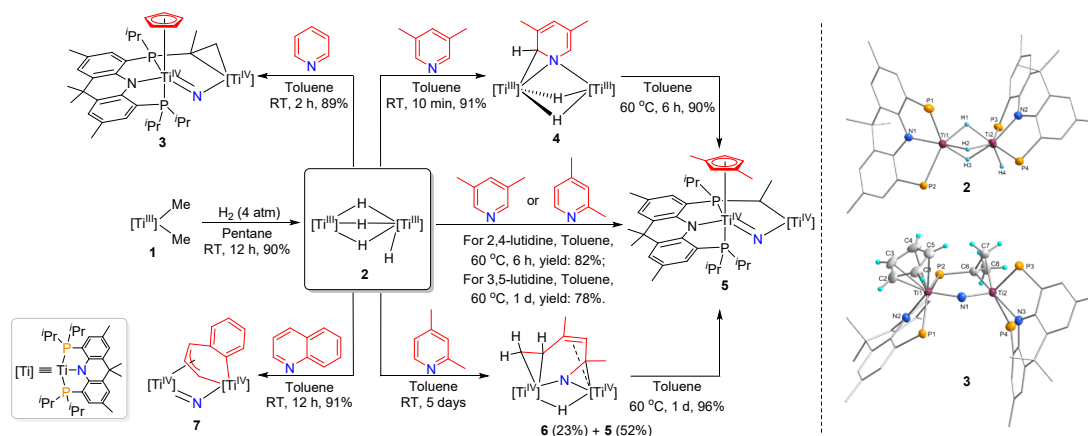


Transformation of Pyridines to Cyclopentadienyl Units by Denitrogenation in a PNP-Ligated Ditunganium Hydride Framework

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Investigating the reactions of aromatic N-heterocycles with transition metal hydrides is of fundamental interest and practical importance, given its relevance to important industrial processes such as hydrodenitrogenation (HDN).¹ Here, we report the synthesis of a novel PNP-ligated dititanium tetrahydride complex **2** and its unique reactivity towards pyridines. The hydrogenolysis of titanium dimethyl complex **1** [(*acri*PNP)TiMe₂]² with H₂ afforded complex **2** in high yield. Reaction of **2** with pyridine led to the formation of the cyclopentadienyl (Cp) complex **3**, in which pyridine was directly denitrogenated to a Cp unit by the cleavage of the two N–C bonds and formation of a new C–C bond. When 3,5-lutidine or 2,4-lutidine was subjected to the reaction with complex **2**, the 1,3-dimethyl-substituted Cp product **5** was obtained. In these reactions, two key intermediates, i.e., an intermediate **4** derived from pyridine unit coordination and an intermediate **6** derived from the cleavage of one C–N bond, were isolated successfully. Reaction of **2** with quinoline gave a metalacyclic complex **7** through the cleavage of both C–N bonds of quinoline. The mechanistic details of these pyridine skeletal editing reactions were clarified by DFT calculations. This work may provide insights for designing new catalysts for the HDN of aromatic N-heterocycles under milder conditions as well as for other useful chemical transformations.



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