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Hydroboration of carbon dioxide enabled by molecular zinc dihydrides

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Neutral molecular zinc(II) dihydrides supported by N-heterocyclic carbene ligands bearing a pendant phosphine group were synthesized and then reacted with carbon dioxide to afford zinc diformates. The zinc dihydrides were found to be active catalysts for hydroboration of carbon dioxide under mild conditions, selectively giving boryl formate, bis(boryl)acetal, or methoxy borane compounds by changing the nature of the borane reductant.

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The use of carbon dioxide (CO_2) as a cheap, nontoxic, and renewable C1 feedstock has attracted considerable attentions from both academia and industry.^{1,2} Great effort has been expended exploring selective and efficient methodologies for the reduction of CO_2 to value-added C1 chemicals such as formic acid, formaldehyde, methanol, and their derivatives.³ Direct hydrogenation of CO_2 with molecular hydrogen (H₂) most atom-economical represents the pathway to corresponding reduction products, but usually requires harsh conditions.⁴ To this end, replacement of H₂ by silanes⁵ or boranes⁶ as reductants has been explored and realized under mild conditions because of the formation of strong Si-O or B-O bonds. In the last decade, hydroboration of CO₂ using a variety of boranes has flourished and excellent performance in terms of activity and selectivity has been achieved.7 In addition, the resulting reduction products can be easily transformed to other valuable organic compounds. To date, a number of transition-metal complexes (including Ni,^{7a,7h} Pd,^{7d,7j} Cu,^{7c} Fe,^{7f} Ru,^{7b,7e,7g} and Co⁷ⁱ), alkali metal hydridoborates,⁸ and maingroup frustrated Lewis pairs9 have been successfully used as catalysts for this transformation. Considering the abundance, biocompatibility and environmental friendliness of metal ions, the use of zinc-based complexes for CO2 transformation is highly attractive. For example, zinc-based complexes can be used for copolymerization of CO_2 with epoxides¹⁰ and homogeneous hydrosilylation of CO_2 .¹¹ However, hydroboration of CO_2 by using a zinc catalyst remains scarce.¹² Herein, we design and synthesize zinc(II) dihydrides supported by an *N*-heterocyclic carbene (NHC) bearing a pendant phosphine group, which are found active for the catalytic hydroboration of CO_2 . Furthermore, the reactions can selectively give different levels of reduction products, for example, boryl formate, bis(boryl)acetal, and methoxy-borane compounds, by simply varying the borane reductant.

Okuda and coworkers showed that molecular zinc(II) dihydrides or monohydride cations can be stabilized by using NHC ligands well-known such as 1.3-bis(2.6diisopropylphenyl)imidazol-2-ylidene) (IPr) and 1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene) (IMes).¹³ These complexes were found to be reactive toward CO₂, resulting in the formation of formate species. However, only one precedent for the catalytic transformation of CO₂ has been reported: the hydrosilylation of CO₂ using a trinuclear cationic zinc hydride cluster under harsh conditions (40 bar CO_2 , 60 °C, 64 h).^{13b} By introducing a pendant phosphine arm on to NHC ligands, we prepared corresponding zinc dihydrides using a wellestablished method, as shown in Scheme 1. Reactions of NHC ligands with an equimolar amount of ZnEt₂ gave zinc dialkyl complexes 1, which were easily converted into zinc diaryloxides **2** by adding two equivalents of 2,6diisopropylphenol. Finally, metathesis reactions of 2 with PhSiH₃ afforded the desired dihydride complexes 3 in high yields (82% for 3a and 76% for 3b).

Complexes **1** - **3** were fully characterized by elemental analysis and multinuclear NMR spectroscopy. The structure of complex **2b** was further confirmed by single-crystal X-ray diffraction (XRD); the molecular structure is depicted in the Supporting Information. In the solid state, the phosphine arm of **2b** was bound to the zinc center with a Zn-P bond distance of 2.636(5) Å, which hampered the formation of dimeric structure obtained in the case of previously reported [(IMes)Zn(μ -OBn)]₂ complex.¹⁴ A solution ¹³C{¹H} NMR spectrum of **2b** showed a carbene carbon resonance at δ 174.1 ppm as a doublet with a ²J_{PC} coupling constant of 48.7 Hz,

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possibly indicating the retention of the Zn-P interaction in the solution. Attempts to obtain single crystals of zinc dihydrides 3 suitable for XRD measurements failed. Nevertheless, the solution behavior of complexes 3 was investigated to elucidate their structures. In ¹H NMR spectra, two distinct hydride signals were observed at δ 4.15 and 3.50 ppm for 3a and δ 4.32 and 3.46 ppm for **3b** in d_8 -toluene at -30 °C. However, these signals were not detected when the temperature was raised to 0 °C (see the Supporting Information for details). This observation is consistent with the behavior of Okuda's complex [IMesZnH₂]₂.^{13a} Complexes **3** featured ³¹P NMR resonances at δ -20.0 ppm (3a) and -19.5 ppm (3b), which were shifted negligibly compared with those of the parent NHC ligands (-22.1 ppm for NHC^a and -22.7 ppm for NHC^b), indicating the absence of Zn-P interactions in 3. Therefore, we proposed that complexes 3 contain a binuclear hydride bridged core structure in solution, like that in Okuda's complexes. Moreover, the diffusion coefficient of complex 3b $(4.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})$ determined by DOSY NMR was smaller than that for monomeric **2b** ($5.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), which is consistent with this hypothesis.¹⁵ Zinc dihydrides **3** were not thermally stable and decomposed when heated at 50 °C in solution for 2 h.

We subsequently monitored the reactions of zinc dihydrides **3** with CO_2 (1 bar) at room temperature (Scheme 2). Complex **3a** resulted in the formation of diformate **4** in 69% isolated yield. The ¹H NMR spectrum of **4** showed a characteristic



Scheme 2. Reactions of zinc dihydrides 3 with CO₂

downfield resonance of a formate unit at $\delta 8.31_{i}$ ppm $(-13C_{i})$ 167.6 ppm) with an integration ratio with the With Oligan of 2:1. The ³¹P NMR spectrum of **4** featured a singlet at δ -20.1 ppm, which was almost identical to that of starting dihydride 3a (-20.0 ppm). When the mesityl-substituted NHC zinc complex was used, the situation changed markedly. Reaction of 3b with CO₂ rapidly gave trinuclear complex 5 with concomitant formation of the NHC·CO₂ adduct 6. Complex 5 was isolated and characterized by single-crystal XRD and its molecular structure contained three zinc centers, six formate moieties, and two NHC ancillary ligands, as shown in Figure 1. The structure of complex 5 is guite similar to that of the reported addition product of [IPrZnH₂]₂ with CO₂.^{13a} The central zinc adopted an octahedral geometry and was coordinated by six n¹-formate ligands, whereas the other two zinc centers were tetrahedrally coordinated by one NHC ligand and three formate ligands. Adduct 6 was also isolated and further confirmed by independent reaction of NHC^b with CO₂ (see the Supporting Information for details).



Figure 1. Molecular structure of complex 5. Hydrogen atoms (except formates) are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level. Symmetry code: 2-x, 1-y and 1-z.

Because zinc dihydrides **3** are highly active toward CO_2 , we decided to investigate their catalytic performance for hydroboration of CO_2 . All the reactions were conducted in C_6D_6 at room temperature and the yields of reduction products determined by ¹H were NMR spectroscopy using hexamethylbenzene as an internal standard (Table 1). Initially, 3a (5 mol% based on Zn) was exposed to 1 bar of CO₂ with pinacol borane (HBpin) as a reductant.¹⁶ The reaction predominantly produced boryl formate HCOOBpin [A, ¹H: δ 8.14 ppm (HCOO-)] in 68% yield after 48 h (entry 1), along with the concomitant formation of a small amount of diborate ether (Bpin)₂O (13%, ¹H: δ 1.01 ppm) and trace amounts of unidentified species. No bis(boryl)acetal [B, ¹H: δ 5.49 ppm (-OCH₂O)]^{7b} or methoxy borane [C, ¹H: δ 3.51 ppm (CH₃O-)]^{7b} was detected during the reaction. Under analogous conditions (1 bar of CO₂, room temperature, 48 h), complex 3b resulted in a much lower yield of HCOOBpin (37%, entry 2) which was probably caused by the dissociation of the NHC ligand during the reaction. To promote the reaction, the CO₂ pressure was

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increased to 10 bar when 3a was used as a catalyst. As expected, this reaction selectively gave HCOOBpin in 85% yield within a short reaction time (12 h), along with a trace amount of (Bpin)₂O (ca. 2%) (entry 3). In addition, the resulting boryl formate A can be directly used as a formylation reagent for Nmethylaniline (see the Supporting Information for details). The isolated CO₂ addition product 4 was also active toward CO₂ borylation and did not noticeably change the reaction results in terms of selectivity and activity compared with the case for parent zinc dihydride 3a (entries 4 vs 3). This result suggests that the Zn-H insertion product serves as an intermediate for the catalytic hydroboration. It has been reported that NHC alone can be used as an efficient organocatalyst for reductive hydrosilylation of CO2.17 Therefore, compound NHC^a was investigated under identical conditions, but it showed much lower activity than that of 3a in the hydroboration reaction (entry 5). To make further comparisons, three previously reported zinc hydrides were also used for the hydroboration of CO2 with HBpin. Okuda's zinc dihydride [IMesZnH2]2 afforded a 31% yield of boryl formate A after 48 h (entry 6). Its analogue [IPrZnH₂]₂ only gave (Bpin)₂O in 27% yield and no signals of A, B, or C was observed (entry 7). A zinc monohydride complex [(DIPP-nacnac)ZnH]¹⁸ supported by a conventional βdiketiminato ligand was also prepared and tested, but proved to be inactive for the hydroboration of CO₂ (entry 8). Overall, zinc dihydride 3a exhibited much better performance than other zinc hydrides under the explored conditions. We tentatively propose that this is because the NHC ligand in 3a is less sterically hindered than IMes, IPr, and DIPP-nacnac ligands.

Controlling the selectivity of the reduction of CO_2 is of considerable interest and can be achieved by some late transition-metal catalysts by reagent control.^{7i,7j} Thus, zinc dihydride **3a**-mediated hydroboration reactions with different borane reagents were carried out under our typical conditions

Table 1 Zinc-catalyzed reduction of CO₂ with hydroboranes^a

$HBR_2 + CO_2$	[catalyst] C ₆ D ₆ , r. t.	$H \xrightarrow{O} OBR_2 + R_2BO'$	∩ _{OBR₂}	+ H ₃ CO-BR ₂
Entry	Borane	Catalyst	Time (h)	Yield (%) ^b A/B/C
1	HBpin	3a	48	68/0/0
2	HBpin	3b	48	37/0/0
3 ^c	HBpin	3a	12	85/0/0
4 ^c	HBpin	4	12	83/0/0
5	HBpin	NHC ^a	48	34/0/0
6	HBpin	[(IMes)ZnH ₂] ₂	48	31/0/0
7	HBpin	[(IPr)ZnH ₂] ₂	48	0/0/0
8	HBpin	(DIPP-nacnac)ZnH	48	0/0/0
9	HBcat	3a	12	0/0/85
10	9-BBN	3a	4	0/75/6
11	$BH_3 \cdot SMe_2$	3a	48	0/0/0

^aReaction conditions: unless noted otherwise, [catalyst] = 0.0075 mmol (based on Zn), [Borane] = 0.15 mmol, 1 bar of CO₂, C₆D₆, room temperature. ^bDetermined by ¹H NMR integration using hexamethylbenzene as an internal standard. ^c10 bar of CO₂ was used.

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(1 bar of CO_2 , room temperature, C_6D_6 as the solvent). The reaction using catechol borane (HBEat) 193033/DPEductant selectively produced six-electron reduction product methoxy borane **C** [¹H: δ 3.32 ppm (CH₃O-)] in 85% yield within 12 h (entry 9), along with diborate ether (Bcat)₂O and trace amount undefined boron-containing species.¹⁹ Subsequent of treatment of the reaction mixture with excess water rapidly gave the hydrolysis product methanol (see the Supporting Information). Remarkably, the challenging four-electron reduction product bis(boryl)acetal **B** [¹H: δ 5.34 ppm (-OCH₂O-)] was obtained as the major product (75%) when 9borabicyclo[3.3.1]nonane (9-BBN) was used ลร а hydroboration reagent, along with the formation of a small amount of methoxy borane (6%) within 4 h (entry 10). The bis(boryl)acetal form generated in the hydroboration of CO₂ is relatively rare compared with the formation of formic acid or methanol.^{7f,7h} Finally, borane reagent BH₃·SMe₂ was investigated in the present hydroboration reaction; no reduction product was detected after 48 h (entry 11). Based on the above preliminary observations, we tentatively propose that the mechanistic framework of hydroboration of CO₂ using our zinc dihydride catalyst also involves three sequential catalytic cycles that are responsible for the formation of products with different reduction levels (Scheme S10 in the Supporting Information), similar to CO₂ hydroboration using other transition-metal hydrides.⁷ HBcat promotes CO₂ reduction to methanol level probably because it is less steric hindrance and electron rich compared with HBpin.

In summary, molecular Zn(II) dihydrides based on neutral NHC ligands bearing a tethered phosphine arm were synthesized that underwent stoichiometric reactions with CO2 to give zinc diformates. Remarkably, Zn(II) dihydride 3a was found to be an active catalyst for the hydroboration of CO_2 under mild conditions. The selectivity of the hydroboration reactions can be easily controlled by varying the borane reagent used and the resulting reduction products were able to be converted into other valuable organic compounds using facile approaches. Although the details of this hydroboration reaction currently remain unclear, we propose that a tandem reaction containing three catalytic cycles is involved, as in the case of late transition-metal hydrides-catalyzed hydroboration. Our study represents the first examples of zinc hydrides as catalysts in the hydroboration of CO₂. Further investigation of the reactivity of these zinc dihydrides and mechanistic studies of the hydroboration reaction are underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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