



HAL
open science

Implications of CO₂ Activation by Frustrated Lewis Pairs in the Catalytic Hydroboration of CO₂: A View Using N/Si + Frustrated Lewis Pairs

N von Wolff, G Lefèvre, J.-C Berthet, Pierre Thuéry, T Cantat

► **To cite this version:**

N von Wolff, G Lefèvre, J.-C Berthet, Pierre Thuéry, T Cantat. Implications of CO₂ Activation by Frustrated Lewis Pairs in the Catalytic Hydroboration of CO₂: A View Using N/Si + Frustrated Lewis Pairs. ACS Catalysis, 2016, 6, pp.4526-4535. 10.1021/acscatal.6b00421 . cea-01338153

HAL Id: cea-01338153

<https://cea.hal.science/cea-01338153>

Submitted on 30 Jan 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 Using N/Si⁺ Frustrated Lewis Pairs

*von Wolff, N. ; Lefèvre, G. ; Berthet, J.-C.; Thuéry, P. ; Cantat T.**

NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette, France

Fax: (+33) 1.6908.6640

Abstract

A series of base-stabilized silylium species were synthesized and their reactivity towards CO₂ explored, yielding in the characterization of a novel N/Si⁺ FLP-CO₂ adduct. These silicon species are active catalysts in the hydroboration of CO₂ to the methoxide level with 9-BBN, catecholborane (catBH) and pinacolborane (pinBH). Both experiments and DFT calculations highlight the role of the FLP-CO₂ adduct in the catalysis. Depending on the nature of the hydroborane reductant, two distinct mechanisms have been unveiled. While 9-BBN and catBH are able to reduce an intermediate FLP-CO₂ adduct, the hydroboration of CO₂ with pinBH follows a different and novel path where the B-H bond is activated by the silicon-based Lewis acid catalyst. In these mechanisms, the formation of a highly stabilized FLP-CO₂ adduct is found detrimental to the kinetics of the reaction.

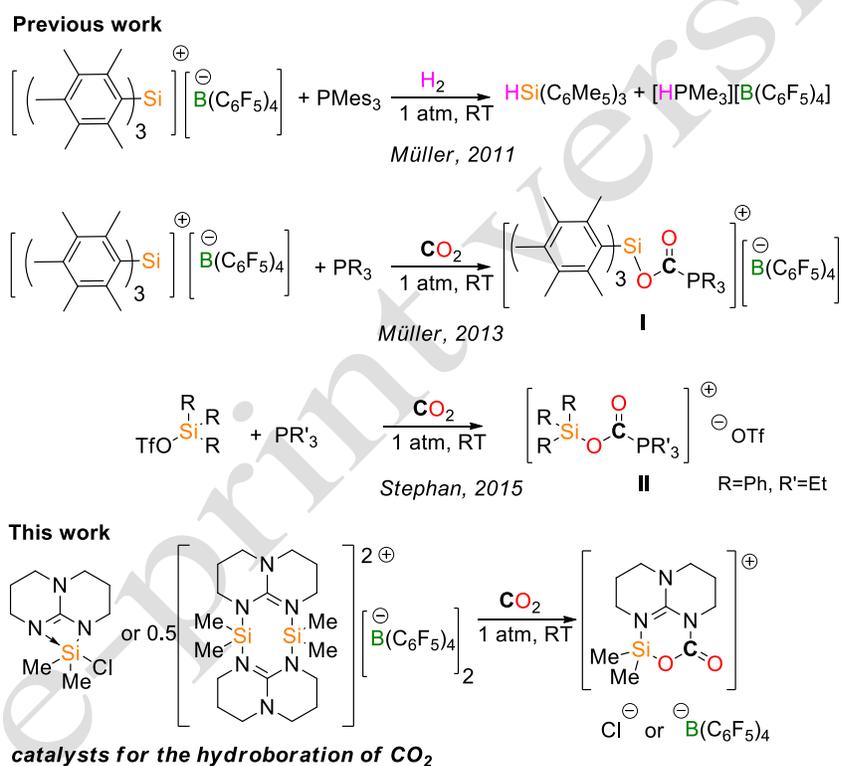
Keywords

Organocatalysis, CO₂, hydroboration, mechanisms, DFT calculations

Introduction

Carbon dioxide is an abundant, inexpensive, low toxic and renewable carbon feedstock and therefore an appealing C1-building block in organic chemistry.¹⁻³ The efficient reduction of CO₂ to important raw materials for the chemical industry or to value-added chemicals is however hampered by its high thermodynamic stability and kinetic inertness towards reduction. This drawback calls for efficient reduction catalysts able to synchronize C–O bond cleavage with C–H and C–C bond formation, at a high kinetic rate and with a low energy demand. While CO₂ activation and reduction at a metal center has been thoroughly investigated over the last four decades,^{2,4-8} organic systems able to perform this task, based on main group elements (e.g. B, N, O, P, Si), remain sporadic and underexplored. Many different coordination modes have been unveiled for the interaction of CO₂ with a transition metal or an f-element, based on the nature of the metal ion and the redox state of the CO₂ ligand.^{9,10} In organic chemistry, CO₂ activation is quite monotonous and relies on the formation of stable adducts with organic Lewis bases, such as guanidines or N-heterocyclic carbenes (NHCs).¹¹⁻¹³ Nevertheless, most progress has been gained *via* the synergistic action of Lewis pairs, able to coordinate both the C and O centers of CO₂. Within the concept of Frustrated Lewis Pairs (FLPs), introduced by Stephan and Erker,¹⁴⁻¹⁷ several CO₂ adducts have been successfully isolated over the last 6 years, in which the C atom is attached to a C, N or P donor while one or two O atoms coordinate a group XIII Lewis acid (B or Al).¹⁸⁻²⁸ Although FLP-CO₂ adducts are commonly proposed as catalytic intermediates in the reduction of

CO₂ with hydrosilanes or hydroboranes, their possible involvement and role in the catalysis remain yet unclear.²⁹⁻³⁴ Experimentally, FLPs that catalyze the hydroelementation of CO₂ do not form observable adducts with CO₂ and, conversely, only a single N/B FLP-CO₂ adduct has been reported so far to promote the catalytic hydroboration of CO₂, by our group.^{27,35} Mechanistically, CO₂ adducts may have a decreased reactivity compared to free CO₂ in the presence of a reductant and reactive CO₂ adducts that are not thermodynamically favored under catalytic conditions may form without being detected.



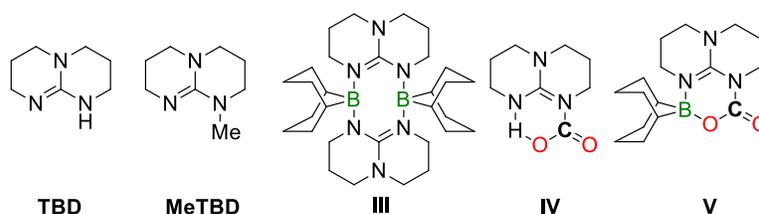
Scheme 1. Silylium-based FLP systems for the activation of small molecules (CO₂ and H₂).

In order, to better address the role and influence of CO₂ adducts in the metal-free catalytic reduction of CO₂, we have thus sought stable CO₂ adducts able to perform as catalysts in the hydroboration of CO₂. Whereas FLP-CO₂ adducts mostly feature borane or alane Lewis acids, we reasoned that an isolobal and isoelectronic silylium cation (R₃Si⁺) would exhibit a stronger Lewis

acidity and a greater affinity for the O-center in CO₂. In addition, the versatile synthesis of organosilicon compounds may facilitate the access to structures exhibiting different affinities for CO₂. In fact, a few FLP systems involving highly electrophilic silyl cations in combination with phosphines as Lewis base were reported to activate small molecules. In 2011, Müller and coworkers demonstrated that triarylsilylium cations in combination with bulky phosphines could activate H₂ and the same system was shown recently to activate CO₂ in the formation of an adduct (**I**) with the intermolecular P/Si⁺ FLP (Scheme 1).^{36,37} Recently, Stephan and co-workers characterized P/Si⁺ FLP-CO₂ adducts (**II**) starting from basic phosphines (namely PEt₃ and P*t*-Bu₃) and silyl triflates.³⁸ Further Ashley et al. reported on a phosphine stabilized silylium species able to cleave H₂.³⁹ We report herein the formation of novel intramolecular FLP-CO₂ adducts by reaction of CO₂ with nitrogen stabilized silyl cations. These systems exhibit excellent catalytic activity in the hydroboration of CO₂ and the catalytic involvement of FLP-CO₂ adducts is addressed, based on mechanistic experimental and DFT investigations (Scheme 1).

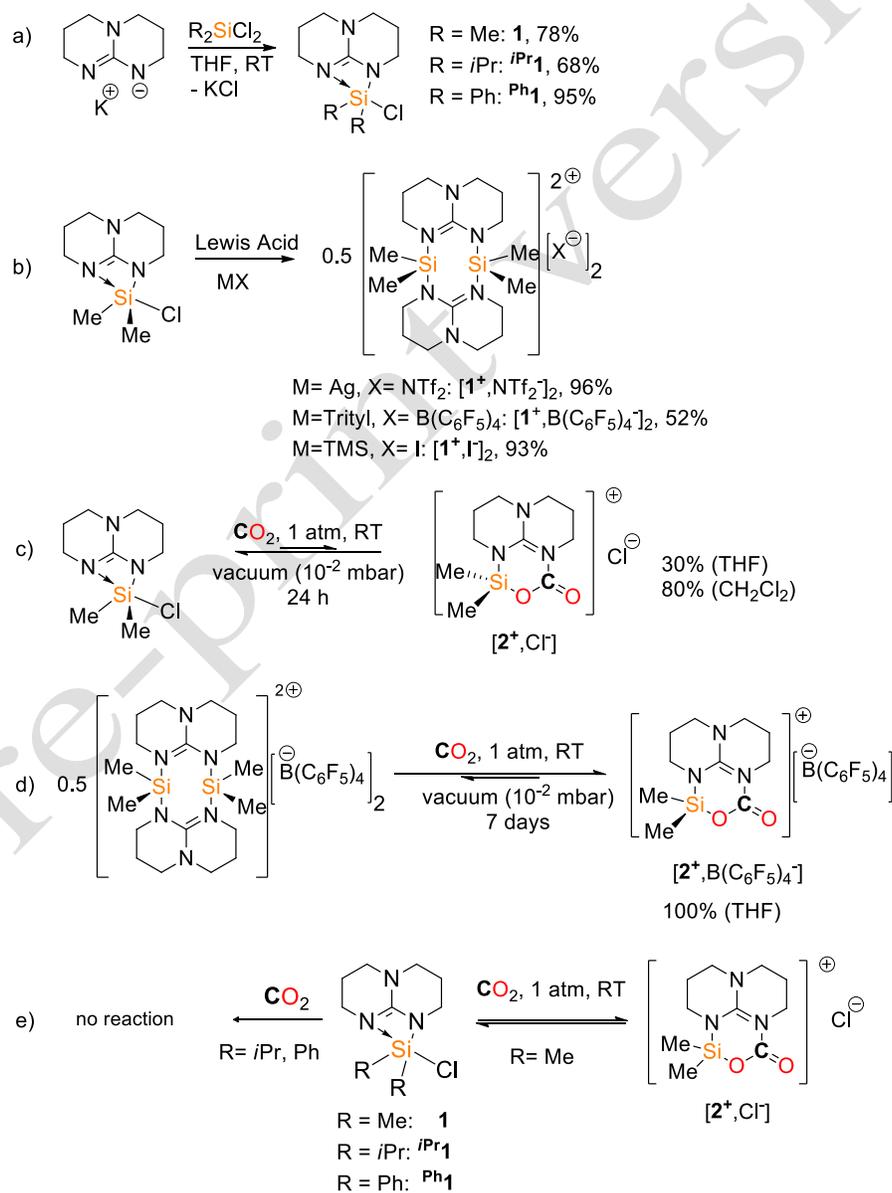
Results and discussion

Synthesis of novel FLP-CO₂ adducts. We recently reported that both 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and guanidine substituted borane **III** are able to bind CO₂ to afford adducts **IV** and **V**, respectively (Scheme 2).²⁷ Importantly, these species are highly active hydroboration catalysts and they promote the reduction of CO₂ to the methanol level with 9-borabicyclo[3.3.1]nonane 9-BBN, at room temperature. In order to increase the activation of the C–O bond in CO₂, the replacement of the organoborane Lewis acid with a more oxophilic silyl cation was envisioned. Unstabilized silyl cations are strong σ and π acceptors⁴⁰ and can undergo unwanted side reactions with the solvent.^{41,42}



Scheme 2. TBD and TBD-substituted borane **II** form CO₂-adducts **III** and **IV**.

The formation of base stabilized silyl species with modulated reactivity was thus attempted by reacting the guanidinate [K⁺,TBD⁻] with various dichlorosilanes (Scheme 3a).



Scheme 3. Synthesis of hypervalent silanes and their reaction with CO₂

Following the procedure developed by Andell and coworkers,⁴³ the hypervalent chlorosilane **1** was isolated from [K⁺,TBD⁻] and Me₂SiCl₂. Replacing Me₂SiCl₂ with *i*-Pr₂SiCl₂ and Ph₂SiCl₂ led to the isolation of the analogous compounds ^{*i*}Pr**1** and Ph**1**, respectively. Crystals of **1**, grown from a pentane solution, revealed a monomeric structure with a hypervalent silicon center bound to two methyl groups, the two nitrogen donors of TBD and one chloride (Figure 1).⁴⁴ The silicon center adopts a distorted trigonal bipyramidal geometry, the Cl1 and N2 atoms occupying the axial positions with a Cl–Si–N2 bond angle of 159.20(4)°. The Si–N2 bond length is significantly longer than the Si–N1 bond length (1.9843(12) vs 1.7914(12) Å) and the Si–Cl bond is elongated in comparison to Si–Cl bonds in tetravalent chlorosilanes (2.2783(5) vs *e.g.* 2.01(2) Å in SiCl₄). Taken together, these data indicate a 3c/4e ω-interaction for the axial bonding.^{45,46} A Natural Bond Orbital (NBO) analysis indeed confirms a notable acidity at the Si atom with a positive charge of +1.89. A similar structure was found for ^{*i*}Pr**1** (see SI). Treating **1** with a Lewis acid (*i.e.* AgNTf₂, [Ph₃C][B(C₆F₅)₄] or Me₃SiI) readily led to the formation of dimeric dicationic species in agreement with the reported ease of halogen-silicon bond ionization of base-stabilized halosilanes (Scheme 3b).⁴⁷ Crystals suitable for X-ray analysis were obtained for both [1⁺,B(C₆F₅)₄⁻]₂ and [1⁺,NTf₂⁻]₂ (Fig. 1 and SI). A dicationic dimeric structure is also proposed for [1⁺,I⁻]₂ due to its very poor solubility in common polar solvents, such as THF, DMSO, acetonitrile and pyridine.⁴⁸

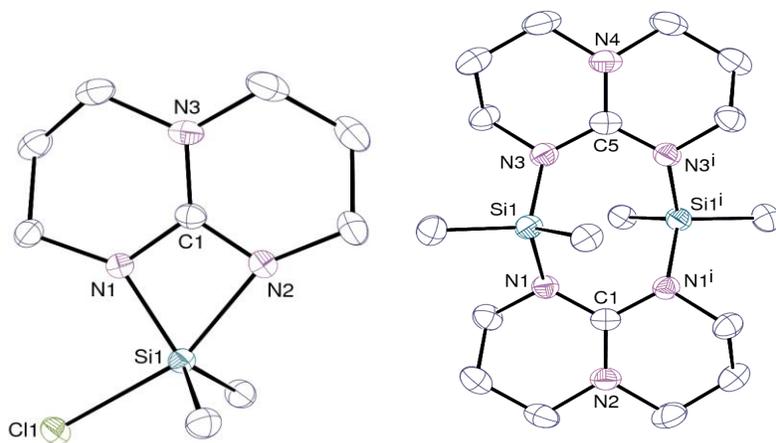


Figure 1. ORTEP view of **1** (left) and cation (1^+)₂ in [1^+ ,B(C₆F₅)₄⁻]₂·C₄H₈O₂ (right). The solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) in **1**: Si1–Cl1 2.2783(5), Si1–N1 1.7914(12), Si1–N2 1.9843(12), N1–C1 1.3578(17), N2–C1 1.3087(18), N1–Si1–N2 69.09(5); in (1^+)₂: Si1–N1 1.7714(13), Si1–N3 1.7796(13), N1–C1 1.3628(16), N3–C5 1.3598(17).

Having in hand a series of base-stabilized chlorosilanes and silyl cations, the activation of CO₂ was explored. Exposing a *d*₈-THF solution of **1** to an atmosphere of CO₂ readily produces a novel species, namely [**2**⁺,Cl⁻], in 30 % conversion, according to the ¹H and ¹³C NMR spectra of the crude solution (see SI, Figure S20). Crystals suitable for X-ray diffraction were successfully obtained by slow diffusion of pentane into a concentrated pyridine solution of **1** under a CO₂ atmosphere. As depicted in Figure 2, [**2**⁺,Cl⁻] is a novel CO₂ adduct where the carbon atom coordinates to a N-donor on the TBD backbone while one oxygen atom binds to the silylium center.

The formation of **2**⁺ also reveals that **1** can act as an intramolecular FLP. The addition of CO₂ is reversible and **1** is recovered after evaporating a THF solution of [**2**⁺,Cl⁻] under high vacuum (10⁻² mbar) overnight (Scheme 3c). Interestingly, the formation of [**2**⁺,Cl⁻] is more favored in CH₂Cl₂ compared to THF and it reaches a conversion of 80 % (see SI, Figure S22). This is in agreement with the observed ease of ionization of Si–Cl bonds by polar solvents reported by Kummer and co-workers⁴⁷ and the more polar CH₂Cl₂ solvent might thus shift the equilibrium towards the

ionized CO₂-adduct. Starting from [1⁺,B(C₆F₅)₄⁻]₂, CO₂-adduct [2⁺,B(C₆F₅)₄⁻] is obtained quantitatively under a CO₂ atmosphere (see SI, Figure S24). This adduct shows a much greater stability as 7 days under reduced pressure (10⁻² mbar) are needed to promote the decarboxylation of [2⁺,B(C₆F₅)₄⁻]. While adducts **I** and **II**, reported by Müller *et al.* and Stephan *et al.*, respectively, were found unstable and could not be characterized structurally,³⁸ [2⁺,Cl⁻] and [2⁺,B(C₆F₅)₄⁻] (Scheme 3d) represent the only examples of N/Si⁺ FLP-CO₂ adducts, which are characterized structurally in the solid state. The bonding of CO₂ in adduct 2⁺ resembles that of **V** and **IV**, with a more pronounced activation of the C–O bonds. Indeed, the activation of CO₂ with FLPs bends the linear CO₂ molecule and the O–C–O bond angle is smaller in 2⁺ (121.4(3) °) compared to **V** (128.6(2) °) and **IV** (129.9(2) °). In parallel the C–O bond activated by the Lewis acid is somewhat longer in 2⁺ (1.322(4) Å), compared to **V** (1.299(3) Å) and **IV** (1.257(3) Å), while the C=O bond is shorter (1.206(4) vs 1.222(2) in **V** and 1.229(2) Å in **IV**). These data confirm the stronger Lewis acidity of the silyl cation in the activation of CO₂, compared to the N/B system **V**. Spectroscopically, the ¹³C resonance for CO₂ is shifted upfield in 2⁺ (145.3 ppm, see SI Figures S25 or S23), compared to **V** and **IV** (153.1 and 154.4 ppm, respectively).

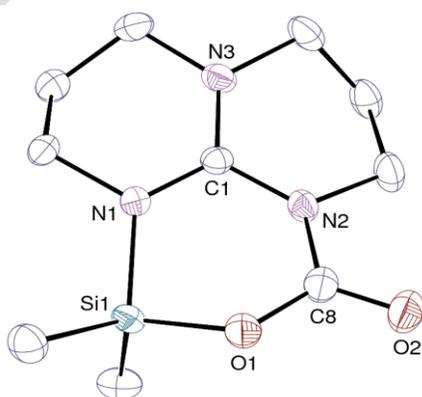
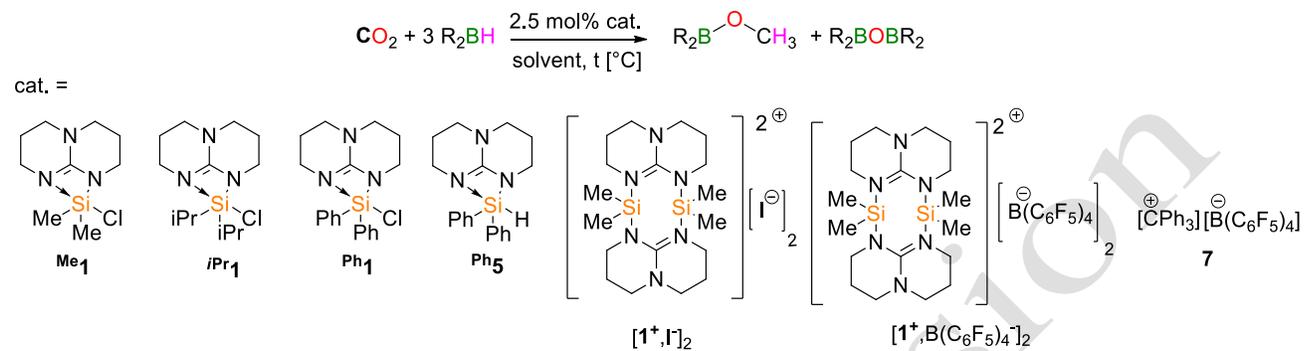


Figure 2. ORTEP view of cation 2⁺ in [2⁺,Cl⁻] 0.5C₃H₅N. The solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–O1 1.671(2), Si1–N1

1.756(2), O1–C8 1.322(4), O2–C8 1.206(4), N1–C1 1.331(4), N2–C1 1.392(4), Si1–O1–C8 125.7(2), O1–C8–O2 121.4(3).

Table 1. Catalyst screening for the hydroboration of CO₂ to methoxyboranes.



| Entry | Catalyst | Borane | T[°C] | t[h] | Yield[%] ^a | TOF(h ⁻¹) ^b |
|-----------------|--|--------|--------|---------|-----------------------|------------------------------------|
| 1 | 1 | 9-BBN | 20 | 23(6.5) | 100(77) | 1.3 (3.7) |
| 2 ^c | 1 | 9-BBN | 20 | 78 | 17.5 | 0.1 |
| 3 ^d | 1 | 9-BBN | 20 | 78 | 0 | 0.0 |
| 4 ^e | 1 | 9-BBN | 20 | 78 | 83 | 0.3 |
| 5 ^f | 1 | 9-BBN | 20 | 78 | 43 | 0.2 |
| 6 | iPr1 | 9-BBN | 20 | 24 | 60 | 0.7 |
| 7 | Ph1 | 9-BBN | 20 | 24 | 56 | 0.8 |
| 8 | 0.5[1 ⁺ ,B(C ₆ F ₅) ₄ ⁻] ₂ | 9-BBN | 20 | 72(3) | 30(6) | 0.1(0.9) |
| 9 | 0.5[1 ⁺ ,I] ₂ | 9-BBN | 20 | 24 | 100 | 1.3 |
| 10 | 1 | catBH | 70 | 120 | 74 | 0.5 |
| 11 | iPr1 | catBH | 70 | 67 | 31 | 0.3 |
| 12 | Ph1 | catBH | 70 | 96 | 44 | 0.3 |
| 13 | 0.5[1 ⁺ ,B(C ₆ F ₅) ₄ ⁻] ₂ | catBH | 70 | 42 | 18 | 0.2 |
| 14 | [1 ⁺ ,I] ₂ | catBH | 70 | 96 | 49 | 0.3 |
| 15 | 1 | pinBH | 90(70) | 28(28) | 75(21) | 0.8(0.2) |
| 16 | iPr1 | pinBH | 90(70) | 16(28) | 100(78) | 2(0.8) |
| 17 | Ph1 | pinBH | 90 | 28 | 82 | 0.9 |
| 18 | 0.5[1 ⁺ ,B(C ₆ F ₅) ₄ ⁻] ₂ | pinBH | 90 | 90 | 50 | 0.6 |
| 19 | 0.5[1 ⁺ ,I] ₂ | pinBH | 90 | 96 | 40 | 0.5 |
| 20 | Ph5 | catBH | 70 | 96 | 40 | 0.3 |
| 21 ^g | 7 | catBH | 90 | 24 | 10 | 0.1 |

Values in parentheses correspond to shorter reaction times with corresponding yields. ^aReaction conditions: catalyst (2.5 mol%) in 400 μL of THF, (0.48 mmol of B-H), 1 atm CO₂. Yields determined by ¹H-NMR vs internal standard (mesitylene). ^bTOFs were calculated under steady-state regime as the derivative of TON (B-H bond used) vs reaction time. ^cin CH₃CN. ^din pyridine. ^ein DCM. ^fin toluene. ^gin benzene.

It is notable that the formation of CO₂ adducts with the intramolecular N/Si⁺ FLPs seems sensitive to the steric crowding around the silylium center. In fact, no adduct is observed when the isopropyl or phenyl derivatives ⁱPr $\mathbf{1}$ or ^{Ph} $\mathbf{1}$ are exposed to an atmosphere of CO₂ (Scheme 3e). This behavior provides FLP systems for which activation of CO₂ is disfavored and hence a platform to study the occurrence and catalytic importance of CO₂ activation by FLPs (*vide infra*).

Catalytic hydroboration of CO₂

The catalytic hydroboration of CO₂ is an efficient method to reduce CO₂ to the methanol level under mild reaction conditions, to produce methoxyboranes or methylamines (in the presence of an amine source). This catalytic reaction, first unveiled by the Guan group in 2010 with nickel(II) catalysts,^{49,50} has attracted much attention and a variety of organometallic catalysts have been proposed.⁵¹⁻⁵³ Interestingly, in 2013, our group²⁷ has shown in parallel with the work of Fontaine and coworkers³¹ that simple organic catalysts such as TBD, Me-TBD or N/B and P/B FLPs (e.g. **V**) could also serve as efficient catalysts in this reductive process. As shown with the synthesis and chemical behaviour of **1**, **1**⁺, ⁱPr $\mathbf{1}$, ^{Ph} $\mathbf{1}$ and **2**⁺, the introduction of a silyl cation on the guanidine backbone of TBD enables a fine tuning in the activation of CO₂. Whereas a strong coordination of CO₂ is observed in **2**⁺, no reaction with CO₂ is observed in the case of ⁱPr $\mathbf{1}$ and ^{Ph} $\mathbf{1}$ showing that the corresponding adducts are not thermodynamically favored (although they could exist as meta-stable intermediates). These compounds therefore constitute a suitable platform to investigate the effect of CO₂-adduct formation in the catalytic reduction of CO₂.

In the presence of 9-BBN and 1 atm of CO₂ in THF, 2.5 mol% of **1** catalyzes the hydroboration of CO₂ to the corresponding methoxyborane MeOBBN in >99 % yield, after 20 h at 20 °C (Table 1, entry 1, TOF = 1.3 h⁻¹).⁵⁴ THF is the best solvent under these conditions, as both

more polar (CH₃CN, pyridine) and less polar solvents (toluene, CH₂Cl₂) gave lower TOFs (Table 1, entries 2-5, TOFs up to 0.3 h⁻¹). In fact, as shown in the work of Kummer and co-workers,⁴⁷ the solvent (Gutmann donor and acceptor number) can have an important influence on the ionization of the Si–Cl bond and hence on the Lewis acidity of the silicon center. The observed solvent effects could however not be correlated to the respective solvent acceptor (nor donor) numbers and might therefore be due to differences in CO₂ and borane solubility. Increasing the steric bulk around silicon leads to a lower reactivity for the hydroboration of CO₂ using 9-BBN. After 24 h at 20 °C, MeOBBN was obtained in 60 % yield using isopropyl compound ***i*Pr1** (TOF = 0.7 h⁻¹) and in 56 % yield with the phenyl analogue ***P*h1** (TOF = 0.8 h⁻¹) (Table 1 entries 6 and 7). The nature of the anion X⁻ also has a drastic influence on the catalytic performances and replacing the chloride ligand in **1** with the non-coordinating B(C₆F₅)₄⁻ anion inhibits the catalytic hydroboration of CO₂ (Entries 8, Table 1, TOFs up to 0.1 h⁻¹).⁵⁵ Poorly soluble in THF, [**1**⁺,I⁻]₂ promotes the reduction of CO₂ to MeOBBN, after an induction period of about 3 h, in 100 % yield, after 24 h (TOF=1.3 h⁻¹ after induction period). [**1**⁺,NTf₂⁻]₂ does not react with CO₂ and shows no catalytic activity, in the presence of 9-BBN, presumably because of its very poor solubility in THF.

When 9-BBN is replaced with catechol borane (catBH), the selective reduction of CO₂ to methoxycatecholborane (MeOBcat) proved less efficient requiring 26 h at 70 °C in 74 % yield (TOF = 0.5 h⁻¹, Entry 10, Table 1). Although the catalytic performances are modest, these results are interesting as neither the parent guanidine base TBD, nor the dimeric boron analogue **III**, nor the N/B FLP-CO₂ adduct **V** (Scheme 2) show any catalytic activity with catBH and pinBH.²⁷ The same trends in reactivity are observed for catBH and 9-BBN when catalyst **1** is replaced with ***i*Pr1**, ***P*h1**, [**1**⁺,I⁻]₂ or [**1**⁺,B(C₆F₅)₄⁻]₂ and the catalytic activity plummets in the presence of poorly-coordinating anions or with bulky silyl cations (Entries 11-14 in Table 1). All together, these

results suggest that the formation of a CO₂-adduct (e.g. **2**) facilitates the catalytic hydroboration of CO₂ with 9-BBN and catBH. Nevertheless, catalysts binding strongly to CO₂ such as [**1**⁺,B(C₆F₅)₄⁻]₂) are sluggish.

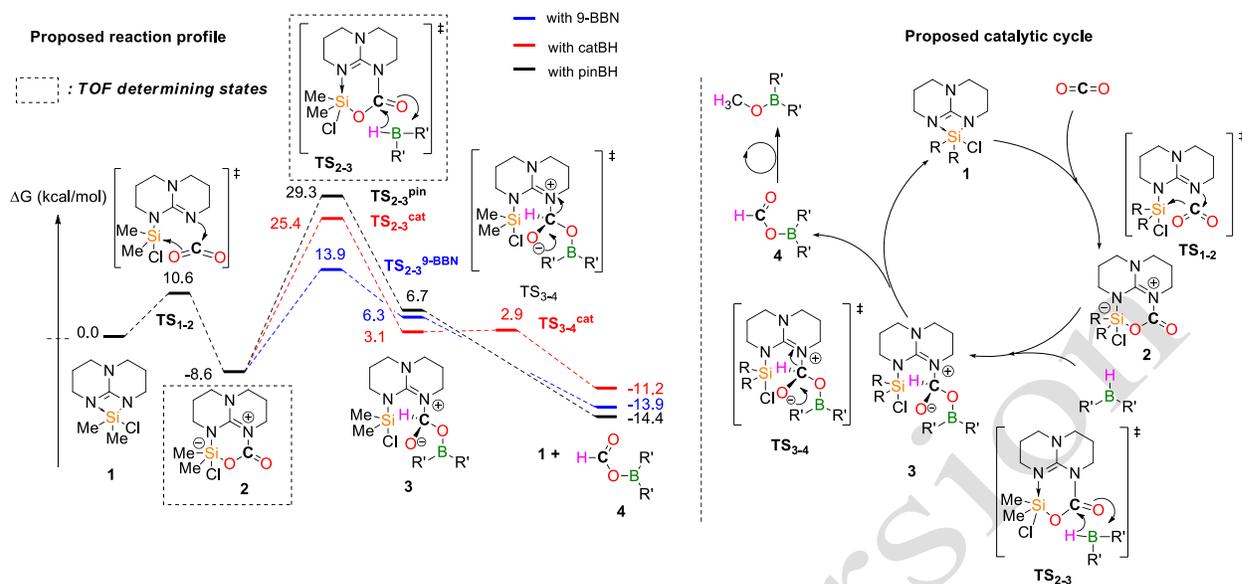
Although pinacolborane (pinBH) presents a much lower hydridic character and a weaker Lewis acidity at boron than 9-BBN or catBH,⁵⁶ it was found to be an efficient hydride source in the hydroboration of CO₂ with **1**. 75 % MeOBpin was obtained selectively after 28 h at 90 °C under 1 atm of CO₂, from pinBH and 2.5 mol% **1** (Entry 15 in Table 1, TOF = 0.8 h⁻¹). Whereas metal-based catalysts have been shown to effectively catalyse the hydroboration of CO₂ using a variety of borane sources (e.g., (9-BBN)₂, BH₃SMe₂ and catBH), few catalysts exist that utilize pinacolborane. For example, Sabo-Etienne, Bontemps *et al.* have reported a ruthenium hydride complex able to afford MeOBpin in a low 40 % yield after 5 h at 70 °C (TOF = 5 h⁻¹).⁵² Only three metal-free systems have been described so far as catalysts in the hydroboration of CO₂ with pinBH: Stephan *et al.* designed a ring expanded-carbene providing a mixture of two- four- and six-electron reduction products,³⁰ whereas Fontaine *et al.* prepared a phosphino-borane FLP producing 60 % pinBOMe at 70 °C (TOF = 21 h⁻¹).^{29,31} Recently the group of Wegner reported a bidentate borane catalyst able to reduce CO₂ to the methanol level in 89 % with pinBH at 70 °C with high reactivity (TOF = 93 h⁻¹).³³ As the catalyst itself possesses six active B–H bonds, this TOF-value must be considered with caution and a TOF of around 16 h⁻¹ is calculated per active B–H bond, facilitating its comparison with other catalysts bearing only one active site.

Strikingly, catalysts ^{*i*}Pr**1** and ^{*Ph*}1 perform better than **1** in the hydroboration of CO₂ with pinBH, while the opposite effect was noted with 9-BBN and catBH. MeOBpin is formed in 82 and 100 % yield within 28 h at 90 °C with ^{*Ph*}1 and ^{*i*}Pr**1** respectively, corresponding to TOFs of 0.9 and 2 h⁻¹ (Entries 16 and 17 in Table 1). Although the amino-borane catalyst of Fontaine and co-workers

showed higher catalytic activity (TOF = 21 h⁻¹, at 70 °C),³¹ *i*Pr $\mathbf{1}$ is able to promote the formation of MeOBpin quantitatively without the formation of other reduction side-products within only 16 h. In contrast to reactions with 9-BBN and catBH, the influence of the anion is less marked in the case of pinBH. Both compounds [$\mathbf{1}^+$,B(C₆F₅)₄⁻]₂ and [$\mathbf{1}^+$,I⁻]₂ exhibit a catalytic activity comparable to that of $\mathbf{1}$, affording pinBOMe in 40 and 50 % yield respectively after 24 h (TOFs of 0.5 and 0.6 h⁻¹ respectively, Table 1 entries 18 and 19). It is remarkable that pinBH imposes different demands on the nature of the catalyst and, unlike 9-BBN and catBH, catalysts showing no CO₂ activation (e.g. *i*Pr $\mathbf{1}$ and Ph $\mathbf{1}$) are more efficient for the hydroboration of CO₂ with pinBH.

Reaction mechanism and DFT calculations

The catalytic hydroboration of CO₂ with $\mathbf{1}$, $\mathbf{1}^+$, *i*Pr $\mathbf{1}$ and Ph $\mathbf{1}$ constitutes an appropriate system to explore the role and impact of FLP-CO₂ adducts in the reduction of CO₂, because these four active catalysts interact differently with CO₂. Whereas $\mathbf{1}$ and $\mathbf{1}^+$ form stable adducts with CO₂, replacing the methyl groups on the silicon atom in $\mathbf{1}$ with *i*-Pr or Ph substituents provides *i*Pr $\mathbf{1}$ and Ph $\mathbf{1}$, which do not react with CO₂. In addition, different behaviours and trends were noticed for 9-BBN and pinBH suggesting that different mechanisms might take place in this important transformation. Regardless of the nature of the hydroborane R₂BH, the formoxyborane HCOOBR₂ and the acetal H₂C(OBR₂)₂ are intermediates in the formation of MeOBR₂. In addition, the distribution of the products over time reveals that the reduction of CO₂ to methoxyborane is kinetically controlled by the first hydroboration step, yielding HCOOBR₂ (see ESI Page 6). The mechanism of the catalytic hydroboration of CO₂ to formoxyboranes has thus been investigated using both DFT calculations and stoichiometric reactions.

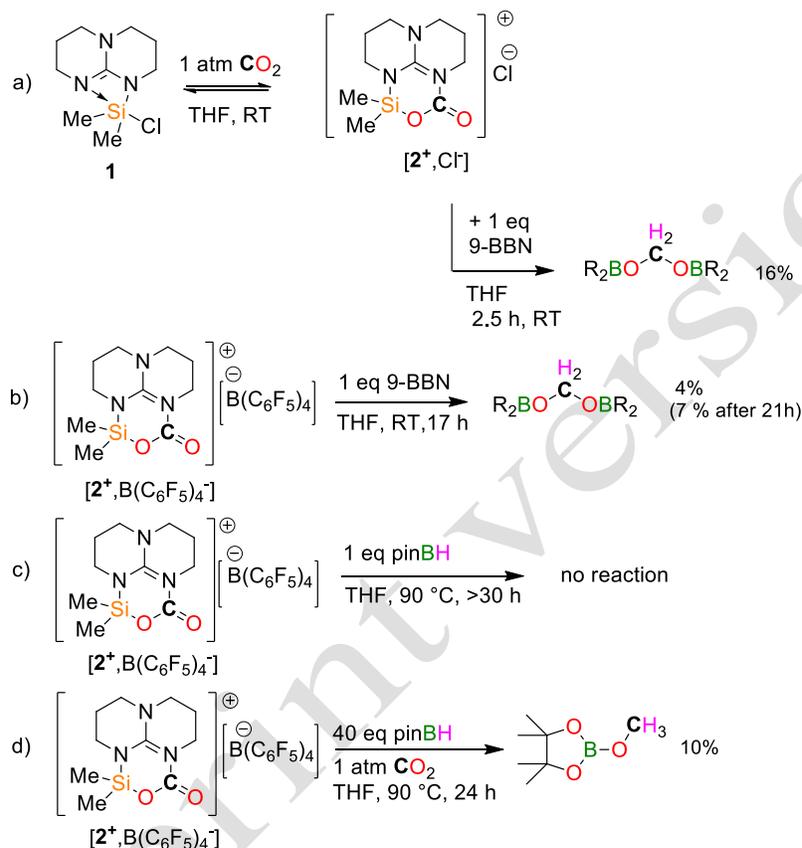


Scheme 4. Computed pathway for the catalytic hydroboration of CO₂ *via* CO₂ activation (M05–2X/PCM THF). Values given are Gibbs Free Energies using **1** as a reference ($G=0.0$ kcal/mol).

Mechanism involving the activation of CO₂. CO₂-adducts are often described as key-intermediates in the catalytic cycle of CO₂ reduction processes^{25,57} and both adducts **IV** and **V** were shown to react with an electrophilic borane (9-BBN) to yield formate species.²⁷ In light of these data and the reaction chemistry of **1** described above, activation of CO₂ by **1** is a reasonable starting point for the hydroboration of CO₂ with **1** (Scheme 4). DFT calculations, performed at the M05–2X/PCM=THF/6-31+G* (6-311++G** for the active hydride) level of theory, confirm that the formation of a CO₂ adduct [**2**⁺,Cl⁻] from **1** is indeed exergonic by -6.1 kcal/mol with a low activation barrier of only 10.6 kcal/mol (Scheme 4). Interestingly, the coordination of the chloride anion to the silylium center is also possible and the corresponding CO₂ adduct **2** lies at -8.6 kcal/mol. These data are consistent with the experimental results showing a reversible CO₂ activation with **1** and the possible formation of hypervalent guanidinate chlorosilanes. Reduction of the activated CO₂ molecule in **2** with 9-BBN was found to involve the addition of the B–H bond to the unbound C=O functionality with a low lying transition state (TS₂₋₃) at 13.9 kcal/mol. The

resulting intermediate **3** features a tetrahedral carbon. Elimination of the product HCOOBBN (**4**) from **3** is essentially barrier-less and favoured by the thermodynamics of the overall process ($\Delta G = -13.9$ kcal/mol). The hydroboration of CO₂ with 9-BBN catalyzed by **1** thus involves three successive steps, namely the activation of CO₂ by the intramolecular FLP, the addition of the hydroborane and, finally, the elimination of HCOOBBN to regenerate catalyst **1** (Scheme 4). Reduction of **3** before release by a second equivalent of hydride might therefore also be likely, although experimentally the first hydride transfer is rate determining (see SI). As depicted in Scheme 4, CO₂ adduct **2** and TS₂₋₃ are the rate determining states and they control the kinetics of the catalysis.⁵⁸⁻⁶¹ The computed energy span of 22.5 kcal/mol is much lower than the one required for the uncatalyzed addition of 9-BBN to CO₂ (30.8 kcal/mol)²⁷ and is consistent with a fast reaction at room temperature (computed TOF of 0.7 h⁻¹).⁵⁷ Notably, as CO₂ adduct **2** constitutes a TOF determining intermediate (TDI), increasing its stability is detrimental to the catalytic performances. Computationally, removing the chloride anion in the energy surface depicted in Scheme 4, an energy span of 24.7 kcal/mol (**1**⁺ as 0.0 kcal/mol reference, see Figure S37) is obtained, that is 2.2 kcal/mol higher than with catalyst **1**. This result is in excellent agreement with the experimental findings pointing to a significant diminution of the catalytic performance when **1** is replaced with [**1**⁺,B(C₆F₅)₄⁻]₂. Moreover, the addition of one equivalent of 9-BBN (monomer) to a 70:30 equilibrium mixture of **1**/[**2**⁺,Cl⁻] results in the fast formation of the acetal CH₂(OBBN)₂ after only 2.5 h at RT while a reaction time of 17 h is required for [**1**⁺,B(C₆F₅)₄⁻]₂ (Scheme 5a,b). The formation of CO₂ adducts from ^{*i*}Pr**1** and ^{Ph}**1** is around 4 kcal/mol higher in energy compared to **2** (see SI Table S1). Although this destabilization could have a positive effect on the catalysis, it also results in a lower degree of activation of the CO₂ molecule and, hence, in a greater activation barrier of 25.2 and 22.6 kcal/mol for the rate determining C–H bond formation, for the *i*Pr and Ph

substituted systems, respectively (see ESI Page 8 for detailed span values). Again, these results are in good qualitative agreement with the catalytic data showing a lower catalytic activity for ***i*Pr1** and **Ph1** compared to **1** and they underline the necessity for a fine balance in the activation of CO₂.

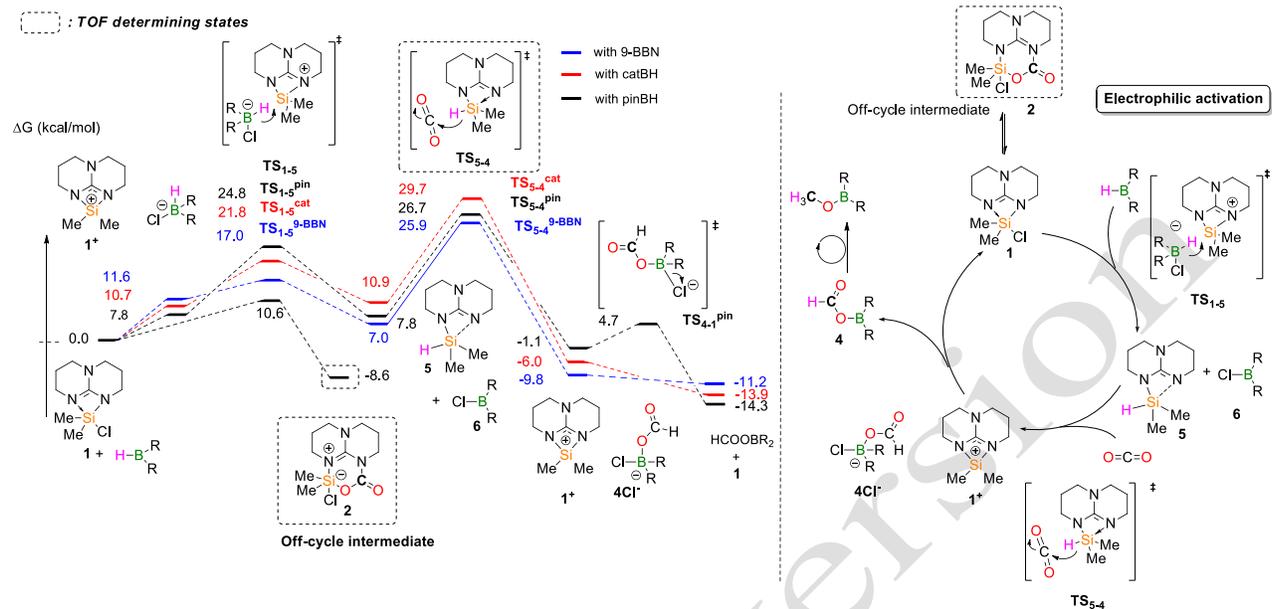


Scheme 5. Stoichiometric and catalytic reactions between **1**, **2⁺**, CO₂ and hydroboranes.

Obviously, changing 9-BBN with catBH or pinBH does not modify the energy level of the CO₂ adduct **2**. Nevertheless, it affects the position of the corresponding TS for the hydride transfer to CO₂ (**TS₂₋₃**). Both catBH and pinBH possess a boron atom that is less Lewis acidic than 9-BBN, because the π lone pairs on the oxygen substituents are delocalized into the boron vacant p orbital. As such, coordination of the hydroborane to the C=O group of the activated CO₂ molecule is disfavoured and the TOF determining **TS₂₋₃^{cat}** and **TS₂₋₃^{pin}** are higher in energy than **2** (spans of 34.0 and 37.9 kcal/mol for catBH and pinBH, respectively). The computed order of reactivity 9-

BBN > catBH > pinBH is thus in agreement with the experimental observations. Nonetheless, a span of 39.7 kcal/mol is relatively high for a catalytic reaction proceeding at 70 °C, thereby questioning the validity of a mechanism relying on CO₂ activation for pinBH. In addition, while *i*^{Pr}**1** presents a better catalytic performance than **1** with pinBH, its computed energy span is 1.8 kcal/mol higher in energy (37.9 kcal/mol). Experimentally, no reaction is observed upon mixing [2⁺,B(C₆F₅)₄⁻]₂ with pinBH for >30 h at 90 °C, although 2.5 mol% [1⁺,B(C₆F₅)₄⁻]₂ efficiently catalyze the reduction of CO₂ to MeOBpin at 90 °C (Scheme 5 and Table 1, entry 18). These facts definitively rule out a mechanism relying on CO₂ activation for the hydroboration of CO₂ with pinBH and an alternative pathway was sought.

Pre-print version



Scheme 6. Computed pathway for the electrophilic activation of hydroboranes in the reduction of CO_2 to formoxyboranes (M05–2X/PCM THF). Values given are Gibbs Free Energies with respect to **1** (0.0).

Mechanism involving the electrophilic activation of the hydroborane. In order to account for the catalytic activity of **1** and $[\mathbf{1}^+, \text{B}(\text{C}_6\text{F}_5)_4]^-$ in the reduction of CO_2 with pinBH, an alternative mechanism was explored based on the potential electrophilic activation of the B–H bond with the catalyst (Scheme 6). Indeed, the ionization of the silicon–chloride bond is readily accessible in hypervalent chlorosilanes.⁴⁷ Starting from **1**, such dissociation would be also favoured by the presence of an electrophile such as a hydroborane, to yield masked silylium ion $\mathbf{1}^+$. The hydride transfer from R_2BHCl^- to $\mathbf{1}^+$ was computed for the three hydroborane reagents, to form hydrosilane **5** (Scheme 6). The formation of **5** and chloroborane R_2BCl (**6**) by-product is slightly endergonic for the three hydroborane sources (+7.0 kcal/mol for 9-BBN, +10.9 kcal/mol for catBH and +7.8 kcal/mol for pinBH, Scheme 6). Nevertheless, the respective transition states energies are all

accessible, suggesting that it is a viable intermediate on the hypersurface (17.0 kcal/mol for 9-BBN, 21.8 kcal/mol for catBH and 24.8 kcal/mol for pinBH, Scheme 6). Species **5** appears to be a potent reductant and outersphere hydride transfer from the Si–H group in **5** to an incoming CO₂ molecule yields silylium **1**⁺ and the formate anion with a low energy barrier of 18.9 kcal/mol, in agreement with the reported reactivity of other hypervalent hydrosilanes towards CO₂.⁶² Subsequent salt metathesis between HCOO[−], R₂BCl and **1**⁺ finally regenerates catalyst **1** and releases formoxyborane HCOOBR₂, without any significant energy barrier (<6 kcal/mol).

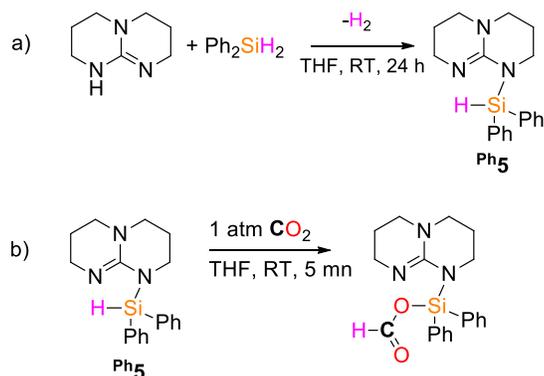
TS₅₋₄ associated with the reduction of CO₂ with **5** constitutes the highest energy rate determining state in this pathway.⁶³ Interestingly, the structure of TS₅₋₄ does not depend on the nature of the hydroborane although its energy level is indirectly dictated by the formation of the chloroborane co-product R₂BCl (**6**). Although catalyst **1** is the lowest energy state in this pathway, CO₂ adduct **2** easily forms under the applied conditions, as revealed by ¹H NMR spectroscopy, and it should therefore be included on the energy surface. **2** is thus an off-cycle intermediate that further enlarges the surface landscape yielding energetic spans of 34.5 kcal/mol (9-BBN), 35.3 kcal/mol (pinBH) and 38.3 kcal/mol (catBH) for the different hydroboranes.

This mechanistic route hence highlights two important experimental observations. First, an electrophilic pathway significantly lowers the energetic span (35.3 kcal/mol) by about 3 kcal/mol for the hydroboration of CO₂ with pinBH compared to a route where CO₂ is activated *via* the formation of an adduct (37.9 kcal/mol). Second, a stable CO₂-adduct hampers reaction kinetics in CO₂ hydroboration under electrophilic activation, as witnessed by the lower reactivity of [1⁺,B(C₆F₅)₄[−]]₂ compared to **1**. In fact, such mechanism also explains the differences in reactivity between **1**, ^{*i*}Pr**1** and ^{Ph}**1**, but care has to be taken to avoid quantitative conclusions, as the calculated spans are close in energy. Computationally, the energy span for the catalytic hydroboration of CO₂

with pinBH decreases from 35.3 kcal/mol with **1** to 34.2 and 32.4 kcal/mol with **Ph1** and ***i*Pr1**, respectively. The DFT model is thus consistent with the experimental data providing the following order of reactivity: ***i*Pr1** > **Ph1** > **1**. The DFT model is thus consistent with the experimental data providing the following order of reactivity: ***i*Pr1** > **Ph1** > **1**. Although the order of reactivity is reproduced correctly, these results have to be taken as a qualitative measure, given the accuracy of the DFT models. It is notable that, although the TOF-limiting transition state with ***i*Pr1** corresponds to the hydride abstraction from pinBH (TS₅₋₄), the main factor governing its higher catalytic activity is the destabilization of CO₂-adduct ***i*Pr2** (+3.7 kcal/mol with respect to **2**) (see SI, Table S1).

To further underline the feasibility of CO₂ reduction by a based-substituted silane **5** (Scheme 7), the synthesis of such a species was attempted. Guanidine substituted hydrosilane **Ph5** is easily accessible through dehydrogenative coupling of TBD with diphenylsilane and shows a characteristic hydride peak at 5.03 ppm in the ¹H NMR (Scheme 7, Figure S26). Crystals suitable for X-ray analysis were obtained by slowly cooling down a concentrated acetonitrile solution of **Ph5** from 90 °C to room temperature (Figure 3). With bond angles of 97.4, 114.7(2)° and 116.8(2) for N1–Si–H1, N1–Si–C8a and N1–Si–C14a, respectively, the silicon geometry is slightly distorted from a tetrahedron, although a ω-bond as in **1** or ***i*Pr1** is less likely due to a small bond angle of 153.6 ° for N2–Si–H1 and a long N2–Si distance of 2.648(5) Å. Under one atmosphere of CO₂, a THF solution of **Ph5** evolves within minutes at room temperature to yield a formate species (Scheme 7, Figure S28). In the absence of an electrophilic scavenger, such as a chloroborane, this species then converts to formylated TBD by deoxygenation of the formate anion (Figure S28). This chemical behaviour demonstrates the strong reductive capability of **Ph5** in the presence of CO₂⁶⁴, in agreement with the DFT model depicted in Scheme 6.

Pre-print version



Scheme 7. Reduction of CO₂ with **Ph5** to a formate species.

The catalytic implication of **Ph5** was further assessed in the reduction of CO₂ with catBH. **Ph5** shows comparable activity as the related phenyl catalyst **Ph1** (TOF = 0.3 h⁻¹ in both cases) providing CH₃OBcat in 40 % yield after 96 h at 70 °C (44% for **Ph1**, Table 1 entries 20 and 12).

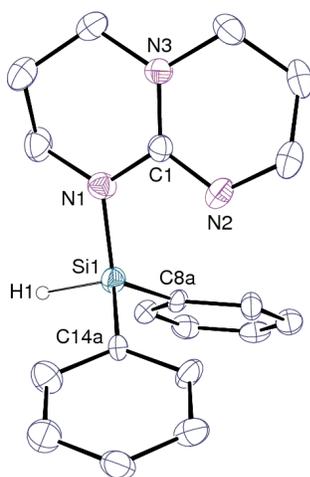
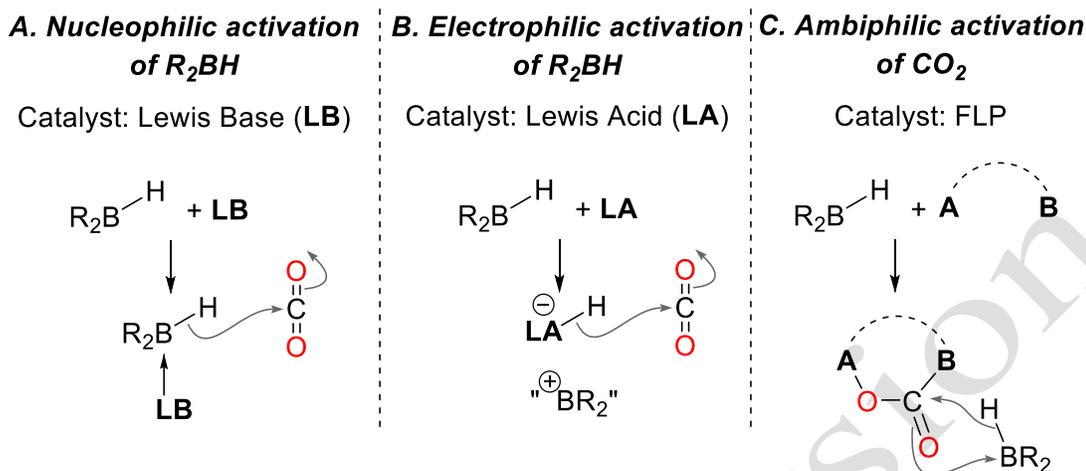


Figure 3. ORTEP view of **Ph5**. Only one position of the disordered groups is represented (see SI for details). Selected bond lengths (Å): Si1–N1 1.722(3), Si1–H1 1.427, N1–C1 1.341(4), N2–C1 1.323(4).

Overall, the mechanistic route depicted in Scheme 6 relies on the abstraction of a hydride from the hydroborane reagent with the Lewis acid catalyst and its subsequent transfer to CO₂ for the reduction of a C=O bond. This route is hence reminiscent of the work of Piers and Gevorgyan

groups on the hydrosilylation of C=O and C–O bonds, where the electrophilic borane ($B(C_6F_5)_3$) abstracts the hydride from the hydrosilane.⁶⁴⁻⁷⁰ Here DFT calculations suggest that the inverse reaction should also be possible. With the work of Oestreich and co-workers^{71,72} on the transient formation of such Si–H–B species during the hydrosilylation of carbonyl functional groups and the recent isolation and characterization of such a species by Piers and co-workers,⁷³ the availability of a transition state (TS₁₋₅) for the hydride transfer from a chloroborate (e.g. [pinBH–Cl][–]) to the masked silylium **1**⁺ is further accredited. Interestingly, such mechanism relying on an electrophilic activation of a hydroborane reductant is unprecedented in hydroboration chemistry, although it resembles the mode of action of Lewis acid catalysts in hydrosilylation chemistry. It is found to be favoured for electron rich boranes such as pinBH (and possibly catBH, although DFT calculation don not allow to draw a final conclusion), with a boron center stabilized by electron donors.



Scheme 8. Different modes of action of an organocatalyst in the hydroboration of CO_2 .

Altogether, these results provide a clearer perspective on the role of FLP- CO_2 adducts in the catalytic reduction of CO_2 and on the different mechanisms at play in the organocatalytic hydroboration of CO_2 . Organic catalysts have been shown to promote the hydroboration of CO_2 via three different modes (Scheme 8). First, strong nucleophiles favor the hydride transfer to CO_2 by increasing the hydricity of the B–H linkage by coordination to the boron center (Scheme 8A). As an example, catalyst Me-TBD or pro-azaphosphatranes operate through this process.^{27,74} In a recent study by Bourissou and Fontaine³² the importance of an intermediate formaldehyde adduct was highlighted, which can also serve as a Lewis base. In contrast, Lewis acids may abstract the hydride of the B–H bond to yield a boron electrophile and convert the catalyst to a strong hydride donor, as observed for iPr_1 with pinBH (Scheme 8B). In these two mechanisms, the formation of stable CO_2 adducts hampers the catalysis by stabilizing the catalyst's resting state. Finally, the organocatalyst can also activate the CO_2 molecule, directly. As CO_2 is a weak Lewis base, this mode of action usually involves a bifunctional activation of CO_2 with the cooperative effect of a Lewis base and a Lewis acid (Scheme 8C). Catalysts **1**, **2**⁺ and **IV** were shown to follow this path,

with 9-BBN. Importantly, the degree of activation of the CO₂ molecule must be finely tuned to open this reduction path. Indeed, the “*activation*” of CO₂ in the form of an adduct is both deleterious and necessary to the catalytic activity, as it stabilizes the lowest intermediate in the potential energy surface yet prepares CO₂ for the subsequent reduction step by removing electron density from the carbon by coordination to the Lewis acid. It is noteworthy that future catalytic systems based on this approach should thus target compounds that show a low affinity for CO₂, based on thermodynamics, yet increase the electrophilicity of the carbon center with strong Lewis acids.

Conclusion

A novel class of intramolecular nitrogen-silylium FLPs, e.g. TBDSiR₂Cl (R = Me, ⁱPr, Ph) and their cationic derivatives, have been reported and their reactivity with CO₂ has been investigated. Formation and stability of the CO₂-adducts can be modulated with the steric and electronic environment at the silicon center and only the methylated CO₂-FLP have been observed and characterized. All of these novel silicon species were shown to promote the catalytic hydroboration of CO₂ to the methoxide level, in high yield under mild reaction conditions. DFT calculations were carried out, in support to experimental results, to better explore the role of FLP-CO₂ adducts in the catalytic reduction of CO₂ with 3 different boranes (9-BBN, catBH, pinBH). To date, CO₂-adducts **2**⁺ and **V**, where CO₂ is activated by a N/Si⁺ or N/B intramolecular FLP, remain the only two examples of stable FLP-CO₂ adducts exhibiting a catalytic activity in the hydro-elementation of CO₂.

From a mechanistic point of view, the reduction of CO₂ by 9-BBN with **1** relies on a hydride transfer from boron to carbon through a [2+2] mechanism, where the B–H bond adds to the C=O

bond of the activated CO₂ molecule in the FLP-CO₂ adduct. On the other hand, using pinBH with **iPr**1 as catalyst a novel electrophilic pathway is at play. For catBH and other catalyst a clear distinction between both pathways cannot be made. Nevertheless, a strong stabilization of CO₂ in the form of an adduct is deleterious to the catalytic activity in all cases.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization of compounds, kinetic profile of catalytic CO₂ hydroboration, crystallographic data, Cartesian coordinates of all optimized stationary points and transition states with the corresponding energies and lowest frequencies, overview of the energetic spans of the different proposed reaction mechanisms including different catalysts and hydroboranes sources, as well as an alternative reaction pathway. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Thibault Cantat, NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette, France

Fax: (+33) 1.6908.6640

E-mail: thibault.cantat@cea.fr

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

For financial support of this work, we acknowledge CEA, CNRS, the University Paris-Saclay, the CHARMMMAT Laboratory of Excellence and the European Research Council (ERC Starting Grant Agreement no. 336467). T.C. thanks the Fondation Louis D. – Institut de France for its formidable support. N. v. W. thanks S. Kozuch for providing the Autotof software.

REFERENCES

- (1) Fiorani, G.; Guo, W.; Kleij, A. W. *Green Chem.* **2015**, *17*, 1375-1389.
- (2) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636-637.
- (3) Tlili, A.; Blondiaux, E.; Frogneux, X.; Cantat, T. *Green Chem.* **2015**, *17*, 157-168.
- (4) Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257-284.
- (5) Walther, D. *Nach. Chem. Tech. Lab.* **1992**, *40*, 1214-1227.
- (6) Walther, D.; Ruben, M.; Rau, S. *Coord. Chem. Rev.* **1999**, *182*, 67-100.
- (7) Fernandez-Alvarez, F. J.; Aitani, A. M.; Oro, L. A. *Catal. Sci. Tech.* **2014**, *4*, 611-624.
- (8) Vaska, L. *J. Mol. Catal.* **1988**, *47*, 381-388.
- (9) Gibson, D. H. *Coord. Chem. Rev.* **1999**, *185-186*, 335-355.
- (10) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063-2096.
- (11) Gerd Weyers, M. S., Norbert Kuhn *Z. Naturforsch.* **199**, *54b*, 427.
- (12) Villiers, C.; Dognon, J.-P.; Pollet, R.; Thuéry, P.; Ephritikhine, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 3465-3468.
- (13) Murphy, L. J.; Robertson, K. N.; Kemp, R. A.; Tuononen, H. M.; Clyburne, J. A. *C. Chem. Commun.* **2015**, *51*, 3942-3956.
- (14) Stephan, D. W. *Dalton Transactions* **2009**, 3129-3136.
- (15) Stephan, D. W. *Organic Biomol. Chem.* **2008**, *6*, 1535-1539.
- (16) Erker, G. *Comptes Rendus Chimie* **2011**, *14*, 831-841.
- (17) Stephan, D. W. *Acc. Chem. Res.* **2015**, *48*, 306-316.
- (18) Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A. *Chem. Eur. J.* **2014**, *20*, 2990-2996.

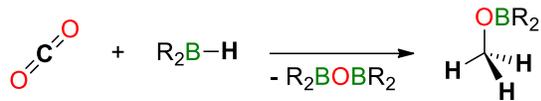
- (19) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 6643-6646.
- (20) Theuergarten, E.; Bannenberg, T.; Walter, M. D.; Holschumacher, D.; Freytag, M.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Dalton Transactions* **2014**, *43*, 1651-1662.
- (21) Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032.
- (22) Ménard, G.; Gilbert, T. M.; Hatnean, J. A.; Kraft, A.; Krossing, I.; Stephan, D. W. *Organometallics* **2013**, *32*, 4416-4422.
- (23) Travis, A. L.; Binding, S. C.; Zaher, H.; Arnold, T. A. Q.; Buffet, J.-C.; O'Hare, D. *Dalton Transactions* **2013**, *42*, 2431-2437.
- (24) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem. Int. Ed.* **2011**, *50*, 3925-3928.
- (25) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796-1797.
- (26) Bertini, F.; Lyaskovskyy, V.; Timmer, B. J. J.; de Kanter, F. J. J.; Lutz, M.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. *J. Am. Chem. Soc.* **2012**, *134*, 201-204.
- (27) Das Neves Gomes, C.; Blondiaux, E.; Thuéry, P.; Cantat, T. *Chem. Eur. J.* **2014**, *20*, 7098-7106.
- (28) Barnett, B. R.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Chem. Commun.* **2015**, *51*, 541-544.
- (29) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2014**, *136*, 10708-10717.
- (30) Wang, T.; Stephan, D. W. *Chem. Eur. J.* **2014**, *20*, 3036-3039.
- (31) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2013**, *135*, 9326-9329.
- (32) Declercq, R.; Bouhadir, G.; Bourissou, D.; Légaré, M.-A.; Courtemanche, M.-A.; Nahi, K. S.; Bouchard, N.; Fontaine, F.-G.; Maron, L. *ACS Catal.* **2015**, *5*, 2513-2520.
- (33) Lu, Z.; Hausmann, H.; Becker, S.; Wegner, H. A. *J. Am. Chem. Soc.* **2015**, *137*, 5332-5335.
- (34) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660-10661.
- (35) Cantat, T.; Gomes, C.; Blondiaux, E.; Jacquet, O.; C07F 5/02 (2006.01), C07B 59/00 (2006.01), G01N 33/60 (2006.01) ed.; CEA, Ed. 2014; Vol. WO/2014/162266
- (36) Reißmann, M.; Schäfer, A.; Jung, S.; Müller, T. *Organometallics* **2013**, *32*, 6736-6744.
- (37) Schäfer, A.; Reißmann, M.; Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 12636-12638.
- (38) Weicker, S. A.; Stephan, D. W. *Chem. Eur. J.* **2015**, *21*, 13027-13034.
- (39) Herrington, T. J.; Ward, B. J.; Doyle, L. R.; McDermott, J.; White, A. J. P.; Hunt, P. A.; Ashley, A. E. *Chem. Commun.* **2014**, *50*, 12753-12756.
- (40) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188-1190.
- (41) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917-1918.
- (42) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325-332.
- (43) Maaranen, J.; Andell, O. S.; Vanne, T.; Mutikainen, I. *J. Organomet. Chem.* **2006**, *691*, 240-246.

- (44) Andell and coworkers solved a dimeric structure of **1** by cooling down a refluxing pentane solution to -30 °C. This might indicate a higher thermodynamic stability of the dimeric structure.
- (45) Pounds, A. J. *J. Chem. Educ.* **2007**, *84*, 43.
- (46) Frank Weinhold; Landis, C. R. *Valency and Bonding A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: United Kingdom at the University Press, Cambridge, 2005.
- (47) Kummer, D.; Abdel Halim, S. H.; Kuhs, W.; Mattern, G. *J. Organomet. Chem.* **1993**, *446*, 51-65.
- (48) Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated solution of $[1^+, \Gamma]_2$ in DMF. However the solved structure shows the decomposition of $[1^+, \Gamma]_2$ in DMF with complete deoxygenation of several DMF molecules and four TBD residues, as well as four iodides in the unit cell.
- (49) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, *132*, 8872-8873.
- (50) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z.-X.; Guan, H. *Inorg. Chem.* **2011**, *50*, 3816-3825.
- (51) Shintani, R.; Nozaki, K. *Organometallics* **2013**, *32*, 2459-2462.
- (52) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 1671-1674.
- (53) Sgro, M. J.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 11343-11345.
- (54) We choose to calculate the TOF following the proposition of Kozuch and Martin (see ref. 62), i.e. as the derivative of the number of turnovers (number of B-H bonds used) per catalyst with respect to the reaction time under steady state regime.
- (55) $[1^+, \text{NTf}_2^-]_2$ is almost insoluble in THF and showed no catalytic activity under the employed reaction conditions.
- (56) Plumley, J. A.; Evanseck, J. D. *J. Phys. Chem. A* **2009**, *113*, 5985-5992.
- (57) Lu, Z.; Wang, Y.; Liu, J.; Lin, Y.-j.; Li, Z. H.; Wang, H. *Organometallics* **2013**, *32*, 6753-6758.
- (58) Kozuch, S.; Shaik, S. *Acc. Chem. Res.* **2011**, *44*, 101-110.
- (59) Uhe, A.; Kozuch, S.; Shaik, S. *J. Comput. Chem.* **2011**, *32*, 978-985.
- (60) Stephan, D. W.; Erker, G. *Chemical Science* **2014**, *5*, 2625-2641.
- (61) Kozuch, S. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 795-815.
- (62) Kozuch, S.; Martin, J. M. L. *ACS Catal.* **2012**, *2*, 2787-2794.
- (63) The formation of hypervalent hydrosilanes has also been proposed as a competent catalytic pathway in the hydrosilylation of CO₂, based on DFT calculation. See: Q. Zhou and Y. Li, *J. Am. Chem. Soc.*, **2015**, *137*, 10182-10189.
- (64) Arya, P.; Boyer, J.; Corriu, R. J. P.; Lanneau, G. F.; Perrot, M. *J. Organomet. Chem.* **1988**, *346*, C11-C14.
- (65) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919-8922.
- (66) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179-6186.
- (67) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672-1675.

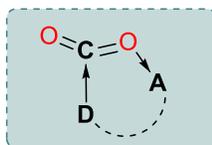
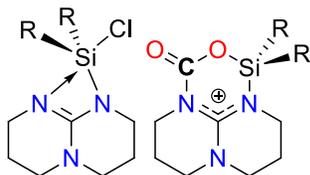
- (68) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887-4892.
- (69) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921-3923.
- (70) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090-3098.
- (71) Hog, D. T.; Oestreich, M. *Eur. J. Org. Chem.* **2009**, *2009*, 5047-5056.
- (72) Rendler, S.; Oestreich, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 5997-6000.
- (73) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. *M. Nat. Chem.* **2014**, *6*, 983-988.
- (74) Blondiaux, E.; Pouessel, J.; Cantat, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 12186-12190.

Pre-print version

TOC GRAPHIC



catalysts:



Stability and role

The synthesis and catalytic activity of novel CO₂ adducts with N/Si+ Frustrated Lewis Pairs is reported, in the hydroboration of CO₂. The results unveil the role of FLP-CO₂ adducts in the hydroboration of CO₂.