

An Efficient Nickel Catalyst for the Reduction of Carbon Dioxide with a Borane

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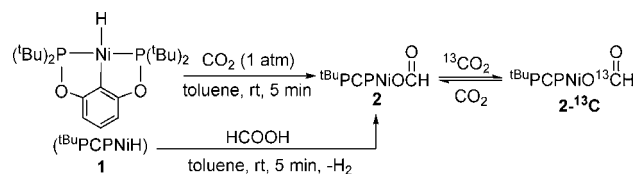
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The conversion of carbon dioxide to polymers, chemicals, and fuels is an attractive means of making biodegradable materials, synthesizing value-added products, and storing energy.¹ In addition, it could help reverse the negative impact of human activities on the earth's atmosphere. Of particular interest to us is the development of highly efficient methods for the reduction of CO₂. Transition-metal-catalyzed homogeneous hydrogenation of CO₂ often leads to either formic acid that is thermodynamically stabilized by a base² or CO via the reverse process of the water-gas shift reaction.³ Transforming CO₂ into methane, the most reduced form of carbon, under homogeneous conditions can be accomplished using silanes as the reducing reagents.⁴ Reducing CO₂ to methanol would be even more desirable for the advantages of transporting a liquid fuel rather than a gas. Catalytic hydrosilylation of CO₂ to methoxysilyl species is feasible with Ir(CN)(CO)(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane] at 40 °C, albeit with limited turnover numbers.⁵ More efficient hydrosilylation reactions are catalyzed by N-heterocyclic carbenes (metal-free) at ambient temperature with turnover frequencies (TOFs) as high as 25.5 h⁻¹ (based on Si–H), and methanol is produced from the hydrolysis of the initial reduction products.⁶ The recent development of frustrated Lewis acid–base pair (FLP) chemistry⁷ has led to alternative strategies for the reduction of CO₂ to the methoxy level given either H₂⁸ or H₃NBH₃⁹ as a hydrogen source. These reactions are presumably promoted by the formation of strong MeO–B and MeO–Al bonds for the FLP systems involving 2,2,6,6-tetramethylpiperidine/B(C₆F₅)₃⁸ and PMes₃/AlX₃ (Mes = 2,4,6-Me₃C₆H₂; X = Cl, Br),⁹ respectively. On the other hand, cleavage of these robust chemical bonds has proven to be difficult, and therefore, stoichiometric amounts of FLPs are required. In this paper, we report a highly efficient nickel system for the catalytic hydroboration of CO₂ to methoxyboranyl species using a simple borane. The reactions operate at room temperature with TOFs at least 1 order of magnitude higher than those of the related reactions described above.

Insertion of CO₂ into a metal–hydrogen bond constitutes a critical step in many transition-metal-catalyzed reductions of CO₂.² Despite the high thermodynamic stability of CO₂, we found that the reaction of PCP-pincer nickel hydride (**1**)¹⁰ with CO₂ proceeds rapidly at room temperature to give a nickel formate complex (**2**) as the sole product (Scheme 1). The related complexes *trans*-(C₃P)₂Ni(H)(Ph)¹¹ and [2,6-(^tBu₂PCH₂)₂C₆H₃]PdH¹² show similar reaction patterns with CO₂. In contrast, the interaction between CO₂ and [(^tBu₂PCH₂SiMe₂)₂N]NiH, a PNP-pincer nickel hydride, gives rise to a hydridonickel cyanate complex through an N/O transposition.¹³ The CO₂ insertion in our system is reversible, as evidenced by the following observations: (1) mixing ¹³C-labeled nickel formate (**2**-¹³C) with CO₂ (~1 atm) at room temperature resulted in the formation of nonlabeled **2**, and (2) heating a solid sample of **2** under vacuum at 60 °C for 5 h generated **1** in a nearly quantitative yield. Compound **2** was also independently synthesized by rapid protonation of **1** with 1 equiv of HCO₂H. X-ray analysis of single crystals of **2** (Figure 1) revealed a distorted square-planar geometry for Ni, with

Scheme 1



the O3 atom displaced 0.41 Å out of the least-squares plane defined by the P1, C1, Ni, and P2 atoms;¹⁴ however, the long through-space Ni···O4 distance [3.271(3) Å] would argue against a potential η² coordination mode for the formato group. The bond lengths of C23–O3 [1.250(4) Å] and C23–O4 [1.236(4) Å] are fairly close as a result of a significant degree of electron density delocalization within the formate moiety;¹⁵ however, these bonds are slightly shorter than the C–O bond lengths in HCO₂Na (1.27 Å).¹⁶

Regenerating **1** from **2** would complete a potential catalytic cycle for the reduction of CO₂. To test this hypothesis, we investigated the reactions between **2** and various reducing reagents at room temperature. When catecholborane (HBcat) was used at 1 equiv with respect to Ni, **1** was observed along with a new boron species that was assigned as HCOOBcat. Interestingly, when HBcat was employed in large excess, a new resonance appeared at 3.34 ppm (singlet) in the ¹H NMR spectrum of the reaction, consistent with the formation of a methanol derivative. To further understand this process, we carried out a series of NMR experiments involving ¹³CO₂. When **2**-¹³C (generated in situ from **1** and ¹³CO₂) was treated with 4 equiv of HBcat, the corresponding ¹H NMR spectrum exhibited a doublet (¹J_{C–H} = 145.2 Hz) at 3.34 ppm (Figure 2). The same reaction monitored by ¹³C NMR spectroscopy revealed a singlet at 53.6 ppm in the ¹H-decoupled spectrum (Figure 3) and a quartet (¹J_{C–H} = 145.2 Hz) in the ¹H-coupled spectrum, confirming the presence of a methoxy group. Thus, the reduction product was identified as ¹³CH₃OBCat, the spectra of which are consistent with those reported in the literature¹⁷ as well as those

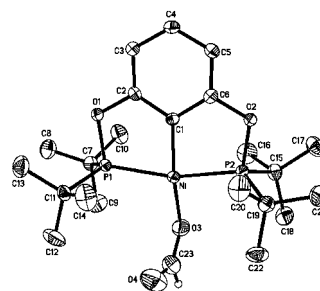


Figure 1. ORTEP view of complex **2** (50% probability level). Selected bond lengths (Å) and angles (deg): Ni–C1, 1.886(2); Ni–P1, 2.2040(7); Ni–P2, 2.1817(8); Ni–O3, 1.920(2); C23–O3, 1.250(4); C23–O4, 1.236(4); P1–Ni–P2, 164.02(3); O3–C23–O4, 128.0(3). Through-space Ni···O4 distance: 3.271(3) Å.

obtained for CH₃OBCat that was independently synthesized from CH₃ONa and ClBcat.¹⁸ The byproduct of the CO₂ reduction process was catBOBcat, which resulted in a downfield shift of the resonances of 2-¹³C (Figures 2 and 3), presumably through a Lewis acid–base interaction. ¹³CH₃OBCat proved to be hygroscopic; it absorbed moisture quickly from the air and generated ¹³CH₃OH, as confirmed by mass spectroscopy.¹⁸

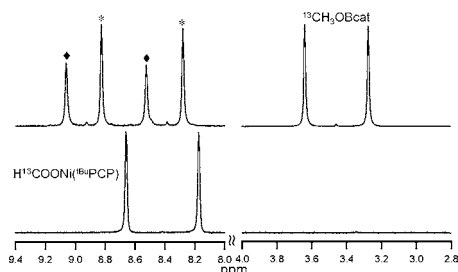


Figure 2. ¹H NMR spectra of 2-¹³C in C₆D₆ (bottom) and 2-¹³C with added HBcat in C₆D₆ [top; ♦ denotes H¹³COOBcat and * denotes H¹³COONi(^tBuPCP)·catBOBcat].

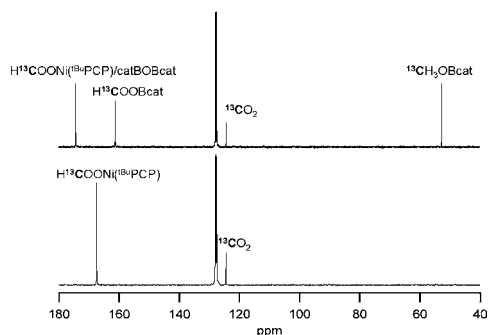
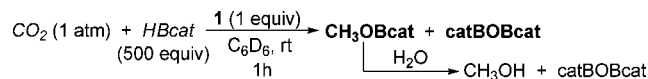


Figure 3. ¹³C{¹H} NMR spectra of 2-¹³C (with residual ¹³CO₂) in C₆D₆ (bottom) and 2-¹³C with added HBcat in C₆D₆ (top).

We also discovered that the reduction of CO₂ with HBcat was catalytic in nickel. The mixture of HBcat and **1** in a ratio of 500:1 under 1 atm CO₂ generated CH₃OBCat with 495 turnovers (based on B–H) in 1 h, while the other boron product (catBOBcat) precipitated from the C₆D₆ solution (Scheme 2). A control experiment showed no reaction in the absence of **1**, confirming that the reduction was indeed catalyzed by the nickel hydride. The initial reduction products were further hydrolyzed in a large excess of water, and vacuum distillation of the resulting mixture yielded 0.28 M methanol in C₆D₆ (i.e., 61% yield based on HBcat).

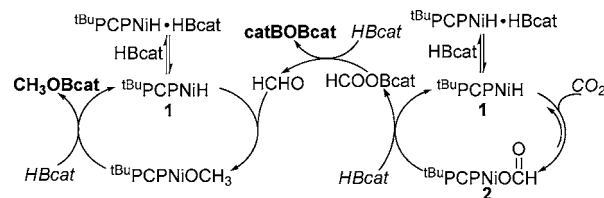
Scheme 2



Catalytic cycles consistent with our observations are outlined in Scheme 3. The catalytic reduction of CO₂ begins with a reversible insertion of CO₂ into a Ni–H bond. The subsequent cleavage of the Ni–O bond with HBcat regenerates **1** and releases HCOOBcat, which is reduced to formaldehyde by another HBcat. A second cycle involves the hydroboration of formaldehyde, which is analogous to the nickel-catalyzed hydrosilylation of aldehydes reported earlier.¹⁰ In accord with this mechanistic hypothesis, the reduction of paraformaldehyde with HBcat in the presence of **1** also gave CH₃OBCat. Two possible equilibria outside the catalytic loops, the formation of the adducts **1**·HBcat and **2**·catBOBcat (not shown), were separately tested.¹⁸ When HBcat was depleted in the solution, the nickel species rested as

2·catBOBcat, and further addition of HBcat reinitiated the reaction with no loss of catalytic activity. In fact, the independently synthesized **2** exhibited a catalytic efficiency comparable to that of **1**, an advantage in our catalytic system as compound **2** is air-stable.

Scheme 3



In summary, we have shown the first catalytic hydroboration of CO₂, with the highest TOF (495 h⁻¹ based on B–H) reported to date for the reduction of CO₂ to the methoxide level. Further studies to elucidate the mechanistic details and improve the catalytic efficiencies are in progress.

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Supporting Information Available: Experimental details, complete ref 1a, and crystallographic data for **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For recent reviews of chemical utilization of CO₂, see: (a) Marks, T. J.; et al. *Chem. Rev.* **2001**, *101*, 953–996. (b) Louie, J. *Curr. Org. Chem.* **2005**, *9*, 605–623. (c) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365–2387. (d) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–2410. (e) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975–2992.
- (2) For reviews of the hydrogenation of CO₂, see: (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259–272. (b) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207–2221. (c) Jessop, P. G.; Joó, F.; Tai, C.-C. *Coord. Chem. Rev.* **2004**, *248*, 2425–2442.
- (3) For discussions of homogeneously catalyzed water-gas shift reactions, see: (a) Ford, P. C.; Trabuco, E.; Mdeleeni, M. M. *Water Gas Shift Reaction—Homogeneous*. In *Encyclopedia of Catalysis*, 1st ed; Horváth, I. T., Ed.; Wiley Interscience: Hoboken, NJ, 2003; Vol. 6, pp 651–658. (b) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022–4047.
- (4) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362–12363.
- (5) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, *8*, 1822–1824.
- (6) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 3322–3325.
- (7) Stephan, D. W. *Dalton Trans.* **2009**, 3129–3136.
- (8) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839–9843.
- (9) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796–1797.
- (10) Chakraborty, S.; Krause, J. A.; Guan, H. *Organometallics* **2009**, *28*, 582–586.
- (11) Darensbourg, D. J.; Darensbourg, M. Y.; Goh, L. Y.; Ludvig, M.; Wiegrefe, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 7539–7540.
- (12) Johansson, R.; Wendt, O. F. *Organometallics* **2007**, *26*, 2426–2430.
- (13) Laird, M. F.; Pink, M.; Tsvetkov, N. P.; Fan, H.; Caulton, K. G. *Dalton Trans.* **2009**, 1283–1285.
- (14) The deviation from planarity for the P1, C1, Ni, and P2 atoms was calculated to be 0.0148 Å.
- (15) In the related complex [2,6-(Me₂NCH₂)₂C₆H₃]NiOCHO, the C–O bond lengths are 1.270(3) and 1.209(3) Å for the Ni-bonded and nonbonded C–O bonds, respectively. See: Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoot, R.; Spek, A. L. *Organometallics* **1984**, *3*, 1003–1009.
- (16) Zachariassen, W. H. *J. Am. Chem. Soc.* **1940**, *62*, 1011–1013.
- (17) For ¹H and ¹³C NMR spectra of nonlabeled CH₃OBCat (prepared from HBcat and CH₃OH), see: Povie, G.; Villa, G.; Ford, L.; Pozzi, D.; Schiesser, C. H.; Renaud, P. *Chem. Commun.* **2010**, *46*, 803–805.
- (18) See the Supporting Information.

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