N-Methylation of Amines *via* Reductive Carbon Dioxide Fixation Catalyzed by Lanthanum Hydridotriarylborate Complexes bearing a Nitrogen Tridentate Ligand

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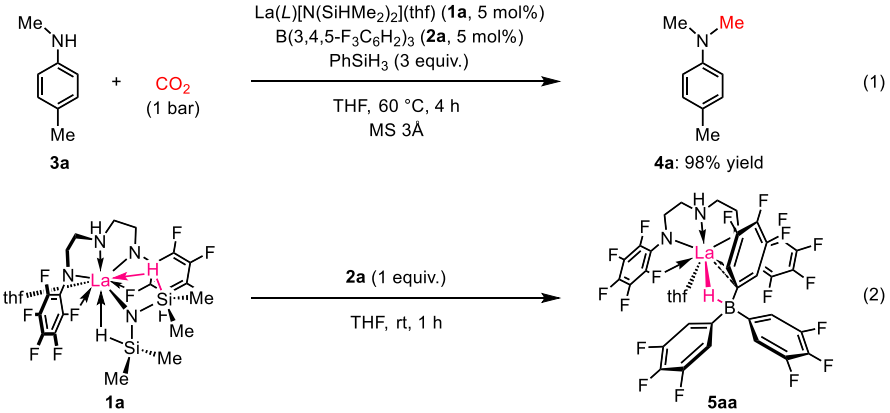
Carbon dioxide is an inexpensive and nontoxic C1 resource for producing various chemical compounds. Reductive transformation of carbon dioxide have been developed by using many kinds of reductants, such as hydrosilanes, hydroboranes, and dihydrogen, to give formic acid, methanol, and methane.[1] Another transformation is the reduction of carbon dioxide in the presence of amines for accessing to *N*-methylamines.[2] Herein, we report that lanthanum complexes bearing *N,N''*-bis(pentafluorophenyl)diethylenetriamine dianion and a hydridotriarylborate anion serve as catalysts for the hydrosilylation of CO_2 in the presence of *N*-methylanilines to give the corresponding *N,N*-dimethylanilines.

We used La(*L*)[N(SiHMe$_2$)$_2$](thf) (**1a**: *L* = *N,N''*-bis(pentafluorophenyl)diethylenetriamine dianion) and an equimolar amount of various triarylboranes **2** for a catalytic *N*-methylation of *N*-methyl-*p*-toluidine (**3a**) under atmospheric pressure of CO_2 with $PhSiH_3$ (3 equiv.) in the presence of MS 3Å to afford *N,N*-dimethyl-*p*-toluidine (**4a**). After screening triarylboranes for the catalytic reaction, B(3,4,5-F$_3$C$_6$H$_2$)$_3$ (**2a**) was found to be the best in terms of catalytic activity and selectivity to afford **4a** in 98% yield (eq. 1). Concerning to a reaction mechanism, we conducted a stoichiometric reaction of **1a** with **2a** to yield a lanthanum hydridotriarylborate complex, La(*L*)[HB(3,4,5-F$_3$C$_6$H$_2$)$_3$](thf) (**5aa**), which showed almost the same catalytic activity as the *in-situ* mixture catalyst system (eq. 2). We disclose substrate scope as well as the influence of Lewis acidity of triarylboranes toward the catalytic activity.



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