

(Electronic supplementary information)

“Titanium N-heterocyclic carbene complexes incorporating an imidazolium-linked bis(phenol)”

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Synthesis of N-(3,5-di-*tert*-buty-2-salicyl)-imidazole.

A 500 mL three-necked round-bottom flask, containing a magnetic stirring bar and imidazole (4.8 g, 70 mmol), anhydrous sodium bicarbonate (6.2 g, 74 mmol) was fitted with serum-cup, a dropping funnel, and a reflux condenser connected to a three-way stopcock with a balloon filled with nitrogen. After THF (50 mL) was introduced, the mixture was refluxed with stirring. To the suspension, a solution of 2-bromomethyl-4,6-di-*tert*-butylphenol (20 g, 67 mmol) in THF (100 mL) was slowly added from a dropping funnel. The mixture was stirred for 12 h. After cooling to room temperature, the mixture was poured into water and extracted with ether. The organics was dried over Na₂SO₄, and the solvent was evaporated to dryness to give off-white solid. Recrystallization of the crude product from ether/n-hexane gave white powder (96%, 18.3 g, 64 mmol). ¹H NMR (500 MHz, C₆D₆) δ 1.30 (s, 9H), 1.66 (s, 9H), 4.56 (s, 2H), 6.35 (s, 1H), 6.63 (s, 1H), 6.71 (s, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H). Anal. Calcd for C₁₈H₂₈N₂O: C, 75.48; H, 9.15; N, 9.78. Found: C, 74.48; H, 9.07; N, 9.69.

Synthesis of 1,3-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)imidazolium bromide [H₃L]Br 1.

A 500 mL three-necked round-bottom flask, containing a magnetic stirring bar and N-(3,5-di-*tert*-buty-2-hydroxyphenylmethyl)-imidazole (10.0 g, 35 mmol) was fitted with serum-cup, a dropping funnel, and a reflux condenser connected to a three-way stopcock with a

balloon filled with nitrogen. After THF (25 mL) was added, the mixture was refluxed with stirring. To the suspension, a solution of 2-bromomethyl-4,6-di-*tert*-butylphenol (9.0 g, 30 mmol) in THF (50 mL) was slowly added from a dropping funnel, then the mixture was stirred for 12 h. After being cool to room temperature, the solvent was evaporated to dryness to give the crude product. Washing of the crude by toluene, then n-hexane gave fine colorless powder of [H₃L]Br (63%, 11.0 g, 19 mmol). ¹H NMR (500 MHz, CDCl₃) δ 1.25 (s, 18H), 1.38 (s, 18H), 5.53 (s, 4H), 6.95 (brs, 2H, OH), 7.07 (d, *J* = 2.4 Hz, 2H), 7.12 (d, *J* = 1.2 Hz, 2H), 7.32 (d, *J* = 2.4 Hz, 2H), 9.51 (brs, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 30.3 (CH₃), 31.7 (CH₃), 34.5, 35.1, 51.3 (CH₂), 122.3, 121.4 (CH), 125.3 (CH), 125.7 (CH), 136.0, 139.1 (CH, imidazolium), 143.4, 151.4. Anal. Calcd for C₃₃H₄₉N₂O₂Br: C, 67.68; H, 8.43; N, 4.78. Found: C, 67.39; H, 8.41; N, 4.74.

1,2-Benzyl Migration in Ligand

To a suspension of **1** (3.0 g, 5.12 mmol) in THF (50 mL) was slowly added 1.0 M solution of NaN(SiMe₃)₂ in THF (15.4 mmol, 15.4 mL) at -78 °C. The mixture was allowed to return to ambient temperature and stirred for further 3 h. Then the mixture was poured into water and extracted with ether. Solvent was evaporated to dryness, and recrystallization of the crude gave 1,2-disubstituted imidazole as white crystals. ¹H NMR (500 MHz, CDCl₃) δ 1.15 (s, 9H), 1.21 (s, 9H), 1.42 (s, 9H), 1.43 (s, 9H), 4.01 (s, 2H), 5.16 (s, 2H), 6.60 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 1.5 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 1.5 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H). Anal. Calcd for C₃₃H₄₈N₂O₂: C, 78.53; H, 9.59; N, 5.55. Found: C, 78.41; H, 9.67; N, 5.55.

Synthesis of Ti(L)Cl₂(thf) **3**

To a suspension of **1** (1.93 g, 3.30 mmol) in THF (30 mL) was slowly added 1.0 M solution of NaN(SiMe₃)₂ in THF (9.9 mmol, 9.9 mL) at -78 °C for 30 min. Keeping the temperature -78 °C, the solution of the ligand was transferred by cannula to a flask containing a solution of TiCl₄(thf)₂ (1.10 g, 3.29 mmol) in THF (20 mL). The mixture was allowed to warm up to room temperature and stirred for further 8 h. After an insoluble material was

removed by centrifugation, the red solution was evaporated to dryness. The residue was recrystallized from THF/n-hexane to give **3** as orange crystals (74%, 1.87 g). ^1H NMR (500 MHz, CDCl_3 at rt) δ 1.26 (s, 18H, *t*Bu), 1.52 (s, 18H, *t*Bu), 1.84 (brs, 4H, THF CH_2), 3.76 (brs, 4H, THF CH_2), 4.5-6.0 (m, 4H, CH_2), 6.94 (brs, 2H, Ar H), 7.06 (brs, 2H, CH), 7.35 (brs, 2H, Ar H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 25.8 (CH_2), 31.1 (CH_3), 31.6 (CH_3), 34.7, 35.7, 53.0 (CH_2), 68.4 (CH_2), 119.3 (CH), 124.3 (CH), 124.5, 125.1 (CH), 137.8, 144.8, 164.0 (carbene). Crystals of this compound are solvated by THF. Hence accurate elemental analytical data is difficult to obtain due to partial loss of solvate during analysis. The amount of THF in the isolated solid of **3** was estimated by ^1H NMR spectroscopy. Anal. Calcd for $\text{C}_{37}\text{H}_{54}\text{Cl}_2\text{N}_2\text{O}_3\text{Ti}$: C, 64.07; H, 7.85; N, 4.04. Found: (1st) C, 64.33; H, 8.51; N, 3.42. (2nd) C, 64.55; H, 8.59; N, 3.03. (3rd) C, 64.48; H, 8.31; N, 3.69.

Synthesis of $\text{Ti}(\text{L})(\text{CH}_2\text{Ph})_2$ **4**

To a solution of **3** (694 mg, 1.0 mmol) in toluene (40 mL) was slowly added 1.53 M solution of PhCH_2MgCl in ether (2.0 mmol, 1.307 mL) at $-78\text{ }^\circ\text{C}$. The mixture was allowed to return to ambient temperature and stirred for further 8 h. After an insoluble material was removed by centrifugation, the reddish brown solution was evaporated to dryness. The residue was recrystallized from toluene/n-hexane to give **3** as light yellow crystals (30%, 220 mg, 0.30 mmol). ^1H NMR (500 MHz, C_6D_6 at rt) δ 1.47 (s, 18H, *t*Bu), 1.99 (s, 18H, *t*Bu), 2.10 (s, toluene), 3.33 (br, 2H, CH_2), 3.43 (br, 2H, CH_2), 3.45 (br, 2H, CH_2), 4.15 (br, 2H, CH_2), 5.37 (s, 2H, CH), 6.71 (m, toluene), 6.88 (m, ArH+toluene), 7.77 (d, $J = 2.5$ Hz, 2H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 30.9 (CH_3), 31.9 (CH_3), 34.4, 36.1, 52.8 (CH_2), 85.2 (CH_2), 118.9 (CH), 121.6 (CH), 124.3 (CH), 124.5 (CH), 126.3 (CH), 127.6 (CH), 140.9, 145.8, 161.4, 188.3 (carbene). Anal. Calcd for $\text{C}_{54}\text{H}_{68}\text{N}_2\text{O}_2\text{Ti}$: C, 78.61; H, 8.31; N, 3.40. Found: C, 78.15; H, 8.61; N, 3.23.

Analysis of the Fluxionality of **4 in Solution.** Complex **4** was dissolved in toluene- d_8 , and the tube was sealed under an argon atmosphere. ^1H NMR spectra were taken at

9 temperatures ranging from 0 to 100 °C. Line shape analysis of the methylene region was carried out at each temperature using a *gNMR* program. The k_1 values obtained at given temperature are as follows: 0°C, 5; 5 °C, 10; 10 °C, 16; 25°C, 45; 40°C, 150; 50°C, 400; 60°C, 1000; 80°C, 4000; 100°C, 1800. Activation parameters were determined from Eyring plots of the above data.

Fig. S1 MWT distribution of polyethylene (using **1** activated by MMAO; Al:Ti = 1000:1, 0.5 h, 1L of toluene, 30°C, 9 bar)

