

Electronic Supplementary Information (ESI) for New Journal of Chemistry

Electronic Supplementary Information

Synthesis of Ti, Zr, and Hf complexes with a new tetra-azane ligand by one-pot HCl-elimination and their properties as catalysts for production of UHMWPE

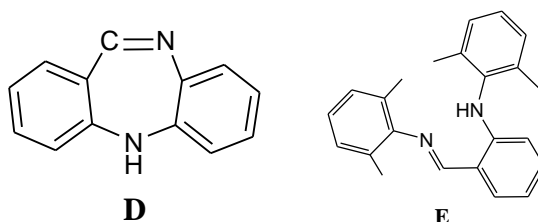
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**1. A typical procedure for the attempted synthesis of free ligands
1,2-[(2-(2,6-R₂C₆H₃N=CH)C₆H₄NH)₂C₆H₄ (R = Me, Et)**

ⁿBuLi (10 mL, 20 mmol) in *n*-hexane was added to a solution of *o*-phenylenediamine (1.08 g, 10 mmol) in 50 mL of THF at -78 °C. The reaction mixture was allowed to warm to room temperature and canula transferred into a solution of *ortho*-C₆H₄F(CH=NC₆H₃Me₂-2,6) (2.27g, 10 mmol) in 50 mL of THF at 50 °C. After the mixture was stirred for 6 h, another equiv of ⁿBuLi (5 mL, 10 mmol) was added at -78 °C. The resulted reaction mixture was warmed to room temperature and one more equiv of *ortho*-C₆H₄F(CH=NC₆H₃Me₂-2,6) (2.27 g, 10 mmol) was added. The reaction mixture was stirred at 60 °C for 10 hours and the solvent was removed under vacuum. The residue was quenched with H₂O (40 mL) and extracted with CH₂Cl₂ (3 × 20ml). The combined organic phase was dried with anhydrous MgSO₄, filtered and concentrated by distillation under reduced pressure to give the residue as a deep yellow solid. The residue was isolated and purified by column chromatography on silica gel eluting with ethyl acetate/petroleum ether (v/v = 1:15, 1% Et₃N) to give pure byproducts **D** (0.8 g, 36.6%) and **E** (1.8 g, 41.4%), but no expected product. **D**: Anal. Calcd for C₁₃H₉N₂ (193.08): C, 80.81; H, 4.69; N, 14.50. Found: C, 80.43; H, 4.61; N, 14.65. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 12.02 (s, 1H, ArNHAr), 8.74 (s, 1H, CH=NAr), 7.72 (d, *J* = 8.4 Hz, 1H, ArH), 7.70 (d, *J* = 8.4 Hz, 1H, ArH), 7.48 (d, *J* = 8.4 Hz, 1H, ArH), 7.22-7.33 (m, 3H, ArH), 7.00 (t, *J* = 14.4 Hz, 1H, ArH), 6.85 (t, *J* = 14.4 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃, 298 K): 159.62, 144.47, 140.01, 137.10, 135.76, 132.17, 126.99, 121.90, 119.45, 117.68, 117.27, 117.02, 112.52ppm. **E**: Anal. Calcd for C₂₃H₂₄N₂ (328.19): C, 84.11; H, 7.37; N, 8.53. Found: C, 84.33; H, 7.51; N, 8.45. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 10.52 (s, 1H, ArNHAr), 8.37 (s, 1H, CH=NAr), 7.34 (d, *J* = 8.4 Hz, 1H, ArH), 7.07-7.18 (m, 4H, ArH), 6.96 (t, *J* = 13.4 Hz, 1H, ArH), 6.71 (t, *J* = 14.4 Hz, 1H, ArH), 6.27 (d, *J* = 8.4 Hz, 1H, ArH), 2.24 (s, 6 H, ArCH₃), 2.19 (s, 6 H, ArCH₃). ¹³C NMR (100 MHz, CDCl₃, 298 K): 165.94, 150.79, 148.47, 137.49, 135.76, 134.54, 132.20, 128.37, 128.11, 127.66, 126.33, 123.79, 116.71, 115.34, 111.76, 18.52, 18.33 ppm.



2. Molecular geometries of compound **E**

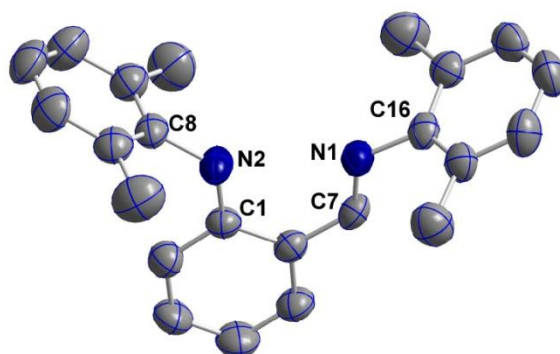


Figure S1. Perspective view of **E** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. The selected bond lengths (\AA) and angles (deg.): C1–N2 1.365(3), C7–N1 1.272(3), C8–N2 1.425(3), C16–N1 1.425(3); C7–N–C16 119.8(2), C1–N2–C8 123.5(2).

3. A typical DSC curve of polyethylene

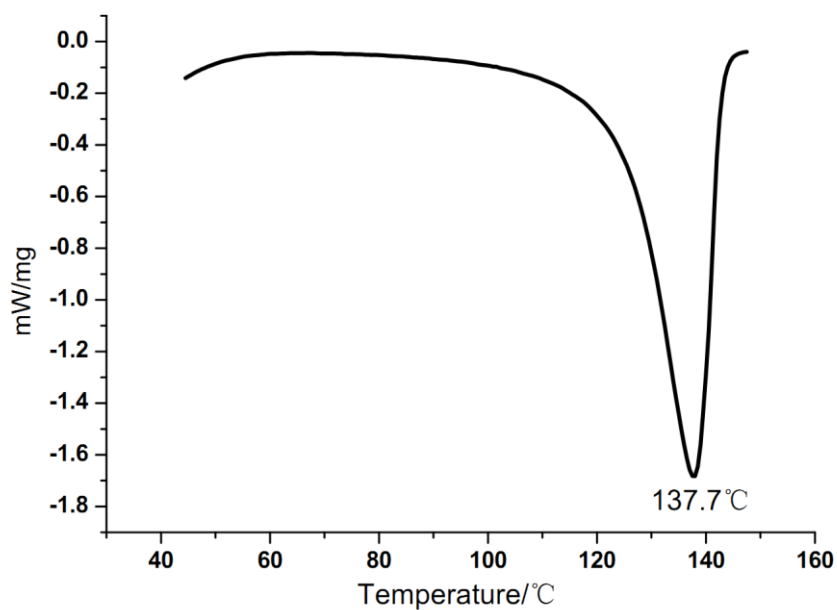


Figure S2. DSC curve of the polyethylene sample from entry 7 in Table 3.

4. NMR spectrum of a typical polyethylene sample

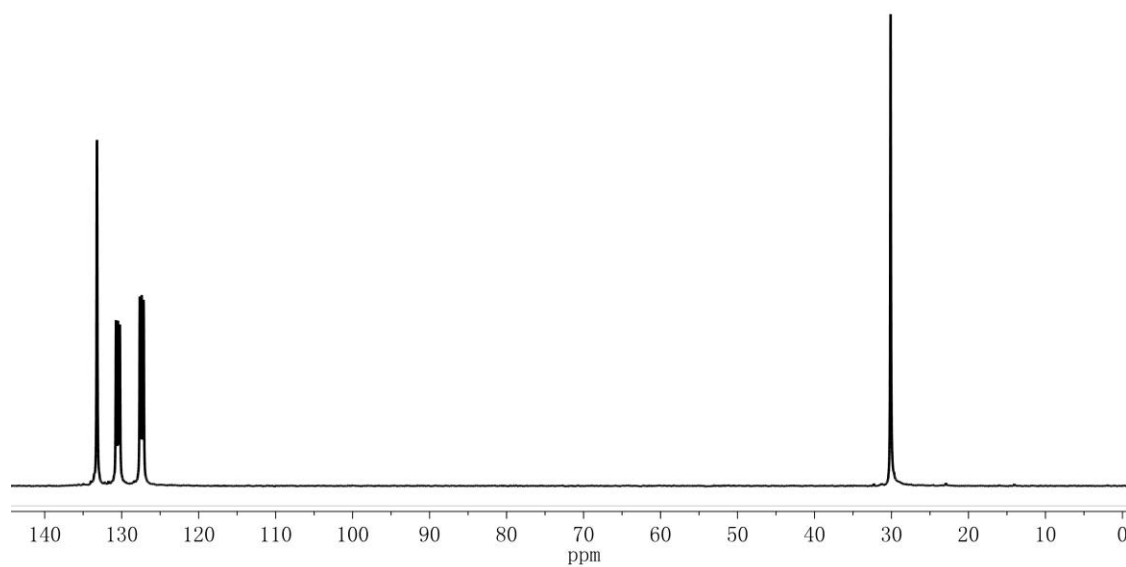


Figure S3. ^{13}C NMR spectrum of the polyethylene sample from entry 1 in Table 3 at 135 °C with $o\text{-C}_6\text{D}_4\text{C}_2\text{H}_2$ as the solvent.