Trialkylborane-Assisted CO₂ Reduction by Late Transition Metals

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Supporting Information

NMR spectra to accompany Experimental Section.

**Figure S1.** Reaction of 2 with CO₂: ¹H NMR of 1•(HCO₂).
Figure S2. Reaction of 2 with CO$_2$: $^{31}$P{$^1$H} NMR of 1•(HCO$_2$).

Figure S3. Reaction of [1][BF$_4$] with [Bu$_4$N][HCO$_2$]: $^1$H NMR of 1•(HCO$_2$).
Figure S4. Reaction of [I][BF₄] and [HNi(dmpe)₂][PF₆] with CO₂ in C₆D₅Cl: Time course (¹H NMR excerpts).

Figure S5. Reaction of [I][BF₄] and [HNi(dmpe)₂][PF₆] with CO₂ in C₆D₅Cl: ¹H NMR of 1•(HCO₂)(pyridine).
**Figure S6.** Reaction of [1][BF₄] and [HNi(dmpe)₂][PF₆] with CO₂ in C₆D₅Cl: ³¹P{¹H} NMR of 1•(HCO₂)(pyridine).

**Figure S7.** Reaction of [HNi(dmpe)₂][PF₆] with CO₂ in C₆D₅Cl (¹H NMR). Spectrum shows almost entirely unreacted Ni hydride, with trace formate.
Figure S8. Reaction of \([\text{HNi(dmpe)}_2][\text{PF}_6]\) (δ 24.68) with \(\text{CO}_2\) in \(\text{C}_6\text{D}_5\text{Cl}\) (\(^{31}\text{P NMR}\)).

Figure S9. Reaction of \([\text{HNi(dmpe)}_2][\text{PF}_6]\) with \(^1\text{Bu(CH}_2)_2\text{B(C}_8\text{H}_{14})\) and \(\text{CO}_2\): Time course (\(^1\text{H NMR alkyl region}\)).
Figure S10. Reaction of \([\text{HNi}(\text{dmpe})_2][\text{PF}_6]\) with \(\text{tBu(CH}_2)_2\text{B(C}_8\text{H}_{14})\) and \(\text{CO}_2\): Time course (\(^1\text{H NMR formate and hydride region)\).

Figure S11. Reaction of \([\text{HNi}(\text{dmpe})_2]^+\) with \(\text{tBu(CH}_2)_2\text{B(C}_8\text{H}_{14})\) and \(\text{CO}_2\): \(^1\text{H NMR after addition of [hept}_4\text{N}[\text{Br}]\) (inset shows hydride region).
Figure S12. Reaction of [Bu₄N][HCO₂] with 'Bu(CH₂)₂B(C₈H₁₄) in C₆D₅Cl: 'H NMR of [Bu₄N][HCO₂BR₃].

Figure S13. Reaction of [Bu₄N][HCO₂] with 'Bu(CH₂)₂B(C₈H₁₄) in C₆D₅Cl: '³C{'H} NMR of [Bu₄N][HCO₂BR₃].
Figure S14. Reaction of [Bu₄N][HCO₂] with 'Bu(CH₂)₂B(C₈H₁₄) in C₆D₅Cl: ¹¹B NMR of [Bu₄N][HCO₂BR₃].

Figure S15. Titration of [Bu₄N][HCO₂] with 'Bu(CH₂)₂B(C₈H₁₄) in C₆D₅Cl (formate region).
Figure S16. Titration of [Bu₄N][HCO₂] with tBu(CH₂)₂B(C₈H₁₄) in C₆D₅Cl (alkyl region omitted).

Figure S17. Reaction of [HNi(dmpe)₂]⁺ and BPh₃ before CO₂ addition (bottom); 5 hours after addition (middle); 2 days after addition (top).
Figure S18. Reaction of [HNi(dmpe)$_2$]$^+$, BMes$_3$, and CO$_2$: $^1$H NMR.

Figure S19. Reaction of [HNi(dmpe)$_2$]$^+$, BMes$_3$, and CO$_2$: $^1$H NMR (blow-up).
Figure S20. Reaction of $\text{[HNi(dmpe)$_2$]}^+$ with $\text{B(C}_6\text{F}_3)_3$ and $\text{CO}_2$: $^1$H NMR.

Figure S21. Reaction of $\text{[HNi(dmpe)$_2$]}^+$ with $\text{B(C}_6\text{F}_3)_3$ and $\text{CO}_2$: $^{19}$F NMR.
Figure S22. Reaction of $[\text{HNi(dmpe)}_2]^+$ with B($C_6F_5)_3$ and CO$_2$: $^{11}$B NMR.

Figure S23. Reaction of $[\text{HNi(dmpe)}_2]^+$ with $^t$Bu(CH$_2$)$_2$B($C_8H_{14}$) and CO$_2$ in MeCN: Overlay ($^1$H NMR, formate region) of reactions at equilibrium with 0 (red), 1 (green) and 10 (blue) equiv $^t$Bu(CH$_2$)$_2$B($C_8H_{14}$).
Figure S24. Reaction of [HNi(dmpe)$_2$]$^+$ with $^t$Bu(CH$_2$)$_2$B(C$_8$H$_{14}$) and CO$_2$ in MeCN: Comparison ($^1$H NMR) of reactions at equilibrium with 0 (bottom), 1 (middle) and 10 (top) equiv $^t$Bu(CH$_2$)$_2$B(C$_8$H$_{14}$).

Figure S25. Reaction of [HNi(dmpe)$_2$]$^+$ with $^t$Bu(CH$_2$)$_2$B(C$_8$H$_{14}$) and CO$_2$ in MeCN: Comparison ($^3$P$^1$H$^1$ NMR) of reactions at equilibrium with 0 (bottom), 1 (middle) and 10 (top) equiv $^t$Bu(CH$_2$)$_2$B(C$_8$H$_{14}$).
Figure S26. Reaction of [Ni(dmpe)$_2$][PF$_6$]$_2$ with [Bu$_4$N][HCO$_2$]: $^1$H NMR.

Figure S27. Reaction of [Ni(dmpe)$_2$][PF$_6$]$_2$ with [Bu$_4$N][HCO$_2$]: $^{31}$P{$^1$H} NMR.
Figure S28. Reaction of $[\mathrm{HNi(dmpe)}_2]^+$ with $^t\mathrm{Bu}(\mathrm{CH}_2)_2\mathrm{B}(\mathrm{C}_8\mathrm{H}_{14})$ and $\mathrm{CO}_2$: $^1\mathrm{H}$ NMR (formate region) before (red) and after (blue) addition of $[\mathrm{Bu}_4\mathrm{N}][\mathrm{HCO}_2]$.

Figure S29. Reaction of $[\mathrm{HNi(dmpe)}_2]^+$ with $^t\mathrm{Bu}(\mathrm{CH}_2)_2\mathrm{B}(\mathrm{C}_8\mathrm{H}_{14})$ and $^{13}\mathrm{CO}_2$: $^1\mathrm{H}$ NMR (formate region) after 12 hours.
**Figure S30.** Reaction of [HNi(dmpe)$_2$]$^+$ with $^t$Bu(CH$_2)_2$B(C$_8$H$_{14}$) and $^{13}$CO$_2$: $^{13}$C{$^1$H} NMR after 12 hours.

**Figure S31.** Attempted catalysis in CD$_3$CN: $^1$H NMR time course (over 3 days).
Figure S32. Attempted catalysis in CD$_3$CN: $^1$H NMR time course (over 3 days).

Figure S33. Attempted catalysis in C$_6$D$_5$Cl: $^1$H NMR time course.
**Figure S34.** H₂ cleavage by [Ni(dmpe)₂][BAR₄F]₂: ¹H NMR time course (excess NEt₃ cut off) before H₂ addition (bottom), 30 minutes after H₂ addition (middle), and 12 hours after H₂ addition (top).

**Figure S35.** Reaction of [Rh(dmpe)₂]⁺ with CO₂ and H₂: ¹H NMR overlay (formate and hydride regions), after 3 hours (red), 24 hours (green), 4 days (blue).
**Figure S36.** Reaction of $[\text{Rh(dmpe)}_2]^+$ with CO$_2$ and H$_2$: $^{31}$P{$^1$H} NMR after 24 hours.

**Figure S37.** Reaction of $[\text{Rh(dmpe)}_2]^+$ with $'\text{Bu(CH}_2)_2\text{B(C}_8\text{H}_{14})$, CO$_2$ and H$_2$: $^1$H NMR time course (aliphatic region); red: before H$_2$/CO$_2$ addition. green, 1.5 hrs after H$_2$/CO$_2$ addition. yellow, 18 hrs after H$_2$/CO$_2$ addition.
**Figure S38.** Reaction of $[\text{Rh(dmpe)}_2]^+$ with $^t\text{Bu(CH}_2)_2\text{B(C}_8\text{H}_{14})$, CO$_2$ and H$_2$: $^1$H NMR time course (formate and hydride regions); red: before H$_2$/CO$_2$ addition. green, 1.5 hrs after H$_2$/CO$_2$ addition. yellow, 18 hrs after H$_2$/CO$_2$ addition.

**Figure S39.** Reaction of $[\text{Rh(dmpe)}_2]^+$ with $^t\text{Bu(CH}_2)_2\text{B(C}_8\text{H}_{14})$, CO$_2$ and H$_2$: $^{31}$P NMR (partially decoupled) after 18 hours.