

## Hydroaminoalkylation of Alkenes Using Titanium-Aluminum Catalysts

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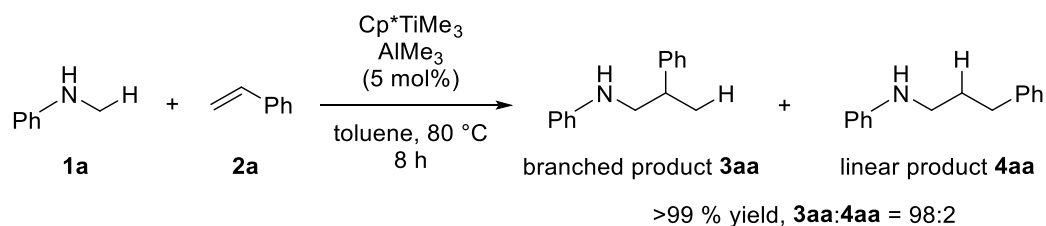
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$\beta$ -Branched alkylamines are synthetically useful building blocks for producing biologically active compounds. One of ideal synthetic methods is metal-catalyzed branch selective hydroaminoalkylation of  $\alpha$ -olefins *via*  $\alpha$ -C–H bond activation of alkylamines. Homoleptic amidometal complexes of group 4 and 5 metals were reported by Nugent *et al.* as the first catalysts for the branch-selective hydroaminoalkylation of 1-pentene with  $\text{HNMe}_2$ ,<sup>1</sup> and then various catalysts of group 4 and 5 metals have been developed; however, these catalysts often needed high temperature and elongated reaction time.<sup>2</sup> We here report that a combination of  $\text{Cp}^*\text{TiMe}_3$  and  $\text{AlMe}_3$  became an active catalyst with a high branch-selectivity for hydroaminoalkylation of alkenes with *N*-methylaniline derivatives.

Treatment of styrene and *N*-methylaniline in toluene at 80 °C in the presence of catalytic amounts of  $\text{Cp}^*\text{TiMe}_3$  (5 mol%) and  $\text{AlMe}_3$  (5 mol%) gave the corresponding  $\beta$ -branched hydroaminoalkylation product **3aa** and the corresponding linear product **4aa** in 98:2 ratio (Scheme 1). Trimethylaluminum plays an important role in both catalytic efficiency and selectivity; in the absence of  $\text{AlMe}_3$ , we found low yield (12%) and low selectivity (branch:linear = 64:36) for hydroaminoalkylated products **3aa** and **4aa** even if  $\text{Cp}^*\text{TiMe}_3$  (10 mol%) was employed. Other trialkylaluminum reagents such as  $\text{AlEt}_3$  and  $\text{Al}^i\text{Bu}_3$  served well as effective additives with keeping a high branch-selectivity, whereas  $\text{AlClEt}_2$  and  $\text{Al}(\text{OEt})\text{Et}_2$  resulted in low activity and poor selectivity. We applied this  $\text{Cp}^*\text{TiMe}_3/\text{AlMe}_3$  catalyst system for various 1-alkenes and 1,3-dienes, selectively producing the corresponding  $\beta$ -branched amines.

**Scheme 1.** Hydroaminoalkylation of Alkenes Catalyzed by  $\text{Cp}^*\text{TiMe}_3$  and  $\text{AlMe}_3$



[1] Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, 2, 161–162. [2](a) Chong, E.; Garcia, P.; Schafer, L. L. *Synthesis* **2014**, 46, 2884–2896. (b) Edwards, P. M.; Schafer, L. L. *Chem. Commun.* **2018**, 54, 12543–12560.