ORGANOMETALLICS

Trialkylborane-Assisted CO₂ Reduction by Late Transition Metal Hydrides

Alexander J. M. Miller, Jay A. Labinger,* and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

ABSTRACT: Trialkylborane additives promote reduction of CO_2 to formate by bis(diphosphine) Ni(II) and Rh(III) hydride complexes. The late transition metal hydrides, which can be formed from dihydrogen, transfer hydride to CO_2 to give a formate—borane adduct. The borane must be of appropriate Lewis acidity: weaker acids do not show significant hydride transfer enhancement, while



stronger acids abstract hydride without CO_2 reduction. The mechanism likely involves a pre-equilibrium hydride transfer followed by formation of a stabilizing formate-borane adduct.

INTRODUCTION

Efficient catalytic conversion of CO_2 to fuels and chemicals could be a major contributor toward achieving carbon neutrality.¹ We have recently reported (stoichiometric) reactions relevant to conversion of syngas to organic products, making use of a combination of a metal carbonyl complex, a nucleophilic late transition metal hydride, and an intramolecularly appended Lewis acid.² Because some syngas conversion catalysts are known to convert CO_2 as well—for example, the common CuO/ZnO/Al₂O₃ catalyst can effectively convert a mixture of H₂, CO₂, and CO to methanol³ we thought it might be worthwhile to examine the chemistry of our CO-reducing systems with CO₂.

The two main approaches to CO_2 reduction currently under consideration are electrocatalytic reduction,^{1a} in which protons and electrons are added sequentially (and/or concertedly), and direct hydrogenation.^{1b,c} Most of the electrocatalytic systems operate at quite reducing potentials to generate CO and H₂O, while hydrogenation (under forcing pressures) more commonly produces formic acid (Scheme 1). Lewis (particularly those based on alkali and alkaline earth metals) and Brønsted acids have shown promise in improving electrocatalytic CO_2 reduction, notably with low-valent Fe porphyrins.⁴ Bimetallic catalysts, including the active site of the enzyme [NiFe] CO dehydrogenase, appear to function by having one metal bound to C while the other acts as a Lewis acid to bind O.⁵ Lewis acids such as AlO_x and TiO_x appear to play an important role in heterogeneous catalysts that convert CO_2 (and CO) to CH_4 .⁶

Several examples involving boron compounds have also been reported. The conversion of a diboronyl $B-B^7$ or secondary borane $B-H^8$ bond to a B-O bond helps drive CO_2 reduction by homogeneous Cu- and Ni-based catalysts, respectively. Activation of dihydrogen by "frustrated Lewis pairs" can also lead to reduction of CO_2 ; products include methanol (after hydrolysis).⁹ All of these reactions are stoichiometric in boron; catalysis is precluded by the difficulty of cleaving the strong B-O bonds, unless strong Si-O bonds are formed using silane additives.¹⁰

We report here that the late transition metal hydrides, as well as the partially reduced metal carbonyl components of our CO reductive coupling system, are able to reduce CO_2 to formate, with Lewis acidic trialkylboranes playing a key role. Although no catalysis has yet been achieved, the formate—borane adducts obtained appear to be considerably less strongly bound than in the above-discussed systems, suggesting that this may be a promising new approach to CO_2 reduction.

RESULTS AND DISCUSSION

The Re carbonyl cation $[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4]$ -[BF₄] ([1][BF₄]), bearing pendent alkylboranes in the secondary coordination sphere of the metal, reacts with [HPt(dmpe)_2][PF₆] (dmpe = 1,2-bis(dimethylphosphino)ethane), but not with the analogous Ni hydride, to give boroxycarbene 2 (Scheme 2).^{2a} (Complex 2 can also be prepared by reduction of 1 with Na-HBEt₃.) Similarly, DuBois has found that CO₂ is reduced to [HCO₂]⁻ by [HPt(dmpe)_2][PF₆], whereas [Bu₄N][HCO₂] transfers hydride to [Ni(dmpe)_2]²⁺ to yield [HNi(dmpe)_2]⁺ (Scheme 3).¹¹ The hydride donor strengths (ΔG_{H-} ; smaller values correspond to stronger hydride donors) of [HPt(dmpe)_2]⁺, [HNi(dmpe)_2]⁺, and [HCO₂]⁻ have been determined to be 42.5, 50.9, and 44.2 kcal·mol⁻¹ respectively¹² (the last value is estimated from the observation that [HCO₂]⁻ has a ΔG_{H-} similar to that of [HPt(depe)_2]⁺ (depe = 1,2-bis(diethylphosphino)ethane),¹¹ the ΔG_{H-} of which was recalculated from the originally published value^{12a} using DuBois' more recent pK_a value^{12c}).

Boroxycarbene 2 can serve as a hydride source, releasing H_2 upon treatment with water or weak acids,^{2d} but the above results show that it is intermediate in hydride strength between $[HNi(dmpe)_2][PF_6]$ and $[HPt(dmpe)_2][PF_6]$; is it strong enough to reduce CO₂? Admission of 1 atm of CO₂ to a thoroughly

```
        Received:
        May 2, 2011

        Published:
        July 18, 2011
```

ACS Publications © 2011 American Chemical Society





hydrogenation of CO₂



Scheme 2



Scheme 3



degassed solution of 2 (formed *in situ* from [1][BF₄] and Na-HBEt₃ in C₆D₅Cl) led after a few minutes to a new ¹H NMR resonance at δ 8.44. ³¹P NMR showed complete consumption of 2 and formation of a new species with a single signal whose chemical shift was similar to that for [1]⁺; IR spectroscopy indicated a [*trans*-L₂Re(CO)₄]⁺ substructure (a single strong stretch at 1993 cm⁻¹) as well as a reduced C=O functionality (1620 cm⁻¹). These data are consistent with hydride transfer from 2 to CO₂, giving 1 · (HCO₂) (Scheme 4); the same species could be obtained by addition of [Bu₄N][HCO₂] to [1][BF₄] in C₆D₅Cl. The apparent symmetry exhibited by the NMR spectra suggests the operation of a fluxional process that exchanges formate between boranes, likely via reversible oligomerization (Scheme 4). After about an hour, large amounts of precipitate formed along with disappearance of the NMR signals assigned to 1 · (HCO₂); probably Scheme 4



this is due to formation of an oligomeric species $[1 \cdot (HCO_2)]_{nv}$ with -B-OC(H)O-B- linkages. Similar behavior has been observed for some of the CO reduction products studied previously.^{2d}

The observation that **2** reacts with CO_2 to yield $[1 \cdot (HCO_2)]$ does not necessarily indicate that 2 is a stronger hydride donor than $[HCO_2]^-$, since the B–O interaction in $1 \cdot (HCO_2)$ (and the two B–O interactions in $[1 \cdot (HCO_2)]_n$ presumably afford-(s) additional stabilization. Similarly, although transfer of hydride from $[HNi(dmpe)_2]^+$ to CO₂ should be uphill by $\sim 7 \text{ kcal} \cdot \text{mol}^{-1}$, addition of CO_2 to a mixture of $[HNi(dmpe)_2][PF_6]$ and [1]- $[BF_4]$ produced significant amounts of $1 \cdot (HCO_2)$ over 24 h at room temperature. This reaction did not proceed to completion, as evidenced by the presence of unreacted $[HNi(dmpe)_2]^+$; the chemical shifts for the (single) remaining Re-containing species were intermediate between those for $[1]^+$ and $1 \cdot (HCO_2)$, suggesting an equilibrium between these species. (No boroxycarbene 2 was observed.) The precipitate that again formed over time could be partially dissolved by addition of pyridine; the resulting solution showed a slightly shifted ¹H NMR signal for the formate group (δ 8.88) and *two* ³¹P NMR signals (δ 1.95 d, 2.98 d, $J_{\rm PP}$ = 77 Hz), consistent with formation of the asymmetric pyridine adduct $1 \cdot (HCO_2)(C_5H_5N)$ (Scheme 5).

Similar chemistry is promoted by a simple trialkylborane, which could imply that Re may simply be a spectator in the reaction involving $[1]^+$: when $[HNi(dmpe)_2][PF_6]$ was allowed to react with CO₂ (1 atm) in the presence of ^tBu(CH₂)₂B(C₈H₁₄) in C₆D₅Cl, over a few hours a new ¹H NMR resonance at δ 8.73 grew in, the hydride resonance of $[HNi(dmpe)_2]^+$ diminished, and $[Ni(dmpe)_2][PF_6]_2$ precipitated. The reaction did not go to completion; the ultimate yield of formate (assessed by integration of NMR spectra) was about 50%. As the reaction proceeded, the ¹H NMR peak attributed to formate gradually shifted upfield

Scheme 5



Figure 1. ¹¹B NMR spectra of a mixture of $[HNi(dmpe)_2][PF_6]$ and ^tBu(CH₂)₂B(C₈H₁₄) in C₆D₅Cl before CO₂ addition (red), 2 h after addition of CO₂ (1 atm) (green), and after 18 h (blue).

(δ 8.73 at 2 h, 8.66 at 18 h), while that for the *tert*-butyl group of the borane shifted downfield (δ 0.89 before reaction, 0.95 at 2 h, 0.97 at 18 h). Concurrently the ¹¹B NMR signal shifted upfield (δ 88.2 before reaction, 65 at 2 h, 51 at 18 h) and broadened considerably (Figure 1). Addition of one equivalent of ^tBu(CH₂)₂-B(C₈H₁₄) to [Bu₄N][HCO₂] in C₆D₅Cl shifted the ¹H NMR resonance for [HCO₂]⁻ from δ 9.58 to δ 8.89, consistent with some formate—borane interaction.

Several other boranes, of varying Lewis acidity, were also examined. Addition of CO₂ to a mixture of isopropyl pinacol borane and $[\text{HNi}(\text{dmpe})_2]^+$ did not significantly increase the amount of formate produced relative to the reaction in the absence of any Lewis acid, although the small ¹H NMR signal for $[HCO_2]^-$ was shifted upfield (δ 8.74 vs 8.84 without borane). Trimesitylborane also failed to effect significant CO₂ reduction, but produced a larger upfield shift (δ 8.63), quite similar to that in the trialkylborane reactions. It appears that these formate—borane adducts are considerably

Scheme 6



less robust, as might be expected for less acidic or more sterically crowded Lewis acids. Triphenylborane did give substantial conversion to formate, but the NMR spectral data indicated formation of unidentified side products as well. The much stronger acid $B(C_6F_5)_3$ exhibited only hydride transfer from Ni to B and no CO_2 reduction.

The results for the trialkylborane, above, clearly indicate formation of a formate-borane adduct (Scheme 6). To further probe this interaction, aliquots of ${}^{t}Bu(CH_2)_2B(C_8H_{14})$ were added sequentially to a C₆D₅Cl solution of formate. Upon addition of borane, a second $[HCO_2]^-$ signal appeared upfield of the original signal for free formate; the new signal increased in intensity, while the first decreased correspondingly, and both signals broadened and shifted upfield as more borane was added, up to one equivalent. At and beyond one equivalent of borane, only a single sharp resonance was observed, which shifted still further upfield as more borane was added. Addition of 10 equivalents of pyridine caused the peak to shift back to approximately the same position observed after addition of one equivalent of borane, along with substantial broadening. (Spectra are shown in the SI, Figure S15.) These observations appear most consistent with formation of a strong monoborane adduct, [HCO₂BR₃]⁻, which does not exchange with free $[HCO_2]^-$ on the NMR time scale, and a weaker bis(borane) adduct, $[HCO_2(BR_3)_2]^-$, which *does* rapidly exchange with the mono adduct; only the latter interaction is cleaved by addition of pyridine. This model does not fully explain the NMR behavior, particularly the changing peak shifts below one equivalent of added borane, but we have observed that other factors (such as counterion speciation and precipitation) can have an effect on NMR shifts (the $[Bu_4N]^+$ resonances also shift with added borane in the above experiment), which could account for these details.

In the absence of any borane, the reaction of $[HNi(dmpe)_2]$ -[PF₆] with 1 atm of CO₂ gave only about 2% formate product; with borane and the addition of tetraheptylammonium bromide it proceeded to completion, accompanied by precipitation of [Ni-(dmpe)₂][Br]₂. Under the latter conditions the formate ¹H NMR signal (δ 8.79) is close to the shift observed for the stoichiometric combination of formate and borane (δ 8.89).

In an attempt to eliminate some of these complications, we investigated CO₂ reduction in acetonitrile, in which all of the constituents are soluble (although there was a concern that MeCN would bind the borane too tightly to permit any acid assistance). Reaction of [HNi(dmpe)₂][PF₆] with CO₂ and no added borane led to ~5% conversion to [Ni(dmpe)₂]²⁺ and [HCO₂]⁻ (δ 8.40; cf. [Bu₄N][HCO₂] δ 8.68), while addition of a single equivalent of ^tBu(CH₂)₂B(C₈H₁₄) gave 60% conversion to [HCO₂(BR₃)_n]⁻ (δ 8.29), and 10 equivalents of borane effected essentially complete conversion (δ 8.22). Addition of one equivalent of [Bu₄N]-[HCO₂] at the end of the last reaction resulted in approximately

doubling the peak intensity with a negligible change in position; when the reaction was carried out with one equivalent of ${}^{13}\text{CO}_2$, the ¹H NMR signal at δ 8.21 appeared as a doublet (${}^{1}J_{\text{CH}} =$ 202 Hz) and a new intense ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR signal appeared at δ 174.16. These findings establish conclusively that the signal around δ 8.2 is indeed due to formate generated by reduction of CO₂. The ¹¹B NMR resonance of the free borane in CD₃CN is far upfield from that in C₆D₅Cl, consistent with formation of a CD₃CN adduct; that must be weaker than the formate—borane adduct, however, since the ¹¹B NMR resonance shifts further upfield (by ~3 ppm) as formate is produced.

In principle reduction of CO_2 by H_2 could be made catalytic in nickel, by employing a suitable base in concert with $[Ni(dm-pe)_2]^{2+}$ to cleave H_2 , ^{12c} followed by hydride delivery to CO_2 (Scheme 7). The base must be of sufficient steric bulk to inhibit

Scheme 7



Scheme 8



Scheme 9

strong adduct formation with the borane and/or nucleophilic attack at CO₂. When a mixture of $[Ni(dmpe)_2]^{2+}$, 5 equiv of NEt₃, and 5 equiv of ^tBu(CH₂)₂B(C₈H₁₄) in CD₃CN was exposed to H₂/CO₂ (1 atm of a 1:1 mixture), slow conversion to small amounts of formate (~8% relative to Ni) was observed over 3 days. The slow reaction is due (at least in part) to slow formation of $[HNi(dmpe)_2]^+$ under these conditions: a solution of $[Ni(dmpe)_2][PF_6]_2$ and NEt₃ (4 equiv) in CD₃CN under 1 atm of H₂ was only 30% converted to $[HNi(dmpe)_2][PF_6]$ after 3 days.

In contrast, the reaction of $[Ni(dmpe)_2][BAr^F_4]_2$ (BAr^F₄ = tetrakis(3,5-trifluoromethylphenyl)borate) and NEt₃ with H₂ proceeded far faster in C₆D₅Cl, with high conversion to $[HNi-(dmpe)_2]^+$ in 3 h and full conversion after 18 h. We ascribe the difference to coordination of solvent (Scheme 8): the adduct $[Ni(dmpe)_2(MeCN)]^{2+}$ has been structurally characterized, and its formation constant was estimated by electrochemical techniques as $K_{eq} = 0.3$, whereas in chlorobenzene $[Ni(dmpe)_2]^{2+}$ would be present as the four-coordinate square-planar complex (whose structure has also been determined).^{12a} Counteranion effects appear to be unimportant: $[Ni(dmpe)_2][BAr^F_4]_2$ reacts at roughly the same rate as $[Ni(dmpe)_2][PF_6]_2$ with NEt₃ under H₂ in CD₃CN.

Disappointingly, a solution of $[Ni(dmpe)_2][BAr^F_4]_2$, ^tBu $(CH_2)_2B(C_8H_{14})$, and NEt₃ under H_2/CO_2 in C_6D_5Cl did not produce any detectable formate, despite the steady growth of $[HNi(dmpe)_2]^+$ over a few days. It is unclear why no formate is generated. Reactions in CD_2Cl_2 led to formation of CD_2HCl , indicating a hydride transfer side reaction.

Reduction of CO₂ with H₂ could, however, be achieved with the rhodium cation $[Rh(dmpe)_2][OTf]$, without the need for an added base, since its H₂ oxidative addition product, [H₂Rh- $(dmpe)_2$ [OTf], is a hydride donor of strength ($\Delta G_{H-} = 50.4$ kcal mol⁻¹)¹³ similar to that of [HNi(dmpe)₂]⁺. Treatment of $[Rh(dmpe)_2][OTf]$ with H_2/CO_2 (1 atm of a 1:1 mixture) in CD_3CN led to formation of some $[H_2Rh(dmpe)_2][OTf]$ but no formate over 4 days; however, inclusion of ${}^{t}Bu(CH_{2})_{2}B(C_{8}H_{14})$ in the reaction led to the generation of formate (¹H NMR signal at δ 8.24) along with the Rh product of hydride transfer, [HRh- $(dmpe)_2(MeCN)$ ²⁺, over a few hours (Scheme 9). With one equivalent of trialkylborane, the yield of formate was $\sim 25\%$ (by NMR integration). Some $[Rh(dmpe)_2]^+$ remained unconverted during the course of the reaction, consistent with the unfavorable thermodynamics of H₂ oxidative addition (uphill by 0.44 kcal mol⁻¹)¹³ and the low (~0.5 atm) H₂ pressure; 1 atm of H₂ is required for complete conversion.



CONCLUSIONS

The late transition metal bis(diphosphine) hydride complexes $[HNi(dmpe)_2]^+$ and $[H_2Rh(dmpe)_2]^+$ (as well as a rhenium—boroxycarbene complex) are able to reduce carbon dioxide to formate, with the assistance of a trialkylborane that shifts the otherwise unfavorable equilibrium by forming a formate—borane adduct. Furthermore, H₂ can be used directly in these systems to reduce CO₂. As judged by NMR spectroscopy, the formate—borane adduct is relatively weak (in comparison to those generated in the CO reductions studied previously) and hence might be broken sufficiently easily to close a catalytic cycle. While overall catalysis has so far eluded us, the prospects for developing catalytic systems based on this chemistry appear promising.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line or Schlenk techniques or in a glovebox under a nitrogen atmosphere. All reactions were carried out in an inert atmosphere, unless otherwise noted. Under standard glovebox conditions, petroleum ether, diethyl ether, benzene, toluene, and tetrahydrofuran were used without purging, such that traces of those solvents were in the atmosphere, and could be found intermixed in the solvent bottles. The solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or calcium hydride or by the method of Grubbs.¹⁴ All NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. Chlorobenzene- d_5 (C₆D₅Cl) and dichloromethane- d_2 (CD₂Cl₂) were freeze-pump-thaw degassed three times before being run through a small column of activated alumina. Tetrahydrofuran- d_8 (THF- d_8) was purchased in a sealed ampule and dried by passage through activated alumina. Unless noted, other materials were used as received. [1][BF₄],^{2a} 2, [Pt(dmpe)₂][PF₆],¹⁵ [HPt(dmpe)₂][PF₆],¹⁵ [Ni(dmpe)₂][BF₄],¹² [HNi(dmpe)₂][PF₆],¹⁵ tBu(CH₂)₂B(C₈H₁₄),¹⁶ [HNi(dmpe)₂][PF₆],¹⁵ tBu(CH₂)₂B(C₈H₁₄),¹⁶ [HNi(dmpe)₂][PF₆],¹⁵ tBu(CH₂)₂B(C₈H₁₄),¹⁶ [HNi(dmpe)₂],¹² [HNi(dmpe)₂][PF₆],¹⁵ tBu(CH₂)₂B(C₈H₁₄),¹⁶ [HNi(dmpe)₂],¹⁵ [H $[Bu_4N][HCO_2],^{17}[Ni(dmpe)_2][BAr^F_4]_2,^{20}$ and $[Rh(dmpe)_2][OTf]^{13,18}$ were synthesized by literature methods. All other materials were readily commercially available, and used as received. ¹H and ¹³C NMR spectra were recorded on Varian Mercury 300 MHz, 400-MR 400 MHz, INOVA 500 MHz, or INOVA 600 MHz spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to residual internal protio solvent for ¹H and ${}^{13}C{{}^{1}H}$ spectra. Other nuclei were referenced to an external standard: H₃PO₄ (³¹P), 15% BF₃ • Et₂O/CDCl₃ (^{11}B) , CFCl₃ (^{19}F) , all at 0 ppm.

EXPERIMENTAL PROCEDURES

CO2 Reduction Involving Rhenium Carbonyl Complexes. Reaction of 2 with CO2. A 10 mL vial was charged with 26.4 mg (0.0251 mmol) of [1][BF₄] and ~0.6 mL of C₆D₅Cl. With stirring, 25.1 µL (0.0251 mmol) of NaHBEt₃ (1.0 M in toluene) was added dropwise to provide a pale yellow solution. The reaction mixture was transferred to a J-Young NMR tube, and initial spectroscopic measurements showed clean conversion to boroxycarbene 2. The tube was placed under vacuum for 1 min with gentle shaking to degas, and 1 atm of CO₂ was then admitted to the tube. NMR spectroscopy after 5 min showed complete conversion to $1 \cdot (HCO_2)$, most of which precipitated overnight. ¹H NMR (C₆D₅Cl, 500 MHz): toluene and BEt₃ are omitted, but overlap with some aliphatic peaks, preventing good integration; δ 0.69 (br s, 4H), 1.59 (br s, overlapping), 1.84 (br, overlapping), 2.05 (br m, overlapping), 2.73 (br, 4H), 7.41 (br, 12H), 8.45 (s, 1H, HCO_2^{-}). ³¹P{¹H} NMR (C₆D₅Cl, 121 MHz): δ 2.2. IR (C₆D₅Cl): $\nu_{\rm CO}$ 1993, 1620 cm⁻¹. ¹³C NMR spectra could not be acquired because of the low solubility of the product.

Reaction of [1][BF₄] with [Bu₄N][HCO₂]. A J-Young NMR tube was charged with 29.1 mg (0.0276 mmol) of [1][BF₄], 7.9 mg (0.0276 mmol) of [Bu₄N][HCO₂], and ~0.6 mL of C₆D₅Cl. After 15 min, ¹H and ³¹P{¹H} NMR spectroscopy showed essentially complete conversion to 1 · (HCO₂). After about 30 min some precipitates were observed, and precipitation of white solids continued over the next 3 h. At this time, the solution was decanted, and IR spectroscopy showed resonances that matched the preparation of 1 · (HCO₂) from CO₂; an additional peak at 1660 cm⁻¹ is unidentified, however. ¹H NMR (C₆D₅Cl, 400 MHz): [Bu₄N]⁺ peaks omitted; δ 0.68 (br, 4H), 0.95 (br, 4H), 1.58 (br, 4H), 1.83 (br, 16H), 2.03 (br, 4H), 2.75 (br, 4H), 7.1–7.2 (m, 12H), 7.4 (m, 8H), 8.49 (s, 1H, [HCO₂]⁻). ³¹P{¹H} NMR (C₆D₅Cl, 162 MHz): δ 2.4. IR (C₆D₅Cl): ν_{CO} 1993, 1660, 1621 cm⁻¹.

Reaction of $[1][BF_4]$ and $[HNi(dmpe)_2][PF_6]$ with CO_2 in C_6D_5CI . A J-Young NMR tube was charged with 24.3 mg (0.0231 mmol) of [1]-[BF₄], 11.6 mg (0.0231 mmol) of [HNi(dmpe)₂][PF₆], and ~0.6 mL of C₆D₅Cl. The tube was sealed, and initial NMR spectroscopic measurements showed no reaction. One atmosphere of CO₂ was added; after \sim 20 min some formate was observed, which grew in over a few hours. During this time precipitates formed, and after about 12 h there was essentially no formate-containing product in solution. The solids were collected, washed with CD₃CN (to extract $[Ni(dmpe)_2][PF_6]_2$) and C_6D_5Cl , and treated with C_6D_5Cl containing 3.8 μ L (0.0462 mmol, 2 equiv) of pyridine, which dissolved most of the solids. An asymmetric product was observed by NMR spectroscopy that was assigned as $1 \cdot (HCO_2)$ (pyridine). ¹H NMR (C₆D₅Cl, 300 MHz): δ 0.44 (br, 2H, Ph₂-PCH₂CH₂BR₂), 0.68 (br, 2H, Ph₂PCH₂CH₂BR₂), 0.95 (2H, Ph₂PCH₂-CH₂BR₂), 1.09 (2H, Ph₂PCH₂CH₂BR₂), 1.34 (6H, Ph₂PCH₂CH₂BR₂), 1.5-2.0 (m, 18H, Ph₂PCH₂CH₂BR₂), 2.1 (br, 4H, Ph₂PCH₂CH₂BR₂), 2.47 (br, 2H, Ph₂PCH₂CH₂BR₂), 2.93 (m, 2H, Ph₂PCH₂CH₂BR₂), 6.5-7.5 (m, mixture of Ph_2PR , free and bound C_6H_5N), 8.41 (m, 2H, C_6H_5N), 8.88 (1H, HCO₂). ³¹P{¹H} NMR (C₆D₅Cl, 121 MHz): δ 1.95 (d, J_{PP} = 77 Hz), 2.98 (d, $J_{\rm PP}$ = 76 Hz).

CO₂ Reduction by Nickel and Boranes in Chlorobenzene. *Reaction of* [*HNi*(*dmpe*)₂][*PF*₆] *with CO*₂. A J-Young NMR tube was charged with 12.2 mg (0.0242 mmol) of [*HNi*(*dmpe*)₂][*PF*₆] and ~0.6 mL of C_6D_5Cl . The tube was degassed by exposure to vacuum briefly with gentle shaking, and 1 atm of CO₂ was admitted to the tube. The tube was sealed, shaken well, and monitored by NMR spectroscopy. A small resonance assigned to formate was observed at δ 8.84, integrating 1–2% relative to the Ni hydride. No increase in the formate resonance was observed over 48 h.

Reaction of $[HNi(dmpe)_2][PF_6]$ with ${}^{t}Bu(CH_2)_2B(C_8H_{14})$ and CO_2 . A solution of 6.7 mg (0.0327 mmol) of ${}^{t}Bu(CH_2)_2B(C_8H_{14})$ in ~0.6 mL of C₆D₅Cl was added to 16.5 mg (0.0327 mmol) of solid [HNi(dm pe_{2} [PF₆]. The reaction mixture was transferred to a J-Young NMR tube, and initial spectroscopic measurements were made. After two freeze-pump-thaw cycles, 1 atm of CO2 was admitted to the tube, and the reaction was monitored by NMR spectroscopy. After 24 h the reaction had reached partial conversion (with the formate resonance shifting from δ 8.73 to 8.66), which did not change over 4 days. Addition of \sim 16.0 mg (0.0327 mmol, 1 equiv nominal; about 2 equiv by NMR integration) of [hept₄N][Br] led to significant further growth of [hept₄N][HCO₂(BR₃)_n], which (along with excess [hept₄N][Br]) was the only soluble product (all hydride was consumed). The spectra agreed well with independently synthesized $[Bu_4N][HCO_2(BR_3)_n]$ (see below). ¹H NMR (C_6D_5Cl , 400 MHz): δ 0.78 (m, 2H, ^tBuCH₂CH₂B(C_8H_{14})), 0.88 (t, J = 6.8 Hz, $[\text{hept}_4\text{N}]^+$), 1.04 (s, 9H, ${}^tBuCH_2CH_2B(C_8H_{14})$), 1.1 (br, 2H, ^tBuCH₂CH₂B(C₈H₁₄)), 1.2-1.3 (br m, [hept₄N]⁺), 1.39 (m, 2H, ^tBuCH₂CH₂B(C₈H₁₄)), 1.5 (br, [hept₄N]⁺), 1.76 (br, 2H, ^tBu-CH₂CH₂B(C₈H₁₄)), 1.94 (br, 4H, ^tBuCH₂CH₂B(C₈H₁₄)), 2.2 (br, 6H, $^{t}BuCH_{2}CH_{2}B(C_{8}H_{14})), 3.11 (m, [hept_{4}N]^{+}), 8.83 (1H, [HCO_{2}(BR_{3})_{n}]^{-}).$ No discernible signals were observed by ¹¹B NMR spectroscopy, presumably

due to broadening and overlapping with the borosilicate glass in the probe construction.

Reaction of [*Bu*₄*N*][*HCO*₂] *with* ^t*Bu*(*CH*₂)₂*B*(*C*₈*H*₁₄) *in C*₆*D*₅*Cl*. A J-Young NMR tube was charged with 15.8 mg (0.0549 mmol) of [*Bu*₄*N*][*HCO*₂], 11.3 mg (0.0549 mmol) of ^t*Bu*(*CH*₂)₂*B*(*C*₈*H*₁₄), and ~0.6 mL of *C*₆*D*₅*Cl*. NMR spectroscopy revealed a formate resonance at δ 8.89, well upfield of [*Bu*₄*N*][*HCO*₂] in the absence of borane (δ 9.58). ¹H NMR (*C*₆*D*₅*Cl*, 500 MHz): δ 0.76 (m, ^t*BuCH*₂*CH*₂*B*(*C*₈*H*₁₄), 2H), 0.86 (t, *J* = 7.3 Hz, N(*CH*₂*CH*₂*CH*₂*CH*₃)₄, 12H), 1.04 (s, ^t*BuCH*₂*CH*₂*B*(*C*₈*H*₁₄), 9H), 1.25 (q, *J* = 7.2 Hz, N(*CH*₂*CH*₂*CH*₂*CH*₂*B*(*C*₈*H*₁₄), overlapping), 1.83 (br, ^t*BuCH*₂*CH*₂*B*(*C*₈*H*₁₄), 2H), 1.97 (br, ^t*BuCH*₂*CH*₂*B*(*C*₈*H*₁₄), 4H), 2.28 (br, ^t*BuCH*₂*CH*₂*B*(*C*₈*H*₁₄), 6H), 3.00 (m, N(*CH*₂*B*(*C*₈*H*₁₄), 4H), 2.28 (br, ^t*BuCH*₂*CH*₂*B*(*C*₈*H*₁₄), 6H), 3.00 (m, N(*CH*₂*CH*₂*CH*₂*CH*₃)₄), 8.89 (s, [*HCO*₂(*BR*₃)_{*n*}]⁻, 1H). ¹³*C*-{¹H</sup>} NMR (*C*₆*D*₅*Cl*, 126 MHz): δ 13.66, 19.87, 23.91, 26.80, 30.05, 31.35, 33.0 (br), 40.75, 58.66, 168.48. ¹¹B NMR (*C*₆*D*₅*Cl*, 160 MHz): δ 2.7.

Titration of $[Bu_4N][HCO_2]$ with ${}^tBu(CH_2)_2B(C_8H_{14})$ in C_6D_5Cl . A J-Young NMR tube was charged with 22.1 mg (0.0769 mmol) of $[Bu_4N][HCO_2]$ and 0.600 mL of C_6D_5Cl . Initial NMR spectra were collected. A 1.0 M solution of ${}^tBu(CH_2)_2B(C_8H_{14})$ in C_6D_5Cl was prepared, and ~19 μ L (~0.25 equiv) was added by syringe, followed by collection of NMR spectra. Integration showed that 0.20 equiv was added. This procedure was repeated so that spectra with 0, 0.2, 0.75, 1.5, 2.4, 3.4, 5.1, and 7.0 equiv of borane (by NMR integration) were obtained. Spectra are shown in the SI as Figure S15.

General Procedure for Reactions of $[HNi(dmpe)_2][PF_6]$ with CO_2 and Other Boranes. A solution of borane (~0.03 mmol) in ~0.6 mL of C_6D_5Cl was added to an equimolar amount of solid $[HNi(dmpe)_2]$ - $[PF_6]$. The reaction mixture was transferred to a J-Young NMR tube, and initial spectroscopic measurements were made. After two freeze– pump–thaw cycles, 1 atm of CO_2 was admitted to the tube, and the reaction was monitored by NMR spectroscopy.

Isopropyl Pinacol Borate. The reaction proceeded essentially the same as that with no borane added. The formate resonance appears between δ 8.70 and 8.74 during the reaction.

Triphenylborane. Complete disappearance of $[HNi(dmpe)_2]^+$ was observed, along with the appearance of a presumed formate resonance at δ 8.8 and some unidentified peaks (δ 5–6).

Trimesity/borane. No change in conversion was observed as compared to the reaction without borane. A minor formate resonance was observed at δ 8.63.

 $B(C_6F_5)_3$. Shortly after mixing $B(C_6F_5)_3$ and $[HNi(dmpe)_2][PF_6]$, a mixture of [Ni(dmpe)₂]²⁺ and [HNi(dmpe)₂]⁺ was observed by ¹H NMR spectroscopy. ¹⁹F and ¹¹B NMR showed complete consumption of $B(C_6F_5)_3$ and were consistent with formation of a four-coordinate borate. The observed ¹¹B NMR resonance is slightly downfield from the expected chemical shift of $[HB(C_6F_5)_3]^-$, and the resonance is broadened beyond being able to observe coupling (probably due to exchange with some free borane). Even after CO2 addition, no formate was observed after ~ 12 h at room temperature. ¹H NMR (C₆D₅Cl, 500 MHz): δ -14.40 ([*H*Ni(dmpe)₂]⁺), 1.0 (m, [Ni(*Me*₂PCH₂CH₂P*Me*₂)₂]²⁺), 1.18 (m, $[HNi(Me_2PCH_2CH_2PMe_2)_2]^+$), 1.28 (m, $[Ni(Me_2PCH_2CH_2-H_2)_2]^+$) $PMe_{2}_{2}^{2^{+}}$), 1.55 (m, [HNi(Me_{2}PCH_{2}CH_{2}PMe_{2})_{2}]^{+}). ³¹P{¹H} NMR $(C_6D_5Cl, 121 \text{ MHz}): \delta 24.3 ([HNi(dmpe)_2]^+), 43.0 ([Ni(dmpe)_2]^{2+}).$ ¹⁹F NMR (C₆D₅Cl, 282 MHz): δ –165.35 (m, 6F), –160.38 (t, J_{FF} = 20.6 Hz, 3F), -134.64 (m, 6F). ¹¹B NMR (C₆D₅Cl, 160 MHz): $\delta - 0.48$ (br).

CO₂ Reductions by Nickel and Boranes in Acetonitrile. General Procedure for Reactions of $[HNi(dmpe)_2][PF_6]$ in Acetonitrile. A J-Young NMR tube was charged with $[HNi(dmpe)_2][PF_6]$ (~0.03 mmol), the appropriate amount of ^tBu(CH₂)₂B(C₈H₁₄) (0, 1, 10 equiv), and ~0.6 mL of CD₃CN. The tube was sealed, initial NMR measurements were taken, and the atmosphere was replaced with 1 atm of CO₂ (after freeze-pump-thaw degassing twice). The reactions were monitored periodically by multinuclear NMR spectroscopy until equilibrium was reached (under 24 h), with conversion at equilibrium estimated by integration.

 CO_2 without borane. In the absence of trialkylborane, only about 5% hydride transfer was observed. The only two species observed in solution were unreacted [HNi(dmpe)₂]⁺ and small amounts of [Ni(dmpe)₂]²⁺.

One equivalent of ${}^{t}Bu(CH_{2})_{2}B(C_{8}H_{14})$ and CO_{2} . When 1 equiv of trialkylborane was added, about 65% hydride transfer was observed.

Ten equivalents of ${}^{t}Bu(CH_2)_2B(C_8H_{14})$ and CO_2 . When excess trialkylborane was added, nearly quantitative hydride transfer was observed. Only a trace of unreacted $[HNi(dmpe)_2]^+$ was observed.

Reaction of [Ni(dmpe)₂][PF₆]₂ with [Bu₄N][HCO₂]. A small vial was charged with 19.7 mg (0.0359 mmol) of [Ni(dmpe)₂][PF₆]₂, and 10.3 mg (0.0359 mmol), and ~0.6 mL of CD₃CN. As the mixture was stirred, a color change from yellow to dark orange was observed. The mixture was transferred to a J-Young NMR tube and monitored. The color faded to a lighter orange over a few minutes. After 15 min, almost complete conversion (~95%) to [HNi(dmpe)₂][PF₆] was observed, although a slight excess of [HCO₂]⁻ (δ 8.58) was still present.

Addition of $[Bu_4N][HCO_2]$ after Reduction. A 1:10 mixture of [HNi-(dmpe)₂][PF₆] and ¹Bu(CH₂)₂B(C₈H₁₄) was treated with CO₂ according to the general procedure. After the reaction was complete the tube was brought into a glovebox and 1 equiv of $[Bu_4N][HCO_2]$ was added to the tube. The resonance at δ 8.210 roughly doubled in intensity (and shifted by only 0.003 ppm), thereby confirming that formate is the product of CO₂ reduction.

Reaction of $[HNi(dmpe)_2]^+$ and ${}^tBu(CH_2)_2B(C_8H_{14})$ with ${}^{13}CO_2$. A J-Young NMR tube was charged with 18.9 mg (0.0374 mmol) of $[HNi(dmpe)_2][PF_6]$, 38.6 mg (0.187 mmol, 5 equiv) of ${}^tBu(CH_2)_2$ -B (C_8H_{14}) , and ~0.6 mL of CD₃CN. After initial NMR spectroscopic measurements, the tube was subjected to two freeze–pump–thaw cycles, and 0.0187 mmol (0.5 equiv) of ${}^{13}CO_2$ was condensed from a 2.87 mL calibrated gas bulb (11.8 mmHg). About 5% conversion to $[Ni(dmpe)_2][PF_6]_2$ had occurred after 30 min, and a small doublet could be seen by 1 H NMR. After 12 h, a large doublet at δ 8.21 (202 Hz) was visible, consistent with formation of $[H^{13}CO_2(BR_3)_n]^-$.

Attempted Catalytic Reactions. Attempted Catalysis in Acetonitrile. A J-Young NMR tube was charged with 5.0 mg (0.0102 mmol, 1 equiv) of [Ni(dmpe)₂][BF₄]₂, 7.1 μ L (0.0511 mmol, 5 equiv) of NEt₃, 10.5 mg (0.0511 mmol, 5 equiv) of ^tBu(CH₂)₂B(C₈H₁₄), and ~0.6 mL of CD₃CN. The tube was subjected to two freeze–pump–thaw cycles, and 1 atm of a 1:1 H₂/CO₂ mixture (mixed in a large round bulb on a vacuum line) was admitted. The reaction was monitored by NMR spectroscopy, and a small formate peak gradually grew in over 3 days, along with another product, $\delta \sim 6.8$. Heating the tube to 60 °C for ~24 h generated visible amounts of [HNi(dmpe)₂]⁺, but also several unidentified products.

Attempted Catalysis in Chlorobenzene. A J-Young NMR tube was charged with 35.5 mg (0.0174 mmol, 1 equiv) of $[Ni(dmpe)_2][BAr^F_4]_2$, 10.0 μ L (0.0695 mmol, 4 equiv) of NEt₃, 3.6 mg (0.0174, 1 equiv) of ^tBu(CH₂)₂B(C₈H₁₄), and ~0.6 mL of C₆D₅Cl. The Ni²⁺ formed a yellow oil at the bottom of the tube if it was allowed to settle. The tube was subjected to two freeze–pump–thaw cycles, and 1 atm of a 1:1 mixture of H₂/CO₂ (mixed in a large round bulb on a vacuum line) was admitted to the tube. NMR spectroscopic monitoring showed steady generation of [HNi(dmpe)₂][BAr^F₄], but no evidence of formate was observed.

Hydrogen Cleavage Reactions. Hydrogen Cleavage in Acetonitrile. A J-Young NMR tube was charged with 32.6 mg (0.0159 mmol) of $[Ni(dmpe)_2][Bar^F_4]_2$, 8.9 μ L (0.0639 mmol, 4 equiv) of NEt₃, and ~0.6 mL of CD₃CN. The tube was subjected to two freeze–pump– thaw cycles, and 1 atm of H₂ was admitted. The reaction was monitored by NMR spectroscopy, revealing about 30% conversion to $[HNi(dm-pe)_2]^+$ over 3 days.

Hydrogen Cleavage in Chlorobenzene. A J-Young NMR tube was charged with 29.0 mg (0.0140 mmol) of $[Ni(dmpe)_2][BAr^F_4]_2$, 7.9 μ L (0.0568 mmol, 4 equiv) of NEt₃, and ~0.6 mL of C₆D₅Cl. The Ni dication was insoluble and formed an oil at the bottom of the tube. Initial NMR measurements detected no Ni species. The tube was subjected to two freeze–pump–thaw cycles, and 1 atm of H₂ was admitted. The tube was sealed and monitored by NMR, which revealed relatively rapid growth of $[HNi(dmpe)_2][BAr^F_4]$. After 18 h, no insolubles were visible, and a large amount of Ni hydride was present. The two-phase reaction prevented precise yields or equilibrium measurements.

CO₂ Reduction by Rhodium and Boranes in Acetonitrile. Reaction of $[Rh(dmpe)_2][OTf]$ with H_2/CO_2 . A J-Young NMR tube was charged with 19 mg (0.0344 mmol) of $[Rh(dmpe)_2][OTf]$ and ~0.6 mL of CD₃CN. The tube was placed under 1 atm of a 1:1 mixture of H₂ and CO₂, mixed by diffusion in a large round bulb on a vacuum manifold. The reaction was monitored by multinuclear NMR, which showed formation of $[H_2Rh(dmpe)_2][OTf]$, but no more than a trace of formate was observed.

Reaction of [Rh(dmpe)_][OTf] with ^tBu(CH₂)₂B(C₈H₁₄) and H₂/CO₂. A J-Young NMR tube was charged with 15.9 mg (0.0288 mmol) of [Rh(dmpe)_][OTf], 5.9 mg (0.0288 mmol) of ^tBu(CH₂)₂B(C₈H₁₄), and ~0.6 mL of CD₃CN. The tube was placed under 1 atm of a 1:1 mixture of H₂ and CO₂, mixed by diffusion in a large round bulb on a vacuum manifold. The reaction was monitored by NMR spectroscopy, which showed growth of signals attributable to $[H_2Rh(dmpe)_2]^+ (\delta - 10.25$, br d, $J_{PH} = 146.4$) and eventually $[HCO_2(BR_3)_n]^- (\delta 8.25)$ and $[HRh(dmpe)_2(MeCN)]^{2+} (\delta - 18.57, m)$.

ASSOCIATED CONTENT

Supporting Information. Accompanying NMR spectra for reactions described in the Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jal@caltech.edu; bercaw@caltech.edu.

ACKNOWLEDGMENT

This research was generously funded by BP through the Methane Conversion Cooperative (MC^2) Program and by the Moore Foundation. The Varian 400-MR spectrometer was purchased through NIH grant RR027690.

REFERENCES

 (a) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Chem. Soc. Rev. 2009, 38, 89. (b) Leitner, W. Angew. Chem., Int. Ed. 1995, 34, 2207. (c) Jessop, P. G.; Joó, F.; Tai, C. Coord. Chem. Rev. 2004, 248, 2425.

(2) (a) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. J. Am. Chem. Soc.
2008, 130, 11874. (b) Elowe, P. R.; West, N. M.; Labinger, J. A.; Bercaw, J. E. Organometallics 2009, 28, 6218. (c) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. J. Am. Chem. Soc. 2010, 132, 3301. (d) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. Organometallics 2010, 29, 4499. (e) West, N. M.; Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. Organometallics 2010, 29, 4499. (e) West, N. M.; Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. Cord. Chem. Rev. 2011, 255, 881. (f) West, N. M.; Labinger, J. A.; Bercaw, J. E. Organometallics 2011, 30, 2690.

(3) Rozovskii, A. Y.; Lin, G. I. Top. Catal. 2003, 22, 137.

(4) (a) Hammouche, M.; Lexa, D.; Momenteau, M.; Saveant, J. M. J. Am. Chem. Soc. **1991**, *113*, 8455. (b) Bhugun, I.; Lexa, D.; Saveant, J.-M. J. Am. Chem. Soc. **1994**, *116*, 5015. (c) Bhugun, I.; Lexa, D.; Saveant, J.-M. J. Phys. Chem. **1996**, *100*, 19981. (d) Bhugun, I.; Lexa, D.;

Saveant, J.-M. J. Am. Chem. Soc. 1996, 118, 1769. (e) Gennaro, A.; Isse,
 A. A.; Severin, M.-G.; Vianello, E.; Bhugun, I.; Saveant, J.-M. J. Chem. Soc.,
 Faraday Trans. 1996, 92, 3963. (f) Saveant, J.-M. Chem. Rev. 2008, 108, 2348. (g) Wong, K.-Y.; Chung, W.-H.; Lau, C.-P. J. Electroanal. Chem.
 1998, 453, 161.

(5) (a) Steffey, B. D.; Curtis, C. J.; DuBois, D. L. Organometallics 1995, 14, 4937. (b) Dubois, M. R.; Dubois, D. L. Acc. Chem. Res. 2009, 42, 1974. (c) Jeoung, J.-H.; Dobbek, H. Science 2007, 318, 1461.

(6) Boffa, A.; Lin, C.; Bell, A. T.; Somorjai, G. A. J. Catal. 1994, 149, 149.

(7) Laitar, D. S.; Muller, P.; Sadighi, J. P. J. Am. Chem. Soc. 2005, 127, 17196.

(8) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. R. J. Am. Chem. Soc. 2010, 132, 8872.

(9) (a) Stephan, D. W.; Erker, G. Angew. Chem., Int. Ed. 2010, 49, 46.
(b) Ashley, A. E.; Thompson, A. L.; O'Hare, D. Angew. Chem., Int. Ed. 2009, 48, 9839. (c) Tran, S. D.; Tronic, T. A.; Kaminsky, W.; Heinekey, D. M.; Mayer, J. M. Inorg. Chim. Acta 2011, 369, 126.

(10) (a) Matsuo, T.; Kawaguchi, H. J. Am. Chem. Soc. 2006, 128, 12362. (b) Berkefeld, A.; Piers, W. E.; Parvez, M. J. Am. Chem. Soc. 2010, 132, 10660.

(11) DuBois, D. L.; Berning, D. E. Appl. Organomet. Chem. 2000, 14, 860.

(12) (a) Berning, D. E.; Noll, B. C.; DuBois, D. L. J. Am. Chem. Soc.
1999, 121, 11432. (b) Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll,
B. C.; Rakowski DuBois, M. C.; DuBois, D. L. Organometallics 2001,
20, 1832. (c) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. J. Am. Chem. Soc. 2002, 124, 1918.

(13) Wilson, A. D.; Miller, A. J. M.; DuBois, D. L.; Labinger, J. A.; Bercaw, J. E. Inorg. Chem. **2010**, *49*, 3918.

(14) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(15) Miedaner, A.; DuBois, D. L.; Curtis, C. J.; Haltiwanger, R. C. Organometallics 1993, 12, 299.

(16) Hirano, K.; Yorimitsu, H.; Oshima, K. Org. Lett. 2005, 7, 4689.
(17) Silavwe, N. D.; Goldman, A. S.; Ritter, R.; Tyler, D. R. Inorg. Chem. 1989, 28, 1231.

(18) DuBois, D. L.; Blake, D. M.; Miedaner, A.; Curtis, C. J.; DuBois, M. R.; Franz, J. A.; Linehan, J. C. *Organometallics* **2006**, *25*, 4414.