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Borane as an efficient directing group. Stereoselective 1,2-addition of organometallic reagents to borane P-stereogenic *N*-phosphanylimines†

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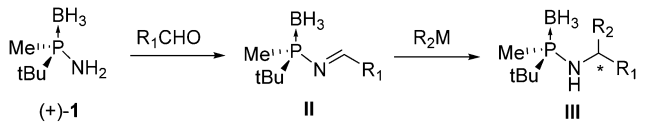
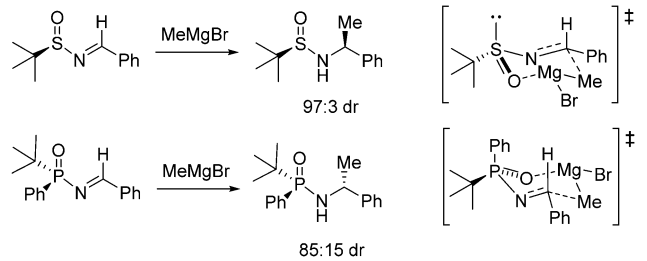
In non-coordinating solvents, borane was shown to be an efficient directing group for the stereoselective 1,2-addition of organolithium reagents to P-stereogenic *N*-phosphanylimines. Selectivity was reversed in coordinating solvents. This process can lead to novel ligand scaffolds for asymmetric catalysis.

The development of more efficient chiral ligands, especially those containing new chiral skeletons, is a key issue in the field of asymmetric catalysis.[1] Our group has recently described the synthesis of optically pure borane-protected amino-phosphane **1** as a valuable P*-building block for ligand synthesis.[2] In this regard, the *tert*-butylmethylphosphane fragment is of particular interest because of the high steric bias provided by the alkyl groups attached to phosphorus.[3] With the aim to selectively build novel carbon skeletons around aminophosphane **1**, we focused on the stereoselective addition of organometallic reagents to type **II** *N*-phosphanylimines (Scheme 1).

In this context, Ellman and co-workers reported that the *tert*-butanesulfinyl group provides excellent stereocontrol upon the addition of Grignard reagents to the corresponding aldimines.[4] Also, Colobert showed that P-stereogenic *N*-phosphinoylaldimines undergo 1,2-addition with moderate selectivity (Scheme 2).[5] In both cases, a six-membered transition state in which the oxygen atom acts as a directing group with coordination to magnesium is invoked to explain the selectivity. Unlike these examples, aldimine **II** does not bear a directing oxygen group but rather a borane-protecting group. The latter is a desirable feature when the resulting phosphane has to be further used as a ligand in metal catalysis;[6] however, its role as a directing group in the 1,2-addition of organometallic reagents is unprecedented.[7]



Scheme 1 Borane *tert*-butyl methyl aminophosphane **1** and its corresponding aldimine.



Scheme 2 Stereoselective 1,2-additions to sulfinyl and phosphanoyl aldimines.

Here we report that borane is in fact an efficient directing group in the stereoselective 1,2-addition of organolithium reagents to type **II** aldimines. In addition, we describe the solvent effect encountered in this process and how this reaction selectively leads to novel ligands for asymmetric metal-catalysis.

The synthesis of imines derived from (+)-**1** was first attempted unsuccessfully by a condensation reaction with several aldehydes using $Ti(O^iPr)_4$, $Ti(OEt)_4$ or $TiCl_4$ as Lewis acids and water scavengers in THF or in toluene solvent. Finally, microwave-promoted condensation using neat $Ti(OEt)_4$ produced the desired imines in a reproducible manner in moderate yields (Scheme 3). Aldimines **2**, **3** and **4** were obtained as single *E* isomers, as shown by ^{1}H NMR of the crude reaction mixture and X-ray analysis.[8] In the ^{1}H NMR spectra, the resulting aldimines showed a sharp H–C═ resonance between 9.0 and 9.2 ppm, with a J_P coupling constant of 26–27 Hz.

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