P Ligands

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Primary and Secondary Aminophosphines as Novel P-Stereogenic Building Blocks for Ligand Synthesis**

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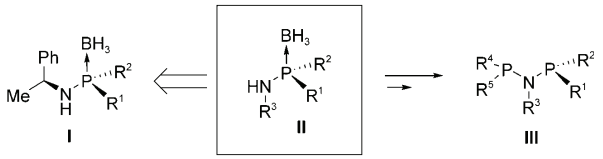
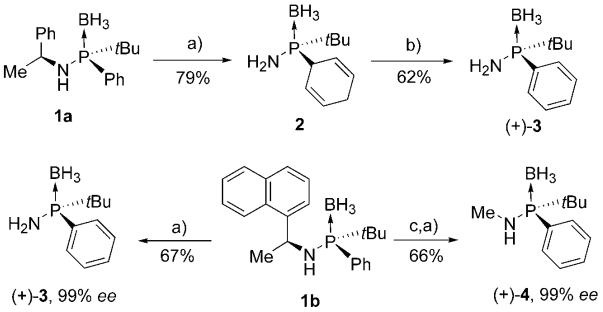
Chiral phosphine ligands are central to asymmetric metal catalysis.[1] The effect of the majority of these ligands arises from the chirality of their backbones; however, P-stereogenic (P*) ligands have garnered renewed interest.[2] After the decisive work of Knowles and co-workers with PAMP and DIPAMP ligands, several efficient syntheses of all-carbon P* compounds have been reported.[3,4] In contrast, P* compounds that contain heteroatoms directly linked to the phosphorus center are scarce, and have found little application in catalysis. This class of substances includes secondary phosphine oxides, which exist in equilibrium with their trivalent phosphinite form.[5] P* aminophosphines, which are the corresponding nitrogen analogues, are even more rare,[6] as free primary aminophosphines tend to dimerize with the evolution of ammonia.[7] However, Kolodiazhnyi et al. have reported that borane aminophosphines of type **I** are stable and that they can be obtained in diastereomerically pure form using 2-phenylethylamine as a chiral amine (Scheme 1).[8] Nonetheless, type **I** compounds do not have any reported applications in asymmetric catalysis, nor has their hydrogenolysis been described. We envisioned that reductive cleavage of the arylethyl fragment should provide borane-protected primary aminophosphines of type **II**, which would be amenable to further transformations and become useful P* building blocks in catalysis. Herein, we report the synthesis of enantiopure P-chiral primary and secondary aminophosphines (**II**) and diphosphinoamines (**III**).



Scheme 1. Strategy explored to synthesize P*-aminophosphine building blocks.

We began by investigating the hydrogenolysis of the known compound **1a**, which contains a *tert*-butyl(phenyl)phosphinamine moiety (Scheme 2), under various reaction conditions; however, all initial attempts failed. We were pleased to find that reaction of **1a** with lithium in ammonia afforded the desired cleavage of the benzylic fragment. Although the phenyl group attached to phosphorus underwent concomitant Birch-type reduction to form the phosphinodiene **2** (Scheme 2), oxidation of **2** with $KMnO_4$ on alumina resulted in **3**; to the best of our knowledge, this is the first report of this compound.[9,10] We were able to circumvent the undesired Birch-type reduction by preparing the naphthyl derivative **1b**. Reductive cleavage of the naphthylethyl fragment in **1b** occurs before the undesired Birch reduction of the phosphine phenyl group. This behavior, which may be attributed to the difference between the reduction potentials of the naphthalene and benzene rings,[11] enabled the efficient syntheses of the primary and secondary aminophosphines **3** and **4**, respectively, from **1b** (Scheme 2). Notably, no isomerization of the phosphorus center was detected under these conditions. Thus, the use of diastereomerically pure **1a** or **1b**



Scheme 2. Synthesis of primary and secondary aminophosphines **3** and **4**. Reagents and conditions: a) Li/NH_3, *t*BuOH, −78 °C, THF; b) $KMnO_4$, Al_2O_3, 0 °C, acetone; c) *n*BuLi, MeI, THF.

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