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Letter

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Di(carbene)-Supported Nickel Systems for CO_2 Reduction Under Ambient Conditions

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Supporting Information Placeholder

ABSTRACT: Di(carbene)-supported nickel species **1** and **2** are efficient catalysts for the room-temperature reduction of CO_2 to methanol in the presence of sodium borohydride. The catalysts feature unusual stability, particularly for a base metal catalyst, enabling > 1.1 million turnovers of CO_2. Moreover, while other systems involve more expensive reducing reagents, sodium borohydride is inexpensive and easily handled. Further, effecting reduction in the presence of water enables direct access to methanol. Preliminary mechanistic data collected are most consistent with a mononuclear nickel active species that mediates rate-determining reduction of a boron formate.

KEYWORDS: carbon dioxide, methanol, nickel, catalyst, borohydride

Global atmospheric CO_2 concentration passed the 400 ppm threshold last year (May, 2015) for the first time on the NOAA record,[1] which highlights effective CO_2 reduction as an important goal for the catalysis community.[2] Most CO_2 reduction products, such as methanol, formic acid, CO, etc., are useful C1 feedstocks in chemical synthesis; among them methanol has the highest volume energy density and is thus a high value product.[3] However, it also is a challenging target, because CO_2 is thermodynamically robust, so its activation requires a strong thermodynamic driving force.[4] Also, selective reduction of CO_2 is problematic; some known catalytic systems afford a mixture of products.[5] Regarding synthetic routes to methanol from CO_2, direct hydrogenation (with H_2) has been observed with a few ruthenium catalysts; these adopt forcing conditions or a multiple catalyst cascade, and they have limited longevity.[6] Excellent, non-renewable routes to methanol via syn gas are possible,[2, 3] but room remains for improvement in renewable CO_2 to methanol conversion.

Certain silanes or boranes can effect CO_2 reduction under much milder conditions.[7] For example, figure 1 shows known, catalytic systems for low temperatures CO_2 to methoxide reduction. More recently, an example appeared wherein BH_3-THF reduces CO_2 to methoxide with $NaBH_4$ as the catalyst.[8] While these catalysts differ structurally, each system involves a silane or borane compound as the stoichiometric reductant. The less expensive and more easily handled $NaBH_4$ has been sparsely investigated for CO_2 reduction in the last century.[9] In 2015 Cummins and Knopf established that CO_2 is reduced by $NaBH_4$ to triformatoborohydride, $HB(OCHO)_3^-$ in anhydrous acetonitrile.[10] We show here how these species can be converted catalytically to methanol at room temperature by nickel catalysts **1** and **2**.

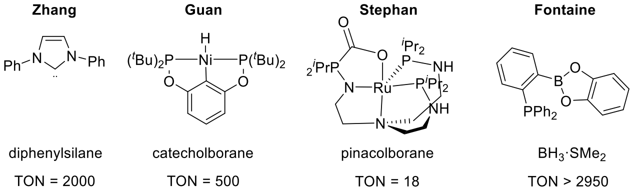
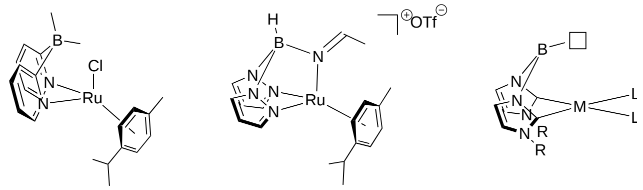


Figure 1. Catalytic CO_2 Reduction with Silanes and Boranes. TONs are based on the number of hydrides delivered.

Our group's strategy for reduction of small molecules involves dual site cooperative hydride delivery.[11] Particularly, we have observed modest reactivity for CO_2 conversion to methoxide with catalysts **3** and **4** in the presence of boranes (TON ca. 20, Figure 2), and surmised that a more electron rich complex featuring an analogous ligand scaffold could improve on these leads. We thus designed a family of nickel complexes supported by strongly donating bis(NHC)borate ligands, conceptually sketched in figure 2.



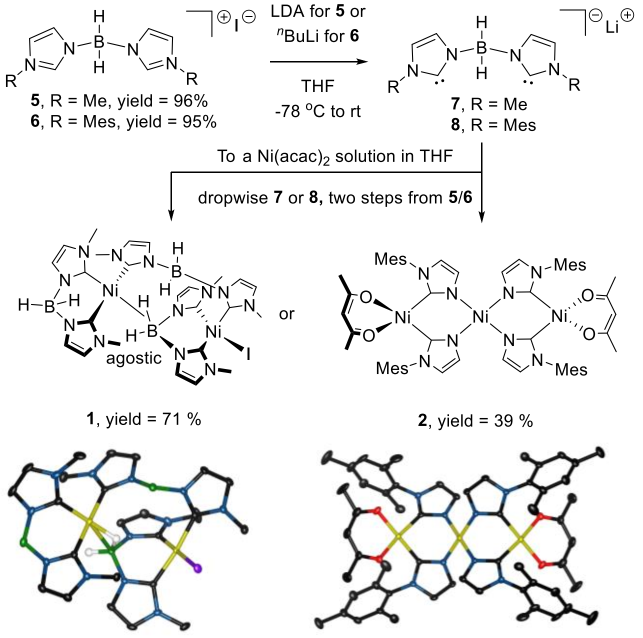
3
CO_2 reduction with NH_3BH_3

4
CO_2 reduction with $NaBH_4$

Proposed scaffold for CO_2 reduction

Figure 2. Dual Center Catalytic Scaffolds for CO_2 Reduction.

Accordingly, we prepared bis(imidazolium)borate cations **5** and **6** (Scheme 1), featuring diverse steric environments. These can be doubly deprotanated to form bis(imidazolium carbene)borate anions, respectively **7** and **8**, which can be treated with $Ni(acac)_2$ to form structurally novel nickel complexes **1** and **2** in preparatively useful yields over 2 steps. Formation of **1**'s nickel iodide bond results from persistence of the iodide counterion that accompanies **5**.



Scheme 1. Syntheses and Structures of Nickel Compounds **1** and **2**. Ellipsoids are drawn at the 50% probability level. Yields of **1** and **2** are based on the ligands.

Nickel(II) complexes **1** and **2** are bimetallic and trimetallic compounds, respectively (Scheme 1). In the solid-state structure of complex **1**, one of three bidentate borate ligands bridges the two nickels. Another structural characteristic of **1** is that a B—H bond from one nickel's ligand interacts with another nickel in an agostic fashion. Quite unlike compound **1**, compound **2** is free of all the boron atoms that are introduced in its synthesis. While not designed based on the enzymes, these multi-metallic structures are reminiscent of nickel-dependent hydrogenases that are reactive catalysts for CO_2 reduction under ambient conditions.[12]

Both **1** and **2** exhibit high reactivity as catalysts for *room-temperature reduction of CO_2* by $NaBH_4$. For example, in two weeks, **1** and **2** can deliver more than 72000 or 143000 turnovers based on methanol product (TOFs are 6.7 min^{-1} and 3.7 min^{-1}), respectively, without apparent loss of reactivity (Figure 3). In a longevity experiment, catalyst **2** reached to a CO_2 TON of 1.1 million over 2 months (3.3 M TONs of hydride), and was still reactive when the reaction mixture was quenched. This TON is over three orders of magnitude more than the highest of CO_2 reduction by metal catalysts and a boron hydride in literature (Figure 1).[7] Also noteworthy in this reaction is that > 90% of the total hydride groups in $NaBH_4$ were converted to C—H bonds, which is superior to a typical $NaBH_4$ reduction of a carbonyl group. The fate of boron containing species is sodium borate, which we can quantitatively crystalize from the mixture.

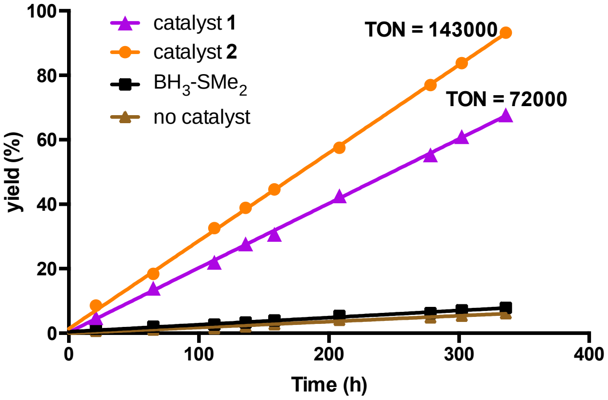


Figure 3. Kinetic Profile of CO_2 Reduction by $NaBH_4$ Catalyzed by **1** and **2** in 2 Weeks. TONs are based on CO_2. Y-axis is yield of methanol based on $NaBH_4$. Loadings of Ni catalysts **1** and **2** and $BH_3 \cdot SMe_2$ are 1.9 μmol, 1.3 μmol, and 20 μmol, respectively.

Nickel catalysts derived from **1** and **2** are exceptionally robust: they work in air and they have high tolerance for water. We take advantage of this fact and reduce CO_2 in presence of a small amount of water to directly synthesize methanol. In a representative NMR experiment, in the presence of 1 vol% H_2O, the reaction yielded ca. 0.1 mmol methanol, instead of boron methoxides (TON 160, TOF 1.2 min^{-1}, see supporting information).

Both nickel and the ligand are important to the mechanism (Table 1), because none of Ni(acac)$_2$, **5**, or a mixture of Ni(acac)$_2$ with **5** or **6** or imidazole effect reduction. When **7** is used to affect the same transformation, we observe stoichiometric conversion of formate to methoxide. We suspect this reactivity is enabled by nucleophilic activation of borohydride by the NHC.[13]

Kinetic studies were conducted on nickel complex **1**. We find that the CO$_2$ pressure has little impact on the reduction: in parallel runs under different CO$_2$ pressures ranging from 15 to 45 psi, the same yield of methoxides is observed at different time points before completion. Complexes **1** and **2** are also effective catalysts for reduction of HCOOH by NaBH$_4$ to methoxides. Sequential protonations of borohydride with HCOOH give the same formates as those generated from CO$_2$: dissolving HCOOH and NaBH$_4$ in acetonitrile affords identical ^{1}H-NMR spectra (see supporting information, Figure S21). This enables formic acid as a convenient liquid surrogate for CO$_2$ for kinetic studies. The formate compounds (Figures S20, S21) are stable at room temperature and do not undergo further reduction until nickel catalyst **1** or **2** is introduced. Thereafter, methoxides form until all formates are consumed. We find this formate reduction to have first order dependence on [formate] and first order dependence on [**1**].

Table 1. Formate Conversion to Methoxides.

$$[\mathrm{HCOOX}] \xrightarrow[\text{25 min, rt}]{\mathrm{CD_3CN}} [\mathrm{H_3COX}]$$

entry	catalyst	conversion	TON
1	**1**	61%	99
2	**2**	64%	104
3	Ni(acac)$_2$	< 5%	N/A
4	Ni(acac)$_2$ + methylimidazole	< 5%	N/A
5	Ni(acac)$_2$ + **5** or **6**	< 5%	N/A
6	**5**	< 5%	N/A
7[a,b]	**7**	6.8%	1[c]
8[d]	**9**	27%	20

Conditions: formates are generated from the reaction between NaBH$_4$ (8.0 mg, 210 μmol) and HCO$_2$H (8.0 μL, 210 μmol) in CD$_3$CN (0.6 mL) in a J. Young tube. For the conversion of formates, catalyst (1.3 μmol) is added. Reaction progress is monitored by disappearance of formate peaks in ^{1}H NMR. [a] CO$_2$ is used instead of FA to avoid protonation of **7**. [b] The initial [formate] is 0.30 M. [c] TON is based on two carbenes per molecule of **7**. [d] 2.6 μmol catalyst is added.

When **2** is treated with a stoichiometric amount of NaBH$_4$, we see rapid conversion of BH$_4^-$ to a new borane species (^{11}B-NMR, Figure S26) and a new, broad hydride peak in ^{1}H-NMR at $\delta(^1H)$ = - 13.8 ppm, suggesting the formation of Ni-H species, which is consistent with a hydrogen bridging Ni and B (Figure S25).[7c] This Ni—H species, if charged with 1 atm CO$_2$, yields formate and methoxide peaks in ^{1}H-NMR (Figure S27). Similarly, in an isotope labelling experiment, sodium formate-d_1 (DCOONa) was clearly reduced by this Ni—H system to a methoxide-d_1 product (Figure S30). These data show us that our conditions result in the formation of a nickel hydride intermediate that is capable of reduction of both CO$_2$ and our formate species. While we don't know that it is a resting state, we propose that this is part of our catalytic cycle.

We have isolated two nickel(II) species from the working reaction conditions, tetra(carbene) species **9** and **10** (Figure 4). Complex **9** shows only modest reactivity in formate reduction: its reaction rate is ca. 5 times slower than **1**, and we have only observed a modest TON (72) in 24 h with it. Compound **10** is not long-lived: while we were fortunate enough to obtain crystallography data; it was not sufficiently robust to test in catalysis. We speculate that the active catalyst is a monomeric nickel carbene complex with a reactive nickel hydride in its reducing form. We base this on the observation of first order kinetic dependence on [**1**], the isolations of **9** and **10**, and the observation of a hydride in stoichiometric model reactions, although these data are not conclusive of a monomeric active catalyst. We suspect that dimer **1** cleaves to make species **9** and a bis(carbene)nickel species, e.g. **11**, which is reduced to give an active hydride (**12**, Scheme 2). Although we do not observe free ligands in the catalytic solution, we expect that **9** can slowly convert to **11**, which then goes on to reduce formate. While our mechanistic proposal remains speculative at this point, it is ironic to see that, while this design concept of a bifunctional transition metal borate (figure 2) led us to our initial design, our mechanistic data effectively eliminate this boron atom's participation in the mechanism, a situation we find frequently.[11d]

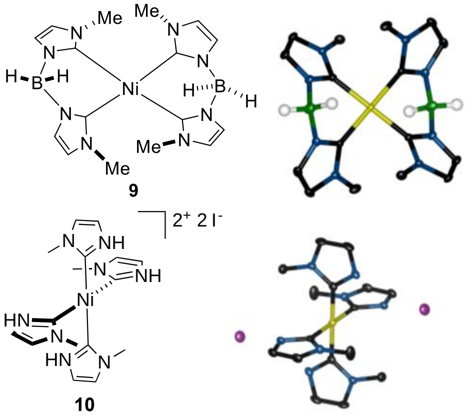
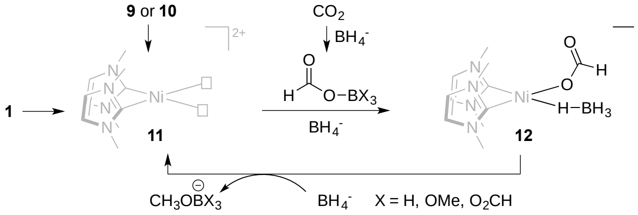


Figure 4. Nickel Complexes **9**, **10** and their Crystal Structures. ORTEP ellipsoids drawn at the 50% probability level.



Scheme 2. Mechanistic Speculation.

In conclusion, we report the synthesis and structural characterization of two novel NHC supported nickel complexes, **1** and **2**. These nickel complexes can catalyze CO_2 reduction to methoxides with $NaBH_4$ under ambient conditions. The catalysts feature unprecedented stability, enabling a stunning > 1 million turnovers. Ultimately we would like to transition this system to H_2 as the reducing agent, until then, the reaction features sodium borohydride, which has superior cost and convenience relative to more complex and sensitive borane and silane reagents. While work remains for the full understanding of the system's catalytic mechanism, preliminary data accommodate a single, probably mononuclear catalyst that enables rate-determining reduction of a boron formate. Further development of this system will involve the identification of a co-catalyst that will enable its turnover based on H_2 itself.

ASSOCIATED CONTENT

Supporting Information.

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

Experimental procedures, graphical and tabular characterization information, and CIF files. CDCC #1455844 (**1**), #1455845 (**2**), #1455846 (**6**), #1455847 (**9**), and #1455848 (**10**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interests.

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