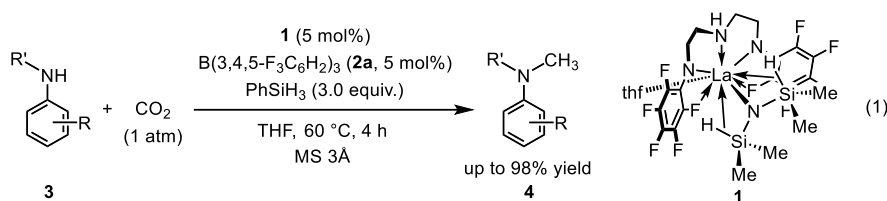


N-Methylation of Amines *via* CO₂ Fixation Catalyzed by Lanthanum Hydridotriarylborate Complexes Supported by a *N,N'*-Diarylethylenetriamine Ligand

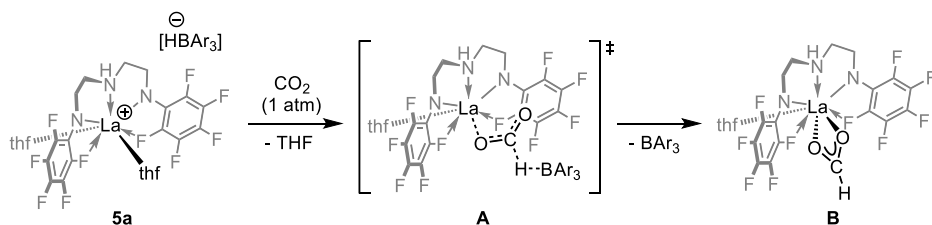
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Carbon dioxide (CO₂) is an inexpensive and renewable C1 feedstock for producing various chemical compounds, although its thermodynamic stability makes it difficult to directly fix into organic compounds.^{1,2} Transition metal-catalyzed hydrosilylation of CO₂ using hydrosilanes as reductants is one of synthetically effective methods to produce silylformates (HCO₂SiR₃) and bis(silyl)acetals (CH₂(OSiR₃)₂), both of which are useful C1 sources. Herein, we report *N*-methylation of anilines *via* the reduction of CO₂ by PhSiH₃, which was catalyzed by a lanthanum complex, La(L)[N(SiHMe₂)₂](thf) (L = a dianionic *N,N'*-bis(pentafluorophenyl)diethylenetriamine ligand), upon treated with B(3,4,5-F₃C₆H₂)₃ (eq. 1). Lanthanum hydridoborate complex, [La(L)(thf)₂][HB(3,4,5-F₃C₆H₂)₃] (**5a**), was characterized by NMR measurements as a key intermediate. DFT calculations revealed that the transition state species **A** involves the coordination of CO₂ to the lanthanum center through an interaction of the electrophilic carbon of CO₂ with hydride on the borate anion, and subsequent elimination of B(3,4,5-F₃C₆H₂)₃ generates lanthanum formate species **B** (Scheme 1). Details of substrate scope and reaction mechanism are discussed in this presentation.



Scheme 1. CO₂ Reduction Step Clarified by the DFT Calculations (Ar = 3,4,5-F₃C₆H₂)



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