Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Multifaceted chelating μ-(η^3:η^3-*antifacial*)-(*cis*-$C_4R_2H_2$) coordination motif in binuclear complexes

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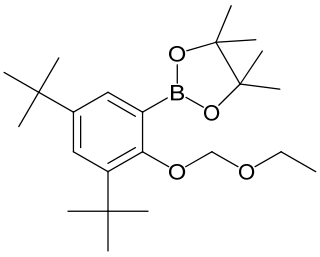
Contents

Experimental Section

General Considerations. All reactions were performed using standard Schlenk techniques under an argon atmosphere or in a Braun dry-box under a nitrogen atmosphere. All solvents were appropriately dried and distilled then degassed prior to use. ^{1}H, ^{13}C (referenced to residual solvent peaks) and ^{19}F (external trifluoroacetic acid reference) NMR spectra were recorded at 295 K on a Bruker Avance 400 FT-NMR spectrometer (ppm). Peak assignments were based on combinations of [^{1}H,^{13}C]-HSQC, -HMBC, 135-DEPT, COSY and NOESY experiments. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer. UV-vis absorption spectra were obtained on an Agilent 8453 diode array spectrophotometer. Elemental analyses were performed on a Vario EL elemental analyzer (Elementar Analysensysteme GmbH). For polymer analysis, gel permeation chromatographs were obtained on a PL-GPC 220 instrument versus polyethylene standards at 160 ^{o}C in 1,2,4-trichlorobenzene.

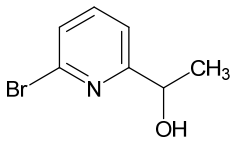
Density Functional Theory Calculations. The structures and energies of all molecular species are calculated at the B3LYP[1] level with the LanL2DZ basis sets[2] for Ti, Zr and Hf and 6-31G(d) basis sets for non-metal atoms. All calculations are performed with Gaussian 09 package of program.[3] Natural Bond Orbital (NBO) analysis and Natural Resonance Theory (NRT) calculations are performed using NBO 5.9 program[4] implemented in Gaussian 09.

Synthesis of I-1



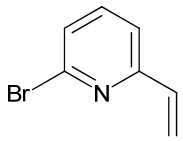
Compound **I-1** was prepared by modification of literature methods.[5,6] A solution of *n*-butyllithium (2.4 M in *n*-hexane, 19.6 mL, 47.0 mmol) was added dropwise to a solution of 1-bromo-3,5-di-tert-butyl-2-(methoxyethoxy)benzene (12.9 g, 37.6 mmol) in diethyl ether (100 mL) at −78 °C under an argon atmosphere. The mixture was stirred for 1 hour at −78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.7 mL, 52.6 mmol) was added, and the resultant mixture was stirred at room temperature for 12 hours. The product was extracted with diethyl ether, washed by brine and water, and dried over magnesium sulfate. Evaporation of volatiles gave a pale yellow oil, which was purified by silica gel flash chromatography using *n*-hexane as eluent to give a white solid. Yield: 11.1 g, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.0 Hz, 3H, $OCH_2\mathit{CH_3}$), 1.31 (s, 9H, *t*-Bu), 1.35 (s, 12H, $BOC(C\mathit{H_3})_2$), 1.43 (s, 9H, *t*-Bu), 3.81 (q, *J* = 7.2 Hz, 2H, $O\mathit{CH_2}CH_3$), 5.21 (s, 2H, OCH_2O), 7.46 (d, *J* = 2.8 Hz, 1H), 7.53 (d, *J* = 2.8 Hz, 1H).

Synthesis of I-2



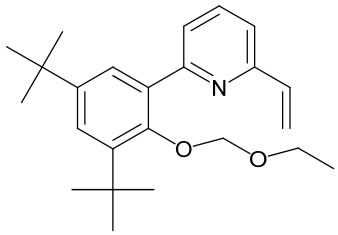
Compound **I-2** was prepared by modification of a literature method.[7] A solution of 2,6-dibromopyridine (2.5 g, 10.6 mmol) in diethyl ether (50 mL) was added dropwise to *n*-butyllithium (2.4 M in *n*-hexane, 4.8 mL, 11.6 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred for 1 hour, after which acetaldehyde (1.2 mL, 21.1 mmol) was added. The resultant mixture was stirred for 12 hours at room temperature, and dilute hydrochloric acid was then added. The product was extracted with diethyl ether, washed by brine and water and dried over magnesium sulfate. The product was obtained as a colorless oil after purification by silica gel flash chromatography using *n*-hexane:ethyl acetate (100:1) as eluent. Yield: 1.7 g, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (d, *J* = 6.8 Hz, 3H, CH_3), 3.43 (s, 1H), 4.87 (d, *J* = 6.0 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H).

Synthesis of I-3



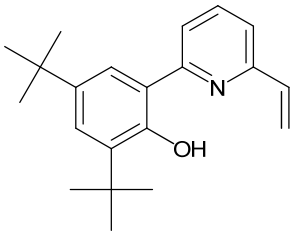
Compound **I-3** was prepared by modification of a literature method.[7] Concentrated sulphuric acid (10 mL) was added dropwise to **I-2** (1.62 g, 8.02 mmol) at 0 °C. The resultant mixture was heated at 120 ^{o}C for 18 hours, after which water was added slowly. The product was extracted with diethyl ether, neutralized by potassium hydroxide, washed by brine and water and dried over magnesium sulphate. The product was obtained as a colourless oil after purification by silica gel flash chromatography using n-hexane as eluent. Yield: 1.2 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (d, *J* = 10.8 Hz, 1H), 6.24 (d, *J* = 17.2 Hz, 1H), 6.69–6.76 (m, 1H), 7.26–7.28 (m, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H).

Synthesis of I-4



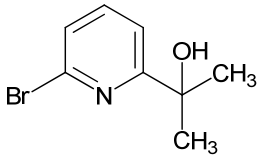
A mixture of **I-1** (2.00 g, 5.22 mmol), **I-3** (0.80 g, 4.35 mmol), potassium carbonate (3.01 g, 21.7 mmol) and Pd(dppf)Cl_2 (0.09 g, 0.11 mmol) in dioxane (40 mL) and deionized water (4 mL) was heated at 100 °C for 48 hours under an argon atmosphere. The resultant black mixture was extracted with dichloromethane, washed by brine and water, and dried over magnesium sulfate. After evaporation of volatiles, the crude product was purified by silica gel flash chromatography using *n*-hexane:ethyl acetate (10:1) as eluent to give a colorless oil. Yield: 1.4 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.0 Hz, 3H, $OCH_2\mathit{CH_3}$), 1.34 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu), 3.52 (q, *J* = 7.1 Hz, 2H, $O\mathit{CH_2}CH_3$), 4.60 (s, 2H, OCH_2O), 5.46–5.59 (br, 1H), 6.27 (d, *J* = 17.6 Hz, 1H), 6.82–7.00 (br, 1H), 7.28–7.38 (br, 1H), 7.43–7.46 (m, 2H), 7.55–7.63 (br, 1H), 7.63–7.76 (br, 1H).

Synthesis of H_2L^H



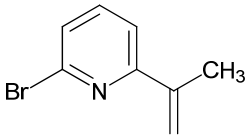
Compound **I-4** (1.40 g, 3.81 mmol) in ethanol (20 mL) and HCl (5 mL) was heated at 80 ^oC for 12 hours. The resultant mixture was extracted with dichloromethane, washed by brine and water, and dried over magnesium sulfate. The product was obtained as a yellow solid after purification by silica gel flash chromatography using *n*-hexane:ethyl acetate (100:1) as eluent. Yield: 1.1 g, 93%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 5.58 (d, J = 10.8 Hz, 1H), 6.23 (d, J = 17.6 Hz, 1H), 6.80–6.87 (m, 1H), 7.23 (dd, J = 6.6 Hz, 1.4 Hz, 1H), 7.41 (d, J = 2.4 Hz, 1H), 7.66 (d, J = 2.4 Hz, 1H), 7.76–7.82 (m, 2H), 14.77 (s, 1H, OH).

Synthesis of I-5



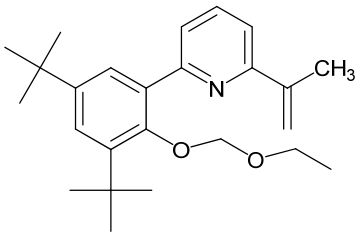
The procedure for the synthesis of **I-2** was adopted using 2,6-dibromopyridine (4.0 g, 16.89 mmol) and acetone (2.5 mL, 33.8 mmol). Yield: 3.1 g, 85%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.54 (s, 6H, CH_3), 3.42–4.43 (br, 1H, OH), 7.35 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H).

Synthesis of I-6



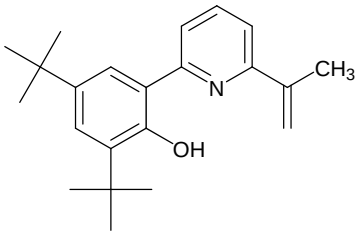
The procedure for the synthesis of **I-3** was adopted using **I-5** (1.84 g, 8.52 mmol). Yield: 1.5 g, 90%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (d, J = 0.8 Hz, 3H, CH_3), 5.33 (quintet, J = 1.4 Hz, 1H), 5.93 (quintet, J = 0.8 Hz, 1H), 7.34 (dd, J = 7.8 Hz, 0.6 Hz, 1H), 7.39 (dd, J = 7.6 Hz, 0.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H).

Synthesis of I-7



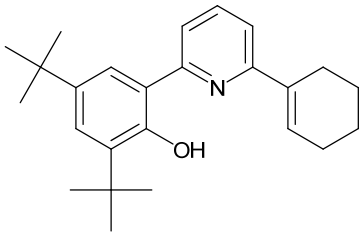
The procedure for the synthesis of **I-4** was adopted using **I-1** (3.15 g, 8.06 mmol) and **I-6** (1.5 g, 7.67 mmol). Yield: 1.8 g, 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 1.34 (s, 9H, *t*-Bu), 1.48 (s, 9H, *t*-Bu), 2.27 (s, 3H, CH_3), 3.56 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 4.61 (s, 2H, OCH_2O), 5.32 (s, 1H), 5.98 (s, 1H), 7.40–7.42 (m, 2H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.61–7.69 (m, 2H).

Synthesis of H_2L^{Me}



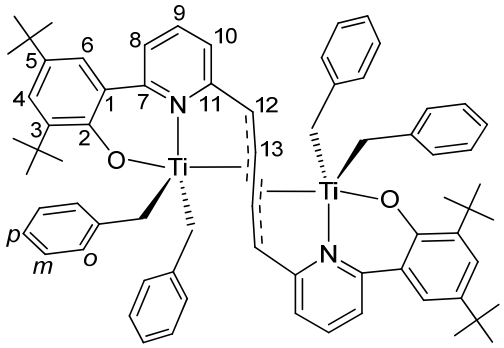
The procedure for the synthesis of $\mathbf{H_2L^H}$ was adopted using **I-7** (1.1 g, 2.88 mmol). Yield: 0.8 g, 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 9H, *t*-Bu), 1.49 (s, 9H, *t*-Bu), 2.28 (s, 3H, CH_3), 5.40 (s, 1H), 5.88 (s, 1H), 7.39–7.42 (m, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.77–7.82 (m, 2H), 14.75 (br, 1H, OH).

Synthesis of H_2L^{Cy}



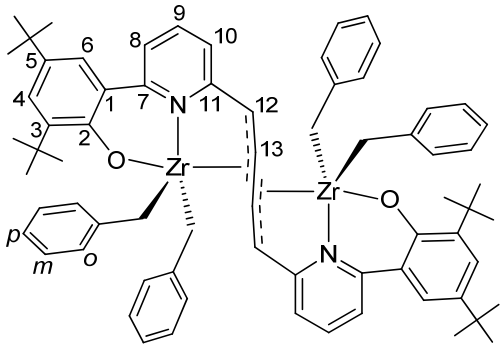
The procedure for the synthesis of $\mathbf{H_2L^H}$ and $\mathbf{H_2L^{Me}}$ was adopted. Yield: 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 1.66–1.74 (m, 2H), 1.81–1.87 (m, 2H), 2.29–2.34 (m, 2H), 2.54–2.57 (m, 2H), 6.69–6.71 (m, 1H), 7.29–7.33 (m, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.73–7.77 (m, 2H), 14.86 (s, 1H, OH).

Synthesis of Complex Ti_2^H



A solution of H_2L^H (0.08 g, 0.26 mmol) in *n*-pentane (10 mL) was added dropwise at −78 °C to $Ti(CH_2Ph)_4$ (0.11 g, 0.27 mmol) in *n*-pentane (5 mL). The reaction mixture was stirred for 1 hour at −78 °C and for 12 hours at room temperature. Filtration and concentration of the resultant mixture, and storage at −25 °C for 2 days, gave a black-purple crystalline solid, which was collected and dried under vacuum. Yield: 0.16 g, 57%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.23 (s, 18H, 5-*t*-Bu), 1.87 (s, 18H, 3-*t*-Bu), 2.93 (d, *J* = 9.2 Hz, 2H, CH_2), 3.14 (d, *J* = 9.2 Hz, 2H, CH_2), 3.29 (d, *J* = 9.2 Hz, 2H, CH_2), 3.91 (d, *J* = 9.2 Hz, 2H, CH_2), 5.27 (m, *J* = 6.3, 4.1 Hz, 2H, H^{12}), 5.42 (d, *J* = 8.0 Hz, 2H, H^{10}), 6.13 (t, *J* = 8.0 Hz, 2H, H^9), 6.24 (d, *J* = 7.6 Hz, 2H, H^8), 6.56–6.60 (m, 6H, *o*-Ph and *p*-Ph), 6.78 (t, *J* = 7.6 Hz, 4H, *m*-Ph), 6.83 (d, *J* = 2.4 Hz, 2H, H^6), 6.99 (d, *J* = 7.2 Hz, 4H, *o*-Ph), 7.05 (t, *J* = 7.4 Hz, 2H, *p*-Ph), 7.12 (m, *J* = 6.3, 4.1 Hz, 2H, H^{13}), 7.37 (t, *J* = 7.6 Hz, 4H, *m*-Ph), 7.61 (d, *J* = 2.4 Hz, 2H, H^4). ^{13}C NMR (101 MHz, C_6D_6; 4º carbons assigned using [^{1}H,^{13}C]-HMBC): δ 30.7 (3-C*Me*$_3$), 31.6 (5-C*Me*$_3$), 34.4 (5-*C*Me$_3$), 35.8 (3-*C*Me$_3$), 82.7 ($^1J_{C,H}$ = 128.3 Hz, CH_2), 95.2 ($^1J_{C,H}$ = 128.3 Hz, CH_2), 95.8 (C^{12}), 114.3 (C^8), 119.5 (C^{10}), 122.0 (*p*-Ph), 122.5 (*p*-Ph), 124.7 (*o*-Ph), 125.0 (C^6), 125.1 (C^4), 126.7 (C^{13}), 126.8 (C^1), 127.7 (*m*-Ph), 127.8 (*o*-Ph), 128.9 (*m*-Ph), 134.7 (C^9), 136.7 (C^3), 142.8 (C^5), 149.9 (*ipso*-Ph), 151.7 (*ipso*-Ph), 152.9 (C^7), 158.3 (C^2), 163.8 (C^{11}). Anal. Calcd for $C_{70}H_{78}N_2O_2Ti_2$ (1075.12): C, 78.20; H, 7.31; N, 2.61. Found: C, 78.40; H, 6.91; N, 2.32.

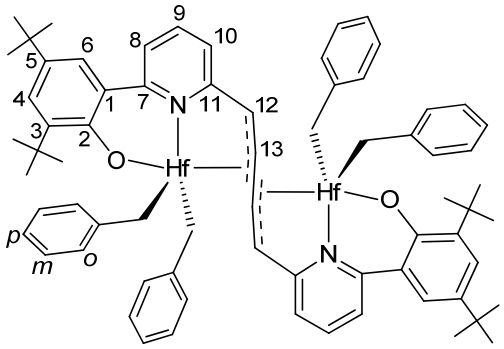
Synthesis of Complex Zr_2^H



A solution of H_2L^H (0.11 g, 0.35 mmol) in *n*-pentane (10 mL) and diethyl ether (2 mL) was added

dropwise at −78 °C to $Zr(CH_2Ph)_4$ (0.17 g, 0.37 mmol) in *n*-pentane (6 mL). The reaction mixture was stirred for 1 hour at −78 °C and for 12 hours at room temperature. Filtration and concentration of the resultant mixture, and storage at −25 °C for 2 days, gave a deep orange crystalline solid, which was collected and dried under vacuum. Yield: 0.18 g, 44%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.31 (s, 18H, 5-*t*-Bu), 1.72 (s, 18H, 3-*t*-Bu), 2.31 (d, J = 10.2 Hz, 2H, CH_2), 2.68 (d, J = 10.8 Hz, 2H, CH_2), 2.74 (d, J = 10.8 Hz, 2H, CH_2), 2.93 (d, J = 10.2 Hz, 2H, CH_2), 5.36 (m, J = 6.4, 4.4 Hz, 2H, H^{12}), 5.41 (d, J = 8.0 Hz, 2H, H^{10}), 5.56 (m, J = 6.4, 4.4 Hz, 2H, H^{13}), 6.13 (d, J = 7.6 Hz, 2H, H^8), 6.40 (t, J = 8.0 Hz, 2H, H^9), 6.74 (t, J = 7.2 Hz, 2H, *p*-Ph), 6.82 (d, J = 7.6 Hz, 4H, *o*-Ph), 6.91−7.01 (m, 12H, *o*-Ph, *m*-Ph, *p*-Ph and H^6), 7.23 (t, J = 7.6 Hz, 4H, *m*-Ph), 7.68 (d, J = 2.4 Hz, 2H, H^4). ^{13}C NMR (101 MHz, C_6D_6; 4º carbons assigned using [^{1}H,^{13}C]-HMBC): δ 31.0 (3-C*Me*$_3$), 31.8 (5-C*Me*$_3$), 34.4 (5-*C*Me$_3$), 35.8 (3-*C*Me$_3$), 66.1 ($^1J_{C,H}$ = 124.8 Hz, CH_2), 75.4 ($^1J_{C,H}$ = 119.7 Hz, CH_2), 85.4 (C^{12}), 115.6 (C^{13}), 116.5 (C^8), 120.1 (C^{10}), 122.26 (*p*-Ph), 122.34 (*p*-Ph), 124.7 (C^6), 125.8 (C^1), 126.0 (*o*-Ph), 126.1 (C^4), 128.1 (*o*-Ph), 128.8 (*m*-Ph), 129.3 (*m*-Ph), 134.2 (C^9), 137.1 (C^3), 141.5 (C^5), 144.1 (*ipso*-Ph), 147.6 (*ipso*-Ph), 151.7 (C^7), 153.9 (C^2), 159.8 (C^{11}). Anal. Calcd for $C_{70}H_{78}N_2O_2Zr_2$ (1161.83): C, 72.36; H, 6.77; N, 2.41. Found: C, 72.01; H, 6.54; N, 2.26.

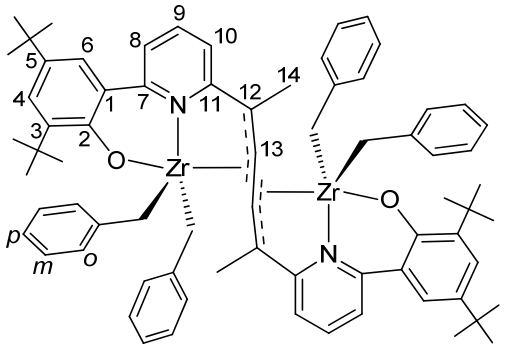
Synthesis of Complex Hf_2^H



A solution of H_2L^H (0.10 g, 0.32 mmol) in *n*-pentane (10 mL) and diethyl ether (2 mL) was added dropwise at −78 °C to $Hf(CH_2Ph)_4$ (0.18 g, 0.34 mmol) in *n*-pentane (6 mL). The reaction mixture was stirred for 1 hour at −78 °C and for 12 hours at room temperature. Filtration and concentration of the resultant mixture, and storage at −25 °C for 2 days, gave a deep orange crystalline solid, which was collected and dried under vacuum. Yield: 0.16 g, 37%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.28 (s, 18H, 5-*t*-Bu), 1.71 (s, 18H, 3-*t*-Bu), 2.09 (d, J = 10.4 Hz, 2H, CH_2), 2.56–2.61 (m, 4H, CH_2), 2.65 (d, J = 11.6 Hz, 2H, CH_2), 5.04 (m, J = 6.2, 4.6 Hz, 2H, H^{12}), 5.47 (d, J = 7.6 Hz, 2H, H^{10}), 5.61 (m, J = 6.2, 4.6 Hz, 2H, H^{13}), 6.13 (d, J = 7.2 Hz, 2H, H^8), 6.33 (t, J = 7.8 Hz, 2H, H^9), 6.65 (t, J = 7.2 Hz, 2H, *p*-Ph), 6.84–6.99 (m, 16H, two sets of *o*-Ph, *m*-Ph, *p*-Ph and H^6), 7.34 (t, J =

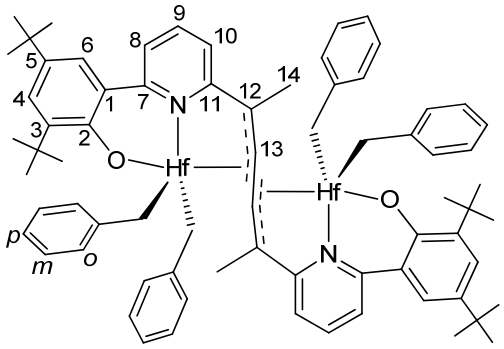
7.6 Hz, 4H, *m*-Ph), 7.66 (d, *J* = 2.0 Hz, 2H, H^4). ^{13}C NMR (101 MHz, C_6D_6; 4º carbons assigned using [^1H,^{13}C]-HMBC): δ 30.9 (3-C*Me*$_3$), 31.7 (5-C*Me*$_3$), 34.3 (5-*C*Me$_3$), 35.7 (3-*C*Me$_3$), 72.1 ($^1J_{C,H}$ = 124.8 Hz, CH_2), 82.3 ($^1J_{C,H}$ = 119.7 Hz, CH_2), 85.2 (C^{12}), 115.0 (C^{13}), 116.3 (C^8), 120.3 (C^{10}), 122.0 (*p*-Ph), 122.2 (*p*-Ph), 124.7 (C^6), 125.8 (C^1), 126.08 (*o*-Ph), 126.12 (C^4), 128.1 (*o*-Ph), 128.2 (*m*-Ph), 128.9 (*m*-Ph), 134.4 (C^9), 137.8 (C^3), 141.7 (C^5), 144.5 (*ipso*-Ph), 148.3 (*ipso*-Ph), 152.0 (C^7), 153.9 (C^2), 160.5 (C^{11}). Anal. Calcd for $C_{70}H_{78}N_2O_2Hf_2$ (1336.36): C, 62.91; H, 5.88; N, 2.10. Found: C, 62.78; H, 5.43; N, 1.98.

Synthesis of Complex Zr_2^{Me}



A solution of H_2L^{Me} (0.18 g, 0.56 mmol) in *n*-pentane (13 mL) and diethyl ether (0.8 mL) was added dropwise at −78 °C to $Zr(CH_2Ph)_4$ (0.27 g, 0.58 mmol) in *n*-pentane (6 mL). The reaction mixture was stirred for 1 hour at −78 °C and for 12 hours at room temperature. Concentration and filtration of the resultant mixture, storage at −25 °C for 18 hours, gave a dark turquoise crystalline solid, which was collected and dried under vacuum. Yield: 0.21 g, 60%. ^1H NMR (400 MHz, C_6D_6): δ 1.36 (s, 18H, 5-*t*-Bu), 1.45 (d, *J* = 11.2 Hz, 2H, CH_2), 1.67 (s, 18H, 3-*t*-Bu), 1.79 (d, *J* = 11.2 Hz, 2H, CH_2), 1.92 (s, 6H, H^{14}), 2.63 (d, *J* = 10.2 Hz, 2H, CH_2), 2.78 (d, *J* = 10.2 Hz, 2H, CH_2), 5.10 (s, 2H, H^{13}), 5.85 (d, *J* = 8.4 Hz, 2H, H^{10}), 6.10 (d, *J* = 7.6 Hz, 2H, H^8), 6.52 (d, *J* = 7.2 Hz, 4H, *o*-Ph), 6.55−6.61 (m, 4H, *p*-Ph and H^9), 6.74 (t, *J* = 7.6 Hz, 4H, *m*-Ph), 6.98 (t, *J* = 7.2 Hz, 2H, *p*-Ph), 7.11 (d, *J* = 2.4 Hz, 2H, H^6), 7.14 (d, *J* = 7.6 Hz, 4H, *o*-Ph), 7.20 (t, *J* = 7.4 Hz, 4H, *m*-Ph), 7.57 (d, *J* = 2.4 Hz, 2H, H^4). ^{13}C NMR (101 MHz, C_6D_6; 4º carbons assigned using [^1H,^{13}C]-HMBC): δ 19.1 (C^{14}), 30.1 (3-C*Me*$_3$), 31.4 (5-C*Me*$_3$), 34.1 (5-*C*Me$_3$), 35.3 (3-*C*Me$_3$), 63.9 ($^1J_{C,H}$ = 122.3 Hz, CH_2), 69.3 ($^1J_{C,H}$ = 129.3 Hz, CH_2), 92.8 (C^{12}), 107.2 (C^{13}), 111.9 (C^{10}), 112.4 (C^8), 121.1 (*p*-Ph), 122.4 (C^6), 123.7 (*p*-Ph), 124.9 (C^1), 125.6 (C^4), 126.5 (*o*-Ph), 127.0 (*o*-Ph), 127.8 (*m*-Ph), 130.7 (*m*-Ph), 135.8 (C^9), 137.4 (C^3), 141.8 (C^5), 143.9 (*ipso*-Ph), 145.9 (*ipso*-Ph), 150.9 (C^7), 151.6 (C^{11}), 155.6 (C^2). Anal. Calcd for $C_{72}H_{82}N_2O_2Zr_2$ (1189.88): C, 72.68; H, 6.95; N, 2.35. Found: C, 72.97; H, 6.61; N, 2.12.

Synthesis of Complex Hf_2^{Me}

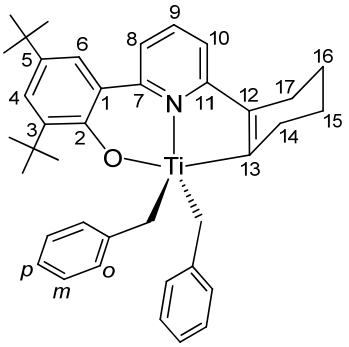


A solution of H_2L^{Me} (0.14 g, 0.42 mmol) in *n*-pentane (10 mL) was added dropwise at −78 °C to $Hf(CH_2Ph)_4$ (0.24 g, 0.44 mmol) in *n*-pentane (6 mL) and diethyl ether (2 mL). The reaction mixture was stirred for 1 hour at −78 °C and for 12 hours at room temperature. Filtration of the resultant mixture gave a dark indigo crystalline solid, which was collected and dried under vacuum. Yield: 0.24 g, 41%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.33 (s, 18H, 5-*t*-Bu), 1.68–1.70 (m, 20H, 3-*t*-Bu and CH_2), 1.85 (d, J = 12.8 Hz, 2H, CH_2), 2.00 (s, 6H, H^{14}), 2.37 (d, J = 12.0 Hz, 2H, CH_2), 2.55 (d, J = 12.0 Hz, 2H, CH_2), 5.13 (s, 2H, H^{13}), 5.79 (d, J = 8.4 Hz, 2H, H^{10}), 6.06 (d, J = 7.2 Hz, 2H, H^8), 6.48–6.54 (m, 8H, *o*-Ph, *p*-Ph and H^9), 6.76 (t, J = 7.6 Hz, 4H, *m*-Ph), 6.96 (t, J = 6.8 Hz, 2H, *p*-Ph), 7.06 (d, J = 2.2 Hz, 2H, H^6), 7.28–7.34 (m, 8H, *o*-Ph and *m*-Ph), 7.58 (d, J = 2.2 Hz, 2H, H^4). ^{13}C NMR (101 MHz, C_6D_6; 4º carbons assigned using [^{1}H,^{13}C]-HMBC): δ 19.4 (C^{14}), 30.4 (3-C*Me*$_3$), 31.7 (5-C*Me*$_3$), 34.4 (5-*C*Me$_3$), 35.7 (3-*C*Me$_3$), 74.3 ($^1J_{C,H}$ = 118.7 Hz, CH_2), 77.7 ($^1J_{C,H}$ = 119.7 Hz, CH_2), 94.0 (C^{12}), 104.5 (C^{13}), 111.8 (C^8), 112.6 (C^{10}), 121.7 (*p*-Ph), 122.6 (C^6), 123.1 (*p*-Ph), 124.9 (C^1), 126.2 (C^4), 127.0 (*o*-Ph), 127.3 (*o*-Ph), 127.9 (*m*-Ph), 129.8 (*m*-Ph), 135.8 (C^9), 138.6 (C^3), 142.3 (C^5), 145.5 (*ipso*-Ph), 146.2 (*ipso*-Ph), 150.1 (C^7), 151.1 (C^{11}), 155.5 (C^2). Anal. Calcd for $C_{72}H_{82}N_2O_2Hf_2$ (1364.41): C, 63.38; H, 6.06; N, 2.05. Found: C, 63.76; H, 5.98; N, 2.01.

Attempted Synthesis of Complex Ti_2^{Me}

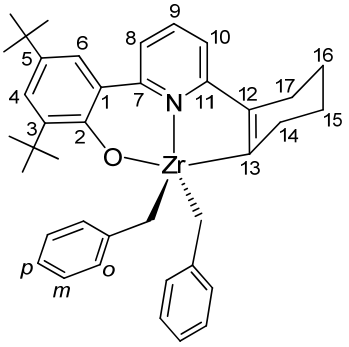
The procedure for the synthesis of $\mathbf{Ti_2^H}$ was adopted using H_2L^{Me} and $Ti(CH_2Ph)_4$ in a variety of different solvents (*n*-pentane, *n*-pentane/diethyl ether, toluene, benzene), but ^{1}H NMR characterization of the resultant reaction mixture gave broad or minimal resonances.

Synthesis of Complex Ti^{Cy}



A solution of H_2L^{Cy} (0.08 g, 0.22 mmol) in toluene (5 mL) was added dropwise at −78 °C to $Ti(CH_2Ph)_4$ (0.10 g, 0.23 mmol) in toluene (5 mL). The reaction mixture was stirred for 5 minutes at −78 °C and for 1 hour at room temperature. The resultant mixture was evacuated to dryness to afford the product as a dark purple crystalline solid. Yield: 0.13 g, 99%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.35 (s, 9H, 5-*t*-Bu), 1.59–1.70 (m, 4H, H^{15} and H^{16}), 1.72–1.76 (m, 2H, H^{17}), 1.77 (s, 9H, 3-*t*-Bu), 3.39–3.48 (m, 2H, H^{14}), 3.78 (d, *J* = 8.4 Hz, 2H, CH_2), 3.82 (d, *J* = 8.4 Hz, 2H, CH_2), 5.97 (d, *J* = 7.6 Hz, 1H, H^{10}), 6.53 (t, *J* = 7.4 Hz, 2H, *p*-Ph), 6.70–6.76 (m, 5H, *m*-Ph and H^9), 6.98 (d, *J* = 7.6 Hz, 4H, *o*-Ph), 7.11 (d, *J* = 7.2 Hz, 1H, H^8), 7.48 (d, *J* = 2.2 Hz, 1H, H^6), 7.67 (d, *J* = 2.2 Hz, 1H, H^4). ^{13}C NMR (101 MHz, C_6D_6; 4º carbons assigned using [^{1}H,^{13}C]-HMBC): δ 23.3 (C^{16}), 24.4 (C^{15}), 24.5 (C^{17}), 30.8 (3-C*Me*$_3$), 31.8 (5-C*Me*$_3$), 34.6 (5-*C*Me$_3$), 35.7 (3-*C*Me$_3$), 36.0 (C^{14}), 91.9 ($^1J_{C,H}$ = 133.3 Hz, CH_2), 113.0 (C^{10}), 120.3 (C^8), 123.7 (*p*-Ph), 123.9 (C^6), 126.7 (C^4), 128.5 (*m*-Ph), 129.7 (C^1), 129.8 (*o*-Ph), 135.7 (C^3), 137.1 (C^{12}), 138.5 (*ipso*-Ph), 139.4 (C^9), 141.8 (C^5), 156.3 (C^2), 157.8 (C^7), 165.5 (C^{11}), 220.8 (C^{13}). Anal. Calcd for $C_{39}H_{45}NOTi$ (591.65): C, 79.17; H, 7.67; N, 2.37. Found: C, 79.36; H, 7.32; N, 2.20.

Synthesis of Complex Zr^{Cy}



A solution of H_2L^{Cy} (0.20 g, 0.55 mmol) in *n*-pentane (10 mL) and diethyl ether (1 mL) was added dropwise at −78 °C to $Zr(CH_2Ph)_4$ (0.26 g, 0.58 mmol) in *n*-pentane (4 mL). The reaction mixture

was stirred for 15 minutes at −78 °C and for 12 hours at room temperature. Filtration of the resultant mixture gave an orange solid, which was collected and dried under vacuum. Yield: 0.25 g, 68%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.37 (s, 9H, 5-*t*-Bu), 1.47−1.52 (m, 2H, H^{15}), 1.60−1.63 (m, 11H, 3-*t*-Bu and H^{16}), 1.87 (t, *J* = 6.2 Hz, 2H, H^{17}), 2.38 (d, *J* = 9.6 Hz, 2H, CH_2), 2.51 (d, *J* = 9.6 Hz, 2H, CH_2), 2.66 (t, *J* = 5.4 Hz, 2H, H^{14}), 6.37 (d, *J* = 7.6 Hz, 1H, H^{10}), 6.71 (t, *J* = 7.0 Hz, 2H, *p*-Ph), 6.88−6.96 (m, 9H, *o*-Ph, *m*-Ph and H^9), 7.22 (d, *J* = 7.6 Hz, 1H, H^8), 7.48 (d, *J* = 2.4 Hz, 1H, H^6), 7.62 (d, *J* = 2.4 Hz, 1H, H^4). ^{13}C NMR (101 MHz, C_6D_6; 4º carbons assigned using [^{1}H,^{13}C]-HMBC): δ 23.4 (C^{16}), 23.6 (C^{15}), 26.1 (C^{17}), 30.3 (3-C*Me*$_3$), 31.8 (5-C*Me*$_3$), 33.6 (C^{14}), 34.5 (5-*C*Me$_3$), 35.5 (3-*C*Me$_3$), 66.4 ($^{1}J_{C,H}$ = 133.3 Hz, CH_2), 114.8 (C^{10}), 121.1 (C^8), 123.5 (*p*-Ph), 125.0 (C^6), 126.1 (C^1), 126.5 (C^4), 128.6 (*m*-Ph), 130.1 (*o*-Ph), 136.9 (C^3), 139.0 (C^{12}), 139.1 (*ipso*-Ph), 139.7 (C^9), 141.4 (C^5), 156.1 (C^2), 157.7 (C^7), 165.7 (C^{11}), 209.1 (C^{13}). Anal. Calcd for $C_{39}H_{45}NOZr$ (635.01): C, 73.77; H, 7.14; N, 2.21. Found: C, 73.71; H, 6.86; N, 2.12.

Formation of Ti_2^H by NMR Reaction

A solution of $Ti(CH_2Ph)_4$ (12.4 mg, 30.07 μmol) in C_6D_6 (0.3 mL) was added to a J. Young NMR tube containing H_2L^H (9.1 mg, 29.41 μmol) in C_6D_6 (0.1 mL) at −30 °C. The tube was sealed and shaken vigorously, and the solution changed from pale yellow to black immediately. The resultant mixture was allowed to react for 1 hour at room temperature, after which the product was characterized by ^{1}H NMR spectroscopy (Figure S1).

Formation of Hf_2^{Me} by NMR Reaction

A solution of $Hf(CH_2Ph)_4$ (9.0 mg, 16.57 μmol) in C_6D_6 (0.3 mL) was added to a J. Young NMR tube containing H_2L^{Me} (5.3 mg, 16.38 μmol) in C_6D_6 (0.1 mL) at −30 °C. The tube was sealed and shaken vigorously, and the solution changed from pale yellow to deep indigo immediately. The resultant mixture was allowed to react for 1 hour at room temperature, after which the product was characterized by ^{1}H NMR spectroscopy (Figure S2).

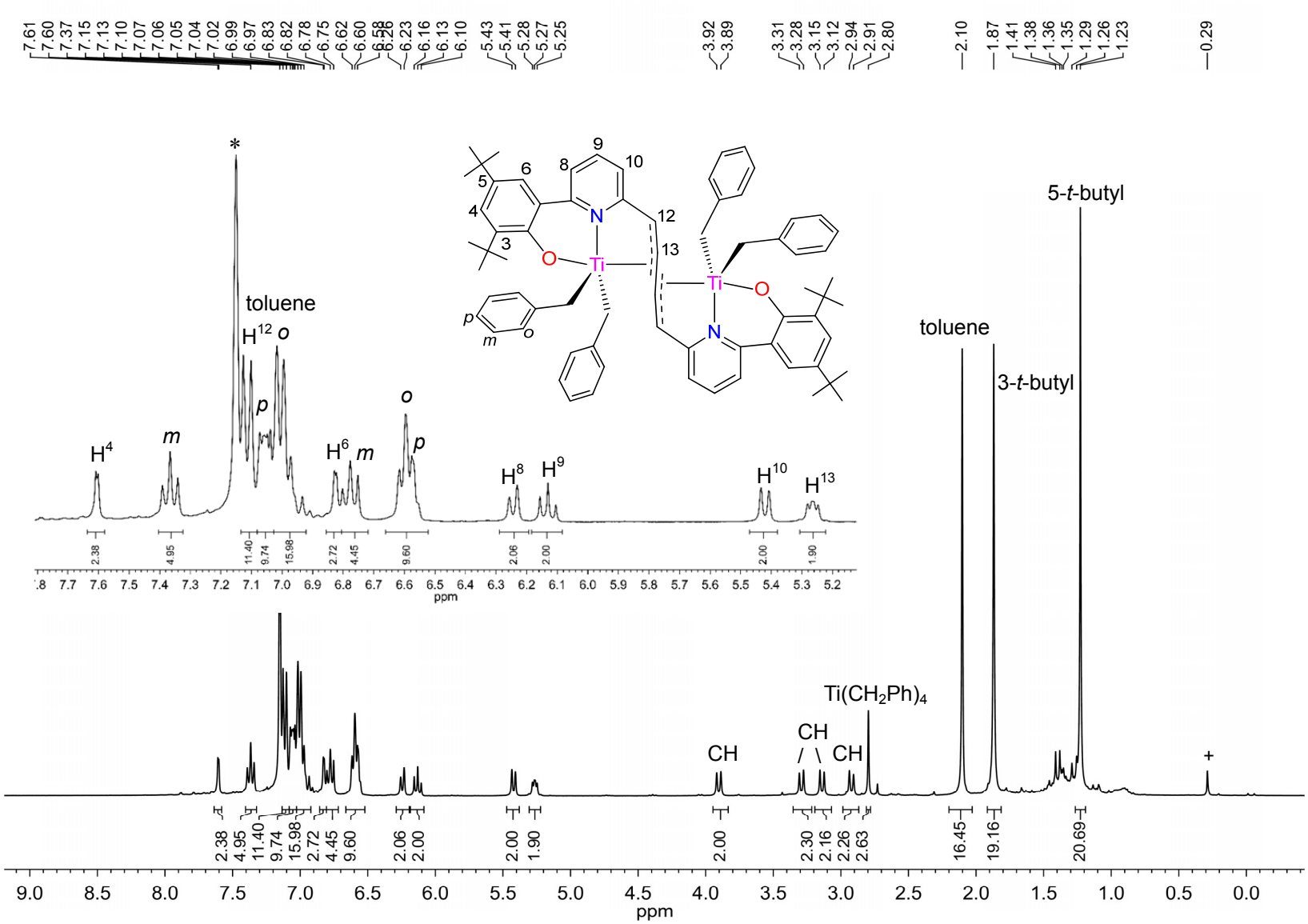


Figure S1. Full and expanded (inset) ^{1}H NMR spectra of **Ti_2^H** generated by NMR reaction of $Ti(CH_2Ph)_4$ with H_2L^H, for comparison with Figure S3 (400 MHz, C_6D_6* [silicone grease^{+}], 295 K).

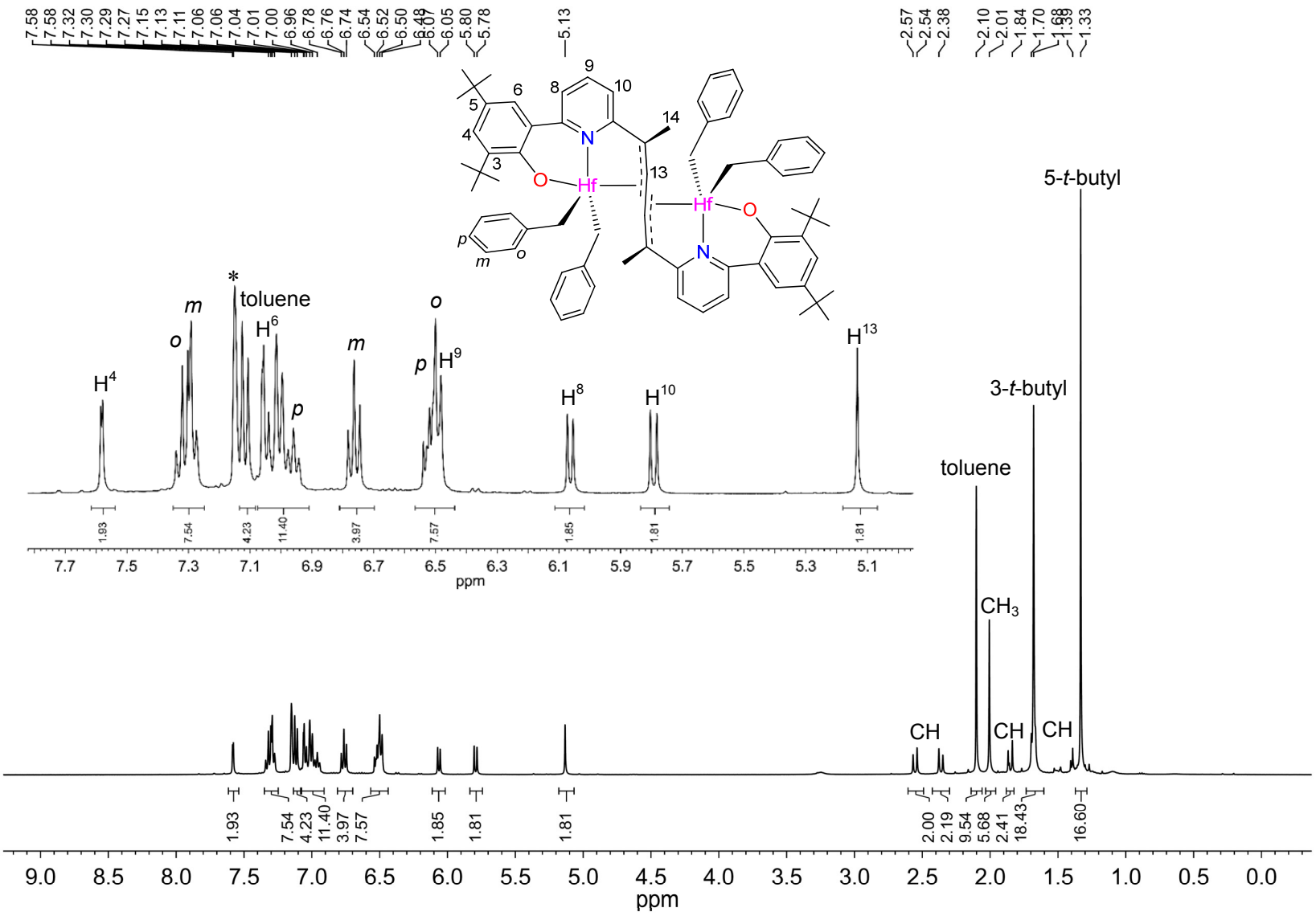


Figure S2. Full and expanded (inset) ^{1}H NMR spectra of **Hf_2^{Me}** generated by NMR reaction of $Hf(CH_2Ph)_4$ with H_2L^{Me}, for comparison with Figure S4 (400 MHz, C_6D_6,* 295 K).

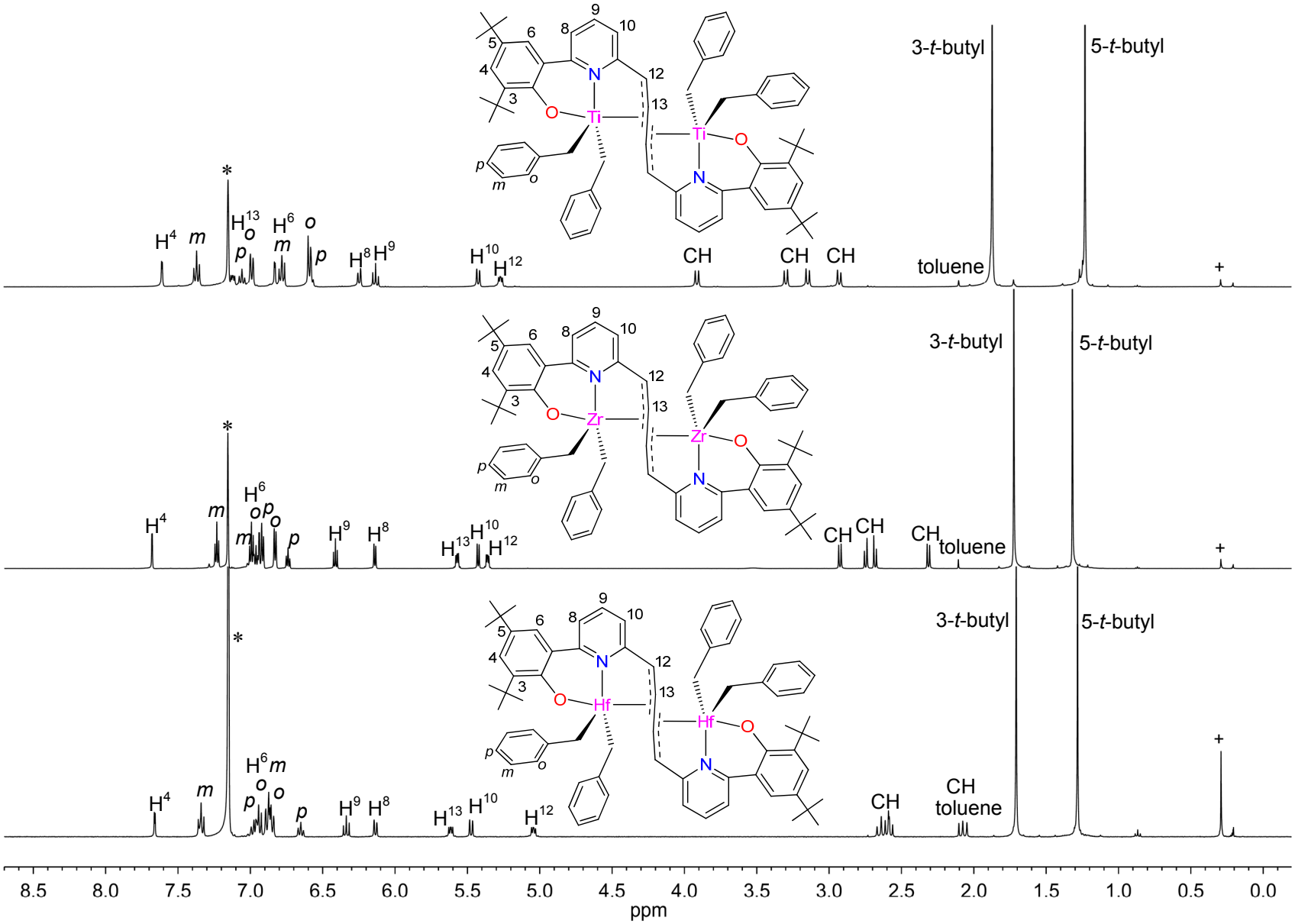


Figure S3. ^{1}H NMR spectra of $\mathbf{M_2^H}$ (400 MHz, C_6D_6* [silicone grease^{+}], 295 K).

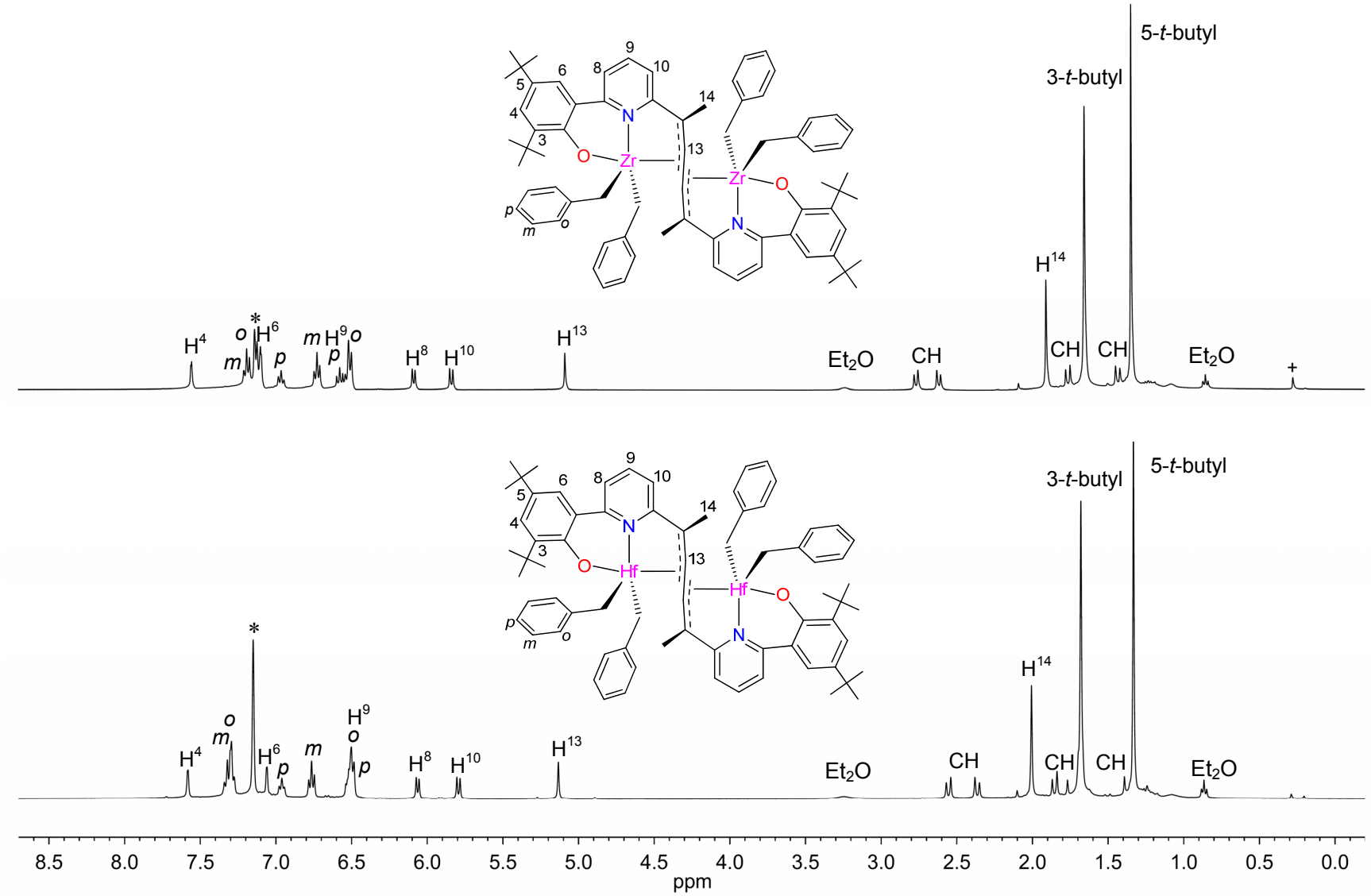


Figure S4. ^{1}H NMR spectra of $\mathbf{M_2}^{\mathbf{Me}}$ (400 MHz, C_6D_6* [silicone grease^{+}], 295 K).

Figure S5. Gas-phase potential energy surface for the formation of binuclear complex $\mathbf{Zr_2^H}$ by dimerization (via *cis-syn*-TS [black pathway] and *cis-anti*-TS [blue pathway]), at B3LYP level using LanL2DZ basis set (metals) and 6-31G(d) basis set (non-metals). All energies are in kcal/mol and selected bond lengths are in Å.

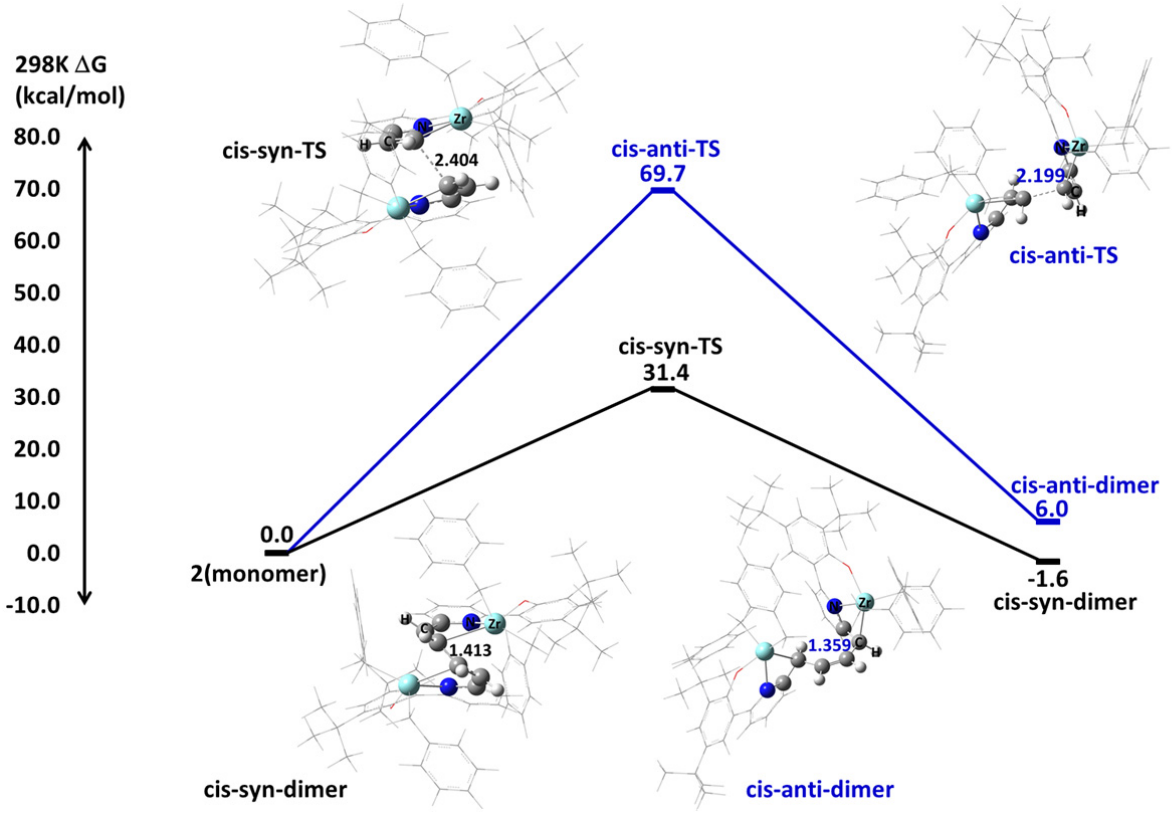
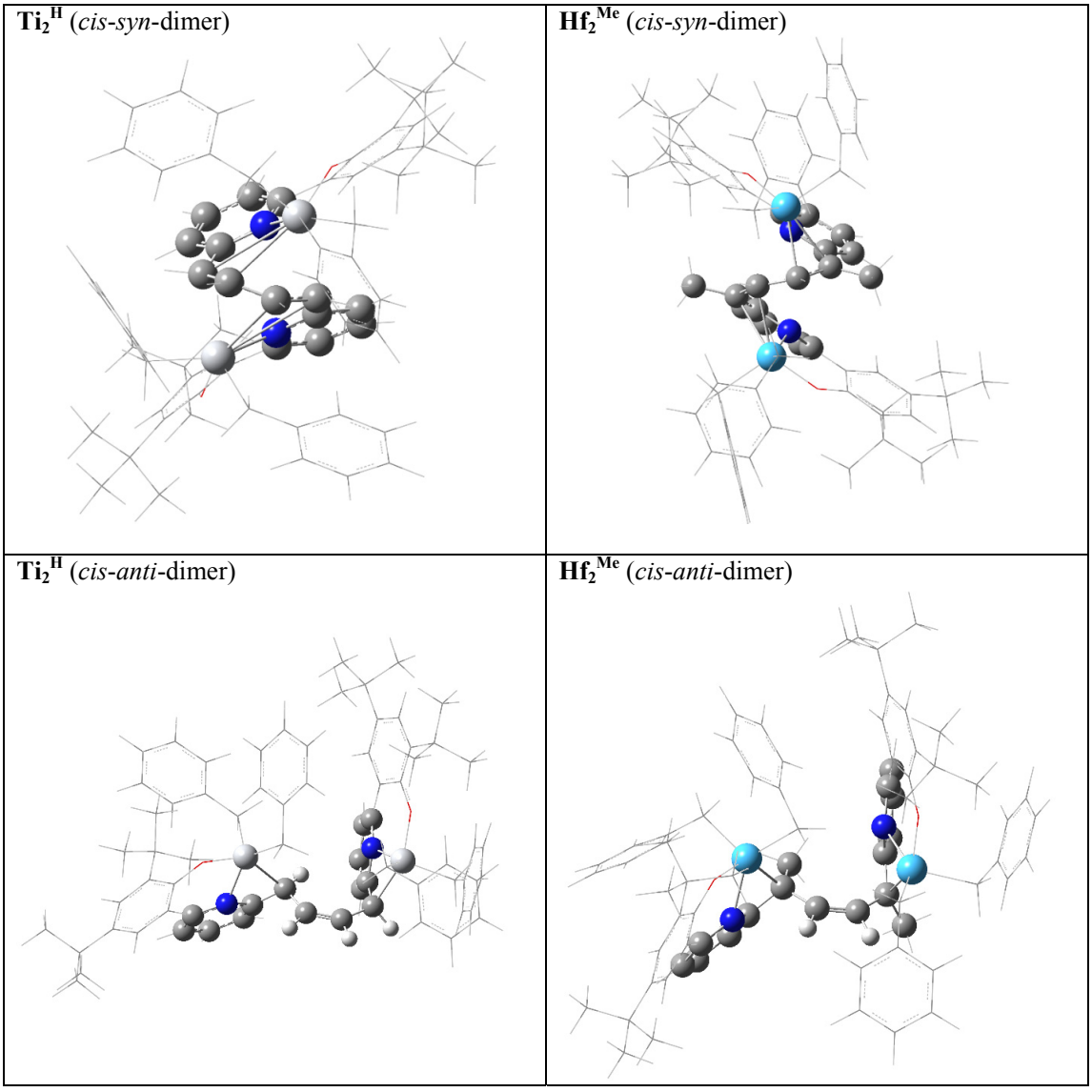


Table S1. Reaction energies (kcal/mol) at B3LYP level using LanL2DZ basis set (metals) and 6-31G(d) basis set (non-metals) [$\mathbf{Ti_2}^{\mathbf{Me}}$ complex has not been synthesized; transition state structure for *trans-syn* dimer could not be located].

	$\Delta G_{298}^{\ddagger}$ (*cis-syn*-TS)	ΔG_{298}° (*cis-syn*-dimer)	$\Delta G_{298}^{\ddagger}$ (*cis-anti*-TS)	ΔG_{298}° (*cis-anti*-dimer)	$\Delta G_{298}^{\ddagger}$ (*trans-anti*-TS)	ΔG_{298}° (*trans-anti*-dimer A)
$\mathbf{Ti_2}^{\mathbf{H}}$	37.4	7.6	77.0	9.3	78.1	–1.8
$\mathbf{Zr_2}^{\mathbf{H}}$	31.4	–1.6	69.7	6.0	65.1	–3.7
$\mathbf{Hf_2}^{\mathbf{H}}$	28.7	3.3	74.8	11.4	50.5	8.2
$\mathbf{Zr_2}^{\mathbf{Me}}$	34.3	9.0	74.9	18.8	71.2	12.0
$\mathbf{Hf_2}^{\mathbf{Me}}$	36.3	15.1	78.8	25.0	64.1	15.8
[$\mathbf{Ti_2}^{\mathbf{Me}}$]	40.1	19.0	83.0	25.9	78.2	17.9



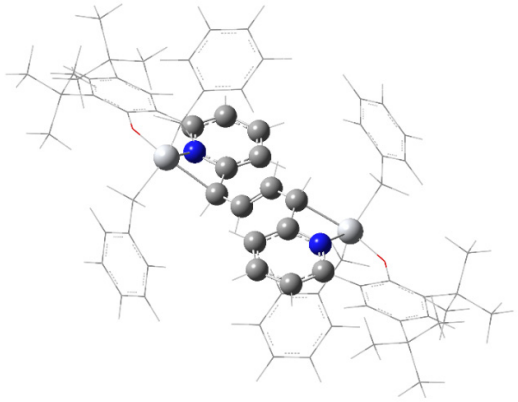
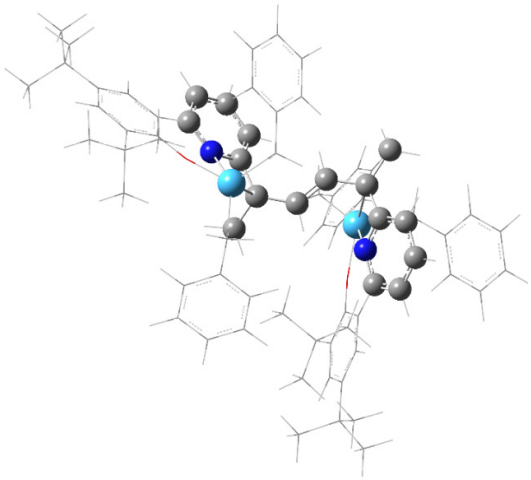
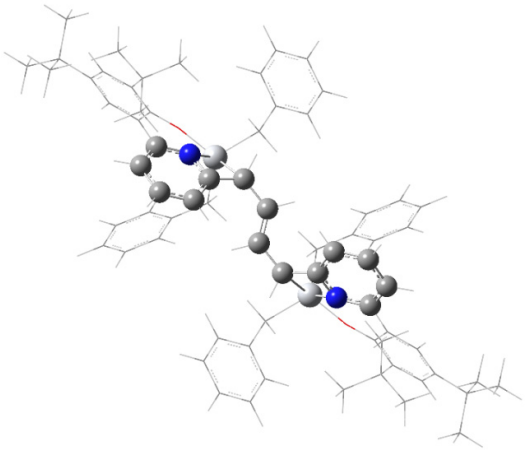
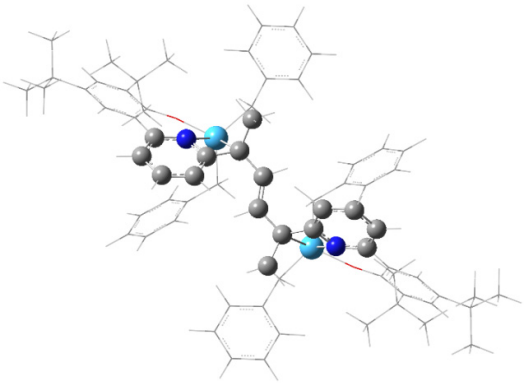
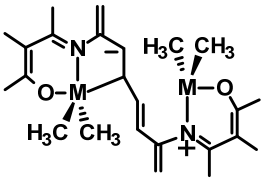
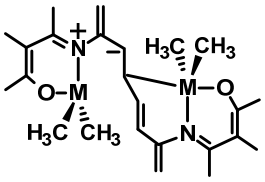
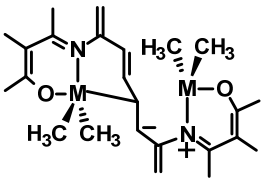
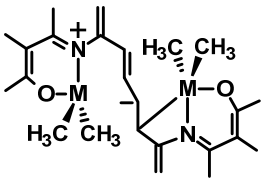
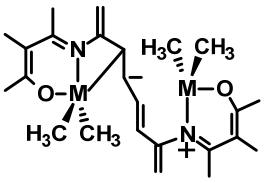
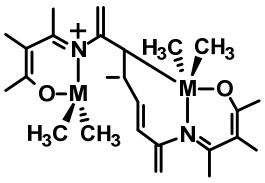
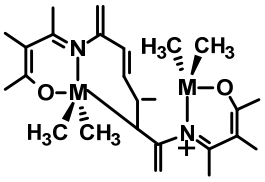
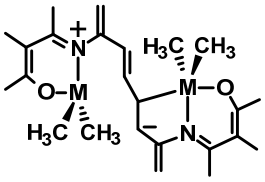
Ti_2^H (*trans-anti*-dimer A)	**Hf_2^{Me}** (*trans-anti*-dimer A)
	
Ti_2^H (*trans-anti*-dimer B)	**Hf_2^{Me}** (*trans-anti*-dimer B)
	

Table S2. Resonance structures for $\mathbf{M_2^{H\prime}}$ (model complexes of $\mathbf{M_2^{H}}$; simplified structure is used to disregard resonance forms within pyridine, phenolate and benzyl systems) from natural resonance theory calculations. A number of resonance structures have been located (highest resonance weight % are shown), and these structures can be classified as resonance forms with (d^0, d^0) or (d^1, d^1) metal centers (see Table S3)**.**

d^0, d^0					
					
$Ti_2^{H\prime}$	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**	**$Ti_2^{H\prime}$**	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**
8.31%	6.84%	9.71%	8.21%	5.55%	2.67%
					
$Ti_2^{H\prime}$	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**	**$Ti_2^{H\prime}$**	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**
7.89%	6.14%	2.05%	6.53%	9.38%	2.67%
					
$Ti_2^{H\prime}$	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**	**$Ti_2^{H\prime}$**	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**
6.44%	8.84%	2.05%	5.54%	5.80%	7.71%
					
$Ti_2^{H\prime}$	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**	**$Ti_2^{H\prime}$**	**$Zr_2^{H\prime}$**	**$Hf_2^{H\prime}$**
5.56%	6.71%	7.63%	5.20%	7.30%	8.41%

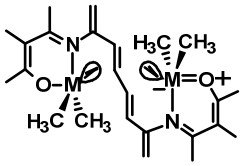
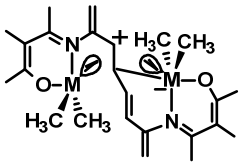
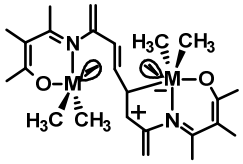
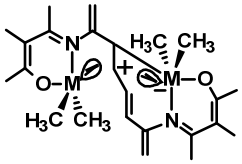
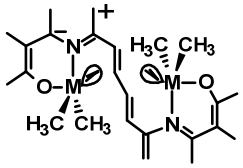
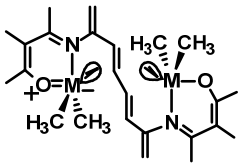
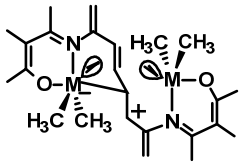
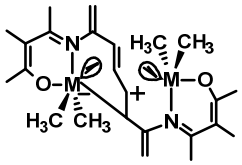
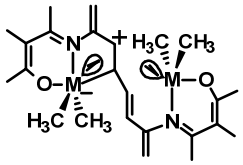
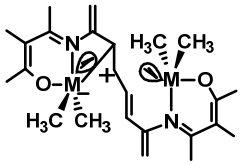
d^1, d^1					
					
$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$	$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$
3.90%	2.33%	1.94%	2.78%	0.66%	0.35%
					
$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$	$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$
2.52%	0.94%	0.76%	1.40%	0.62%	0.28%
					
$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$	$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$
1.39%	1.46%	0.88%	3.71%	2.02%	1.94%
					
$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$	$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$
2.42%	1.09%	1.02%	2.16%	1.11%	0.20%
					
$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$	$Ti_2^{H\prime}$	$Zr_2^{H\prime}$	$Hf_2^{H\prime}$
1.69%	1.26%	0.58%	1.78%	1.27%	0.18%

Table S3. Summary of resonance weight (%) for $\mathbf{M_2^{H\prime}}$ (model complexes of $\mathbf{M_2^{H}}$). The resonance weighting for (d^0, d^0):(d^1, d^1) metal centers increases from $\mathbf{Ti_2^{H\prime}}$ (1.31) to $\mathbf{Zr_2^{H\prime}}$ (1.74) to $\mathbf{Hf_2^{H\prime}}$ (1.84), thus implying that d^1 character decreases from $\mathbf{Ti_2^{H\prime}}$ to $\mathbf{Zr_2^{H\prime}}$ to $\mathbf{Hf_2^{H\prime}}$.

$Ti_2^{H\prime}$		$Zr_2^{H\prime}$		$Hf_2^{H\prime}$	
d^0, d^0	d^1, d^1	d^0, d^0	d^1, d^1	d^0, d^0	d^1, d^1
56.3	43.0	63.2	36.3	64.4	35.0

Table S4. MO composition (%; MO density map (isovalue = 0.03) shown for $\mathbf{Ti_2^H}$) for $\mathbf{M_2^H}$ complexes at B3LYP level using LanL2DZ basis set (metals) and 6-31G(d) basis set (non-metals).

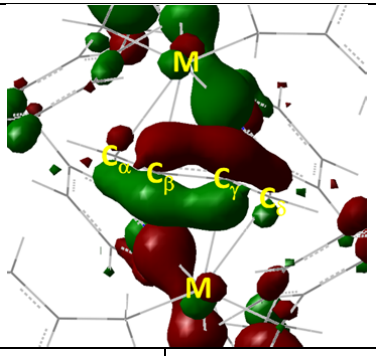
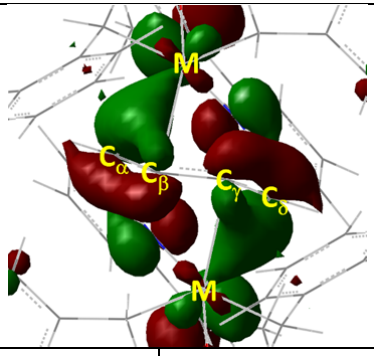
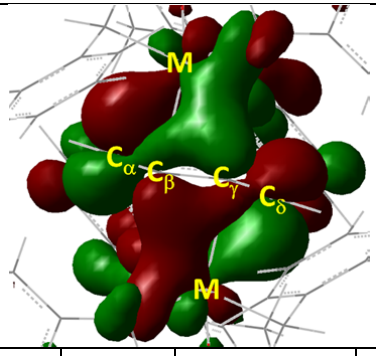
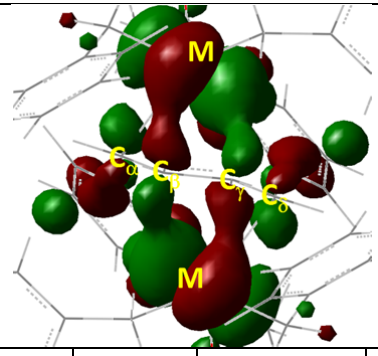
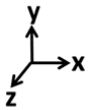
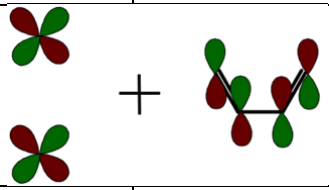
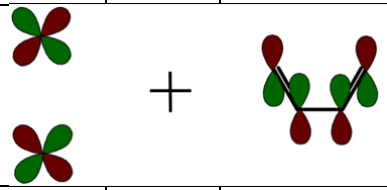
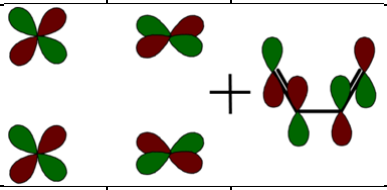
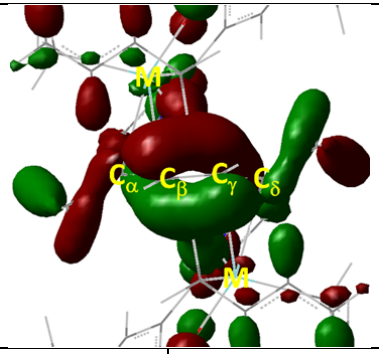
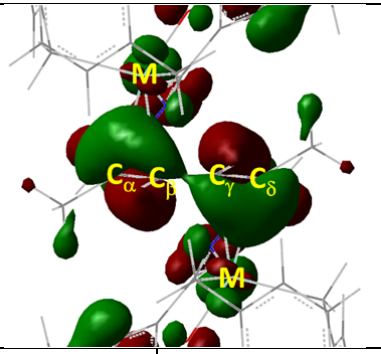
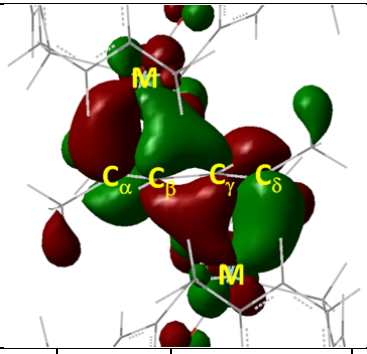
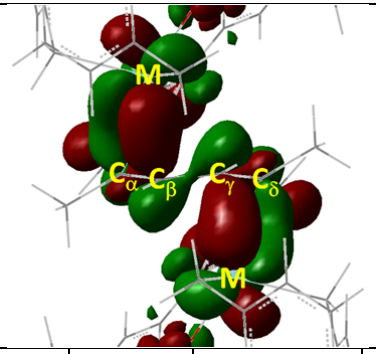
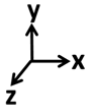
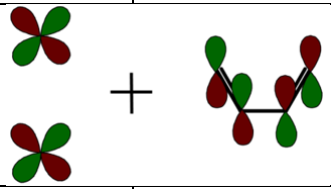
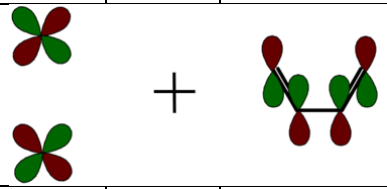
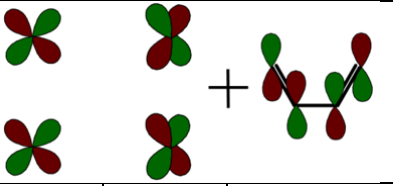
	HOMO–43		HOMO–13		HOMO				LUMO			
												
MO composition	d_{xy}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	d_{xy}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	d_{xy}^M	d_{xz}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	π_{py}^*	d_{xy}^M	d_{xz}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	π_{py}^*
												
$\mathbf{Ti_2^H}$	0.1	9.0	4.8	13.0	10.2	2.1	30.2	20.3	14.5	38.1	7.4	15.0
$\mathbf{Zr_2^H}$	0.1	26.8	4.8	17.6	8.2	2.6	31.8	21.8	6.0	12.5	17.3	28.3
$\mathbf{Hf_2^H}$	0.2	20.7	4.2	14.8	5.2	1.6	28.8	22.8	6.5	3.5	11.5	44.2

Table S5. MO composition (%; MO density map (isovalue = 0.03) shown for $\mathbf{Zr_2^{Me}}$) for $\mathbf{M_2^{Me}}$ complexes at B3LYP level using LanL2DZ basis set (metals) and 6-31G(d) basis set (non-metals).

	HOMO–46		HOMO–7		HOMO				LUMO			
												
MO composition	d_{xy}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	d_{xy}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	d_{xy}^M	d_{yz}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	π_{py}^*	d_{xy}^M	d_{yz}^M	$\pi_{C_\alpha C_\beta C_\gamma C_\delta}$	π_{py}^*
												
$\mathbf{Zr_2^{Me}}$	0.5	19.3	1.2	22.9	8.6	3.8	32.0	28.9	11.6	14.0	16.5	27.5
$\mathbf{Hf_2^{Me}}$	0.1	13.5	1.5	23.4	6.6	2.6	32.8	31.7	9.8	7.5	19.7	38.1

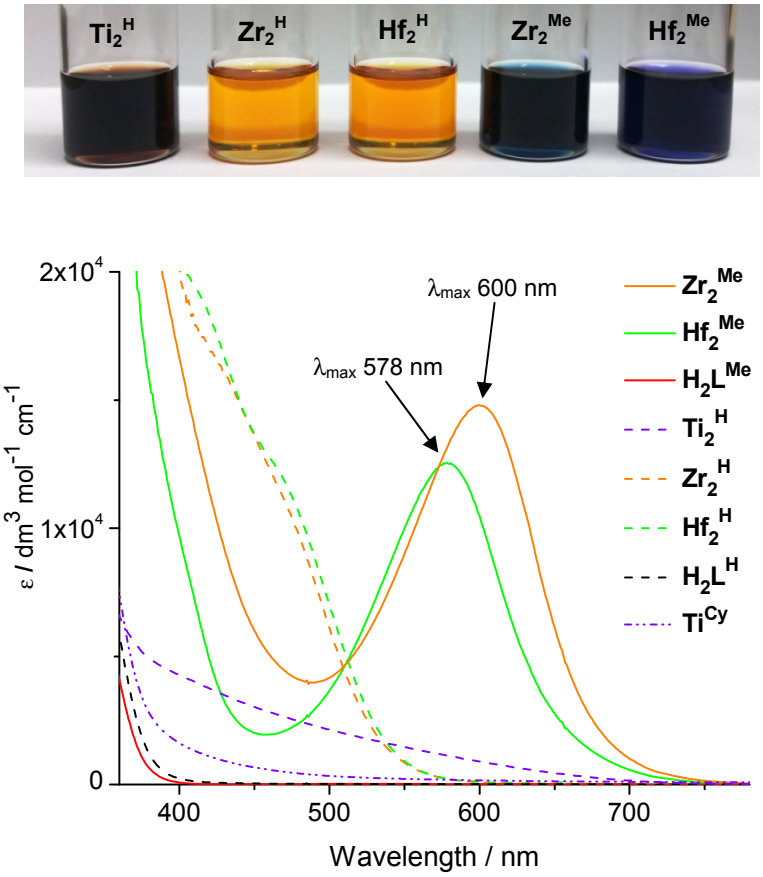
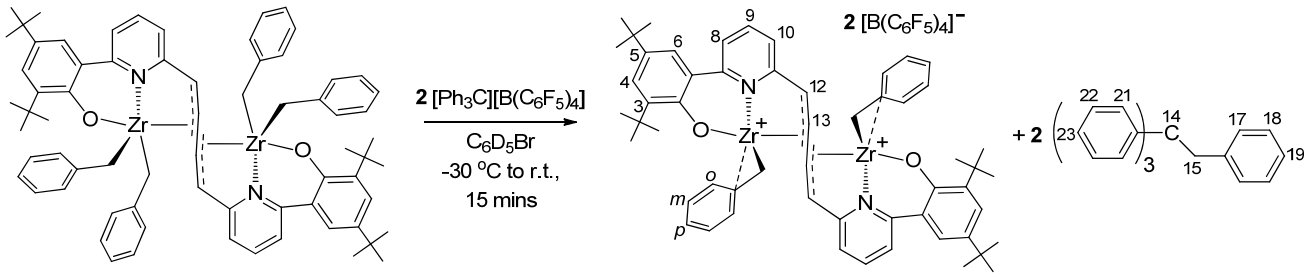


Figure S6. UV-vis absorption spectra of $\mathbf{M_2^R}$ (top: photograph showing solutions in toluene), H_2L^R and $\mathbf{Ti^{Cy}}$ (toluene, 298 K, N_2).

Reaction of Zr_2^H with Trityl Borate (NMR Reaction)



A solution of $[Ph_3C][B(C_6F_5)_4]$ (6.9 mg, 7.52 μmol) in C_6D_5Br (0.2 mL) was added to a J. Young NMR tube containing $\mathbf{Zr_2^H}$ (3.8 mg, 3.27 μmol) in C_6D_5Br (0.2 mL) at −30 °C. The tube was sealed and shaken vigorously, and the solution changed from orange to red-brown immediately and remained homogeneous. The resultant mixture was allowed to react for 15 mins at room temperature, then characterized by multinuclear NMR spectroscopy (Figure S7). ^{1}H NMR (400 MHz, C_6D_5Br): δ 1.50 (s, 18H, 5-*t*-Bu), 1.75 (s, 18H, 3-*t*-Bu), 2.76 (d, J = 9.0 Hz, 2H, CH_2), 2.80 (d, J = 9.0 Hz, 2H, CH_2), 4.05 (s, 4H, H^{15}), 4.72–4.83 (br, 2H, H^{12}), 5.49–5.59 (br, 2H, H^{13}), 6.10 (d, J = 8.0 Hz, 2H, H^{10}), 6.57–6.66 (br, 4H, *o*-Ph), 6.68 (t, J = 8.0 Hz, 2H, H^9), 6.85 (d, J = 7.6 Hz, 4H, H^{17}), 6.91–6.95 (m, 2H, H^{19}), 6.98–7.06 (br, 2H, *p*-Ph), 7.07–7.11 (m, 6H, H^8 and H^{18}), 7.15–7.17 (m, 2H, H^6), 7.20–7.36 (m, 22H, *m*-Ph, H^{22} and H^{23}), 7.40–7.42 (m, 12H, H^{21}), 7.82 (d, J = 1.6 Hz, 2H, H^4). ^{13}C NMR (101 MHz, C_6D_5Br): δ 30.4 (3-C*Me*$_3$), 31.3 (5-C*Me*$_3$), 34.7 (5-*C*Me$_3$), 35.4 (3-*C*Me$_3$), 46.5 (C^{15}), 72.1 (CH_2), 89.8 (C^{12}), 112.8 (C^{13}), 118.1 (C^8), 122.2 (C^{10}), 126.03 (C^6), 126.2 (C^{23}), 127.6 (C^{18}), 127.9 (C^{22}), 128.45 (C^4), 130.0 (C^{21}), 131.5 (C^{17}), 132.1 (C^{19}), 138.7 (C^9); 4º carbons: 58.8 (C^{14}), 121.0, 122.6, 122.8, 124.4, 125.0, 125.97, 128.0, 128.3, 128.51, 128.5, 136.7 (d, $J_{C,F}$ = 246.5 Hz, $B(C_6F_5)_4$), 137.3 (C^3), 138.6 (d, $J_{C,F}$ = 251.5 Hz, $B(C_6F_5)_4$), 139.5, 146.9, 147.9 (C^5), 148.8 (d, $J_{C,F}$ = 242.5 Hz, $B(C_6F_5)_4$). ^{19}F NMR (376 MHz, C_6D_5Br): δ −131.3, −161.2, −165.2.

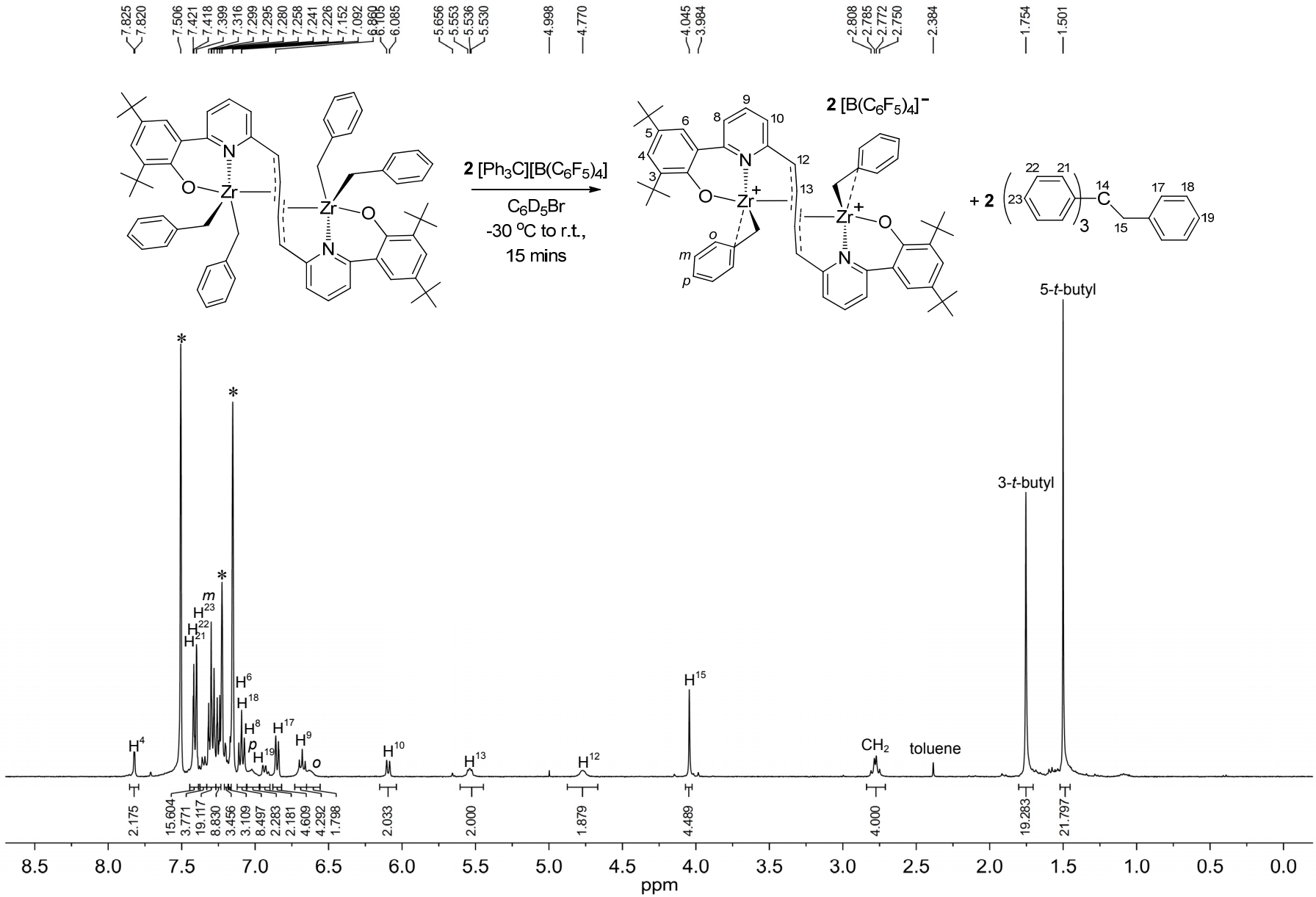


Figure S7. ^{1}H NMR spectrum (400 MHz, C_6D_5Br,* 295 K) for dication derived from reaction of $\mathbf{Zr_2^H}$ with 2 equiv. of trityl borate.

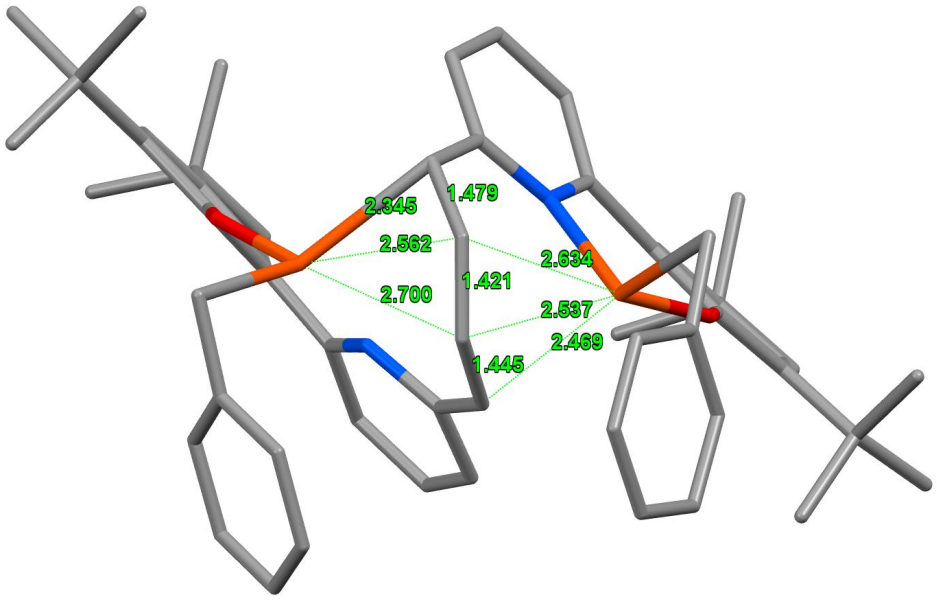


Figure S8. Energy-minimized calculated (Gaussian) structure of dication derived from $\mathbf{Zr_2^H}$, after benzyl abstraction from each Zr center [Zr: orange; N: blue; O: red]. Compared with the molecular structure of $\mathbf{Zr_2^H}$, structural changes include the hapticity of the μ-C_4H_4 moiety (Zr–C_α coordination is significantly stronger) and slight contraction of the Zr···Zr distance (4.517 Å).

ESI References

1 A. D. Beck, *J. Chem. Phys*., 1993, **98**, 5648.

2 (*a*) P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 270; (*b*) P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 284; (*c*) P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 299.

3 *Gaussian 09, Revision B.1*, M. J. Frisch et al., Gaussian, Inc., Wallingford, CT, USA, 2009.

4 *NBO 5.9*. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales and F. Weinhold, (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2009; http://www.chem.wisc.edu/~nbo5)

5 L.-C. So, C.-C. Liu, M. C. W. Chan, J. C. Y. Lo, K.-H. Sze and N. Zhu, *Chem. Eur. J*., 2012, **18**, 565.

6 R. C. Klet, D. G. VanderVelde, J. A. Labinger and J. E. Bercaw, *Chem. Commun*., 2012, **48**, 6657.

7 D. M. Kang, J.-W. Kang, J. W. Park, S. O. Jung, S.-H. Lee, H.-D. Park, Y.-H. Kim, S. C. Shin, J.-J. Kim and S.-K. Kwon, *Adv. Mater*., 2008, **20**, 2003.