

Supporting Information

Zirconocene Mediated Acetylboron Chemistry

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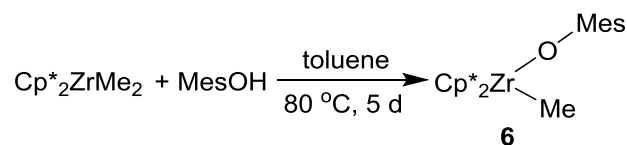
General Information: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Toluene, CH₂Cl₂, Et₂O, pentane and THF were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. All solvents were stored under an argon atmosphere. NMR spectra were recorded on a Varian Inova 500 (¹H: 500 MHz, ¹³C: 126 MHz, ³¹P: 202 MHz, ¹⁹F: 470 MHz, ¹¹B: 160 MHz) or a Varian Inova 600 (¹H: 600 MHz, ¹³C: 151 MHz, ³¹P: 243 MHz, ¹⁹F: 564 MHz, ¹¹B: 192 MHz). ¹H NMR and ¹³C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ³¹P NMR: chemical shifts δ are given relative to H₃PO₄ (external reference), ¹⁹F NMR: chemical shifts δ are given relative to CFCl₃ (external reference), ¹¹B NMR: chemical shifts δ are given relative to BF₃·Et₂O (external reference). NMR assignments were supported by additional 1D (NOESY and TOCSY) and 2D (gCOSY, gHSQC and gHMBC) NMR experiments. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series).

X-Ray diffraction: For compound **6** data sets were collected with a Bruker APEX II CCD diffractometer. Data sets for compounds **7**, **9b** and **13** were collected with a D8 Venture CMOS diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution SHELXT-2015 (Sheldrick, **2015**); structure refinement SHELXL-2015 (Sheldrick, **2015**) and graphics, XP (Bruker AXS Inc., **2015**). *R*-values are given for observed reflections, and *wR*² values are given for all reflections.

Exceptions and special features: For compounds **6** and **7** one Cp* groups and for compound **13** one pentane molecule were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compound **9b** one badly disordered dichloromethane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek (**2015**) *Acta Cryst.*, C71, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule.

Materials: Bis(pentafluorophenyl)borane (HB(C₆F₅)₂)^{1,2} was prepared according to the literature procedure. H₃C-B(C₆F₅)₂ was synthesized by known procedure.^{3,4} Dimethyl bis(pentamethylcyclopentadienyl)zirconium (Cp*₂ZrMe₂) was synthesized according to the known procedure.⁵ Bis(pentamethylcyclopentadienyl)zirconium dihydride (Cp*₂ZrH₂) was synthesized according to the known procedure.⁶ 2,4,6-Trimethylphenol (MesOH) was purchased from Sigma Aldrich and dried prior to use by CaH₂ and then sublimation. All other reagents were commercially available and used as received. [(1) Parks, D. J.; von H. Spence, R. E.; Piers W. E. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809. (2) Daniel, J.; Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492. (3) von H. Spence, R. E.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics*, **1998**, *17*, 2459. (4) Chen, C.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2010**, *132*, 13594. (5) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D. Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (6) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818.]

Preparation of complex 6



Scheme S1

One equiv. of MesOH (272 mg, 2.0 mmol) was slowly added to a solution of Cp*₂ZrMe₂ (784 mg, 2.0 mmol) in toluene (10 mL) at room temperature. After stirring at 80 °C for 5 d, the colorless solution had become yellow. The solvent was removed in vacuo to give a yellow solid, which was recrystallized from pentane at -35 °C to afford yellow crystal product **6**. Yield: 765 mg, 75 %.

Elemental analysis: calc. for C₃₀H₄₄OZr (510.2 g mol⁻¹): C, 70.39; H, 8.66. Found: C, 70.13; H, 8.51.

¹H NMR (600 MHz, 299 K, C₆D₆, 7.15 ppm): δ = 6.83 (m, 1H, *m*-Mes), 6.75 (m, 1H, *m*-Mes), 2.21 (s, 3H, *p*-CH₃-Mes), 2.19 (s, 3H, *o*-CH₃-Mes), 2.07 (s, 3H, *o*-CH₃-Mes), 1.75 (s, 30H, C₅(CH₃)₅), 0.18 (s, 1H, Zr-Me).

¹³C{¹H} NMR (151 MHz, 299 K, C₆D₆, 128.0 ppm): δ = 157.3 (*i*-Mes), 129.8 (*m*-Mes), 129.2 (*m*-Mes), 126.6 (*o*-Mes), 126.5 (*p*-Mes), 122.7 (*o*-Mes), 118.3 (C₅(CH₃)₅), 32.5 (Zr-CH₃), 20.6 (*p*-CH₃-Mes), 19.3 (*o*-CH₃-Mes), 18.3 (*o*-CH₃-Mes), 11.3 (C₅(CH₃)₅).

¹H, ¹³C gHMBC (600 MHz/151 MHz, 299 K, C₆D₆) [selected traces]: δ¹H / δ¹³C = 6.83 and 6.75 / 157.3 (*m*-Mes / *i*-Mes), 2.21 / 126.5 (*p*-CH₃-Mes / *p*-Mes), 2.19 / 122.7 (*o*-CH₃-Mes / *o*-Mes), 2.07 / 126.6 (*o*-CH₃-Mes / *o*-Mes), 1.75 / 118.3 (C₅(CH₃)₅ / C₅(CH₃)₅).

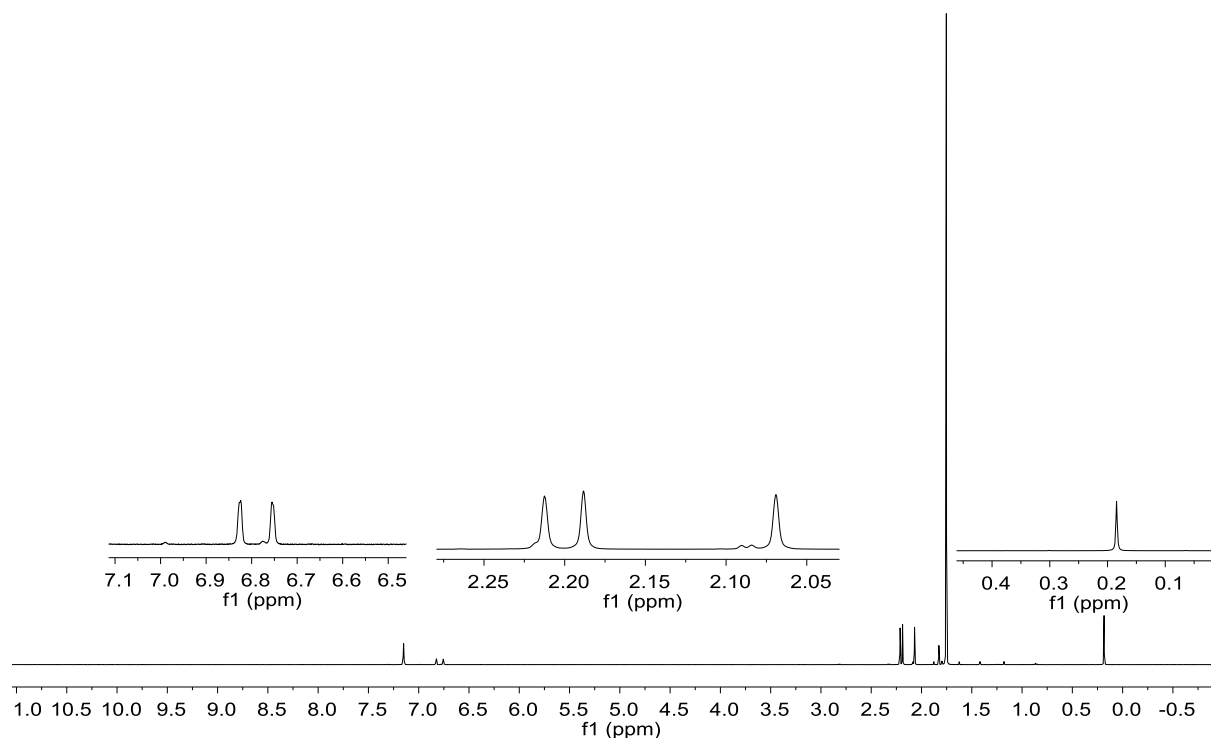


Figure S1. ¹H NMR (600 MHz, 299 K, C₆D₆) spectrum of complex **6**.

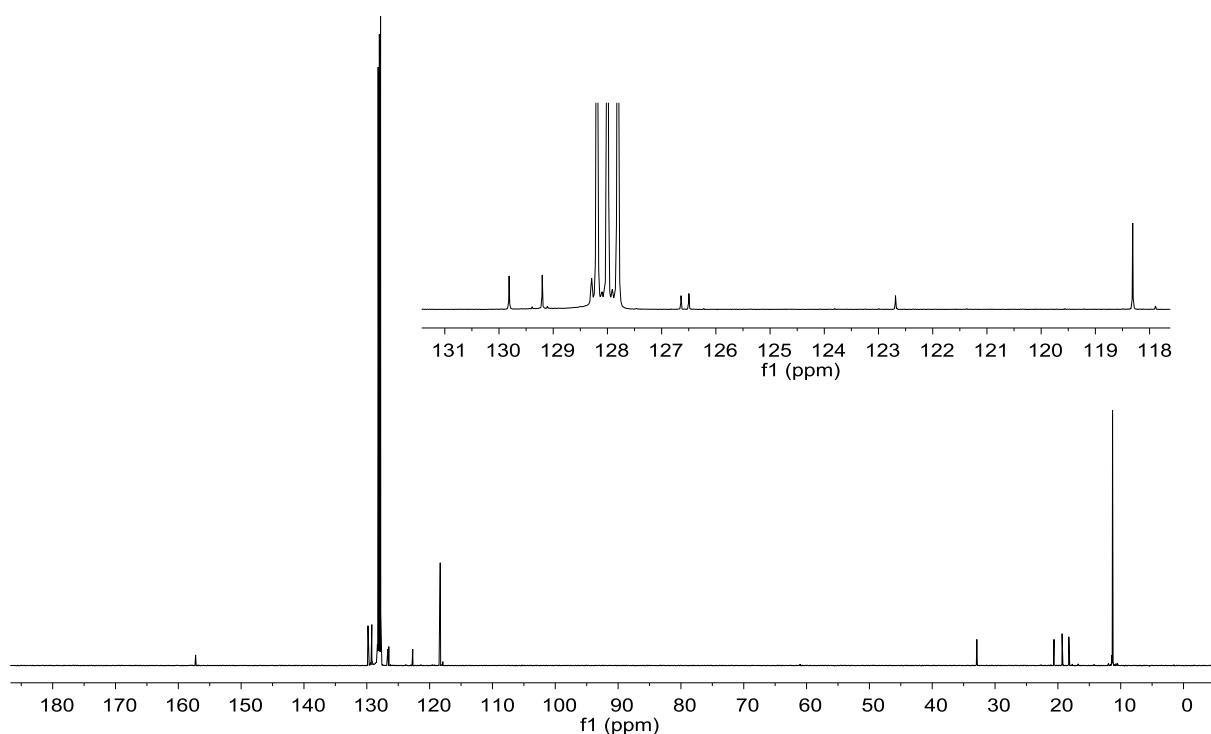


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of complex **6**.

Crystals of complex **6** suitable for the X-ray crystal structure analysis were obtained from a solution of complex **6** in pentane at $-35\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of 6 (erk8843): A yellow prism-like specimen of $\text{C}_{30}\text{H}_{44}\text{OZr}$, approximate dimensions 0.120 mm x 0.180 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1631 frames were collected. The total exposure time was 18.25 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 41299 reflections to a maximum θ angle of 66.79° (0.84 \AA resolution), of which 4675 were independent (average redundancy 8.834, completeness = 99.6%, $R_{\text{int}} = 3.60\%$, $R_{\text{sig}} = 1.79\%$) and 4569 (97.73%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.6735(4)\text{ \AA}$, $b = 32.9368(15)\text{ \AA}$, $c = 9.8794(5)\text{ \AA}$, $\beta = 110.658(2)^\circ$, volume = $2640.9(2)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9235 reflections above $20\sigma(I)$ with $5.366^\circ < 2\theta < 133.4^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.861. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5380 and 0.6760. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with $Z = 4$ for the formula unit, $\text{C}_{30}\text{H}_{44}\text{OZr}$. The final anisotropic full-matrix least-squares refinement on F^2 with 399 variables converged at $R1 = 2.89\%$, for the observed data and $wR2 = 7.03\%$ for all data. The goodness-of-fit was 1.075. The largest peak in the final difference electron density synthesis was $1.100\text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.600\text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.060\text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.287 g/cm^3 and $F(000)$, 1088 e^- . CCDC Nr.: 1832832.

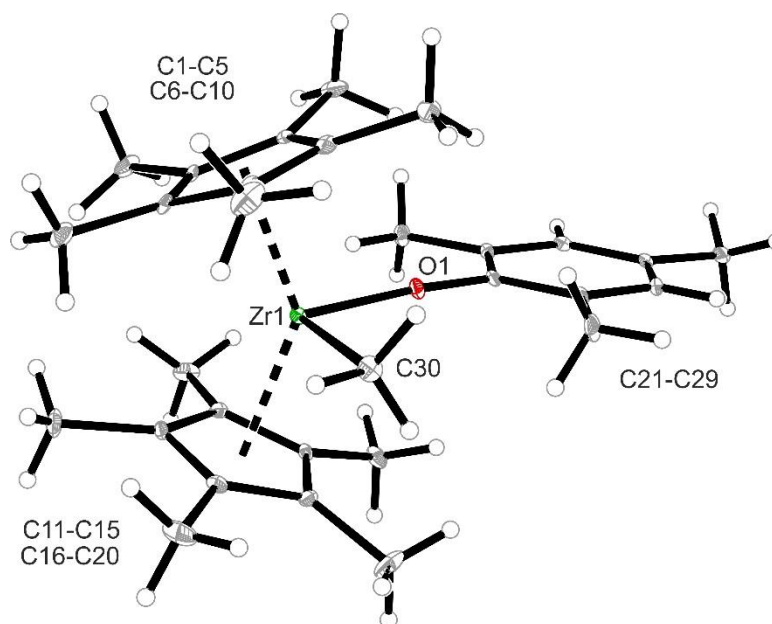
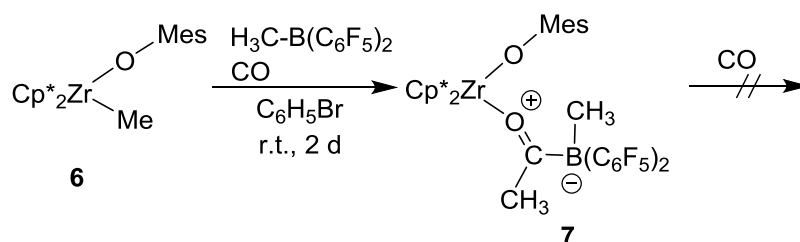


Figure S3. A view of the molecular structure of complex **6** (thermal ellipsoids are shown with 15% probability).

Preparation of complex **7**



Scheme S2

1) Preparation of complex **7:** In a Schlenk tube, complex **6** (256 mg, 0.5 mmol) and $\text{H}_3\text{C-B}(\text{C}_6\text{F}_5)_2$ (160 mg, 0.5 mmol) were mixed and dissolved in bromobenzene (5 mL) at room temperature. The obtained solution was evacuated at $-78\text{ }^\circ\text{C}$, and then refilled by a CO atmosphere (1.5 bar) at room temperature. After stirring for 2 d, the solvent was removed in vacuo to give a red solid, which was recrystallized twice from a mixture of CH_2Cl_2 and pentane at $-35\text{ }^\circ\text{C}$ to afford the resulting yellow crystal product **7**. Yield: 332 mg, 74 %.

Elemental analysis: calc. for $\text{C}_{44}\text{H}_{47}\text{BF}_{10}\text{O}_2\text{Zr}$: C, 58.73; H, 5.26. Found: C, 57.94; H, 5.13.

^1H NMR (600 MHz, 299 K, CD_2Cl_2 , 5.32 ppm): δ = 6.73 (s, 2H, *m*-Mes), 2.70 (s, 3H, O=C- CH_3), 2.18 (s, 3H, *p*- CH_3 -Mes), 2.14 (s, 3H, *o*- CH_3 -Mes), 2.02 (s, 3H, *o*- CH_3 -Mes), 1.89 (s, 30H, $\text{C}_5(\text{CH}_3)_5$), 0.50 (br s, 3H, BCH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2 , 53.8 ppm): δ = 289.3 (m, O=C), 157.1 (*i*-Mes), 148.5 (dm, $^1J_{\text{FC}} \sim 238\text{ Hz}$, C_6F_5), 138.8 (dm, $^1J_{\text{FC}} \sim 245\text{ Hz}$, C_6F_5), 137.3 (dm, $^1J_{\text{FC}} \sim 244\text{ Hz}$, C_6F_5), 129.8 (*m*-Mes), 129.2 (*m*-Mes), 128.7 (*p*-Mes), 126.1 (br s, *i*- C_6F_5), 125.7 ($\text{C}_5(\text{CH}_3)_5$), 125.4 (*o*-Mes), 123.8 (*o*-Mes), 41.6 ($^{\text{O}}\text{CCH}_3$), 20.3 (*p*- CH_3 -Mes), 20.0 (*o*- CH_3 -Mes), 19.8 (*o*- CH_3 -Mes), 12.0 ($\text{C}_5(\text{CH}_3)_5$), 9.4 (br, BCH_3).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ = -12.1 ($\nu_{1/2} \sim 50\text{ Hz}$).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): $\delta = -128.5$ (m, 2F, *o*- C_6F_5), -161.9 (t, $^3J_{\text{FF}} = 20.4$ Hz, 1F, *p*- C_6F_5), -165.8 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{m,p} = 3.9$].

^1H , ^{13}C gHMBC (600 MHz/151 MHz, 299 K, CD_2Cl_2) [selected traces]: $\delta^1\text{H} / \delta^{13}\text{C} = 2.70 / 289.3$ (O=C- $\text{CH}_3 / \text{O}=\text{C}$), $6.73 / 157.1$ (*m*-Mes / *i*-Mes), $2.18 / 128.7$ (*p*- CH_3 -Mes / *p*-Mes), $2.14 / 123.8$ (*o*- CH_3 -Mes / *o*-Mes), $2.02 / 125.4$ (*o*- CH_3 -Mes / *o*-Mes), $1.89 / 125.7$ ($\text{C}_5(\text{CH}_3)_5 / \text{C}_5(\text{CH}_3)_5$), $0.50 / 126.1$ and 289.3 ($\text{BCH}_3 / i\text{-C}_6\text{F}_5$ and O=C).

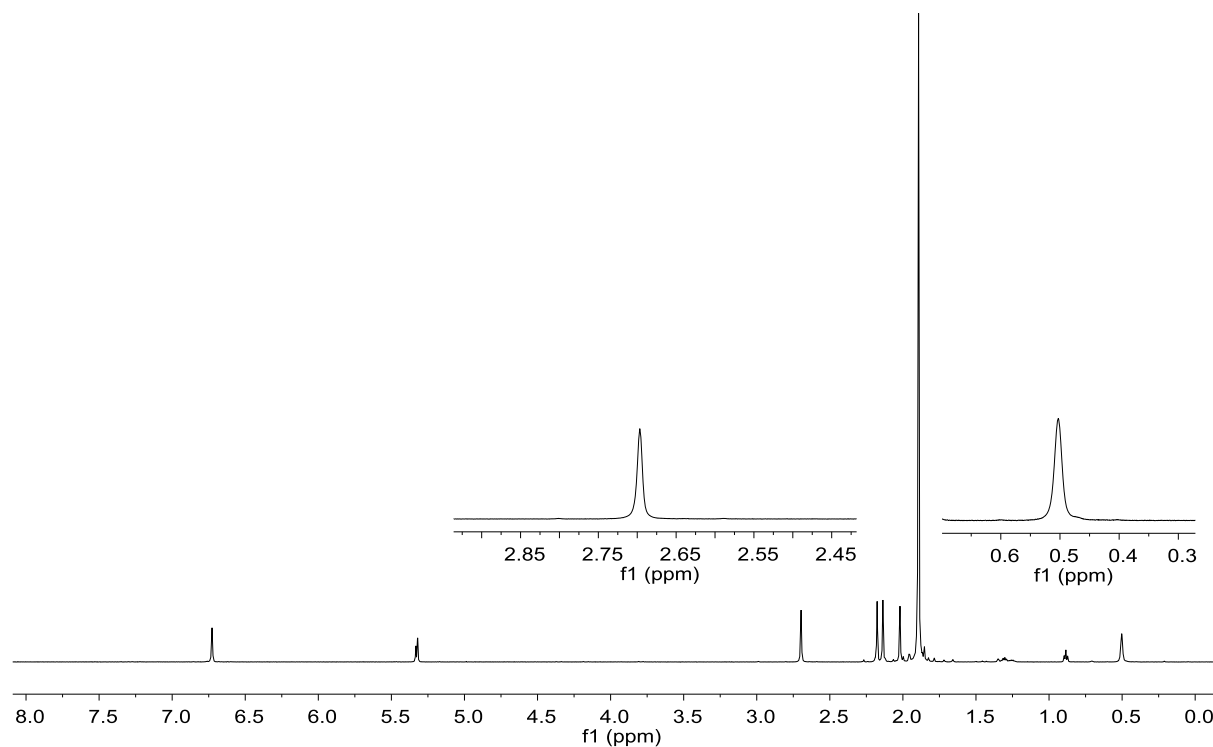


Figure S4. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of complex **7**.

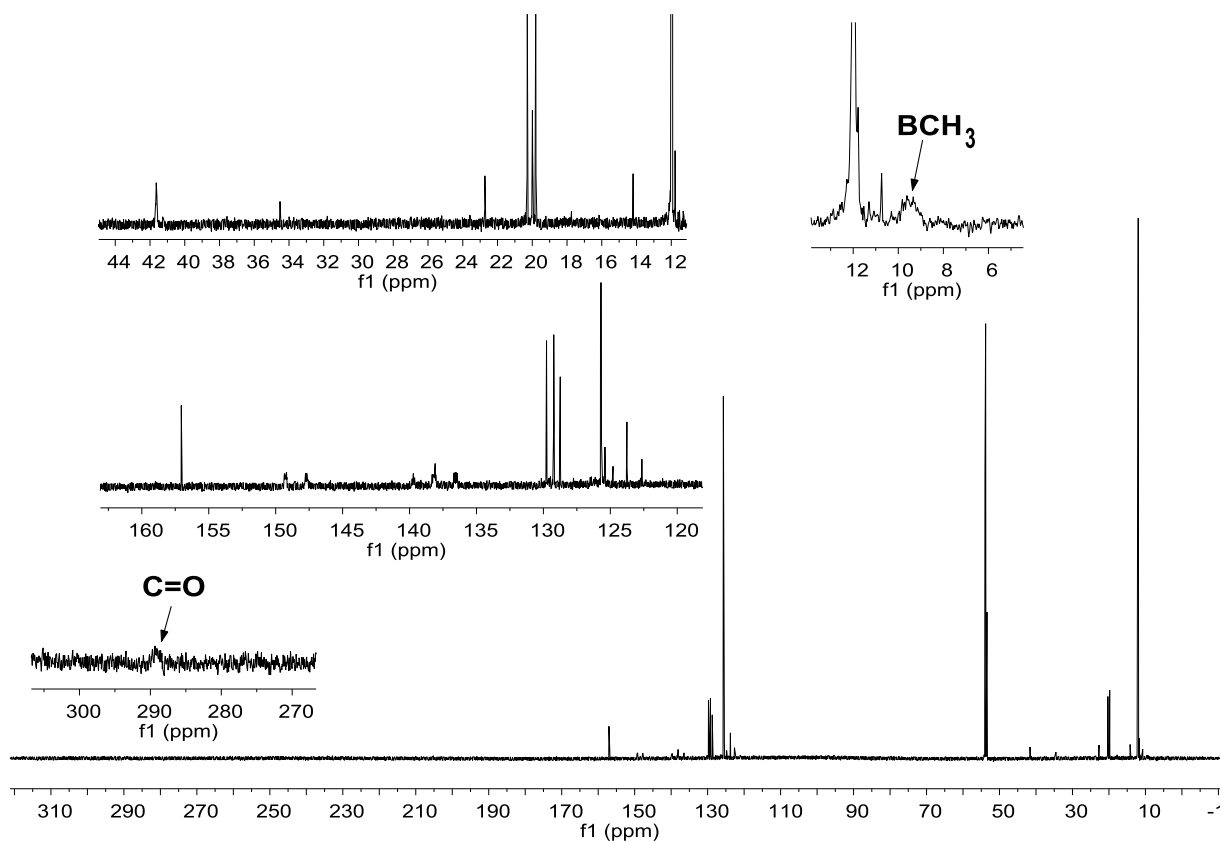


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of complex 7.

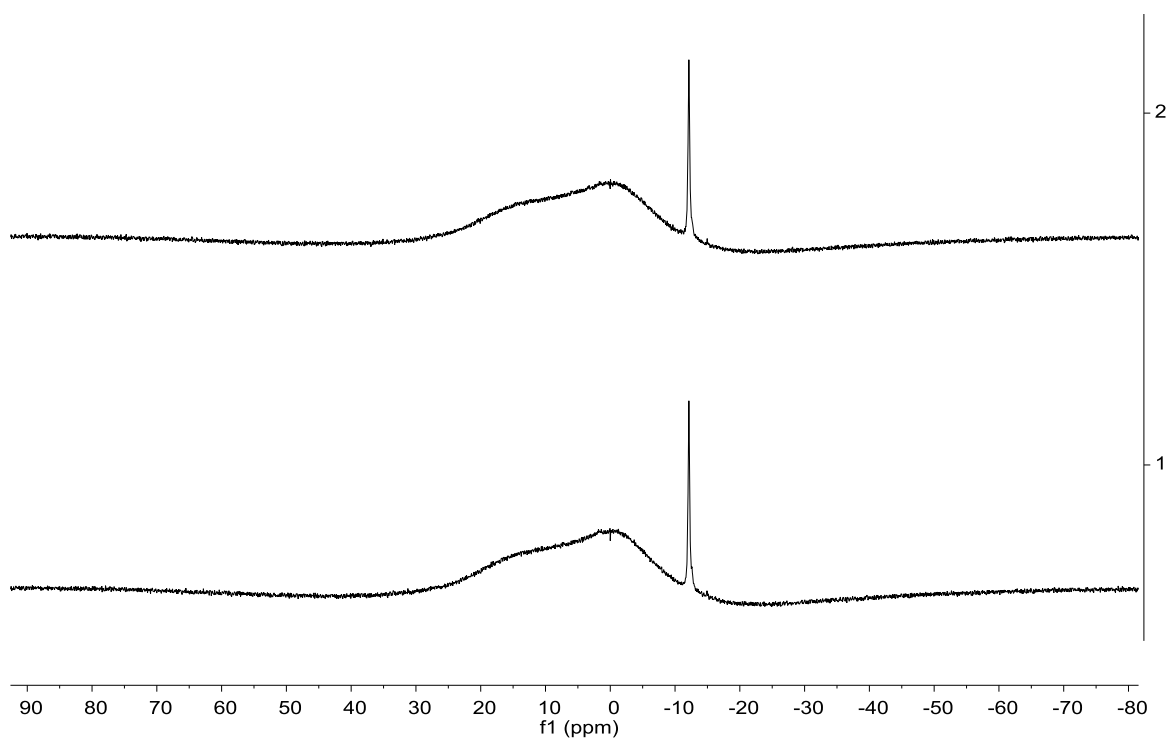


Figure S6. (1) ^{11}B and (2) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of complex 7.

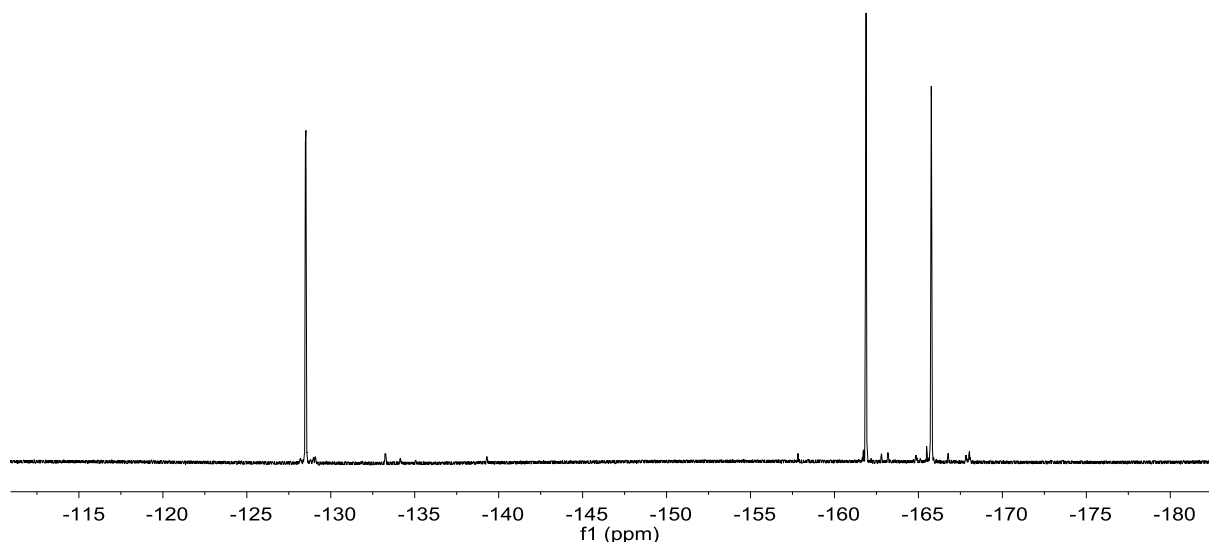


Figure S7. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of complex **7**.

Crystals of complex **7** suitable for the X-ray crystal structure analysis were obtained from the mixture of pentane and CH_2Cl_2 (5 : 1) at room temperature.

X-ray crystal structure analysis of 7 (erk8859): A yellow needle-like specimen of $\text{C}_{44}\text{H}_{47}\text{BF}_{10}\text{O}_2\text{Zr}$, approximate dimensions 0.058 mm x 0.091 mm x 0.295 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 472 frames were collected. The total exposure time was 5.24 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 62038 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 14669 were independent (average redundancy 4.229, completeness = 99.8%, $R_{\text{int}} = 12.25\%$, $R_{\text{sig}} = 9.64\%$) and 9663 (65.87%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 12.4315(6)$ Å, $b = 17.3708(10)$ Å, $c = 21.1666(11)$ Å, $\alpha = 110.538(2)^\circ$, $\beta = 104.768(2)^\circ$, $\gamma = 97.356(2)^\circ$, volume = $4017.8(4)$ Å³, are based upon the refinement of the XYZ-centroids of 9628 reflections above $20 \sigma(I)$ with $4.813^\circ < 2\theta < 51.94^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.883. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9020 and 0.9800. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}$, with $Z = 4$ for the formula unit, $\text{C}_{44}\text{H}_{47}\text{BF}_{10}\text{O}_2\text{Zr}$. The final anisotropic full-matrix least-squares refinement on F^2 with 1161 variables converged at $R1 = 5.34\%$, for the observed data and $wR2 = 11.39\%$ for all data. The goodness-of-fit was 1.028. The largest peak in the final difference electron density synthesis was $0.471 \text{ e}^-/\text{Å}^3$ and the largest hole was $-0.554 \text{ e}^-/\text{Å}^3$ with an RMS deviation of $0.087 \text{ e}^-/\text{Å}^3$. On the basis of the final model, the calculated density was 1.488 g/cm^3 and $F(000)$, 1848 e⁻. CCDC Nr.: 1832833.

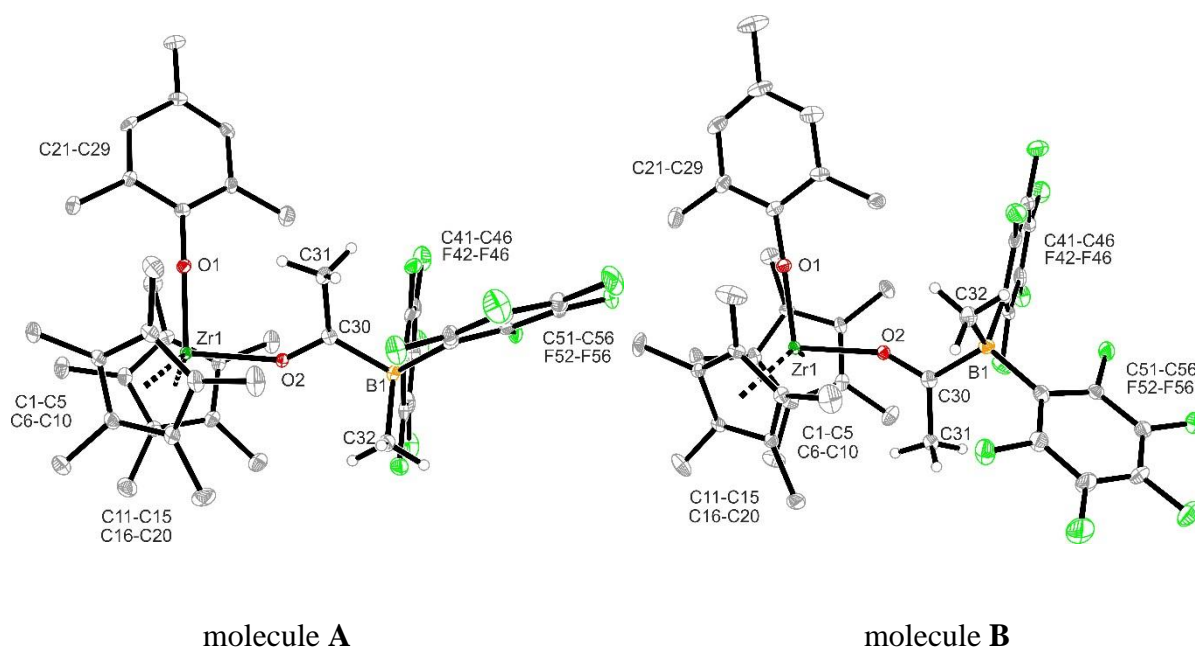


Figure S8. Crystal structure of compound **7** representing both molecules found in the asymmetric unit (molecule **A** (left) and molecule **B** (right)). Hydrogen atoms at Cp* and O-mesityl groups were omitted for clarity (thermal ellipsoids are shown with 30% probability.)

2) **In situ exposure of complex 7 to CO:** In a Young tube, complex **7** (18.0 mg, 0.02 mmol) was dissolved in C_6D_6 (0.5 mL) at room temperature. The solution was evacuated at $-78\text{ }^\circ\text{C}$, and then refilled by a CO atmosphere (1.5 bar) at room temperature. After standing for 2 d, the NMR data were collected, indicating that no further reaction with CO takes place under these conditions.

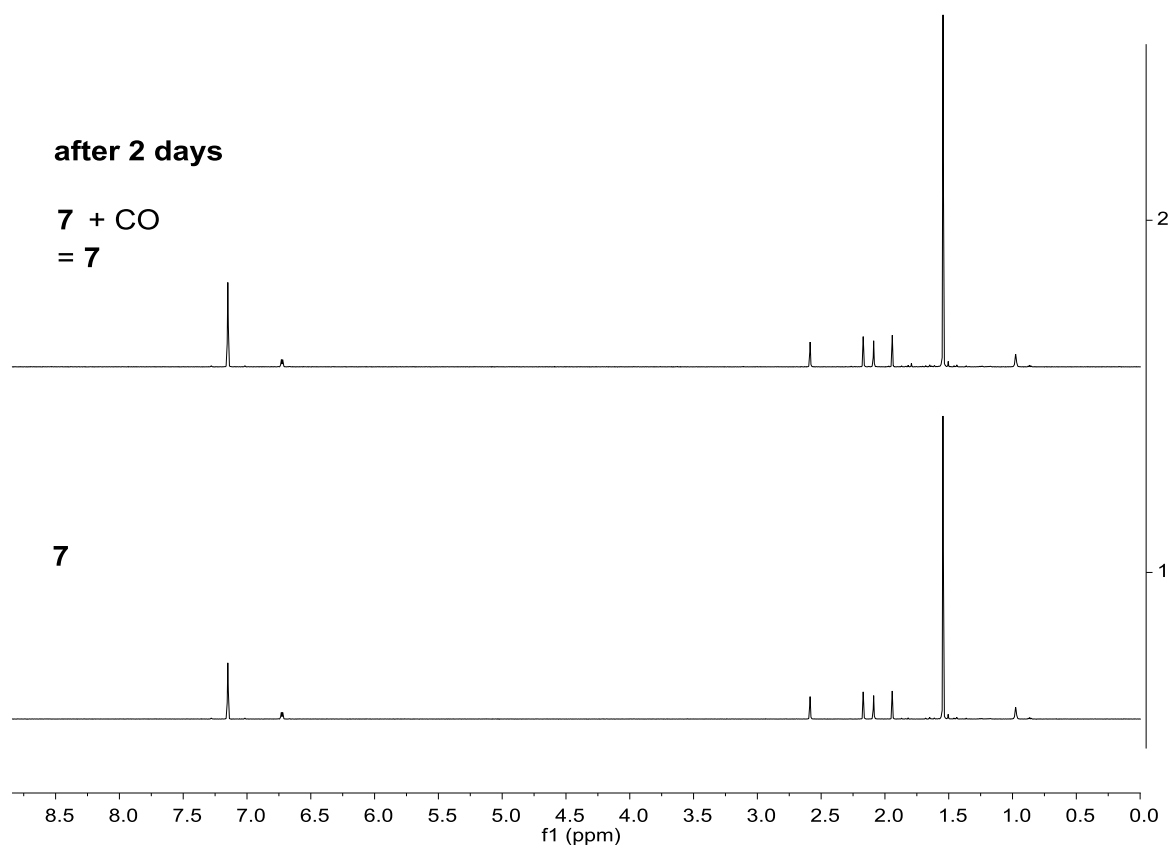


Figure S9. (1) ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of complex **7**; (2) ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of the reaction of complex **7** with CO after 2 days.

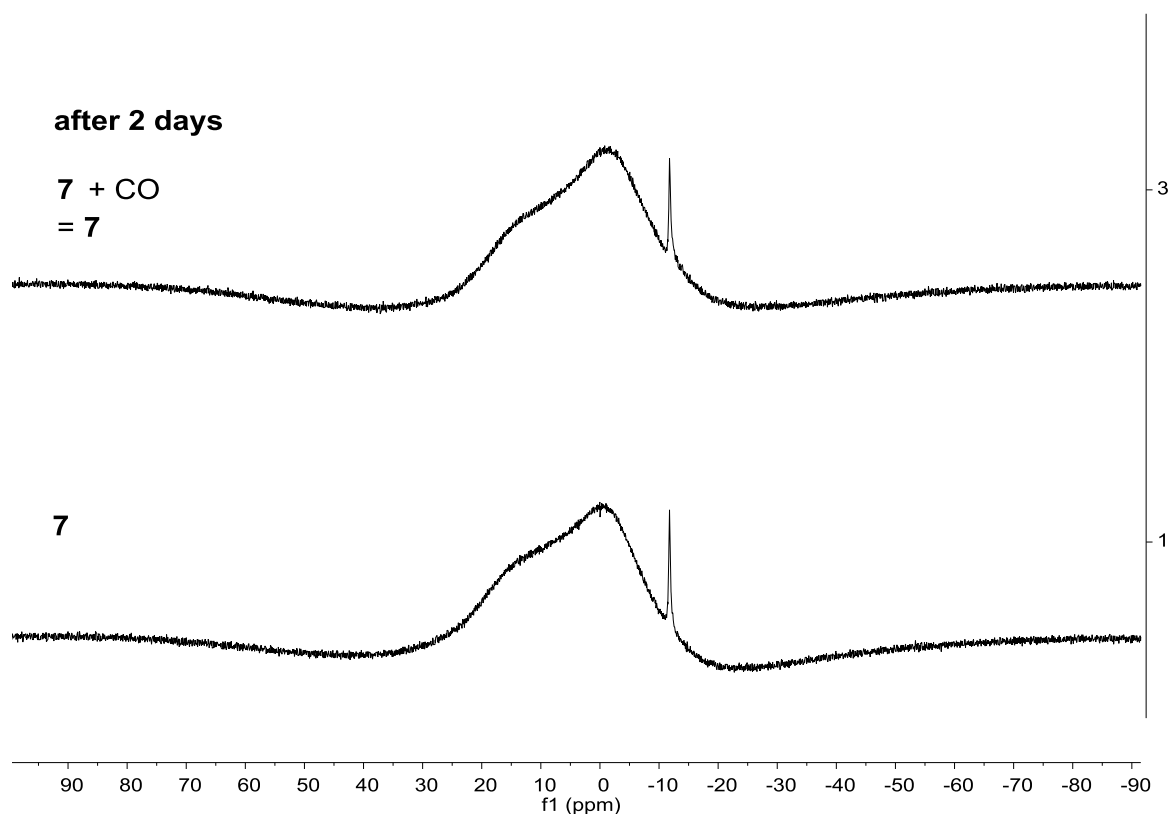


Figure S10. (1) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectrum of complex **7**; (2) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectrum of the reaction of complex **7** with CO after 2 days.

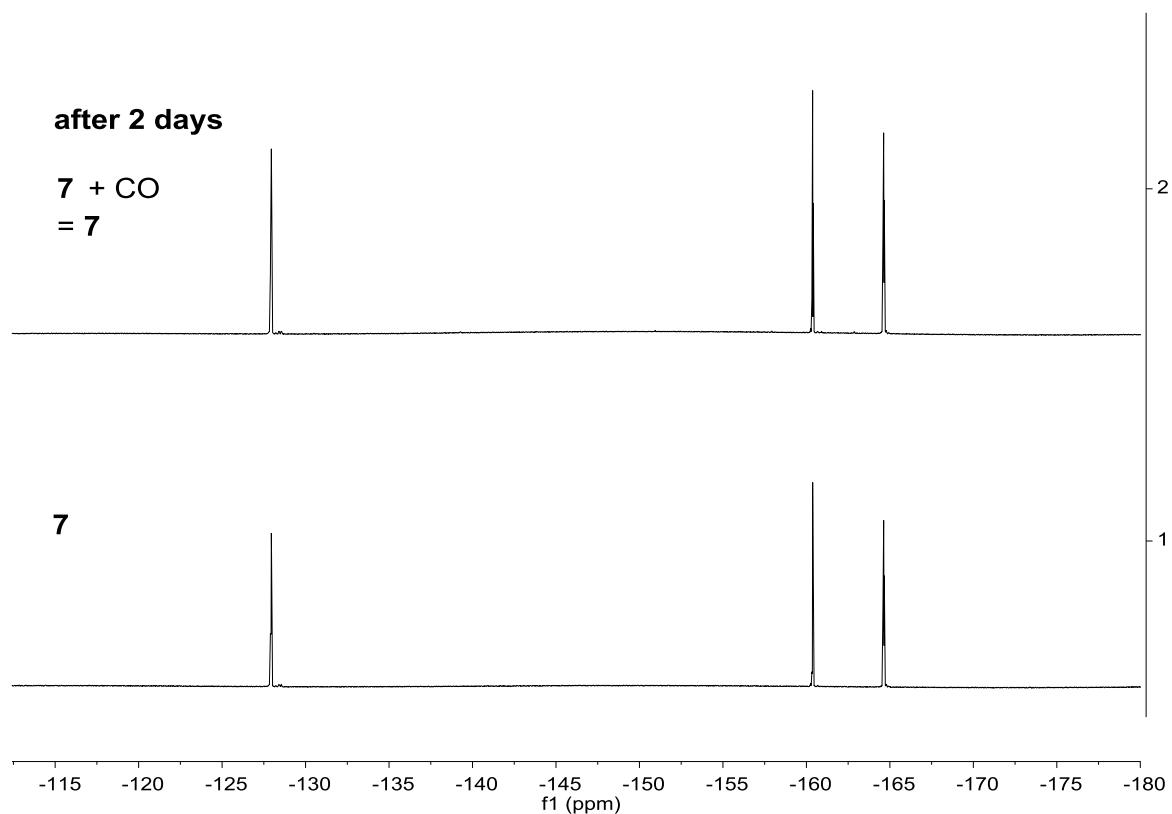
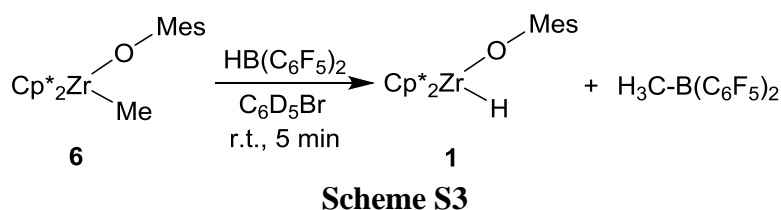


Figure S11. (1) ^{19}F NMR (564 MHz, 299 K, C_6D_6) spectrum of complex **7**; (2) ^{19}F NMR (564 MHz, 299 K, C_6D_6) spectrum of the reaction of complex **7** with CO after 2 days.

Reaction of complex 6 with $\text{HB}(\text{C}_6\text{F}_5)_2$



In a Young tube, complex **6** (10.2 mg, 0.02 mmol) and $\text{HB}(\text{C}_6\text{F}_5)_2$ (7.0 mg, 0.02 mmol) were mixed and dissolved in $\text{C}_6\text{D}_5\text{Br}$ (0.5 mL) at room temperature. After standing for 5 min, the NMR data were collected, indicating the formation of complex **1** and $\text{H}_3\text{C-B}(\text{C}_6\text{F}_5)_2$ via the exchange reaction.

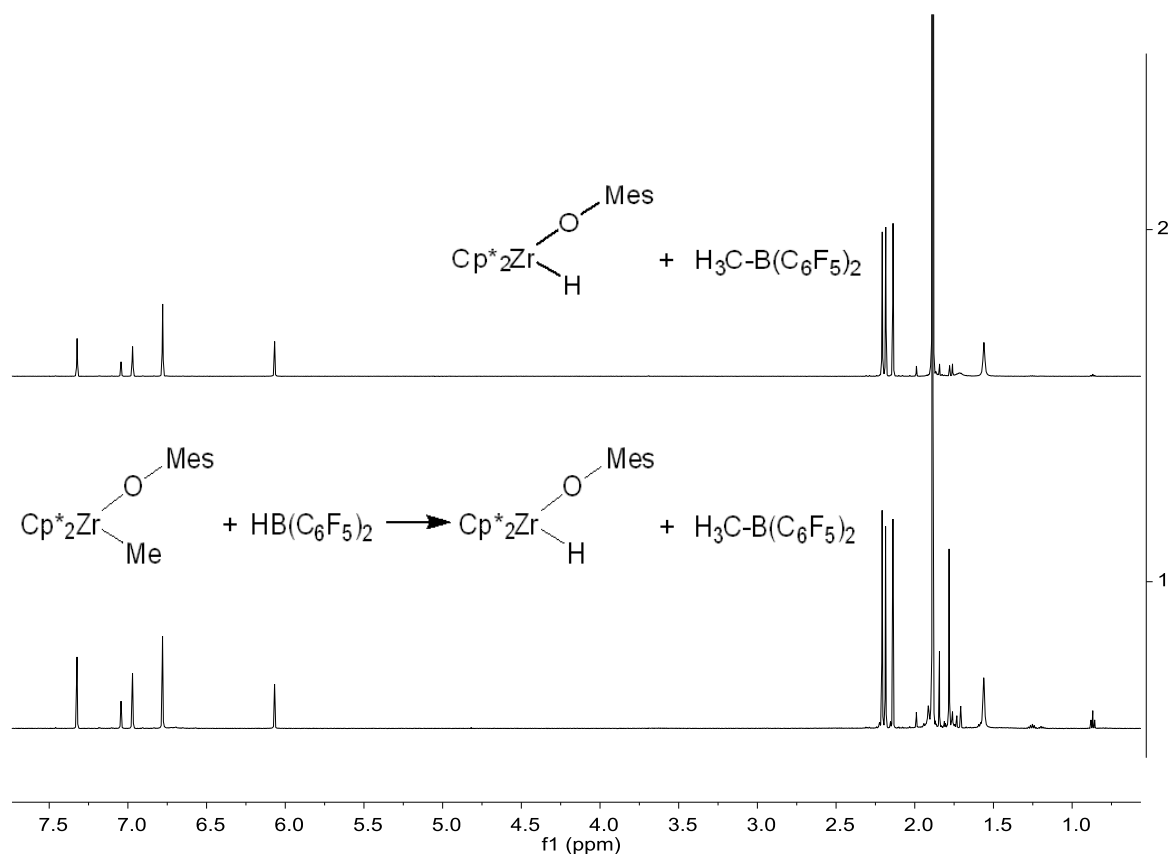


Figure S12. (1) ^1H NMR (600 MHz, 299 K, $\text{C}_6\text{D}_5\text{Br}$) spectrum of the reaction of complex **6** with $\text{HB}(\text{C}_6\text{F}_5)_2$; (2) ^1H NMR (600 MHz, 299 K, $\text{C}_6\text{D}_5\text{Br}$) spectrum of complex **1** with $\text{H}_3\text{C-B}(\text{C}_6\text{F}_5)_2$.

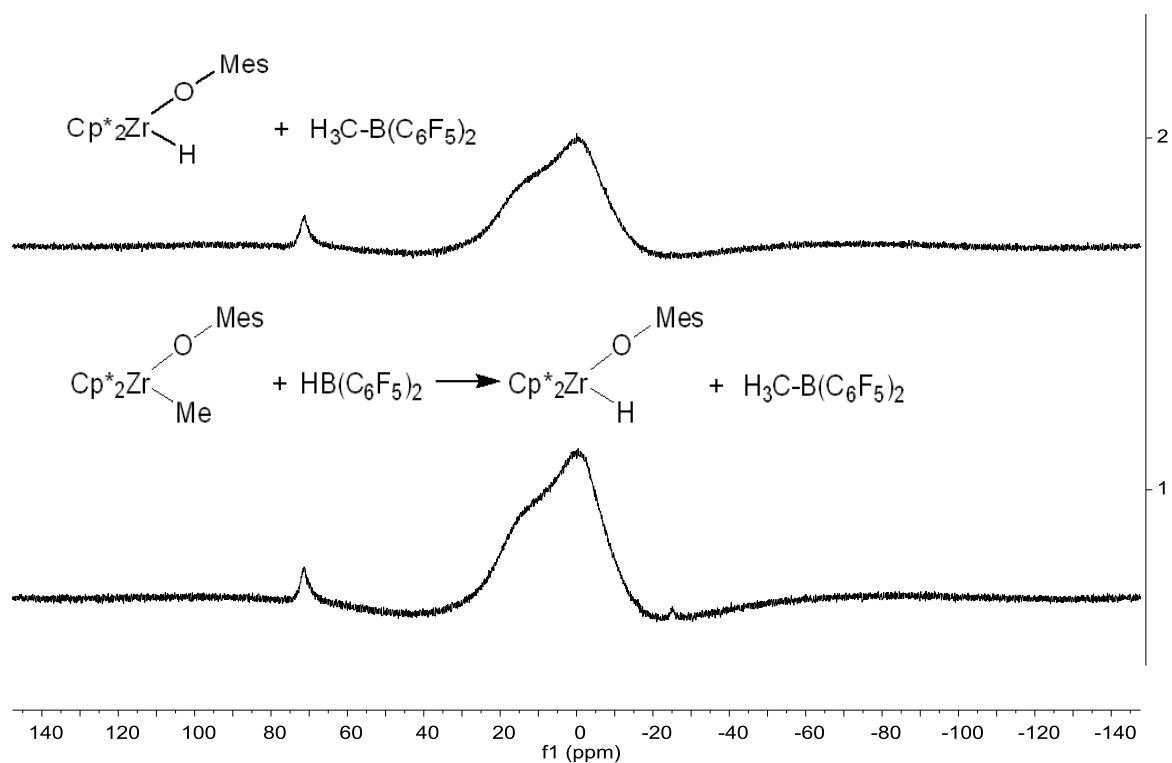


Figure S13. (1) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, $\text{C}_6\text{D}_5\text{Br}$) spectrum of the reaction of complex **6** with $\text{HB}(\text{C}_6\text{F}_5)_2$; (2) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, $\text{C}_6\text{D}_5\text{Br}$) spectrum of complex **1** with $\text{H}_3\text{C}-\text{B}(\text{C}_6\text{F}_5)_2$.

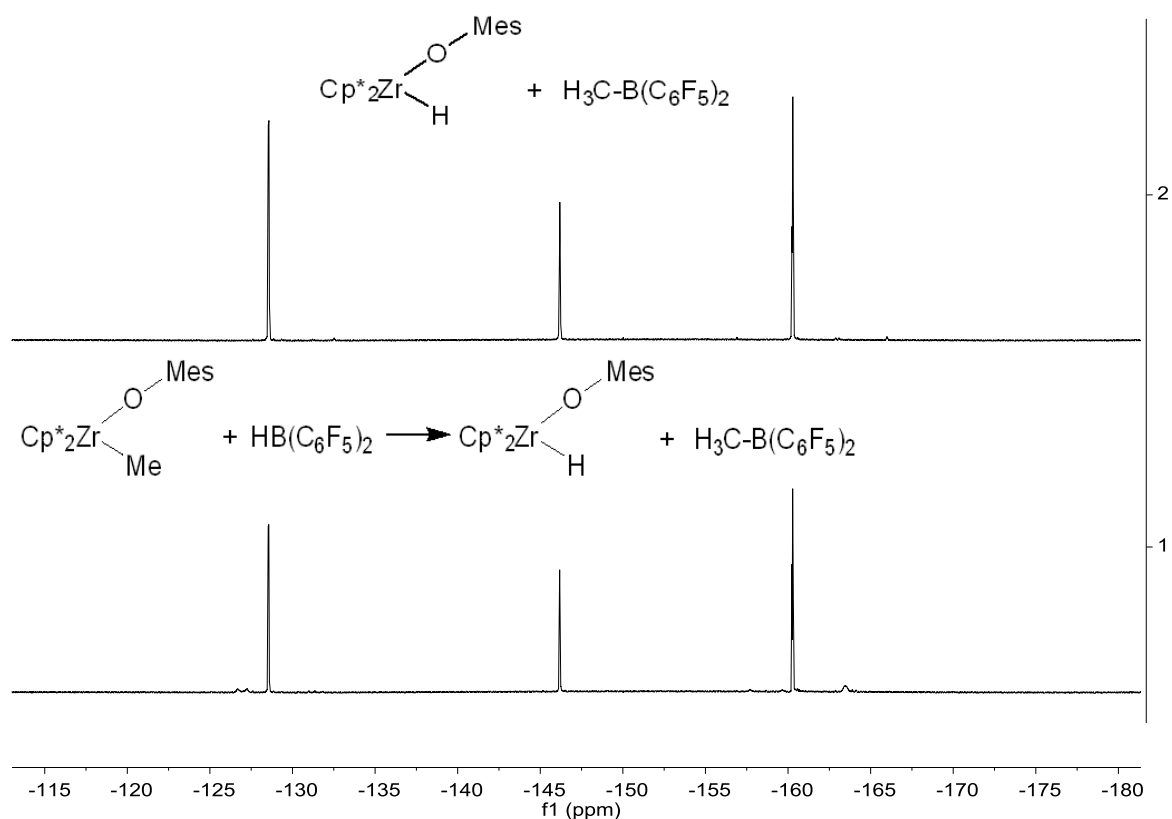
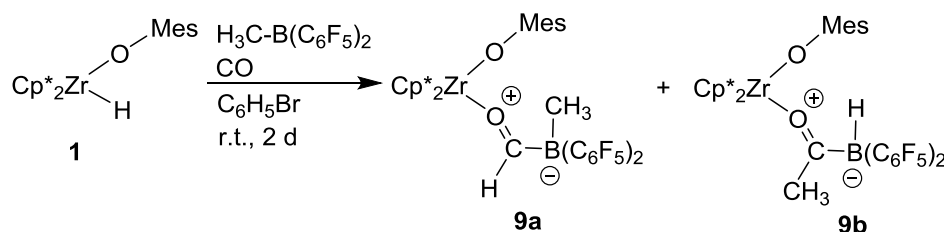


Figure S14. (1) ^{19}F NMR (564 MHz, 299 K, $\text{C}_6\text{D}_5\text{Br}$) spectrum of the reaction of complex **6** with $\text{HB}(\text{C}_6\text{F}_5)_2$; (2) ^{19}F NMR (564 MHz, 299 K, $\text{C}_6\text{D}_5\text{Br}$) spectrum of complex **1** with $\text{H}_3\text{C}-\text{B}(\text{C}_6\text{F}_5)_2$.

Preparation of complexes **9a** and **9b**



Scheme S4

In a Schlenk tube, complex **1** (249 mg, 0.5 mmol) and H₃C-B(C₆F₅)₂ (160 mg, 0.5 mmol) were mixed and dissolved in bromobenzene (5 mL) at room temperature. The obtained solution was evacuated under -78 °C, and then refilled by CO atmosphere (1.5 bar) at room temperature. After stirring for 2 d, the solvent was removed in vacuo to give a red solid, which was recrystallized twice from a mixture of CH₂Cl₂ and pentane at -35 °C to afford the resulting yellow crystalline product **9a** and **9b**. Yield: 238 mg, 54 %.

Elemental analysis: calc. for C₄₃H₄₅BF₁₀O₂Zr • 0.5CH₂Cl₂: C, 56.28; H, 4.99. Found: C, 55.95; H, 4.80.

Comment:

¹H NMR spectrum indicates that the ratio of **9b** to **9a** is 10 : 1 at 299 K.

¹H NMR spectrum indicates that the ratio of **9b** to **9a** is 17 : 1 at 258 K.

9b: ¹H NMR (600 MHz, 258 K, CD₂Cl₂, 5.32 ppm): δ = 6.70 (s, 1H, *m*-Mes), 6.60 (s, 1H, *m*-Mes), 3.29 (br, 1H, BH), 2.71 (s, 3H, O=C-CH₃), 2.13 (s, 3H, *p*-CH₃-Mes), 2.09 (s, 3H, *o*-CH₃-Mes), 1.70 (s, 3H, *o*-CH₃-Mes), 1.87 (s, 30H, C₅(CH₃)₅).

9a: ¹H NMR (600 MHz, 258 K, CD₂Cl₂, 5.32 ppm): δ = 11.56 (s, 1H, O=C-H), 6.74 (s, 1H, *m*-Mes), 6.73 (s, 1H, *m*-Mes), 2.16 (s, 3H, *p*-CH₃-Mes), 2.03 (s, 3H, *o*-CH₃-Mes), 1.90 (s, 3H, *o*-CH₃-Mes), 1.79 (s, 30H, C₅(CH₃)₅), 0.44 (br s, 3H, BCH₃).

9b: ¹³C{¹H} NMR (151 MHz, 258 K, CD₂Cl₂, 53.8 ppm): δ = 290.1 (m, O=C), 156.1 (*i*-Mes), 147.7 (dm, ¹J_{FC} ~ 237 Hz, C₆F₅), 138.8 (dm, ¹J_{FC} ~ 248 Hz, C₆F₅), 136.8 (dm, ¹J_{FC} ~ 249 Hz, C₆F₅), 128.84 (*m*-Mes), 128.78 (*m*-Mes), 127.6 (*p*-Mes), 126.2 (*o*-Mes), 124.4 (C₅(CH₃)₅), 122.7 (*o*-Mes), 121.9 (br s, *i*-C₆F₅), 41.9 (^o=CCH₃), 20.16 (*p*-CH₃-Mes), 19.7 (*o*-CH₃-Mes), 18.5 (*o*-CH₃-Mes), 11.5 (C₅(CH₃)₅).

9a: ¹³C{¹H} NMR (151 MHz, 258 K, CD₂Cl₂, 53.8 ppm): δ = 274.7 (m, O=C), 155.7 (*i*-Mes), 129.01 (*m*-Mes), 128.94 (*m*-Mes), 128.0 (*p*-Mes), 127.4 (*o*-Mes), 124.3 (C₅(CH₃)₅), 122.2 (*o*-Mes), 20.19 (*p*-CH₃-Mes), 19.6 (*o*-CH₃-Mes), 17.9 (*o*-CH₃-Mes), 11.1 (C₅(CH₃)₅), 5.3 (BCH₃). [C₆F₅ signals are not listed]

9b: ¹¹B NMR (192 MHz, 258 K, CD₂Cl₂): δ = -20.4 (d, ¹J_{BH} = 79.7 Hz, BH). ¹¹B{¹H} NMR (192 MHz, 258 K, CD₂Cl₂): δ = -20.4 ($\nu_{1/2}$ ~ 105 Hz).

9a: ¹¹B{¹H} NMR (192 MHz, 258 K, CD₂Cl₂): δ = -11.9

9b: ¹⁹F NMR (564 MHz, 258 K, CD₂Cl₂): δ = -129.7 (m, 2F, *o*-C₆F₅), -160.9 (t, ³J_{FF} = 20.4 Hz, 1F, *p*-C₆F₅), -165.3 (m, 2F, *m*-C₆F₅). [$\Delta\delta^{19}\text{F}_{m,p}$ = 4.4].

9a: ¹⁹F NMR (564 MHz, 258 K, CD₂Cl₂): δ = -131.5 (m, 2F, *o*-C₆F₅), -160.8 (t, ³J_{FF} = 20.4 Hz, 1F, *p*-C₆F₅), -164.9 (m, 2F, *m*-C₆F₅). [$\Delta\delta^{19}\text{F}_{m,p}$ = 4.1].

9b: ^1H , ^{13}C gHMBCAD (600 MHz/151 MHz, 258 K, CD_2Cl_2) [selected traces]: $\delta^1\text{H} / \delta^{13}\text{C} = 2.71 / 290.1$ ($\text{O}=\text{C}-\text{CH}_3 / \text{O}=\text{C}$), 6.70 and 6.60 / 156.1 (*m*-Mes / *i*-Mes), 2.13 / 127.6 (*p*- CH_3 -Mes / *p*-Mes), 2.09 / 122.7 (*o*- CH_3 -Mes / *o*-Mes), 1.70 / 126.2 (*o*- CH_3 -Mes / *o*-Mes), 1.87 / 124.4 ($\text{C}_5(\text{CH}_3)_5 / \text{C}_5(\text{CH}_3)_5$).

9a: ^1H , ^{13}C gHMBCAD (600 MHz/151 MHz, 258 K, CD_2Cl_2) [selected traces]: $\delta^1\text{H} / \delta^{13}\text{C} = 0.44 / 274.7$ ($\text{BCH}_3 / \text{O}=\text{C}$), 6.74 and 6.73 / 155.7 (*m*-Mes / *i*-Mes), 2.16 / 128.0 (*p*- CH_3 -Mes / *p*-Mes), 2.03 / 122.2 (*o*- CH_3 -Mes / *o*-Mes), 1.90 / 127.4 (*o*- CH_3 -Mes / *o*-Mes), 1.79 / 124.3 ($\text{C}_5(\text{CH}_3)_5 / \text{C}_5(\text{CH}_3)_5$).

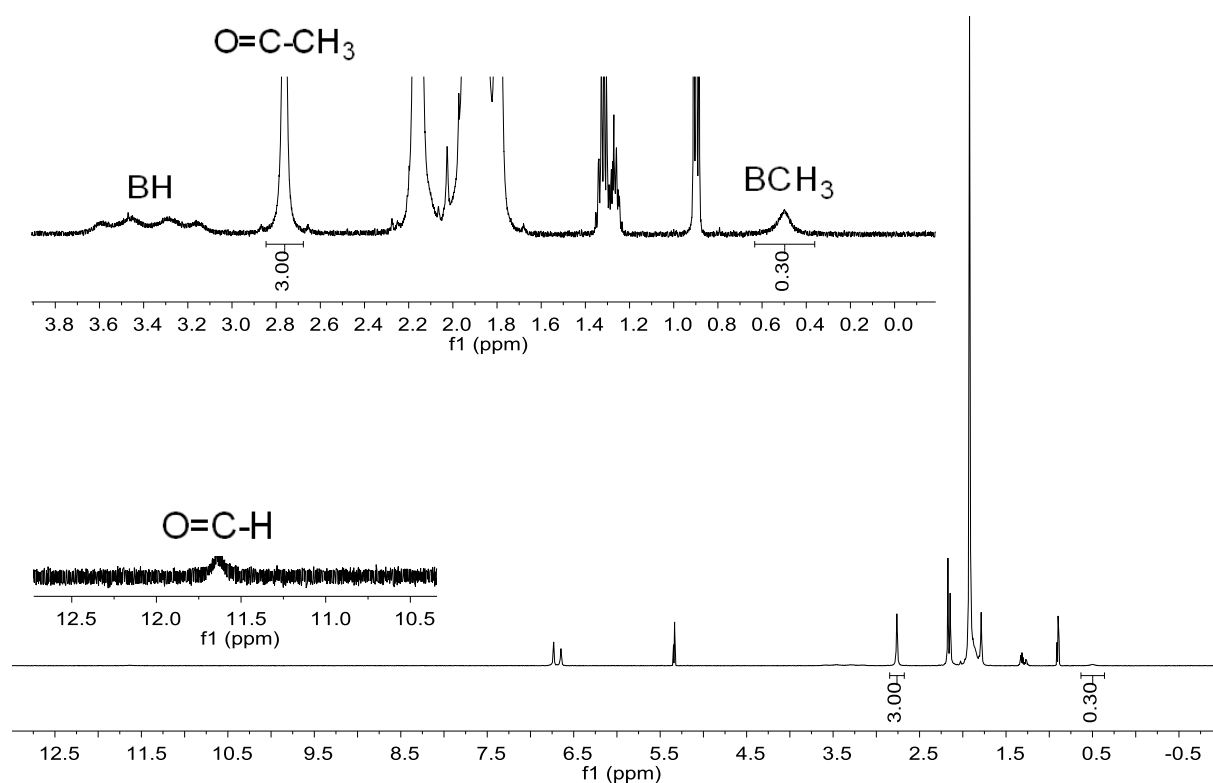


Figure S15. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of complexes **9a** and **9b**.

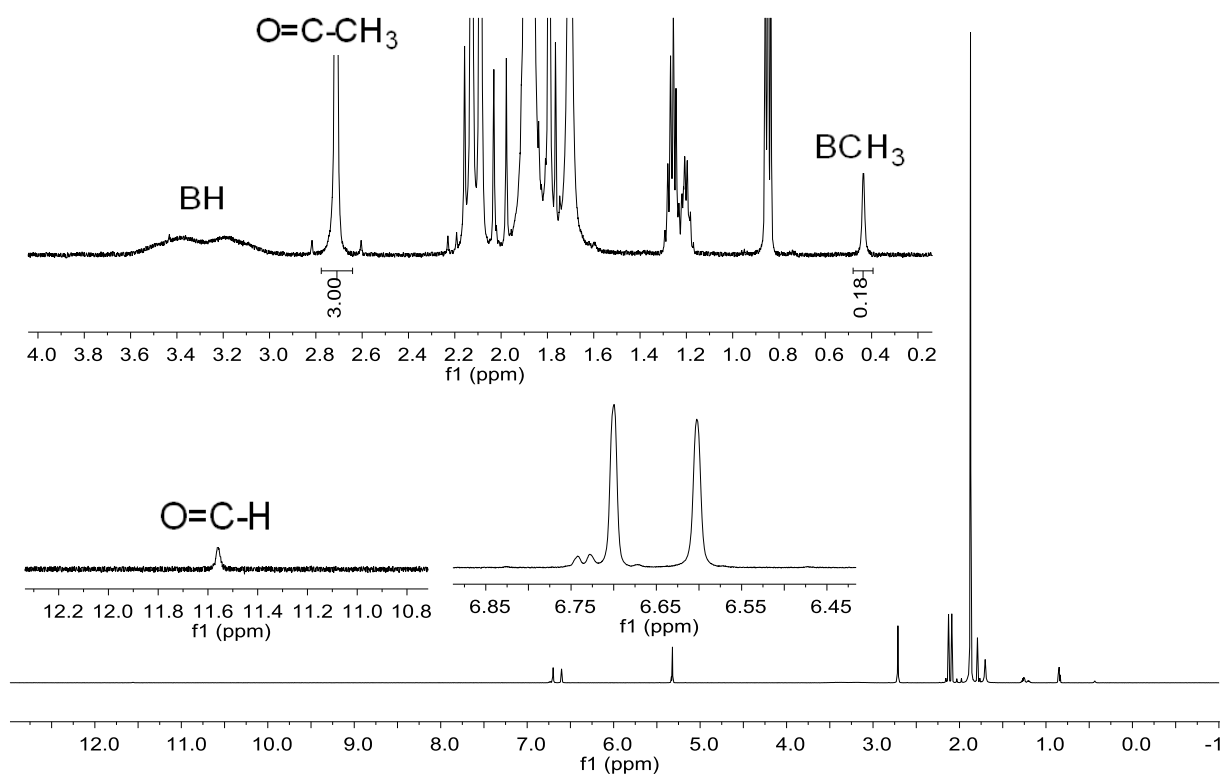


Figure S16. ^1H NMR (600 MHz, 258 K, CD_2Cl_2) spectrum of complexes **9a** and **9b**.

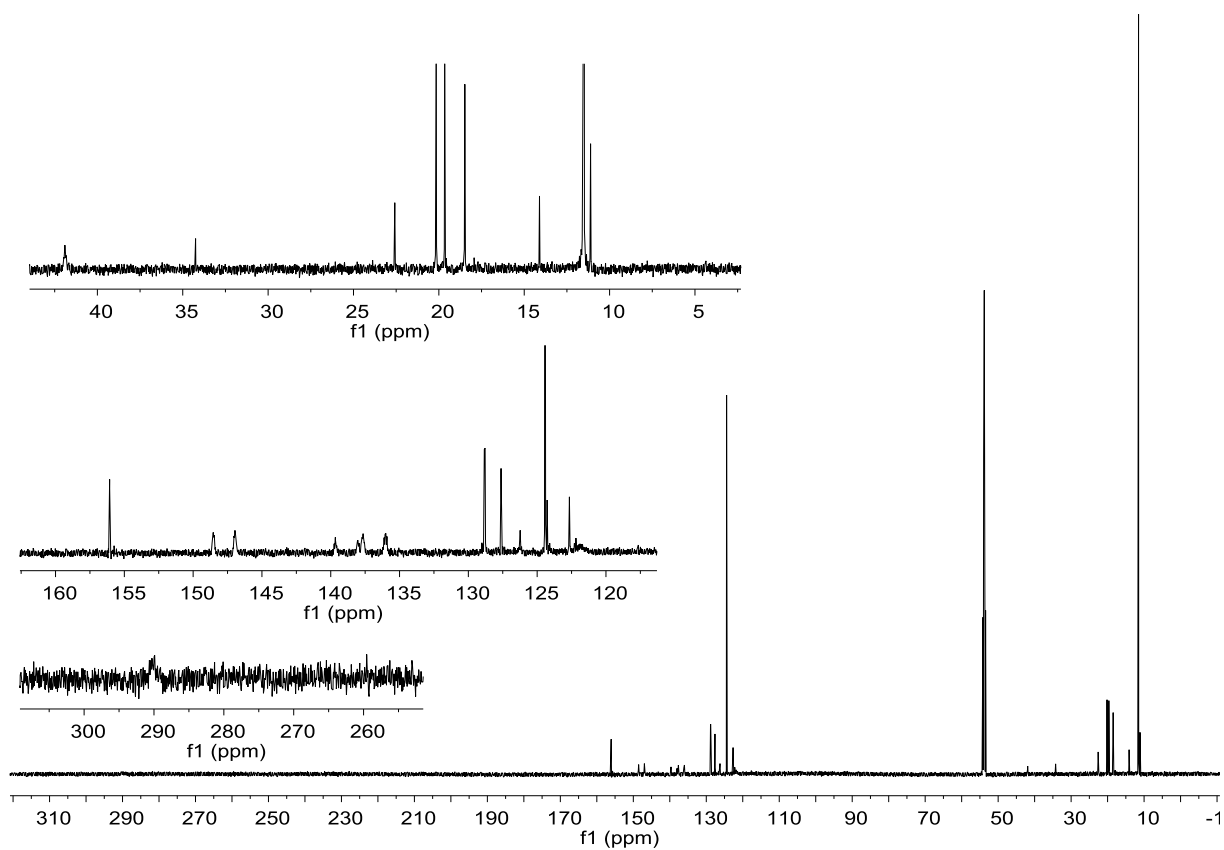


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 258 K, CD_2Cl_2) spectrum of complexes **9a** and **9b**.

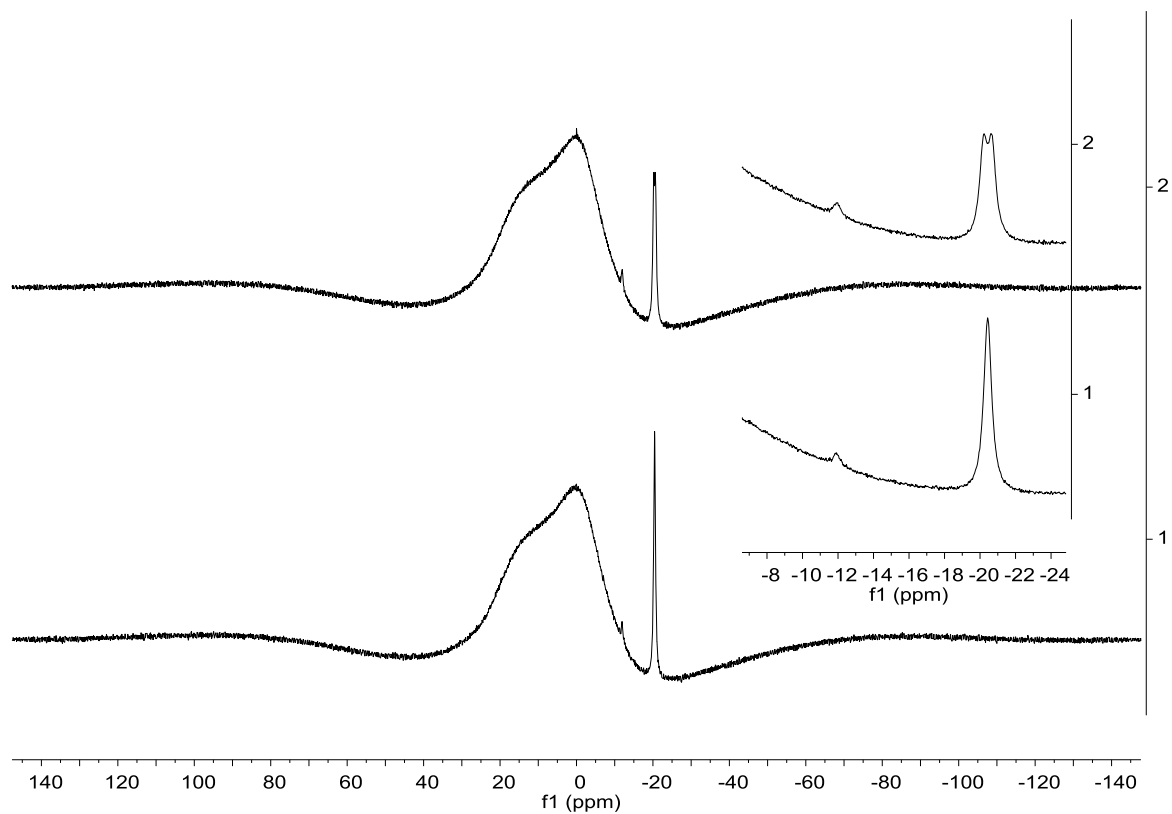


Figure S18. (1) ^{11}B and (2) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 258 K, CD_2Cl_2) spectra of complexes **9a** and **9b**.

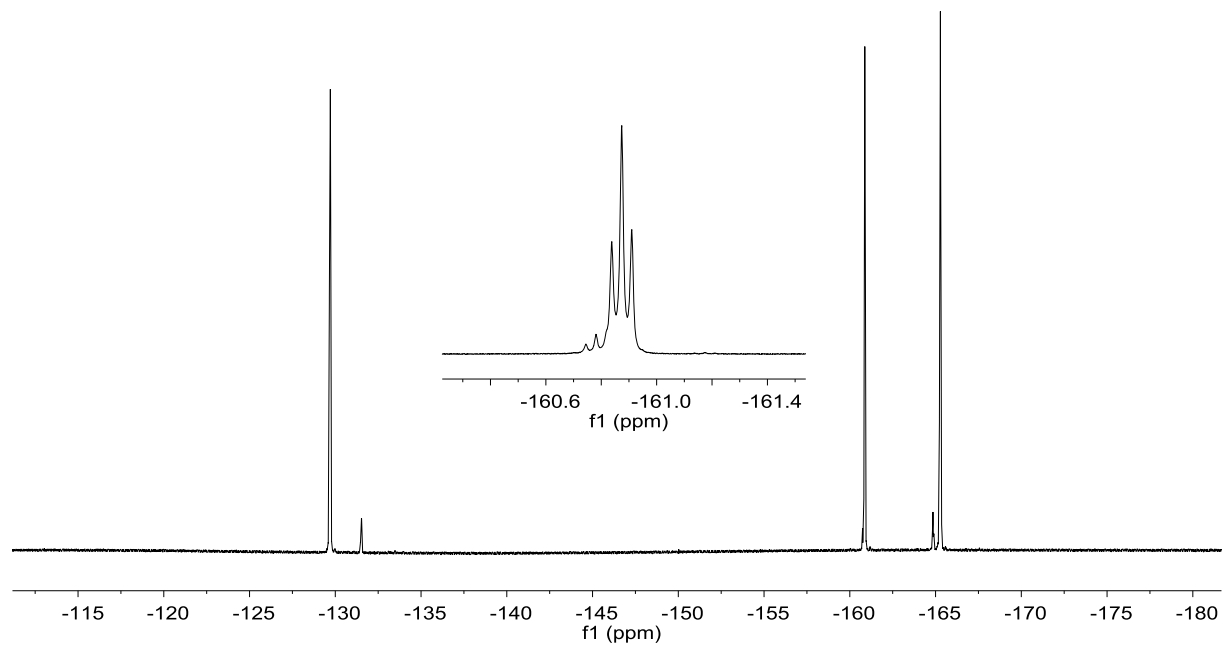


Figure S19. ^{19}F NMR (564 MHz, 258 K, CD_2Cl_2) spectrum of complexes **9a** and **9b**.

Crystals of complex **9b** suitable for the X-ray crystal structure analysis were obtained from the mixture of pentane and CH₂Cl₂ (5 : 1) at -35 °C.

X-ray crystal structure analysis of 9b (erk8818): A yellow prism-like specimen of C₄₃H₄₅BF₁₀O₂Zr, approximate dimensions 0.129 mm x 0.144 mm x 0.403 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 558 frames were collected. The total exposure time was 6.97 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 42813 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 8592 were independent (average redundancy 4.983, completeness = 99.8%, $R_{\text{int}} = 6.11\%$, $R_{\text{sig}} = 4.28\%$) and 6991 (81.37%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 9.9866(5)$ Å, $b = 13.5663(6)$ Å, $c = 17.4676(7)$ Å, $\alpha = 71.1900(10)^\circ$, $\beta = 82.820(2)^\circ$, $\gamma = 69.877(2)^\circ$, volume = 2103.13(17) Å³, are based upon the refinement of the XYZ-centroids of 9874 reflections above $20 \sigma(I)$ with $4.960^\circ < 2\theta < 54.85^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.847. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8750 and 0.9570. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}$, with $Z = 2$ for the formula unit, C₄₃H₄₅BF₁₀O₂Zr. The final anisotropic full-matrix least-squares refinement on F^2 with 532 variables converged at $R1 = 3.89\%$, for the observed data and $wR2 = 8.87\%$ for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was 0.562 e⁻/Å³ and the largest hole was -0.597 e⁻/Å³ with an RMS deviation of 0.064 e⁻/Å³. On the basis of the final model, the calculated density was 1.399 g/cm³ and F(000), 908 e⁻. CCDC Nr.: 1832834.

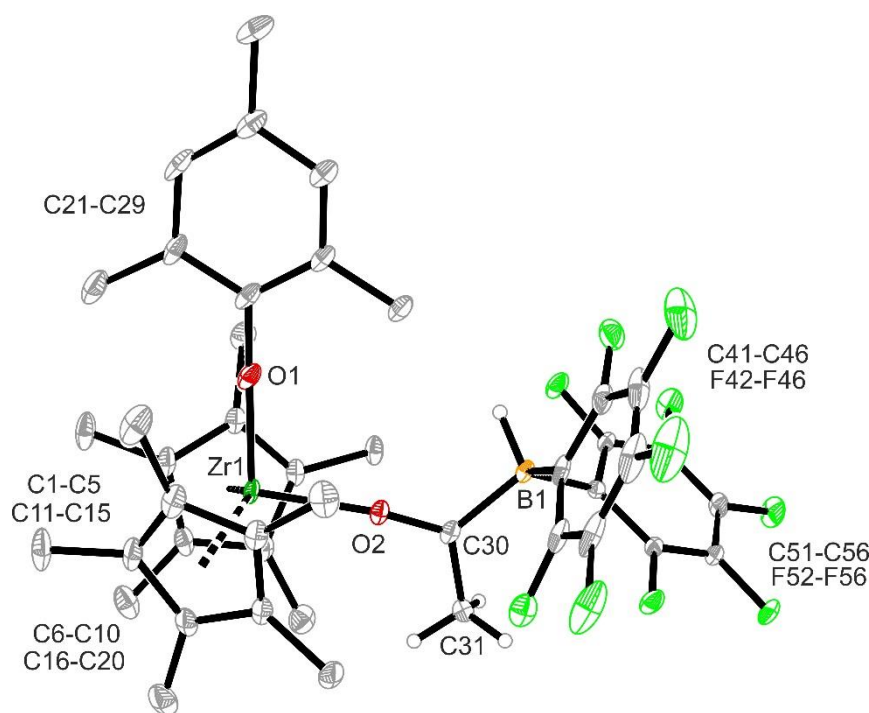
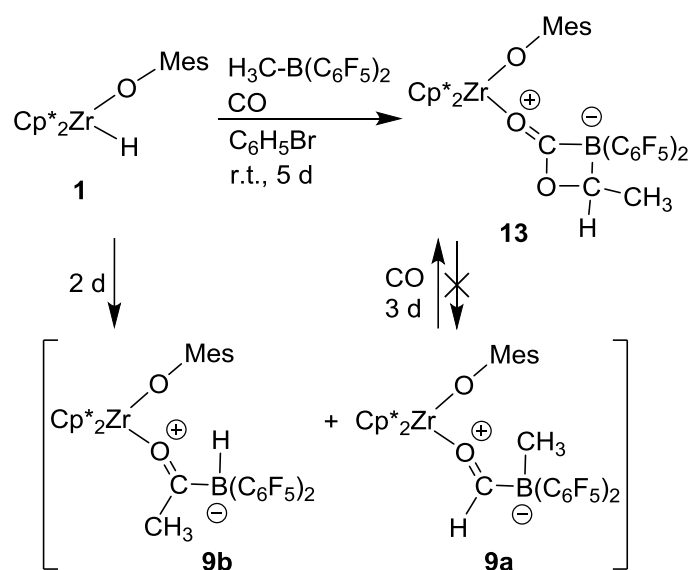


Figure S20. Crystal structure of compound **9b**. Hydrogen atoms at Cp* and O-mesityl groups were omitted for clarity (thermals ellipsoids are shown with 30% probability).

Preparation of complex 13



Scheme S5

1) **In situ reaction of complexes 9a and 9b with CO:** In a Young tube, 17.7 mg of complexes **9a** and **9b** (0.02 mmol) was dissolved in C_6D_6 (0.5 mL). The yellow solution was evacuated at -78°C , and then refilled by CO atmosphere (1.5 bar) at room temperature. After 3 d, the NMR data were collected, indicating the formation of complex **13**.

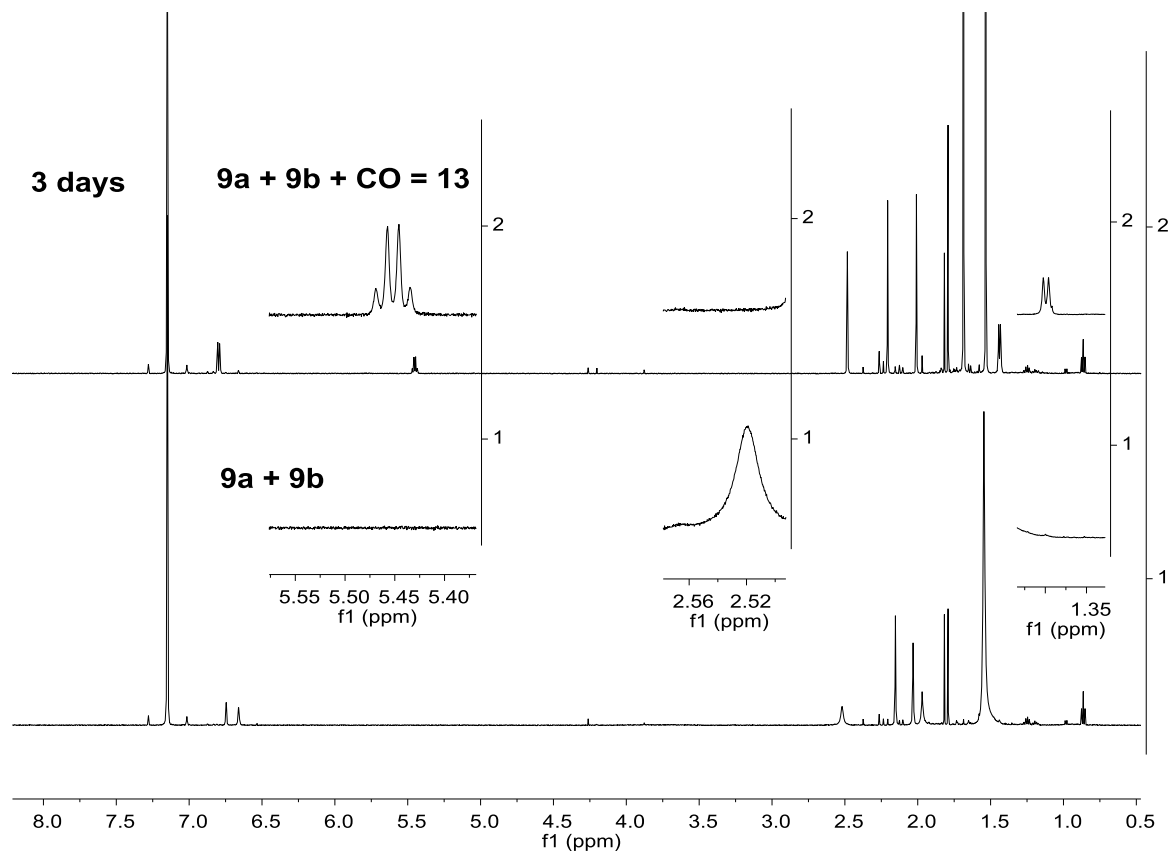


Figure S21. (1) ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of complexes **9a** and **9b**; (2) ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of the reaction of complexes **9a** and **9b** with CO after 3 days.

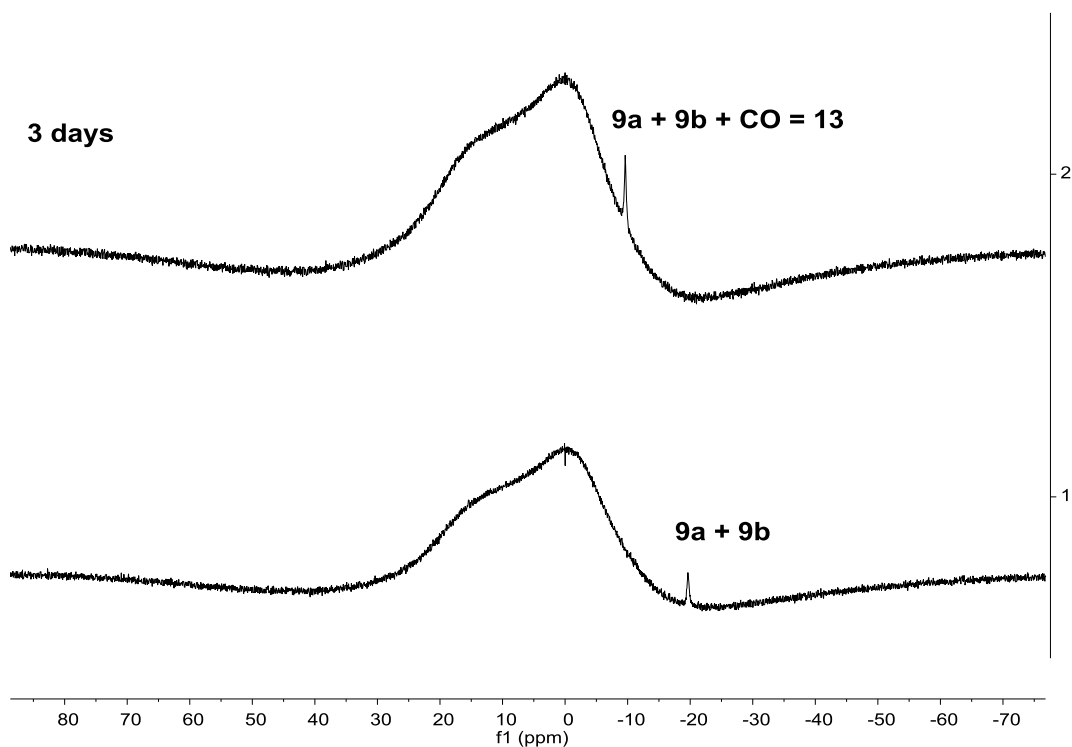


Figure S22. (1) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectrum of complexes **9a** and **9b**; (2) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectrum of the reaction of complexes **9a** and **9b** with CO after 3 days.

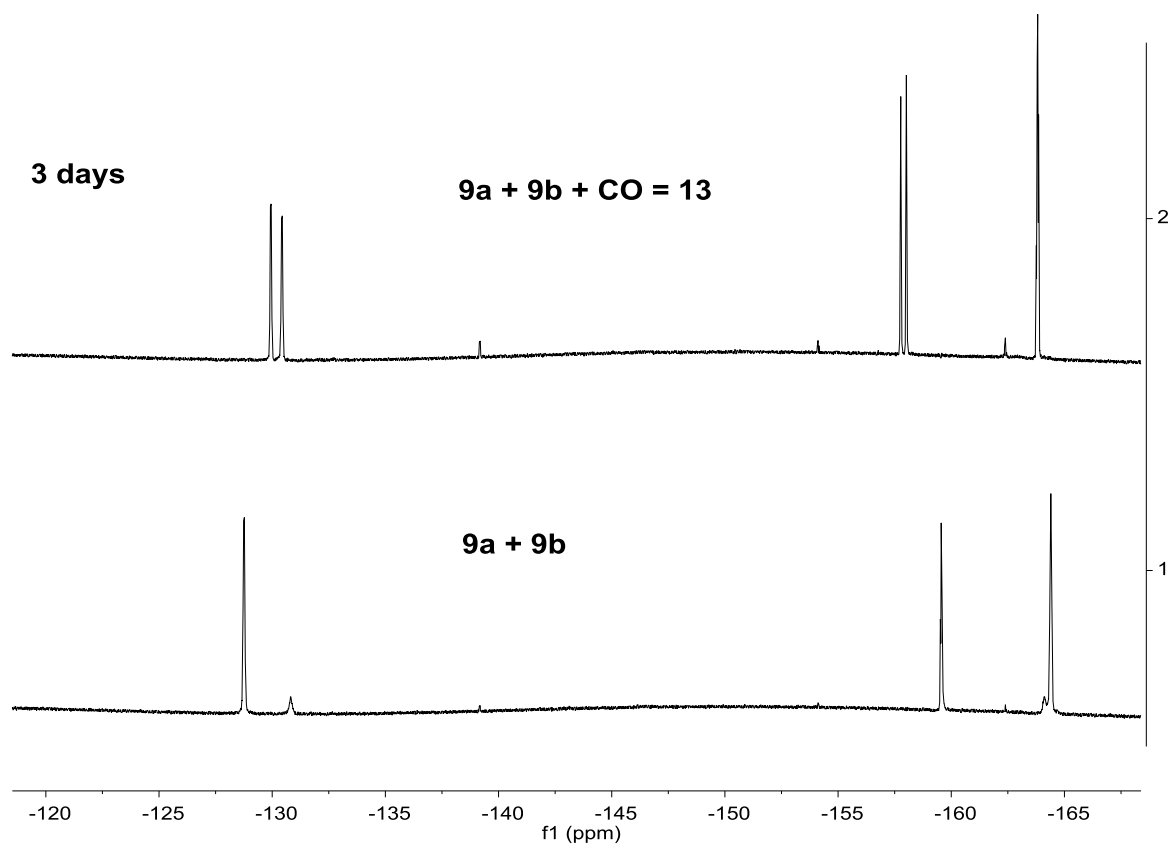


Figure S23. (1) ^{19}F NMR (564 MHz, 299 K, C_6D_6) spectrum of complexes **9a** and **9b**; (2) ^{19}F NMR (564 MHz, 299 K, C_6D_6) spectrum of the reaction of complexes **9a** and **9b** with CO after 3 days.

2) **Synthesis of complex 13 (preparative scale):** In a Schlenk tube, complex **1** (249 mg, 0.5 mmol) and $\text{H}_3\text{C-B}(\text{C}_6\text{F}_5)_2$ (160 mg, 0.5 mmol) were mixed and dissolved in bromobenzene (5 mL) at room temperature. The obtained solution was evacuated at $-78\text{ }^\circ\text{C}$, and then refilled by CO atmosphere (1.5 bar) at room temperature. After stirring for 5 d, the solvent was removed in vacuo to give a red solid, which was recrystallized twice from a mixture of CH_2Cl_2 and pentane at $-35\text{ }^\circ\text{C}$ to afford the resulting yellow crystal product **13**. Yield: 219 mg, 48 %.

Elemental analysis: calc. for $\text{C}_{44}\text{H}_{45}\text{BF}_{10}\text{O}_3\text{Zr} \cdot \text{C}_5\text{H}_{12}$: C, 59.69; H, 5.83. Found: C, 59.87; H, 5.79.

^1H NMR (600 MHz, 299 K, CD_2Cl_2 , 5.32 ppm): δ = 6.75 (s, 1H, *m*-Mes), 6.73 (s, 1H, *m*-Mes), 5.30 (q, $^3J_{\text{HH}} = 6.9$ Hz, 1H, BCH), 2.19 (s, 3H, *p*- CH_3 -Mes), 2.17 (s, 3H, *o*- CH_3 -Mes), 2.12 (s, 3H, *o*- CH_3 -Mes), 1.94 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.79 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.41 (d, $^3J_{\text{HH}} = 6.9$ Hz, 1H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2 , 53.8 ppm): δ = 215.2 (br, C=O), 156.9 (*i*-Mes), 148.1 (dm, $^1J_{\text{FC}} \sim 241$ Hz, C_6F_5), 147.1 (dm, $^1J_{\text{FC}} \sim 240$ Hz, C_6F_5), 139.9 (dm, $^1J_{\text{FC}} \sim 245$ Hz, C_6F_5), 139.6 (dm, $^1J_{\text{FC}} \sim 246$ Hz, C_6F_5), 137.3 (dm, $^1J_{\text{FC}} \sim 250$ Hz, C_6F_5), 129.5 (*m*-Mes), 129.1 (*m*-Mes), 128.1 (*p*-Mes), 127.4 (*o*-Mes), 125.1 ($\text{C}_5(\text{CH}_3)_5$), 124.6 ($\text{C}_5(\text{CH}_3)_5$), 122.8 (*o*-Mes), 118.0 (br s, *i*- C_6F_5), 80.1 (br, BCH), 20.4 (*p*- CH_3 -Mes), 18.9 (*o*- CH_3 -Mes), 18.65 (*o*- CH_3 -Mes), 18.58 (CH_3), 11.6 ($\text{C}_5(\text{CH}_3)_5$), 11.4 ($\text{C}_5(\text{CH}_3)_5$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ = -9.9 ($\nu_{1/2} \sim 55$ Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -130.3 (m, 2F, *o*- C_6F_5), -160.2 (t, $^3J_{\text{FF}} = 20.1$ Hz, 1F, *p*- C_6F_5), -165.2 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{m,p} = 5.0$]. -130.9 (m, 2F, *o*- C_6F_5), -159.3 (t, $^3J_{\text{FF}} = 20.1$ Hz, 1F, *p*- C_6F_5), -165.1 (m, 2F, *m*- C_6F_5). [$\Delta\delta^{19}\text{F}_{m,p} = 5.8$].

^1H , ^{13}C gHMBCAD (600 MHz/151 MHz, 299 K, CD_2Cl_2) [selected traces]: $\delta^1\text{H} / \delta^{13}\text{C} = 6.75$ and $6.73 / 156.9$ (*m*-Mes / *i*-Mes), $5.30 / 215.2$ and 118.0 (BCH / C=O and *i*- C_6F_5), $2.19 / 128.1$ (*p*- CH_3 -Mes / *p*-Mes), $2.17 / 127.4$ (*o*- CH_3 -Mes / *o*-Mes), $2.12 / 122.8$ (*o*- CH_3 -Mes / *o*-Mes), $1.94 / 125.1$ ($\text{C}_5(\text{CH}_3)_5 / \text{C}_5(\text{CH}_3)_5$), $1.79 / 124.6$ ($\text{C}_5(\text{CH}_3)_5 / \text{C}_5(\text{CH}_3)_5$).

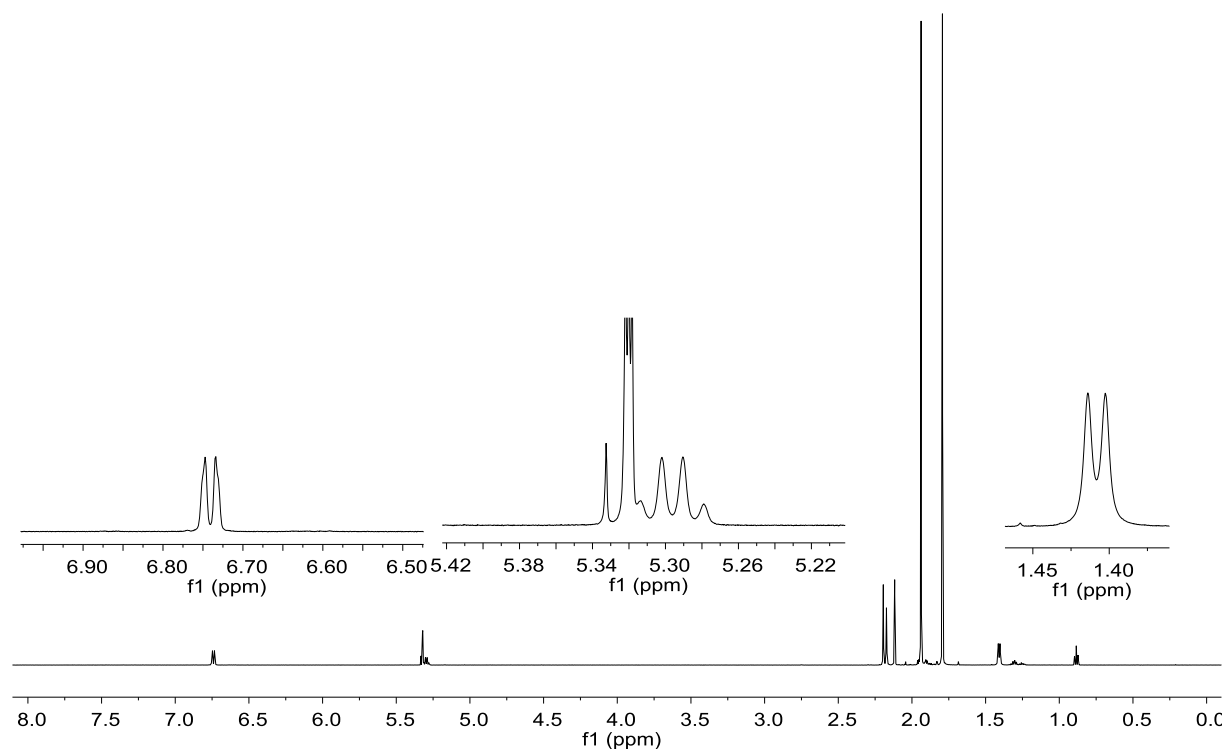


Figure S24. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of complex **13**.

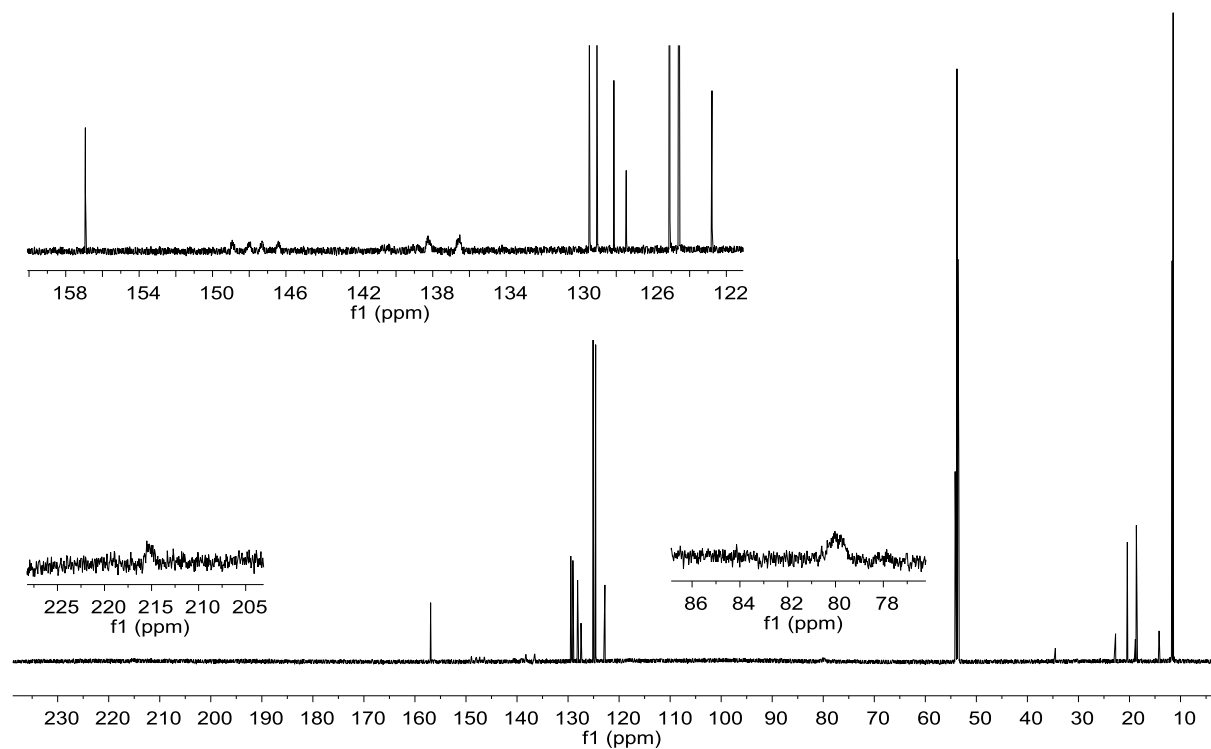


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of complex **13**.

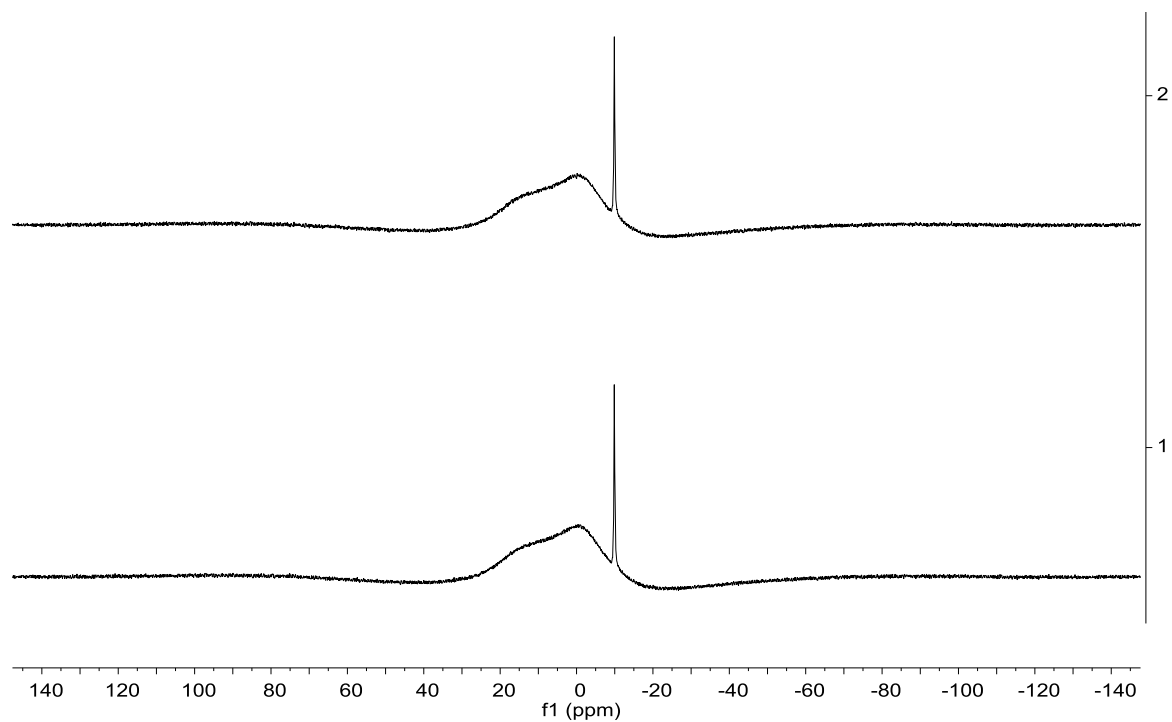


Figure S26. (1) ^{11}B and (2) $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of complex **13**.

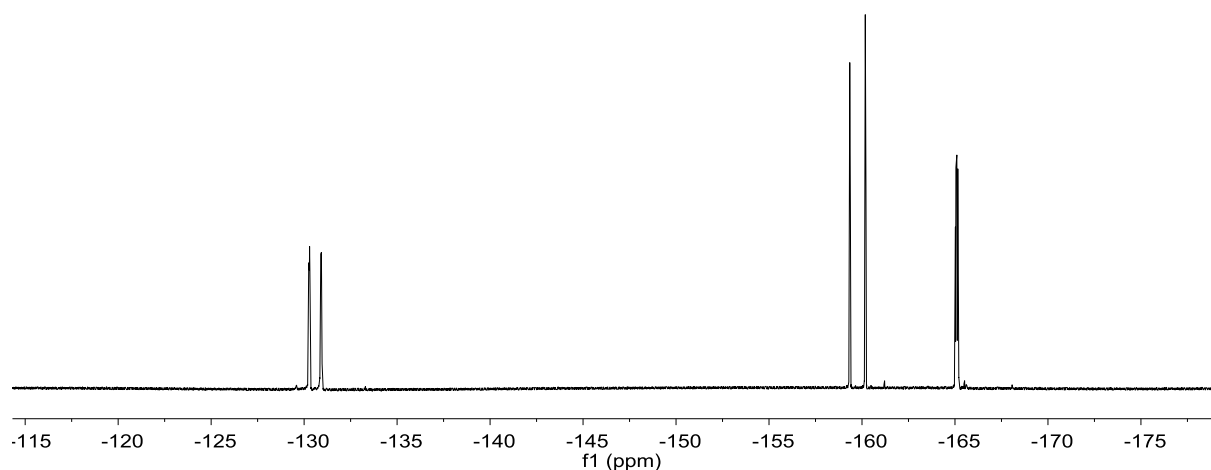


Figure S27. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of complex **13**.

Crystals of complex **13** suitable for the X-ray crystal structure analysis were obtained from pentane at room temperature.

X-ray crystal structure analysis of 13 (erk8840): A colorless plate-like specimen of $\text{C}_{44}\text{H}_{45}\text{BF}_{10}\text{O}_3\text{Zr} \cdot \text{C}_5\text{H}_{12}$, approximate dimensions 0.046 mm x 0.095 mm x 0.113 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 958 frames were collected. The total exposure time was 11.97 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 108115 reflections to a maximum θ angle of 25.35° (0.83 \AA resolution), of which 8368 were independent (average redundancy 12.920, completeness = 99.8%, $R_{\text{int}} = 9.14\%$, $R_{\text{sig}} = 4.32\%$) and 6546 (78.23%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a} = 26.8923(13) \text{ \AA}$, $\underline{b} = 10.9665(5) \text{ \AA}$, $\underline{c} = 31.0978(14) \text{ \AA}$, $\beta = 94.806(2)^\circ$, volume = $9138.9(7) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9855 reflections above $20 \sigma(I)$ with $4.727^\circ < 2\theta < 50.69^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.919. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9640 and 0.9850. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $C2/c$, with $Z = 8$ for the formula unit, $\text{C}_{44}\text{H}_{45}\text{BF}_{10}\text{O}_3\text{Zr} \cdot \text{C}_5\text{H}_{12}$. The final anisotropic full-matrix least-squares refinement on F^2 with 639 variables converged at $R1 = 3.82\%$, for the observed data and $wR2 = 7.35\%$ for all data. The goodness-of-fit was 1.053. The largest peak in the final difference electron density synthesis was $0.418 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.365 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.065 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.433 g/cm^3 and $F(000)$, 4080 e^- . CCDC Nr.: 1832835.

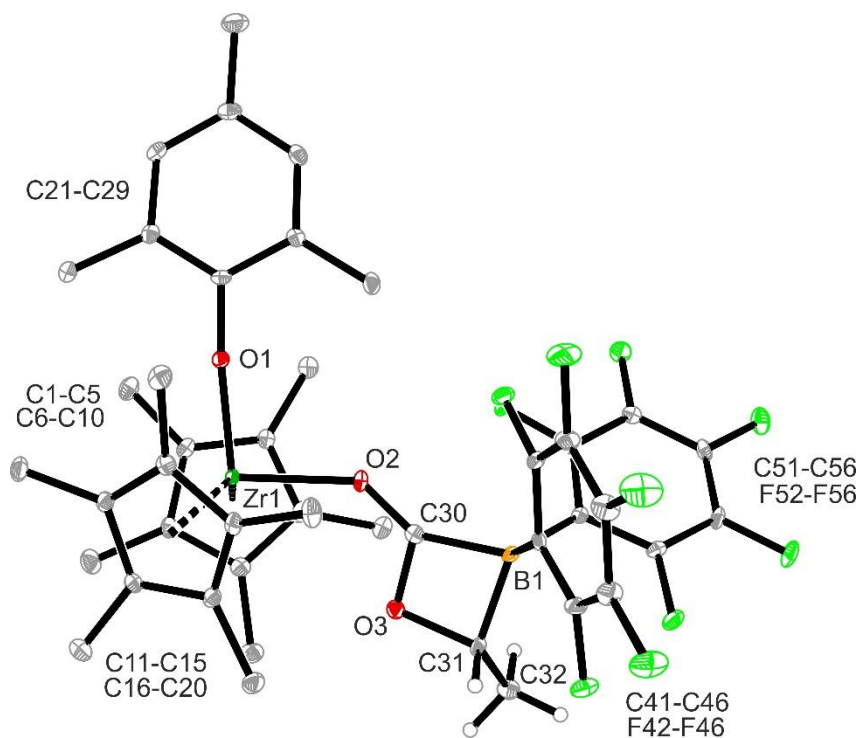


Figure S28. Crystal structure of compound **13**. Hydrogen atoms at Cp* and O-mesityl groups were omitted for clarity (thermal ellipsoids are shown with 30% probability).