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Iron-Catalyzed Reduction of CO_2 into Methylene: Formation of C−N, C−O, and C−C Bonds

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Supporting Information

ABSTRACT: We report herein the use of the (dihydrido) iron catalyst, $Fe(H)_2(dmpe)_2$, for the selective reduction of CO_2 into either bis(boryl)acetal or methoxyborane depending on the hydroborane used as a reductant. In a one-pot two-step procedure, the in situ generated bis(boryl)acetal was shown to be a reactive and versatile source of methylene to create new C−N but also C−O and C−C bonds.

Carbon dioxide is a very abundant and rather nontoxic source of carbon when compared to other C1 sources employed by the chemical industry. Its use has thus attracted interest in various fields of chemistry despite its intrinsic high thermodynamic stability.[1] In the most advanced processes of transformation of CO_2, the O−C−O unit is maintained, as in carbonate or salicylic acid syntheses, and/or the carbon atom remains in the +4 oxidation state as in urea derivatives.[2] However, to fully use CO_2 as a source of carbon, one needs to abstract the oxygen atom(s) and to have access to the full range of carbon oxidation states. As a consequence, homogeneous catalyzed *CO_2 reduction with concomitant oxygen abstraction* was investigated with dihydrogen,[3] silanes,[4] and boranes[5] as reducing agents. Regardless of the reductant, the scope of products resulting from the reduction of CO_2 is still rather limited.[6] The use of dihydrogen as a reductant gave rise to methanol,[7] whereas the addition of amines, imines, or olefins to the hydrogenation process afforded formamides,[8] methylamines,[9] and aliphatic alcohols,[10] thus generating new C−N and C−C bonds. While CO_2 hydrogenation appears as the ideal reaction in terms of atom economy, a sustainable source of "carbon-free" dihydrogen and milder reaction conditions remain to be found. The use of silanes and boranes as reductants allowed significantly milder operating conditions and development of various types of catalysts to afford the complete list of C1 compounds (CO, CH_2O, CH_3OH, and CH_4).[4,5] Key mechanistic insights were gained, and up to four consecutive hydrofunctionalization reactions have been described (Figure 1) yielding formoxy **A**, acetal **B** and/or formaldehyde, methoxy **C**, and ultimately methane, the latter being only obtained in the case of hydrosilanes. Our studies on ruthenium-catalyzed CO_2 hydroboration shed light on the second stage of CO_2 reduction with the first experimental evidence of the formation of a bis(boryl)acetal compound **B**,[11,12] and of formaldehyde.[13] To increase molecular complexity, Cantat et al. and others described the reduction of CO_2 to the formoxy level **A**, with subsequent functionalization with amines to afford formamides, and further reduction to generate methylamines (Figure 1).[14]

In this context, we sought to further enlarge the scope of carbon-containing compounds accessible from CO_2 transformation. We postulated that the selective synthesis of the bis(boryl)acetal **B** would be possible and that such a compound would be a reactive and versatile source of methylene. In addition, we searched for earth abundant based catalytic systems and looked at defined iron complexes featuring hydride ligands to transfer our expertise from ruthenium polyhydride complexes. The use of iron-based catalysts for homogeneous transformation of CO_2 is scarce, and recent studies focused on the formation of formic acid and derivatives.[15] It was also reported that in the presence of multidentate phosphine ligands, the iron precursor $Fe(acac)_2$ was able to catalyze the reductive functionalization of CO_2 into formamide and methylamine.[16] We chose the dihydride iron complex $Fe(H)_2(dmpe)_2$ (**1**) as the catalyst precursor, because it has been shown by Field et al. to react with CO_2,[17] and by us to catalyze the dehydrogenative borylation of arenes.[18] We describe herein the iron-catalyzed selective reduction of CO_2 into bis(boryl)acetal and its subsequent use as a versatile and reactive methylene transfer agent to form not only C−N but also C−O, C−C, C═N, and C═C bonds using a one-pot two-step strategy.

Catalytic hydroboration of CO_2 was carried out with 5 mol % of **1** with three different hydroboranes: catecholborane (HBCat), pinacolborane (HBpin), and 9-borabicyclo[3.3.1]-nonane (9-BBN) (Scheme 1). The reactions were first conducted in C_6D_6 at room temperature under 1 atm of CO_2 in an NMR tube, and the yields of the two main products, bis(boryl)acetal and methoxyborane, were determined by ^1H NMR integrations at full conversion of the corresponding hydroborane.[19] With HBCat, full conversion was observed within 3 h and only methoxyborane was obtained in 59% yield. In the case of HBpin and 9-BBN, complete conversion occurred within 5 h and the corresponding bis(boryl)acetal was favored (30% and 46%, respectively) over methoxyborane (18% and 27%, respectively).

We thus chose 9-BBN for a selective synthesis of the bis(boryl)acetal and optimized the experimental conditions. Among the different parameters tested, the solvent proved to have the most important impact, since the use of THF favored

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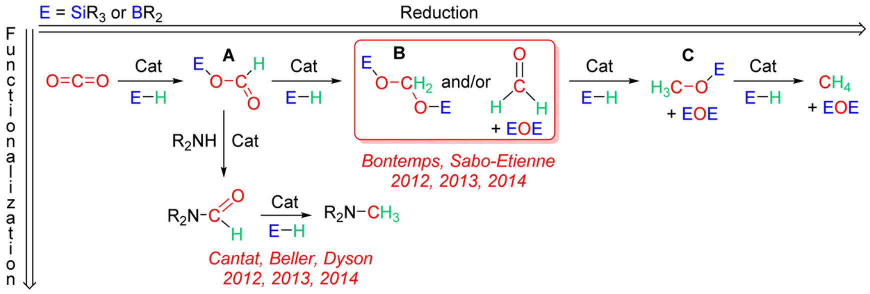
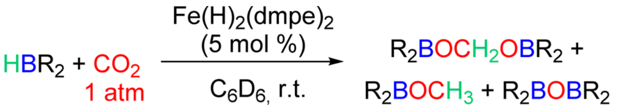


Figure 1. General scheme for the reduction and functionalization of CO_2.

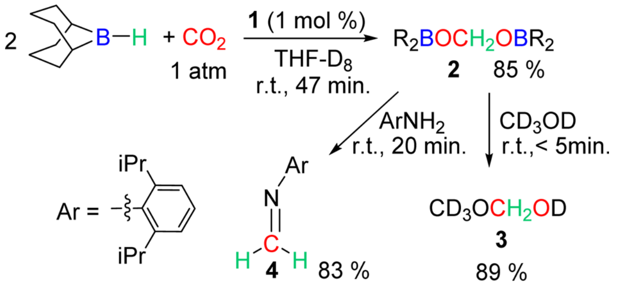
Scheme 1. CO_2 Hydroboration with HBCat, HBpin, and 9-BBN



the formation of the bis(boryl)acetal **2** in terms of both rate and selectivity (Table S3). After 47 min, at full 9-BBN conversion, a yield of 8% in methoxyborane and 85% in compound **2** was determined by ^1H NMR integration compared to an internal standard. It should be noted that, before complete reduction to methoxyborane, transient accumulation of bis(boryl)acetal was recently reported in a catalyzed system using strong bases as catalysts and also 9-BBN as a reductant.[20] In our system, **2** was not further reduced, since, after 15 h, 52% of acetal and only 11% of methoxyborane were observed. Unidentified products featuring methylene and methoxy units were observed in the NMR spectra which might account for the decreased amount of **2**.

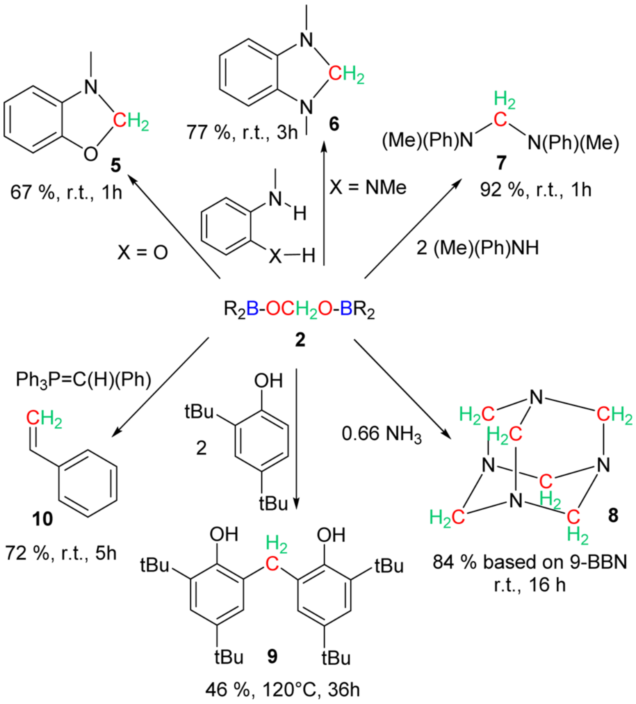
We then probed the ability of **2** to transfer methylene. As described in Scheme 2, the standard CO_2 reduction was carried out and followed by the addition of 0.4 equiv of methanol or diisopropylaniline compared to 9-BBN. This one-pot two-step procedure led to the corresponding hemiacetal **3** and methyleneaniline **4** in 89% (72%) and 83% (66%) NMR yields, based on the trapping agent (and 9-BBN), respectively.

Scheme 2. Iron-Catalyzed Selective Reduction of CO_2 into Bis-borylacetal 2 and Subsequent Functionalization into Compounds 3 and 4



We then studied the reactivity of compound **2** as a surrogate of formaldehyde in a few representative reactions which were first conducted in NMR tubes (Scheme 3). Unless otherwise stated, yields are based on the trapping agent to account for the efficiency of the trapping reaction. In situ generated compound **2** was reacted at room temperature with 2-methylaminophenol or *N*,*N*-dimethyl-1,2-benzenediamine to afford the cyclic hemiaminal and aminal compounds **5** (1 h, 67% yield) and **6** (3 h, 77% yield), respectively. Cyclic aminals are notably used as organic hydride donors or as N-heterocyclic precursors.[21] The acyclic aminal **7** was readily obtained in 92% yield after 1 h at rt by the reaction of 2 equiv of the corresponding secondary amine. Ammonia is an important building block, but its reactivity is difficult to control. However, the reaction of ammonia with formaldehyde is a known reversible condensation which affords the cage compound hexamethylenetetramine **8**, a versatile organic reagent.[22] In situ generated compound **2** exposed to an ammonia solution led after 16 h, at rt, to compound **8** in an 84% yield based on 9-BBN. This compound features six methylene moieties resulting from the reduction of CO_2. The characterization of **3**−**8** completes the list of compounds accessible from the reductive functionalization of CO_2 with amines with the generation of C−N and C−O bonds. With the objective of forming C−C bonds, we turned our attention to phenol reagents. Formaldehyde is indeed used at the industrial scale in phenol resins, via condensation reaction generating C−C bonds. For a proof of concept, we chose to use a *t*-Bu protected phenol in positions 2 and 4. For comparison and an NMR signature in THF, **9** was first generated with an in situ measured yield of 48%, from the reaction of *para*-formaldehyde with the substituted phenol compound in the

Scheme 3. Reactions of in Situ Generated 2 Affording Compounds 5−10



presence of KOH in 16 h at 120 °C. When in situ generated compound **2** was used instead of *para*-formaldehyde, the reaction occurred with the production of **9** in 46% after 36 h at 120 °C without the need for KOH addition. Encouraged by the generation of such C−C bonds from CO_2, we then exposed compound **2** to an ylide and observed the expected outcome of a Wittig reaction with the formation of styrene **10** in very good yield (72%).

We used both $^{13}CO_2$ and $^{12}CO_2$ to confirm by NMR and HRMS that the methylene carbon atom within **3**−**10** resulted from the reduction of CO_2. NMR data for the bis(boryl)acetal **2** and for the resulting compounds **3**−**10** are provided in Table S4. The important variations of ^{13}C and ^{1}H NMR chemical shifts (from $\delta(^{13}C) = 32.6$ and $\delta(^{1}H) = 3.88$ for compound **9** to $\delta(^{13}C) = 156.5$ and $\delta(^{1}H) = 7.73$ for compound **4**), indicating different types of methylene, highlight the versatile reactivity of compound **2**. The experiments performed in NMR tubes allowed detailed and convenient monitoring. In a next stage, we sought isolation of the functionalized products and compounds **8** and **9** were selected. On a 10-fold scale up synthesis, compound **2** was selectively generated at 60 °C in 10 min and subsequently trapped to afford compounds **8** and **9** in 98% and 37% isolated yields based on the trapping agent, respectively. A 100-fold scale up synthesis led to compound **8** in 2 days at room temperature with a 70% (106.2 mg) isolated yield based on 9-BBN.

To conclude, we report herein the use of a (dihydrido)iron complex in the reduction of CO_2 into either bis(boryl)acetal or methoxyborane depending on the hydroborane used as a reductant. Selective reduction of CO_2 to the acetal level and subsequent functionalization in a one-pot two-step procedure allowed CO_2 to be transformed into methylene and to considerably enlarge the scope of accessible functions by generating not only new C−N but also C−O and C−C bonds. Our results further highlight the importance of metal hydride complexes in the controlled transformation of CO_2. We are currently conducting a mechanistic investigation to understand and improve the catalytic system and are pursuing research on the specific reactivity of bis(boryl) and/or bis(silyl)acetal compounds.[23]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06077.

Experimental details and NMR data (PDF)

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Notes

The authors declare no competing financial interest.

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