

**Implications of CO₂ activation by Frustrated Lewis Pairs
in the catalytic hydroboration of CO₂: a view with
N/Si+ Frustrated Lewis Pairs**

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Niklas von Wolff, Guillaume Lefèvre, Pierre Thuéry, Jean-Claude Berthet, Thibault Cantat. Implications of CO₂ activation by Frustrated Lewis Pairs in the catalytic hydroboration of CO₂: a view with N/Si+ Frustrated Lewis Pairs. Journées de Chimie de Coordination de la SCF, Jan 2017, Grenoble, France. cea-02340807

HAL Id: cea-02340807

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Submitted on 31 Oct 2019

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The implications of CO₂ activation by Frustrated Lewis Pairs in the catalytic hydroboration of CO₂ : a view with N/Si⁺ Frustrated Lewis Pairs

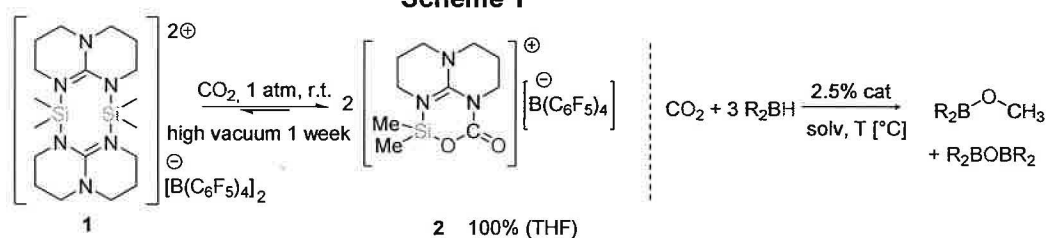
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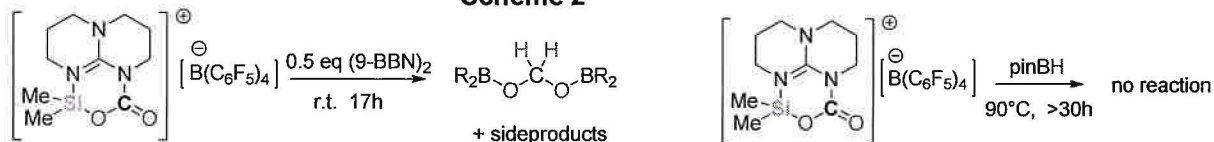
In recent years, silylium species have found application in the design of frustrated Lewis pairs (FLPs) for the activation of small molecules.^[1] Highly electrophilic Si⁺ species are strong σ and π acceptors and tend to undergo unwanted side-reactions in particular with solvents. Nevertheless, the use of base-stabilized silyl cations with tunable reactivity is of interest. Although CO₂ inserts readily into N–Si bonds,^[2] the reactivity of N/Si⁺ FLPs for the reductive transformation of CO₂ and the activation of other small molecules has not yet been explored.

Scheme 1



Using complex **1** as a silyl cation stabilized by an intramolecular nitrogen base (Scheme 1), CO₂ can be inserted to form the isolable N/Si⁺ FLP–CO₂ adduct **2**. Complex **1** catalyzes hydroboration of CO₂^[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 CO₂ adducts during the catalytic cycle of CO₂ hydroboration.^[4]

Scheme 2



Statut : Chercheur

N° adhérent SCF : 11955

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