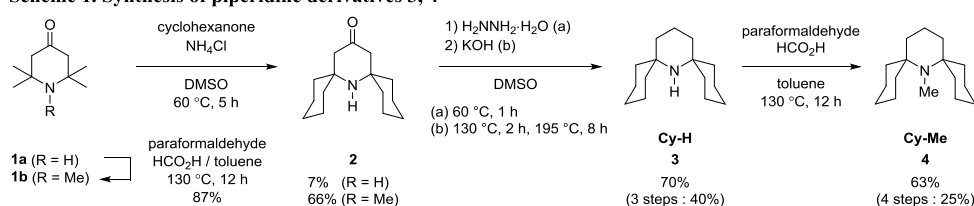
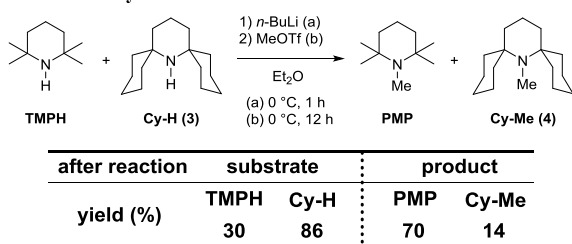
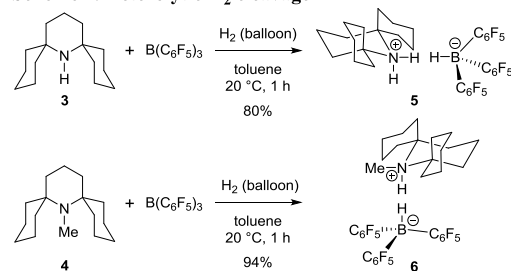


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2,2,6,6-Tetramethylpiperidine (TMPH) is a well-known bulky organic base having methyl groups adjacent to the nitrogen atom. It is often used in organic reactions, such as in regioselective metalation and as the Lewis base moiety in reactions involving Frustrated Lewis Pairs (FLPs). However, we found out that TMPH forms adducts with strong Lewis acids such as SbF₅. To avoid this problem more bulkier analogs are essential.

In this study, 7-Azadispiro[5.1.5⁸.3⁶]hexadecane **3**, a novel bulky organic base with a piperidine core dispiro-fused at the 2 and 6 positions, was prepared from 2,2,6,6-tetramethylpiperidin-4-one **1** in three steps (Scheme 1).^[1] The *N*-methyl analog **4** was also synthesized (Scheme 1). These compounds were structurally identified by X-ray crystal structure analysis. A competitive methylation reaction between the *N*-H base and TMPH resulted in the predominant methylation of the latter TMPH, thereby indicating that the steric hindrance around the nitrogen atom of the novel base is larger than that of TMPH (Table 1). The two newly prepared bulky bases functioned as the Lewis base moiety of Frustrated Lewis Pairs (FLPs) with tris(pentafluorophenyl)borane as the Lewis acid counterpart and hydrogen molecules could be heterolytically cleaved, providing their corresponding piperidinium borate salts **5**, **6** (Scheme 2).^[2] These salts could be characterized by X-ray crystal structure analysis. These salts were found to be exceptionally stable to heat and hydrogen molecules could not be released even at 200°C the decomposition point of these salts. We are currently investigating the use of the lithium amide of the bulky *N*-H base as a sterically hindered base.

Scheme 1. Synthesis of piperidine derivatives **3**, **4**Table 1. Relative ratio of unreacted substrates and products determined by ¹H NMRScheme 2. Heterolytic H₂ cleavage

[1] (a) Crozza, P.; Ferri, G. *Eur. Pat. Appl.* **1996**, 729947. (b) Sakai, K.; Yamada, K.; Yamasaki, T.; Kinoshita, Y.; Mito, F.; Utsumi, H. *Tetrahedron*. **2010**, *66*, 2311-2315.

[2] Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem. Int. Ed.* **2008**, *47*, 6001-6003.