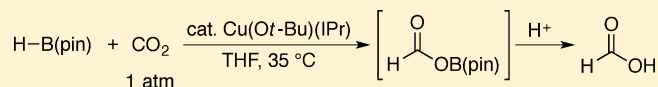# Copper-Catalyzed Hydroboration of Carbon Dioxide

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S *Supporting Information*

ABSTRACT: A copper/N-heterocyclic carbene catalyzed hydroboration of carbon dioxide has been developed to give a formic acid derivative selectively under mild conditions. Investigations directed toward understanding the catalytic cycle of this process have been carried out, and the hydroboration product can be directly used as a formylation reagent for various amines.

$$H-B(pin) + CO_2 \xrightarrow[\text{THF, 35 °C}]{\text{cat. Cu(O}t\text{-Bu)(IPr)}} \left[\underset{H}{\overset{O}{\diagdown}} OB(pin) \right] \xrightarrow{H^+} \underset{H}{\overset{O}{\diagdown}} OH$$
1 atm

Carbon dioxide, the most oxidized and stable form of carbon, is an abundant and inexpensive carbon source,[1] and catalytic reduction of carbon dioxide with hydrogen or hydrides is one of attractive way to utilize it.[1a–g] Among the various approaches to this end, nickel-[2] and ruthenium-catalyzed[3] hydroboration of CO_2 has been recently reported, in addition to the more widely explored catalytic hydrogenation[1c] and hydrosilylation[4] reactions. In contrast to many examples using hydrogen[1c,5] or hydrosilanes[4a–d,6] as the reductant that could give formic acid derivatives as the reduced form of CO_2, both of these hydroboration reactions provide methoxyboranes as the end product by 3-fold reduction of CO_2, but catalytic and selective formation of formic acid equivalents by using hydroboranes has not been reported as far as we are aware. In this context, herein we describe the development of a copper/N-heterocyclic carbene (NHC) complex catalyzed hydroboration of CO_2 to give a formic acid derivative as the product.

RESULTS AND DISCUSSION

Because copper/NHC complexes are reported to be effective catalysts for carboxylation of various carbon nucleophiles by using CO_2,[7] we initially employed Cu(O-t-Bu)(IPr)[8] as a catalyst for the reaction of pinacolborane with CO_2. After some investigation, we successfully found a set of conditions that can selectively provide formic acid by hydroboration of CO_2 followed by protonolysis. Thus, Cu(O-t-Bu)(IPr) (10 mol %) catalyzed a reaction of pinacolborane with CO_2 (1 atm) in THF under mild conditions to give formic acid in 85% yield after acidic workup (Table 1, entry 1). It is worth noting that this reaction proceeds without using a metal alkoxide base, which is usually required for related carboxylation reactions of carbon nucleophiles.[7a–d] The reaction could also be conducted with 5 mol % of the catalyst (entry 2) or in other solvents such as benzene (entry 3). In comparison, the reaction did not proceed by using catecholborane instead of pinacolborane (entry 4). The related Cu(O-t-Bu)(IMes)[7e] showed somewhat lower catalytic activity (entry 5), and CuCl(IPr)[9] was almost inactive for the present hydroboration reaction (entry 6). We have also confirmed that the reaction does not proceed in the absence of

Table 1. Copper-Catalyzed Hydroboration of CO_2

$$H-B(pin) + CO_2 \xrightarrow[\text{35 °C, 24 h}]{\text{Cu-catalyst}} \xrightarrow{\text{HCl}aq} \underset{H}{\overset{O}{\diagdown}} OH$$
1 atm

entry	Cu catalyst (amt (mol %))	solvent	yield (%)[a]
1	Cu(O-t-Bu)(IPr) (10)	THF	85
2	Cu(O-t-Bu)(IPr) (5)	THF	72
3[b]	Cu(O-t-Bu)(IPr) (10)	benzene	57
4[c]	Cu(O-t-Bu)(IPr) (10)	THF	<2
5	Cu(O-t-Bu)(IMes) (10)	THF	32
6	CuCl(IPr) (10)	THF	3
7	none	THF	<2
8	Cu(OAc)$_2$·H$_2$O/dppbz[d] (10/15)	THF	38
9	IPr (10)	THF	35

[a]Determined by ^{1}H NMR against an internal standard (MeNO$_2$). [b]The reaction was quenched with HCl in diethyl ether. [c]Catecholborane was used instead of pinacolborane. [d]dppbz = 1,2-bis-(diphenylphosphino)benzene.

any catalyst (entry 7). The use of Cu(OAc)$_2$·H$_2$O/dppbz, which was reported to be a highly active catalyst for the hydrosilylation of CO_2,[4b] resulted in a significantly lower yield (entry 8), and the reaction using IPr as an organocatalyst, which is also known to be highly effective for the reaction of CO_2 with hydrosilanes,[4e,10] turned out to be much inferior to the reaction catalyzed by Cu(O-t-Bu)(IPr) (entry 9).

A series of stoichiometric reactions were carried out to gain some insight into the catalytic cycle for the present hydroboration of CO_2. The reaction of Cu(O-t-Bu)(IPr) (^{1}H NMR spectrum shown in Figure 1a) with pinacolborane (1.0 equiv) in benzene-d_6 at room temperature under argon instantly produced CuH(IPr)[11] along with generation of (t-BuO)B(pin) (Figure 1b). This copper hydride is known to be thermally unstable in solution,[8] and it indeed started to decompose within 1 h. Successive treatment of CuH(IPr) generated in situ with CO_2 (1 atm) cleanly afforded a new species that corresponds to Cu(O$_2$CH)(IPr) (Figure 1c).[4b,12] Although

a)

b)

c)
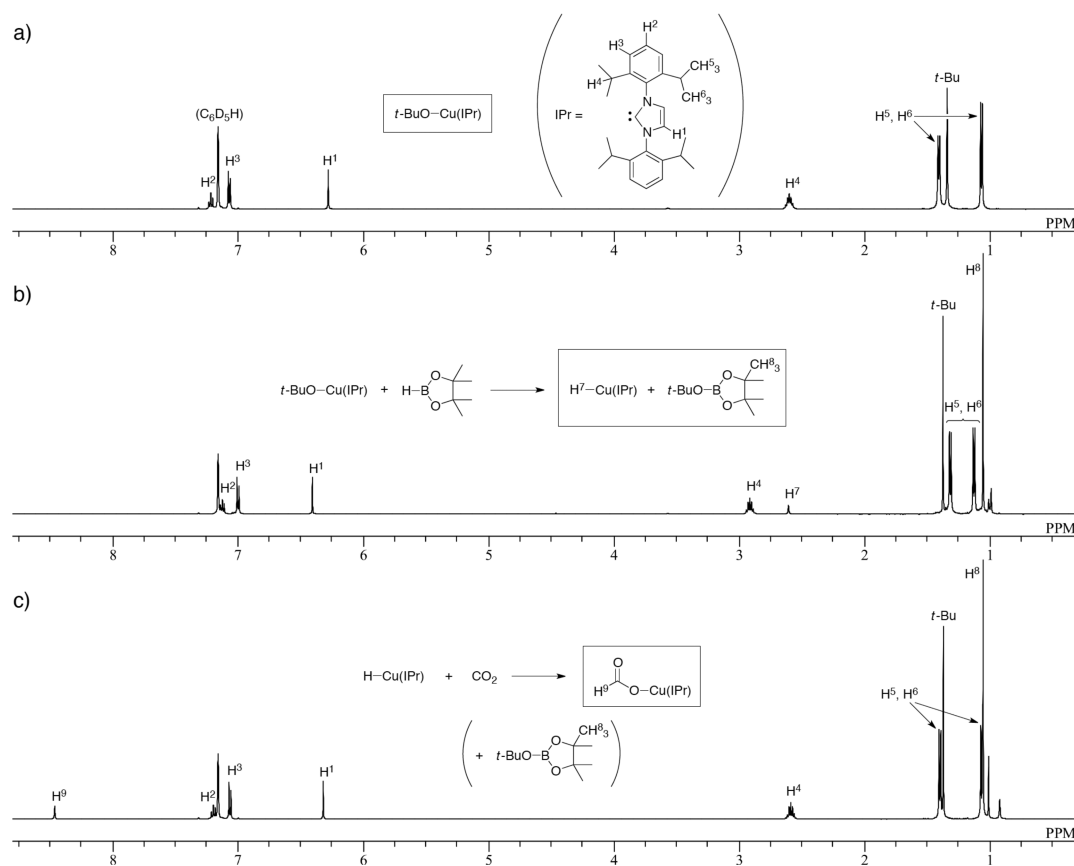
Figure 1. ^{1}H NMR spectra in benzene-d_6 of (a) Cu(O-t-Bu)(IPr), (b) CuH(IPr) and (t-BuO)B(pin) obtained from Cu(O-t-Bu)(IPr) + HB(pin), and (c) Cu(O$_2$CH)(IPr) obtained from CuH(IPr) + CO$_2$.

we expected regeneration of CuH(IPr) by the reaction of this copper formate with pinacolborane in the absence of CO$_2$,[13] we were unable to observe the formation of CuH(IPr) by the addition of pinacolborane (1.0 equiv, and then excess) to a solution of Cu(O$_2$CH)(IPr) in benzene-d_6 under argon. Instead, the majority of this formate complex stayed intact for a while and then gradually decomposed. In order to obtain more information, we independently synthesized Cu(O$_2$CH)-(IPr) by the reaction of CuCl(IPr) and Ag(O$_2$CH) and used it as a catalyst for the present hydroboration of CO$_2$. As shown in eq 1, this copper complex displayed a catalytic activity similar to that of Cu(O-t-Bu)(IPr), giving formic acid in high yield after acidic workup.
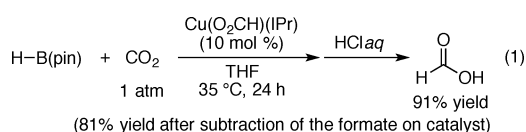
On the basis of these experiments, a proposed catalytic cycle for Cu(O-t-Bu)(IPr)-catalyzed hydroboration of CO$_2$ is illustrated in Scheme 1. Thus, the reaction of Cu(O-t-Bu)(IPr) with pinacolborane generates CuH(IPr), which smoothly undergoes insertion of CO$_2$ to give Cu(O$_2$CH)(IPr). The subsequent turnover-limiting reaction of this species with pinacolborane provides a boron formate as the product along with regeneration of the copper hydride. Although we could not directly observe this elemental step under stoichiometric conditions, considering the result using Cu(O$_2$CH)(IPr) as the catalyst (eq 1), we currently believe this process does occur

Scheme 1. Proposed Catalytic Cycle for the Copper-Catalyzed Hydroboration of CO$_2$[a]
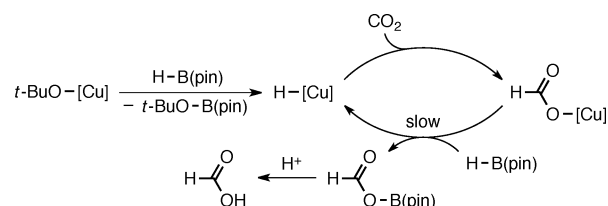
[a][Cu] = Cu(IPr).

during catalysis under CO$_2$.[14] The primary hydroboration product HCO$_2$B(pin) (^{11}B NMR (THF) δ 21.0 ppm (s))[15] becomes formic acid by treatment with aqueous HCl at the end of the reaction.

We have also found that HCO$_2$B(pin) produced in the present catalysis can be directly used as a formylation reagent for various amines, as shown in Table 2.[16] For example, treatment of p-anisidine (**1a**) in the presence of Et$_3$N with a solution of HCO$_2$B(pin) after the catalytic hydroboration of CO$_2$ cleanly afforded the corresponding formamide **2a** in 84% isolated yield (entry 1). Secondary aniline **1b** as well as cyclic amine **1c** also gave formamides **2** in high yield (81−86% yields; entries 2 and 3). In addition, primary alkylamines **1d**−**f** could also be used with high efficiency, regardless of their steric properties (81−98% yields; entries 4−6), and secondary alkylamine **1g** was converted to formamide **2g** in high yield as well (90% yield; entry 7). It is worth noting that the hydroboration−fomylation sequence can also be conducted

Table 2. N-Formylation of Amines 1 via Copper-Catalyzed Hydroboration of CO_2

entry	HNR^{1}R^2 (**1**)	product	yield (%)^a
1	H$_2$N–⬡–OMe (**1a**)	**2a**	84
2^b	HN(Me)(Ph) (**1b**)	**2b**	81
3^b	indoline (**1c**)	**2c**	86
4	H$_2$N–CH$_2$CH$_2$–Ph (**1d**)	**2d**	98
5	H$_2$N–CH(Me)–Ph (**1e**)	**2e**	89
6	H$_2$N–adamantyl (**1f**)	**2f**	81
7	HN(Ph)(CH$_2$Ph) (**1g**)	**2g**	90

^{a}Isolated yield. ^{b}The formylation reaction was conducted at 80 °C.

without pregeneration of HCO$_2$B(pin), as exemplified in eq 2. Thus, the reaction of pinacolborane with CO_2 in the presence of *p*-anisidine (**1a**) provides formamide **2a** in 71% yield.[17]
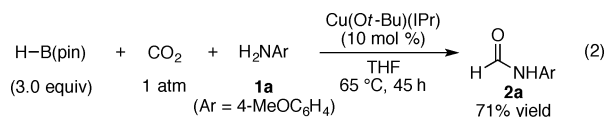
CONCLUSIONS

In summary, we have developed a copper/N-heterocyclic carbene-catalyzed hydroboration of carbon dioxide under mild conditions to give a formic acid derivative selectively for the first time. We have also carried out investigations to gain insights into the catalytic cycle of this process and utilized the hydroboration product as a formylation reagent for various amines as well. Future studies will be directed toward the development of more active catalyst systems for reductive utilization of carbon dioxide.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) This complex is reported to be a dimeric species.[8] See also ref 7e.

(12) Stoichiometric reactions of copper tetrahydroborate complexes with CO_2 giving copper formates have been reported. For examples, see: (a) La Monica, G.; Ardizzoia, G. A.; Cariati, F.; Cenini, S.; Pizzotti, M. *Inorg. Chem.* **1985**, *24*, 3920. (b) Pandey, K. K.; Garg, K. H.; Tiwari, S. K. *Polyhedron* **1992**, *11*, 947.

(13) A related stoichiometric reaction using a nickel formate complex has been reported.[2b]

(14) We do not have a solid explanation for the reactivity differences of the $Cu(O_2CH)(IPr)$ intermediate with pinacolborane in the absence and presence of CO_2. It might be possible that the transient generation of relatively unstable $CuH(IPr)$ is facilitated in the presence of CO_2 by driving the reaction to the subsequent step toward regeneration of $Cu(O_2CH)(IPr)$.

(15) Isolation of $HCO_2B(pin)$ has not been successful. See also ref 2b.

(16) For related formylation of amines using hydrosilanes and CO_2, see: (a) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuéry, P.; Ephritikhine, M.; Cantat, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 187. (b) Reference 4d. (c) Reference 10.

(17) No formylation reaction was observed in the absence of pinacolborane.