**Reaction Intermediates**

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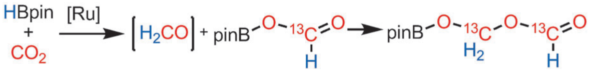
Trapping Formaldehyde in the Homogeneous Catalytic Reduction of Carbon Dioxide



**Formaldehyde detectives**: Evidence for the production of formaldehyde during a ruthenium-catalyzed $CO_2$ reduction process, and for its involvement in the formation of the resulting $C_2$ compound, is disclosed. Ultimately, formaldehyde can be recovered by methanol trapping. HBPin = pinacolborane.

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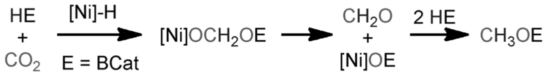
**Reaction Intermediates**

# Trapping Formaldehyde in the Homogeneous Catalytic Reduction of Carbon Dioxide**

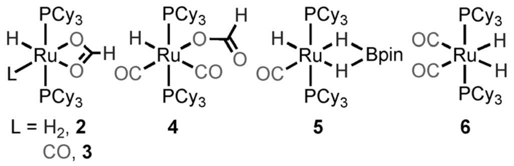
*Sébastien Bontemps* and Sylviane Sabo-Etienne**

The abundance, low cost, and low toxicity of $CO_2$ make it an attractive carbon source.[1] Nature succeeds in transforming $CO_2$ into carbohydrates by photosynthesis,[2] but the reduction of this highly oxidized molecule is a significant challenge for chemists.[3] Following the pioneering studies of Sadighi et al.[4] and Kawagushi et al.,[5] it has been demonstrated that oxygen abstraction from $CO_2$ can be achieved under rather mild conditions by homogeneous catalysis[6] to yield CO,[4,7] $CH_3OH$,[8] and $CH_4$[5,9] with silanes, boranes, silylboranes or aldehydes as reducing agents. Recently, silane-based reductive processes have been used in a so-called diagonal approach for the formylation or methylation of N−H bonds.[10] With dihydrogen as the sole reductant, $CH_3OH$ can also be produced through a cascade reaction involving three different catalysts,[11] or by using a tridentate phosphine ruthenium catalyst precursor under harsher conditions.[12] In the series of $C_1$ molecules derived from $CO_2$, formaldehyde is the missing link. Despite its importance as a $C_1$ building block,[13] $H_2CO$ has not been isolated, or even observed, in any homogeneous catalytic reduction of $CO_2$.[14] More than 20 years ago, Cutler et al. reported the synthesis of a heterobimetallic bridging formaldehyde complex from the stoichiometric reduction of the corresponding carbon dioxide complex.[15] Moreover, the computational mechanistic study by Wang et al.[16] on the Ni/borane system described by Guan et al.,[8c] predicts the reduction of $CO_2$ to formaldehyde, and finally to $CH_3OBCat$, from the decomposition of an acetal $[Ni]OCH_2OBCat$ species (Scheme 1).[17] The nickel acetal complex was not experimentally observed in this particularly active system, but precedents exist for acetal motifs in the reduction of $CO_2$.[5,8a,b,9,18] The "inevitable" formation of formaldehyde from the observed $R_3SiOCH_2OSiR_3$ acetal structure was also highlighted in another computational study by Wang et al. on the NHC/silane reduction process of $CO_2$ to afford $CH_3OSiR_3$.[19]

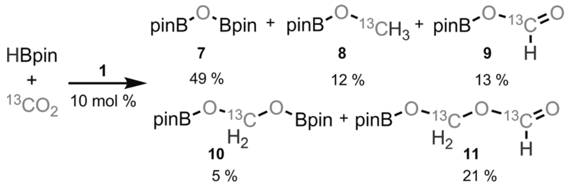


*Scheme 1.* Calculated intermediates in the reduction of $CO_2$ by the [Ni]-H/HBCat system.

We recently reported the catalytic reduction of $CO_2$ by $[RuH_2(H_2)_2(PCy_3)_2]$ (**1**; Cy = cyclohexyl) and pinacolborane (HBpin) reductant.[20] Complexes **2**–**6** (Scheme 2) are crucial to the catalytic cycle affording compounds **7**–**11** (Scheme 3). Compound **10** was the first bis(boryl) acetal structure observed in the reduction of $CO_2$, and the formation of the $C_2$ compound $pinBO^{13}CH_2O^{13}CHO$ (**11**) through the reductive coupling of two molecules of $^{13}CO_2$ was unprecedented.



*Scheme 2.* Complexes **2**–**6** involved in the $CO_2$ reduction by HBpin.



*Scheme 3.* Compounds **7**–**11** obtained after 30 min at RT from the reaction of HBpin with $^{13}CO_2$ (1 atm) using complex **1** as the catalyst precursor.

Herein, we provide direct proof of the production of formaldehyde during the ruthenium-catalyzed $CO_2$ reduction process, and of its involvement in the formation of the $C_2$ compound **11**. Ultimately, formaldehyde can be recovered by methanol trapping.

In the $CO_2$ reduction reported earlier, HBpin was readily transformed (< 30 min.) into compounds **7**–**11**.[20] A slow retransformation of **9**–**11** into **7**–**8** was achieved (22 days). We now observe that any attempt to generate the $C_2$ compound **11** from formaldehyde, HBpin, and any catalyst precursor (**1**–**6**) failed. Notably, no reaction occurred when exposing a solution of complex **3**, the main organometallic species observed during the catalysis, to formaldehyde (8 h, RT). However, when conducting the standard reaction (30 min,

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room temperature, $^{13}CO_2$) to form labeled compounds **3** and **7**–**11**, and subsequently adding $H_2{}^{12}CO$ to the mixture,[21] $^1$H NMR analysis shows that the added $H_2{}^{12}CO$ reacted completely with pinBOCHO (**9**) to generate pinBO$^{12}$CH$_2$O$^{13}$CHO (**11***) within 28 min. $H_2{}^{12}CO$ and $H_2{}^{13}CO$ could be observed in the mixture by NMR spectroscopy after a few hours (Figure 1). Within 12 days, only compounds **7** and **8** were observed, along with pinBO$^{12}$CH$_3$ (**8***). Thus, formaldehyde is formed during the catalysis and readily trapped by compound **9** to yield the $C_2$ compound **11***. Furthermore, the characterization of compound **8*** confirms that compound **11** is reduced to form compound **8**.

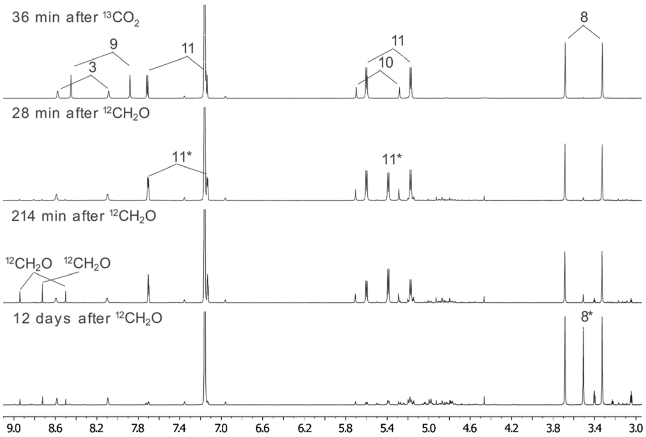
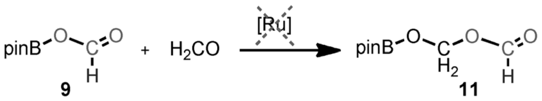


***Figure 1.*** $^1$H NMR spectra of the catalytic mixture leading to **7**–**11** before (top) and after subsequent addition of $H_2{}^{12}CO$.

Compound **9** could be independently prepared by addition of an excess of HBpin to formic acid in $C_6D_6$ over 20 h; 1 equiv of formaldehyde was then added to the resulting solution. This readily resulted in total conversion of **9** into the $C_2$ compound **11**. Thus, the insertion of formaldehyde into **9** to generate **11** does not need to be catalyzed by a metal complex (Scheme 4). During the synthesis of **9**, the excess HBpin does not react with **9**. However, when complex **1** was added to a 1:2 mixture of **9** and HBpin, compounds **7**–**11** were readily formed (< 10 min). This observation is consistent with 1) the need for the ruthenium catalyst in the reduction of compound **9** and 2) the involvement of compound **9** as an intermediate in the catalyzed reduction process, and not as a side product. In an attempt to isolate **9**, a controlled vacuum was applied to remove excess HBpin. As a result, formic acid was detected, along with further reduction of **9**.[21] It appears that the excess of HBpin is required for the stabilization of **9**, which might explain the difficulties in isolating it, as also mentioned by Shintani and Nozaki,[22] as well as by Guan et al.[8c] for the related CatBOCHO compound.



**9** **11**

***Scheme 4.*** Reaction of compound **9** with $H_2CO$.

Formaldehyde can be stabilized in alcohol solutions as the hemiacetal species.[23] Thus, to trap formaldehyde from compound **11**, we added [D$_4$]MeOH to the solution of compound **11** generated in situ and observed its complete and clean conversion into $CD_3OCH_2OD$.[24] We then added $CD_3OD$ to the catalytic mixture of **7**–**11**. Compounds **8** and **9** were transformed into $^{13}CH_3OD$ and $H^{13}COOD$, and to our delight, not only compound **11**, but also compound **10**, were readily converted into $CD_3O^{13}CH_2OD$, as observed by NMR spectroscopy (Figure 2). The latter transformation is direct experimental evidence of the recovery of formaldehyde from an acetal compound.[16,19] Under the standard catalytic conditions (catalyst **1** (10 mol %), 1 atm $CO_2$, RT, 30 min) the hemiacetal species $CD_3O^{13}CH_2OD$ was produced in 10 % yield, as estimated by NMR spectroscopy.[21,25] Upon reducing the catalyst loading to 1 % and increasing the $CO_2$ pressure to 2 atm, 4 h were needed for the complete conversion of HBpin. The catalyst/HBpin/$CO_2$ ratio better favors the formation of compound **11**, which leads to an increased yield of 37 %.

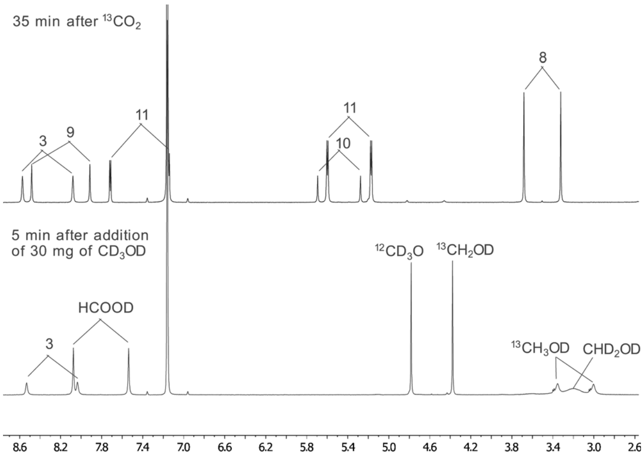


***Figure 2.*** $^1$H NMR spectra before (top) and after (bottom) the addition of $CD_3OD$ to the **7**–**11** mixture.

In summary, through detailed NMR studies using labeled species, we herein disclose direct proof of the formation of formaldehyde, which is readily trapped by compound **9** to afford the $C_2$ compound **11**, during a ruthenium-catalyzed $CO_2$ reduction process. The intermediacy of formaldehyde in the production of **11** could offer new strategies to prepare $C_n$ compounds. Moreover, formaldehyde was shown to be recovered not only from **11**, but also from the acetal compound **10** by methanol trapping. Indeed, this important building block is no longer an elusive molecule in the field of $CO_2$ homogeneous catalysis.

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