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

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Activated olefins directly react with a phenylselenium borane, at room temperature, without any metal or organocatalytic assistance. Up to 10 examples of β-(phenylseleno) substituted ketones and aldehydes have been prepared and theoretical evidence for the mechanism opens up non-existing pathways to create C–heteroatom bonds as a general tool.

Recently, there has been considerable interest in the generation of organoselenium compounds for their extensive applications in organic synthesis, materials 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 of **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, and the molecular structure is shown in Fig. 1. The Se–B distance of 1.950(3) Å is somewhat shortened compared to that of 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 ESI.†

Quaternization of one boron atom in species containing B–B and B–E bonds (E = elements from group 14) facilitates the heterolytic cleavage of these stable bonds.[5] The pull–push effect of diboranes, silaboranes and aminoboranes when reacted with bases, by forming the corresponding Lewis acid–base adducts $[Nu\rightarrow B(OR)_2–B(OR)_2]$,[6] $[Nu\rightarrow B(OR)_2–SiMe_2Ph]$[7] and $[Nu\rightarrow B(OR)_2–NR_2']$,[8] facilitates 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 the assistance of bases, principally alkoxides (^-OMe, $^-O^tBu$) or N-heterocyclic carbenes, to activate the B–B, B–Si or B–N reagent. Now, we have found that the simple addition of α,β-unsaturated carbonyl compounds to the selenium boron species PhSeBpin (**1**) selectively promotes the PhSe transfer (Scheme 1).

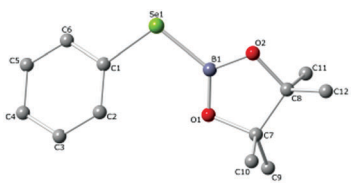

Fig. 1 Ball and stick diagram of **1** with hydrogen atoms omitted for clarity. Selected bond distances (Å): Se(1)–C(1) 1.923(3), Se(1)–B(1) 1.950(3), B(1)–O(2) 1.349(4), B(1)–O(1) 1.349(3); selected bond angles (°): C(1)–Se(1)–B(1) 103.69(12), O(2)–B(1)–O(1) 115.2(2), O(2)–B(1)–Se(1) 118.3(2), O(1)–B(1)–Se(1)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

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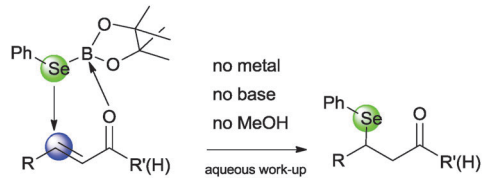


Scheme 1 Hypothetical reactivity of phenylselenium boranes with α,β-unsaturated ketones and aldehydes.

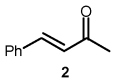
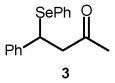
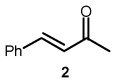
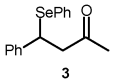
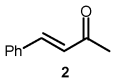
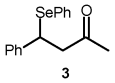
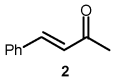
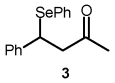
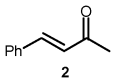
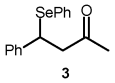
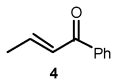
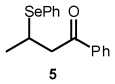
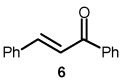
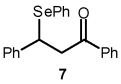
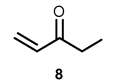
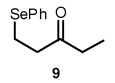
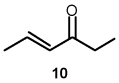
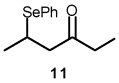
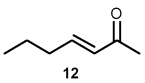
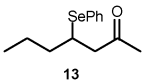
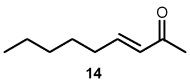
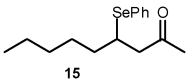
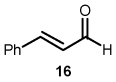
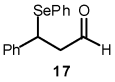
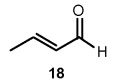
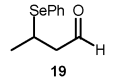
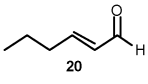
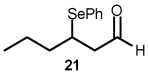
Remarkably, this direct addition does not require the presence of a transition metal complex, base or even co-solvent, such as MeOH, unlike other E-Bpin additions.

With the aim of activating **1** and selectively transferring the PhSe moiety to electron deficient 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, a low percentage of the β-(phenylseleno) substituted ketone was observed (Table 1, entries 1–3). An excess of PhSeBpin reagent (1.5 eq.) or higher reaction temperatures (60 °C) did not improve the product formation.

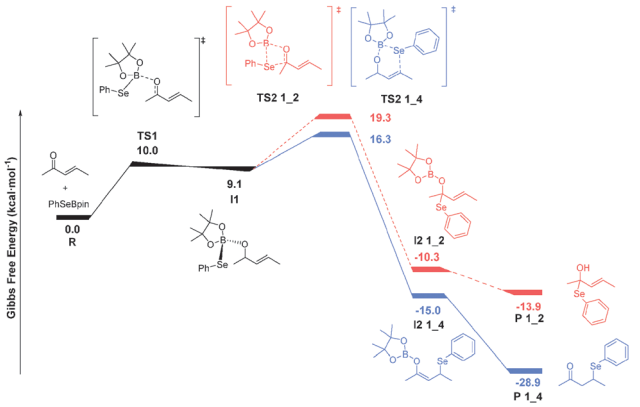
The influence of other α,β-unsaturated ketones on the preparation of β-(phenylseleno) substituted ketones was next examined. As shown in Table 1, the substrate *trans*-1-phenyl-2-buten-1-one (**4**) was more efficiently converted into the corresponding product **5** (Table 1, entry 6) than the analogue 4-phenyl-3-buten-2-one (**2**) (Table 1, entry 3) under the same reaction conditions. Substrates with a Ph group bound to the C═O (**4** and **6**) were converted into the 1,4-product with better conversion values (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** with up to 99% conversion (Table 1, entries 8 and 9). For the bulkiest aliphatic ketones, 3-hepten-2-one (**12**) and 3-nonen-2-one (**14**), the conversion diminished slightly (Table 1, entries 10 and 11), probably as a consequence of the more hindered β-position. Next, we turned our attention to explore the β-selenation of α,β-unsaturated aldehydes. In the case of cinnamaldehyde (**16**), 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 in the C═O interaction with Bpin (Table 1, entries 3 and 12). When the substrate was the aliphatic aldehyde crotonaldehyde (**18**), quantitative transformation into the desired product was observed (99%, Table 1, entry 13), however the conjugate addition of PhSe on *trans*-2-hexenal (**20**) (Table 1, entry 14) was diminished. Unfortunately, when α,β-unsaturated esters were subjected to the same reactivity, the corresponding β-(phenylseleno) substituted esters were 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 ESI†) 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 the gas phase) for the reaction of **1** with 3-penten-2-one, chosen as the 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 (alkoxides, carbenes), thus increasing the nucleophilic character of the PhSe moiety.

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

Entry	Substrate	Product	Solvent	Conv.[b] (%)	I.Y. (%)
1	 **2**	 **3**	$CHCl_3$	27	
2	 **2**	 **3**	Benzene	30	
3	 **2**	 **3**	THF	40	35
4[c]	 **2**	 **3**	THF	24	
5[d]	 **2**	 **3**	THF	29	
6	 **4**	 **5**	THF	69	49
7	 **6**	 **7**	THF	67	60
8	 **8**	 **9**	THF	99	54
9	 **10**	 **11**	THF	95	49
10	 **12**	 **13**	THF	78	70
11	 **14**	 **15**	THF	65	31
12	 **16**	 **17**	THF	41	39
13	 **18**	 **19**	THF	99	68
14	 **20**	 **21**	THF	53	50

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



Scheme 2 Proposed reaction pathway for the reaction of PhSeBpin (**1**) with 3-penten-2-one. All energies are in kcal mol^{-1}.

Indeed, the 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 that of the reactants. Note that the electronic energy profile of this intermediate is 5.8 kcal mol^{-1} more stable than the two separated entities, and it is raised in free energy because of 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, whereupon the bond distance was computed to be Se–B (1.953 Å) in the free reagent. The next step is the boron–selenium bond cleavage, which is concerted with respect to the attack of the nucleophilic selenium on the electrophilic 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 **TS2 1_4** it can be observed that the Se–B distance increases (Se–B = 2.170 Å) while the B–O distance decreases (B–O = 1.551 Å). The electronic rearrangement of the double bond can be observed by the increase of the O–C_2 bond (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 **TS2 1_2** the increase of the Se–B bond (Se–B = 2.223 Å) distance can be observed as well as the decrease of the B–O (B–O = 1.539 Å) and increase of the O–C_2 bond (O–C_2 = 1.282 Å). The optimized structures of **TS1**, **I1**, **TS2 1_2** and **TS2 1_4** are shown in Fig. 2.

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 protonation, becomes a more 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 due to both kinetic and thermodynamic reasons.

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) analogues of PinBSePh (**1**). Fig. 3 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.[9] 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

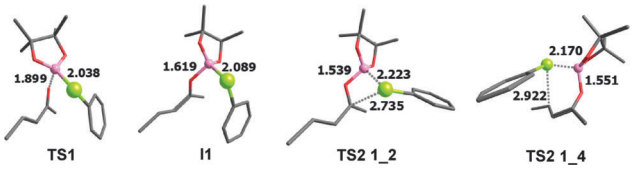


Fig. 2 Optimized structures of **TS1**, **I1**, **TS2 1_2** and **TS2 1_4** with the selected geometric parameters in Å.

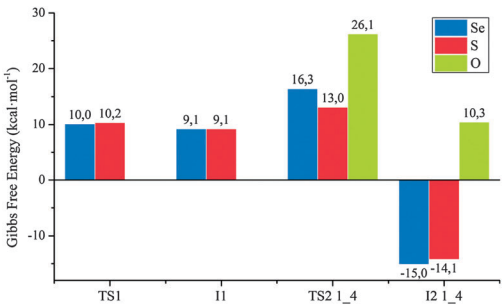
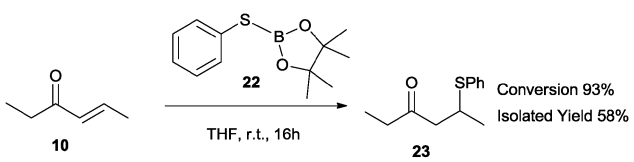


Fig. 3 Relative Gibbs free energies of the most relevant species in the reaction of 3-penten-2-one with PinBSePh (**1**) and its S and O analogous.

same conditions. However, it is important to mention that in the case of the oxygen analogues 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 that 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, we expect that the reaction will probably work for the S–B reagent derivative under the same reaction conditions as observed with the selenium reagent, but it will not work for an oxygen equivalent based reagent.

Indeed, these predictions have been confirmed experimentally for the analogous thioboration reaction. The reagent PhSBpin (**22**)[4] was added to 4-hexen-3-one (**10**) in THF as the solvent, at room temperature, in the absence of any additive. After 16 h the PhS moiety was directly and quantitatively transferred to the activated olefins, to form the corresponding 5-phenylsulphanyl-hexan-3-one (**23**) 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 contrasts with all the previous reports involving 1,4-addition of thiols to α,β-unsaturated carbonyl compounds that require additional catalysts or bases.[10,11] Additional experimental studies are currently underway, particularly with cyclic α,β-unsaturated carbonyl ketones, the results of which will be disclosed in due course.



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

The direct reactivity between *p*-phenylselenium pinacolborane (PhSeBpin) and α,β-unsaturated ketones or aldehydes opens a non-existing pathway towards the selective synthesis of 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] DFT studies propose a plausible mechanism for the reaction and explain the high selectivity towards the 1,4-addition product. Moreover, predictions were made on the reactivity of the sulphur and oxygen analogues. Eventually, an example of the direct reaction between PhSBpin and 4-hexen-3-one corroborates that selenium and sulphur follow the same pathway in the facile 1,4-addition to α,β-unsaturated carbonyl compounds.

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12 Under the same reaction conditions described in Table 1, the cyclic α,β-unsaturated ketone 2-cyclopente-1-one and 2-cyclohexen-1-one were transformed into the β-seleno adducts (65% and 93% conversion respectively). Spectroscopic and theoretical studies are currently being performed to understand the mechanistic pathways in those particular cases. See ESI† for more details.