Implications of C02 activation by Frustrated Lewis Pairs in the catalytic hydroboration of C02 : a view with N/Si+ Frustrated Lewis Pairs

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The implications of CO_2 activation by Frustrated Lewis Pairs in the catalytic hydroboration of CO_2 : a view with N/Si$^+$ Frustrated Lewis Pairs

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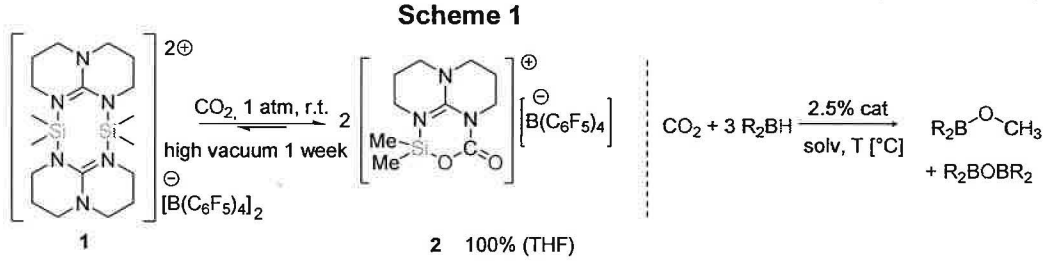
In recent years, silylium species have found application in the design of frustrated Lewis pairs (FLPs) for the activation of small molecules.[1] Highly electrophilic Si$^+$ species are strong σ and π acceptors and tend to undergo unwanted side-reactions in particular with solvents. Nevertheless, the use of base-stabilized silyl cations with tunable reactivity is of interest. Although CO_2 inserts readily into N–Si bonds,[2] the reactivity of N/Si$^+$ FLPs for the reductive transformation of CO_2 and the activation of other small molecules has not yet been explored.

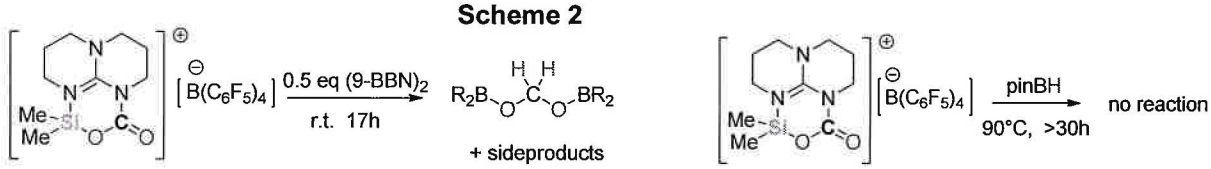
Scheme 1



1 2 100% (THF)

Using complex **1** as a silyl cation stabilized by an intramolecular nitrogen base (Scheme 1), CO_2 can be inserted to form the isolable N/Si$^+$ FLP-CO_2 adduct **2**. Complex **1** catalyzes hydroboration of CO_2[3] to methoxyboranes with 9-Borabicyclo(3.3.1)nonane (9-BBN), pinacolborane (pinBH) and catecholborane (catBH). The influence of the R alkyl groups on the silicon atom, the nature of the counter-ion X^- on the stability of cation **2**$^+$ and the catalytic performances were investigated. Experiments coupled with DFT calculations suggest that two different mechanisms proceed with 9-BBN and pinBH (Scheme 2). A novel electrophilic activation of pinacolborane that forms highly reactive "SiH" species is proposed, highlighting the role of CO_2 adducts during the catalytic cycle of CO_2 hydroboration.[4]

Scheme 2



Statut : Chercheur
N° adhérent SCF : 11955

References :

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