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Palladium Pincer Complex Catalyzed Substitution of Vinyl Cyclopropanes, Vinyl Aziridines, and Allyl Acetates with Tetrahydroxydiboron. An Efficient Route to Functionalized Allylboronic Acids and Potassium Trifluoro(allyl)borates

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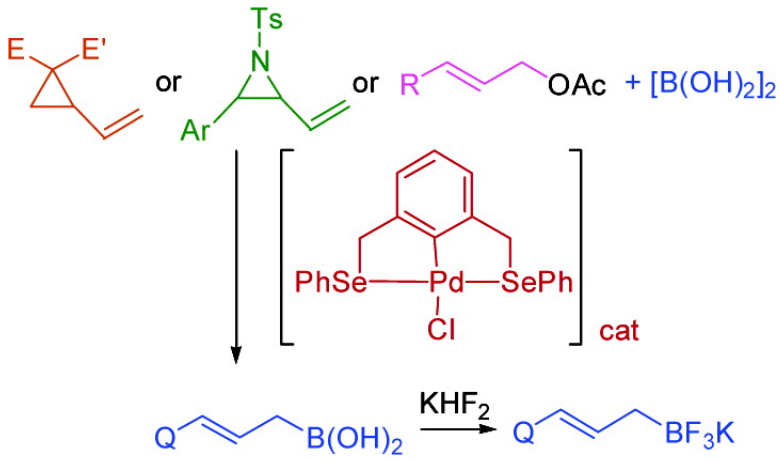

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Palladium Pincer Complex Catalyzed Substitution of Vinyl Cyclopropanes, Vinyl Aziridines, and Allyl Acetates with Tetrahydroxydiboron. An Efficient Route to Functionalized Allylboronic Acids and Potassium Trifluoro(allyl)borates

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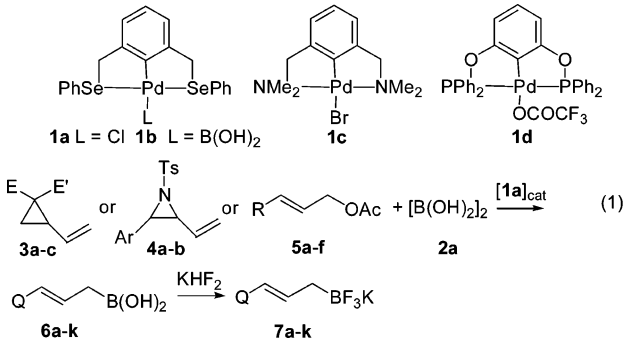
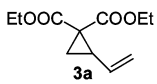
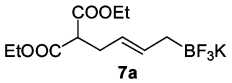
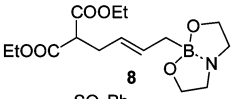
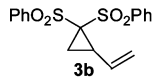
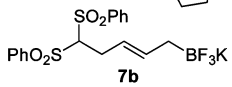
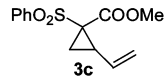
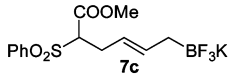
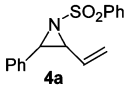
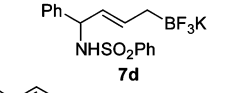
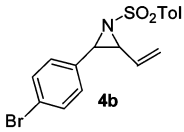
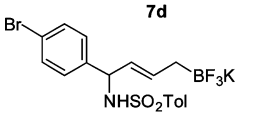
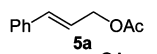
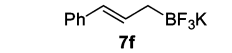
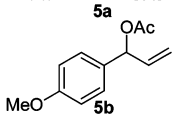
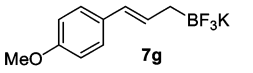
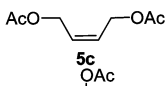
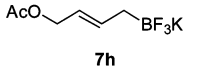
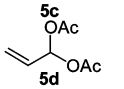
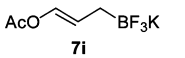
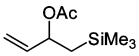
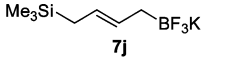
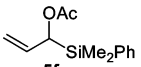
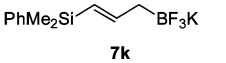
Application of pincer complex catalysts[1] (e.g., **1a**,[1g] **c**[1h]) offers a mild and efficient method for synthesis of functionalized organometallic compounds, such as allyl-, allenyl-, and propargyl stannanes and silanes.[2] Since palladium complexes are known to both create and cleave carbon−metal bonds,[3] the high selectivity of the applied pincer complex catalyst for carbon−metal bond-forming reactions is a prerequisite of a synthetically useful process.



We have now found that pincer complex **1a** readily catalyzes boronate transfer reactions (eq 1) from tetrahydroxydiboron (**2a**) to vinyl cyclopropanes (**3a**−**c**), vinyl aziridines (**4a**−**b**), and functionalized allyl acetates (**5a**−**f**). These reactions afforded allylboronic acids **6a**−**k**, which were subsequently reacted with aqueous KHF_2 to obtain the corresponding potassium trifluoro-(allyl)borate derivatives **7a**−**k** in good to excellent yields (Table 1). Allylboronic acid derivatives are extremely useful precursors for synthesis of allylborane-based building blocks,[4a−g] such as potassium trifluoroborate derivatives[4e−m] and allylboronates including chiral tartrate-based reagents.[4a−d] However, a broad access to functionalized allylboronic acids has been limited by the well-known instability and the high reactivity of these species.[4b] Nevertheless, selective formation of allylboronic acids **6a**−**k** can be observed by ^{1}H NMR spectroscopy (in DMSO-d_6) in the reaction mixture of the above process. Many of these species are surprisingly stable in DMSO solution; however, in concentrated solution or without solvent they completely decompose. Therefore, we converted[4h,l] **6a**−**k** to the corresponding potassium trifluoro(allyl)borate derivatives **7a**−**k**. Most of these compounds are air-stable and soluble in acetone. The exceptions are **7e** and **7j**, which undergo slow decomposition even at low temperature. The resulting allylboronic acids can also be converted to the corresponding allylboronates by using diols instead of KHF_2 (entry 2). Opening of the strained three-membered rings (**3** and **4**) with **2a** proceeds remarkably fast in 2−5 h at 40 °C (entries 1−6), while boronate substitution of the allyl acetates (**5a**−**f**) requires much longer reaction times 16−36 h (entries 7−12). As the boronation reactions proceed under mild and neutral conditions, many functionalities such as Br, COOEt, $ArSO_2(NH)$, OAc, and $SiRMe_2$ are tolerated. Interestingly, in diacetates **5c** and **5d**, only one of the acetate groups is replaced by boronate functionality (entries 9 and 10), and thus orthogonally functionalized products **7h** and **7i** can be obtained. As the silyl functionality of **6j** and **6k** remained unchanged after the KHF_2 treatment,[4m] we were able to prepare useful silyl borane synthons **7j** and **7k**. The regioselectivity of the reaction is excellent, as we obtained only the linear products, even from branched allyl acetates

Table 1. Pincer Complex Catalyzed Synthesis of Allylborates[a]

Entry	Substrate	t [h]	Products	Yield[b]
1	 **3a**	3	 **7a**	82
2[c]	**3a**	3	 **8**	90
3	 **3b**	5	 **7b**	89
4	 **3c**	5	 **7c**	98
5	 **4a**	3	 **7d**	81
6	 **4b**	2	 **7e**	87
7	 **5a**	16	 **7f**	71
8	 **5b**	16	 **7g**	75
9	 **5c**	36	 **7h**	73
10	 **5d**	36	 **7i**	97
11	 **5e**	16	 **7j**	81
12	 **5f**	16	 **7k**	60

[a] Unless otherwise stated, the reactions of **2a** and the corresponding substrates were conducted in the presence of **1a** (5 mol %) in DMSO at 40 °C. After the indicated reaction times, aqueous KHF_2 was added. [b] Isolated yield. [c] Diethanolamine was added instead of KHF_2.

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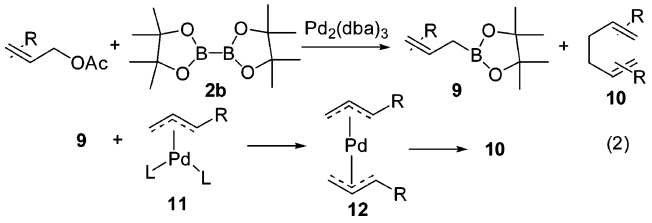
5b, **5e**, and **5f**. Furthermore, the double bond geometry in the products was exclusively trans.

We have also employed other pincer complex catalysts in the above process (eq 1), such as **1c** and **1d**. It was found that **1c** displayed a very low catalytic activity, while **1d** proved to be inactive as catalyst. Miyaura and co-workers[5a,b] have shown that allyl acetates can be converted to allyl pinacolboronates (**9**) in the presence of bis(pinacolato)diboron (**2b**) using $Pd_2(dba)_3$ catalyst (eq 2). The allyl−allyl coupling process is a well-known side reaction of this catalytic transformation. Formation of side product **10** can be explained by the reaction of allylboronate product **9** with allylpalladium intermediate **11** to give bis-allylpalladium complex **12**, which undergoes allyl−allyl coupling (eq 2).[5c] On the other hand, Kabalka and co-workers[4l] obtained densely functionalized allylboronates from palladium-catalyzed cross-coupling of Baylis−Hillman acetate adducts with **2b** without formation of allyl−allyl coupling products (such as **10**). These findings indicate that formation of bis-allylpalladium complexes (such as **12**) can be avoided for certain types of allyl acetate substrates.



We have also attempted the present substitution reactions (eq 1) using $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ catalysts in place of **1a**. These transformations resulted in complex mixtures of several unsaturated products. For example, the reaction of **5c** and **2a** with $Pd(PPh_3)_4$ led to full conversion of the starting material; however, formation of **6h** could not be detected (cf. entry 9). On the other hand, the reaction of $Pd_2(dba)_3$ with allyl acetates **5c**−**f** gave traces (5−30% conversion) of the corresponding allyl boronic acid products (**6c**−**f**). However, these transformations did not proceed with full conversion of the starting materials, because of deactivation of the catalyst accompanied by precipitation of palladium-black, which was also observed for the reaction with **2b**.[5c] The best result with $Pd_2(dba)_3$ was achieved with **5e** giving about 20% isolated yield of **7j**. Interestingly, the reaction of **5c** with $Pd_2(dba)_3$ resulted in a very low conversion (5%) to **6h**; however, we observed formation of a considerable amount of butadiene in the reaction mixture. This finding can be explained by formation of a β-OAc-substituted allylpalladium intermediate (**11**, R = CH_2OAc), which is known[5d] to easily dissociate an acetate ion providing butadiene.

The above results clearly indicate that the catalytic activity and selectivity of pincer complexes **1c**,**d** and palladium(0) catalysts $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ are inferior to that of SeCSe complex **1a** in the presented boronate transfer reactions (eq 1). Although the exact mechanism of the **1a**-catalyzed reaction is not known, several mechanistic features are probably similar to the trimethyltin transfer reactions from hexamethylditin to allylic/propargylic substrates.[2] In these transformations, the catalytic cycle is initiated by transmetalation of the dimetallic reagent to the pincer complex catalyst followed by transfer of the organometallic group to the allylic (propargylic) substrate in an S_N2/S_N2'-type reaction.[2b,c] Accordingly, we assume that the first step of the present boronate transfer process is formation of a boronate coordinated pincer complex intermediate **1b**, and subsequently, the high energy Pd−B σ-bond initiates the transfer of the $B(OH)_2$ group from palladium to the allylic substrate. The high selectivity observed in this reaction can be explained by the finding that electron-rich pincer complexes (such as **1a** and **1c**) are reluctant to undergo transmetallatation with allyl metal species.[6] Thus, the carbon−boron bond of the allylboronic acid products **6** is not cleaved by **1a**, allowing the subsequent isolation of the products (**7** and **8**). The above-described reactivity of **1a** has at least three advantageous features compared to that of palladium(0) catalysts, such as $Pd_2(dba)_3$ and $Pd(PPh_3)_4$: (i) the **1a**-catalyzed reactions proceed without formation of potentially unstable (η^3-allyl)palladium complexes (**11**), (ii) the electron-rich SeCSe complex does not react with the allylboronate products to give bis-allylpalladium (such as **12**) or related complexes, and (iii) the pincer complex catalyst is not reduced to palladium(0) under the applied conditions, and therefore deactivation of the catalyst by precipitation of palladium-black can be avoided. Furthermore, the above presented transformations also widen the synthetic scope of application of **2a** in palladium-catalyzed coupling reactions. As far as we know, the only previous use of **2a** in these types of processes was presented in a patent.[5e]

In summary, we have devised an efficient pincer complex-catalyzed reaction for synthesis of functionalized allylboronates. The primary products (**6**) can be converted to either trifluoro(allyl)-borates (**7**) or other allylboronates (**8**), which are useful, highly selective reagents in advanced organic synthesis and natural product chemistry.[3,4]

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Supporting Information Available: Experimental procedures and characterization and NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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