

Supporting information:

1. Synthetic procedures

a. General procedures

All reactions were done under an inert atmosphere of argon using Schlenk and glovebox techniques with dry and deoxygenated solvents. Hexane and toluene were purified using an SPS Braun system. THF was dried by distillation over sodium/benzophenone under a nitrogen atmosphere and was stored over freshly cut sodium in a glovebox. ^1H and ^{31}P NMR spectra were recorded using a Bruker AV400 spectrometer. Ph_3SiMe is used as internal references relative to $-\text{SiMe}$ for ^1H (C_6D_6 ; $\delta = 0.72$ ppm) chemical shifts (ppm). All other reagents and chemicals were obtained commercially and used as received.

b. X-ray Crystallographic Studies.

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at -88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package [1]. The raw frame data were processed using SAINT and SADABS to yield the reflection data file [2]. The structures were solved by using the SHELXTL program [3]. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at calculated positions and were included in the structure calculations without the further refinement of the parameters. The terminal hydrogen atom in complex **2** has been refined anisotropically. Molecular structures were generated using the OLEX 2 program.

c. Synthesis of Zinc Hydride Complex LZnH (**2**).

To a solution of zinc benzyloxy complex **1** (0.52 g, 0.8 mmol) in THF was added PhSiH_3 (0.108 g, 1.0 mmol) or $(\text{EtO})_3\text{SiH}$ (0.164 g, 1.0 mmol), and the mixture was stirred for 10 h at room temperature. The volatile was removed under reduced pressure, and hexane (5 mL) was added. The white precipitate was isolated by filtration and dried under vacuum (yield, 0.33 g, 76%). Anal. Calcd for $\text{C}_{29}\text{H}_{30}\text{N}_5\text{PZn}$: C, 63.92; H, 5.55; N, 12.85. Found: C, 63.88; H, 5.50; N, 12.83. ^1H NMR (500 MHz, C_6D_6): δ 7.73-7.69 (m, 4H; *o*-PPh₂), 7.53 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 2H; *o*-NPh), 7.03-6.89 (m, 8H; PhH), 6.66 (t, $^3J_{\text{H-H}} = 7.3$ Hz, 1H; *p*-NPh), 5.39 (d, $^3J_{\text{P-H}} = 2.4$ Hz, 1H; Zn-H), 5.29 (s, 2H; Pz-H), 2.22 (s, 6H; Pz-CH₃), 1.89 ppm (s, 6H; Pz-CH₃). ^{31}P NMR (162 MHz, C_6D_6): δ 20.8 ppm.

d. Synthesis of formate Complex LZnOCHO (**3**).

In a Schlenk tube, a solution of complex **2** (0.163 g, 0.3 mmol) of toluene (8 mL) was frozen in a liquid nitrogen bath under vacuum, and ~ 2 bar of CO_2 was added. The mixture was stirred for 3 h at room temperature and concentrated to about 1.0 mL;

then, several drops of hexane were added. White crystals were obtained at $-30\text{ }^{\circ}\text{C}$ 2 days later (yield, 0.081 g, 46%). Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{N}_5\text{O}_2\text{PZn}$: C, 61.18; H, 5.13; N, 11.89%. Found: C, 61.20; H, 5.11; N, 11.93%. ^1H NMR (500 MHz, C_6D_6): δ 9.13 (s, 1H; OCHO), 7.68-7.64 (m, 4H; *m*-PPh₂), 7.33 (d, $^3\text{J}_{\text{H-H}} = 8.4$ Hz, 2H; *o*-NPh), 7.06-6.86 (m, 8H; Ph-H), 6.65 (t, $^3\text{J}_{\text{H-H}} = 7.4$ Hz, 1H; *p*-NPh), 5.24 (s, 2H; Pz-H), 2.33 (s, 6H; Pz-CH₃), 1.83 ppm (s, 6H; Pz-CH₃). ^{31}P NMR (162 MHz, C_6D_6): δ 22.71 ppm.

e. Synthesis of Magnesium Hydride Complex LMgH (**5**)

To a solution of *n*-butyl Magnesium complex **4** (0.384 g, 0.8 mmol) in toluene was added PhSiH_3 (0.108 g, 1 mmol). The mixture was reacted for 12h at room temperature. The white precipitate was isolated by filtration, washed by hexane and dried under vacuum (yield, 0.181 g, 45%). Anal. Calcd for $\text{C}_{29}\text{H}_{30}\text{N}_5\text{O}_2\text{PMg}$: C, 69.13; H, 6.00; N, 13.90%. Found: C, 69.20; H, 5.96; N, 13.93%. ^1H NMR (500 MHz, C_6D_6): δ 7.90-7.86 (m, 4H; *o*-PPh₂), 7.53 (d, $^3\text{J}_{\text{H-H}} = 8.3$ Hz, 2H; *o*-NPh), 7.02-6.85 (m, 8H; PhH), 6.50 (t, $^3\text{J}_{\text{H-H}} = 7.3$ Hz, 1H; *p*-NPh), 6.19 (s, 1H; Mg-H), 5.45 (s, 2H; Pz-H), 2.56 (s, 6H; Pz-CH₃), 1.96 ppm (s, 6H; Pz-CH₃). ^{31}P NMR (162 MHz, C_6D_6): δ 17.82 ppm.

f. Catalytic Hydroboration Reaction of CO_2 with Zinc Hydride Complex **2**.

0.01 mmol of the base catalyst was dissolved in C_6D_6 (~ 1 ml) in a Schlenk tube. The required amount of $\text{BH}_3\cdot\text{SMe}_2$ was then added. The Schlenk tube was frozen in a liquid nitrogen bath under vacuum, and ~2 bar of CO_2 was added. The reaction was followed by NMR spectroscopy. The yields reported by ^1H NMR were according to the integration of both $\text{B}(\text{OMe})_3$ at 3.44 ppm and $(\text{OBOMe})_3$ at 3.34 ppm and compared to the -SiMe of the Ph_3SiMe at 0.70 ppm^[4, 5].

2. X-ray crystallography

Table S1 Crystal data and structure refinement details for complexes **3**.

Parameter	2 ·(Toluene) ₃
Empirical formula	$\text{C}_{44}\text{H}_{47}\text{N}_5\text{O}_2\text{PZn}$
Formula weight	774.20
Temperature/K	173
Crystal system	triclinic
Space group	P-1
<i>a</i> /Å	9.9364(6)
<i>b</i> /Å	12.6486(8)
<i>c</i> /Å	16.9877(11)
$\alpha/^\circ$	108.9870(10)
$\beta/^\circ$	97.2460(10)
$\gamma/^\circ$	96.9120(10)
Volume/Å ³	1972.9(2)
Z	2

$\rho_{\text{calc}}/\text{cm}^3$	1.303
μ/mm^{-1}	0.706
F(000)	814.0
Crystal size/ mm^3	$0.3 \times 0.2 \times 0.1$
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/	3.456 to 52.87
Index ranges	$-12 \leq h \leq 11, -15 \leq k \leq 15, -21 \leq l \leq 13$
Reflections collected	11375
Independent reflections	7887 [$R_{\text{int}} = 0.0152, R_{\text{sigma}} = 0.0298$]
Data/restraints/parameters	7887/272/524
Goodness-of-fit on F^2	1.049
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0370, wR_2 = 0.1048$
Final R indexes [all data]	$R_1 = 0.0391, wR_2 = 0.1066$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.79/-0.88

3. NMR spectra of complexes 2, 3 and 5

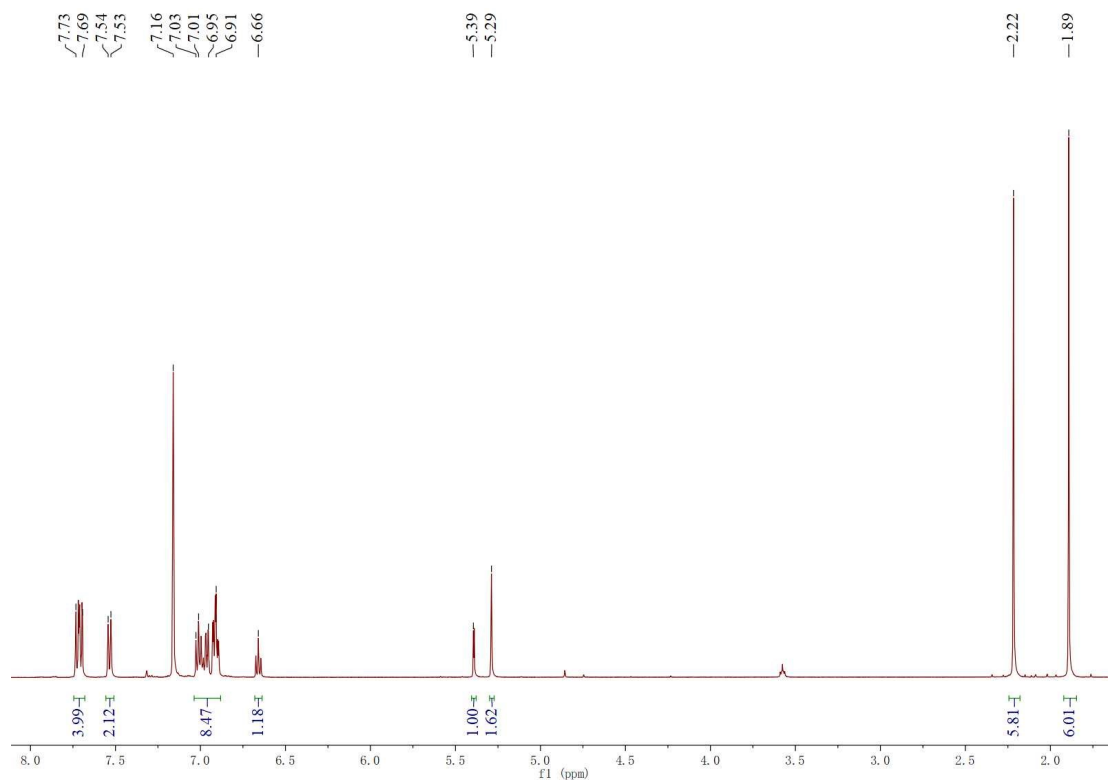


Fig. S1 ^1H NMR spectrum of zinc hydride LZnH (2) (C_6D_6)

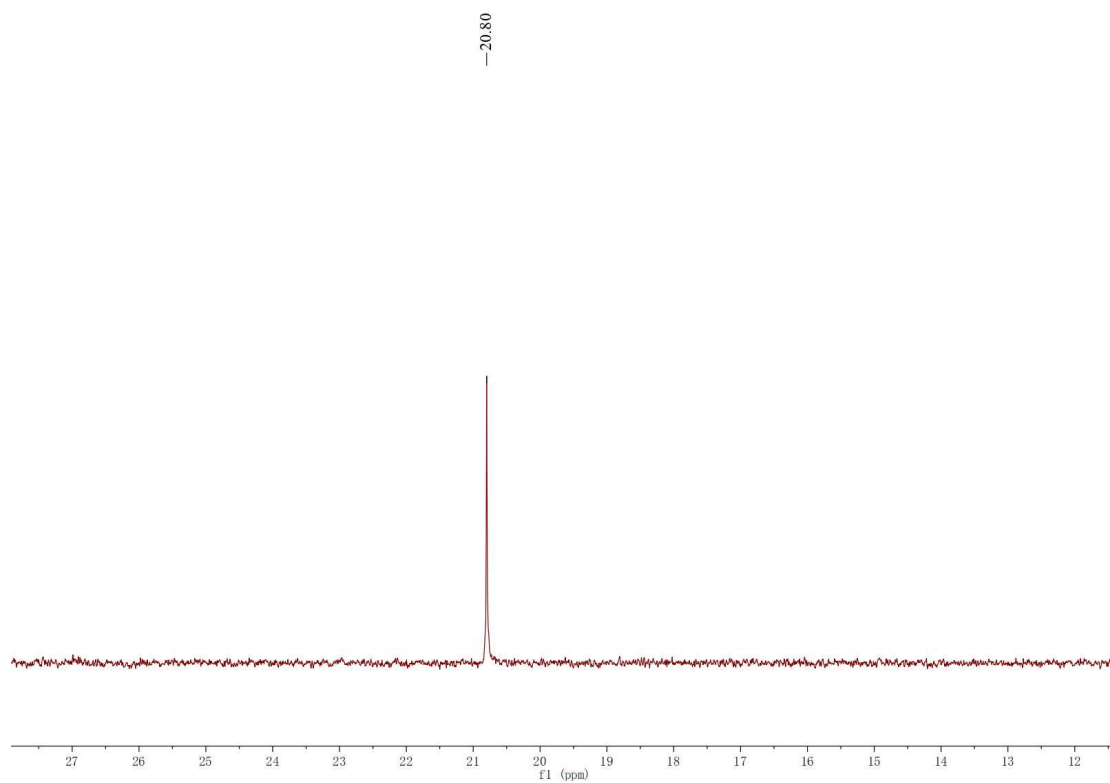


Fig. S2 ³¹P NMR spectrum of zinc hydride LZnH (2) (C₆D₆)

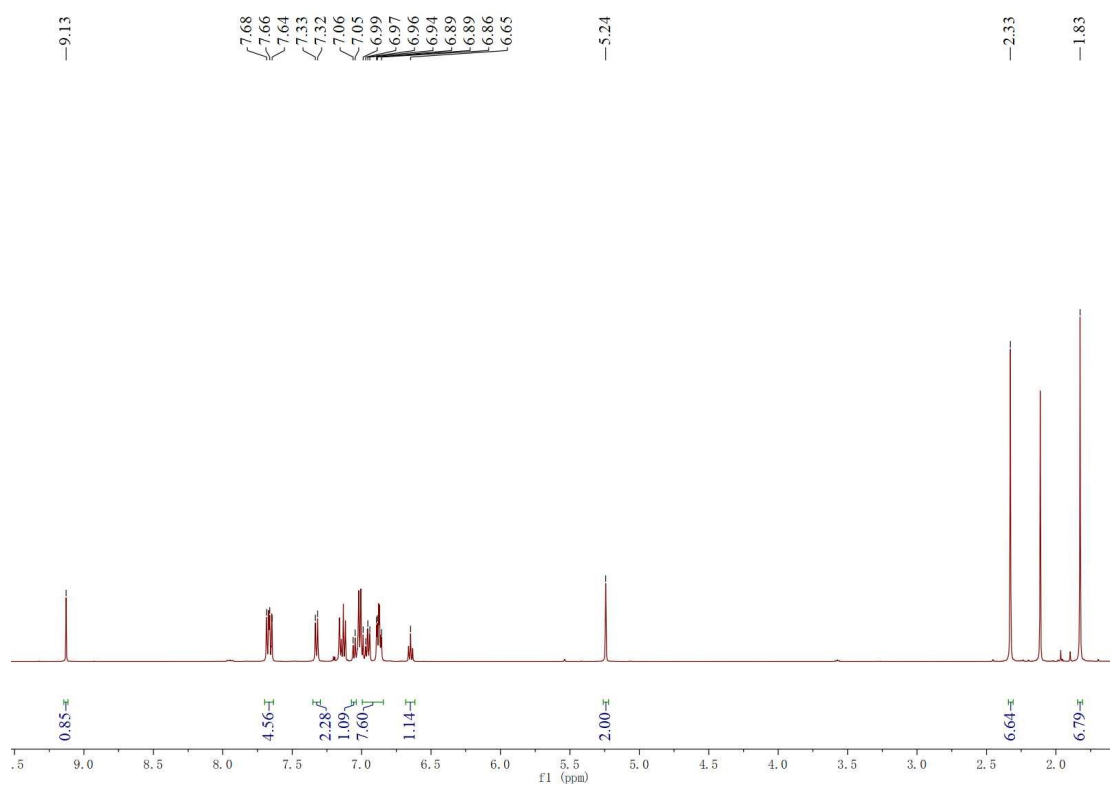


Fig. S3 ¹H NMR spectrum of zinc formate complex LZnOCH(O) (3) (C₆D₆)

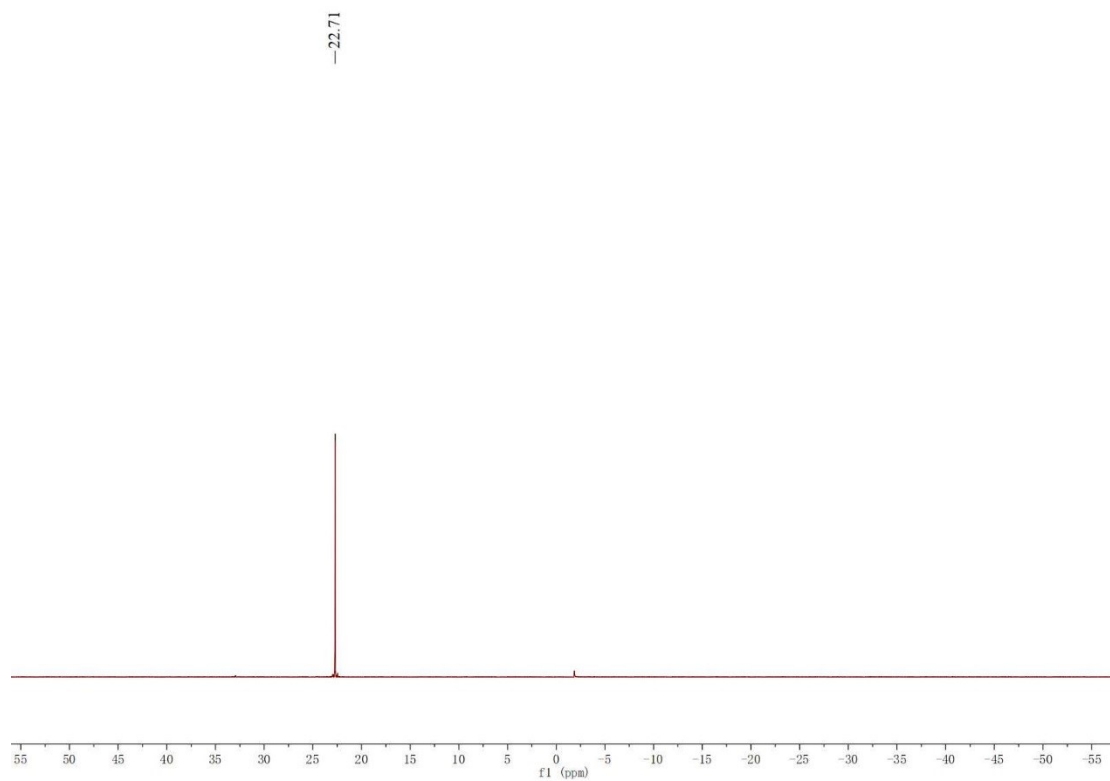


Fig. S4 ³¹P NMR spectrum of zinc formate complex LZnOCH(O) (3) (C₆D₆)

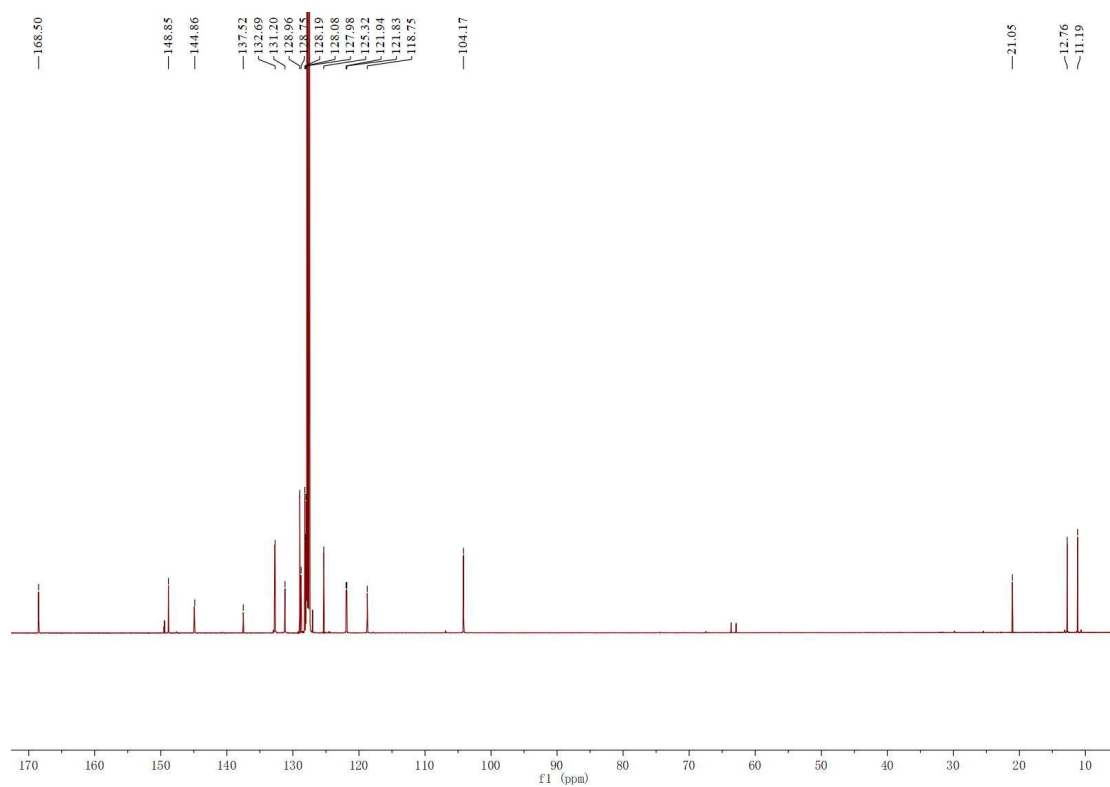


Fig. S5 ¹³C NMR spectrum of zinc formate complex LZnOCH(O) (3) (C₆D₆)

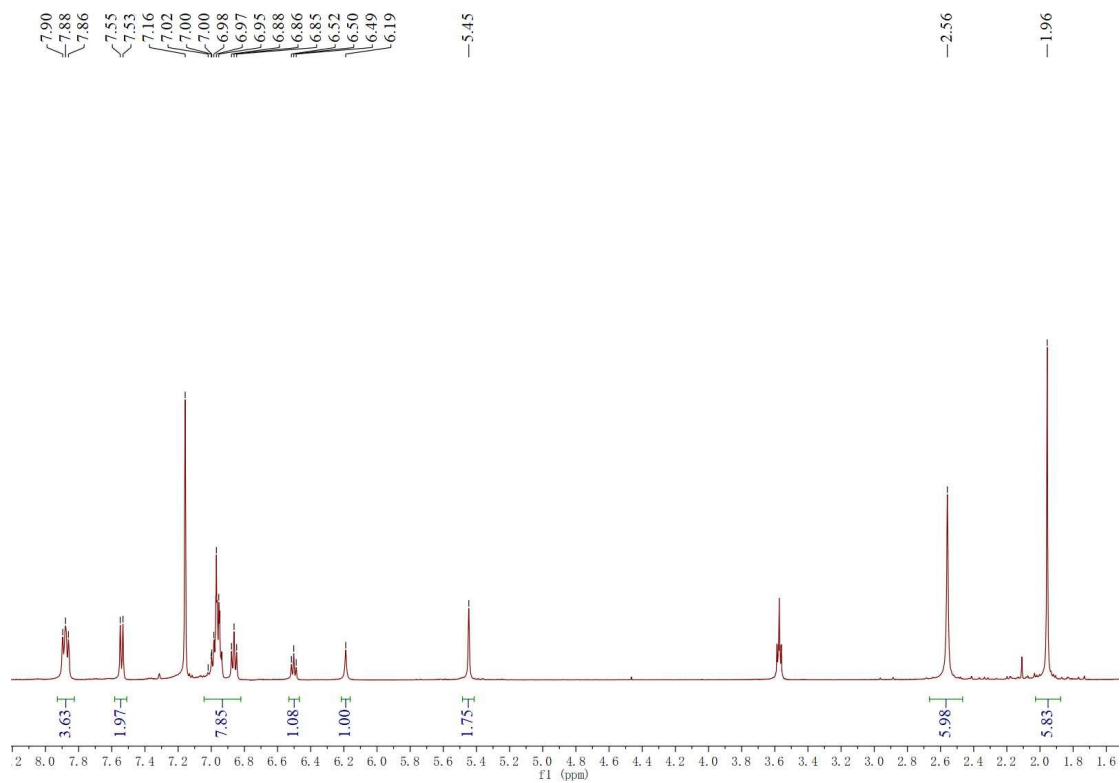


Fig. S6 ^1H NMR spectrum of magnesium hydride LMgH (**5**) (C_6D_6)

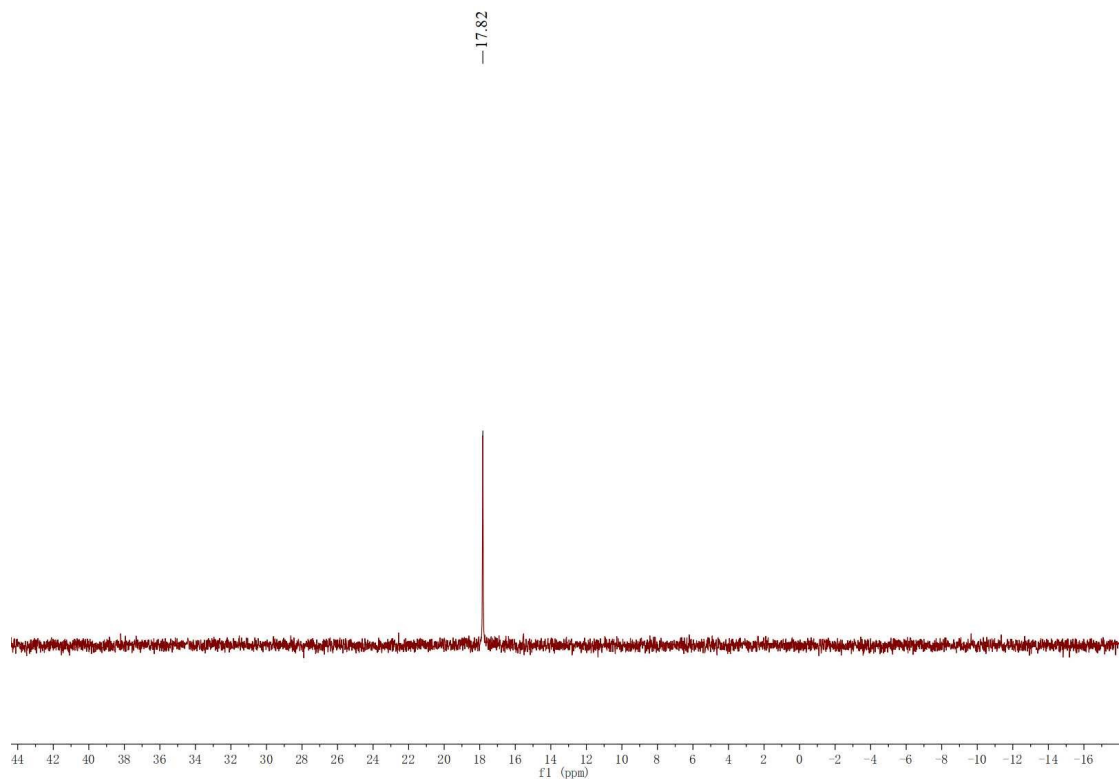


Fig. S7 ^{31}P NMR spectrum of magnesium hydride LMgH (**5**) (C_6D_6)

4. ^1H NMR spectra of hydroboration of CO_2

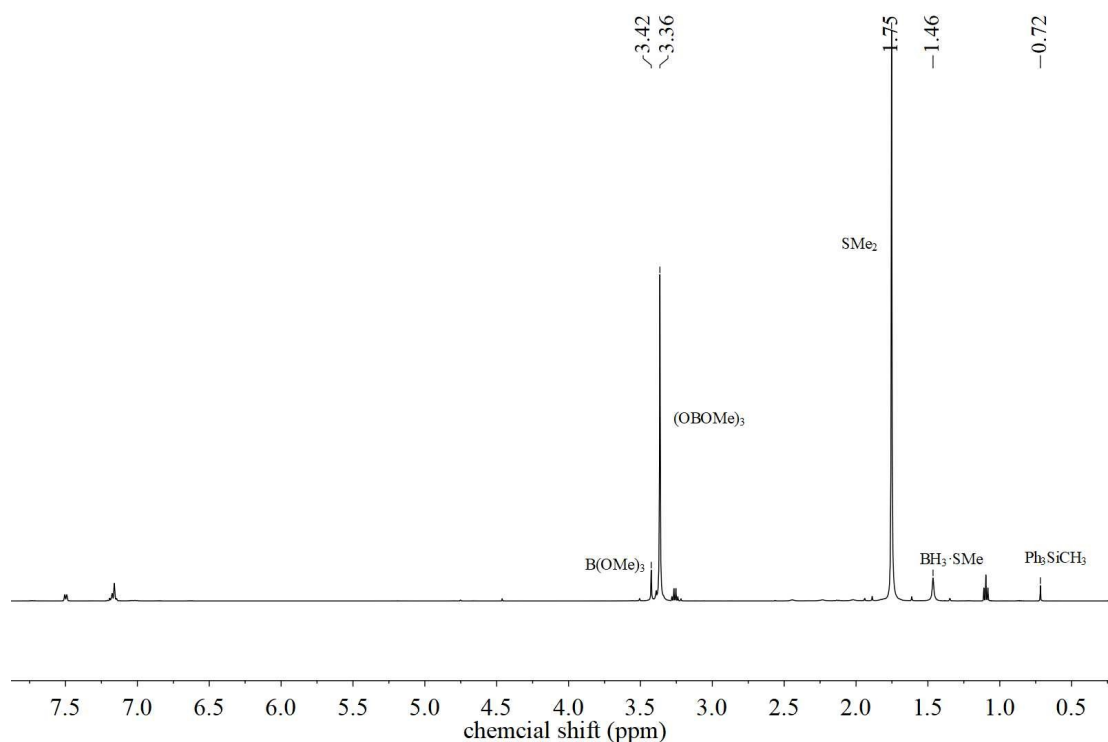


Fig. S8 Typical ¹H NMR spectrum of the carbon dioxide reduction using BH₃·SMe₂. Incomplete reaction at 1/100 of **2**/ BH₃·SMe₂.

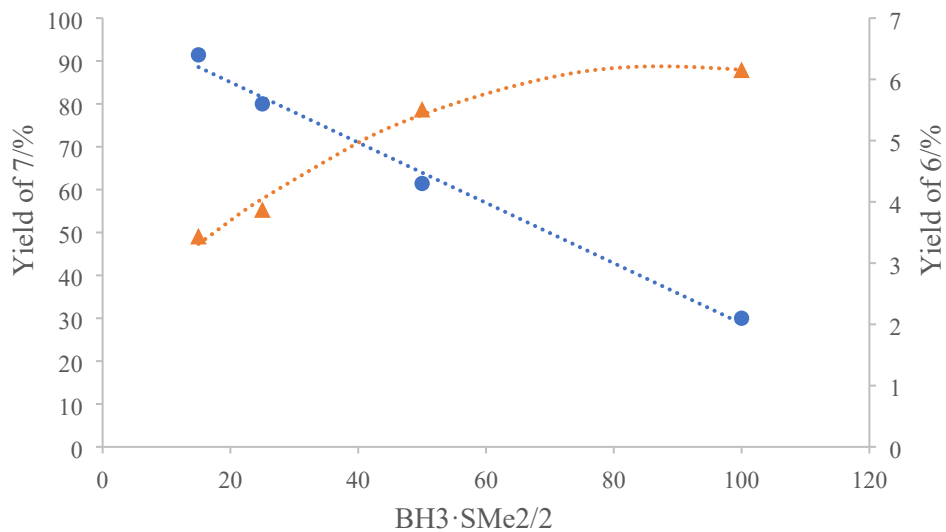


Fig. S9 Plots of BH₃·SMe₂ concentration versus yield (Table 1, run 2-run 5). (blue, B(OMe)₃; orange, (OBOMe)₃).

5. Kinetic study

Table S2. Hydroboration of CO₂ catalyzed by complex **2** at different time.

Run ^a	Time (h)	Yield of 6 (%) ^b	Yield of 7 (%) ^b	Total (%)
1	0.5	1	29	30
2	1.5	1	45	46
3	3	2	65	67
4	4	3	81	84
5	8	4	81	85

^a Reaction conditions: **2** (0.01mmol), **2**/BH₃·SMe₂ = 1/50, T = 25°C, C₆D₆ (1 ml), under ~2 atm CO₂; ^b The yield was obtained by ¹H NMR using methyltriphenylsilane as an internal standard.

6. REFERENCES

- [1] SMART, Version 5.054; Bruker AXS Inc.: Madison, WI, 2000.
- [2] SAINT and SADABS, Version 6.22; Bruker AXS Inc.: Madison, WI, 2000.
- [3] Sheldrick, G. M. SHELXTL NT, Version 6.12; Bruker AXS Inc.: Madison, WI, 2000.
- [4] Chia C C, Teo Y C, Cham N, et al. Aluminum-Hydride-Catalyzed Hydroboration of Carbon Dioxide[J]. *Inorg Chem*, 2021, 60(7): 4569-4577.
- [5] Leong B X, Lee J, Li Y, et al. A Versatile NHC-Parent Silyliumylidene Cation for Catalytic Chemo- and Regioselective Hydroboration[J]. *J Am Chem Soc*, 2019, 141(44): 17629-17636.