interacts with the empty *p* orbital of the boron atom, in the same way as other nucleophiles do (alkoxides, carbenes), thus increasing the nucleophillic character of the PhSe moiety. Indeed, a first intermediate is formed (**I1**, Se-B=2.089 Å, B-O=1.619 Å, O-C_2=1.244 Å) which lies 9.1 kcal·mol^{-1} above the reactants. Note that in the electronic energy profile this intermediate is 5.8 kcal·mol^{-1} more stable than the two separated entities, and it is raised in free energy because the loss of translational entropy. All Gibbs free energy values provided in the manuscript do not include any additional correction. We located a transition state (**TS1**, Se-B=2.039 Å, B-O=1.899 Å, O-C_2=1.234 Å) for the formation of intermediate **I1**, which reflects the activation of the Se-B bond too, its bond distance computed Se-B (1.953 Å) in the free reagent. The next step is the boron-selenium bond cleavage, which is concerted with the attack of the nucleophillic selenium to the electrophillic points of the substrate through a second transition state. Thus, selenium can attack either the β position (**TS2 1_4**) or the carbonylic carbon (**TS2 1_2**). In the **TS2 1_4** it can be observed that the Se-B distance increases (Se-B=2.170 Å) while the B-O decreases (B-O=1.551Å). The electronic rearrangement of the double bond can be observed by the increase of the O-C_2 (O-C_2=1.281 Å) and the decrease of the C_2-C_3 bond distances (ΔC_2-C_3=-0.06 Å). In the **TS2 1_2** the increment of the Se-B bond (Se-B=2.223 Å) distance can be observed as well as the B-O decrease (B-O=1.539 Å) and the O-C_2 increase (O-C_2=1.282 Å). The optimized structures for the **TS1**, **I1**, **TS2 1_2** and **TS2 1_4** are collected in Figure 3.



Scheme 2. Proposed reaction pathway for the reaction of PhSeBpin (**1**) with 3-penten-2-one. The pathway for the direct addition is painted in red and for the conjugate addition is painted in blue. All energies are in kcal·mol^{-1}.

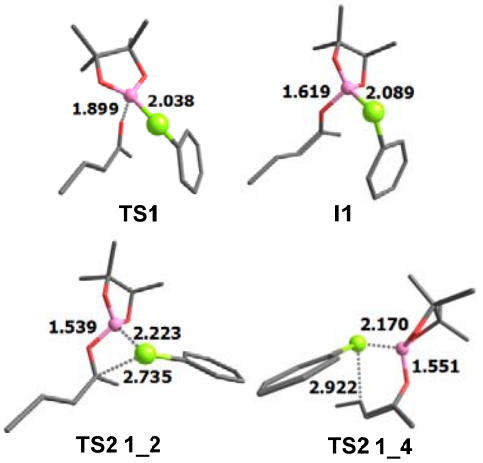


Figure 3. Optimized structures for the **TS1**, **I1**, **TS2 1_2** and **TS2 1_4** with the selected geometric parameters in Å.

It is important to highlight that the 1,4-addition pathway is less energetically demanding than the 1,2-addition, and also it leads to a more stable intermediate **I2 1_4**, which after a work-up becomes the most stable β-selenated ketone (**P 1_4**). In all the cases studied (Table 1) the corresponding seleno-alcohol **P 1_2** was never experimentally observed. Therefore, the 1,4-addition product **P 1_4** is obtained from both kinetic and thermodynamic reasons. The molecular orbital plot in Figure 4 depicts the HOMO of **TS2 1_4** that reflects two interesting features: first, the big lobe located on the nucleophillic Se atom interacting with the β-carbon, and second, the building up of a π orbital between the α and the carbonylic carbon atoms.

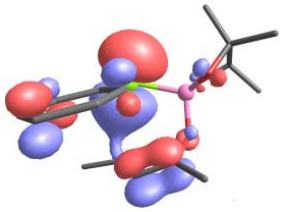


Figure 4. Graphic representation of the HOMO orbital for the **TS2 1_4** corresponding to the interaction of the selenium atom with the β carbon.

At this point we decided to explore theoretically the reaction of the same substrate, 3-penten-2-one, with the sulphur (PinBSPh) and oxygen (PinBOPh) analogous of PinBSePh (**1**). Figure 5 plots graphically the relative Gibbs free energies of the **TS1**, **I1**, **TS2 1_4** and **I2 1_4** structures for selenium, sulphur and oxygen borane reagents. Note that the energies for PinBSePh and PinBSPh are very similar, almost identical, and this would indicate that both reactions might take place under the same conditions. However, it is important to mention that in the case of the oxygen analogous the pathway is clearly different than the other two: no **TS1** was located, and the reaction would occur in only one step. Moreover, the activation energy in this case is much higher than for the Se and S species, and the reaction would lead to a product that is even less stable than the reactants. Based on these theoretical arguments, one should expect that the reaction probably work for the S-borane derivative under the same reaction conditions than the selenium reagent, but it will not work for an oxygen equivalent based reagent.

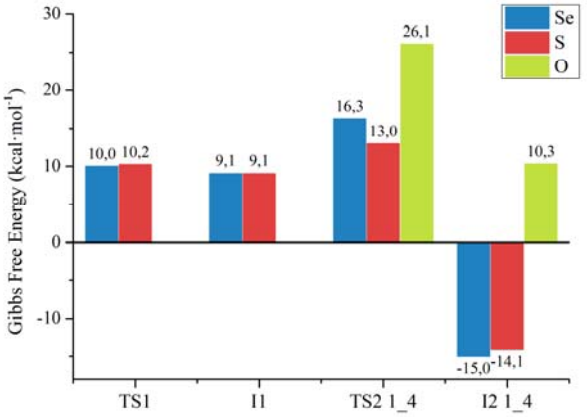
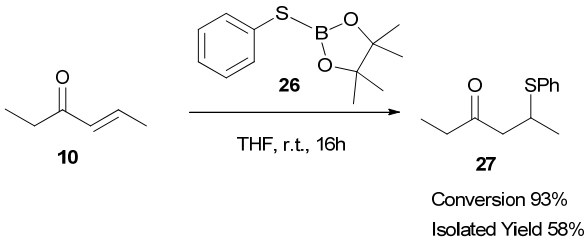


Figure 5. Relative Gibbs free energies of the most relevant species in the reaction of 3-penten-2-one with PinBSePh (**1**) and its S and O analogous.

Indeed, these predictions were confirmed by a single experiment. The reagent PhSBpin (**26**)[4] was added to 4-hexen-3-one (**10**) in THF as solvent, at room temperature, in the absence of any additive. After 16h the PhS moiety was directly and quantitatively transferred to the activated olefins, to form the corresponding 5-phenylsulphanyl-hexan-3-one (**27**) after work-up, as a result of the 1,4-addition reaction (Scheme 3). The simplicity of the chemical operation, confirms the theoretical prediction, but also opens a useful methodology to generate organosulfur compounds in a facile and highly efficient way, which contrast with all the previous reports involving 1,4-addition of thiols to α,β-unsaturated carbonyl compounds, that require additional catalysts or bases.[9,10]



Scheme 3. Extrapolated reactivity of PhSBpin to α,β-unsaturated ketones on the basis of theoretical prediction of direct 1,4-addition reaction

Conclusions

The direct reactivity between *p*-phenylselenium pinacolborane (PhSeBpin) and activated olefins such as α,β-unsaturated ketones or aldehydes opens a non existing pathway towards the selective β-(phenylseleno) substituted carbonyl compounds. The substrate scope of the α,β-unsaturated ketones or aldehydes is wide and includes cyclic and acyclic substrates (12 examples). DFT studies propose a plausible mechanism of the

reaction and explain the high selectivity towards the 1,4-addition product. This is a new method to achieve easily a C-Se bond formation in a selective way without any metal or organocatalyst assistance. Moreover, predictions are made on the reactivity of the sulphur and oxygen analogous. Eventually, an example of direct reaction between PhSBpin and 4-hexen-3-one in corroborates that selenium and sulphur follow the same pathway in the facile 1,4-addtion to α,β-unsaturated carbonyl compounds.

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