Supplementary Information

Synthesis of titanium and zirconium complexes supported by a *p*-terphenoxide ligand and their reactions with N_2, CO_2 and CS_2

Takashi Kurogi, Yutaka Ishida and Hiroyuki Kawaguchi*

Department of Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152-8551, Japan
E-mail: hkawa@chem.titech.ac.jp

Contents

Experimental Section

General procedure

All manipulations were carried out using standard Schlenk techniques or in a glove-box under an atmosphere of dinitrogen or argon. Anhydrous hexane, pentane and toluene were dried by passage through two columns of activated alumina and a Q-5 column, while anhydrous THF, Et_2O and DME were dried by passage through two columns of activated alumina. Anhydrous benzene and deuterated benzene (benzene-d_6) were dried and degassed over a potassium mirror prior to use. Deuterated THF (THF-d_8) and deuterated chloroform (chloroform-d_1) were distilled from calcium hydride prior to use. Labeled $^{15}N_2$ and $^{13}CO_2$ (Cambridge Isotopes) were used as received. Me_2[OO], H_2[OO] and $TiCl_3(THF)_3$ were prepared by the literature procedure.[1, 2] ^1H and ^{13}C NMR spectra were recorded on JEOL ECX-400 and ECX-500 spectrometer. All spectra were referenced to residual protiosolvent (^1H, C_6D_5H in C_6D_6, ^1H (δ) = 7.15; C_4D_7HO in THF-d_8, ^1H (δ) = 1.73, 3.58; $CHCl_3$ in $CDCl_3$, ^1H (δ) = 7.24), solvent (^{13}C) or nitromethane (^{15}N) resonances. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Raman spectra were obtained on a JASCO NRS-2100 with an excitation wavelength of 514.5 nm. UV-visible spectra were obtained on a JASCO V-560 spectrometer at room temperature. Elemental analyses (C, H and N) were carried out on an Elementar VarioMicroCube. Solid-state magnetic susceptibilities were measured on a Sherwood Scientific MSB-AUTO at ambient temperature. Corrections were applied for diamagnetism calculated for Pascal constants.

Synthesis of Me_2[OO]

To a DMF (200 mL) solution of 1,4-benzene-diboronic acid (5.34 g, 32.2 mmol) and 2-bromo-4-methyl-6-*tert*-butyl-anisol (19.3 g, 75.0 mmol) was added $Pd(PPh_3)_4$ (650 mg, 562 μmol) and K_2CO_3 (20.5 g, 148 mmol) in H_2O (15 mL). The reaction mixture was heated to 100 °C. After stirring for 20 h, water (300 mL) was added to precipitate a white solid. The precipitate was collected by filtration. Purification by column chromatography (silica; heptane/CH_2Cl_2, 7:3) afforded a white solid of Me_2[OO] (10.8 g, 25.1 mmol, 78%).

^{1}H NMR (500 MHz, chloroform-d_1): δ 1.42 (s, 18H, ^{t}Bu), 2.33 (s, 6H, Me), 3.29 (s, 6H, OMe), 7.04 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.10 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.58 (s, 4H, C_6H_4). ^{13}C NMR (125 MHz, chloroform-d_1): δ 21.2 (*p*Me), 31.0 (C*Me*$_3$), 35.2 (*C*Me$_3$), 60.4 (OMe), 127.0, 129.1 (ArO), 130.2 (*C*$_6$H$_4$), 132.3, 134.9 (ArO), 138.7 (*C*$_6$H$_4$), 142.8, 155.4 (ArO). Anal. Calcd for $C_{30}H_{38}O_2$: C, 83.67; H, 8.89. Found: C, 83.67; H, 8.95.

Synthesis of H$_2$[OO]

A solution of BBr_3 (1.0M in CH_2Cl_2, 15 mL, 15 mmol) was added to Me$_2$[OO] (2.37 g, 5.50 mmol) in CH_2Cl_2 (50 mL) at 0 °C. After stirring for 24 h at room temperature, the reaction mixture was then quenched with 5% aqueous HCl and extracted with CH_2Cl_2 (3 x 50 mL). The organic fraction was washed with brine and dried over $MgSO_4$. Volatile materials were removed via rotary evaporation. The residue was washed with hexane and dried to give H$_2$[OO] as a white powder (1.67 g, 4.15 mmol, 76%).

^{1}H NMR (500 MHz, chloroform-d_1): δ 1.43 (s, 18H, ^{t}Bu), 2.31 (s, 6H, Me), 5.25 (s, 2H, OH), 6.92 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.12 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.55 (s, 4H, C_6H_4). ^{13}C NMR (125 MHz, chloroform-d_1): δ 20.9 (*p*Me), 29.8 (C*Me*$_3$), 35.0 (*C*Me$_3$), 127.7, 128.1, 128.4, 129.1 (ArO), 130.6 (*C*$_6$H$_4$), 136.3 (ArO), 137.2 (*C*$_6$H$_4$), 148.9 (ArO). IR (cm^{-1}; KBr): 522 (m), 575 (m), 775 (s), 841 (s), 870 (w), 931 (w), 1023 (m), 1085 (s), 1162 (s), 1193 (s), 1126 (s), 1252 (m), 1273 (m), 1329 (s), 1361 (m), 1391 (m), 1468 (s), 1515 (m), 1602 (w), 2959 (s), 3547 (s). Anal. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.29; H, 8.72.

Synthesis of Li$_2$[OO]

Addition of ^{n}BuLi (1.59 M in hexane, 1.10 mL, 1.75 mmol) to a solution of H$_2$[OO] (319 mg, 729 μmol) in Et_2O (20 mL) at 0 °C gave a white suspension. After stirring for 30 min at room temperature, the reaction mixture was evaporated to dryness and washed with Et_2O to give Li$_2$[OO]·3Et$_2$O as a white powder (393 mg, 617 μmol, 85%).

^{1}H NMR (400 MHz, benzene-d_6): δ 0.76 (t, $^3J_{HH}$ = 7 Hz, 18H, Et_2O), 1.69 (s, 18H, ^{t}Bu), 2.36 (s, 6H, Me), 2.93 (q, $^3J_{HH}$ = 2 Hz, 12H, Et_2O), 7.24 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.29 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 8.15 (s, 4H, C_6H_4). ^{13}C NMR (100 MHz, benzene-d_6): 14.1 (Et_2O), 21.0

(*p*Me), 31.2 (C*Me*$_3$), 35.0 (*C*Me$_3$), 65.5 (Et$_2$O), 127.8, 127.9, 128.9 (ArO), 129.4 (*C*$_6$H$_4$), 132.1, 136.8 (ArO), 139.2 (*C*$_6$H$_4$), 158.6 (ArO). ^{7}Li NMR (152 MHz, benzene-*d*$_6$): 3.64. Anal. Calcd for $C_{40}H_{62}O_5Li_2$: C, 75.44; H, 9.81. Found: C, 75.75; H, 9.46.

Synthesis of [OO]TiCl(DME) (1)

To a suspension of $TiCl_3(THF)_3$ (436 mg, 1.18 mmol) in THF (15 mL) was added $Li_2[OO]\cdot 3Et_2O$ (750 mg, 1.18 mmol) in THF (10 mL) at –35 °C. The mixture was stirred for 3 h at room temperature, during which time a color of the solution changed from blue to green. The reaction mixture was evaporated to dryness and extracted with toluene (10 mL). After centrifugation to remove insoluble materials, the green supernatant was evaporated to dryness. The residue was dissolved in DME (3 mL) and stored at room temperature, yielding **5** as pale red crystals (368 mg, 641 μmol, 54%).

IR (cm^{-1}; KBr): 566 (s), 619 (m), 644 (m), 771 (m), 838 (s), 857 (s), 933 (m), 980 (m), 1008 (m), 1032 (s), 1074 (s), 1187 (s), 1208 (s), 1241 (s), 1290 (m), 1322 (m), 1354 (m), 1384 (m), 1407 (s), 1509 (m), 1610 (w), 2947 (s). Anal. Calcd for $C_{32}H_{42}O_4ClTi$: C, 66.96; H, 7.38. Found: C, 66.68; H, 7.70. $\mu_{eff} = 1.71\ \mu_B$.

Synthesis of [(OO)Ti(DME)]$_2$(μ-N$_2$) (2)

To a suspension of **1** (105 mg, 183 μmol) in toluene (20 mL) was added KC_8 (30.0 mg, 222 μmol) in toluene (5 mL) at –30 °C under N_2. The mixture was allowed to warm to room temperature and stirred for 18 h, during which time a color of the solution changed from pale red to dark yellow. The reaction mixture was centrifuged to remove insoluble materials, giving a dark yellow supernatant. After removal of all volatiles, the residue was washed with hexane to give **2** as dark yellow powder (44.8 mg, 40.5 μmol, 44%).

^{1}H NMR (500 MHz, benzene-*d*$_6$): *δ* 1.72 (s, 36H, ^{t}Bu), 2.39 (s, 12H, Me), 2.57 (br, 6H, DME), 2.67 (br, 4H, DME), 2.94 (br, 4H, DME), 3.11 (br, 6H, DME), 7.02 (s, 4H, *m*H), 7.15 (s, overlapped, *m*H and benzene-*d*$_6$), 7.33 (br, 4H, C$_6$H$_4$), 7.49 (br, 4H, C$_6$H$_4$). ^{13}C NMR (125 MHz, benzene-*d*$_6$): *δ* 21.1 (*p*Me), 30.3 (C*Me*$_3$), 35.4 (*C*Me$_3$), 58.6, 67.9, 68.2, 72.0 (DME), 125.9, 127.6, 127.8 (ArO), 128.0 (*C*$_6$H$_4$), 131.0 (ArO), 132.9 (*C*$_6$H$_4$), 135.3, 164.9 (ArO). IR (cm^{-1}; KBr): 570 (s br), 769 (m), 832 (s br), 863 (s), 933 (m), 1054 (m), 1083 (m), 1185 (s), 1244 (s br), 1318 (w), 1358 (m), 1388 (m), 1413 (s br), 1510 (w), 1602 (w), 2952 (s). IR (cm^{-1}; benzene): 566 (w), 846 (m br), 1249 (s), 1409 (m), 2954 (s). Raman (cm^{-1}): 1394 ($\nu_{N\text{-}N}$). Anal. Calcd for $C_{64}H_{84}N_2O_8Ti_2$: C, 69.56; H, 7.66; N, 2.53. found: C, 70.15 H, 7.73; N, 0.51. The amount of nitrogen present in **2** was not determined by elemental analysis.

Synthesis of [(OO)Ti(py)$_2$]$_2$(μ-N$_2$) (3)

To a toleuene (5 mL) solution of **2** (40.0 mg) was added pyridine (1 mL). A color of the solution changed from dark yellow to purple. The mixture was evaporated to dryness to afford **3** as a purple solid quantitatively.

^{1}H NMR (500 MHz, benzene-*d*$_6$): δ 1.43 (s, 36H, ^{t}Bu), 2.29 (s, 12H, Me), 6.27 (s, 8H, C_6H_4), 6.51 (t, $^3J_{HH}$ = 2 Hz, 8H, py), 6.85 (t, $^3J_{HH}$ = 2 Hz, 4H, py), 7.19 (d, $^4J_{HH}$ = 7 Hz, 4H, *m*H), 7.42 (d, $^4J_{HH}$ = 7 Hz, 4H, *m*H), 9.09 (d, $^3J_{HH}$ = 7 Hz, 8H, py). ^{13}C NMR (125 MHz, benzene-*d*$_6$): δ 21.0 (*p*Me), 30.3 (C*Me*$_3$), 35.8 (*C*Me$_3$), 123.6 (py), 125.4, 128.0 (ArO), 129.7 (C_6H$_4$), 134.7 (ArO), 136.4 (py), 138.1, 138.7 (ArO), 138.9 (C_6H$_4$), 150.8 (py), 160.6 (ArO). Raman (cm^{-1}): 1362 ($\nu_{N\text{-}N}$). Anal. Calcd for $C_{64}H_{84}N_6O_8Ti_2$: C, 73.54; H, 6.82; N, 6.77. Found: C, 72.47; H, 6.96; N, 4.37. The amount of nitrogen present in **3** did not agree to the calculated value and it agreed to the amount of pyridine.

Synthesis of [(OO)Ti(L)]$_2$(μ-^{15}N$_2$) (L = DME, 2-^{15}N$_2$; py, 3-^{15}N$_2$)

To a mixture of **1** (500 mg, 873 μmol) and KC_8 (120 mg, 887 μmol) was added toluene (30 mL) *via* vacuum transfer at -196 °C. The reaction mixture was allowed to slowly warm to room temperature under an atmosphere of $^{15}N_2$. After stirring for 24 h at room temperature, insoluble materials were removed by centrifugation. The dark yellow supernatant was evaporated to dryness. The residue was washed with hexane to give **2-^{15}N$_2$** as a dark yellow powder (248 mg, 224 μmol, 51%).

Addition of pyridine (1 mL) to **2-^{15}N$_2$** in toluene (5 mL) followed by evaporation to dryness afforded **3-^{15}N$_2$**.

2-^{15}N$_2$: ^{15}N NMR (50 MHz, C_6D_6): δ 114.7 (μ-$^{15}N_2$). Raman (cm^{-1}): 1352 ($\nu_{N\text{-}N}$)

3-^{15}N$_2$: ^{15}N NMR (50 MHz, C_6D_6): δ 178.1 (μ-$^{15}N_2$). Raman (cm^{-1}): 1320 ($\nu_{N\text{-}N}$).

Synthesis of [OO]Zr(CH_2Ph)$_2$ (4)

To a solution of Zr(CH_2Ph)$_4$ (803 mg, 1.76 mmol) in toluene (10 mL) was added H_2[OO] (715 mg, 1.78 mmol) at room temperature. The mixture was stirred for 1 h at room temperature to give a yellow suspension. After removal of volatiles under vacuum, the residue was washed with hexane to give **4** as a yellow powder (850 mg, 1.26 mmol, 72%).

^{1}H NMR (500 MHz, benzene-*d*$_6$): δ 1.81 (s, 18H, ^{t}Bu), 2.26 (s, 6H, Me), 3.30 (s, 4H, CH_2), 6.56 (s, 4H, C_6H_4), 6.65 (t, $^3J_{HH}$ = 8 Hz, 2H, Bn), 6.71 (t, $^3J_{HH}$ = 8 Hz, 4H, Bn), 7.05 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.18 (d, $^3J_{HH}$ = 8 Hz, 4H, Bn). ^{13}C NMR (125 MHz, benzene-*d*$_6$): δ 20.9 (*p*Me), 31.3 (C*Me*$_3$), 35.2 (*C*Me$_3$), 69.1 (CH_2, $^1J_{CH}$ = 135 Hz), 124.3 (ArO), 124.4 (*p*-Bn), 128.1 (ArO), 128.5 (*m*-Bn), 129.0 (*C*$_6$H$_4$), 129.2 (*o*-Bn), 131.4 (*ipso*-Bn), 134.9, 136.0, 137.0 (ArO), 139.4 (*C*$_6$H$_4$), 156.9 (ArO). Anal. Calcd for $C_{42}H_{46}O_2Zr$: C, 74.84; H, 6.88. Found: C, 74.44; H, 6.88.

Synthesis of [OO]ZrCl$_2$(THF) (5)

To a solution of **4** (500 mg, 742 μmol) in THF (10 mL) was added NEt_3HCl (208 mg, 1.51 mmol) in THF (30 mL) at room temperature. After stirring for 1 h at room temperature, a color of the reaction mixture changed from yellow to colorless. After removal of volatiles under vacuum, the residue was extracted with toluene and centrifuged to remove insoluble materials. The colorless supernatant was evaporated to dryness. The resulting solid was washed with hexane to give **9** as a white powder (399 mg, 629 mmol, 85%).

^{1}H NMR (500 MHz, chloroform-*d*$_1$): δ 1.49 (s, 18H, ^{t}Bu), 1.84 (m, 4H, THF), 2.39 (s, 6H, Me), 3.74 (m, 4H, THF), 7.14 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.22 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.49 (s, 2H, C_6H_4), 7.70 (s, 2H, C_6H_4). ^{13}C NMR (125 MHz, chloroform-*d*$_1$): δ 21.2 (*p*Me), 30.3 (C*Me*$_3$), 35.1 (*C*Me$_3$), 41.7, 73.2 (THF), 124.4, 127.7, 130.3 (ArO), 130.4, 132.2 (*C*$_6$H$_4$), 133.7, 138.3 (ArO), 139.6 (*C*$_6$H$_4$), 156.4 (ArO). IR (cm^{-1}; KBr): 563 (s), 620 (m), 643 (m), 732 (m), 768 (m), 839 (s), 934 (s), 1008 (s), 1083 (s), 1186 (s), 1228 (s br), 1323 (m), 1361 (m), 1389 (m), 1409 (s), 1460 (s), 1507 (w), 1607 (w), 2957 (s). Anal. Calcd for $C_{32}H_{40}O_3Cl_2Zr$: C, 60.55; H, 6.35. Found: C, 60.32; H, 6.75.

Synthesis of $[OO]Zr(THF)_3$ (6)

To a suspension of **5** (300 mg, 473 μmol) in THF (15 mL) was added KC_8 (130 mg, 962 μmol) in THF (5 mL) at -35 °C. The reaction mixture was allowed to warm to room temperature, and a color of the solution changed from colorless to dark green. After stirring for 1 h at room temperature, the solution was centrifuged to remove insoluble materials. The dark green supernatant was concentrated to ca. 1 mL and layered with hexane (3 mL) to give **6** as green crystals (168 mg, 237 μmol, 50%).

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ 1.32 (s, 18H, ^{t}Bu), 1.78 (m, 12H, THF), 2.11 (s, 6H, Me), 3.62 (m, 12H, THF), 5.61 (s, 4H, C_6H_4), 6.55 (s, 2H, *m*H), 6.56 (s, 2H, *m*H). ^{13}C NMR (100 MHz, THF-d_8, 298K): δ 20.3 (*p*Me), 25.4 (THF), 29.7 (C*Me*$_3$), 35.1 (*C*Me$_3$), 67.3 (THF), 105.3 (*C*$_6$H$_4$), 122.0 (*C*$_6$H$_4$, $^1J_{CH}$ = 162 Hz), 123.3, 124.0, 124.3, 133.6, 141.7, 162.6 (ArO). UV-Vis (λ_{max}, nm (ε, M^{-1}cm^{-1}), THF), 659 (343). Anal. Calcd for $C_{40}H_{56}O_5Zr$: C, 67.85; H, 7.97. Found: C, 67.83; H, 8.08.

^{1}H NMR (500 MHz, THF-d_8, 193 K): δ 1.32 (s, 18H, ^{t}Bu), 1.78 (m, 12H, THF), 2.11 (s, 6H, Me), 3.62 (m, 12H, THF), 5.61 (br, $\Delta\nu_{1/2}$ = 60 Hz, 4H, C_6H_4), 6.55 (s, 2H, *m*H), 6.56 (s, 2H, *m*H).

Synthesis of $[OO]_2[(C_6H_3)(ArO)_2]_2Zr_4(\mu\text{-}H)_2(THF)_2$ (7)

Complex **6** (115 mg, 162 μmol) was dissolved in toluene (5 mL). A color of the solution changed from green to brown. After stirring for 15 min at room temperature, the reaction mixture was evaporated to dryness to yield **7** (83.2 mg, 39.4 μmol, 98%) as a brown solid.

^{1}H NMR (500 MHz, benzene-d_6): δ 1.16 (br, 8H, THF), 1.51 (s, 18H, ^{t}Bu), 1.52 (s, 18H, ^{t}Bu), 1.62 (s, 18H, ^{t}Bu), 1.93 (s, 18H, ^{t}Bu), 2.26 (s, 6H, Me), 2.30 (s, 6H, Me), 2.31 (s, 6H, Me), 2.48 (s, 6H, Me), 3.56 (br, 8H, THF), 5.59 (d, $^3J_{HH}$ = 12 Hz, 2H, C_6H_3), 5.75 (d, $^3J_{HH}$ = 12 Hz, 2H, C_6H_3), 6.86 (d, $^3J_{HH}$ = 12 Hz, 2H, ZrH), 6.90 (d, $^3J_{HH}$ = 2 Hz, 2H, *m*H), 6.94 (d, $^4J_{HH}$ = 2 Hz, 4H, *m*H), 6.97 (d, $^3J_{HH}$ = 12 Hz, 2H, C_6H_3), 7.12 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.15

(overlapped, C_6H_4 and benzene-d_6), 7.22 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.24 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.30 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.35 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.39 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 2H, C_6H_4), 7.42 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 7.78 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 2H, C_6H_4), 7.99 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 2H, C_6H_4). ^{13}C NMR (125 MHz, thf-d_8): δ 21.1, 21.2, 21.3, 21.4 (*p*Me), 25.2 (THF), 30.2, 30.4, 30.6, 32.0 (C*Me*$_3$), 34.8, 35.1, 35.2, 35.9 (C*Me*$_3$), 71.6 (THF), 103.0 (C_6H_3), 122.9, 123.0 (ArO), 124.3 (C_6H_4), 124.7, 125.8 (ArO), 126.5 (C_6H_3), 126.8, 127.2, 127.4, 127.6, 128.0, 128.4, 128.6, 128.7, 129.2 (ArO), 129.3 (C_6H_4), 129.8 (ArO), 131.9 (C_6H_3), 132.3 (C_6H_4), 133.8, 133.9, 134.2 (ArO), 136.3 (C_6H_4), 136.8, 136.9, 137.9 (ArO), 138.2 (C_6H_3), 141.7, 143.3 (C_6H_4), 152.0, 158.5, 159.1, 163.4 (ArO), 171.8, 202.7 (C_6H_3). Selected HH COSY NMR chemical shifts (500 MHz, benzene-d_6): δ ^{1}H (δ ^{1}H) 5.59 (6.86), 5.75 (6.97). Selected ^{1}H–^{13}C HMQC NMR chemical shifts (500 MHz, benzene-d_6): δ ^{1}H (δ ^{13}C) 5.59 (103.0), 5.75 (171.7), 6.97 (131.9). Anal. Calcd for $C_{120}H_{144}O_{10}Zr_4$: C, 68.26; H, 6.87. Found: C, 68.40; H, 7.14.

Synthesis of $[(OO)_2(CO_2)]Zr_2(THF)_4$ (8)

A 50 mL flask was charged with **6** (80.0 mg, 113 μmol) and THF (20 mL). The headspace was evacuated, and an atmosphere of CO_2 (1 atm) was introduced. A color of the solution changed from green to yellow. After stirring for 30 min at room temperature, the reaction mixture was evaporated to dryness. The residue was washed with pentane to give **8** as yellow powder (63.2 mg, 48.0 μmol, 85%).

^{1}H NMR (500 MHz, THF-d_8): δ 1.23 (s, 18H, ^{t}Bu), 1.62 (s, 18H, ^{t}Bu), 1.78 (br, 16H, THF), 2.14 (s, 6H, Me), 2.29 (s, 6H, Me), 3.62 (br, 16H, THF), 4.12 (s, 2H, C_6H_4), 4.62 (d, $^3J_{HH}$ = 6 Hz, 2H, C_6H_4), 5.62 (s, 2H, C_6H_4), 5.86 (d, $^3J_{HH}$ = 6 Hz, 2H, C_6H_4), 6.58 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H), 6.73 (d, $^4J_{HH}$ = 2 Hz, 4H, *m*H), 6.75 (d, $^4J_{HH}$ = 2 Hz, 2H, *m*H). ^{13}C NMR (125 MHz, THF-d_8): δ 20.01, 20.2 (*p*Me), 25.4 (THF), 29.5, 29.8 (C*Me*$_3$), 34.2, 34.3 (*C*Me$_3$), 53.0 (C_6H_4), 67.3 (THF), 91.2, 121.4 (C_6H_4), 122.9, 123.6, 124.4, 124.5, 124.8, 125.6 (ArO), 129.5, 133.6 (C_6H_4), 134.3, 134.6 (ArO), 135.4 (C_6H_4), 135.6, 136.0, 163.1, 163.3 (ArO). Selected ^{1}H–^{13}C HMQC NMR chemical shifts (500 MHz, THF-d_8): δ ^{1}H (δ ^{13}C) 4.12 (53.0), 4.62 (91.2), 5.62 (129.5), 5.86 (133.6). Anal. Calcd for $C_{73}H_{96}O_{10}Zr_2$: C, 66.63; H, 7.35. Found: C, 66.56; H, 7.67.

NMR experiment for the reaction of 6 with $^{13}CO_2$

A J. Young valve NMR tube was charged with **6** (10.0 mg, 14.1 μmol) and THF-d_8 (0.5 mL). The headspace was evacuated, and an atmosphere of $^{13}CO_2$ (1 atm) was introduced. The mixture was stored at room temperature for 30 min. The ^{1}H NMR spectrum indicated that the reaction afforded **8-^{13}C** quantitatively.

^{13}C NMR (125 MHz, THF-d_8): δ 173.0 ($[C_6H_4]_2CO_2$).

Synthesis of $[(OO)Zr(THF)]_2(C_2S_4)$ (9)

To a solution of **6** (30.0 mg, 42.4 μmol) in THF (5 mL) was added CS_2 (10.0 μL, 165 μmol) at room temperature. A color of the solution changed from green to yellowish orange. After stirring for 30 min at room temperature, the reaction mixture was evaporated to dryness. The residue was washed with hexane to give a pale orange powder of **9** (20.1 mg, 15.7 μmol, 74%). The pale orange powder was dissolved in benzene (2 mL) and stored at room temperature, yielding **9**·2benzene as green crystals.

^{1}H NMR (500 MHz, benzene-d_6): δ 1.23 (br, 8H, THF), 1.40 (s, 36H, ^{t}Bu), 2.31 (s, 12H, Me), 3.73 (br, 8H, THF), 6.94 (d, $^4J_{HH}$ = 2 Hz, 4H, *m*H), 7.17 (d, $^4J_{HH}$ = 2 Hz, 4H, *m*H), 7.25 (s, 4H, C_6H_4), 8.42 (s, 4H, C_6H_4). Anal. Calcd for $C_{78}H_{92}O_6S_4Zr_2$: C, 65.23; H, 6.46. Found: C, 65.09; H, 6.60. Solubility constraints prevent us from aquiring the ^{13}C NMR spectrum of **9**.

X-ray Crystallography

Crystallographic data for are summarized Table S1. Single crystals of **1**, **3**, **4**, **5**, **6**, **7**, **8** and **9** were obtained from DME, toluene/hexane, toluene/hexane, chloroform, THF/hexane, toluene/pentane, THF/hexane and toluene/pentane respectively. Crystals of these complexes immersed in mineral oil on nylon loop and transferred to a Rigaku Saturn CCD system for **1**, **2**, **3**, **6**, **7**, **8** and **9**, and to a Rigaku Mercury CCD system for **4** and **5** equipped with a Rigaku

GNNP low-temperature device. Data were collected under cold nitrogen stream (123 K) using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). Equivalent reflections were merged, and the images were processed with the CrystalClear (Rigaku) Program. Corrections for Lorentz-polarization effects and absorption were performed.

All calculations were performed using SHELXS[3] and SHELXL[4]. The structures were solved by Patterson and Fourier transform methods. For **1**, two crystallograhically independent, but chemically equivalent molecules are present in the asymmetric unit. For **7**, the methylene groups of the THF molecule were disordered over two positions. Three sites occupied by THF were identified in the asymmetric unit. Two of these sites were fully occupied by two THF molecules. The other site contains considerably disordered THF molecules and were treated by SQUEEZE as a diffuse contribution.[5,6] In the void space, a contribution of 53 e^- per unit cell was found and taken to represent 0.5 THF molecules for each Zr_2 complex, giving a total of 2.5 THF in the asymmetric unit. For **9**, the methylene groups of the THF molecule and the toluene molecule were disordered over two positions. The disordered toluene molecule was fixed with a rigid group model. All non-hydrogen atoms are refined anisotropically, with exception of disordered atoms, which were refined isotropically. All carbon-bound hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. In the case of **7**, the positions of metal-bound hydride and the protons of C_6H_3 unit were found in the Fourier map.

These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disordered groups and crystal solvents. The large values of the second parameter on the SHELXL weighting are due to the poor quality of crystals.

References

(1) M. M. Gruza, J.-C. Chambron, E. Espinosa and E. Aubert, *Eur. J. Org. Chem.* 2009, 6318-6327.

(2) N. A. Jones, S. T. Liddle, C. Wilson and P. L. Arnold, *Organometallics* 2007, **26**, 755-757.

(3) SHELXS-97, G. M. Sheldrick, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany (1997).

(4) SHELXL-97, G. M. Sheldrick, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany (1997).

(5) A. L. Spek, *Acta Cryst.* 2009, **D65**, 148-155.

(6) P. van der Sluis, A. L. Spek, *Acta Cryst.* 1990, **A46**, 194-201.

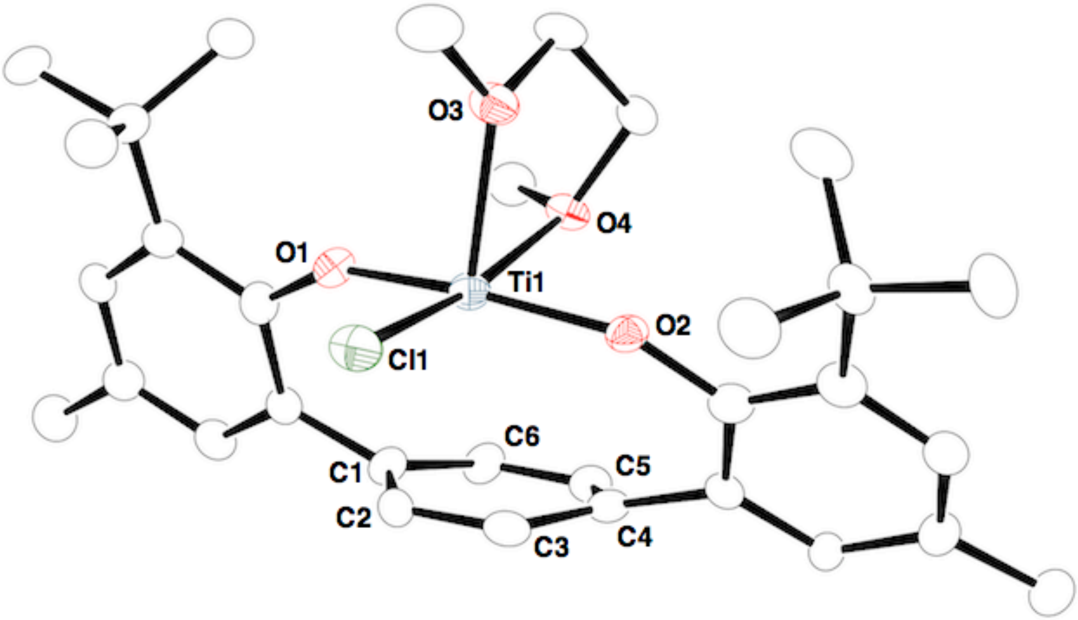

Fig. S1 Molecular structure of **1**. One of two independent molecules in the asymmetric unit is shown. Hydrogen atoms have been omitted for clarity.

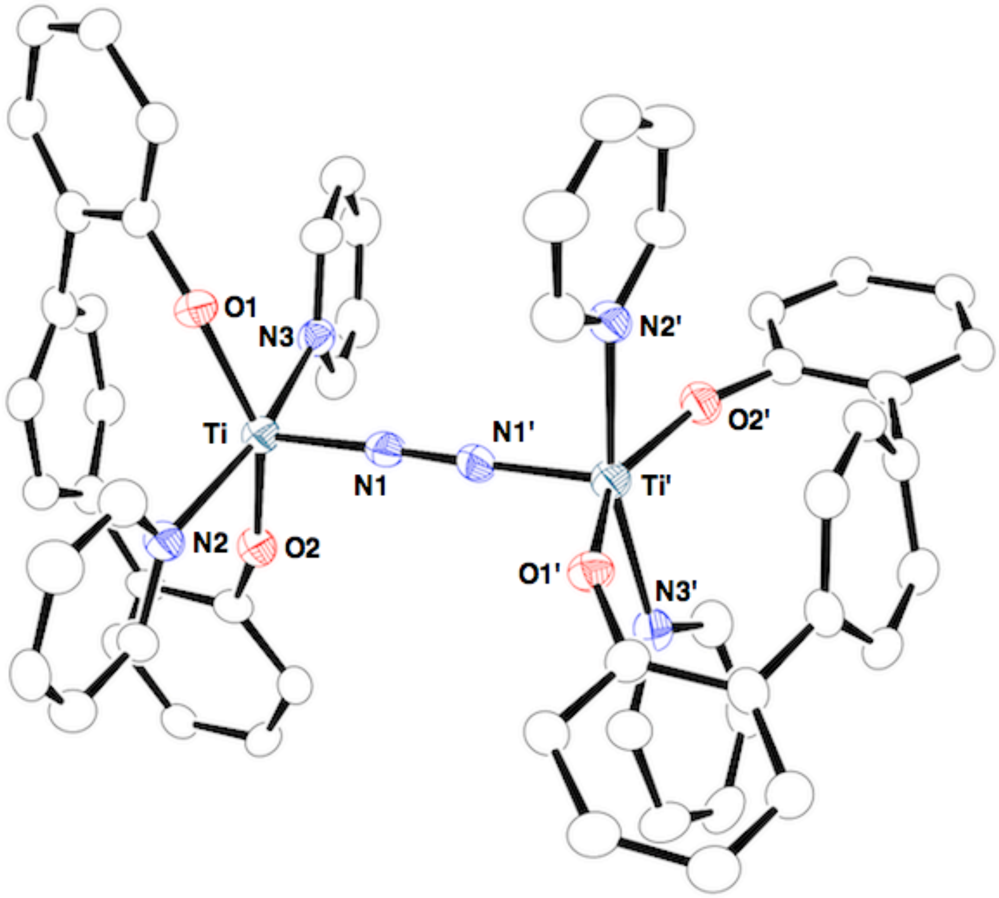

Fig. S2 Molecular structure of **3**. Carbon atoms of *tert*-butyl/methyl substituents and hydrogen atoms have been omitted for clarity.

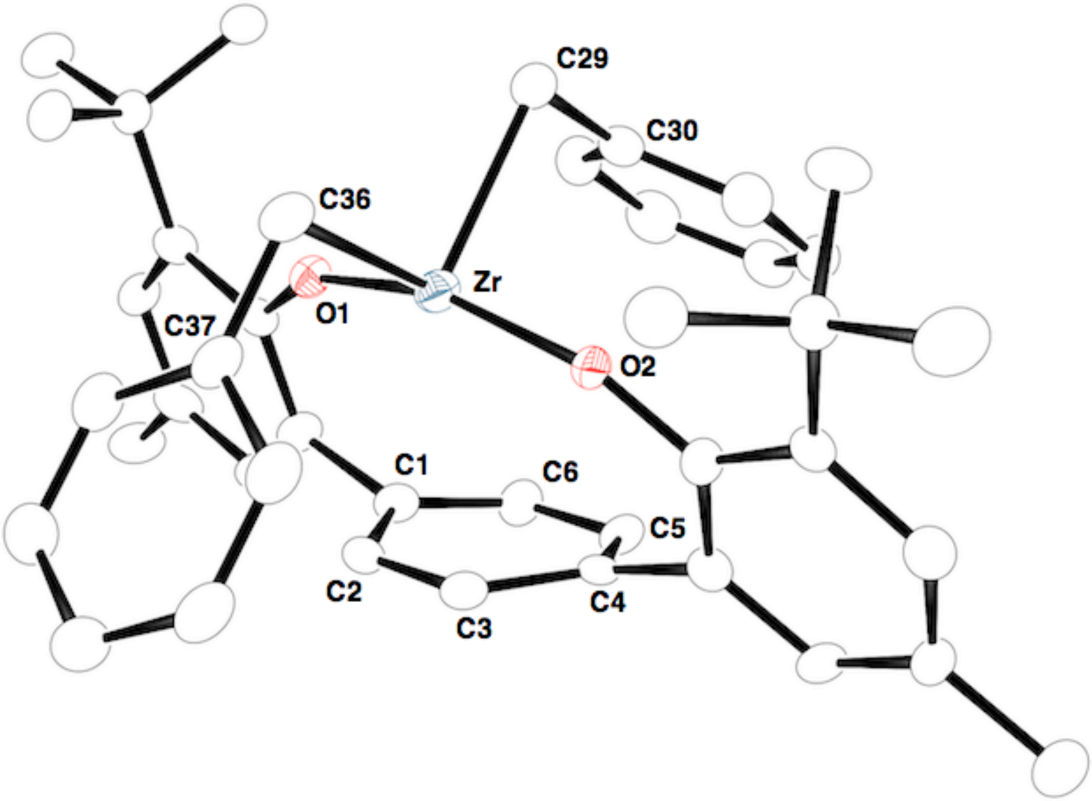

Fig. S3 Molecular structure of **4**. Hydrogen atoms have been omitted for clarity.

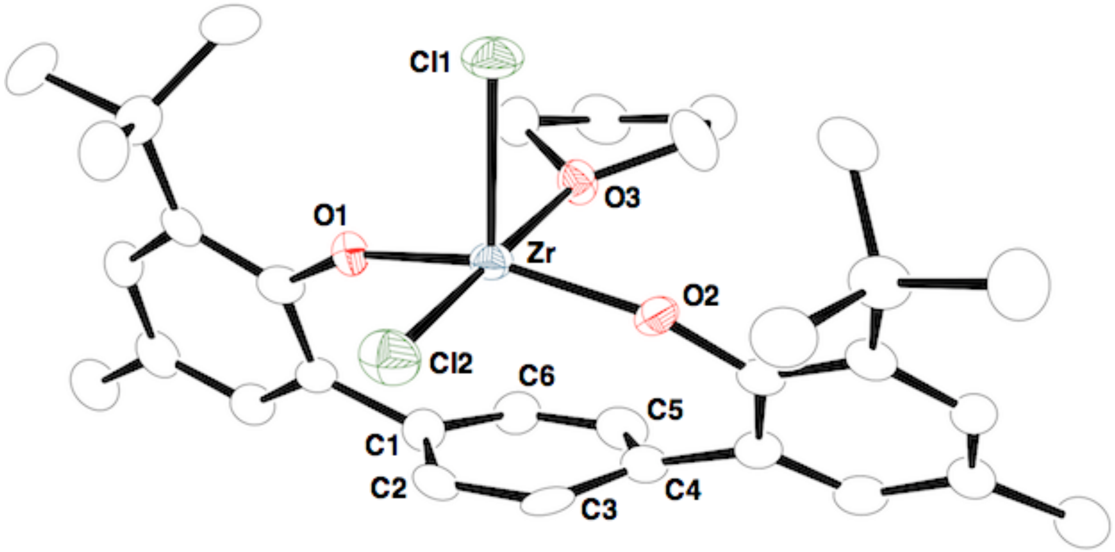

Fig. S4 Molecular structure of **5**. Hydrogen atoms have been omitted for clarity.

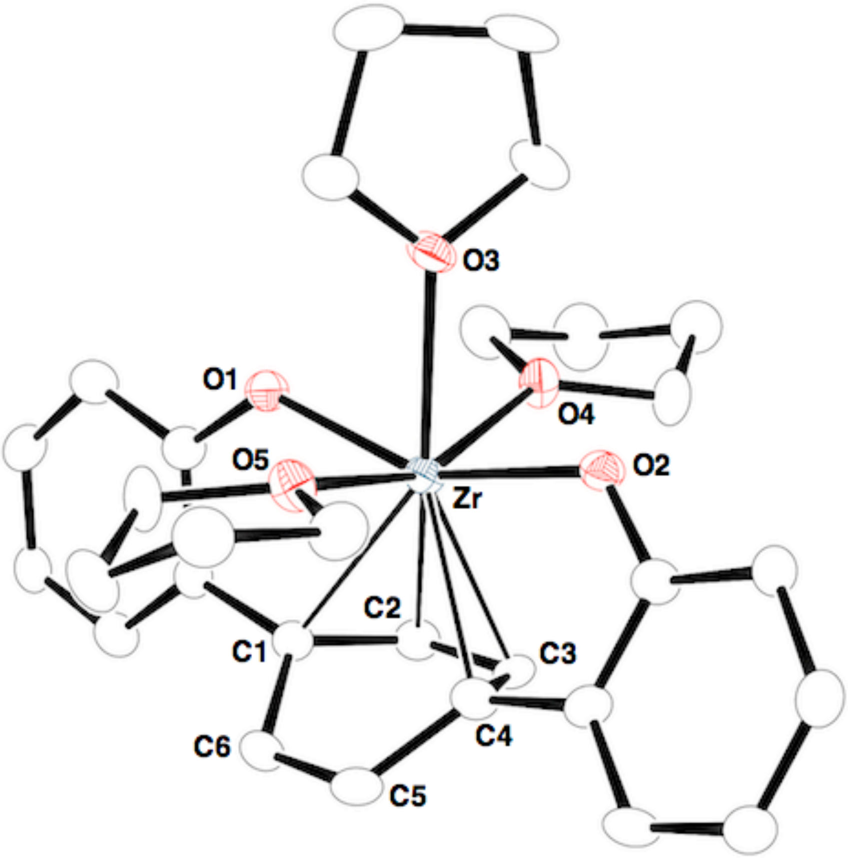

Fig. S5 Molecular structure of **6**. Carbon atoms of *tert*-butyl/methyl substituents and hydrogen atoms have been omitted for clarity.

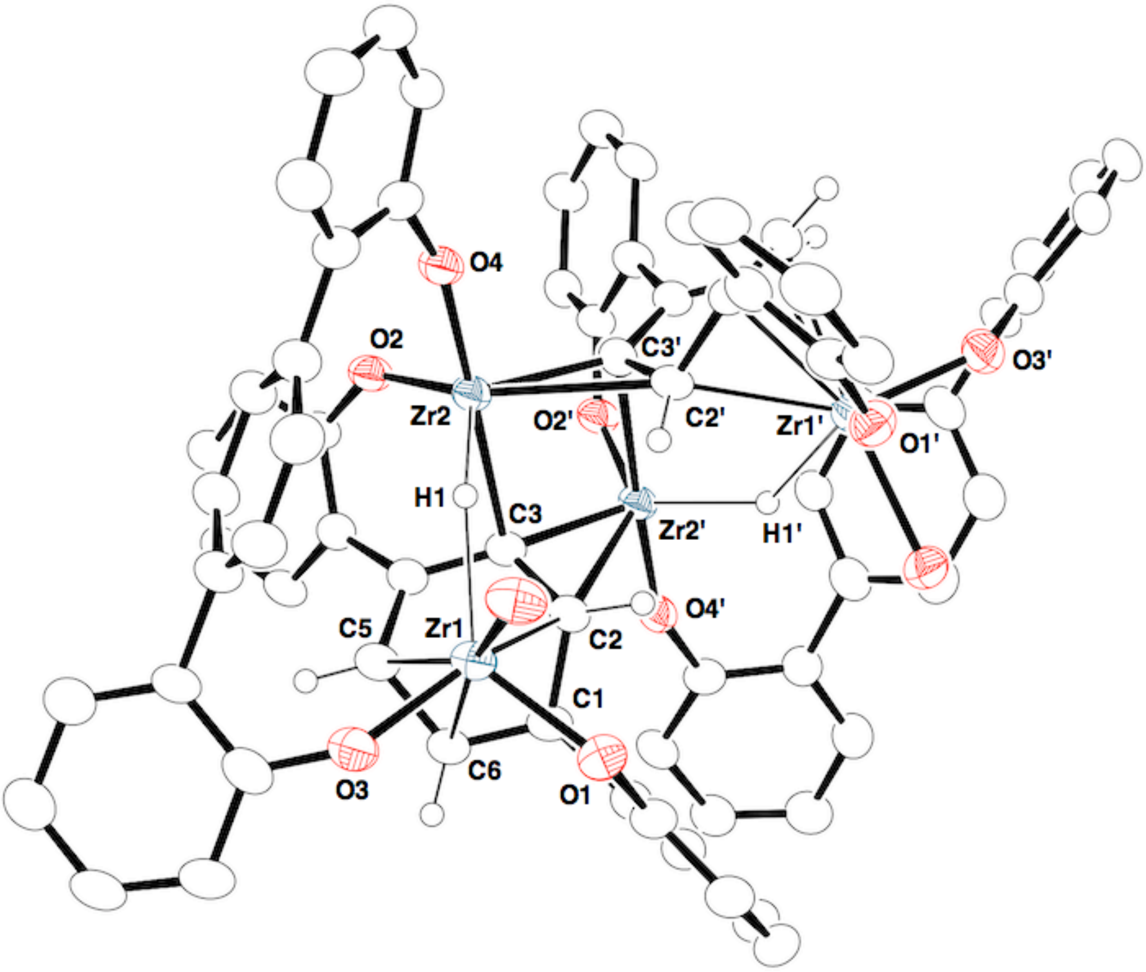

Fig. S6 Molecular structure of **7**. Carbon atoms of *tert*-butyl/methyl substituents and THF and hydrogen atoms except the hydrides and the metalated arene protons have been omitted for clarity.

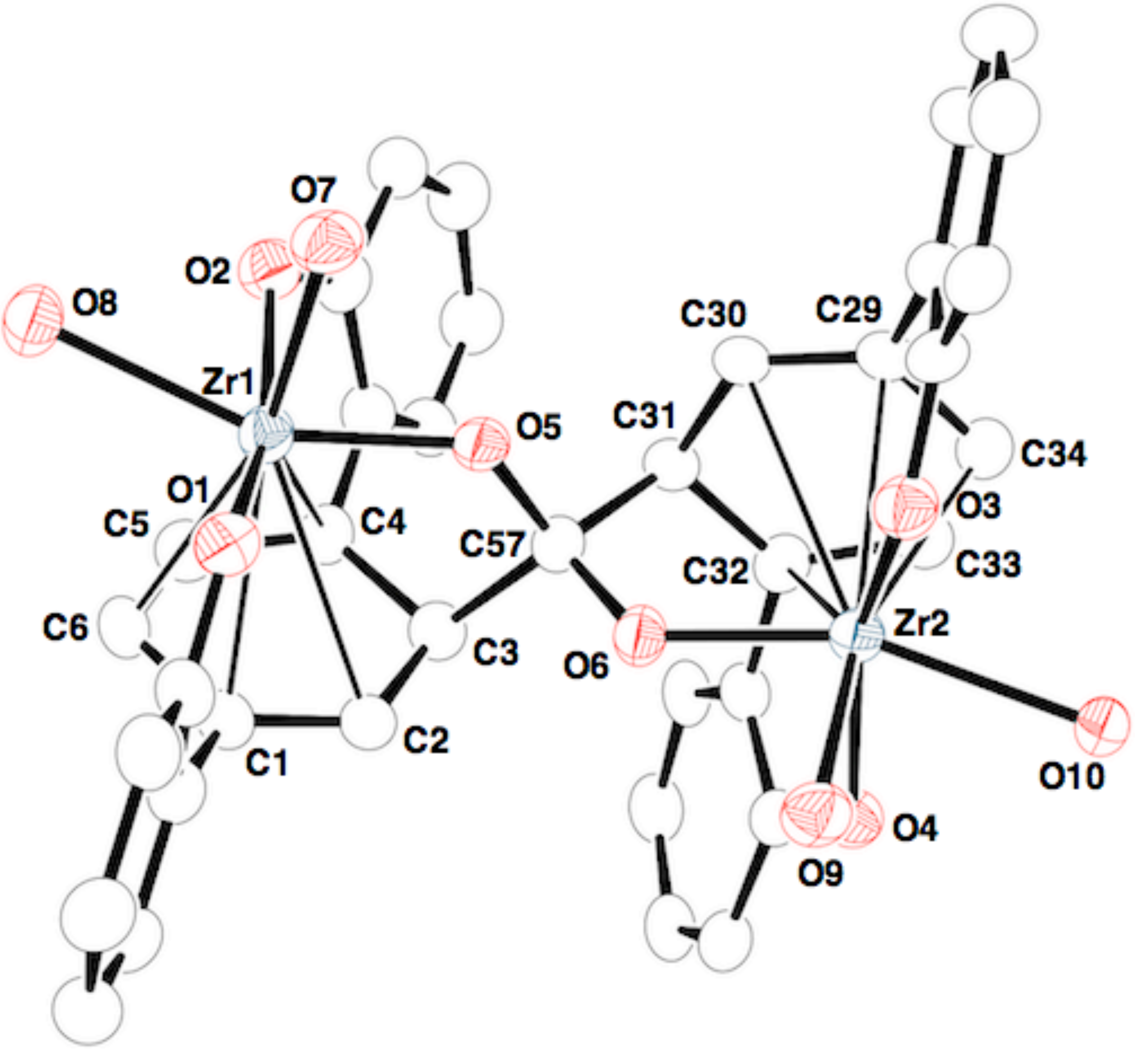

Fig. S7 Molecular structures of **8**. Carbon atoms of *tert*-butyl/methyl substituents and THF and hydrogen atoms have been omitted for clarity.

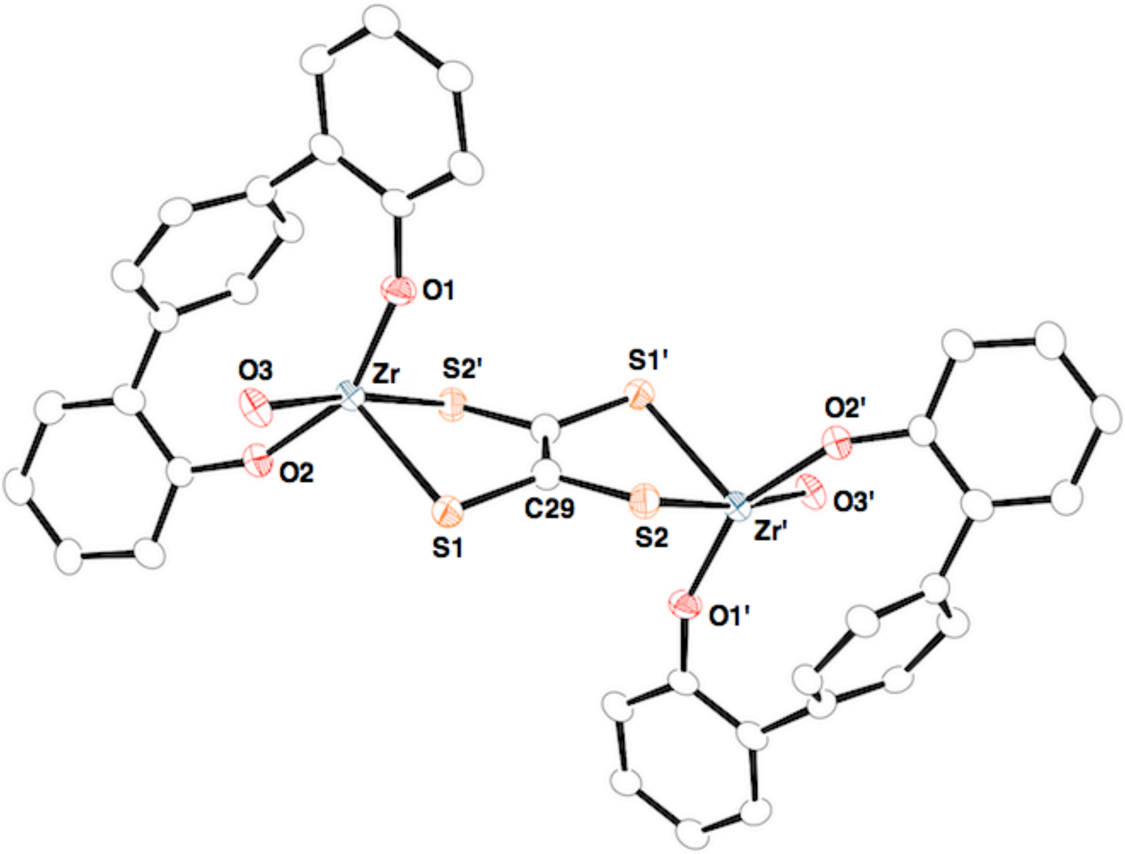

Fig. S8 Molecular structure of **9**. Carbon atoms of *tert*-butyl/methyl substituents and THF and hydrogen atoms have been omitted for clarity.

Table S1. Crystallographic Data.

	1	**3**	**4**
Formula	$C_{32}H_{42}O_4ClTi$	$C_{76}H_{84}N_6O_4Ti_2$	$C_{42}H_{46}O_2Zr$
M	574.01	1241.29	674.01
T/K	123(2)	123(2)	123(2)
Color	red	purple	yellow
Crystal size/mm^3	0.22 x 0.15 x 0.14	0.20 x 0.08 x 0.03	0.14 x 0.13 x 0.09
Crystal system	*Orthorhombic*	*Orthorhombic*	*Monoclinic*
Space group	$Pca2_1$ (No. 29)	$Fdd2$ (No. 43)	$P2_1/c$ (No. 14)
a/Å	26.4628(17)	22.533(5)	10.1726(15)
b/Å	11.6059(6)	50.714(11)	21.898(3)
c/Å	19.5905(12)	11.285(2)	15.189(2)
α/°	90	90	90
β/°	90	90	91.409(6)
γ/°	90	90	90
V/Å^3	6016.7(6)	12896(5)	3382.5(8)
Z	8	8	4
D_c/g cm^{-3}	1.267	1.279	1.324
μ/mm^{-1}	0.407	0.304	0.360
Reflections collected	41404	26369	35970
Independent reflections (R_{int})	13770 (0.1064)	7372 (0.0932)	7752 (0.1139)
Refined parameters	705	405	414
Goodness-of-fit on F^2	1.048	1.056	1.056
R_1 $[I > 2\sigma(I)]^a$	0.0612	0.0756	0.0715
wR_2 (all data)^b	0.1415	0.1638	0.1590
Largest diff. peak and hole/e Å^{-3}	0.447 and −0.525	0.503 and −0.390	1.104 and −0.832

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, [b] w$R_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$

Table S1. Crystallographic Data. (Cont.)

	5	**6**	**7**
Formula	$C_{32}H_{40}O_3Cl_2Zr$	$C_{44}H_{64}O_6Zr$	$C_{144}H_{184}O_{10}Zr_4$
M	634.76	780.17	2439.79
T/K	123(2)	123(2)	123(2)
Color	colorless	green	brown
Crystal size/mm^3	0.14 x 0.13 x 0.09	0.06 x 0.05 x 0.02	0.13 x 0.10 x 0.09
Crystal system	*Monoclinic*	*Monoclinic*	*Orthorhombic*
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pbcn* (No. 60)
a/Å	15.032(2)	24.091(6)	31.709(6)
b/Å	9.1927(15)	9.788(2)	15.741(3)
c/Å	22.154(4)	16.906(4)	25.572(5)
α/°	90	90	90
β/°	90.733(3)	96.277(5)	90
γ/°	90	90	90
V/Å^3	3061.1(8)	3962.4(17)	12763(4)
Z	4	4	4
D_c/g cm^{-3}	1.377	1.308	1.270
μ/mm^{-1}	0.564	0.324	0.375
Reflections collected	24316	30136	83954
Independent reflections (R_{int})	6957 (0.0497)	9065 (0.1012)	14603 (0.0705)
Refined parameters	351	468	711
Goodness-of-fit on F^2	0.990	1.066	1.203
R_1 [$I > 2\sigma(I)$][a]	0.0498	0.0743	0.0845
wR_2 (all data)[b]	0.1460	0.1821	0.2015
Largest diff. peak and hole/e Å^{-3}	1.554 and −0.615	1.493 and −1.028	1.258 and −0.922

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$

Table S1. Crystallographic Data. (Cont.)

	8	**9**
Formula	$C_{83}H_{105}O_{12.5}Zr_2$	$C_{94}H_{112}O_6S_4Zr_2$
M	1485.11	1648.52
T/K	123(2)	123(2)
Color	yellow	blue
Crystal size/mm^3	0.09 x 0.09 x 0.03	0.07 x 0.06 x 0.05
Crystal system	*Monoclinic*	*Triclinic*
Space group	$P2_1/c$ (No. 14)	P-1 (No. 2)
a/Å	17.785(2)	9.498(3)
b/Å	14.4383(19)	14.156(5)
c/Å	29.830(4)	16.469(5)
α/°	90	77.889(15)
β/°	95.8792(19)	80.28(2)
γ/°	90	80.586(14)
V/Å^3	7619.7(17)	2114.9(12)
Z	4	1
D_c/g cm^{-3}	1.295	1.294
μ/mm^{-1}	0.334	0.398
Reflections collected	92813	26318
Independent reflections (R_{int})	17461 (0.0992)	9639 (0.0766)
Refined parameters	819	488
Goodness-of-fit on F^2	0.983	1.071
R_1 [$I > 2\sigma(I)$]^a	0.0934	0.0778
wR_2 (all data)^b	0.2712	0.1901
Largest diff. peak and hole/e Å^{-3}	1.579 and –0.869	1.147 and –0.852

^{a} $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, ^{b}w$R_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$