Supporting information
For
Acetate-catalyzed hydroboration of CO₂ for the selective formation of methanol-equivalent products

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of CO\textsubscript{2} hydroboration to model A’ through the formation of acetate-bridged dinuclear boron model VI’.
Figure S1. $^1$H NMR spectrum ($C_6D_6$) of [TBA][OAc] (1).

Figure S2. $^{13}$C NMR spectrum ($C_6D_6$) of [TBA][OAc] (1).
Figure S3. $^1$H NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (5 mol%). Conditions: C$_6$D$_6$; T = 90 °C; Time: 26 h; Borane conversion (82% conv) to a 11/1/4.7 HCO$_2$Bpin/H$_2$C(OBpin)/MeOBpin mixture. The residual C$_6$D$_6$ peak was used as an internal standard.

Figure S4. $^{11}$B NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (5 mol%). Conditions: C$_6$D$_6$; T = 90 °C; Time: 26 h; Borane conversion: 82%.
Figure S5. $^1$H NMR monitoring data of the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (5 mol%) as a function of time. Conditions: C$_6$D$_6$; T = 90 °C. The residual C$_6$D$_6$ peak was used as an internal standard. *: HCO$_2$Bpin; °: H$_2$C(OBpin)$_2$; °°: MeOBpin.
Figure S6. $^{11}$B NMR monitoring data of the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (5 mol%) as a function of time. Conditions: $\text{C}_6\text{D}_6$; $T = 90^\circ\text{C}$.
Figure S7. $^1$H NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.5 mol%). Conditions: C$_6$D$_6$; T: 90 °C; Time: 2 h; Borane conversion: 40%.

Figure S8. $^{11}$B NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.5 mol%). Conditions: C$_6$D$_6$; T: 90 °C; Time: 2 h; Borane conversion: 40%.
Figure S9. $^1$H NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.5 mol%). Conditions: C$_6$D$_6$; T: 90 °C; Time: 20 h; Borane conversion: 96 %.

Figure S10. $^{11}$B NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.5 mol%). Conditions: C$_6$D$_6$; T: 90 °C; Time: 20 h; Borane conversion: 96 %. Compounds A, B and C correspond to hydroboration products HCO$_2$Bpin (A), H$_2$C(OBpin)$_2$ (B) and MeOBpin (C), respectively.
Figure S11. $^1$H NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.1 mol%). Conditions: C$_6$D$_6$, T = 90 °C, 20 h; Borane conversion: 94%. Internal standard: hexamethylbenzene.

Figure S12. $^{13}$C NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.1 mol%). Conditions: C$_6$D$_6$, T = 90 °C; 46 h; Borane conversion: 94%. Internal standard: hexamethylbenzene.
Figure S13. $^{11}$B NMR spectrum after the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.1 mol%). Conditions: C$_6$D$_6$, T = 90 °C, 46 h; Borane conversion: 94%; Internal standard: hexamethylbenzene.

Figure S14. $^1$H NMR monitoring spectra of the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.1 mol%). Conditions: C$_6$D$_6$, T = 90 °C. Internal standard: hexamethylbenzene.
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Figure S16. $^1$H NMR spectrum of the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.1 mol%) under solvent-free conditions after complete conversion to MeOBpin. Conditions: T = 90 ºC, 19 h. Internal standard: hexamethylbenzene.
Figure S17. $^{11}$B NMR spectrum of the reduction of CO$_2$ in the presence of HBpin and [TBA][OAc] (0.1 mol%) under solvent-free conditions after complete conversion to MeOBpin. Conditions: T = 90 °C, 19 h. Internal standard: hexamethylbenzene.

Figure S18. $^1$H NMR spectrum of the reduction of CO$_2$ in the presence of HBpin and NaOAc (0.1 mol% vs. H-Bpin). Conditions: C$_6$D$_5$Br, 120 °C, 65 h, Borane conv: 96% (hexamethylbenzene, internal standard).
Figure S19. $^{11}$B NMR spectrum of the reduction of CO$_2$ in the presence of HBpin and NaOAc (0.1 mol% vs. H-Bpin). Conditions: C$_6$D$_5$Br, 120 °C, 65 h. Borane conv: 96%.

Figure S20. $^1$H NMR spectrum of the reduction of CO$_2$ in the presence of HBpin and KOAc (0.1 mol% vs. H-Bpin). Conditions: C$_6$D$_5$Br, 120 °C, 65 h. Borane conversion: 94%. Internal standard: hexamethylbenzene.
**Figure S21.** $^1$B NMR spectrum of the reduction of CO$_2$ in the presence of HBpin and KOAc (0.1 mol% vs. H-Bpin). Conditions: C$_6$D$_5$Br, 120 °C, 65 h, 94% conversion to MeOBpin.

**Figure S22.** $^1$H NMR spectrum of the reduction of CO$_2$ by H$_3$B-SMe$_2$ catalyzed by [TBA][OAc] (10 mol% vs. BH$_3$-SMe$_2$). Conditions: C$_6$D$_6$, RT, 17 h. C$_6$Me$_6$ ($\delta$ 2.12) was used as an internal standard. Quantitative conversion to a 70/30 (MeOBO)$_3$/B(OMe)$_3$ mixture.
Figure S23. $^{11}\text{B}$ NMR spectrum of the reduction of CO$_2$ by H$_3$B-SMe$_2$ catalyzed by [TBA][OAc] (10 mol% vs. BH$_3$-SMe$_2$). Conditions: C$_6$D$_6$, RT, 17 h. C$_6$Me$_6$ was used as an internal standard. Quantitative borane conversion to a 70/30 (MeOBO)$_3$/B(OMe)$_3$ mixture.

Figure S24. $^1\text{H}$ NMR spectrum of the reduction of CO$_2$ by H$_3$B-SMe$_2$ catalyzed by [TBA][OAc] (1 mol% vs. BH$_3$-SMe$_2$). Conditions: C$_6$D$_6$, RT, 48 h. C$_6$Me$_6$ was used as an internal standard. 68% borane conversion to reduction product (MeOBO)$_3$. 
Figure S25. $^{11}$B NMR spectrum of the reduction of CO$_2$ by H$_3$B-SMe$_2$ catalyzed by [TBA][OAc] (1 mol% vs. BH$_3$-SMe$_2$). Conditions: C$_6$D$_6$, RT, 48 h. 68% borane conversion to reduction product (MeOBO)$_3$.

Figure S26. $^1$H NMR spectrum of the reduction of CO$_2$ by H$_3$B-SMe$_2$ catalyzed by [TBA][OAc] (0.1 mol% vs. BH$_3$-SMe$_2$). Conditions: C$_6$D$_6$, 60 °C, 20 h. C$_6$Me$_6$ was used as an internal standard. 75 % borane conversion to reduction product (MeOBO)$_3$. 
Figure S27. $^{11}$B NMR spectrum of the reduction of CO$_2$ by H$_3$B-SMe$_2$ catalyzed by [TBA][OAc] (0.1 mol% vs. BH$_3$-SMe$_2$). Conditions: C$_6$D$_6$, 60 °C, 20 h. C$_6$Me$_6$ was used as an internal standard. 75 % borane conversion to reduction product (MeOBO)$_3$. 
NMR data for stoichiometric monitoring reactions: 1/1 [TBA][OAc]/pinB–H; 1/1/1 [TBA][OAc]/pinB–H/CO₂ (1.5 atm)

Figure S28. ¹H NMR spectrum (C₆D₆) of the stoichiometric reaction between [TBA][OAc] and HBpin after 1h at room temperature.

Figure S29. ¹¹B NMR spectrum (C₆D₆) of the stoichiometric reaction between [TBA][OAc] and HBpin (1 h, RT).
Figure S30. $^{13}$C NMR spectrum ($C_6D_6$) after the stoichiometric reaction between [TBA][OAc] and HBpin (1h, RT).

Figure S31. $^1$H NMR spectrum ($C_6D_6$) of the reaction mixture after exposing a 1/1 [TBA][OAc] and HBpin under 1.5 atm of CO$_2$, consistent with the complete formation of the CO$_2$ insertion product [pinB(OAc)(O$_2$CH)]$^-$ (4).
Figure S32. $^1$H NMR spectrum ($\text{C}_6\text{D}_6$) of the reaction mixture after exposing a 1/1 [TBA][OAc] and HBpin under 1.5 atm of CO$_2$, consistent with the complete formation of the CO$_2$ insertion product [pinB(OAc)(O$_2$CH)]$^-$ (4).

Figure S33. $^{13}$C NMR spectrum ($\text{C}_6\text{D}_6$) of the reaction mixture after exposing a 1/1 [TBA][OAc] and HBpin under 1.5 atm of CO$_2$, consistent with the complete formation of the CO$_2$ insertion product [pinB(OAc)(O$_2$CH)]$^-$ (4).
Figure S34. 2D HSQC NMR spectrum (C$_6$D$_6$) of the reaction mixture after exposing a 1/1 [TBA][OAc] and HBpin under 1.5 atm of CO$_2$, consistent with the complete formation of the CO$_2$ insertion product [pinB(OAc)(O$_2$CH)]$^+$ (4).

Figure S35. 2D HMBC NMR spectrum (C$_6$D$_6$) of the reaction mixture after exposing a 1/1 [TBA][OAc] and HBpin under 1.5 atm of CO$_2$, consistent with the complete formation of the CO$_2$ insertion product [pinB(OAc)(O$_2$CH)]$^+$ (4).
Figure S36. Molecular structure of **TS-1** as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)

Figure S37. Molecular structure of **TS-2** as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)
Figure S38. Molecular structure of TS-3 as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)

Figure S39. Molecular structure of TS-4 as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)
**Figure S40.** Molecular structure of **TS-5** as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)

**Figure S41.** Molecular structure of **TS-6** as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)
Figure S42. Molecular structure of TS-7 as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)

Figure S43. Molecular structure of TS-8 as estimated by DFT calculations (wB97xD/def2tzvpp//B3LYP/6-31G*)
**Figure S44.** DFT-estimated mechanism (wB97xD/def2tzvpp//B3LYP/6-31G*, benzene) of acetate-catalyzed CO$_2$ hydroboration to model A’ through the formation of acetate-bridged dinuclear boron model VI’. The values in parenthesis correspond to the energy barriers.