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Expanding the Substrate Scope for Metal-Catalyzed Asymmetric Carbon–Boron Bond Formation

Patrick J. Guiry^{*[a]}

Organoboranes are extremely useful intermediates/reagents in organic synthesis and, as a result, considerable effort has been devoted to their efficient synthesis.^[1] Their most common method of preparation is by uncatalyzed hydroboration, the *syn*-addition of a boron–hydrogen bond across carbon–carbon multiple bonds.^[2] The development of a catalytic hydroboration process was aided by the observation that Wilkinson's catalyst underwent oxidative addition when treated with catecholborane.^[3] However, it was another decade before the landmark development of a rhodium-catalyzed hydroboration process by Männig and Nöth, who reported that Wilkinson's catalyst was effective for the addition of catecholborane to a range of alkenes and alkynes.^[4] This process paved the way for the development of transition metal-catalyzed hydroboration for the conversion of alkenes into organoborane intermediates, some of which have been employed in natural product and drug syntheses.^[5] In addition, organoboranes serve as synthons for numerous functional groups^[6] and are often subject to consecutive carbon–oxygen,^[7] carbon–carbon,^[8] boron–carbon,^[9] or carbon–nitrogen^[10] bond-forming reactions. Critically, such further functionalizations occur with retention of stereochemistry and this has provided the impetus for the development of asymmetric catalytic hydroboration of alkenes.^[11]

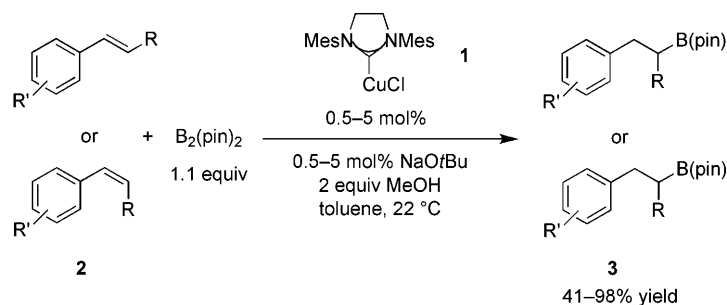
As with many metal-catalyzed asymmetric processes, finding the correct combination of borane, metal and ligand for a broad range of substrates has been

the subject of much investigation. Using catecholborane or pinacolborane, the majority of the reports detailing the development of the enantioselective variant of hydroboration have employed styrenes, aryl-substituted styrenes, β -substituted styrenes, norbornenes, and cyclic vinyl arenes. Rhodium complexes of chiral diphosphine ligands were the initial successful examples with styrene as the substrate, giving enantioselectivities of up to 95% *ee* with excellent regioselectivities favoring the α -regioisomeric product.^[12] Subsequently, rhodium complexes of heterobidentate P,N ligands have afforded even more selective catalysts,^[13] with for example, *ee* values of up to 99.5% being obtained for indene.^[13d]

The next advance in the development of catalytic hydroboration was the recent study on the addition of diboron reagents such as bis(pinacolato)diboron to carbon–carbon multiple bonds.^[14] Morken and co-workers reported the rhodium-catalyzed asymmetric 1,2-diboration of styrene, β -methylstyrene, and monosubstituted alkenes.^[15] However, use of diboron reagents opened up the range of transition metals which could be employed and examples now also include palladium,^[16] with enantiomeric excesses of up to 98% in the asymmetric diboration of allenes, and platinum in the asymmetric 1,4-diboration of 1,3-dienes, albeit with low asymmetric in-

duction (up to 20% *de*).^[17] The metal-catalyzed β -borylation of α , β -unsaturated compounds by use of bis(pinacolato)diboron was a further advance in the substrate scope for hydroboration. The metals investigated included platinum,^[18] rhodium,^[19] and copper (ee values up to 94%).^[20] The chiral ligands employed in these studies were primarily diphosphines or P,N ligands, but the use of N-heterocyclic carbenes as ligands has recently grown in importance. Styrene has again been studied as a substrate by Fernández and, in contrast to the rhodium-catalyzed process, this favored β -selectivity (2.3:1–7.3:1 site selectivity) when catecholborane was employed.^[21]

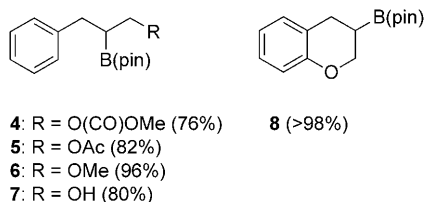
This summarizes the state-of-the-art of asymmetric hydroboration prior to a very significant recent report by Hoveyda and co-workers.^[22] They addressed a real challenge in catalytic hydroboration, namely the highly selective reaction of disubstituted alkenes for the preparation of regioisomers not accessible through existing methods. Using (*E*)- β -methylstyrene as the substrate upon which they performed their developmental work, they found that the NHC complex **1** promoted a highly effective boron addition to acyclic and cyclic β -substituted aryl alkenes **2**, with site selectivity of $>98: <2$, favoring the β -borylated products **3** in short reaction times (10 min to 24 h; Scheme 1).



Scheme 1. β -Borylation of disubstituted alkenes.

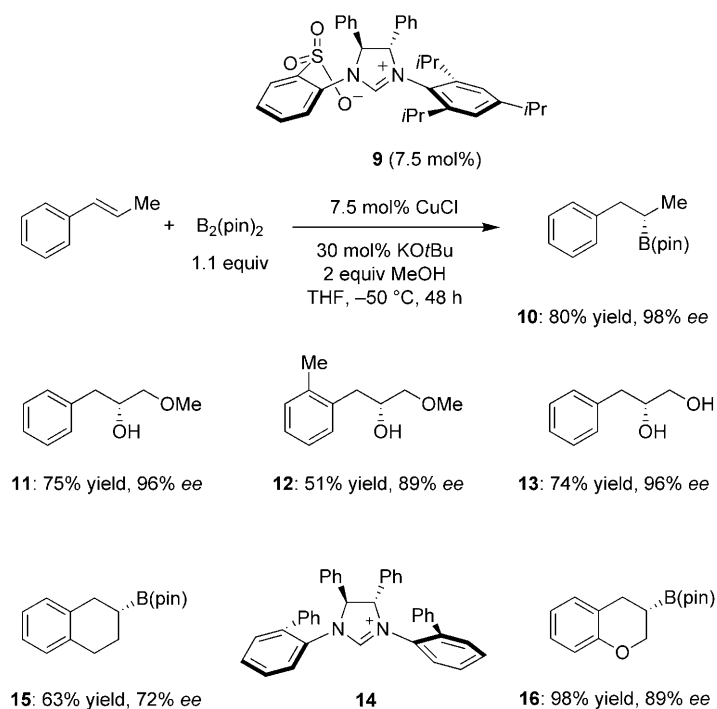
[a] Prof. P. J. Guiry
Centre for Synthesis and Chemical Biology,
School of Chemistry and Chemical Biology
UCD Conway Institute, University College
Dublin, Belfield, Dublin 4 (Ireland)
Fax: (+353) 1-716-2127
E-mail: p.guiry@ucd.ie

Of further importance was the range of substrates, such as allylic carbonates, esters, ethers, and alcohols, to which this β -borylation process could be extended and high to excellent yields of the β -borylated products **4–8** were obtained (Scheme 2).



Scheme 2. Products obtained from the β -borylation of a range of substrates.

As a range of chiral NHC ligands has already been successfully applied in asymmetric catalysis, it was clearly of interest to determine the levels of asymmetry they induced in this process. Gratifyingly, copper complexes of the chiral bidentate NHC ligand **9** afforded the borane **10** and oxidation products **11–13** in yields of 51–80% and with ee values of 89–98%, whereas use of the monodentate NHC ligand **14** gave the boranes **15–16** in 63–98% yields and with ee values of 72–89% (Scheme 3).



Scheme 3. Asymmetric β -borylation of disubstituted alkenes.

A discussion on the reasons/model for the detected regio- and stereoselectivity would undoubtedly have enhanced this study and it is hoped that this will be forthcoming in future publications.

In conclusion, there is no doubt this contribution to catalytic asymmetric hydroboration by Hoveyda will provide further impetus for improving the scope of this important transformation and it will be of interest to see how long it takes before this procedure is widely used in natural product synthesis.

Keywords: asymmetric catalysis • boranes • carbene ligands • hydroboration • regioselectivity

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