Reaction Intermediates Hot Paper

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

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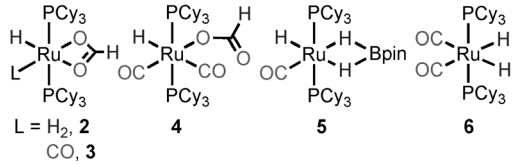
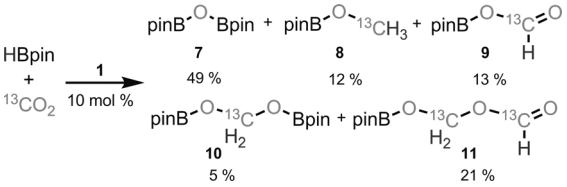
The abundance, low cost, and low toxicity of CO_2 make it an attractive carbon source.[1] Nature succeeds in transforming CO_2 into carbohydrates by photosynthesis,[2] but the reduction of this highly oxidized molecule is a significant challenge for chemists.[3] Following the pioneering studies of Sadighi 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]

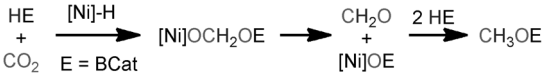
We recently reported the catalytic reduction of CO_2 by $[RuH_2(H_2)_2(PCy_3)_2]$ (**1**; Cy = cyclohexyl) and pinacolborane (HBpin) reductant.[20] Complexes **2**–**6** (Scheme 2) are crucial to the catalytic cycle affording compounds **7**–**11** (Scheme 3). Compound **10** was the first bis(boryl) acetal structure



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.



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

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.

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

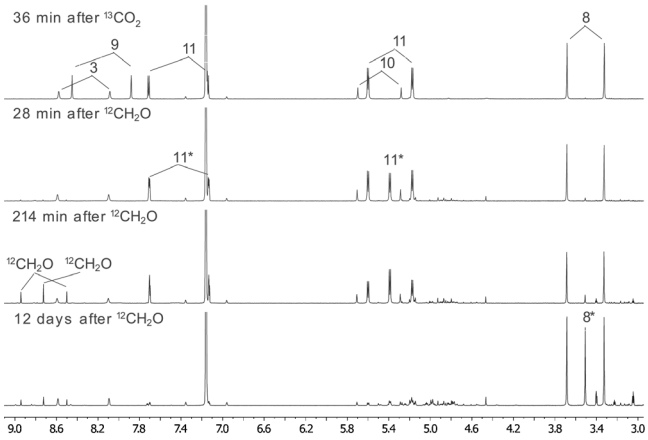
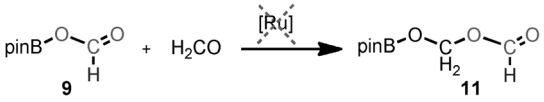


Figure 1. ^{1}H NMR spectra of the catalytic mixture leading to **7–11** before (top) and after subsequent addition of $H_2{}^{12}CO$.

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**.

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



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

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.

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

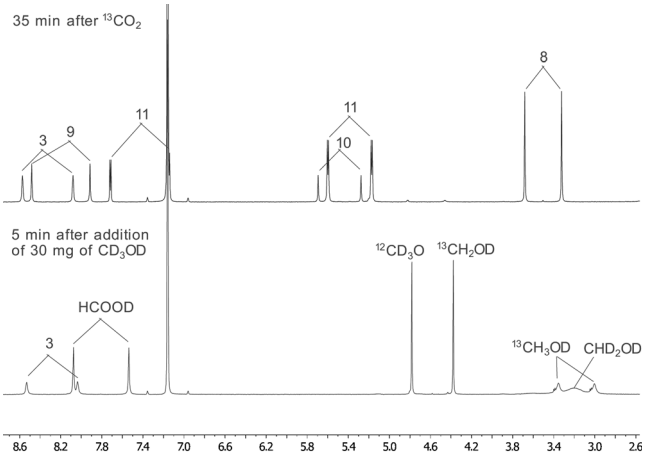


Figure 2. ^{1}H NMR spectra before (top) and after (bottom) the addition of CD_3OD to the **7–11** mixture.

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%.

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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