Selective Reduction of Carbon Dioxide to Bis(silyl)acetal Catalyzed by a PBP-Supported Nickel Complex†‡

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Selective reduction of CO₂ to the formaldehyde level remains an important challenge and to date only a few catalysts have been developed for this reaction. Herein, we report an efficient catalyst that consists of a bis(phosphino)boryl nickel hydride complex in combination with B(C₅F₅)₃ for the highly selective hydrosilation of CO₂ to bis(silyl)acetal derivatives.

The use of carbon dioxide (CO₂) as a non-toxic, renewable and economical carbon source for the synthesis of liquid fuels and value added chemicals has attracted increasing attention over the last years.¹ Regarding the many catalytic transformations involving CO₂, those concerning its selective reduction represent an important challenge. In this sense, a substantial number of efficient transition metal catalysts for the conversion of carbon dioxide to formic acid, employing different reducing agents, have been reported.² Also, great efforts in the design of catalysts for the reduction of CO₂ to methanol³a,b and methane³c–e have been made. Nevertheless, catalysts that are selective enough for the controlled transformation of CO₂ to the formaldehyde level are very rare.⁴ Formaldehyde is an important industrial chemical with a world-wide production greater than 20 million tons per year. Currently, the large-scale synthesis of formaldehyde is based on the catalytic oxidation of methanol at high temperatures.⁵ In this sense, the use of CO₂ as a carbon source for the synthesis of CH₂O acquires great importance from both an industrial and an academic perspective. Recently, Bontemps and Sabo-Étienne reported the selective synthesis of formaldehyde by the borane reduction of CO₂ using ruthenium and iron catalysts.⁶,⁷ Likewise, Oestreich et al. have described the ruthenium-catalyzed reduction of CO₂ to bis(silylacetal) or methyl silyl ether by adjusting the reaction temperature.⁸ Finally, the groups of Berke and Piers applied the frustrated Lewis pair (FLP) concept to the selective hydrosilation of CO₂, employing Rhenium and Scandium complexes in combination with B(C₅F₅)₃ (Scheme 1).

![Scheme 1](image)

We have recently described the synthesis of a nickel methyl complex supported by a bis(phosphino)boryl (PBP) ligand [(PBP)NiMe] (1) that promotes the activation of H₂ through a cooperative metal-boryl mechanism, to form the hydride complex [(PBP)NiH] (2)⁶,⁷ (Scheme 2).

![Scheme 2](image)

We envisioned that 2 could also serve as an efficient catalyst for the activation of carbon dioxide. In this regard, the insertion of CO₂ into a metal-hydrogen bond is assumed to be a key step in the catalytic conversion of CO₂ mediated by transition-metal complexes.⁸ This process is eased by the use of ligands that exert a strong trans-influence decreasing the Ni-H bond strength and increasing the nucleophilic character of the hydride group.⁹ Taking into account that boryl groups are...
among the strongest trans-influence ligands known,\textsuperscript{10} we considered complex 2 an attractive candidate to study the activation of CO\(_2\). Furthermore, from the economical point of view, the replacement of noble metals by earth abundant and cheaper ones is a desired goal in catalysis. In this communication, we describe a proficient nickel catalyst for the selective hydrosilation of carbon dioxide into bis(silyl)acetal derivatives with a catalytic activity comparable to the most effective catalysts reported so far.\textsuperscript{4b}

As we expected, treatment of 2 with CO\(_2\) (1 bar, r.t.) gives the formate complex [\((\text{PBP})\text{Ni(O}_2\text{CH})\)] \((3)\) instantaneously. \(^{1}\text{H}\) and \(^{13}\text{C}\) NMR spectra show resonances at 9.11 and 167.2 ppm respectively, that assign to the formate group. The \(^{31}\text{P}\) and \(^{13}\text{B}\) NMR spectra exhibit signals (\(\delta_{31}\text{P} 85.2\); \(\delta_{31}\text{B} 37.5\) ppm) at higher field than those observed for 2. We remark that while we were immersed in this study, Lin and Peters reported the synthesis and characterization of 3.\textsuperscript{7} In an effort to evaluate the suitability of 3 as a catalyst for hydrosilation of CO\(_2\), we studied the stoichiometric reaction of 3 towards Et\(_3\)SiH. We observed that no reaction occurred at room temperature and heating of the solution at 40 °C provokes the decomposition of 3.\textsuperscript{11} At this point, based on previous work from Piers,\textsuperscript{4b} Berke\textsuperscript{4b} and others,\textsuperscript{5p,5q,5r,5s,5t} we ran this reaction in the presence of B(C\(_3\)F\(_2\))\(_3\).

Thus, the addition of Et\(_3\)SiH (1 equiv) to a solution of 3 and B(C\(_3\)F\(_2\))\(_3\) (one equivalent relative to 3) and CO\(_2\) (4 bar) in C\(_6\)D\(_6\) gives rise to the complete consumption of Et\(_3\)SiH and the selective formation of the bis(silyl)acetal derivative, after heating at 70 °C for 30 minutes (Scheme 3a). We also observed the formation of a new nickel complex generated by reaction of 3, formed due to the presence of CO\(_2\) in solution, with B(C\(_3\)F\(_2\))\(_3\). The nature of this new species will be discussed in detail below. The resonance due to the CH\(_2\) group of (Et\(_3\)SiO)\(_2\)CH\(_2\) appeared at 5.07 ppm in the \(^{1}\text{H}\) NMR spectrum (See S7, Figure S8). Remarkably, no other over reduced products, formed by the hydrosilation of the bis(silyl)acetal catalyzed by free B(C\(_3\)F\(_2\))\(_3\), i.e. methyl silyl ether and methane (Piers-Rubinsztaijn reaction), were detected during the reaction (Scheme 3b).\textsuperscript{12} The high chemoselectivity observed justifies a detailed analysis of the reactions involved to elucidate the mechanism of this process. First, we decided to explore the reaction of 3 with B(C\(_3\)F\(_2\))\(_3\) to understand the precise nature of the catalyst. Thus, monitoring this reaction by NMR spectroscopy we observed the formation of a new complex 4 (Scheme 4). In the \(^{1}\text{H}\) NMR spectrum the signal at 9.11 ppm, corresponding to the formate proton of 3, disappeared and a new signal appeared at 8.45 ppm, as expected for a formato-tetra-coordinated boron atom, respectively.\textsuperscript{31,4b} We were able to obtain crystals of 4, suitable for an X-ray diffraction analysis, by slow evaporation of a toluene solution (Figure 1). The solid-state structure of 4 revealed a slightly distorted square-planar geometry at nickel due to the geometric constrains imposed by the PBP pincer ligand (P-Ni-P angle =158.61(2)\(^\circ\)). The coordination of the formato-borate group is related to that reported by Peters\textsuperscript{36,4b} in which a zwiterring structure is adopted.\textsuperscript{13} Accordingly, the C25–O1 bond length (1.219 (2) Å) is significantly shorter than C25–O2 bond distance (1.283 (2) Å). Likewise, the Ni–O separation is slightly longer than that reported for [\((\text{PBP})\text{Ni(O}_2\text{CH})\)].\textsuperscript{7} The B2–O2 bond length (1.552 (2) Å) is similar to that observed in related zwiterring species formed by CO\(_2\) insertion into Frustrated Lewis pairs adducts.\textsuperscript{14} The structure of 4 was modeled by DFT analysis.\textsuperscript{15} The optimized structure was found to be a local energy minimum and an excellent agreement was obtained between calculated and experimental bond lengths and angles (See S7, table S2).

We explored the catalytic version of this reaction using 0.05 mol % of 4 (relative to silane) under 4 bar of CO\(_2\) at 70 °C in C\(_6\)D\(_6\). We observed transformation to bis(silyl)acetal after 21 hours, corresponding to a turnover number (TON) (based on mol of silane reacted per mol of catalyst) of 1200 and a turnover frequency (TOF) of 56 h\(^{-1}\) (Table 1, entry 1). In order to investigate the scope of this reaction, several silanes were tested. Ph\(_3\)MeSiH leads to comparable selectivity to Et\(_3\)SiH though longer reaction times are required for similar conversions (Table 1, entry 4). On the contrary, a less bulky silane, such as PhMe\(_2\)SiH, reacts faster with CO\(_2\) but small amounts of methyl silyl ether (8%) and methane (14%) are also...
formed together with the bis(silyl)acetal derivative (Table 1, entry 7). Interestingly, we observed that a high concentration of silane in the reaction solution increases considerably the reaction rate (See S8). It should be noted that, compared with the most effective catalyst reported so far, ours gives similar turnover numbers while turnover frequencies are significantly increased.

On the other hand, it is well known the efficiency of B(C₆F₅)₃ as a catalyst for the hydrosilylation of bis(silyl)acetal derivatives to methyl silyl ethers and methane. Recently, Turculet et al. have reported the catalytic reduction of CO₂ using platinum and palladium silyl pincer complexes in combination with B(C₆F₅)₃. At difference with our system, the presence of free borane in solution leads to the reduction of the bis(silyl)acetal derivative to methane and the corresponding bis(silyl)ether. In this sense, the selectivity we observed suggests that no free borane is present or, at least, not in a significant amount during the catalysis.

\[
\text{Eq. 1: } \text{CH}_2\text{SiO} \rightleftharpoons \text{CH}_2\text{SiO} + \text{H}_2\text{SiO} + \text{CH}_2\text{Si} \text{O} \text{H}
\]

Accordingly, in order to evaluate if the equilibrium shown in Equation 1 is operating under the catalytic conditions, a benzene solution of 4-¹³CO₂ (prepared employing ¹³C-enriched CO₂) was heated in a NMR sealed tube during 4 hours at 70 °C. However, analysis by NMR spectroscopy (¹⁹B, ²⁹Si and ¹³C) did not show resonances attributable to free B(C₆F₅)₃. Interestingly, when the NMR tube containing a solution of 4-¹³CO₂ was charged with non-labeled CO₂ (1bar, 70°C, 22h), the incorporation of ¹³CO₂ was observed in a 12 % ratio (See S13, Figure S17), demonstrating that the equilibrium shown in Equation 1 takes place but is shifted to the right side, minimizing the free borane quantity in solution. These experimental observations agree well with the Gibbs energy difference of 15.2 Kcal mol⁻¹ between 4 (−27 Kcal mol⁻¹) and 3 + B(C₆F₅)₃ (−11.8 Kcal mol⁻¹) calculated by DFT analysis.

To gain further insight into the mechanism about the formation of bis(silyl)acetal we monitored the catalytic reaction, by ¹H and ¹³C NMR spectroscopy, employing ¹³C-enriched CO₂ and Et₂SiH as reductant (See Figure 2). After 3h at 70°C, the ¹³C (fully coupled) experiment showed only a triplet signal at 85.5 ppm (J_C,H = 161 Hz) that corresponds to (Et₅SiO)₂CH₂ and the signal for free ¹³CO₂ (δ 124.9 ppm). After 8 h of heating, the signal of ¹³CO₂ decreased considerably in intensity and the major ¹³C-enriched species observable in the spectrum was (Et₅SiO)CH₂. Remarkably, the over reduced products that could be formed due to the presence of free borane in solution were not detected. At this point, B(C₆F₅)₃ (4 equivalents) was intentionally added to the solution resulting in the quantitative reduction of (Et₅SiO)CH₂ into methane and (Et₅Si)₂O, reinforcing the idea that 4 is the major species present in solution during the catalysis. Additionally, an isolated sample of (Et₅SiO)CH₂ was reacted with B(C₆F₅)₃-activated silane yielding the quantitative formation of Et₅SiOSiEt₃ and methane (See S13, Figure S16).

![Figure 2](image_url)
the high selectivity observed implies that subsequent sequestration of \( B(C_3F_3)_3 \) by the metal complex is needed to avoid further reduction of \( (R_3SiO)\text{CH}_2 \), as postulated by Piers for his Scandium catalyst.\(^{40} \) We propose that \( B(C_3F_3)_3 \) is trapped by the metal complex, either as the formaborate complex 4 or as the hydroborate complex \([\text{Ni}]\text{H}B(C_3F_3)_3\), preventing the formation of over reduced products. We are currently investigating both possibilities by DFT calculations.

\[
\text{CO}_2 + (\text{R}_3\text{SiO})\text{CH}_2 \rightarrow B(C_3F_3)_3 + (\text{R}_3\text{SiO})\text{CH}_2
\]

Scheme 5. Proposed mechanism for the selective formation of bis(silyl)acetal.

In summary, an effective nickel catalyst for the selective reduction of \( \text{CO}_2 \) to bis(silyl)acetal derivatives has been developed. The highest TOFs (56 h\(^{-1} \) based on mol of silane) reported so far for this transformation have been achieved. Further mechanistic studies, that will allow a better understanding of the mechanism of this reaction and, in particular, the origin of the high selectivity for the formation of bis(silyl)acetals, are underway.

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Notes and references

1. Q. Liu, R. Jackstell and M. Beller, Nat. Commun. 2015, 6, 5933.
7. When this work was under preparation Peters and Lin reported an alternative preparation of 2 and the insertion of carbon dioxide into the Ni-H bond to form the formate derivative 3: J. Peters, and T-P. Lin, J. Am. Chem. Soc. 2014, 136, 13672.
11. We observed the liberation of free PBP ligand and the presence of unidentified decomposition products.
12. (a) It is well known that \( B(C_3F_3)_2 \) is able to abstract an hydride from a silane to form a borane-activated silane \( B(C_3F_3)_2\cdot\text{HSiR} \) that mediates the hydrosilylation of \( (\text{Et}_3\text{SiO})\text{CH}_2 \) to methane or methyl silyl ether. See references 3f and 3g. (b) D. J. Parks, J. M. Blackwell and W. E. Piers, J. Org. Chem. 2000, 65, 3090. (c) S. Rubinsztajn and J. Cella, Polym. Prep., 2004, 45, 635.
15. The calculations were performed with the Gaussian 09 program: Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2010. The energies are free energies in benzene, relative to \( 2 + \text{CO}_2 + B(C_3F_3)_2 \). The full Gaussian citation can be found in the supplementary information.
17. In the Scandium system reported by Piers, in which a higher degree of \( B(C_3F_3)_2 \) dissociation is observed, a smaller \( \Delta G \) value of 6.4 Kcal mol\(^{-1} \) is obtained. See reference 3g.
18. The resonance of the formate H atom of \( \text{Et}_3\text{SiO}_2\text{CH} \) at 6.78 ppm was detected in small amount at low concentrations of silane indicating the formation of the silyl ester derivative as intermediate. (See S9, Figure S10).