Mechanistic Studies on the Selective Reduction of CO₂ to the Aldehyde Level by a PBP-Supported Nickel Complex

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ABSTRACT: This work describes a thorough investigation of the mechanism of a highly selective hydrosilylation of CO₂ to the formaldehyde level catalyzed by a bis(phosphino)boryl (PBP)Ni(II) complex in the presence of B(C₆F₅)₃. CO₂ activation by insertion into the Ni-H bond of the catalyst precursor **2** is shown to occur very easily due to the *trans* influence exerted by the boryl ligand. During catalysis, the limiting step is B(C₆F₅)₃ dissociation from the active species (PBP)Ni-OCHO·B(C₆F₅)₃ (**4**), which controls the amount of free borane that can lead to over-reduction to methane. Free borane activates the silane by formation of [R₃Si-H···B(C₆F₅)₃], which can then transfer the silylium (R₃Si⁺) fragment to the oxygen atoms of the Ni formate and Ni acetal intermediates. The ion pair [(PBP)Ni][HB(C₆F₅)₃] (**5**) is the key species that activates CO₂ in the catalytic cycle (and silylformate in a second step) with [HB(C₆F₅)₃]⁻ as the source of

hydride. Hydride transfer to $[(\text{PBP})\text{Ni-OCO}]^+$ is virtually barrier-less whereas hydride transfer to $[(\text{PBP})\text{Ni-OCHOSiR}_3]^+$ has the second highest energy barrier of the process ($25.2 \text{ kcal}\cdot\text{mol}^{-1}$). Therefore, the $(\text{PBP})\text{Ni}$ framework is instrumental in both reduction steps of the catalysis and controls the selectivity of the reaction by sequestering $\text{B}(\text{C}_6\text{F}_5)_3$.

KEYWORDS: CO_2 , nickel complexes, boryl ligands, hydrosilylation, mechanisms, DFT calculations

INTRODUCTION

Carbon dioxide (CO_2) is present in the atmosphere and its concentration is increasing as a consequence of the intensive use of fossil fuels. Re-use of this non-toxic, renewable and abundant source of carbon as a C1 building block for the synthesis of liquid fuels and added value chemicals is a goal in chemical synthesis that has attracted considerable attention since the first account of its activation by a metal complex,¹ and increasingly during the last decade.^{2,3} However, the kinetic inertness and thermodynamic stability of CO_2 make its activation and reduction a challenge that has been tackled by the use of metal complexes⁴⁻⁶ and organic systems,⁷⁻⁹ including Frustrated Lewis Pairs (FLP).¹⁰⁻¹⁷ Selective reduction of CO_2 to methanol,¹⁸⁻²² and also to formic acid²³⁻²⁹ and methane³⁰⁻³³ are of great industrial interest, and many efforts have been made to design homogeneous metal catalysts to this end. Formaldehyde is another product of the partial reduction of CO_2 , with a worldwide production of over 20 million tons per year, however its current industrial synthesis is based on the catalytic oxidation of methanol at high temperatures.³⁴ There are comparatively few examples of catalysts capable of reducing CO_2 to the formaldehyde level selectively.^{16,17,35-38} Some representative examples

(Scheme 1) include ruthenium and iron catalysts reported by Bontemps and Sabo-Etienne that yield formaldehyde by the selective reduction of CO₂ with borane,^{36,37} the ruthenium-catalyzed reduction of CO₂ to bis(silyl)acetal or methyl silyl ether (controlled by the reaction temperature) described by Oestreich et al.³⁸ and the rhenium and scandium complexes of Berke¹⁷ and Piers,³⁵ who applied the Frustrated Lewis Pair (FLP) concept to the hydrosilylation of CO₂ with B(C₆F₅)₃ as co-catalyst.

Scheme 1. Examples of catalysts for the selective reduction of CO₂ to the formaldehyde level: **I** Berke, 2013 (reference 17); **II** Piers, 2014 (reference 35); **III** Bontemps and Sabo-Etienne, (reference 37); **IV** Oestreich, 2015 (reference 38) and compound **4** of this work.

Lately we have focused our attention on the reactivity of nickel complexes stabilized by a bis(phosphino)boryl (PBP) ligand.³⁹⁻⁴⁴ Thus, we have reported the synthesis of a nickel methyl complex (PBP)NiMe (**1**), which undergoes hydrogenolysis of its Ni-Me bond with activation of H₂ through a cooperative metal-boryl mechanism to yield the hydride derivative (PBP)NiH (**2**) (Scheme 2).⁴⁵

Scheme 2. Formation of **2** via a Ni(0) σ -borane (**A**).

We expected that the strong *trans* influence of the boryl ligand⁴⁶⁻⁴⁹ would increase the nucleophilicity of the hydride,⁵⁰⁻⁵² which would in turn make **2** a good candidate to serve as catalyst for the activation of CO₂, since insertion of this molecule into a metal-hydrogen bond is often postulated as a key step in the catalytic conversion of CO₂ by transition metal complexes.^{53,54} Indeed, we have recently reported that **2** reacts with CO₂ (1 bar, r.t.) to form the formate complex (PBP)Ni-OCHO (**3**) instantaneously (Scheme 3).⁵⁵ The same species **2** and **3** have been synthesized in the group of J. Peters and **3** has been used as olefin hydrogenation catalyst.⁴⁹

Scheme 3. Synthesis of the catalyst (**4**).

In our case, we have reported that **3** is the precursor of an efficient catalyst for a highly selective hydrosilylation of CO₂ into bis(silyl)acetal with B(C₆F₅)₃ as co-catalyst (Scheme 4).⁵⁵ The catalyst, (PBP)Ni-OCHO·B(C₆F₅)₃ (**4**), was isolated after treatment of **3** with B(C₆F₅)₃ and fully characterized by spectroscopic methods including X-Ray diffraction. Catalyst loadings of 0.05% afford high conversions at 70° with various silanes, with turnover numbers up to 1200 and

turnover frequencies up to 56 h⁻¹, which makes **4** one of the most active catalysts to date for this transformation.³⁵

Scheme 4. Reaction catalyzed by **4**. Me₃SiH was used as a model in the computational study.

In this work we report a detailed investigation of the mechanism of such catalysis, which involves a role for the B(C₆F₅)₃ co-catalyst in activating the silane and the participation of the (PBP)Ni metal framework in the activation of CO₂ and in controlling the selectivity of the process. We will also briefly probe the effect of the boryl functionality in the insertion of CO₂ into the Ni-H bond of **2** by comparing this molecule with related pincer nickel complexes.

COMPUTATIONAL DETAILS

Density Functional Theory (DFT) calculations^{56,57} were carried out using the Gaussian09 (G09) software.⁵⁸ All geometries were optimized without restrictions in the gas phase with the PBE0 functional as implemented in the G09 software.⁵⁹ Non-metal atoms were described with the 6-31G(d,p) basis set with polarization functions and the nickel atom was modelled with the Stuttgart/Dresden SDD basis set and its associated Electron Core Potential.⁶⁰ Vibrational analysis at the same level of theory was carried out to characterize the optimized geometries as minima or saddle points (Transition States, TS) of the Potential Energy Hypersurface as well as for obtaining the corresponding Zero-Point corrections and thermal corrections to Enthalpy and Free Energy. The nature of the species connected by a given TS was established by means of Intrinsic Reaction Coordinate (IRC)⁶¹ calculations or by allowing the TS geometries to vibrate along their imaginary frequency and optimizing the resulting geometries to the nearest minima.

Bulk solvent effects were modelled by single point calculations on the gas phase geometries using Truhlar's SMD continuum solvent model.⁶² Empirical dispersion corrections were shown to have substantial effects on the energy barriers of our systems and have also been introduced with the D3 version of Grimme's dispersion⁶³⁻⁶⁵ by single point calculations on the gas phase geometries (optimizing the molecular geometries with the PBE0-D corrected functional yielded very similar results). Exploratory calculations were carried out using a simplified version of the catalyst in which the ^tBu groups on the phosphorus atoms of the PBP ligand were replaced by Me groups (PBP_{Me}, the corresponding species are denoted by a Me subscript). These calculations were used to favor one mechanistic pathway, which was then recalculated with the real catalyst. Also, we have used Me₃SiH instead of larger silanes, however the use of the real Lewis acid, B(C₆F₅)₃, in the calculations (instead of BF₃) was shown to be critical to account for the experimental results.

Free energy in solution. Translation entropy, while accurately calculated in the gas phase,⁶⁶ is greatly overestimated by standard calculation methods for reactions in solution.⁶⁷ Theoretical⁶⁷⁻⁶⁹ and experimental^{70,71} investigations suggest that a 50% correction^{72,73} to gas phase entropy (3-6 kcal per mole change) yields better agreement between experimental (solution) and calculated (gas phase) data. Some authors choose to omit entropy data entirely and only use enthalpy values.⁷⁴ Throughout the following discussion we will use Zero-Point Energies (with solvent and dispersion corrections) and will indicate 50% corrected-free energy variations (ΔG_{50}) when appropriate.

RESULTS AND DISCUSSION

We have directed our investigations to understanding the role of the (PBP)Ni framework in the reduction of CO₂ and in the selectivity of the catalysis. We begin this section by accounting

for the role of the boryl functionality of **2** in facilitating the insertion of CO₂ into its Ni(II)-H bond. The results described below reflect the prompt formation of precursor **3**. However, it soon became obvious from further experiments that the active species in catalyst is **4**, with B(C₆F₅)₅ being instrumental for the reaction to occur. Therefore, we focused subsequent efforts in analyzing the reactivity of **4** with Me₃SiH, with results that are discussed later.

CO₂ insertion into the Ni-H bond of 2. Effect of the boryl functionality. Studies on the insertion of CO₂ into Ni-H and Ni-L (L ≠ H) bonds of related species have been reported and a relationship has been established between the influence of the ligand *trans* to H and the energy barriers of the reactions.^{54,52} Insertion of CO₂ into Ni-H bonds does not feature in the catalytic cycle that we describe here, as we shall see below. However, we describe here our study the reaction of **2** with CO₂ by DFT methods as a probe of the *trans*-influence of its boryl moiety. Also, for comparison purposes, we calculated the insertion of CO₂ into Ni(II)-H bonds of analogous pincer complexes with different ligands *trans* to H (Scheme 5). Thus, we used model complexes (with methyl groups on P and N atoms replacing larger substituents) derived from our (PBP_{Me})NiH (**2_{Me}**) and other nickel hydrides containing PCP (**2_{PCP,Me}**),⁷⁵ POCOP (**2_{POCOP,Me}**)^{19,76} and PSiP (**2_{PSiP,Me}**)⁷⁷ ligands. Cationic derivatives containing carbene (**2_{PCBImp,Me}**) and pyridine (**2_{PNP,Me}** and **2_{NNN,Me}**) ligands *trans* to H were considered in addition.

Scheme 5. Energies involved in the insertion of CO₂ into the Ni-H of several pincer complexes: $\Delta G^\ddagger$ (red, top) and ΔG^0 (bottom). In the cases in which a two-step process is involved (with $2_{PCP,Me}$ and $2_{PSiP,Me}$) the highest barrier from the reactants is reported.

All insertion reactions are thermodynamically favorable except for the PNP species. Analysis of the insertion mechanism of the reaction with 2_{Me} (Figure 1) reveals that nucleophilic attack of the hydride ligand to CO₂ takes place at the transition state, without involvement of the nickel atom, whereas, in agreement with previous analysis,⁵⁴ the remaining systems feature four-centered transition states with participation of the metal (see the SI for details). Additionally, two-step mechanisms were found for the PSiP and PCP systems at our level of theory, in which formation of the formate ligand is preceded by the generation of an activated [Ni]-H·CO₂ complex with very short H···CO₂ contacts. As expected, the PSiP and 2_{Me} complexes yielded the lowest overall barriers for CO₂ insertion, $\Delta G^\ddagger = 6.1$ and 6.3 kcal·mol⁻¹ respectively, in good agreement with the strong *trans* influence of silyl and boryl ligands.⁴⁶⁻⁴⁹ Additionally, 2_{Me} yields the most stable Ni formate complex of all the species calculated. Cationic species presented higher insertion barriers, with insertion of CO₂ in $2_{PCBImp,Me}$, resulting from the formal

replacement of the boron of **2_{Me}** by a carbon atom, being the most endoergic. Moreover, the trends obtained in this study are consistent with the experimental observations in terms of the time required for the reaction to complete at room temperature; while **2_{Me}** (energy barrier of 6.3 kcal·mol⁻¹) gives the formate **3** in a few seconds,⁵⁵ the PCP (**2_{PCP,Me}**; $\Delta G^\ddagger = 9.1$ kcal·mol⁻¹) and POCOP complexes (**2_{POCOP,Me}**; $\Delta G^\ddagger = 13.2$ kcal·mol⁻¹) require a few minutes⁷⁵ and one hour⁷⁶ respectively.

Figure 1. Front and side views of the transition state for insertion of CO₂ into the Ni-H bond of **2_{Me}**.

Catalysis by 4. Role of B(C₆F₅)₃. The nature of **4**, (PBP)Ni-OCHO·B(C₆F₅)₃, as the catalyst was established experimentally.⁵⁵ Three experimental facts have been taken into consideration to propose mechanistic pathways for the reaction (Scheme 6):

1. Addition of one equivalent of Et₃SiH to a 1:1 mixture of **3** and B(C₆F₅)₃ (**4** forms *in situ*) results in the complete consumption of the silane and formation of the bis(silyl)acetal derivative after heating at 70 °C for 30 min. No silylformate was detected at any stage of this transformation.

2. ^1H NMR-monitoring of the CO_2 reduction in catalytic conditions, using ^{13}C -enriched CO_2 , showed $(\text{Et}_3\text{SiO})_2\text{CH}_2$ as the almost exclusive reduction product.⁷⁸ Intentional addition of $\text{B}(\text{C}_6\text{F}_5)_3$ following consumption of CO_2 (after 8h) resulted in the quantitative reduction of $(\text{Et}_3\text{SiO})_2\text{CH}_2$ to methane.
3. When an NMR sample of **4** synthesized using $^{13}\text{CO}_2$ was charged with non-labelled CO_2 (1 bar), 12% CO_2 exchange was observed after 22 h at 70 °C.

Scheme 6. Relevant experimental observations.

The DFT-optimized geometry of **4** is in agreement with the solid state (X-Ray) data (Figure S4).⁵⁵ Elongation of the Ni-O bond from 1.958 in **3** to 1.997 Å upon $\text{B}(\text{C}_6\text{F}_5)_3$ coordination is also in agreement with experimental data by Peters⁴⁹ and us,⁵⁵ and the linkage of the formaborate group is in agreement with the zwitterionic structure depicted in Scheme 3^{31,35,79} with $\text{NiO}=\text{C}$ and C-OB distances of 1.239 and 1.277 Å respectively. The B-O distance, 1.558 Å, is similar to related species formed by CO_2 insertion into Frustrated Lewis Pairs adducts.^{80,81}

Figure 2. (double column) Initial steps of the pathways considered for the reduction of CO₂ to the formate level by **4**_{Me} and Me₃SiH (model system). Pathway a) (blue trace) involves direct hydrosilylation of the catalyst whereas pathway b) (red trace) requires B(C₆F₅)₃ dissociation. The profiles represent ΔZPE in kcal·mol⁻¹ (ΔG_{50} data in parentheses).

I. Reduction to the formate level. We have considered two possible pathways for the catalysis by **4**. These begin with either: a) *direct* hydrosilylation of the catalyst⁸² or b) silane activation by the borane previously dissociated from the catalyst (Figure 2). The model system (**4**_{Me} + Me₃SiH) was used in these exploratory calculations.

Silane attack to **4**_{Me} (a) was considered to take place from the side of the coordination plane of Ni further away from the B(C₆F₅)₃ fragment, with the Si atom approaching the Ni-coordinated oxygen. At the transition state (Figures 2 and S5), slippage of the formaborate ligand has taken place with splitting of the former Ni-O bond and formation of a new Ni-O interaction with the boron-bonded oxygen ($d_{\text{Ni}\cdots\text{O}} = 2.25$ Å). Simultaneously, a new Si-O bond begins to form ($d_{\text{Si}\cdots\text{O}} = 2.02$ Å) as hydrogen transfer takes place from Si-H to the boryl fragment ($d_{\text{B}\cdots\text{H}} = 1.67$ Å).

The Ni atom does not form a Ni-H bond,⁸³ instead the transition state leads to a Ni(0) species featuring a σ -borane interaction,⁴¹ which forms an adduct with $\text{Me}_3\text{SiOCHOB}(\text{C}_6\text{F}_5)_3$ ($\mathbf{A}_{\text{Me}}$ · $\text{Me}_3\text{SiOCHOB}(\text{C}_6\text{F}_5)_3$). This situation is reminiscent of the mechanism that we described for the hydrogenolysis of $\mathbf{1}$,⁴⁵ in which H_2 was activated at the nickel center, with cooperation of the boryl moiety. The barrier for Si-H activation from $\mathbf{4}_{\text{Me}}$ + Me_3SiH is $\Delta ZPE^\ddagger = 30.1 \text{ kcal}\cdot\text{mol}^{-1}$ ($\Delta G_{50}^\ddagger = 38.2 \text{ kcal}\cdot\text{mol}^{-1}$).

Pathway b) requires dissociation of $\text{B}(\text{C}_6\text{F}_5)_3$ from $\mathbf{4}_{\text{Me}}$ to activate the silane by formation of $[\text{Me}_3\text{Si-H}\cdots\text{B}(\text{C}_6\text{F}_5)_3]$.^{80,84-86} The energy variation in this case is $31.2 \text{ kcal}\cdot\text{mol}^{-1}$ ($\Delta G_{50} = 30.7 \text{ kcal}\cdot\text{mol}^{-1}$). This species increases the electrophilicity of Si, making it more prone to nucleophilic attack by the carbonyl of $(\text{PBP}_{\text{Me}})\text{Ni-OCHO}$ ($\mathbf{3}_{\text{Me}}$).⁸⁷ This process (**TS1b**) can be related to a Frustrated Lewis Pair (FLP) bond activation as described by Piers and Tuononen,⁸⁵ in which the Ni formate complex and the borane are the Lewis base and Lewis acid respectively (Scheme 7).

Scheme 7. Frustrated Lewis Pair-Like Si-H activation allows transfer of silylium (R_3Si^+) to the formate ligand of the catalyst.

While both pathways require overcome comparable initial energy barriers, in pathway a) separation of the **A_{Me}** and Me₃SiOCHOB(C₆F₅)₃ fragments is endothermic by a further 31.7 kcal·mol⁻¹ and, when regeneration of **2_{Me}** from **A_{Me}** (to insert more CO₂) is taken into account, the overall energy barrier from the reactants amounts to 54.8 kcal·mol⁻¹. On the contrary, borane dissociation is the highest energy barrier of pathway b). Thus, FLP-like bond activation of silane at the encounter complex **3_{Me}**·[Me₃Si-H···B(C₆F₅)₃], which lays 15.5 kcal·mol⁻¹ above the origin, occurs with S_N2-like transfer of silylium to (PBP_{Me})Ni-OCHO⁸⁴ (Scheme 7 and Figure 2) with virtually no energy barrier ($\Delta E^\ddagger(\mathbf{TS1b}) < 1$ kcal·mol⁻¹). At the transition state B···H, H···Si and Si···O distances are 1.38, 1.65 and 2.81 Å respectively. The resulting ion pair [(PBP_{Me})Ni-OCHOSiMe₃][HB(C₆F₅)₃] (**B_{Me}**) lays 1.7 kcal·mol⁻¹ above **4_{Me}** + Me₃SiH (Figure S6). These results indicated that pathway a) should be discarded and from this point we will describe the results obtained with the real catalyst for pathway b).

Results with the full catalyst 4. Dissociation of B(C₆F₅)₃ from **4** to yield (PBP)Ni-OCHO (**3**) + [Me₃Si-H···B(C₆F₅)₃] has a calculated energy variation of ca. 30 kcal·mol⁻¹ (Figure 3). As in the model system, this is the most endothermic (and endergonic) step of this pathway. Me₃Si⁺ transfer from [Me₃Si-H···B(C₆F₅)₃] to the O-terminus of **3** yields the ion pair **B**, [(PBP)NiOCHOSiMe₃][HB(C₆F₅)₃], with an energy return of 27.5 kcal·mol⁻¹ from **3** + [Me₃Si-H···B(C₆F₅)₃]. All attempts to locate the corresponding transition state (**TS1b**) resulted either in separation of **3** and [Me₃Si-H···B(C₆F₅)₃] or in evolution of the guessing geometries to **B**. This, in addition to the results of a Relaxed Potential Energy Scan (PES; Figure S7) and the low energy barrier calculated for the model system supports that silylium transfer at this step is very facile. Rearrangement of the relative positions of the cation and anion of **B** affords a geometry for the ion pair, **B'** (Figure S8), that is more stable than the former by 11.6 kcal·mol⁻¹, and from

which the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion can either a) approach the Ni atom with extrusion of Me_3SiOCHO to generate $[(\text{PBP})\text{Ni}][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**5**) (Figure S9), or b) transfer H^- to the formate ligand (**C**) to initiate the second reduction step (Scheme 8). The former step (a) has an energy cost of $25.2 \text{ kcal}\cdot\text{mol}^{-1}$ ($\Delta G_{50}^* = 19.7 \text{ kcal}\cdot\text{mol}^{-1}$) from **B'**, which is similar, as we shall see, to the energy required for H^- transfer (b). However, experiments showing the formation of bis(silyl)acetal, $(\text{Et}_3\text{SiO})_2\text{CH}_2$, as the sole product of the reduction of CO_2 by a 1:1 mixture of **4** and Et_3SiH ⁵⁵ (Scheme 6) strongly indicate that the second reduction process must be faster than extrusion of silylformate followed by regeneration of **4** from **5**.

Figure 3. Energy profile of the first reduction stage calculated with the real catalyst. ΔZPE data in $\text{kcal}\cdot\text{mol}^{-1}$ (ΔG_{50} data in parentheses and dashed trace). The inset represents the optimized geometry of ion pair **B'** (most C-H atoms omitted for clarity).

Scheme 8. Evolution of intermediate **B'** (overall Zero-Point Energies, in kcal·mol⁻¹, from **B'** in parentheses).

II. Second reduction stage. Hydride transfer from the hydroborate [HB(C₆F₅)₃]⁻ to the formate ligand of **B'** yields (PBP)Ni-OCH₂OSiMe₃·BAr₃, **C**·B(C₆F₅)₃, which lays 25.3 kcal·mol⁻¹ ($\Delta G_{50}^0 = 24.6$ kcal·mol⁻¹) above **B'** (Scheme 8 and Figure 4). Unfortunately, no TS has been located for the transfer, however, like in the first silylium transfer step (**TS1b**), calculations on the model system rendered the reverse process (**TS2b**; **C**_{Me}·B(C₆F₅)₃ → **B'**_{Me}) virtually barrierless, which was again supported by a relaxed PES on the real system (Figure S10). The borane is loosely bound to the organometallic fragment of **C**·B(C₆F₅)₃ and can activate a new molecule of silane to form the new encounter complex **C**·[Me₃Si-H···B(C₆F₅)₃] (Figure S11) ($\Delta ZPE^0 = 11.7$ kcal·mol⁻¹ from the origin), from which a second Me₃Si⁺ fragment is transferred, S_N2 fashion, in this case to the Ni-bound oxygen of the acetal ligand (**TS3b**). Again this step is very fast (when solvent and dispersion corrections are applied $\Delta ZPE^\ddagger$ and $\Delta G_{50}^\ddagger$ from **C**·[Me₃Si-H···B(C₆F₅)₃] are nearly zero) and the formation of the new ion pair [(PBP)Ni-O(SiMe₃)CH₂OSiMe₃][HB(C₆F₅)₃] (**D**) is exothermic by 22.7 kcal·mol⁻¹. Interestingly, if dispersion and entropy corrections are not applied, $\Delta G^\ddagger$ for this step exceeds 50 kcal·mol⁻¹ from the origin, whereas if only dispersion corrections are included $\Delta G^\ddagger = 36.9$ kcal·mol⁻¹. The former value of free energy would imply that the reaction cannot take place via any of the two mechanisms considered, and the latter, even if it could be justified, predicts the second reduction stage being slower than the first one (*i.e.* Me₃SiOCHO would be the main product), contrary to the experimental observations. These results highlight the importance of both dispersion

corrections in large systems and also the need for entropy corrections for reactions in solution. In this case, the entropy penalty is larger during the second reduction stage, since the variation in the number of species from the reactants to the products is up to -2, whereas in the first reduction stage is up to -1. Finally, extrusion of $(\text{Me}_3\text{SiO})_2\text{CH}_2$ from **D** yields **5** and is exothermic by 23.1 $\text{kcal}\cdot\text{mol}^{-1}$ from $\text{C}\cdot[\text{Me}_3\text{Si-H}\cdots\text{B}(\text{C}_6\text{F}_5)_3]$ ($\Delta G_{50}^0 = -29.2 \text{ kcal}\cdot\text{mol}^{-1}$). The overall reaction, when regeneration of the catalyst, **4**, from **5** is considered (see below) is exothermic by 46.3 $\text{kcal}\cdot\text{mol}^{-1}$ ($\Delta G_{50}^0 = -39.0 \text{ kcal}\cdot\text{mol}^{-1}$). The overall energy profile, including the regeneration of the catalyst can be found in the supporting information.

Figure 4 (please, double column). Energy profile for the second reduction stage. ΔZPE in $\text{kcal}\cdot\text{mol}^{-1}$ from **4** + Me_3SiH –solid trace– (ΔG_{50} data in parentheses and dashed trace).

III. Regeneration of the catalyst. CO_2 activation by $[(\text{PBP})\text{Ni}][\text{HB}(\text{C}_6\text{F}_5)_3]$ (5**).** The reaction media remains homogeneous for as long as CO_2 is present. Once it is consumed a precipitate appears, which readily re-dissolves when more CO_2 is added, thus regenerating **4**. We

attribute such precipitate to the Ni hydridoborate complex **5**, [(PBP)Ni][HB(C₆F₅)₃]. Evidence of the formation of **5** has been obtained by NMR spectroscopy. ¹H{¹¹B} NMR of the precipitate in toluene-*d*₈ shows the expected signals for the (PBP)Ni core and a broad resonance centered δ 4.38 ppm attributable to the BH. Correspondingly, ¹¹B NMR experiments reveal the characteristic resonance of the boryl boron from the PBP as a singlet at 28.3 in addition to a doublet resonance for the BH at δ -24.4 ppm with ¹J_{BH} = 93 Hz, which simplifies upon ¹H decoupling.^{33,88,89} Unfortunately, small amounts of THF or other ethereal solvents had to be added to the samples of **5** in order to achieve sufficient solubility, therefore amounts of ether-borane adducts are seen by NMR⁹⁰ (see the SI for further details).

We have already shown how **5** must be formed after extrusion of bis(silyl)acetal from **D**, and could also be formed after the first reduction process from **4** (Scheme 8a). According to our calculations, activation of CO₂ by **5** may follow a mechanism which is comparable to that proposed by Piers, Maron and Eisenstein for the analogous reaction with the ion pair [Cp*₂Sc][HB(C₆F₅)₃].³¹ Indeed, **5** is best described as a contact ion pair, in which the hydridoborate may bind the nickel in either κ¹-*F* or κ¹-*H* manners. DFT calculations located two minima for **5** within 1.4 kcal·mol⁻¹, featuring κ¹-*F* and κ¹-*H* interactions between the metal and hydridoborate fragments (Figure 5).

Figure 5. Molecular geometry of $[(\text{PBP})\text{Ni}][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**5**). H atoms have been omitted for clarity.

Insertion of CO_2 in the pocket between these fragments is exothermic by $4.6 \text{ kcal}\cdot\text{mol}^{-1}$ (from $\kappa^1\text{-F}$ coordinated **5** + CO_2 ; $\Delta G_{50}^0 = 0.0 \text{ kcal}\cdot\text{mol}^{-1}$), and yields **E**, $[(\text{PBP})\text{Ni-OCO}][\text{HB}(\text{C}_6\text{F}_5)_3]$ (Figure 6) featuring $\kappa^1\text{-O}$ CO_2 coordination to the metal.⁹¹ An early transition state (**TS4**) was located for H^- transfer from the borohydride to coordinated CO_2 , $0.4 \text{ kcal}\cdot\text{mol}^{-1}$ above the previous minimum. At this TS, the B-H bond is very slightly elongated by $0.03 \text{ \AA}$, the O-C-O angle is 160° and the $\text{C}\cdots\text{H}$ distance is still long at $1.77 \text{ \AA}$. In the product of this step (**F**), which lays $6.1 \text{ kcal}\cdot\text{mol}^{-1}$ below **5** + CO_2 , the new HCO_2^- ligand interacts with $\text{B}(\text{C}_6\text{F}_5)_3$ through a $\text{H}\cdots\text{B}$ contact of $2.36 \text{ \AA}$. Borane coordination to the O-termini of the formate is very exothermic and requires overcoming a barrier of only $2.3 \text{ kcal}\cdot\text{mol}^{-1}$. The overall process is nearly barrierless and has an energy return of ca. $35 \text{ kcal}\cdot\text{mol}^{-1}$ ($\Delta G_{50}^0 = 30.4 \text{ kcal}\cdot\text{mol}^{-1}$), in agreement with the observed instantaneous re-dissolution of **5** to regenerate **4** upon CO_2 addition to the reaction mixture, and with the CO_2 exchange equilibrium (3) of Scheme 6, as the limited incorporation of $^{13}\text{CO}_2$ in **4** indicates that the reverse reaction of CO_2 dissociation presents a high barrier.

Figure 6 (please, double column). Energy profile for CO₂ activation by the ion pair [(PBP)Ni][HB(C₆F₅)₃] (**5**) to regenerate the catalyst **4**. ΔZPE in kcal·mol⁻¹ –solid line– (ΔG₅₀ in parentheses –dashed line–).

The overall catalytic cycle is represented in Scheme 9: borane dissociation from the catalyst allows the formation of small amounts of [Me₃Si-H···B(C₆F₅)₃], which readily transfer silylium to the formate ligand of **3**. Hydride transfer to the silylformate of the intermediate **B** gives C·B(C₆F₅)₃ and must be faster than extrusion of the organic fragment with formation of the ion pair [(PBP)Ni][HB(C₆F₅)₃], **5**. Then, a second molecule of silane reacts with C·B(C₆F₅)₃ to yield more [Me₃Si-H···B(C₆F₅)₃], which transfers a second silylium to the silylacetal ligand of **C**. Extrusion of the bis(silyl)acetal yields **5**, which is able to activate CO₂ to close the cycle.

Scheme 9. Overall catalytic cycle.

IV. Origin of the selectivity. Due to its remarkable stability, the first step in CO₂ reduction is often the most difficult. In our case, it seems clear that the (PBP)Ni framework is responsible for this process, either by facile CO₂ insertion into the Ni-H bond of **2** thanks to the *trans* influence that the boryl moiety exerts on this bond, or via CO₂ insertion into the components of the contact ion complex [(PBP)Ni][HB(C₆F₅)₃] (**5**) followed by hydride transfer, as we have described before. However, most reactions that reduce CO₂ with silanes and B(C₆F₅)₃ co-catalyst yield methane.^{30-33,80,92} This is due in most cases to the formation of [R₃Si-H...B(C₆F₅)₃], which is an active catalyst in the reduction of carbonyl groups,^{84,85,93} although it is not capable of activating CO₂ on its own.¹⁵ Therefore, sequestration of B(C₆F₅)₃ by the metal framework is required for selectivity control. Thus Piers, Maron and Eisenstein reported³¹ that a ca. 1:1 (Et₂SiO)₂CH₂:CH₄ mixture was formed in the reduction of CO₂ by [Cp*Sc]·[HB(C₆F₅)₃] with Et₃SiH in the absence of added borane, and calculated that B(C₆F₅)₃ dissociation from [Cp*ScOCOH]·B(C₆F₅)₃ is relatively accessible with $\Delta G^0 = 6.4 \text{ kcal}\cdot\text{mol}^{-1}$. In a subsequent work Piers et al. argued that increased selectivity towards bis(silyl)acetal was achieved thanks to a more effective trapping of B(C₆F₅)₃ by a modified Sc catalyst.³⁵

In our case, we have already indicated that borane dissociation from **4** (Scheme 10, eq. 1) is highly disfavored. The same is true for borane dissociation from **5** to give **2** (Scheme 10, eq 2). ΔG_{50}^0 for these processes are 27.9 and 24.2 kcal·mol⁻¹ respectively. In addition, activation of CO₂ and Me₃SiOCHO compete favorably with the latter process. Dissociation of borane could also occur from (PBP)Ni-OCH₂OSiMe₃·B(C₆F₅)₃ (C·B(C₆F₅)₃), but the process from (**4**) + 2Me₃SiH is again endoergic, with $\Delta G_{50}^0 = 22.3$ kcal·mol⁻¹. When this process is combined with the formation of Me₃SiOCHO from (**4**) + Me₃SiH (Scheme 10, eq. 3) the overall free energy involved amounts to $\Delta G_{50}^0 = 38.4$ kcal·mol⁻¹. Formation of (Me₃SiO)₂CH₂ via reduction of Me₃SiOCHO with [Et₃Si-H···B(C₆F₅)₃] is not exoergic enough ($\Delta G_{50}^0 = -17.7$ kcal·mol⁻¹) to make the overall process thermodynamically favorable. These data support that in our case both CO₂ reduction processes are metal mediated, and explain how over reduction is controlled by our catalyst.

Scheme 10. Relevant equilibria related to B(C₆F₅)₃ release and ΔG_{50} (kcal·mol⁻¹) for the forward reaction.

CONCLUDING REMARKS

We have described a mechanism for the selective reduction of CO₂ to the formate level with silanes, catalyzed by a (PBP)Ni complex with B(C₆F₅)₃ as co-catalyst.⁵⁵ From a computational point of view the use of empirical dispersion corrections has proven to be necessary to account

for the experimental results, as well as it is important to correct the translational entropy, which is overestimated in reactions taking place in solution. The role of the boryl ligand in lowering the energy barrier for stoichiometric insertion of CO₂ into the Ni-H bond of the catalyst precursor **2** has been shown. More importantly, the metal framework has been revealed to be instrumental in the reduction steps during catalysis via FLP-like bond activation steps involving silylium transfer from [R₃Si-H...B(C₆F₅)₃], followed by hydride transfer from [HB(C₆F₅)₃]⁻ at contact ion pairs like [(PBP)Ni][HB(C₆F₅)₃]³¹, which is the species responsible for CO₂ activation. The metal framework is also involved in determining the selectivity of the catalysis, since it does effectively sequester B(C₆F₅)₃, thus limiting the amount of [R₃Si-H...B(C₆F₅)₃] in the reaction medium, and preventing that the latter species catalyzes the reduction of carbonyl groups to CH₄. Therefore, the metal complex takes part in both reduction steps, from CO₂ to R₃SiOCHO and from there to (R₃SiO)₂CH₂. We are currently expanding the scope of the (PBP)Ni framework as a catalyst in small molecule activation reactions.

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The manuscript was written through contributions of all authors.

ASSOCIATED CONTENT

Supporting Information. XYZ coordinates and potential energy of calculated species.

Additional computational and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC GRAPHIC

A mechanism for the selective hydrosilylation of CO₂ to the aldehyde level by a bisphosphinoboryl (PBP) nickel complex is described. The results reveal the origin of the selectivity and the roles of [(PBP)Ni]⁺ and [HB(C₆F₅)₃]⁻ in the sequence of hydride and silylium (R₃Si⁺) transfers to CO₂ and formate ligands that lead to reduction.