Supporting Information

Molecular Zinc Hydride Cations \([\text{ZnH}]^+\): Synthesis, Structure, and \(\text{CO}_2\) Hydrosilylation Catalysis

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General Remarks

All reactions were performed under dry argon atmosphere using standard Schlenk technique or under argon in a glovebox, unless otherwise stated. Prior to use, glassware were dried at 130 °C overnight. Solvents were dried, distilled and degassed using standard methods or using a MB SPS-800 solvent purification system. TMEDA (N,N,N',N'-tetramethylethylenediamine) and TEEDA (N,N,N',N'-tetraethylethylenediamine) were purchased from Sigma-Aldrich. [ZnH$_2$]$_n$,$^4$$^{[5]}$ [NEt$_3$H][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$],$^{[52]}$ Et$_3$SiH,$^{[53]}$ and B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$,$^{[54]}$ were synthesized following literature procedures. $^1$H, $^{13}$C($^1$H), $^{11}$B($^1$H), $^{19}$F($^1$H) and $^{29}$Si($^1$H) NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance III HD 400 spectrometer in J. Young style NMR tubes at ambient temperature unless otherwise stated. Chemical shifts (δ in ppm) in the $^1$H and $^{13}$C($^1$H) NMR spectra were referenced internally to the residual signals of the deuterated solvents. Chemical shifts in the $^{11}$B($^1$H) and $^{29}$Si($^1$H) spectra were referenced externally to BF$_3$(OEt$_2$) or tetramethylsilane, respectively. The resonances in the $^1$H and $^{13}$C($^1$H) NMR spectra were assigned based on two-dimensional NMR experiments (COSY, HSQC, HMBC). Abbreviations for multiplicities of NMR signals are as follows: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), br (broad). IR spectra were recorded as KBr pellets using an AVATAR 360 FT-IR spectrometer. Elemental analysis were performed on an elementar vario EL machine.
Experimental Procedures and Spectroscopic Data

Synthesis of [(TMEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1a).

To a stirred solution of [NEt$_3$H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1.50 g, 1.55 mmol) in Et$_2$O (5 mL) was added dropwise TMEDA (0.27 g, 2.32 mmol) in Et$_2$O (2 mL) and the mixture was stirred overnight at room temperature. The solution was concentrated in vacuo. Addition of $n$-pentane resulted in the precipitation of a solid. The supernatant was decanted off, the residue was washed with $n$-pentane (2 x 3 mL) and dried in vacuo to give [(TMEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] as colorless solid (1.50 g, 1.52 mmol). Yield: 98%.

$^1$H NMR (400 MHz, [D$_3$]acetonitrile): δ = 2.46 (s, N-CH$_3$, 12H), 2.75 (s, N-CH$_2$, 4H), 3.64 (br, NH, 1H), 7.67 (s, para-C$_6$H$_3$, 4H), 7.69 (s, ortho-C$_6$H$_3$, 8H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, [D$_3$]acetonitrile): δ = 44.86 (N-CH$_3$), 55.27 (N-CH$_2$), 118.72 (para-C$_6$H$_3$), 124.16 (q, $^1$J$_{C-F}$ = 271.6 Hz, CF$_3$), 130.08 (qq, $^2$J$_{C-F}$ = 31.6 Hz, $^3$J$_{C-B}$ = 2.8 Hz, meta-C$_6$H$_3$), 135.70 (ortho-C$_6$H$_3$), 162.66 (q, $^1$J$_{B-C}$ = 50.1 Hz, ipso-C$_6$H$_3$) ppm.

$^{11}$B($^1$H) NMR (128 MHz, [D$_3$]acetonitrile): δ = -6.67 ppm.

$^{19}$F($^1$H) NMR (377 MHz, [D$_3$]acetonitrile): δ = -63.27 ppm.

IR (KBr): ν = 2973 cm$^{-1}$ (br, NH).

Anal. Calcd. for C$_{38}$H$_{29}$N$_2$BF$_4$ (980.44 g ∙ mol$^{-1}$): C, 46.55; H, 2.98; N, 2.86. Found: C, 46.77; H, 3.05; N, 3.21%.

Figure S1: $^1$H NMR spectrum of [(TMEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1a) in [D$_3$]acetonitrile (*).
Figure S2: $^{13}$C($^1$H) NMR spectrum of [(TMEDA)$^-$][B(3,5-(CF$_3$_2)C$_6$H$_3$)$_4$] (1a) in [D$_3$]acetonitrile.

Figure S3: $^{11}$B($^1$H) NMR spectrum of [(TMEDA)$^-$][B(3,5-(CF$_3$_2)C$_6$H$_3$)$_4$] (1a) in [D$_3$]acetonitrile.
Figure S4: $^{19}$F($^1$H) NMR spectrum of [(TMEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1a) in [D$_3$]acetonitrile.

Figure S5: IR spectrum (KBr pellet) of [(TMEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1a).

Synthesis of [(TEEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1b).

To a stirred solution of [NEt$_3$H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (0.500 g, 0.517 mmol) in Et$_2$O (5 mL) was added a solution of TEEDA (0.131 g, 0.760 mmol) in Et$_2$O (2 mL) and the mixture was stirred overnight at room temperature. The solution was concentrated in vacuo. Addition of n-pentane resulted in the precipitation of a solid. The supernatant was decanted off, the residue washed
with n-pentane (2 × 3 mL) and dried in vacuo to give [(TEEDA)H][B(3,5-(CF₃)₂-C₆H₃)₄] as a colorless solid (0.523 g, 0.504 mmol). Yield: 97%.

¹H NMR (400 MHz, [D₃]acetonitrile): δ = 1.13 (t, ³J_H-H = 7.2 Hz, N-CH₂CH₃, 12H), 2.51 (q, ³J_C-H = 7.2 Hz, N-CH₂CH₃, 8H), 2.89 (s, N-CH₂CH₂, 4H), 4.92 (br, NH, 1H), 7.67 (s, para-C₆H₃, 4H), 7.70 (s, ortho-C₆H₃, 8H) ppm.

¹³C(¹H) NMR (101 MHz, [D₃]acetonitrile): δ = 10.27 (N-CH₂CH₃), 47.57 (N-CH₂CH₃), 48.75 (N-CH₂), 118.71 (para-C₆H₃), 125.49 (q, ¹J_C-F = 271.7 Hz, CF₃), 129.95 (qq, ²J_C-F = 31.5 Hz, ³J_C-B = 2.8 Hz, meta-C₆H₃), 135.68 (ortho-C₆H₃), 162.63 (q, ¹J_B-C = 49.8 Hz, ipso-C₆H₃) ppm.

¹³B(¹H) NMR (128 MHz, [D₃]acetonitrile): δ = -6.67 ppm.

¹⁹F(¹H) NMR (377 MHz, [D₃]acetonitrile): δ = -63.67 ppm.

IR (KBr): ν = 2976 cm⁻¹ (br, NH).

Anal. Calcd. for C₄₂H₃₇N₂BF₂₄ (1036.54 g · mol⁻¹): C, 48.67; H, 3.60; N, 2.70. Found: C, 48.16; H, 4.05; N, 2.94%.

Figure S6: ¹H NMR spectrum of [(TEEDA)H][B(3,5-(CF₃)₂-C₆H₃)₄] (1b) in [D₃]acetonitrile (*)
Figure S7: $^{13}$C($^1$H) NMR spectrum of [(TEEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1b) in [D$_3$]acetonitrile.

Figure S8: $^{11}$B($^1$H) NMR spectrum of [(TEEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1b) in [D$_3$]acetonitrile.
Figure S9: $^{19}$F($^1$H) NMR spectrum of [(TEEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1b) in [D$_3$]acetonitrile.

Figure S10: IR spectrum (KBr pellet) of [(TEEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1b).
Synthesis of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a).

To a suspension of [ZnH$_2$]$_n$ (34 mg, 0.51 mmol) in THF (5 mL) was added dropwise a solution of [(TMEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (0.500 g, 0.51 mmol) in THF (5 mL) at room temperature. After gas evolution had ceased (approximately 15 min) the reaction mixture was filtered. The solution was concentrated in vacuo and subsequent addition of n-pentane resulted in the precipitation of a colorless solid. The solvent was removed by decantation. Drying under reduced pressure gave [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] as a colorless solid (535 mg, 0.48 mmol). Yield: 94%.

$^1$H NMR (400 MHz, [D$_8$]THF): $\delta$ = 1.78 (m, THF, 4H), 2.60 (s, N-CH$_3$, 12H), 2.87 (s, N-CH$_2$, 4H), 3.65 (m, THF, 4H), 3.68 (s, Zn-H, 1H) 7.59 (s, para-C$_6$H$_3$, 4H), 7.80 (s, ortho-C$_6$H$_3$, 8H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, [D$_8$]THF): $\delta$ = 26.43 (thf), 47.37 (N-CH$_3$), 57.97 (N-CH$_2$CH$_2$), 68.27 (thf), 118.26 (para-C$_6$H$_3$), 125.58 (q, $^1$J$_{C-F}$ = 272 Hz, CF$_3$), 130.08 (qq, $^2$J$_{C-F}$ = 31.6 Hz, $^3$J$_{C-B}$ = 3.5 Hz, meta-C$_6$H$_3$), 135.66 (ortho-C$_6$H$_3$), 162.88 (q, $^1$J$_{B-C}$ = 50 Hz, ipso-C$_6$H$_3$) ppm.

$^{11}$B($^1$H) NMR (128 MHz, [D$_8$]THF): $\delta$ = -6.48 ppm.

$^{19}$F($^1$H) NMR (377 MHz, [D$_8$]THF): $\delta$ = 63.42 ppm.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 1.99 (m, THF, 4H), 2.56 (s, N-CH$_3$, 12H), 2.75 (s, N-CH$_2$, 4H), 3.56 (s, Zn-H, 1H), 4.03 (m, THF, 4H), 7.58 (s, para-C$_6$H$_3$, 4H), 7.73 (s, ortho-C$_6$H$_3$, 2.1, 8H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ = 25.87 (THF), 47.97 (N-CH$_3$), 57.84 (N-CH$_2$), 72.61 (THF), 118.12 (para-C$_6$H$_3$), 125.24 (q, $^1$J$_{C-F}$ = 272.4 Hz, CF$_3$), 129.46 (qq, $^2$J$_{C-F}$ = 31.5 Hz, $^3$J$_{C-B}$ = 2.5 Hz, meta-C$_6$H$_3$), 135.44 (ortho-C$_6$H$_3$), 162.39 (q, $^1$J$_{B-C}$ = 49.8 Hz, ipso-C$_6$H$_3$) ppm.

$^{11}$B($^1$H) NMR (128 MHz, CD$_2$Cl$_2$): $\delta$ = -6.47 ppm.

$^{19}$F($^1$H) NMR (377 MHz, CD$_2$Cl$_2$): $\delta$ = -63.42 ppm.

IR (KBr): $\nu$ = 1804, 1609 cm$^{-1}$ (m, ZnH).

Anal. Calcd. for C$_{42}$H$_{37}$BF$_{24}$ON$_2$Zn (1117.92 g mol$^{-1}$): C, 45.12; H, 3.34; N, 2.51. Found: C, 44.41; H, 3.68; N, 2.98%.
Figure S11: $^1$H NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in [D$_8$]THF.

Figure S12: $^{13}$C($^1$H) NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in [D$_8$]THF.
**Figure S13:** $^{11}$B($^1$H) NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in [D8]THF.

**Figure S14:** $^{19}$F($^1$H) NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in [D8]THF.
Figure S15: $^1$H NMR spectrum of [(TMEDA)$\text{ZnH(thf)}$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in CD$_2$Cl$_2$.

Figure S16: $^{13}$C($^1$H) NMR spectrum of [(TMEDA)$\text{ZnH(thf)}$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in CD$_2$Cl$_2$. 
Figure S17: $^{11}$B($^1$H) NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in CD$_2$Cl$_2$.

Figure S18: $^{19}$F($^1$H) NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (2a) in CD$_2$Cl$_2$. 
Figure S19: IR spectrum (KBr pellet) of [(TMEDA)ZnH(thf)][B(3,5-(CF₃)₂-C₆H₃)] (2a).

Synthesis of [(TEEDA)ZnH][B(3,5-(CF₃)₂-C₆H₃)₄] (2b).
To a suspension of [ZnH₂]n (26 mg, 385 µmol) in THF (5 mL) was added dropwise a solution of [(TEEDA)H][B(3,5-(CF₃)₂-C₆H₃)] (400 mg, 385 µmol) in THF (5 mL) at room temperature. After gas evolution had ceased (approximately 15 min) the reaction mixture was filtered and the solvent volume reduced in vacuo. Addition of n-pentane resulted in the precipitation of a colorless solid which could be isolated by decantation and subsequent drying under reduced pressure. The title complex was recrystallized by layering a solution of [(TEEDA)ZnH][B(3,5-(CF₃)₂-C₆H₃)₄] in CD₂Cl₂ with n-pentane at –30 ℃ to give colorless crystals (392 mg, 355 µmol). Yield: 92%.

¹H NMR (400 MHz, [D₈]THF): δ = 1.17 (t, ³J_HH = 7.2 Hz, N-CH₂C₂H₅, 24H), 2.84 – 2.95 (AA’BB’, N-CH₂CH₃, 8H), 2.96 (s, N-CH₂CH₂, 8H), 2.98 – 3.11 (AA’BB’, N-CH₂CH₃, 8H), 3.73 (s, Zn-H, 2H), 7.59 (s, para-C₆H₃, 8H), 7.80 (s, para-C₆H₃, 16H) ppm.

¹³C(¹H) NMR (101 MHz, [D₈]THF): δ = 8.87 (N-CH₂CH₃), 46.97 (N-CH₂CH₃), 51.64 (N-CH₂CH₂), 118.28 (para-C₆H₃), 125.61 (q, ¹J_C-F = 272.2 Hz, CF₃), 129.99 (qq, ²J_C-F = 31.52 Hz, ³J_C-B = 2.81 Hz, meta-C₆H₃), 135.69 (ortho-C₆H₃), 162.89 (q, ¹J_B-C = 49.9 Hz, ipso-C₆H₃) ppm.

¹¹B(¹H) NMR (128 MHz, [D₈]THF): δ = -6.50 ppm.

¹⁹F(¹H) NMR (377 MHz, [D₈]THF): δ = -63.44 ppm.
$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 1.23$ (t, $^3J_{H-H} = 7.2$ Hz, N-CH$_2$CH$_3$, 24H), 2.95 (p, $^3J_{H-H} = 7.1$ Hz, N-CH$_2$CH$_3$, 16H), 3.03 (s, N-CH$_2$CH$_2$, 8H), 4.28 (s, Zn-H, 2H), 7.58 (s, para-C$_6$H$_3$, 8H), 7.73 (s, ortho-C$_6$H$_3$, 16H). ppm.

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 10.92$ 87 (N-CH$_2$CH$_3$), 50.14 (N-CH$_2$CH$_3$), 51.64 (N-CH$_2$CH$_2$), 118.12 (para-C$_6$H$_3$), 125.24 (q, $^1J_{C-F} = 272.4$ Hz, CF$_3$), 129.50 (qq, $^2J_{C-F} = 31.66$ Hz, $^3J_{C-B} = 2.90$ Hz, meta-C$_6$H$_3$), 135.44 (ortho-C$_6$H$_3$), 162.37 (q, $^1J_{B-C} = 49.9$ Hz, ipso-C$_6$H$_3$ ppm.

$^{11}$B($^1$H) NMR (128 MHz, CD$_2$Cl$_2$): $\delta = -6.60$ ppm.

$^{19}$F($^1$H) NMR (377 MHz, CD$_2$Cl$_2$): $\delta = -63.44$ pp.

IR (KBr): $\nu = 1798$, 1607 cm$^{-1}$ (m, ZnH).

Anal. Calcd. for C$_{84}$H$_{74}$B$_2$F$_{48}$N$_4$Zn$_2$ (2203.85 g ∙ mol$^{-1}$): C, 45.78; H, 3.38; N, 2.54. Found: C, 44.42; H, 4.82; N, 3.32%.

Figure S20: $^1$H NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (2b) in [D$_8$]THF.
Figure S21: $^{13}$C($^1$H) NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (2b) in [D$_8$]THF.

Figure S22: $^{11}$B($^1$H) NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (2b) in [D$_8$]THF.
Figure S23: $^{19}$F($^1$H) NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (2b) in [D$_8$]THF.

Figure S24: $^1$H NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (2b) in CD$_2$Cl$_2$. 
Figure S25: $^{13}$C{($^1$H)} NMR spectrum of [($\text{TEEDA}$)$\text{ZnH}$]$\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_4]$ (2b) in CD$_2$Cl$_2$.

Figure S26: $^{11}$B{($^1$H)} NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (2b) in CD$_2$Cl$_2$. 
Figure S27: $^{19}$F($^1$H) NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (2b) in CD$_2$Cl$_2$.

Figure S28: IR spectrum (KBr pellet) of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (2b).
Synthesis of [(TMEDA)$_2$Zn$_2$H$_3$][(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a).

**Method A:** To a suspension of [ZnH$_2$]$_n$ (70 mg, 1.03 mmol) in THF (5 mL) was added dropwise a solution of [(TMEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (500 mg, 0.51 mmol) and TMEDA (59 mg, 0.51 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature until gas evolution ceased (approximately 15 min). The reaction mixture was filtered and the filtrate concentrated in vacuo. Addition of n-pentane resulted in the precipitation of a colorless solid which could be isolated by decantation and subsequent drying under reduced pressures. Recrystallization from CD$_2$Cl$_2$/n-pentane at -30 °C gave [(TMEDA)$_2$Zn(H)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] as a colorless solid (554 mg, 0.45 mmol). Yield: 88%.

**Method B:** To a suspension of [ZnH$_2$]$_n$ (6 mg, 89 µmol) and TMEDA (10 mg, 89 µmol) in THF (5 mL) was added a THF solution of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (1a) (100 mg, 89 µmol). The solvent was removed in vacuo and the residue was recrystallized from CD$_2$Cl$_2$/n-pentane at -30 °C. The supernatant was decanted off and the crystalline solid was dried under reduced pressure a colorless solid (105 mg, 85 µmol). Yield: 96%.

$^1$H NMR (400 MHz, [D$_8$]THF): δ = 2.58 (s, N-CH$_3$, 24H), 2.83 (s, N-CH$_2$, 8H), 3.68 (s, Zn-H, 3H), 7.59 (s, para-C$_6$H$_3$, 4H), 7.80 (s, ortho-C$_6$H$_3$, 8H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, [D$_8$]THF): δ = 48.10 (N-CH$_3$), 58.01 (N-CH$_2$), 118.25 (para-C$_6$H$_3$), 125.58 (q, $^1$J$_{C-F}$ = 272.2 Hz, CF$_3$), 130.13 (qq, $^2$J$_{C-F}$ = 31.2 Hz, $^3$J$_{B-C}$ = 3.4 Hz, meta-C$_6$H$_3$), 135.66 (ortho-C$_6$H$_3$), 163.37 (q, $^1$J$_{B-C}$ = 50.1 Hz, ipso-C$_6$H$_3$) ppm

$^{11}$B($^1$H) NMR (128 MHz, [D$_8$]THF): δ = -6.52 ppm.

$^{19}$F($^1$H) NMR (377 MHz, [D$_8$]THF): δ = -63.42 ppm.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.56 (s, N-CH$_3$, 24H), 2.74 (s, N-CH$_2$, 8H), 3.58 (s, Zn-H, 3H), 7.58 (s, para-C$_6$H$_3$, 4H), 7.73 (s, ortho-C$_6$H$_3$, 8H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$): δ = 48.59 (N-CH$_3$), 57.82 (N-CH$_2$), 117.97 (para-C$_6$H$_3$), 125.24 (q, $^1$J$_{C-F}$ = 272.3 Hz, CF$_3$), 129.48 (qq, $^2$J$_{C-F}$ = 31.5 Hz, $^3$J$_{B-C}$ = 2.8 Hz, meta-C$_6$H$_3$), 135.44 (ortho-C$_6$H$_3$), 162.40 (q, $^1$J$_{B-C}$ = 49.9 Hz, ipso-C$_6$H$_3$) ppm

$^{13}$B($^1$H) NMR (128 MHz, CD$_2$Cl$_2$): δ = -6.60 ppm.

$^{19}$F($^1$H) NMR (377 MHz, CD$_2$Cl$_2$): δ = -62.80 ppm.

IR (KBr): ν = 1758 (m, ZnH), 1606 cm$^{-1}$ (m, ZnH).

Anal. Calcd. for C$_{64}$H$_{47}$BF$_{24}$N$_4$Zn$_2$ (1229.42 g ∙ mol$^{-1}$): C, 42.99; H, 3.85; N; 4.56. Found: C, 43.61; H, 4.46; N, 4.61%.
Figure S29: $^1$H NMR spectrum of \([\text{TMEDA})_2\text{Zn}_2\text{H}_3]\text{[B}(3,5-\text{(CF}_3)_2\text{-C}_6\text{H}_3)\text{]}_4\) (3a) in [D8]THF (* denotes n-pentane).

Figure S30: $^{13}$C($^1$H) NMR spectrum of \([\text{TMEDA})_2\text{Zn}_2\text{H}_3]\text{[B}(3,5-\text{(CF}_3)_2\text{-C}_6\text{H}_3)\text{]}_4\) (3a) in [D8]THF (* denotes n-pentane.)
Figure S31: $^{11}$B($^1$H) NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a) in [D$_8$]THF.

Figure S32: $^{19}$F($^1$H) NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a) in [D$_8$]THF.
Figure S33: $^1$H NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a) in CD$_2$Cl$_2$.

Figure S34: $^{13}$C($^1$H) NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a) in CD$_2$Cl$_2$. 
Figure S35: $^{11}$B($^1$H) NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a) CD$_2$Cl$_2$.

Figure S36: $^{19}$F($^1$H) NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a) in CD$_2$Cl$_2$. 
Figure S37: IR spectrum (KBr pellet) of [(TMEDA)$_2$Zn$_3$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a).

Figure S38: Variable-temperature $^1$H NMR spectrum of [(TMEDA)$_2$Zn$_3$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3a) in CD$_2$Cl$_2$. 
Synthesis of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (3b).

Method A: To a suspension of [ZnH$_2$]$_n$ (26 mg, 385 µmol) in THF (5 mL) was added dropwise a solution of [(TEEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (200 mg, 192 µmol) and TEEDA (33.2 mg, 192 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature until gas evolution had ceased (approximately 15 min), filtered and concentrated in vacuo. Addition of n-pentane resulted in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressures. Recrystallization from toluene/n-pentane at -30 °C gave [(TEEDA)$_2$ZnH$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] as a colorless solid (284 mg, 211 µmol). Yield: 74%.

Method B: To a suspension of [ZnH$_2$]$_n$ (6 mg, 91 µmol) and TEEDA (16 mg, 91 µmol) in THF (5 mL) was added a solution of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)]$_2$ (100 mg, 45 µmol) in THF (mL). After stirring the reaction mixture for 15 min at room temperature, the solvent was removed in vacuo. The residue was recrystallized from CD$_2$Cl$_2$/n-pentane at -30 °C. The supernatant was decanted off and the crystalline solid was dried under reduced pressure to give colorless crystals (121 mg, 90 µmol). Yield: 98%.

$^1$H NMR (400 MHz, [D$_8$]THF): δ = 1.14 (t, $^3$J$_{HH}$ = 7.1 Hz, N-CH$_2$-CH$_3$, 24H), 2.83 (m, N-CH$_2$CH$_3$, 8H), 2.90 (s, N-CH$_2$, 8H), 3.06 (m, N-CH$_2$CH$_3$, 8H), 3.65 (s, Zn-H, 3H), 7.60 (s, para-C$_6$H$_3$, 4H), 7.81 (s, ortho-C$_6$H$_3$, 8H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, [D$_8$]THF): δ = 9.19 (N-CH$_2$CH$_3$), 47.78 (N-CH$_2$CH$_3$), 51.72 (N-CH$_2$CH$_2$), 118.28 (para-C$_6$H$_3$), 125.62 (q, $^1$J$_{C-F}$ = 272.2 Hz, CF$_3$), 130.27 (qq, $^2$J$_{C-F}$ = 31.5 Hz, $^3$J$_{C-C}$ = 2.8 Hz, meta-C$_6$H$_3$), 135.70 (ortho-C$_6$H$_3$), 162.90 (q, $^1$J$_{C-C}$ = 49.8 Hz, ipso-C$_6$H$_3$) ppm.

$^{11}$B($^1$H) NMR (128 MHz, [D$_8$]THF): δ = -6.50 ppm.

$^{19}$F($^1$H) NMR (377 MHz, [D$_8$]THF): δ = -63.44 ppm.

IR (KBr): ν = 1758 (m, ZnH), 1610 cm$^{-1}$ (m, ZnH).

Anal. Calcd. for C$_{58}$H$_{76}$B$_2$F$_{48}$N$_6$Zn$_3$ (2209.86 g · mol$^{-1}$): C, 46.55; H, 4.73; N, 4.18. Found: C, 46.02; H, 4.52; N, 4.22%. 

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Figure S39: $^1$H NMR spectrum of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (3b) in [D8]THF.

Figure S40: $^{13}$C($^1$H) NMR spectrum of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (3b) in [D8]THF.
Figure S41: $^{11}$B($^1$H) NMR spectrum of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] in [D8]THF.

Figure S42: $^{19}$F($^1$H) NMR spectrum of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (3b) in [D8]THF.
Figure S43: IR spectrum (KBr pellet) of [(TEEDA)₂Zn₃H₃][B(3,5-(CF₃)₂-C₆H₃)] (3b).

Synthesis of [(TMEDA)₃Zn₃H₆][B(3,5-(CF₃)₂-C₆H₃)₄]₂ (4a).

**Method A:** To a suspension of [ZnH₂]ₙ (21 mg, 306 µmol) in THF (5 mL) was added a solution of [(TMEDA)H][B(3,5-(CF₃)₂-C₆H₃)₄] (200 mg, 204 µmol) and TMEDA (12 mg, 102 µmol) in THF (5 mL). After gas evolution had ceased (ca. 15 min), the reaction mixture was filtered and the volume of the filtrate reduced in vacuo. Addition of n-pentane resulted in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressure to give colorless platelets (201 mg, 91 µmol). Yield: 90%.

**Method B:** To a suspension of [ZnH₂]ₙ (3 mg, 44 µmol) and TMEDA (5 mg, 44 µmol) in THF (5 mL) was added a solution containing [(TMEDA)ZnH(thf)][B(3,5-(CF₃)₂-C₆H₃)₄] (100 mg, 89 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 30 min. After filtration the solvent was removed in vacuo to give [(TMEDA)₃Zn₃H₆][B(3,5-(CF₃)₂-C₆H₃)₄]₂ as colorless platelets (92 mg, 42 µmol). Yield: 94%.

¹H NMR (400 MHz, [D₈]THF): δ = 2.50 (s, N-CH₃, 36H), 2.73 (s, N-CH₂, 12H), 3.62 (s, Zn-H, 4H), 7.60 (s, para-C₆H₃, 8H), 7.80 (s, ortho-C₆H₃, 16H) ppm.

¹³C{¹H} NMR (101 MHz, [D₈]THF): δ = 47.52 (N-CH₃), 58.26 (N-CH₂), 118.29 (para-C₆H₃), 125.61 (q, ¹J_C-F = 272.2 Hz, CF₃), 130.12 (qq, ²J_C-F = 31.5 Hz, ³J_B-C = 2.8 Hz, meta-C₆H₃), 135.68 (ortho-C₆H₃), 162.90 (q, ¹J_B-C = 49.8 Hz, ipso-C₆H₃) ppm.
$^{11}$B($^1$H) NMR (128 MHz, [D8]THF): δ = -6.50 ppm.

$^{19}$F($^1$H) NMR (377 MHz, [D8]THF): δ = -63.42 ppm.

IR (KBr): ν = 1778 (m, ZnH), 1606 cm$^{-1}$ (m, ZnH).

Anal. Calcd. for C$_{82}$H$_{76}$B$_2$F$_{48}$N$_6$Zn$_3$ (2209.86 g ∙ mol$^{-1}$): C, 44.57; H, 3.47; N, 3.80. Found: C, 44.17; H, 4.36; N, 4.69%.

**Figure S44**: $^1$H NMR spectrum of [(TMEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (4a) in [D8]THF.

**Figure S45**: $^{13}$C($^1$H) NMR spectrum of [(TMEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (4a) in [D8]THF.
Figure S46: $^{11}$B($^1$H) NMR spectrum of [(TMEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (4a) in [D8]THF.

Figure S47: $^{19}$F($^1$H) NMR spectrum of [(TMEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (4a) in [D8]THF.
Figure S48: IR spectrum (KBr pellet) of [(TMEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$] (4a).

Synthesis of [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$] (4b).

Method A: To a suspension of [ZnH$_2$]$_n$ (19 mg, 289 µmol) in THF (5 mL) was added dropwise a solution containing [(TEEDA)H][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (200 mg, 192 mmol) and TEEDA (17 mg, 96 µmol) in THF (5 mL). After gas evolution had ceased (approximately 15 min) the reaction mixture was filtered and the volume of the filtrate reduced in vacuo. Addition of n-pentane results in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressure to give a colorless solid (217 mg, 89 µmol). Yield: 92%.

Method B: To a suspension of [ZnH$_2$]$_n$ (3 mg, 45 µmol) and TEEDA (8 mg, 45 µmol) in THF (5 mL) was added a solution of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$] (100 mg, 45 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 30 min. After filtration the solvent was removed in vacuo giving [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$] as a colorless solid (103 mg, 42 µmol). Yield: 98%.

$^1$H NMR (400 MHz, [D$_8$]THF): $\delta = 1.15$ (t, $^3$J$_{HH} = 7.1$ Hz, N-CH$_2$-C$_6$H$_3$, 36H), 2.88 (m, N-CH$_2$CH$_3$, 12H), 2.92 (s, N-CH$_2$, 12H), 3.03 (m, N-CH$_2$CH$_3$, 12H), 3.66 (s, Zn-H, 4H), 7.58 (s, para-C$_6$H$_3$, 8H), 7.79 (s, ortho-C$_6$H$_3$, 16H) ppm.
$^{13}$C$[^1]$H NMR (101 MHz, [D8]THF): $\delta = 9.09$ (N-CH$_2$CH$_3$), 47.46 (N-CH$_2$CH$_3$), 51.67 (N-CH$_2$CH$_3$), 118.26 (para-C$_6$H$_3$), 125.59 (q, $^1$J$_{CF} = 272.2$ Hz, CF$_3$), 130.09 (qq, $^2$J$_{CF} = 31.5$ Hz, $^3$J$_{BC} = 2.8$ Hz, meta-C$_6$H$_3$), 135.67 (ortho-C$_6$H$_3$), 162.88 (q, $^1$J$_{BC} = 49.8$ Hz, ipso-C$_6$H$_3$) ppm.

$^{11}$B$[^1]$H NMR (128 MHz, [D8]THF): $\delta = -6.48$ ppm.

$^{19}$F$[^1]$H NMR (377 MHz, [D8]THF): $\delta = -63.42$ ppm.

IR (KBr): $\nu = 1766$ (m, ZnH), 1610 cm$^{-1}$ (m, ZnH).

Anal. Calcd. for C$_{94}$H$_{100}$B$_2$F$_{48}$N$_6$Zn$_3$: C, 46.20; H, 4.13; N, 3.44. Found: C, 46.10; H, 4.71; N, 3.59%.

Figure S49: $^1$H NMR spectrum of [(TEEDA)$_2$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (4b) in [D8]THF.
Figure S50: $^{13}$C($^1$H) NMR spectrum of [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)]$_2$ (4b) in [D8]THF.

Figure S51: $^{11}$B($^1$H) NMR spectrum of [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)]$_2$ (4b) in [D8]THF.
**Figure S52**: $^{19}$F($^1$H) NMR spectrum of [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$] (4b) in [D$_8$]THF.

**Figure S53**: IR spectrum (KBr pellet) of [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$] (4b).
Synthesis of [(TEEDA)Zn(µ-H₂)][(TMEDA)ZnH₂][B(3,5-(CF₃)₂-C₆H₃)]₂ (4c).
To a suspension of [ZnH₂]₃ (3 mg, 45 µmol) and TEEDA (8 mg, 45 µmol) THF (5 mL) was added a solution of [(TMEDA)ZnH(thf)][B(3,5-(CF₃)₂-C₆H₃)₄] (100 mg, 89 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature until all solid material had dissolved (approximately 15 min). The solvent volume was reduced in vacuo. Addition of n-pentane resulted in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressure to give colorless solid (102 mg, 43 µmol). Yield: 95%.

¹H NMR (400 MHz, [D₈]THF): δ = 1.14 (t, ³Jₜ-H = 7.1 Hz, N-CH₂CH₃, 12H), 2.59 (s, N-CH₆, 24H), 2.84 (s, N-CH₂, 8H), 2.86–2.90 (m, N-CH₂CH₃, 4H), 2.92 (s, N-CH₂, 4H), 2.97–3.09 (m, N-CH₂CH₃, 4H), 3.67 (s, Zn-H, 4H), 7.59 (s, para-C₆H₃, 8H), 7.80 (s, ortho-C₆H₃, 16H).

¹³C(¹H) NMR (101 MHz, [D₈]THF): δ = 9.14 (N-CH₂CH₃), 47.58 (N-CH₂CH₃), 48.13 (N-CH₃), 51.71 (N-CH₂), 58.02 (N-CH₂), 118.28 (para-C₆H₃), 125.60 (q, ¹Jₖ-C = 272.2 Hz, CF₃), 130.06 (qq, ¹Jₖ₃ = 31.5 Hz, ³Jₘ₈-C = 2.8 Hz, meta-C₆H₃), 135.68 (ortho-C₆H₃), 162.89 (q, ¹Jₖ-C = 49.8 Hz, ipso-C₆H₃) ppm.

¹¹B(¹H) NMR (128 MHz, [D₈]THF): δ = -6.49 ppm.

¹⁹F(¹H) NMR (377 MHz, [D₈]THF): δ = -63.38 ppm.

IR (KBr): ν = 1774 (m, ZnH), 1611 cm⁻¹ (m, ZnH).

Anal. Calcd. for C₆₆H₄₂B₂F₄₈N₆Zn₃ (2331.34 g · mol⁻¹): C, 44.31; H, 3.63; N, 3.60. Found: C, 42.99; H, 3.79; N, 3.74%.
Figure S54: $^1$H NMR spectrum of $\left[(\text{TEEDA})\text{Zn}(\mu-H_2)\right]\left[(\text{TMEDA})\text{ZnH}\right)_2\left[B(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)\right]_2$ (4c) in [D8]THF.

Figure S55: $^{13}$C($^1$H) NMR spectrum of $\left[(\text{TEEDA})\text{Zn}(\mu-H_2)\right]\left[(\text{TMEDA})\text{ZnH}\right)_2\left[B(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)\right]_2$ (4c) in [D8]THF.
**Figure S56:** $^{11}$B($^1$H) NMR spectrum of $[[\text{TEEDA}]\text{Zn(µ-H}_2\text{)}][(\text{TMEDA})\text{ZnH}_2]]\text{[B(3,5-(CF}_3\text{)C}_6\text{H}_3\text{)]}_2}$ (4c) in [D8]THF.

**Figure S57:** $^{19}$F($^1$H) NMR spectrum of $[[\text{TEEDA}]\text{Zn(µ-H}_2\text{)}][(\text{TMEDA})\text{ZnH}_2]]\text{[B(3,5-(CF}_3\text{)C}_6\text{H}_3\text{)]}_2}$ (4c) in [D8]THF.
Figure S58: IR spectrum (KBr pellet) \(\{(\text{TEEDA})\text{Zn(μ-H)}\}_2\{(\text{TMEDA})\text{ZnH}_2\}_2\)\[\text{B}(\text{3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3)\]_2 (4c).
Molecular structure of 4c. Displacement parameters of the zinc and nitrogen atoms are set at 40% probability level. The borate anions and hydrogen atoms except of H1, H2, H3 and H4 are omitted for clarity. Selected bond distances [Å] and angles [°]: Zn1-H1 1.75(6), Zn1-H3 1.89(2), Zn3-H3 1.78(6), Zn3-H4 1.62(6), Zn2-H4 1.78(2), Zn2-H2 1.61(6), H1-Zn1-H3 125(3), H3-Zn3-H4 130(3), H4-Zn2-H2 118(3).
Synthesis of [(TMEDA)Zn(OCHO)]₂[B(3,5-(CF₃)₂-C₆H₃)₄] (5a).
A solution of [(TMEDA)₂ZnH(thf)][B(3,5-(CF₃)₂-C₆H₃)₄] (200 mg, 179 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO₂ (1 bar). The reaction mixture was layered with n-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying in vacuo to give [(TMEDA)₂Zn(OCHO)]₂[B(3,5-(CF₃)₂-C₆H₃)₄] as a colorless solid (185 mg, 84 µmol). Yield: 94%.

¹H NMR (400 MHz, [D₈]THF): δ = 2.62 (s, N-C₆H₃, 24H), 2.91 (s, N-C₆H₃, 8H), 7.58 (s, para-C₆H₃, 4H), 7.79 (s, ortho-C₆H₃, 8H), 8.26 (s, Zn-OCHO, 2H) ppm.

¹³C{¹H} NMR (101 MHz, [D₈]THF): δ = 47.34 (N-C₆H₃), 57.60 (N-C₆H₃), 118.24 (para-C₆H₃), 125.59 (q, ¹J_C-F = 272.2 Hz, CF₃), 130.27 (qq, ²J_C-F = 31.8 Hz, ³J_B-C = 2.9 Hz, meta-C₆H₃), 135.67 (ortho-C₆H₃), 162.88 (q, ¹J_B-C = 49.8 Hz, ipso-C₆H₃), 171.87 (Zn-OCHO) ppm.

¹¹B{¹H} NMR (128 MHz, [D₈]THF): δ = -6.48 ppm.

¹⁹F{¹H} NMR (377 MHz, [D₈]THF): δ = -63.41 ppm.

IR (KBr): ν = 1649 cm⁻¹ (s, ZnOCHO).

Anal. Calcd. for C₇₈H₅₈B₂F₄₈N₄O₄Zn₂ (2179.65 g · mol⁻¹): C, 42.98; H, 2.68; N, 2.57. Found: C, 43.62; H, 3.67; N, 2.38%.

Figure S59: ¹H NMR spectrum of [(TMEDA)Zn(OCHO)]₂[B(3,5-(CF₃)₂-C₆H₃)₄] (5a) in [D₈]THF.
Figure S60: $^{13}$C$({}^1\text{H})$ NMR spectrum of [(TMEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (5a) in [D8]THF.

Figure S61: $^{11}$B$({}^1\text{H})$ NMR spectrum of [(TMEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$]$_2$ (5a) in [D8]THF.
**Figure S62**: $^{19}$F($^1$H) NMR spectrum of [(TMEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (5a) in [D8]THF.

**Figure S63**: IR spectrum (KBr pellet) of [(TMEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (5a).
Synthesis of [(TEEDA)Zn(OCHO)]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2 (5b).
A solution of [(TEEDA)ZnH][B(3,5-(CF_3)_2-C_6H_3)_4]_2 (200 mg, 91 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO_2 (1 bar). The reaction mixture was layered with n-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying in vacuo to give [(TEEDA)_2Zn(OCHO)]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2 as a colorless solid (201 mg, 88 µmol). Yield: 96%.

^1^H NMR (400 MHz, [D8]THF): δ = 1.16 (t, ^3^J_H-H = 7.1 Hz, N-CH_2CH_3, 24H), 3.02 (m br., N-C_6H_2CH_3, 16H), 3.07 (s, N-CH_2CH_2, 8H), 7.59 (s, para-C_6H_3, 4H), 7.79 (s, ortho-C_6H_3, 8H), 8.23 (s, Zn-OCHO, 2H) ppm.

^1^3^C(^1^H) NMR (101 MHz, [D8]THF): δ = 7.74 (N-CH_2CH_3), 46.06 (N-CH_2CH_3), 50.34 (N-CH_2CH_2), 117.21 (para-C_6H_3), 124.53 (q, ^1^J_C-F = 272.2 Hz, CF_3), 129.04 (qq, ^2^J_C-F = 31.5 Hz, ^3^J_C-C = 2.8 Hz, meta-C_6H_3), 134.61 (ortho-C_6H_3), 161.82 (q, ^1^J_B-C = 49.9 Hz, ipso-C_6H_3), 170.19 (Zn-OCHO) ppm.

^1^1^B(^1^H) NMR (128 MHz, [D8]THF): δ = -6.48 ppm.

^1^9^F(^1^H) NMR (377 MHz, [D8]THF): δ = -63.39 ppm.

IR (KBr): ν = 1625 cm^{-1} (s, ZnOCHO).

Anal. Calcd. for C_{86}H_{74}B_2F_{48}N_4O_4Zn_2 (2291.87 g ∙ mol^{-1}): C, 45.07; H, 3.25; N, 2.44. Found: C, 45.28; H, 3.44; N, 2.79%.
Figure S 64: $^1$H NMR spectrum of [(TEEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (5b) in [D$_8$]THF.

Figure S65: $^{13}$C($^1$H) NMR spectrum of [(TEEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (5b) in [D$_8$]THF.
**Figure S66**: $^{11}$B($^1$H) NMR spectrum of [(TEEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (5b) in [D$_8$]THF.

**Figure S67**: $^{19}$F($^1$H) NMR spectrum of [(TEEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (5b) in [D$_8$]THF.
Synthesis of [(TMEDA)₂Zn(OCHO)]₂[B(3,5-(CF₃)₂-C₆H₃)₄] (6a).

A solution of [(TMEDA)₂Zn₂H₃][B(3,5-(CF₃)₂-C₆H₃)₄] (200 mg, 163 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO₂ (1 bar). The reaction mixture was layered with n-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying in vacuo to give [(TMEDA)₂Zn₅(OCHO)]₂[B(3,5-(CF₃)₂-C₆H₃)₄] as colorless rods (212 mg, 156 µmol). Yield: 92 %.

¹H NMR (400 MHz, [D₈]THF): δ = 2.49 (s, N-CH₃, 24H), 2.76 (s, N-CH₂, 8H), 7.58 (s, para-C₆H₃, 4H), 7.79 (s, ortho-C₆H₃, 8H), 8.26 (s, Zn-OCHO, 3H) ppm.

¹³C(¹H) NMR (101 MHz, [D₈]THF): δ = 47.04 (N-CH₃), 57.02 (N-CH₂), 118.23 (para-C₆H₃), 125.58 (q, ¹J_C-F = 272.2 Hz, CF₃), 130.10 (qq, ²J_C-F = 31.5 Hz, ³J_B-C = 2.8 Hz, meta-C₆H₃), 135.66 (ortho-C₆H₃), 162.88 (q, ¹J_B-C = 49.9 Hz, ipso-C₆H₃), 170.70 (Zn-OCHO) ppm.

¹¹B(¹H) NMR (128 MHz, [D₈]THF): δ = -6.60 ppm.

¹⁹F(¹H) NMR (377 MHz, [D₈]THF): δ = -63.43 ppm.

IR (KBr): ν = 1653 cm⁻¹ (s, ZnH).
Anal. Calcd. for $C_{47}H_{47}BF_{24}N_4O_6Zn_2$ (1361.45 g · mol$^{-1}$): C, 41.96; H, 3.48; N, 4.12. Found: C, 41.55; H, 3.96; N, 4.14%.

Figure S69: $^1$H NMR spectrum of [[(TMEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (6a) in [D8]THF.

Figure S70: $^{13}$C($^1$H) NMR spectrum of [[(TMEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (6a) in [D8]THF.
Figure S71: $^{11}$B($^1$H) NMR spectrum of [(TMEDA)$_2$Zn$_2$(OCHO)$_3$]B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$ (6a) in [D8]THF.

Figure S72: $^{19}$F($^1$H) NMR spectrum of [(TMEDA)$_2$Zn$_2$(OCHO)$_3$]B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$ (6a) in [D8]THF.
Figure S73: IR spectrum (KBr pellet) of [(TMEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (6a).

**Synthesis of [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (6b).**

A solution of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (200 mg, 149 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO$_2$ (1 bar). The reaction mixture was layered with n-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying in vacuo to give [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] as a colorless solid (204 mg, 138 µmol). Yield: 96%.

$^1$H NMR (400 MHz, [D$_8$]THF): $\delta$ = 1.11 (t, $^3$J$_{H-H}$ = 7.1 Hz, N-CH$_2$CH$_3$, 24H), 2.97 (m, N-CH$_2$, 24H), 7.60 (s, para-C$_6$H$_3$, 4H), 7.81 (s, ortho-C$_6$H$_3$, 8H), 8.30 (s, Zn-OCHO, 3H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, [D$_8$]THF): $\delta$ = 8.84 (N-CH$_2$CH$_3$), 46.94 (N-CH$_2$CH$_3$), 50.97 (N-CH$_2$CH$_2$), 118.28 (para-C$_6$H$_3$), 125.62 (q, $^1$J$_{C-F}$ = 272.2 Hz, CF$_3$), 130.13 (q, $^2$J$_{C-F}$ = 31.5 Hz, $^3$J$_{C-B}$ = 2.8 Hz, meta-C$_6$H$_3$), 135.70 (ortho-C$_6$H$_3$), 162.90 (q, $^1$J$_{B-C}$ = 49.8 Hz, ipso-C$_6$H$_3$), 171.45 (Zn-OCHO) ppm.

$^{11}$B($^1$H) NMR (128 MHz, [D$_8$]THF): $\delta$ = -6.48 ppm.

$^{19}$F($^1$H) NMR (377 MHz, [D$_8$]THF): $\delta$ = -63.38 ppm.
IR (KBr): $\nu = 1594 \text{ cm}^{-1}$ (s, ZnH).

Anal. Calcd. for $C_{55}H_{63}BF_{24}N_4O_6Zn_3$ (1473.66 g · mol$^{-1}$): C, 44.83; H, 4.13; N 3.80. Found: C, 44.73; H, 4.27; N, 3.78%.

Figure S74: $^1$H NMR spectrum of [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-$C_6$H$_3$)$_4$] (6b) in [D8]THF.

Figure S75: $^{13}$C($^1$H) NMR spectrum of [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-$C_6$H$_3$)$_4$] (6b) in [D8]THF.
Figure S76: $^{11}$B($^1$H) NMR spectrum of [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (6b) in [D$_8$]THF.

Figure S77: $^{19}$F($^1$H) NMR spectrum of [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (6b) in [D$_8$]THF.
Figure S78: IR spectrum (KBr pellet) of [(TEEDA)₂Zn₂(OCHO)₃][B(3,5-(CF₃)₂-C₆H₃)₄] (6b).

**Synthesis of [(TMEDA)Zn(OCHO)₂] (7a).**

**Method A:** A solution of [(TMEDA)₃Zn₃H₄][B(3,5-(CF₃)₂-C₆H₃)₄]₂ (200 mg, 88 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO₂ (1 bar). The solvent was removed in vacuo and the residue was extracted with benzene (3 x 3 mL) The solvent was removed in vacuo and the residue was extracted with diethyl ether (3 x 3 mL) to separate the title compound [(TMEDA)Zn(OCHO)]₂[B(3,5-(CF₃)₂-C₆H₃)₄]₂ from 5a. The combined ethereal extracts were filtered and the solvent removed in vacuo. Repeated recrystallization and drying under reduced pressure gave [(TEMDA)₂Zn(OCHO)₂] as a solid (19 mg, 70 µmol). Yield: 80 % (based on the maximum theoretical yield).

**Method B:** A suspension of [ZnH₂]ₙ (20 mg, 296 µmol) and TMEDA (35 mg, 296 µmol) in CH₂CH₂ (2 mL) was transferred into a Schlenk tube equipped with a stir bar, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO₂ (1 bar). The suspension was stirred at room temperature until all solid material had dissolved (approximately 20 min). The solvent was removed in vacuo to give [(TEEDA)Zn(OCHO)₂] as a colorless solid (79 mg, 290 µmol). Yield: 98 %.
\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 2.53\) (s, N-CH\(_3\), 12H), 2.73 (s, N-CH\(_2\), 4H), 8.29 (s, Zn-OCHO, 2H) ppm.

\(^{13}\)C\(^{(1)}\)H NMR (101 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 47.12\) (N-CH\(_3\)), 57.27 (N-CH\(_2\)), 169.70 (Zn-OCHO) ppm.

IR (KBr): \(\nu = 1608\) cm\(^{-1}\) (s, ZnOCHO).

Anal. Calcd. for C\(_8\)H\(_{18}\)N\(_2\)O\(_4\)Zn (271.62 g \cdot mol\(^{-1}\)): C, 35.38; H, 6.68; N 10.31. Found: C, 35.11; H, 6.60; N, 10.45%.

Figure S79: \(^1\)H NMR spectrum of [(TMEDA)Zn(OCHO)\(_2\)] (7a) in CD\(_2\)Cl\(_2\).

Figure S80: \(^{13}\)C\(^{(1)}\)H NMR spectrum of [(TMEDA)Zn(OCHO)\(_2\)] (7a) in CD\(_2\)Cl\(_2\).
Figure S81: IR spectrum (KBr pellet) of [(TMEDA)Zn(OCHO)_2] (7a).

Molecular structure of 7a. Displacement parameters atoms are set at 50% probability level. The hydrogen atoms except of the formate hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Zn1-O1 1.986(3), Zn1-N1 2.101(4), N1-Zn1-O1 102.89(14), N1'-Zn1-O1 113.13(15).[55]

Synthesis of [(TEEDA)Zn(OCHO)_2] (7b).
A solution of [(TEEDA)_3Zn_3H_4][B(3,5-(CF_3)_2-C_6H_3)_4]_2 (200 mg, 82 μmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and
pressurized with CO₂ (1 bar). The solvent was removed in vacuo and the residue was extracted with diethyl ether (3 x 3 mL) to separate the title compound [(TEEDA)Zn(OCHO)]₂[B(3,5-(CF₃)₂-C₆H₃)]₂ from 5b. The combined ethereal extracts were filtered and the solvent removed in vacuo. Repeated recrystallization and drying under reduced pressure gave [(TEEDA)₂Zn(OCHO)]₂ as colorless solid (12 mg, 68 µmol). Yield: 83 % (based on the maximum theoretical yield).

Method B: A suspension of [ZnH₂₅] (20 mg, 296 µmol) and TEEDA (51 mg, 296 µmol) in CH₂CH₂ (2 mL) was transferred into a Schlenk tube equipped with a stir bar, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO₂ (1 bar). The suspension was stirred at room temperature until all solid material had dissolved (approximately 20 min). The solvent was removed in vacuo to give [(TEEDA)₂Zn(OCHO)]₂ as a colorless solid (94 mg, 287 µmol). Yield: 98 %.

¹H NMR (400 MHz, CD₂Cl₂): δ = 1.08 (t, ³J_H,H = 7.1 Hz, N-CH₂CH₃, 12H), 2.79 (m, N-CH₂CH₃, 4H), 2.87 (s, N-CH₂, 4H), 3.17 (m, N-CH₂CH₃, 4H), 8.31 (s, Zn-OCHO, 2H) ppm.

¹³C(¹H) NMR (101 MHz, CD₂Cl₂): δ = 8.78 (N-CH₂CH₃), 46.18 (N-CH₂CH₃), 51.02 (N-CH₂CH₃), 168.48 (Zn-OCHO) ppm.

IR (KBr): ν = 1633 cm⁻¹ (s, ZnOCHO).

Anal. Calcd. for C₁₂H₂₆N₂O₄Zn (327.73 g · mol⁻¹): C, 43.98; H, 8.00; N 8.55. Found: C, 42.84; H, 7.68; N, 8.60%.

Figure S82: ¹H NMR spectrum of [(TEEDA)Zn(OCHO)]₂ (7b) in CD₂Cl₂.
Figure S83: $^{13}$C{^1}H NMR spectrum of [(TEEDA)Zn(OCHO)$_2$] (7b) in CD$_2$Cl$_2$.

Figure S84: IR spectrum (KBr pellet) of [(TEEDA)Zn(OCHO)$_2$] (7b).
Synthesis of silanes

Synthesis of \( \text{\textsuperscript{\(n\)}} \text{BuMe}_2\text{SiH}\)\textsuperscript{[S6]}

To a suspension of LiAlH\(_4\) (302 mg, 7.9 mmol) tetruglyme was added dropwise \( \text{\textsuperscript{\(n\)}} \text{BuMe}_2\text{SiCl} \) (1000 mg, 6.6 mmol) and stirred over night at roomtemperature. The title compound was distilled directly from the reaction mixture under reduced preassure as a colorless liquid. Yield: 740 mg, 6.4 mmol, 96%.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 0.06 \) (d, \( J_{\text{HH}} = 3.7 \) Hz, 6H, Si-\( \text{CH}_3 \)), 0.44 – 0.63 (m, 2H, Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 0.89 (t, \( J_{\text{HH}} = 7.0 \) Hz, 3H, Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 1.18 – 1.44 (m, 6H, Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 3.84 (hept, \( J = 3.6 \) Hz, 1H, Si-\( \text{H} \)) ppm.

\(^{13}\)C\(^{\{1\}}\)H NMR (101 MHz, CDCl\(_3\)): \( \delta = -4.28 \) (Si-\( \text{CH}_3 \)), 13.96 (Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 14.02 (Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 26.33(Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 26.75 (Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)) ppm.

\(^{29}\)Si\(^{\{1\}}\)H (DEPT 45) NMR (79 MHz, CDCl\(_3\)): \( \delta = -13.06 \) ppm.

\(^{29}\)Si\(^{\{1\}}\)H (inverse gated) NMR (79 MHz, CDCl\(_3\)): \( \delta = -13.06 \) ppm.

Figure S85: \(^1\)H NMR spectrum of \( \text{\textsuperscript{\(n\)}} \text{BuMe}_2\text{SiH} \) in CDCl\(_3\).
Figure S86: $^{13}$C($^1$H) NMR spectrum of $^n$BuMe$_2$SiH in CDCl$_3$.

Figure S87: $^{29}$Si($^1$H) NMR spectrum (DEPT 45) of $^n$BuMe$_2$SiH in CDCl$_3$. 
Synthesis of \( ^{7} \text{BuMe}_2 \text{Si(OCHO)} \)[\( \text{S7} \)]

To Na(OCHO) (541 mg, 7.9 mmol) in tetraglyme was added \( ^{7} \text{BuMe}_2 \text{SiCl} \) (1000 mg, 6.6 mmol) and reaction mixture was stirred for 48 h at 90°C. The title compound was distilled direct from the reaction mixture as a colorless liquid. Yield: 999 mg, 6.2 mmol, 94%.

\(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 0.30 \) (s, 6H, Si-\( \text{CH}_3 \)), 0.74 – 0.82 (m, 2H, Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 0.85 – 0.95 (m, 3H), 1.28 – 1.42 (m, 4H, Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 8.08 (s, 1H, Si-OCHO) ppm.

\(^{13}\text{C}(^1\text{H}) \) NMR (101 MHz, CDCl\(_3\)): \( \delta = -1.64 \) (Si-\( \text{CH}_3 \)), 13.83 (Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 15.82 (Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 25.01 (Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 26.25 (Si-\( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 161.19 (Si-OCHO) ppm.

\(^{29}\text{Si}(^1\text{H}) \) (DEPT 20) NMR (79 MHz, CDCl\(_3\)): \( \delta = 26.19 \) ppm.

\(^{29}\text{Si}(^1\text{H}) \) (inverse gated) NMR (79 MHz, CDCl\(_3\)): \( \delta = 26.19 \) ppm.
Figure S89: $^1$H NMR spectrum of $^n$BuMe$_2$Si(OCHO) in CDCl$_3$.

Figure S90: $^{13}$C($^1$H) NMR spectrum of $^n$BuMe$_2$Si(OCHO) in CDCl$_3$. 
Figure S91: $^{29}$Si($^1$H) NMR spectrum (DEPT 20) of $^n$BuMe$_2$Si(OCHO) in CDCl$_3$.

Figure S92: $^{29}$Si($^1$H) NMR spectrum (inverse gated) of $^n$BuMe$_2$Si(OCHO) in CDCl$_3$. 
Synthesis of \( \text{"BuMe}_2\text{Si(OCH}_3\text{)} \)\[^{[S8]}\]

To NaOCH\(_3\) (430 mg, 7.9 mmol) in tetraglyme was added dropwise \( \text{"BuMe}_2\text{SiCl} \) (1000 mg, 6.6 mmol) and stirred for 48 h at 80°C. The title compound was directly distilled from the reaction mixture as a colorless liquid. Yield: 912 mg, 6.2 mmol, 94%.

\(^1\text{H NMR (400 MHz, CDCl}_3\): } \delta = 0.09 \text{ (s, 6H, Si-CH}_3\text{), 0.54 – 0.65 (m, 2H, Si-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{), 0.83 – 0.95 (m, 3H, Si-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{), 1.23 – 1.43 (m, 4H, Si-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{), 3.42 (s, 3H, Si-OCCH}_3\text{) ppm.}

\(^{13}\text{C}[^{1}\text{H}]\text{ NMR (101 MHz, CDCl}_3\): } \delta = -2.54 \text{ (Si-CH}_3\text{), 13.93 (Si-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{), 15.73 (Si-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{), 25.50 (Si-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{), 26.54 (Si-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{), 50.41 (Si-OCCH}_3\text{) ppm.}

\(^{29}\text{Si}[^{1}\text{H}]\text{ (DEPT 20) NMR (79 MHz, CDCl}_3\): } \delta = 19.79 \text{ ppm.}

\(^{29}\text{Si}[^{1}\text{H}]\text{ (inverse gated) NMR (79 MHz, CDCl}_3\): } \delta = 19.80 \text{ ppm.}

\textbf{Figure S93: } \(^1\text{H NMR spectrum of } \text{"BuMe}_2\text{Si(OCH}_3\text{) in CDCl}_3\text{.}\)
Figure S94: $^{13}$C($^1$H) NMR spectrum of $^n$BuMe$_2$Si(OCH$_3$)$_2$ in CDCl$_3$.

Figure S95: $^{29}$Si($^1$H) NMR spectrum (DEPT20) of $^n$BuMe$_2$Si(OCH$_3$)$_2$ in CDCl$_3$. 
Figure S96: $^{29}$Si($^1$H) NMR spectrum (inverse gated) of $^6$BuMe$_2$Si(OCH$_3$) in CDCl$_3$. 
Catalysis of CO₂ Hydrosilylation

Typical procedure for CO₂ hydrosilylation

In a glovebox, a J. Young-style NMR tube was charged with hydrosilane (0.18 mmol) and hexamethylbenzene (0.06 mmol). 0.5 mL of a catalyst stock solution in [D8]THF was added. The mixture was degassed by three cycles of “freeze-pump-thaw” and pressurized with 1 bar of CO₂. The reaction progress was monitored by NMR spectroscopy. Selected spectra of the catalytic reaction mixture are provided below.

Typical procedure for twostep CO₂ hydrosilylation

In a glovebox, a J. Young-style NMR tube was charged with silane (0.18 mmol) and hexamethylbenzene (0.06 mmol). 0.5 mL of a catalyst stock solution in [D8]THF was added. The mixture was degassed by three cycles of “freeze-pump-thaw” and pressurized with 1 bar of CO₂. When hydrosilane was consumed CO₂ was removed by three cycles of “freeze-pump-thaw” and the reaction mixture charged with silane. The reaction progress was monitored by NMR spectroscopy. Selected spectra of the catalytic reaction mixture are provided below.

Catalytic hydrosilylation using nBuMe₂SiH:

Figure S97: ¹H NMR spectra of the catalytic reaction mixture with nBuMe₂SiH ($$: hexamethylbenzene as internal standard); a): at the start, b) after 6h.
Figure S98: $^{29}$Si($^1$H) NMR spectrum (inverse gated) of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 6 h.

Figure S99: $^{29}$Si($^1$H) NMR spectrum (DEPT20) of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 6 h.
**Figure S100**: $^{29}$Si$^1$H HMBC spectrum of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 6 h.

**Figure S101**: $^1$H NMR spectra of the catalytic reaction mixture with $^n$BuMe$_2$SiH ($$: hexamethylbenzene as internal standard). a): Start of the reaction; b): after 6 h and full consumption of silane; c): 16 h and addition of 1 equiv. silane and catalyst.
Figure S102: $^1$H NMR spectrum after 16 h of the catalytic reaction mixture with $^n$BuMe$_2$SiH ($$: hexamethylbenzene as internal standard).

Figure S103: $^{29}$Si($^1$H) NMR spectrum (DEPT20) of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 16 h.
Figure S104: $^{29}$Si($^1$H) NMR spectrum (inverse gated) of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 16 h.

Figure S105: $^1$H NMR spectra of the catalytic reaction mixture with $^n$BuMe$_2$SiH ($$: hexamethylbenzene as internal standard). a): reaction mixture after 16 h and added silane and catalyst; b): after 24 h and excess silane (2 equiv.) and catalyst.
Figure S106: $^{29}$Si($^1$H) NMR spectrum (DEPT20) of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 24 h.

Figure S107: $^{29}$Si($^1$H) NMR spectrum (inverse gated) of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 24 h.
Figure S108: $^{29}$Si$^1$H HMBC spectrum of the catalytic reaction mixture using $^n$BuMe$_2$SiH after 24 h and addition of excess silane (2 equiv.) and catalyst.
Catalytic hydrosilylation using EtMe₂SiH:

Figure S109: ¹H NMR spectra of the catalytic reaction mixture with EtMe₂SiH ($: hexamethylbenzene as internal standard); a): at the start; b): after 4h.

Figure S110: ¹H NMR spectra of the catalytic reaction mixture with EtMe₂SiH ($: hexamethylbenzene as internal standard) after 4h.
Figure S11: $^{29}\text{Si}[^1\text{H}]$ NMR spectrum (inverse gated) of the catalytic reaction mixture using EtMe$_2$SiH after 4h.

Figure S12: $^{29}\text{Si}[^1\text{H}]$ NMR spectrum (DEPT20) of the catalytic reaction mixture using EtMe$_2$SiH after 4h.
**Figure S113**: $^{29}$Si$^1$H HMBC spectrum of the catalytic reaction mixture using EtMe$_2$SiH after 4h.

**Figure S114**: $^1$H NMR spectra of the catalytic reaction mixture with EtMe$_2$SiH ($$: hexamethylbenzene as internal standard). a): Start of the reaction; b): after 4h and full consumption of silane; c): after 8h and addition of silane and catalyst.
Figure S115: $^1$H NMR spectrum after 8h of the catalytic reaction mixture with EtMe$_2$SiH ($$: hexamethylbenzene as internal standard).

Figure S116: $^{29}$Si($^1$H) NMR spectrum (DEPT 20) of the catalytic reaction mixture using EtMe$_2$SiH after 8 h.
Figure S117: $^{29}$Si($^1$H) NMR spectrum (inverse gated) of the catalytic reaction mixture using EtMe$_2$SiH after 8 h.

Figure S118: $^{29}$Si$^1$H HMBC spectrum of the catalytic reaction mixture using EtMe$_2$SiH after 8h.
**Figure S119**: $^1$H NMR spectra of the catalytic reaction mixture with EtMe$_2$SiH (S: hexamethylbenzene as internal standard). a): reaction mixture after 8 h and added silane and catalyst; b): after 14 h and excess silane (2 equiv.) and catalyst.

**Figure S120**: $^{29}$Si($^1$H) NMR spectrum (DEPT 20) of the catalytic reaction mixture using EtMe$_2$SiH after 14 h.
Figure S121: $^{29}$Si$^1$H NMR spectrum (inverse gated) of the catalytic reaction mixture using EtMe$_2$SiH after 14 h.

Figure S122: $^{29}$Si$^1$H HMBC spectrum of the catalytic reaction mixture using EtMe$_2$SiH after 14 h.
Catalytic hydrosilylation using Et₃SiH:

Figure S123: ¹H NMR spectra of the catalytic reaction mixture with Et₃SiH ($$: hexamethylbenzene as internal standard); a): at the start; b): after 48 h.

Figure S124: ¹H NMR spectra at the after 48 h of the catalytic reaction mixture with Et₃SiH ($$: hexamethylbenzene as internal standard).
Figure S125: $^{29}$Si($^1$H) NMR spectrum (inverse gated) of the catalytic reaction mixture using Et$_3$SiH after 48 h.

Figure S126: $^{29}$Si$^1$H HMBC spectrum of the catalytic reaction mixture using Et$_3$SiH after 48 h.
Background Catalysis

Figure S127: $^1$H NMR spectra at the start and after 60 h of the catalytic reaction mixture with $^6$BuMe$_2$SiH [Zn(OTf)$_2$] (10 mol%) as catalyst.

Figure S128: $^1$H NMR spectra at the start and after 60 h of the catalytic reaction mixture with $^6$BuMe$_2$SiH [NEt$_3$H][B(3,5-CF$_3$-C$_6$H$_3$)$_4$] (10 mol%) as catalyst.
Figure S 129: $^1$H NMR spectra of with $^n$BuMe$_2$SiH and B(3,5-CF$_3$-C$_6$H$_3$)$_3$ (10mol%) as catalyst: a) immediately after mixing; b) 20 min after mixing.
Stoichiometric reaction

Reaction of formate complex 2a with 1 equiv. of \textsuperscript{6}BuMe\textsubscript{2}Si(OCHO):

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure130.png}
\caption{\textsuperscript{1}H NMR spectra of the reaction of 1 eq. 2a with 1 equiv. of \textsuperscript{6}BuMe\textsubscript{2}Si(OCHO) (a): 10 min after mixing; b): 20 min after mixing) in [D\textsubscript{8}]THF.}
\end{figure}
\end{center}

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure131.png}
\caption{\textsuperscript{29}Si NMR spectra (DEPT 20) of the reaction of 1 equiv. 2a with 1 equiv. of \textsuperscript{6}BuMe\textsubscript{2}SiH (a): 10 min after mixing; b): 20 min after mixing) in [D\textsubscript{8}]THF.}
\end{figure}
\end{center}
Figure S132: $^1$H NMR spectrum of the reaction of 1 equiv. 2a with 1 equiv. of $^n$BuMe$_2$SiH: 20 min after mixing in [D8]THF.

Reaction of 2a with 1 equiv. of $^n$BuMe$_2$Si(OCH$_3$):

Figure S133: $^1$H NMR spectra of $^n$BuMe$_2$Si(OCH$_3$) and 2a in [D8]THF; (a): 10 min after mixing; b): 6 h after mixing.
Reaction of \( \text{nBuMe}_2\text{Si(OCHO)} \) and \( \text{nBuMe}_2\text{Si(OCH}_3\text{)} \) in presence of 2a:

**Figure S134:** \(^1\text{H NMR spectra of the reaction of } \text{nBuMe}_2\text{S(OCH}_3\text{)} \text{ with of } \text{nBuMe}_2\text{S(OCHO)} \text{ in the presence of } 2\text{a in [D8]THF; (a): 10 min after mixing; b): 24 h at 70 °C.} 

Reaction of \( \text{nBuMe}_2\text{Si(OCHO)} \) and \( \text{nBuMe}_2\text{Si(OCH}_3\text{)} \) in presence of 5a:

**Figure S135:** \(^1\text{H NMR spectra of the reaction of } \text{nBuMe}_2\text{S(OCH}_3\text{)} \text{ with of } \text{nBuMe}_2\text{S(OCHO)} \text{ in the presence of } 5\text{a in [D8]THF; (a): 10 min after mixing; b): 3 d at 70 °C.} 

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Reaction of \( \text{BuMe}_2\text{Si(OCHO)} \) and \( \text{BuMe}_2\text{Si(OCH}_3\text{)} \) without presence of a catalyst:

**Figure S136:** \(^1\text{H NMR spectra of } \text{BuMe}_2\text{Si(OCH}_3\text{)} \text{ of } \text{BuMe}_2\text{Si(OCHO)} \text{ in [D8]THF; (a): 10 min after mixing; b): 7 d at 70 °C.}**
Single Crystal X-ray Diffraction

X-ray diffraction data were collected at 100 K on an Eulerian 4-circle diffractometer STOE STADIVARI in ω-scan mode with Cu-Kα radiation (2a, 2b, 3a, 4a, 4c, 5a, 6a) or with Mo-Kα radiation (7a). The structures were solved by direct methods using SHELXT\textsuperscript{[59]} and all refinements were carried out against F\textsuperscript{2} with SHELXL\textsuperscript{[510]} as implemented in the program system Olex2.\textsuperscript{[511]} The packing of 2b contains CH\textsubscript{2}Cl\textsubscript{2}, the packing of 3a contains co-crystallized n-hexane, the packing of 4a contains co-crystallized CH\textsubscript{2}Cl\textsubscript{2}, and the packing of 4c contains co-crystallized n-pentane. The co-crystallized solvent in 6a could not be modelled reasonably well; in this case the routine “solvent mask” as implied in Olex2 was used. The molecular cation in 2b shows crystallographic \(\overline{1}\) symmetry, the molecular cation in 6a shows crystallographic \(C\) symmetry with the \(C\) axis through the atoms C1 and C2, and the molecule 7a shows crystallographic \(C\) symmetry with the \(C\) axis through the metal atom Zn1. The packing of 3a contains two crystallographically independent molecules, of which one \(C_{12}H_{35}N_4Zn_2\) unit is disordered (involving the atoms Zn4, N8, C54 and C55). The disorder was resolved by using split positions, also for the for CF\textsubscript{3} groups involving atoms F22, F23 and F24 in 2a, F13, F14 and F15 in 2b, F10, F11, F12 and F13, F14 and F15 in 3a. Further disorder that was resolved involved the carbon atoms C10 and C11, the fluorine atoms F1, F2, F3, F4, F5, F6, F7, F8, F9, F10, F12, F22, F23, F24, F40, F41, F42, F44, F45 in 4a, the fluorine atoms F46, F47 F48 in 4c, as well as the fluorine atoms F22, F23, F24 in 5a and the carbon atoms C4, C5, C6, C7, C8 in 6a. The carbon atoms of the co-crystallized solvent molecule n-pentane in 4c (C88 – C91) were also refined with split positions. All non-hydrogen atoms were refined with anisotropic displacement parameters. Only the disordered atoms C54B, C55B, C56B in 3a, F46, F47, F48 in 4c, C4, C5, C6, C7, C8 in 6a, as well as those of the solvent molecule n-pentane in 4c (C88 – C91) were refined with isotropic displacement parameters, because attempted refinement with anisotropic displacement parameters did not lead to physically meaningful values. The reflections 2 0 0, 2 0 2, 2 0 4 and 1 0 4 in 2a, as well as 1 0 1 in 4a were omitted from the refinement, because they were most likely affected by the beam stop. The hydrogen atoms were included in calculated positions and treated as riding throughout the refinement. Only the hydride atoms H1 in 2a, H1 in 2b, H1, H2 and H3 in 3a, as well as H1, H2, H3 and H4 in 4a were located in a Fourier difference map and were refined with isotropic displacement parameters. For the refinement of the anisotropic displacement parameters of the fluorine atoms of disordered CF\textsubscript{3} groups, restraints were used (F13, F14 and F15 in 2b, F10, F13, F14, F15, F46 and F47 in 3a, F1, F2, F3, F4, F5, F6, F9, F10, F11, F12, F22, F23, F24, F40, F41, F42, F44, F45 in 4a). Restraints were also used in the refinement of the anisotropic displacement parameters of Zn4 in 3a. Distance restraints were employed in the refinement of 3a (involving the carbon atoms C53, C54, C89, C90, C91, C92, C93 and C94),
in the refinement of 4c (involving the fluorine atoms F46, F47, F48 and the carbon atoms of the co-crystallized solvent molecule n-pentane (C87 – C91)) and in the refinement of 6a (involving the nitrogen atoms N1, N2 and the carbon atoms C7 and C8). Refinement results are given in Tables S1 – S3. Graphical representations were performed with the program DIAMOND. CCDC 2022679 – 2022686 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S1. Crystallographic data of 2a, 2b and 3a.

|            | 2a                          | 2b                          | 3a                          |
|------------|-----------------------------|-----------------------------|-----------------------------|
| formula    | C_{10}H_{25}N_{2}OZn, C_{32}H_{12}BF_{24} | C_{10}H_{25}N_{2}Zn, C_{32}H_{12}BF_{24}, CH_{2}Cl_{2} | 2(C_{10}H_{25}N_{2}Zn), 2(C_{32}H_{12}BF_{24}), C_{6}H_{14} |
| Fw / g mol\(^{-1}\) | 1117.91                     | 1186.84                     | 2544.98                     |
| crystall. color, habit | colorless plate             | colorless plate             | colorless block             |
| crystal size / mm          | 0.05 × 0.11 × 0.22           | 0.08 × 0.14 × 0.21          | 0.15 × 0.21 × 0.33          |
| crystal system      | orthorhombic                | triclinic                   | triclinic                   |
| space group          | Pbca                        | P\(-\)                      | P\(-\)                      |
| a / Å                | 18.8785(3)                  | 13.7238(4)                  | 12.6330(2)                  |
| b / Å                | 19.1191(3)                  | 13.7498(5)                  | 18.7331(4)                  |
| c / Å                | 25.6643(4)                  | 13.8331(5)                  | 23.7463(4)                  |
| α / °                | 79.572(3)                   | 89.246(2)                   | 89.246(2)                   |
| β / °                | 67.574(3)                   | 87.985(2)                   | 87.985(2)                   |
| γ / °                | 85.890(3)                   | 80.892(2)                   | 80.892(2)                   |
| V / Å\(^3\)         | 926.3(3)                    | 2373.03(15)                 | 5545.24(18)                 |
| Z                    | 8                           | 2                           | 2                           |
| \(d_{calc}\) / Mg m\(^{-3}\) | 1.603                       | 1.661                       | 1.524                       |
| \(\mu\)(CuKα) / mm\(^{-1}\) | 1.963                       | 2.950                       | 2.130                       |
| \(F(000)\)          | 4496                        | 1192                        | 2580                        |
| θ range / °          | 4.63, 72.17                 | 3.48, 72.00                 | 3.55, 71.99                 |
| index ranges         | -23 ≤ h ≤ 15, -22 ≤ k ≤ 19, -31 ≤ l ≤ 26 | -16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -17 ≤ l ≤ 12 | -15 ≤ h ≤ 11, -22 ≤ k ≤ 19, -29 ≤ l ≤ 26 |
| reflns              | 33170                       | 20641                       | 54441                       |
| independ. reflns (R\(_{int}\)) | 8754 (0.0401)              | 8723 (0.0238)              | 20267 (0.0186)              |
| observed reflns     | 6570                        | 7291                        | 15543                       |
| data/ restr./ param. | 8754 / 0 / 677              | 8723 / 42 / 693             | 20267 / 77 / 1549           |
| \(R\(_{1}\), wR\(_2\) [\(> 2\sigma(I)\)] | 0.0558, 0.1508               | 0.0547, 0.1416               | 0.0546, 0.1515               |
| \(R\(_{1}\), wR\(_2\) (all data) | 0.0720, 0.1604               | 0.0658, 0.1512               | 0.0682, 0.1574               |
| Goof on \(F\(^2\)\) | 1.019                       | 1.049                       | 1.078                       |
| largest diff. peak, hole / e Å\(^3\) | 0.980, -0.795               | 0.647, -0.960               | 2.287, -1.089               |
| CCDC number         | 2022679                     | 2022680                     | 2022681                     |
### Table S2. Crystallographic data of 4a, 4c and 5a.

|       | 4a                                           | 4c                                           | 5a                                           |
|-------|----------------------------------------------|----------------------------------------------|----------------------------------------------|
| formula | C₁₈H₅₂N₆Zn₃, 2(C₃₀H₁₂BF₂₄), C₅H₁₂Cl₂         | 2(C₃₀H₁₂N₆Zn₃), 4(C₃₀H₁₂BF₂₄), C₅H₁₂       | C₁₅H₃₈N₄O₆Zn₂, C₃₂H₁₂BF₂₄                   |
| Fw/mol⁻¹ | 2360.14                                      | 4726.72                                      | 1361.43                                      |
| crystal color, habit | colorless plate                             | colorless plate                              | colorless plate                              |
| crystal size / mm | 0.04 × 0.18 × 0.34                          | 0.07 × 0.28 × 0.45                          | 0.04 × 0.16 × 0.33                          |
| crystal system | triclinic                                    | triclinic                                    | triclinic                                    |
| space group | P₁                                      | P₁                                        | P₁                                        |
| a/Å | 13.6357(4)                                   | 12.6823(12)                                  | 10.4089(3)                                  |
| b/Å | 17.9663(4)                                   | 17.7306(16)                                  | 16.4176(4)                                  |
| c/Å | 21.9342(5)                                   | 23.497(3)                                    | 16.7899(4)                                  |
| α/° | 71.9835(17)                                  | 96.087(8)                                    | 75.5569(19)                                 |
| β/° | 76.0546(19)                                  | 91.887(9)                                    | 82.161(2)                                   |
| γ/° | 71.3749(17)                                  | 103.611(7)                                   | 89.192(2)                                   |
| V/Å³ | 4781.7(2)                                    | 5097.1(9)                                    | 2752.10(13)                                 |
| Z     | 2                                           | 1                                           | 2                                           |
| dcalc/Mg m⁻³ | 1.639                                      | 1.540                                       | 1.643                                       |
| μ(CuKα)/mm⁻¹ | 2.672                                       | 2.037                                       | 2.278                                       |
| F(000) | 2368                                        | 2382                                        | 1372                                        |
| θ range/° | 2.15, 72.09                               | 2.58, 71.41                                 | 2.64, 71.89                                 |
| index ranges | -16 ≤ h ≤ 12, -22 ≤ k ≤ 21, -27 ≤ l ≤ 26 | -15 ≤ h ≤ 15, -16 ≤ k ≤ 20, -28 ≤ l ≤ 27 | -9 ≤ h ≤ 12, -19 ≤ k ≤ 20, -20 ≤ l ≤ 20 |
| reffns | 50574                                       | 42734                                       | 24803                                       |
| Independent reffns (Rint) | 17716 (0.0490)                              | 18149 (0.0223)                              | 10009 (0.0175)                              |
| observed reffns | 10530                                       | 14082                                       | 8299                                        |
| data/restr./param. | 17716 / 198 / 1528                         | 18149 / 37 / 1346                            | 10009 / 0 / 793                             |
| R₁, wR₂ [I>2σ(I)] | 0.0376, 0.0751                             | 0.0779, 0.2149                              | 0.0439, 0.1206                              |
| R₁, wR₂ (all data) | 0.0691, 0.0796                             | 0.0946, 0.2277                              | 0.0520, 0.1243                              |
| GooF on F² | 0.784                                       | 1.076                                       | 1.098                                       |
| largest diff. peak, hole / eÅ³ | 0.511, -0.543                              | 2.140, -1.125                               | 0.910, -0.762                               |
| CCDC number | 2022682                                     | 2022683                                     | 2022684                                     |
Table S3. Crystallographic data of 6a and 7a.

|                | 6a                                              | 7a                                              |
|----------------|------------------------------------------------|------------------------------------------------|
| Formula        | 0.5(C_{14}H_{34}N_{4}O_{4}Zn_{2}), C_{32}H_{12}BF_{24} \ (+ solvent)] | C_{4}H_{18}N_{2}O_{4}Zn_{3}                     |
| Fw /g mol\(^{-1}\) | 1089.92                                         | 271.61                                          |
| cryst. color, habit | colorless rod                                  | colorless plate                                  |
| crystal size / mm | 0.05 \times 0.14 \times 0.29                  | 0.05 \times 0.11 \times 0.19                    |
| crystal system  | monoclinic                                      | monoclinic                                       |
| space group    | C\(_2/c\)                                       | C\(_2/c\)                                        |
| a / Å          | 24.289(5)                                       | 14.6808(19)                                     |
| b / Å          | 14.3638(6)                                      | 7.1067(6)                                       |
| c / Å          | 28.4787(6)                                      | 12.0225(16)                                     |
| \(\beta\) / ° | 92.8825(18)                                     | 109.443(10)                                     |
| V / Å\(^3\)    | 9923(3)                                         | 1182.8(3)                                       |
| Z              | 8                                               | 4                                               |
| \(d_{calc}\) / Mg m\(^{-3}\) | 1.459                                           | 1.525                                           |
| \(\mu\) (CuK\(\alpha\)) / mm\(^{-1}\) | 1.835                                           |                                                  |
| \(\mu\) (MoK\(\alpha\)) / mm\(^{-1}\) |                                                  | 2.074                                           |
| \(F(000)\)     | 4352                                            | 568                                             |
| \(\theta\) range / ° | 3.11, 72.02                                    | 2.94, 30.42                                     |
| index ranges   | -29 \(\leq h \leq 29\),                        | -20 \(\leq h \leq 17\),                        |
|                | -17 \(\leq k \leq 13\),                       | -9 \(\leq k \leq 9\),                         |
|                | -35 \(\leq l \leq 34\)                        | -15 \(\leq l \leq 16\)                        |
| refln.         | 48330                                           | 4076                                            |
| Independ. reflns \((R_m)\) | 9500 \(0.0297\)                               | 1600 \(0.0672\)                                |
| observed reflns | 5854                                           | 857                                             |
| data/ restr. / param. | 9500 / 6 / 622                                 | 1600 / 0 / 71                                   |
| \(R_1\), \(wR_2\) \([I > 2\sigma(I)\)] | 0.0638, 0.1873                                 | 0.0614, 0.1386                                  |
| \(R_1\), \(wR_2\) (all data) | 0.0902, 0.1980                                 | 0.1067, 0.1499                                  |
| Goof on \(F^2\) | 1.05                                           | 0.863                                           |
| largest diff. peak, hole / e Å\(^3\) | 1.210, -0.878                                  | 0.849, -1.276                                   |
| CCDC number    | 2022685                                         | 2022686                                         |
DFT Calculations

Computational details: Zinc was treated with a Stuttgart–Dresden pseudopotential in combination with their adapted basis set. The basis set has been augmented by a set of polarization functions (f for Zn). All other atoms have been described with a 6–31G(d,p) double–ζ basis set. Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91. Geometry optimizations were carried out without any symmetry restrictions, the nature of the extrema (minimum) was verified with analytical frequency calculations. All these computations have been performed with the Gaussian 09 suite of programs. The bonding situation was analyzed using the NBO technique.

\([(\text{TMEDA})\text{ZnH(thf)}]^+\)

![DIAMOND representation of the optimized molecular structure of \([(\text{TMEDA})\text{ZnH(thf)}]^+\).](image)

Natural Charge: 
- Zn = 1.00
- H = -0.39

Wiberg Bond Index: Zn1–H1: 0.77

Bond: 
- (1.86963) BD(1) Zn1–H1
  - (25.52%) 0.5051*Zn1 s(38.53%)p1.53(58.77%)d0.07(2.70%)f0.00(0.00%)
  - (74.48%) 0.8630*H1 s(99.98%)p0.00(0.02%)

Analysis of the Bonding:
This is a classical terminal Zn–H bond as found in the two species presented below; Wiberg bond indices and bond description are similar (see below).
### Optimized Molecular Coordinates

| atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| Zn1  | 12.685256000 | 16.027308000 | 14.085514000 |
| O1   | 13.983852000 | 17.490842000 | 14.973146000 |
| N1   | 12.098397000 | 14.904403000 | 15.826862000 |
| N2   | 10.659244000 | 16.771158000 | 14.085435000 |
| C1   | 15.371290000 | 17.034615000 | 15.057001000 |
| C2   | 13.958536000 | 18.906963000 | 14.630808000 |
| C3   | 10.752106000 | 15.421711000 | 16.169726000 |
| C4   | 13.007069000 | 15.039875000 | 16.982637000 |
| C5   | 12.034320000 | 13.483237000 | 15.426610000 |
| C6   | 9.954238000  | 15.766054000 | 14.919252000 |
| C7   | 10.145781000 | 16.730676000 | 12.695366000 |
| C8   | 10.461010000 | 18.129493000 | 14.630980000 |
| C9   | 16.205604000 | 18.161411000 | 14.470382000 |
| C10  | 15.382628000 | 19.397674000 | 14.838990000 |
| H1   | 13.367513000 | 15.423531000 | 12.839856000 |
| H2   | 15.450448000 | 16.095040000 | 14.503219000 |
| H3   | 15.597854000 | 16.860766000 | 16.114316000 |
| H4   | 13.225314000 | 19.393542000 | 15.278156000 |
| H5   | 13.647844000 | 19.007108000 | 13.583588000 |
| H6   | 10.885584000 | 16.312648000 | 16.790784000 |
| H7   | 10.197263000 | 14.691068000 | 16.774832000 |
| H8   | 13.986625000 | 14.632655000 | 16.723174000 |
| H9   | 12.623692000 | 14.491476000 | 17.853231000 |
| H10  | 13.121125000 | 16.094115000 | 17.242670000 |
| H11  | 11.368965000 | 13.351021000 | 14.569143000 |
| H12  | 11.675039000 | 12.857576000 | 16.254015000 |
| H13  | 13.028740000 | 13.143008000 | 15.126962000 |
| H14  | 9.805923000  | 14.870779000 | 14.307956000 |
| H15  | 8.955626000  | 16.128606000 | 15.200091000 |
| H16  | 10.669658000 | 17.474398000 | 12.092492000 |
| H17  | 9.069541000  | 16.945475000 | 12.667951000 |
| H18  | 10.328737000 | 15.746249000 | 12.260426000 |
| H19  | 10.850273000 | 18.196837000 | 15.649818000 |
| H20  | 9.401395000  | 18.399055000 | 14.637627000 |
| H21  | 11.000288000 | 18.851040000 | 14.009261000 |
| H22  | 17.216497000 | 18.179740000 | 14.883840000 |
| H23  | 16.282991000 | 18.056548000 | 13.383370000 |
| H24  | 15.545141000 | 19.674436000 | 15.885232000 |
| H25  | 15.610297000 | 20.267082000 | 14.217443000 |
\[(\text{TEEDA})\text{Zn}_2\text{H}_2\]^{2+}

**Figure S138**: DIAMOND representation of the optimized molecular structure of \[(\text{TEEDA})\text{Zn}_2\text{H}_2\]^{2+}.

**Natural Charge:**

\begin{align*}
\text{Zn}1 &= 0.91761 \\
\text{Zn}2 &= 0.91761 \\
\text{H}1 &= -0.36259 \\
\text{H}2 &= -0.36259
\end{align*}

**Natural Electron Configuration:**

\begin{align*}
\text{Zn}1 &\quad \text{[core]}4s(0.49)3d(9.97)4p(0.01)5s(0.01)5p(0.01)6d(0.01) \\
\text{Zn}2 &\quad \text{[core]}4s(0.49)3d(9.97)4p(0.01)5s(0.01)5p(0.01)6d(0.01)
\end{align*}

**Wiberg Bond Indices:**

\begin{align*}
\text{Zn}1-\text{Zn}2 &= 0.2829 \\
\text{Zn}1-\text{H}1 &= 0.3904 \\
\text{Zn}1-\text{H}2 &= 0.3846 \\
\text{Zn}2-\text{H}1 &= 0.3846 \\
\text{Zn}2-\text{H}2 &= 0.3846 \\
\text{Zn}1 &= 1.8583 \\
\text{Zn}2 &= 1.8584 \\
\text{H}1 &= 0.8720 \\
\text{H}2 &= 0.8720
\end{align*}
Bond:

1. (1.65185) BD(1) Zn2–H1

(18.26%) Zn2 s(32.49%)p2.02(65.73%)d0.05(1.77%)f0.00(0.00%)
(81.74%) H1 s(99.98%)p0.00(0.02%)

2. (1.65720) BD(1) Zn2–H2

(18.60%) Zn2 s(35.16%)p1.79(62.97%)d0.05(1.87%)f0.00(0.00%)
(81.40%) H2 s(99.98%)p0.00(0.02%)

Donation:

Donation from s orbitals Zn1 → Zn2: 9.02 kcal/mol
Donation from s orbitals of Zn2 → Zn1: 33.2 kcal/mol
Donation from d orbitals of Zn2 → Zn1: 2.74 kcal/mol
Donation from the bond Zn2–H1 → Zn1: 283.91 kcal/mol
Donation from the bond Zn2–H2 → Zn1: 266.48 kcal/mol

Optimized Molecular Coordinates

76
C20H20N4Zn2
Zn1 13.77827 12.95281 0.20210
Zn2 15.64070 14.47647 -0.20210
N1 11.73827 13.16377 0.20550
N2 13.55915 10.90184 0.23324
N3 17.68070 14.26551 -0.20550
N4 15.85982 16.52744 -0.23324
C1 11.30515 11.81773 -1.21033
C2 11.31336 13.40716 -1.21033
C3 11.17130 14.19353 1.13720
C4 14.32291 10.26361 -0.89514
C5 12.08335 10.70665 0.03026
C6 13.94524 10.30214 1.55578
C7 18.11382 15.61154 -0.70476
C8 18.10561 14.02212 -0.70476
C9 18.24766 13.23575 -1.13720
C10 15.09606 17.16297 0.89514
C11 17.33562 16.72263 -0.03026
C12 15.47373 17.12714 -1.55578
C13 9.82142 13.35100 -1.47761
C14 11.55618 15.60680 0.78419
C15 13.95529 8.81708 -1.20907
C16 15.32498 10.69973 2.03360
C17 19.59755 14.07827 1.47761
C18 17.86279 11.82427 -0.78419
C19 15.46368 18.61219 1.20907
C20 14.09399 16.72955 -2.03360
H1 14.84034 14.03522 1.65285
H2 14.57863 13.39406 -1.65285
H3 10.35854 11.69917 0.53078
H4 11.44058 11.77010 1.66420
H5 11.74972 12.75053 -1.77641
H6 11.63761 14.28201 -1.47887
H7 11.47454 14.00169 2.03865
H8 10.20296 14.12252 1.13090
H9 15.26752 10.30327 -0.68459
H10 14.18112 10.79749 -1.69572
LUMO, $E = -0.2414$

HOMO, $E = -0.4921$
The HOMO is not shown because it involves mainly the interaction between the metal centers and the ligands TEEDA.
Figure S139: DIAMOND representation of the optimized molecular structure of (TMEDA)$_2$Zn$_2$H$_3$.$^+$

Natural Charge:
Zn1: 0.76
Zn2: 0.76
H1: -0.36
H2: -0.40
H3: -0.36

Wiberg Bond Indices:
Zn1–H1: 0.76
Zn1–H2: 0.37
Zn2–H2: 0.37
Zn2–H3: 0.76

Bond:
(1.89755) BD(1) Zn1–H1
(28.71%) 0.5358*Zn1 s(43.09%) p1.29(55.39%) d0.04(1.52%) f0.00(0.00%)
(71.29%) 0.8444*H1 s(99.98%) p0.00(0.02%)

(1.90166) BD(1) Zn2–H3
(28.87%) 0.5373*Zn2 s(43.84%) p1.25(54.59%) d0.04(1.57%) f0.00(0.00%)
(71.13%) 0.8434*H3 s(99.98%) p0.00(0.02%)
Second Order Study:
Donation from lone pair of the bridging H2 to an empty sp orbital (7.6% s, 91.3% p) at Zn1: 81.98 kcal/mol
Donation from lone pair of the bridging H2 to an empty sp orbital (7.6% s, 91.3% p) at Zn2: 79.18 kcal/mol

Analysis of the Bonding:
Donation from the s lone pair of the bridging H2 to the empty sp orbitals of Zn1 and Zn2 leads to a 3c-2e bond between Zn1–H2–Zn2. In line with a 3c-2e bond, the Wiberg bond indices of 0.37 correspond to half of that of a normal 2c-2e Zn–H bond.

Optimized Structure
53
Zn1C12N4H35
Zn1 2.223870000 0.004002000 14.511442000
Zn2 -0.038889000 -1.433080000 15.318682000
N1 4.272935000 0.324455000 15.187741000
N2 1.900508000 2.052461000 15.170133000
N3 -0.556291000 -2.880354000 16.876005000
N4 0.056049000 -3.167495000 14.020782000
C1 4.373963000 1.800820000 15.258220000
C2 4.546765000 -0.265434000 16.509786000
C3 5.221956000 -0.223953000 14.199631000
C4 3.147557000 2.433332000 15.870522000
C5 0.738136000 2.230560000 16.060958000
C6 1.703976000 2.866867000 13.952487000
C7 -0.331898000 -4.200425000 16.246698000
C8 -1.982028000 -2.683777000 17.205955000
C9 0.249996000 -2.745469000 18.100976000
C10 -0.709245000 -4.188676000 14.770000000
C11 -0.614124000 -2.852068000 12.742330000
C12 1.429506000 -3.626939000 13.744394000
H1 2.090063000 -0.245331000 12.973405000
H2 1.590304000 -1.031965000 15.727508000
H3 -1.172288000 -0.404584000 15.012871000
H4 5.279752000 2.116324000 15.764625000
H5 4.479442000 2.150710000 14.194292000
H6 3.836613000 0.104705000 17.251174000
H7 5.567363000 -0.032022000 16.844988000
H8 4.435150000 -1.350171000 16.450727000
H9 5.136828000 -1.312717000 14.178934000
H10 6.258026000 0.042349000 14.451136000
H11 4.980746000 0.157551000 13.205358000
H12 3.059986000 2.106030000 16.910988000
H13 3.265599000 3.526524000 15.891745000
H14 -0.169282000 1.913229000 15.544038000
H15 0.631299000 3.280260000 16.368233000
H16 0.858588000 1.609876000 16.951898000
H17 2.544478000 2.744003000 13.267163000
H18 1.598073000 3.930793000 14.206665000
H19 0.803405000 2.529842000 13.435937000
H20 0.727491000 -4.449413000 16.361008000
H21 -0.900953000 -4.984295000 16.767637000
H22 -2.126028000 -1.678034000 17.605366000
H23 -2.318550000 -3.420295000 17.949221000
H24 -2.598631000 -2.772573000 16.310131000
H25 1.311091000 -2.836486000 17.857998000
H26 -0.015276000 -3.510790000 18.843909000
|    | X        | Y        | Z        |  |   |
|----|----------|----------|----------|---|---|
| H27| 0.077800000 | -1.760966000 | 18.542360000 |  |   |
| H28| -1.772555000 | -3.956006000 | 14.655767000 |  |   |
| H29| -0.552766000 | -5.188632000 | 14.339482000 |  |   |
| H30| -1.613918000 | -2.458366000 | 12.937318000 |  |   |
| H31| -0.690921000 | -3.743601000 | 12.104665000 |  |   |
| H32| -0.038976000 | -2.086607000 | 12.217291000 |  |   |
| H33| 1.971049000  | -2.834392000 | 13.223490000 |  |   |
| H34| 1.423721000  | -4.530536000 | 13.118266000 |  |   |
| H35| 1.956279000  | -3.847955000 | 14.675059000 |  |   |

\[\text{[(TMEDA)}_3\text{Zn}_3\text{H}_4\]^{2+}\]

**Figure S140:** DIAMOND representation of the optimized molecular structure of \([\text{[(TMEDA)}_3\text{Zn}_3\text{H}_4]\]^{2+}\).

**Natural Charge:**
- Zn1 = 0.87
- Zn2 = 0.97
- Zn3 = 0.87
- H1 = -0.39
- H2 = -0.45
- H3 = -0.45
- H4 = -0.39
**Wiberg Bond Indices:**

- Zn1–H1: 0.70
- Zn1–H2: 0.29
- Zn2–H2: 0.40
- Zn2–H3: 0.40
- Zn3–H3: 0.29
- Zn3–H4: 0.70
- Zn1–Zn2: 0.12
- Zn2–Zn3: 0.12

**NBO Analysis:**

(1.92788) BD(1) Zn1–H1

(29.32%) 0.5415*Zn1  s(74.12%)p0.33(24.57%)d0.02(1.31%)f0.00(0.00%)

(70.68%) 0.8407*H1  s(99.98%)p0.00(0.02%)

(1.73783) BD(1) Zn2–H2

(17.17%) Zn2  s(43.41%)p(55.32%)d(1.27%) H2  s(99.99%)p(0.01%)

A bond exists between Zn2 and H2.

**Second Order Study for H2:**

→ Donation from the Zn2–H2 bond to the empty sp orbital (25%s, 75%p) at Zn1: 75.58 kcal/mol

(1.92839) BD(1) Zn3–H4

(29.32%) 0.5414*Zn3  s(74.13%)p0.33(24.56%)d0.02(1.31%)f0.00(0.00%)

(70.68%) 0.8407*H4  s(99.98%)p0.00(0.02%)

(1.73764) BD(1) Zn2–H3

(17.21%) Zn2  s(43.57%)p(55.14%)d(1.29%) H3  s(99.99%)p(0.01%)

A bond exists between Zn2 and H3.

**Second Order Study for H3:**

→ Donation from the Zn2–H3 bond to the empty sp orbital (25%s, 75%p) at Zn3: 75.82 kcal/mol.

**Analysis of the Bonding:**

The structure can be defined as an adduct between a neutral ZnH₂ fragment and two [ZnH]⁺ cations. The two Zn-H bonds of the Zn₃H₂ (Zn2–H1 and Zn2–H3) moiety are weakened because of the donation to the empty sp orbitals of the Zn cations (Zn1 and Zn3).

**Optimized Structure**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| Zn1  | 21.689880000 | 7.529445000 | 6.452191000 |
| Zn2  | 24.109301000 | 9.252877000 | 5.767868000 |
| Zn3  | 21.802620000 | 11.106810000 | 4.986130000 |
| N1   | 20.596890000 | 6.636427000 | 4.836727000 |
| N2   | 21.844086000 | 5.513451000 | 7.224777000 |
| N3   | 25.708618000 | 9.024864000 | 4.348404000 |
| N4   | 25.652735000 | 9.412606000 | 7.257376000 |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| N5 | 20.707132000 | 12.053347000 | 6.563246000 |
| N6 | 22.089433000 | 13.103961000 | 4.217857000 |
| C1 | 20.282709000 | 5.263915000 | 5.310781000 |
| C2 | 21.392071000 | 6.591890000 | 3.591660000 |
| C3 | 19.341749000 | 7.378322000 | 4.575926000 |
| C4 | 21.444846000 | 4.656655000 | 6.082882000 |
| C5 | 20.885315000 | 5.389936000 | 8.346859000 |
| C6 | 23.185082000 | 5.125359000 | 7.700116000 |
| C7 | 25.545956000 | 9.869206000 | 3.145897000 |
| C8 | 26.912147000 | 9.448216000 | 5.109871000 |
| C9 | 25.824786000 | 7.611503000 | 3.927140000 |
| C10| 25.802962000 | 10.816440000 | 7.692037000 |
| C11| 25.405359000 | 8.569468000 | 8.446345000 |
| C12| 26.872995000 | 8.948681000 | 6.547699000 |
| C13| 21.457446000 | 12.053062000 | 7.836635000 |
| C14| 20.486278000 | 13.441755000 | 6.082520000 |
| C15| 19.404741000 | 11.381173000 | 6.776677000 |
| H1 | 21.117649000 | 8.640688000 | 7.383256000 |
| H2 | 23.332935000 | 7.788726000 | 5.794798000 |
| H3 | 23.408541000 | 10.754396000 | 5.703808000 |
| H4 | 21.211846000 | 10.016324000 | 4.034589000 |
| H5 | 20.019356000 | 4.615140000 | 4.464477000 |
| H6 | 19.395372000 | 5.324762000 | 5.947377000 |
| H7 | 21.634864000 | 7.612637000 | 3.285240000 |
| H8 | 20.827355000 | 6.105225000 | 2.785486000 |
| H9 | 23.321177000 | 6.040840000 | 3.752751000 |
| H10| 18.760302000 | 7.455292000 | 5.497402000 |
| H11| 19.738245000 | 6.869372000 | 3.813218000 |
| H12| 19.587046000 | 8.385578000 | 4.228105000 |
| H13| 21.173388000 | 3.649130000 | 6.428030000 |
| H14| 22.316853000 | 4.546142000 | 5.430480000 |
| H15| 21.190630000 | 6.053792000 | 9.157856000 |
| H16| 20.851410000 | 4.358041000 | 8.720275000 |
| H17| 19.882789000 | 5.685823000 | 8.034905000 |
| H18| 23.914816000 | 5.254366000 | 6.897072000 |
| H19| 23.203020000 | 4.078119000 | 8.029953000 |
| H20| 23.466255000 | 5.755961000 | 8.546371000 |
| H21| 24.648820000 | 9.563399000 | 2.602786000 |
| H22| 26.410375000 | 9.775779000 | 2.475789000 |
| H23| 25.440835000 | 10.914821000 | 3.441767000 |
| H24| 26.951947000 | 10.541222000 | 5.089120000 |
| H25| 27.826478000 | 9.087805000 | 4.619046000 |
| H26| 25.942487000 | 6.950633000 | 4.794189000 |
| H27| 26.685473000 | 7.472921000 | 3.260116000 |
| H28| 24.916826000 | 7.315899000 | 3.398145000 |
| H29| 25.982500000 | 11.469511000 | 6.835036000 |
| H30| 26.636621000 | 10.921328000 | 8.398665500 |
| H31| 24.883449000 | 11.146320000 | 8.180690000 |
| H32| 24.497172000 | 8.906984000 | 8.950728000 |
| H33| 26.242284000 | 8.627083000 | 9.154218000 |
| H34| 25.273910000 | 7.530006000 | 8.139498000 |
| H35| 26.876277000 | 7.854766000 | 6.569881000 |
| H36| 27.776782000 | 9.279179000 | 7.077549000 |
| H37| 21.634779000 | 11.020307000 | 8.144562000 |
| H38| 20.890109000 | 12.567526000 | 8.623512000 |
| H39| 22.419618000 | 12.554334000 | 7.712014000 |
| H40| 20.233587000 | 14.104276000 | 6.921287000 |
|   | 19.617727000 | 13.431485000 | 5.417941000 |
|---|-------------|-------------|-------------|
| H42| 18.852621000 | 11.338864000 | 5.835155000 |
| H43| 18.803657000 | 11.920605000 | 7.520121000 |
| H44| 19.581943000 | 10.363087000 | 7.128651000 |
| H45| 21.461499000 | 12.593746000 | 2.268554000 |
| H46| 21.196537000 | 14.305371000 | 2.696006000 |
| H47| 20.144311000 | 13.029039000 | 3.356840000 |
| H48| 21.502667000 | 15.003705000 | 4.997708000 |
| H49| 22.561193000 | 14.040372000 | 6.027968000 |
| H50| 24.160697000 | 13.262532000 | 4.601980000 |
| H51| 23.540305000 | 14.464174000 | 3.442945000 |
| H52| 23.733835000 | 12.771689000 | 2.943645000 |
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