



HAL
open science

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

Niklas von Wolff, Guillaume Lefèvre, Pierre Thuéry, Jean-Claude Berthet,
Thibault Cantat

► To cite this version:

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

<https://cea.hal.science/cea-02340807>

Submitted on 31 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

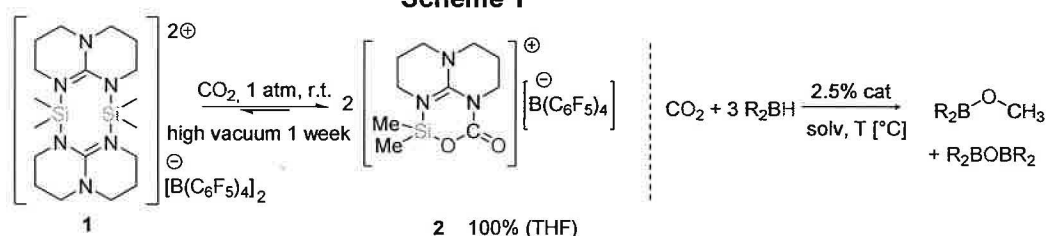
Niklas von Wolff, Guillaume Lefèvre, Pierre Thuéry, Jean-Claude Berthet, Thibault Cantat*

NIMBE, CEA, CNRS-UMR 3685, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette

E-mail: jean-claude.berthet@cea.fr; thibault.cantat@cea.fr

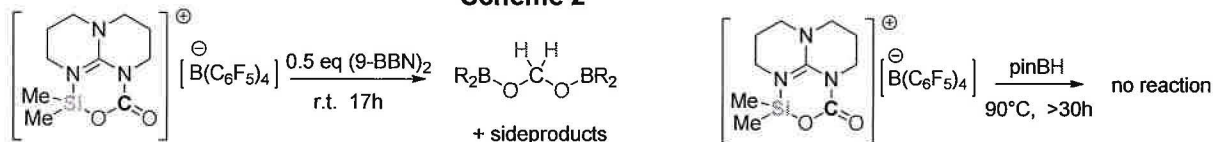
In recent years, silylium species have found application in the design of frustrated Lewis pairs (FLPs) for the activation of small molecules.^[1] Highly electrophilic Si⁺ species are strong σ and π acceptors and tend to undergo unwanted side-reactions in particular with solvents. Nevertheless, the use 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

References :

- [1] T. Müller et al., *Angew. Chem. Int. Ed.*, **2011**, *50*, 12636; T. Müller et al., *Organometallics*, **2013**, *32*, 6736; A. E. Ashley et al., *Chem. Comm.* **2014**, *50*, 12753; T. Müller et al., *Chem. Eur. J.* **2014**, 9381.
- [2] E. A. V. Ebsworth, G. Rocktäschel, J. C. Thompson, *J. Chem. Soc. (A)* **1967**, 362; L. Birkhofer et al. *J. Organomet. Chem.* **1975**, *99*, C1–C4; W. Kaim et al. *J. Organomet. Chem.* **1995**, 283.
- [3] T. Cantat et al., *Chem. Eur. J.* **2014**, *20*, 10708; M. J. Sgro, D. W. Stephan, *Angew. Chem. Int. Ed.*, **2012**, *51*, 11343; F. G. Fontaine et al., *J. Am. Chem. Soc.* **2013**, *135*, 9326; F. G. Fontaine et al., *J. Am. Chem. Soc.* **2014**, *136*, 10708; D. W. Stephan, G. Ménard, *J. Am. Chem. Soc.* **2010**, *132*, 1796; S. Bontemps, L. Vendier, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2012**, *51*, 1671.
- [4] N. von Wolff, G. Lefèvre, P. Thuéry, J.-C. Berthet, T. Cantat, *ACS Catal.* **2016**, *6*, 4526.