

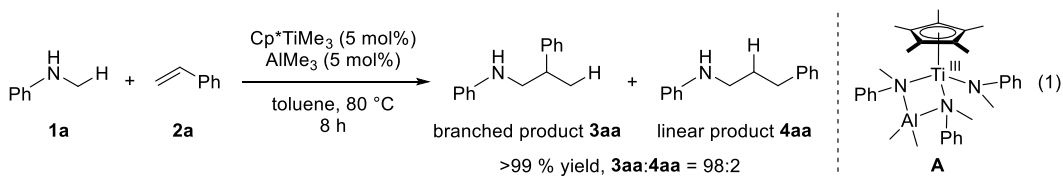
Mechanistic Study on Branch-selective Hydroaminoalkylation of Styrenes Catalyzed by Cp*TiMe₃/AlMe₃

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Keywords: Hydroaminoalkylation; Alkyltitanium complexes; Alkylaluminum; C–H bond activation; Branch-selective

Alkylamines are ubiquitous and useful building blocks in biologically active compounds, and their synthetic methods in a stoichiometric and catalytic manners have been continuously investigated. One of the most attractive catalytic reactions is hydroaminoalkylation of alkenes *via* the activation of C–H bond at α -position to the amine nitrogen atom. Since the early discoveries on the hydroaminoalkylation of 1-alkenes with dimethylamine upon using homoleptic dimethylamido complexes of zirconium, niobium, and tantalum,¹ various group 4 and 5 metal complexes have been developed as catalysts for hydroaminoalkylation of alkenes with secondary alkylamines.² Even though, it is still a challenging task to improve the catalytic efficiency and control branch/linear selectivity on such the catalytic hydroaminoalkylation. Herein, we report that a half-titanocene complex, Cp*TiMe₃, upon combined with AlMe₃ became a catalyst for branch-selective hydroaminoalkylation of styrenes and 1-alkenes with *N*-methylanilines under mild reaction conditions, and we disclose d¹ titanium(III) species as the catalytically active species.

Reaction of styrene and *N*-methylaniline in toluene at 80 °C for 8 h in the presence of Cp*TiMe₃ (5 mol%) and AlMe₃ (5 mol%) gave the β -branched hydroaminoalkylation product **3aa** and the linear one **4aa** in 98:2 ratio (eq. 1). This catalyst system was applicable for various 1-alkenes, selectively producing the corresponding β -branched amines. We found that a half-titanocene(III) species was generated as a catalytically active species based on the EPR analyses as well as DFT calculations, by which trimethylaluminum played an important role as a reductant to form amido-bridged Ti(III)-Al active species **A** and one of two bridging amido groups worked as a base to abstract a proton from the N–Me moiety of the non-bridging anilido ligand. Noteworthy was that the activation energy for the transition state in the C–H bond activation step was lower than that calculated for a titanium species without any interaction with AlMe₃. Details of the mechanism will be disclosed in this presentation.



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