

Article

Phosphine-Thiophenolate Half-Titanocene Chlorides: Synthesis, Structure, and Their Application in Ethylene (Co-)Polymerization

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Abstract: A series of novel half-titanocene complexes $\text{CpTiCl}_2[\text{S-2-R-6-(PPh}_2\text{)C}_6\text{H}_3]$ ($\text{Cp} = \text{C}_5\text{H}_5$, **2a**, $\text{R} = \text{H}$; **2b**, $\text{R} = \text{Ph}$; **2c**, $\text{R} = \text{SiMe}_3$) have been synthesized by treating CpTiCl_3 with the sodium of the ligands, $2\text{-R-6-(PPh}_2\text{)C}_6\text{H}_3\text{SNa}$, which were prepared by the corresponding ligands and NaH. These complexes have been characterized by ^1H , ^{13}C and ^{31}P NMR as well as elemental analyses. Structures for **2a–b** were further confirmed by X-ray crystallography. Complexes **2a–b** adopt five-coordinate, distorted square-pyramid geometry around the titanium center, in which the equatorial positions are occupied by sulfur and phosphorus atoms of the chelating phosphine-thiophenolate and two chlorine atoms, and the cyclopentadienyl ring is coordinated on the axial position. The complexes **2a–c** were investigated as the catalysts for ethylene polymerization and copolymerization of ethylene with norbornene in the presence of MMAO or $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/\text{Bu}_3\text{Al}$ as the cocatalyst. All complexes exhibited low to moderate activities towards homopolymerization of ethylene. However, they displayed moderate to high activities towards copolymerization of ethylene with norbornene.

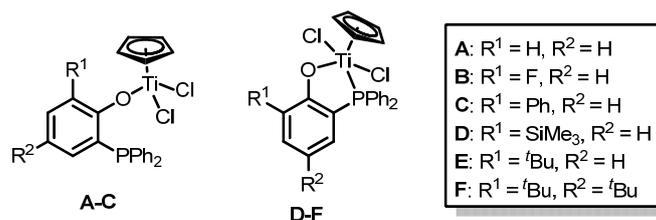
Keywords: copolymerization; catalysts; ethylene

1. Introduction

The development of well-defined, single-site group 4 metal catalysts has attracted much attention for olefin polymerization [1–3]. Many studies have also been focused on the relationship between the structure and catalytic properties of a given catalyst with respect to polymer chain composition and architecture [4–7]. Recent studies of half-metallocenes, having one cyclopentadienyl moiety and one monoanionic ligand have led to new classes of catalysts. [8–40] The bridged half-sandwich group 4 metal complexes “constrained geometry” catalysts (CGCs) have proven to be a very successful class of catalysts which exhibit high activities and high comonomer incorporations [8]. Recently, non-bridged half-sandwich group 4 metal complexes containing anionic ancillary donor ligands have become a hot topic because of their easy modifications and remarkable catalytic activity for olefin (co)polymerization [9–40]. For instance, Nomura *et al.* found that the half-titanocenes containing aryloxo ligands exhibited remarkable catalytic activity in olefin polymerization and efficient comonomer incorporation in ethylene/ α -olefin copolymerization [10,29]. Gibson and his coworkers reported a series of bis(phosphanylphenoxide) group 4 metal dichloride complexes, and further suggested that the use of ancillary ligands with softer L donors, such as phosphorus and sulfur, might offer beneficial stabilization of the highly reactive metal center [41,42]. Subsequently, our group found that high-temperature living ethylene/norbornene copolymerization could be achieved by using bis(phenoxy-phosphine)-titanium complexes as the catalysts in the presence of MMAO [43].

To combine the advantages of metallocene and phenoxy-phosphine ligands, we reported a series of *o*-di(phenyl)phosphanylphenolate-based half-titanocene complexes, CpTiCl₂[*O*-2-R¹-4-R²-6-(PPh₂)C₆H₂] (Cp = C₅H₅, **A**: R¹ = R² = H; **B**: R¹ = F, R² = H; **C**: R¹ = Ph, R² = H; **D**: R¹ = SiMe₃, R² = H; **E**: R¹ = ^tBu, R² = H; **F**: R¹ = R² = ^tBu), supported by bidentate ligands with softer donor atoms (Chart 1) [28]. We found that all complexes exhibited low to moderate activities towards homopolymerization of ethylene, but displayed excellent ability to copolymerize ethylene with norbornene, and catalytic activity was more than 100 times greater than that of ethylene homopolymerization in the case of Ph₃CB(C₆F₅)₄/^tBu₃Al as cocatalyst, affording the copolymers with high comonomer incorporations. To further investigate the electronic effect of the ligand on polymerization behaviors, we synthesized some half-titanocene complexes containing phosphine-thiophenolate ligands. Herein, we thus described the synthesis and characterization of some novel phosphine-thiophenolate-based half-titanocene complexes, CpTiCl₂[S-2-R-6-(PPh₂)C₆H₃] (Cp = C₅H₅, **2a**, R = H; **2b**, R = Ph; **2c**, R = SiMe₃), and explored their application in ethylene polymerization and ethylene/NBE copolymerization.

Chart 1. Structures of complexes A–F.



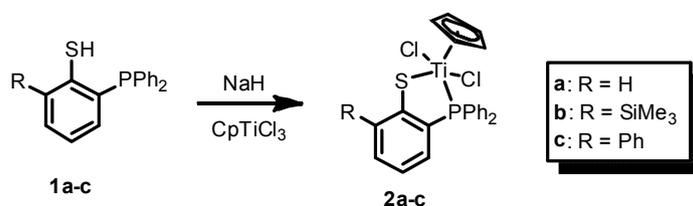
2. Results and Discussion

A series of novel half-titanocene complexes $\text{CpTiCl}_2[\text{S-2-R-6-(PPh}_2\text{)C}_6\text{H}_3]$ ($\text{Cp} = \text{C}_5\text{H}_5$, **2a**, $\text{R} = \text{H}$; **2b**, $\text{R} = \text{Ph}$; **2c**, $\text{R} = \text{SiMe}_3$) have been synthesized in high yields (76–85%) by treating CpTiCl_3 with the sodium of the ligands, 2-R-6-(PPh_2) $\text{C}_6\text{H}_3\text{SNa}$, which were prepared by the corresponding ligands and NaH , as shown in Scheme 1. The resultant complexes were identified by ^1H , ^{13}C and ^{31}P NMR spectra and elemental analysis. The ^1H NMR spectra of these complexes showed no complexity, and the integration of complexes confirms a 1:1 ratio of cyclopentadienyl to phosphine-thiophenolate ligand. A doublet for the Cp hydrogens was observed for complexes **2a–c** (**2a**, δ 6.47 ppm, $J_{\text{HP}} = 2.5$ Hz; **2b**, δ 6.45 ppm, $J_{\text{HP}} = 2.3$ Hz; **2c**, δ 6.44 ppm, $J_{\text{HP}} = 2.3$ Hz), which suggests phosphorus is coordinated to titanium. The observed results were an interesting contrast to those found in the analogues containing *o*-di(phenyl)phosphanylphenolate ligands in which the phosphorus in **A** and **C** is not coordinated to Ti. In addition, all signals in the ^{31}P NMR spectra of complexes **2a–c** (**2a**, δ 44.33 ppm; **2b**, δ 43.32 ppm; **2c**, δ 42.53 ppm) were shifted substantially downfield from the values found for the corresponding ligands **1a–c** (**1a**, δ -13.1 ppm; **1b**, δ -12.20 ppm; **1c**, δ -13.6 ppm).

2.1. Synthesis and Characterization of Half-Titanocene Complexes $\text{CpTiCl}_2[\text{S-2-R-6-(PPh}_2\text{)C}_6\text{H}_3]$

Crystals of **2a–b** suitable for crystallographic analysis were grown from the chilled concentrated CH_2Cl_2 -hexane mixture solution. The crystallographic data together with the collection and refinement parameters are summarized in Table 1. Selected bond distances and angles for **2a–b** and **C–D** [28] were summarized in Table 2. If the centroid of the cyclopentadienyl ring is considered as a single coordination site, complexes **2a–b** adopt five-coordinate, distorted square-pyramid geometry around the titanium center, where the equatorial positions are occupied by sulfur and phosphorus atoms of the ligands and two chlorine atoms. The cyclopentadienyl group is coordinated on the axial position, as shown in Figures 1–2. The configurations of **2a–b** in the solid state were in line with the results observed in the ^{31}P NMR spectra. These results are very different from those for complexes **A–F**, in which the steric bulk in R position is required in generation of five-coordinate, distorted square-pyramid geometry around the titanium center. However, for phosphine-thiophenolate-based half-titanocene complexes, the steric bulk in R position is not essential to generate distorted square-pyramid geometry around the titanium center.

Scheme 1. Synthesis of complexes **2a–c**.



Ti(1)-S(1) bond distance in complex **2b** (2.4359(9) Å) is slightly longer than that in **2a** (2.4188(10) Å). Ti-Cp (centroid) distances in **2a–b** (**2d**: 2.027, **2e**: 2.029) are longer than that in **C** (2.016 Å), but somewhat shorter than that in **D** (2.034 Å). The five-membered C_2SPTi chelate ring in **2a–b** has an envelope conformation with the metal lying *ca.* 1.132–1.136 Å (**2a**: 1.136, **2b**: 1.132 Å) out of the C_2SP plane in the direction of Cp ring, whereas the metal lies *ca.* 0.549–0.603 Å (**D**: 0.549, **E**: 0.603, **F**: 0.593 Å)

out of the C₂OP plane in **D–F**. The Ti(1)-P(1) bond length in **2a–b** is slightly affected by the R group of the ligand (**2a**: 2.5769(9), **2b**: 2.5630(10) Å), which is shorter than that in **D–F** (**D**: 2.6446(6), **E**: 2.6208(12), **F**: 2.6285(8) Å). The Ti(1)-P(1) bond distances in **2a–b** appear in the range of 2.5630–2.5769 Å, indicative of significant coordination of phosphorus atom to the metal center in the solid state. These results indicate that Ti-P bond in **2a–b** is stronger than that in **D–F**, which is also consistent with the results of ³¹P NMR. However, the S(1)-C(1) and P(1)-C(2) bond lengths in **2a–b** change slightly with the variation in R group, as shown in Table 2. The two Ti(1)-Cl bond lengths in **2a–b** are statistically identical (**2a**: 2.3121(10) and 2.3139(10) Å, **2b**: 2.3106(10) and 2.3207(9) Å to Cl(1) and Cl(2), respectively). The bond angles for Cl(1)-Ti(1)-Cl(2) in **2a–b** (**2a**: 91.73(4)°, **2b**: 91.87(3)°, respectively) are much smaller than that for complex **C** (101.45(4)°), but larger than that for complex **D** (88.96(2)°). The bond angles for Ti(1)-S(1)-C(1) in **2a–b** (**2a**: 110.27(11)°, **2b**: 110.66(10)°, respectively) are much smaller than that for Ti(1)-O(1)-C(1) in **D** (134.99(11)°). However, the bond angles for Ti(1)-P(1)-C(2) in **2a–b** (**2a**: 107.67(11)°, **2b**: 109.24(11)°, respectively) are larger than that in **D** (97.11(6)°).

Table 1. Crystal data and structure refinements of complexes **2a–b**.

| | 2a | 2b |
|---|---|--|
| Empirical formula | C _{23.50} H ₂₀ Cl ₃ PSTi | C ₂₉ H ₂₃ Cl ₂ PSTi |
| Formula weight | 519.68 | 553.30 |
| Crystal system | Pna2(1) | P2(1) |
| Space group | orthorhombic | monoclinic |
| a (Å) | 19.6852(10) | 8.0269(7) |
| b (Å) | 22.8729(12) | 13.6834(11) |
| c (Å) | 10.3207(6) | 11.5902(9) |
| α (°) | 90.00 | 90.00 |
| β (°) | 90.00 | 97.3240(10) |
| γ (°) | 90.00 | 90.00 |
| V (Å ³), Z | 4647.0(4), 8 | 1262.63(18), 2 |
| Density _{calcd} (Mg/m ³) | 1.486 | 1.455 |
| Absorption coefficient (mm ⁻¹) | 0.881 | 0.714 |
| F (000) | 2120 | 568 |
| Crystal size (mm) | 0.30 × 0.21 × 0.15 | 0.30 × 0.24 × 0.18 |
| θ range for data collection (°) | 1.78 to 26.01 | 1.77 to 26.03 |
| Reflections collected | 27237 | 8126 |
| Independent reflections | 9135 | 4698 |
| Data/restraints/ parameters | 9135/1/532 | 4698/1/307 |
| Goodness-of-fit on F ² | 1.041 | 1.030 |
| Final R indices [<i>I</i> > 2σ(<i>I</i>): R1, wR2] | 0.0385, 0.0972 | 0.0350, 0.0847 |
| Largest diff. Peak and hole (e Å ⁻³) | 0.553 and -0.366 | 0.337 and -0.191 |

Table 2. Selected Bond Distances (Å) and Angles (deg) for complexes **2a-b** and **C-D** [28].

| | 2a | 2b | C | D |
|----------------------------|------------|------------|------------|------------|
| <i>Bond Distances in Å</i> | | | | |
| Ti(1)-S(1)/O(1) | 2.4188(10) | 2.4359(9) | 1.795(2) | 1.8708(13) |
| Ti(1)-P(1) | 2.5769(9) | 2.5630(10) | | 2.6446(6) |
| Ti(1)-Cl(1) | 2.3121(10) | 2.3106(10) | 2.2582(11) | 2.3320(6) |
| Ti(1)-Cl(2) | 2.3139(10) | 2.3207(9) | 2.2478(11) | 2.3453(6) |
| Ti(1)-Cp(centroid) | 2.027 | 2.029 | 2.016 | 2.034 |
| S(1)/O(1)-C(1) | 1.768(4) | 1.778(3) | 1.369(4) | 1.360(2) |
| P(1)-C(2) | 1.813(3) | 1.808(3) | 1.835(3) | 1.7994(19) |
| <i>Bond Angles in °</i> | | | | |
| Cl(1)-Ti(1)-Cl(2) | 91.73(4) | 91.87(3) | 101.45(4) | 88.96(2) |
| O(1)/S(1)-Ti(1)-P(1) | 73.49(3) | 72.69(3) | | 72.85(4) |
| Ti(1)-S(1)/O(1)-C(1) | 110.27(11) | 110.66(10) | 161.39(19) | 134.99(11) |
| Ti(1)-P(1)-C(2) | 107.67(11) | 109.24(11) | | 97.11(6) |
| Cl(1)-Ti(1)-S(1)/O(1) | 129.59(4) | 131.62(4) | 104.48(7) | 127.96(5) |
| Cl(2)-Ti(1)-S(1)/O(1) | 81.09(4) | 82.09(3) | 103.92(7) | 90.17(4) |
| Cl(1)-Ti(1)-P(1) | 80.08(3) | 79.39(3) | | 78.40(2) |
| Cl(2)-Ti(1)-P(1) | 138.03(4) | 135.69(4) | | 144.48(2) |
| S(1)/O(1)-C(1)-C(2) | 121.0(2) | 118.7(2) | 117.8(3) | 118.22(16) |
| P(1)-C(2)-C(1) | 111.7(2) | 112.8(2) | 117.7(2) | 111.70(14) |

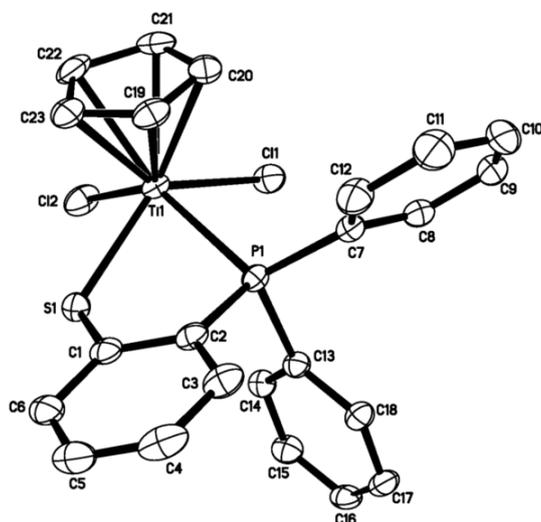
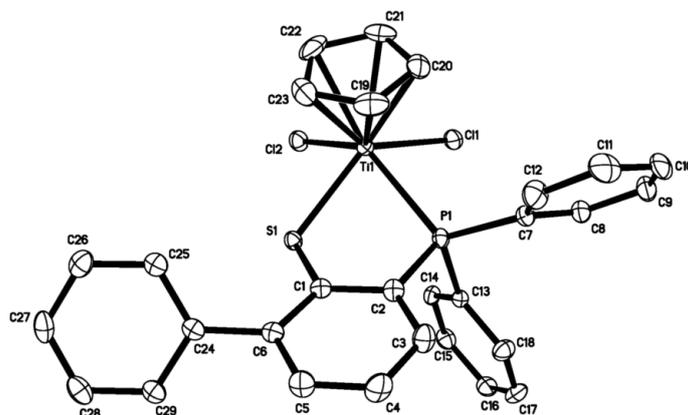
Figure 1. Molecular structure of complex **2a** with thermal ellipsoids at 30% probability level. The hydrogen atoms and the solvent molecule are omitted for clarity.

Figure 2. Molecular structure of complex **2b** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.



2.2. Ethylene (Co)Polymerization Catalyzed by 2a–c

To explore the catalytic behaviors of complexes **2a–c**, ethylene polymerizations were carried out in the presence of modified methylaluminoxane (MMAO). Complex **2a** showed moderate catalytic activity (**2a**, 190 kg/mol_{Ti}·h) for ethylene polymerization (conditions: ethylene 4 atm, MMAO/Ti = 1000, $V_{\text{total}} = 50$ mL, 20 °C, 10 min). Introducing bulk group in R position decreased the activity (**2c**: 140 kg/mol_{Ti}·h). Complex **2b**, bearing phenyl group in both R position, exhibited lowest activity among these catalysts (**2b**: 40 kg/mol_{Ti}·h). These data suggested that both the steric bulk effect and the electron-donating effect of R group play a key role to the enhanced catalytic activity. Using $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/{}^i\text{Bu}_3\text{Al}$ in place of MMAO as the cocatalyst, complexes **2a–c** only produced trace polymers for ethylene polymerization under the similar conditions ($[\text{Al}]/[\text{B}]/[\text{Ti}] = 100/2/1$). Generally, the activities of ethylene homopolymerization by complexes **2a–c** were lower than those by corresponding *o*-di(phenyl)phosphanylphenolate-based half-titanocene complexes [28]. Ethylene copolymerization with norbornene has also been carried out by complexes **2a–c** in the presence of $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/{}^i\text{Bu}_3\text{Al}$ or MMAO under similar conditions with complexes **A–F**. The polymerization results are depicted in Table 3.

Copolymerizations of ethylene with NBE by complex **2a**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/{}^i\text{Bu}_3\text{Al}$ took place at different NBE concentrations in feed. The activity increased upon the increasing the NBE concentration in feed from 0.3 to 0.5 mol/L (entries 1–2, Table 3), and decreased upon further increasing the NBE concentration (entries 3–4). This result was somewhat different from those by **A**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/{}^i\text{Bu}_3\text{Al}$ catalyst system, in which the highest activity was observed at NBE concentration of 1.0 mol/L in feed [28]. The thiophenolate catalysts were less active than the phenolate catalysts. It was assumed that the electronegativity of sulfate is higher than that of oxygen, therefore, the cationic active species of thiophenolate catalysts is less electron deficient. In addition, the NBE incorporation was lower than that obtained by complex **A**, especially at NBE concentration of 1.0 mol/L (**2a**: 33.8%, **A**: 53.2%, respectively). The resultant copolymers possessed relatively high molecular weights (MWs) with unimodal molecular weight distributions (MWDs), and the MW of the copolymers decreased upon the increasing NBE concentration (entries 1–4). The trace amount of polymer was obtained if changing the molar ratio of $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/{}^i\text{Bu}_3\text{Al}$ in system. Suitable amount of both $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ and ${}^i\text{Bu}_3\text{Al}$ was

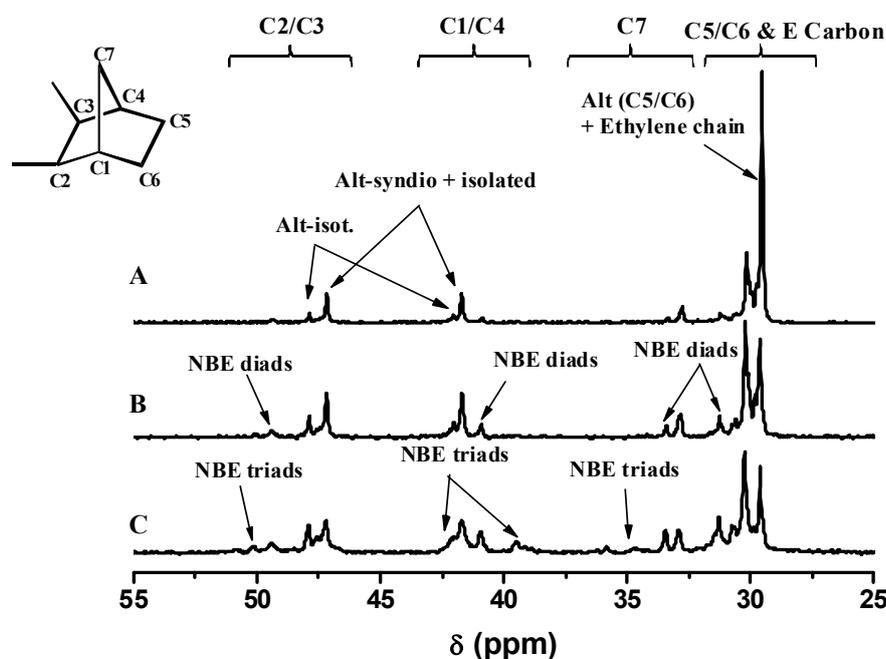
thus required to optimize the polymerization conditions (entries 2 vs. 5). The copolymerization by **2a**/MMAO was also carried out, and the observed activity calculated on the basis of the polymer yield was almost 20 times lower than that by **2a**/Ph₃CB(C₆F₅)₄^tBu₃Al system. However, either the MW or the NBE incorporation by **2a**/MMAO system was much higher than that by **2a**/Ph₃CB(C₆F₅)₄^tBu₃Al.

Table 3. Copolymerization of ethylene with NBE using **2a–c**/Ph₃CB(C₆F₅)₄^tBu₃Al ^a.

| Entry | Cat. | Al/Ti (molar ratio) | NBE (mol/L) | Yield (mg) | Activity (kg/mol _{Ti} ·h) | M _w ^b (kg/mol) | M _w /M _n | NBE Incorp. (mol%) ^c |
|----------------|-----------|------------------------|----------------|---------------|---------------------------------------|---|--------------------------------|------------------------------------|
| 1 | 2a | 100 | 0.3 | 387 | 1858 | 225 | 2.9 | 12.0 |
| 2 | 2a | 100 | 0.5 | 605 | 2904 | 169 | 2.5 | 24.3 |
| 3 | 2a | 100 | 0.7 | 337 | 1618 | 143 | 2.2 | 31.2 |
| 4 | 2a | 100 | 1.0 | 135 | 648 | 112 | 1.8 | 33.8 |
| 5 | 2a | 50 | 0.5 | trace | - | - | - | - |
| 6 ^d | 2a | 100 | 0.5 | 163 | 782 | 121 | 2.4 | 31.8 |
| 7 ^e | 2a | 1000 | 0.5 | 130 | 160 | 256 | 2.8 | 30.1 |
| 8 | 2b | 100 | 0.5 | 90 | 432 | 109 | 2.0 | 26.4 |
| 9 | 2c | 100 | 0.5 | 288 | 1382 | 299 | 1.8 | 28.5 |

^a Conditions: Ph₃CB(C₆F₅)₄^tBu₃Al as cocatalyst, catalyst 2.5 μmol, [B]/[Ti] = 2/1, ethylene pressure 4 atm., 20 °C, 5 min, V_{total} = 50 mL. ^b Weight-average molecular weights and polydispersity indexes determined by high temperature GPC at 150 °C in 1,2,4-C₆Cl₃H₃ vs. narrow polystyrene standards. ^c NBE content (mol%) estimated by ¹³C NMR spectra. ^d 40 °C. ^e MMAO as cocatalyst, catalyst 5.0 μmol, 10 min.

Figure 3. ¹³C NMR spectra of E/NBE copolymer with different NBE incorporations produced by **2a** (A, 12.0%, entry 1; B, 24.3%, entry 2; C: 33.8%, entry 4 in Table 3, respectively).



Complex **2b** with a phenyl group in R position showed much lower activity than complex **2a**. The MWs of the resultant copolymers by **2b** were also relatively lower than those by **2a** under similar conditions, whereas the NBE incorporation was higher than that by **2a** (entries 2 vs. 9). Replacement of

a phenyl group at the R position in complex **2b** with a -SiMe₃ group (**2c**) led to higher activity. Moreover, **2c** in combination with Ph₃CB(C₆F₅)₄/ⁱBu₃Al could provide a high molecular weight ethylene-norbornene copolymer, M_w 299 × 10³, with 1380 kg of polymer/mol of cat·h activity at a NBE content of 28.5 mol%.

The typical ¹³C NMR spectra of poly(ethylene-*co*-NBE)s with different NBE incorporations are illustrated in Figure 3. [44–56] Figure 3A showed that the microstructures of the COCs formed using **2a** under low NBE concentration of 0.3 mol/L possessed alternating ethylene-NBE sequences and isolated NBE units. In contrast, resonances ascribed to NBE diads or triads were observed for the copolymers prepared at high NBE concentration of 0.5–1.0 mol/L (Figures 3B–C), and the microstructures thus possessed a mixture of NBE repeat units in addition to the alternating, isolated NBE sequences.

3. Experimental

3.1. General Procedures and Materials

All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. The NMR data of the ligands and complexes used were obtained on a Bruker 300 MHz, 400 MHz or 600 MHz spectrometer at ambient temperature, with CDCl₃ as the solvent (dried by MS 4Å). The NMR data of the polymers were obtained on a Varian Unity-400 MHz spectrometer at 135 °C, with *O*-C₆D₄Cl₂ as a solvent. Elemental analyses were recorded on an elemental Vario EL spectrometer. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific Inc). The weight-average molecular weights (M_w) and the polydispersity indices (PDIs) of polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10-μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd., Kawasaki, Japan). CpTiCl₃ were purchased from Aldrich. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Commercial ethylene was directly used for polymerization without further purification. The other reagents and solvents were commercially available.

3.2. Synthesis of Half-Titanocene Complexes

3.2.1. Synthesis of Ligands **1a–c**

Various Phosphine-thiophenol ([S,P]) ligands bearing different substituents on R position, 2-R-6-(PPh₂)C₆H₃SH (**1a**, R = H; **1b**, R = Ph; **1c**, R = SiMe₃), prepared according to literature procedures [44,48]. Compound **1b** (R = Ph) was prepared via a procedure similar to that for **1a** and the characterizations of the compound are followed:

Synthesis of ligands **1b** (2-Ph-6-(PPh₂)C₆H₃SH). Yield: 68%. ¹H NMR (300 MHz, CDCl₃, 298K): δ 7.49–7.30 (m, 15H, Ar-H), 7.20 (dd, J = 7.6, 1.3 Hz, 1H, Ar-H), 7.08 (t, J = 7.6 Hz, 1H, Ar-H), 6.85–6.78 (m, 1H, Ar-H), 4.38 (s, 1H, SH). ¹³C NMR (101 MHz, CDCl₃, 298K): δ 141.62 (d, J = 3.6 Hz),

141.19 (d, $J = 2.2$ Hz), 138.07, 137.78, 135.66 (d, $J = 9.4$ Hz), 134.10 (d, $J = 19.6$ Hz), 133.19, 130.88, 129.50, 129.18, 128.85 (d, $J = 7.2$ Hz), 128.57, 127.85, 125.06. ^{31}P NMR (162 MHz, CDCl_3 , 298K): $\delta -12.20$. Anal. Calcd. For $\text{C}_{24}\text{H}_{19}\text{PS}$: C, 77.81; H, 5.17. Found: C, 77.85; H, 5.15.

3.2.2. Synthesis of Half-Titanocene Complexes **2a–c**

Synthesis of half-titanocene complex **2a** ($\text{CpTiCl}_2[\text{S-6-(PPh}_2\text{)C}_6\text{H}_4]$). To a stirred solution of 6-(PPh_2) $\text{C}_6\text{H}_4\text{SH}$ (0.294 g, 1.00 mmol) in dried tetrahydrofuran (THF) (15 mL) was added NaH (0.048 g, 2.00 mmol) at 0 °C, and the mixture was allowed to warm up to room temperature and stirred for an additional 6 hours. And then the mixture was filtered to remove residual NaH, and the filtrate cooled to 0°C, and 15 mL THF solution of CpTiCl_3 (0.219 g, 1.00 mmol) was added slowly. The cooler bath was removed, and the resultant mixture was warmed up to room temperature and stirred overnight. The solvents were removed under vacuum, and the residue was extracted with CH_2Cl_2 (3×10 mL). The combined filtrates were concentrated under vacuum to about 5 mL, and 20 mL hexane was layered with this solution for several days at -30 °C to precipitate dark red crystals of **2a** (Yield: 85%). ^1H NMR (300 MHz, CDCl_3 , 298K): δ 7.91–7.79 (m, 4H, Ar-H), 7.61–7.53 (m, 1H, Ar-H), 7.52–7.42 (m, 6H, Ar-H), 7.40–7.36 (m, 1H, Ar-H), 7.35–7.27 (m, 1H, Ar-H), 7.21–7.13 (m, 1H, Ar-H), 6.47 (d, $J = 2.5$ Hz, 5H, C_5H_5). ^{13}C NMR (151 MHz, CDCl_3 , 298K): δ 156.71 (d, $J = 34.2$ Hz), 135.64, 135.28, 133.90 (d, $J = 7.4$ Hz), 131.74, 131.28, 131.06, 129.25 (d, $J = 7.7$ Hz), 128.79 (d, $J = 9.0$ Hz), 125.16, 120.69. ^{31}P NMR (162 MHz, CDCl_3 , 298K): δ 44.33. Anal. Calcd. For $\text{C}_{23}\text{H}_{19}\text{Cl}_2\text{PSTi}$: C, 57.89; H, 4.01. Found: C, 57.98; H, 4.05.

Synthesis of half-titanocene complex **2b** ($\text{CpTiCl}_2[\text{S-2-Ph-6-(PPh}_2\text{)C}_6\text{H}_3]$) was carried out according to the same procedure as that of **2a**, except that 2-Ph-6-(PPh_2) $\text{C}_6\text{H}_3\text{SH}$ (0.370 g, 1.00 mmol) was used in place of 6-(PPh_2) $\text{C}_6\text{H}_4\text{OH}$. Complex **2b** was obtained as black red crystals in 80% yield. ^1H NMR (600 MHz, CDCl_3 , 298K): δ 7.93–7.82 (m, 4H, Ar-H), 7.55 (t, $J = 6.7$ Hz, 1H, Ar-H), 7.49 (m, 6H, Ar-H), 7.41–7.36 (m, 4H, Ar-H), 7.35–7.30 (m, 2H, Ar-H), 7.23 (td, $J = 7.5$, 1.6 Hz, 1H, Ar-H), 6.45 (d, $J = 2.3$ Hz, 5H, C_5H_5). ^{13}C NMR (151 MHz, CDCl_3 , 298K): δ 154.70 (d, $J = 33.6$ Hz), 141.88 (d, $J = 8.5$ Hz), 140.38, 137.56, 137.19, 134.15, 133.53, 131.26, 130.08, 129.52, 128.77 (d, $J = 9.1$ Hz), 128.19, 127.72, 125.61 (d, $J = 6.0$ Hz), 120.47. ^{31}P NMR (162 MHz, CDCl_3 , 298K): δ 43.32. Anal. Calcd. For $\text{C}_{29}\text{H}_{23}\text{Cl}_2\text{PSTi}$: C, 62.95; H, 4.19. Found: C, 62.90; H, 4.23.

Synthesis of half-titanocene complex **2c** ($\text{CpTiCl}_2[\text{S-2-SiMe}_3\text{-6-(PPh}_2\text{)C}_6\text{H}_3]$) was carried out according to the same procedure as that of **2a**, except that 2-SiMe₃-6-(PPh_2) $\text{C}_6\text{H}_3\text{SH}$ (0.367, 1.00 mmol) was used in place of 6-(PPh_2) $\text{C}_6\text{H}_4\text{SH}$. Complex **2c** was obtained as black red crystals in 76% yield. ^1H NMR (300 MHz, CDCl_3 , 298K): δ 7.86–7.81 (m, 4H, Ar-H), 7.61–7.32 (m, 8H, Ar-H), 7.13 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.44 (d, $J = 2.3$ Hz, 5H, C_5H_5), 0.37 (s, 9H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (151 MHz, CDCl_3 , 298K): δ 163.77 (d, $J = 33.6$ Hz), 140.98 (d, $J = 4.5$ Hz), 137.83, 136.26, 135.90, 134.05, 131.92, 131.14, 128.70 (d, $J = 9.0$ Hz), 124.45 (d, $J = 4.1$ Hz), 120.45, -0.17 . ^{31}P NMR (162 MHz, CDCl_3 , 298K): δ 42.53. Anal. Calcd. For $\text{C}_{26}\text{H}_{27}\text{Cl}_2\text{PSSiTi}$: C, 56.84; H, 4.95. Found: C, 56.91; H, 4.91.

3.2.3. Ethylene (Co-)Polymerization

A 200 mL stainless steel autoclave was heated under vacuum up to 150 °C for 6 h and then was cooled to and maintained at the desired reaction temperature. The reactor was charged with toluene and

comonomer if desired under vacuum, and then the stirring motor was engaged to facilitate heat transfer. For single-component trials, a toluene solution of the catalyst was injected to the reactor, for co-catalyst-activated trials, a toluene solution of MMAO or $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/\text{Bu}_3\text{Al}$ was also added, after which ethylene was fed continuously, which was manually adjusted to maintain a desired constant pressure. Temperature control was conducted by internal cooling water coils. After the prescribed reaction time, the stirring motor was stopped and the reactor was vented. The solid polyethylene was obtained by filtration after precipitation from ethanol, washed with ethanol and acetone, dried at 60 °C for 10 h under vacuum.

3.2.4. Crystallographic Studies

Single crystals of complexes **2b**, **2e** and **3g** suitable for X-ray structure determination were grown from CH_2Cl_2 and hexane solution in a glove box, thus maintaining a dry, O_2 -free environment. The crystallographic data, collection parameters, and refinement parameters are listed in Table 1. The intensity data were collected with the ω scan mode (186 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). Lorentz, polarization factors were made for the intensity data, and absorption corrections were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least-squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

4. Conclusions

A series of novel half-titanocene complexes $\text{CpTiCl}_2[\text{S-2-R-6-(PPh}_2\text{)C}_6\text{H}_3]$ ($\text{Cp} = \text{C}_5\text{H}_5$, **2a**, $\text{R} = \text{H}$; **2b**, $\text{R} = \text{SiMe}_3$; **2c**, $\text{R} = \text{Ph}$) have been synthesized in high yields. The ^1H and ^{31}P NMR spectra indicated that the phosphorus is coordinated to titanium in complexes **2a-c**. Additionally molecular structures show that complexes **2a-b** adopted five-coordinate distorted square-pyramid geometry around the titanium center. The complexes **2a-c** were investigated as the catalysts for ethylene polymerization and copolymerization of ethylene with norbornene in the presence of MMAO or $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4/\text{Bu}_3\text{Al}$ as the cocatalyst. All complexes exhibited low to moderate activities towards ethylene polymerization. Note that these complexes displayed moderate to high activities towards copolymerization of ethylene with norbornene, affording relatively high-molecular-weight copolymers with unimodal molecular weight distributions.

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