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Cobalt catalysed reduction of CO₂ via hydroboration

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We report an operationally convenient reduction of CO_2 to methanol via cobalt catalysed hydroboration which occurs under mild reaction conditions. Addition of NaHBEt₃ to Co(acac)₃ generates an active hydroboration catalyst, which is proposed to be a "Co-H" species on the basis of infrared spectroscopy. The reduction of CO₂ in the presence of various boranes showed that BH₃.SMe₂ afforded near quantitative conversion (98 % NMR yield) to methanol upon hydrolysis.

The chemical utilization of carbon dioxide (CO_2) as a synthetic building block is an attractive undertaking for a variety of reasons.¹ The deleterious environmental impacts of CO_2 are now well established; the ability to employ CO_2 as a useful C1 building block to make new chemical bonds is a juxtaposition to its harmful role in climate change.

There are various chemical methodologies that have been CO_2^2 : hydrosilylation,³ explored in remediation of hydrogenation,⁵ hydroboration,⁴ carboxylation,⁶ and carbonylation.⁷ However, the conversion of CO₂ to methanol remains an unsolved problem despite sustained research effort; even the most successful approaches typically require harsh reaction conditions $^{\rm 5c,\ 8}$ and generate a mixture of reduced products.⁹ The challenge remains in developing catalytic systems that can effect efficient reduction of CO₂ to methanol (and methanol derivatives) under mild conditions. Sanford demonstrated a direct hydrogenation of CO₂ to CH₃OH via the formation of a carbamate salt. The turnover number (TON) for the reduction of CO₂ to CH₃OH was reported to be 550 after 54 hrs of catalysis.¹⁰ However, Olah and Prakash improved the overall TON of this catalytic system by using a different base.¹¹ Simple replacement of K_3PO_4 with pentaethylenehexamine as

base afforded both increased catalytic activity (TON = 1060 at 155°C) and the ability to effect CO_2 reduction from air. ¹¹

An alternative to direct hydrogenation of CO₂ would be the use of hydrogen surrogates, such as organoboranes, as the ultimate source of hydrogen. A hydroboration strategy avoids the use of elevated pressures of gaseous hydrogen and, furthermore, organoborates play a key role as intermediates in the transformations of a wide array of important organic substrates. Recent examples of the catalytic reduction of CO₂ via hydroboration include both precious (Ru,^{4a, 4c, 4g, 5b} and Pd^{4I}) and first row transition metals (Ni,^{4e} Cu,^{4b, 4j} and Fe^{4f}), frustrated Lewis pairs (FLPs),^{3h, 12} and organocatalysts.¹³



The efficient borylation of CO_2 to afford methanol has been reported using a bis(phosphonate) pincer ligated Pd complex; Guan reported a turnover frequency (TOF) up to 1780 h⁻¹ in the catalysed reduction of CO_2 in the presence of catecholborane (HBCat) to CH₃OBCat.¹⁵ Similarly, Chen reported a bis(phosphonate) pincer ligated Ni complex was capable of the reduction of CO_2 in the presence of HBCat with a TOF of 2400 h⁻¹, the highest TOF reported to date.¹⁶ Mizuta reported reduction of CO_2 to methoxide derivatives, (CH₃OBO)₃, in the presence of BH₃·THF at 0.5 mol % loading of NaBH₄; hydrolysis yielded 87 % of CH₃OH.¹⁷ Williams and coworkers disclosed NHC-supported

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Ni complexes to be highly effective for reduction of CO_2 in the presence of excess NaBH₄. These complexes demonstrated longevity with a high TON of 1.1 million over two months.¹⁸

In our recent efforts to explore base metal catalysts, we have been investigating hydroboration chemistry using simple metal salts of the first-row elements.¹⁹ Herein, we report a simple cobalt precatalyst, Co(acac)₃, may be employed in the reduction of CO₂. The activation of the cobalt precatalyst using sodium triethylborohydride (NaHBEt₃), proved essential to generation of an effective catalyst.²⁰

Our initial experiments (see Table 1) were conducted by charging a J-Young NMR tube with $Co(acac)_3$ (10 mol %), NaHBEt₃ (10 mol %), and HBPin (1.00 mmol) prior to admitting CO_2 (1 atm). This preliminary study was monitored using ¹¹B NMR spectroscopy (Figure S1). The progress of the reaction was monitored for 10 hours after the addition of CO_2 ; > 95 % of HBPin was converted within 10 hrs. The presence of a peak at 21.2 ppm in the ¹¹B NMR spectrum suggested the formation of a boron bound to three oxygen atoms, ²¹ comparison with the literature initially insinuated the formation of HCOOBPin (1).²²

Table 1 Cobalt-catalysed hydroboration of CO_2 employing $Co(acac)_3$ as precatalyst and NaHBEt₃ as activator.

0	B-0 Co(acac) ₃ NaHBEt ₃ 50°C, THF	0 - H - C - (1)		0 0		о В о Н (4)
Entry	mol %	mol %	Time	1 ^b	3 ^b (%)	4 ^b
	Co(acac)₃	NaHBEt₃	(h)	(%)		(%)
1	10	10	10	n.d.	n.d.	n.d.
2	10	0	10	n.d.	n.d.	n.d.
3	0	10	120	0	23	13
4	0	0	120	23	14	0
5	1	1	16	27	63	4
6	1	1	21	0	15	0
7	1	1	21	0	24	0
8	1	1	21	0	trace	0
9	1	1	21	0	trace	0
10	1	1	21	0	7	0

Reaction conditions: CO₂ (1 atm), HBPin (0.1 mmol), Co(acac)₃ (1 mol %), NaHBEt₃ (1 mol %), THF- d_8 (0.7 mL). ^a1.0 mmol HBPin. ^bConversion was determined by ¹H NMR against an internal standard (mesitylene). ^ctoluene- d_8 . ^dbenzene- d_6 . ^edichloromethane- d_2 . ^fchloroform-d. ^gcyclohexane- d_{12} . n.d. = not detected.

A control experiment in the absence of NaHBHEt₃ showed minimal catalytic activity (Figure S2). Reaction between NaHBEt₃ (10 mol %) and HBPin (1.0 mmol) afforded both **3** (13 %), and **2** (23 %) based on ¹H NMR spectroscopy; multinuclear NMR analysis revealed the presence of significant amount of unreacted HBPin even after 5 days of heating at 50 °C (Figures S3 and S4). Upon lowering the catalyst loading to 1 mol %, we were pleased to find that ¹¹B and ¹H NMR spectroscopy revealed the formation of both PinBOBPin (**2**) and HCOOBPin (**1**). The formation of CH₃OBPin (**3**) was detected after ~5 hrs (Figure S5 and S6). Little to no reactivity was observed in a variety of common organic solvents (toluene- d_8 , benzene- d_6 , dicholormethane- d_2 , chloroform- d_1 , and cycolohexaner d_{12}) has monitored by ¹H, and ¹¹B NMR as well: (Figures SIT 20): Intriguingly, when a control reaction was conducted using lower loading of NaHBEt₃ (1 mol %) in the presence of 0.1 mmol HBPin, ¹H NMR and ¹¹B spectra showed the formation of **1** (18 %) and **2** (34 %); the formation of **3** (4 %) was observed after 12 hrs (Figures S8 and S9). It should also be noted that the activity of NaHBEt₃ could be dependent on the choice of solvent as previously reported by Turculet and coworkers.¹⁴

In the absence of both Co(acac)₃ and NaHBEt₃ a background reaction between CO₂ and HBPin was observed; the background reaction was sluggish and yielded **1** (23 %) and **2** (14 %) after 5 days (Figure S10 and 11). Therefore, the addition of both Co(acac)₃ and NaHBEt₃ is necessary for effective and efficient catalytic hydroboration of CO₂.

 Table 2 Cobalt-catalysed hydroboration of CO2 employing different boranes.

0 R 6 + B 0 H	-R Co(acac) ₃ NaHBEt ₃ 50°C, THF	0 ^{∽ BR} 2 H ^{−C} ≈0 (1)	R ₂ B ₀ BR ₂ (2)	0 ^{−^{BR}₂ H[−]L_H H[−]H_H}	H ₃ CO _B O _B OCH ₃ I O _B O I OCH ₃ (4)	
Entry	Borane	Time	1 (%) ^a	2 (%) ^a	3 (%) ^a	4 (%) ^a
		(h)				
1	HBPin	16	27	63	4	0
2	HBCat	72	0	56	25	0
3	BH₃·S(Me)₂ ^b	20	0	0	0	98 ^{c,d,e}
4	B.Pin.	10	0	0	0	0

Reaction conditions: A J-Young tube was charged with Co(acac)₃ (1 mol %), borane (0.1 mmol), NaHBEt₃ (1 mol %), THF-*d*₈ (0.7 mL). The reaction mixture was degassed three times by freeze-pump-thaw, and backfilled with CO₂ (1 atm). ^aYield was determined by addition of mesitylene as internal standard. ^b Pre-catalyst and salt loading 0.33 mol % relative to B-H functionality. ^cYield of MeOD after hydrolysis with 50 μ L of D₂) in DCl. ^dTON calculated based upon hydrides transferred: 300. ^eTOF calculated by TON/time: 15 h⁻¹.

Next, we explored the use of several different borylating reagents: bis(pinacalotodiboron) (B₂Pin₂), HBCat, and borane dimethylsulfide (BH₃·S(Me)₂) (Table 2). The reaction of $BH_3 \cdot S(Me)_2$ with CO_2 was monitored using ¹H and ¹¹B NMR spectroscopy which revealed the exclusive formation of $(CH_3OBO)_3$ (Figure 2a). The ¹³C NMR spectrum reveals a peak at 51.7 ppm which corresponds to the the -OCH₃ peak.¹⁷ The hydrolysis of (CH₃OBO)₃ to methanol was easily achieved by the addition of 20 % DCl in D₂O to the reaction mixture. A new peak corresponding to the formation of MeOD was observed at 3.27 ppm (Figure 2c). The reaction of HBCat proceeded at a somewhat slower relative rate and was sluggish, ¹H and ¹¹B NMR spectra showed a substantial amount of unreacted HBCat even after 20 hrs of heating (Figure S27 and 28); 25 % of 3 was formed after 72 hours of catalysis. Monitoring the reaction using ¹H NMR spectroscopy revealed the rapid formation of **2** in the initial phases of catalysis; however, as the reaction progresses, the amount of 2 decreases concomitant with an increase in the amount of **3** (Figure S24). Though, we did not observe evidence of HCHO, which has been reported to be generated prior to the formation of methoxide derivate,²³ the presence of a new peak at 3.79 ppm (¹H NMR) and 53.2 ppm Journal Name

(¹³C NMR) indicated the formation of **3**. No reaction was observed to occur with B_2Pin_2 (Figure S27) presumably due to the lack of hydride transfer from the boryl source to regenerate the active Co-H species for catalysis (*vida infra*).



76 74 72 70 68 65 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 25 24 22 20 18 16 14 12 10 08

Fig 2 Top: ¹¹B NMR for hydroboration of CO₂ in the presence of BH₃·SMe₂. (a) prior to addition of CO₂; (b) T = 20 h (•) represents the ¹¹B resonance for (CH₃OBO)₃ at 19.3 ppm, and (•) represents the peak for BH₃·S(Me)₂ at -21.3 ppm. Bottom: ¹¹H NMR after 20 h. (c) after addition of 50 μ L of DCL; (d) after hydrolysis. (*) represents the peak for mesitylene and (0) represents the resonance for $-OCH_3$.

The reaction using BH₃·S(Me)₂ as the borane source in our newly developed catalytic system warrants further discussion. The reaction of BH₃·THF with NaBH₄ as reported by Mizuta was proposed to follow a mechanism in which the BH₄⁻ anion catalytically reduces CO₂ into **4**.¹⁷ Similarly, Williams also proposed the addition of stoichiometric amount of NaBH₄ to generate an active Ni-H species, which was capable of reducing CO₂ to formoxyborane, and subsequently to the reduced methoxy derivatives.¹⁸ Brown and co-workers showed that upon addition of formic acid to BH₃·THF at 0°C, the formation of trimethoxyboroxine was observed.²⁴ Moreover, in the presence of NaBH₄, BH₃·CO adduct was found to yield trimethylboroxine, (CH₃BO)₃, after reduction.²⁵

Based upon our experimental observations and consistent with prior experimental and computational reports, 4e,4g,23b we tentatively propose the mechanism shown below (Scheme 1). The addition of NaHBEt₃ to a solution of Co(acac)₃ will lead to the formation of a Co-H complex. ¹¹B NMR spectroscopy reveals the formation of free BEt_3 after the precatalyst has been activated, indicating the transfer of hydride from NaHBEt₃ to Co(acac)_{3.} Moreover, we do not observe any evidence of unreacted or newly formed borohydride species upon precatalyst activation nor do we observe any formation of BH4 species during catalysis. The generation of paramagnetic species made locating a "Co-H" species by NMR spectroscopy difficult. We subsequently turned to IR spectroscopy but the appearance of a new signal in the IR spectrum at ~1900 cm⁻¹ could not be definitively assigned as arising from a "Co-H".²⁶ A control experiment in the absence of Co(acac)₃ showed limited reactivity; ¹¹B NMR revealed unreacted BH₃·S(Me)₂,even after 30 hrs of reaction at 50°C (Figure S24). The 9h sertion / 6f CO29A to the Co-H bond to generate a cobalt formate complex has ample precedent in studies where Co-H species have emerged as powerful catalysts in CO₂ hydrogenation.^{27,28} Subsequent transmetallation of the formate complex using H-BR₂ affords 1 with concomitant reformation of Co-H. Insertion of 1 into a Co-H bond will form a metal acetal, which can undergo β -alkoxy elimination to generate free formaldehyde and the metal alkoxyborane; transmetallation using H-BR₂ affords **2** and Co-H once more. Insertion of the free formaldehyde into a Co-H bond provides access to the MeOH-level products (3 and 4) via a similar insertion-transmetallation strategy. The presence of 4 in the case of BH₃·S(Me)₂ suggests all three B-H bonds are available for insertion into CO₂. This is particularly interesting since BH₃ has the highest hydrogen content of any hydroborane.



Scheme 1. Proposed mechanism for CO₂ hydroboration.

To put the synthetic utility of our system into context, a brief comparison to previously reported hydroboration catalysts is warranted. Impressive TON and TOF values have been disclosed using the well-defined palladium-based catalysts of Guan (TOF = 1780 h⁻¹),¹⁵ and Hazari (TON = 60,000).⁴¹ In stark contrast, we achieve maximum TON and TOF of 300 and 15 h⁻¹, respectively (Table 2, Entry 3). Although this certainly lags the best catalysts in the field, we can compare the work of Mizuta¹⁷ and Cantat²⁹ a bit more directly. Mizuta employed both a commercially available catalyst and BH₃·S(Me)₂ in the hydroboration of CO₂ and achieved TON and TOF of 174 and 14.5 h⁻¹, respectively.¹⁷ Cantat's report,²⁹ is the only other example we could find of Cocatalyzed CO₂ hydroboration; highest TON and TOF values reported were 66 and 2.8 h⁻¹, respectively.

In summary, we have shown an effective and efficient reduction of CO_2 into methanol by an *in-situ* generated Co-H complex under mild conditions. The activity exhibited by simply activating $Co(acac)_3$ is remarkable. Moreover, the versatility of the system to effect reduction of CO_2 with various boranes also shows the robustness of the system. Future studies will focus on: a) more fully elucidating the reaction mechanism and b) utilizing this catalytic system further to incorporate CO_2 as a C1building block.

Conflicts of interest

There are no conflicts to declare.

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