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# Synthesis of Heterocyclic-Fused Cyclopentadienyl Scandium Complexes and the Catalysis for Copolymerization of Ethylene and Dicyclopentadiene

Runhai Chen,<sup>†,‡</sup> Changguang Yao,<sup>†,||</sup> Meiyang Wang,<sup>§</sup> Hongyan Xie,<sup>†,||</sup> Chunji Wu,<sup>\*,†</sup> and Dongmei Cui<sup>\*,†</sup>

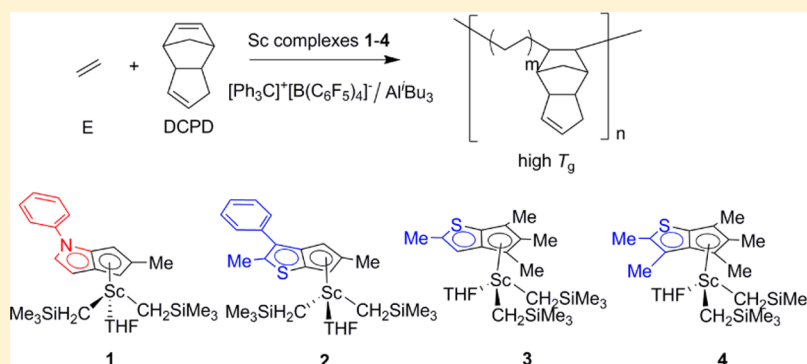
<sup>†</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

<sup>‡</sup>School of Chemical Engineering, Shandong University of Technology, Zibo 255049, People's Republic of China

<sup>§</sup>Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130022, China

<sup>||</sup>University of the Chinese Academy of Sciences, Changchun Branch, Changchun 130022, People's Republic of China

## Supporting Information



**ABSTRACT:** Heterocyclic-fused cyclopentadienyl scandium bis(alkyl) complexes  $L^{1-4}Sc(CH_2SiMe_3)_2THF$  ((5-Me-1-Ph-cyclopenta[*b*]pyrrol-4-yl)Sc( $CH_2SiMe_3$ )<sub>2</sub>THF (1), (2,5-Me<sub>2</sub>-3-Ph-6H-cyclopenta[*b*]thiophenyl)Sc( $CH_2SiMe_3$ )<sub>2</sub>THF (2), (2,4,5,6-Me<sub>4</sub>-4H-cyclopenta[*b*]thiophenyl)Sc( $CH_2SiMe_3$ )<sub>2</sub>THF (3), (2,3,4,5,6-Me<sub>5</sub>-4H-cyclopenta[*b*]thiophenyl)Sc( $CH_2SiMe_3$ )<sub>2</sub>THF (4)) were facilely synthesized by alkane elimination reaction of  $Sc(CH_2SiMe_3)_3(THF)_2$  with the heterocyclic-fused cyclopentadienyl ligands **HL**<sup>1-4</sup> in high yields. Complexes 1–4 were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and X-ray diffraction analyses as THF-solvated monomers, adopting a half-sandwich geometry. Upon activation of  $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ , these half-sandwich scandium complexes displayed various activities toward the copolymerization of ethylene (E) and dicyclopentadiene (DCPD). Complex 1, supported by the phenyl-substituted pyrrole-fused cyclopentadienyl ligand, showed a slightly higher activity than the phenyl-substituted thiophene-fused cyclopentadienyl complex 2. Among the thiophene-fused cyclopentadienyl complexes 2–4, 4, bearing pentamethyl substituents, showed the highest activity of  $2.9 \times 10^6$  g/mol<sub>Sc</sub>·h·bar. The resultant copolymers had adjustable DCPD incorporation varying from 14.0 up to 46.1 mol %, of which the alternating poly(E-*alt*-DCPD) had a high *T*<sub>g</sub> of 166 °C. In addition, no cross-linking was observed in the copolymers, suggesting that these catalytic systems were highly regioselective for the two active double bonds within DCPD.

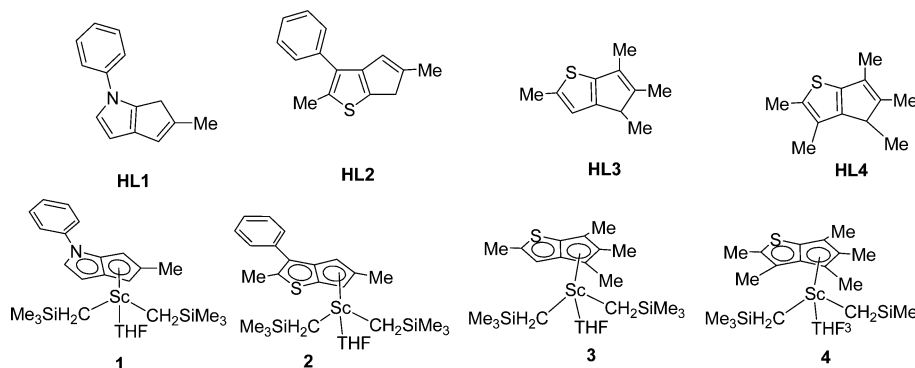
## INTRODUCTION

Dicyclopentadiene (DCPD), generated from spontaneous Diels–Alder reactions of cyclopentadiene, is a major constituent in the C5 stream of naphtha cracking and commercially available at a low price.<sup>1</sup> However, for a long time, the C5 stream has not been used as a chemical source but is incinerated as an energy source. Meanwhile, the copolymerizations of ethylene (E) with cyclic olefins such as norbornene (NB) and DCPD afford typical polymer materials, the cyclic olefin copolymers (COCs), which have found wide applications because of their excellent properties such as high chemical resistance, good UV resistance, low dielectric constant, high

glass transition temperature, excellent transparency, large refractive index, and low birefringence.<sup>2</sup> Among COCs, poly(E-*co*-NB)s have been deeply investigated. High NB incorporation leads to a high glass transition temperature (*T*<sub>g</sub>) but arouses the detrimental effect of increasing brittleness of the material.<sup>3</sup> Compared to poly(E-*co*-NB)s, poly(E-*co*-DCPD)s are more promising and attractive; they possess higher *T*<sub>g</sub>'s at the same incorporation of the cyclic olefins because of the bulkier DCPD, leading to improved mechanical

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Chart 1. Molecular Structure of Thiophene and Pyrrole-Fused Cyclopentadienes and Scandium Complexes 1–4



performances and avoiding the brittleness problem. In addition, poly(*E-co*-DCPD)s bearing reactive double bonds as the side groups readily allow postpolymerization modification to functional polymers. Therefore, polymerizations of DCPD from the C5 stream to afford value-added polymer materials have attracted the increasing interest of both industry and academic fields.

The copolymerization of ethylene and DCPD was originally achieved in 1999 by Shino with zirconocene catalysts such as  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ ,  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ , and  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$  under the activation of MAO, whereas the incorporation of DCPD within the copolymer is low (13 mol %), leading to low  $T_g$  (43.6 °C).<sup>4a</sup> Thereafter, research has been focused on catalyst systems based on group 4 transition metal precursors to improve the catalyst performances.<sup>4,5</sup> The half-sandwich Ti-based catalysts such as  $(t\text{-BuNSiMe}_2\text{CpMe}_4)\text{TiCl}_2$  were investigated, which unfortunately showed low selectivity to the two double bonds of DCPD to give cross-linking products.<sup>4c,d</sup> Breakthrough work was attributed by Hou et al., who used  $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  to obtain the copolymer possessing a high  $T_g$  (125 °C) and high DCPD incorporation of up to 45 mol %.<sup>6</sup> Recently, Li reported a similar copolymer with a 48 mol % DCPD content prepared by using a non-cyclopentadienyl bis( $\beta$ -enaminoketonato) titanium complex combined with MMAO.<sup>5a</sup> To date,  $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  is still the only rare-earth metal catalyst system capable of catalyzing the copolymerization of ethylene and DCPD. Hence, developing novel catalysts for copolymerization of ethylene and DCPD, in particular those based on rare-earth elements, to access COCs with a higher  $T_g$  is a challenging subject.<sup>7</sup>

Monocyclopentadienyl (Cp) half-sandwich rare-earth metal complexes have attracted growing interest. Upon activation with organoborate or  $\text{AlR}_3$ , they generate cationic (or pseudocationic) derivatives that have shown high activities for the homo- and copolymerization of alkenes and styrene.<sup>8–11</sup> The effects of substituents<sup>12a,c,f–h</sup> and the types of heteroatoms<sup>12b,d,e</sup> and the amino or ether functional side arms<sup>8a</sup> on the stability of the active metal centers and their catalytic performances have also been deeply investigated. The heterocyclic-fused cyclopentadienyl ligands have not been employed in constructing rare-earth metal catalysts as far as we know, although heterocyclic-fused cyclopentadienyl ligated Ti or Zr complexes have exhibited enhanced activity for alkene polymerization due to the strong electron-donating nature of the heteroatom-fused cyclopentadienyl rings.<sup>13,14</sup> Herein, we reported the synthesis and characterization of the first half-

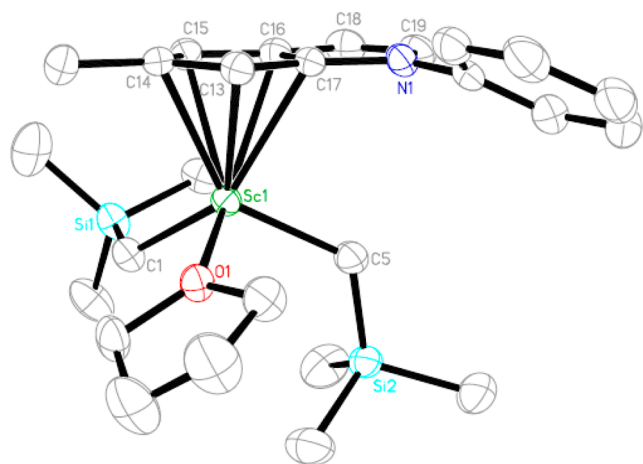
sandwich scandium complexes bearing thiophene- and pyrrole-fused cyclopentadienyl ligands and their catalysis toward the copolymerization of ethylene and DCPD.

## RESULTS AND DISCUSSION

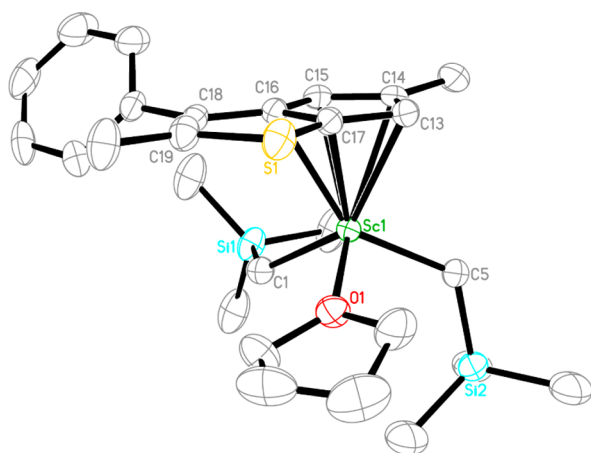
### Synthesis and Characterization of Sc Complexes.

Substituted thiophene- and pyrrole-fused cyclopentadiene compounds (Chart 1) were synthesized according to previously reported methods.<sup>14b,15b</sup> The alkane elimination reaction of compounds **HL**<sup>1–4</sup> with  $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$  at 10 °C for 1 day gave the bis(alkyl) scandium complexes **L**<sup>1–4</sup>  $\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$  ((5-Me-1-Ph-4H-cyclopenta[*b*]pyrrole)- $\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}$  (**1**), (2,5-Me<sub>2</sub>-3-Ph-6H-cyclopenta[*b*]thiophenyl) $\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}$  (**2**), (2,4,5,6-Me<sub>4</sub>-4H-cyclopenta[*b*]thiophenyl) $\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}$  (**3**), (2,3,4,5,6-Me<sub>5</sub>-4H-cyclopenta[*b*]thiophenyl) $\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}$  (**4**)) in high yields (75–95%). All these scandium complexes were fully characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR analyses. The disappearance of the Cp–CH (around 3.0–3.3 ppm) protons of the ligands from the reaction mixture indicates the completeness of the reaction. The methylene protons of the remaining scandium alkyl moieties  $\text{Sc}-\text{CH}_2\text{SiMe}_3$  in all complexes **1–4** appear in the narrow region from –0.2 to –0.4 ppm, while the silyl methyl  $\text{Sc}-\text{CH}_2\text{SiMe}_3$  protons give sharp singlet resonances at the downfield region from 0.2 to 0.3 ppm. It is interesting to note that substituents on cyclopentadiene can significantly affect rotation of the  $\eta^5$ (centroid)–Sc axis. In complexes **1** and **2**, rotation about the  $\eta^5$ (centroid)–Sc axis is so fast that the two  $\text{CH}_2\text{SiMe}_3$  auxiliary ligands are equivalent. However, the two methylene protons on a  $\text{CH}_2\text{SiMe}_3$  are diastereotopic and appear at –0.27/–0.37 and –0.21/–0.26 ppm for **1** and **2**, consequently exhibiting an AB spin pattern, because of planar chirality of the attached  $\eta^5$ -ring. In complex **4**, the rotation about the  $\eta^5$ (centroid)–Sc axis is restricted because of the presence of many methyl groups and the two  $\text{CH}_2\text{SiMe}_3$  are not equivalent. Therefore, two methylene signals are separately observed at –0.25/–0.38 and –0.23 ppm, and one of these exhibits an AB spin pattern, while the other is a singlet (Figures S5 and S6). In complex **3**, the rotation is slow, generating broad methylene signals between the pattern observed for complex **2** and that observed for complex **4**. The <sup>13</sup>C NMR spectra analyses further confirmed the above <sup>1</sup>H NMR analyses. The methylene carbons of  $\text{Sc}-\text{CH}_2\text{SiMe}_3$  in complexes **1–3** show one resonance around 41 ppm, while complex **4** exhibits two signals at 41.14 and 39.68 ppm, and all the signals of the  $\text{SiMe}_3$  fragments appear around 4 ppm.

The molecular structures of complexes **1**, **2**, and **3** were further confirmed by X-ray diffraction analyses. The crystallographic data are summarized in Table S1 (see Supporting Information). The ORTEP drawings of their molecular structures together with the data of the selected bond lengths and angles are shown in Figures 1–3. All complexes exhibit the

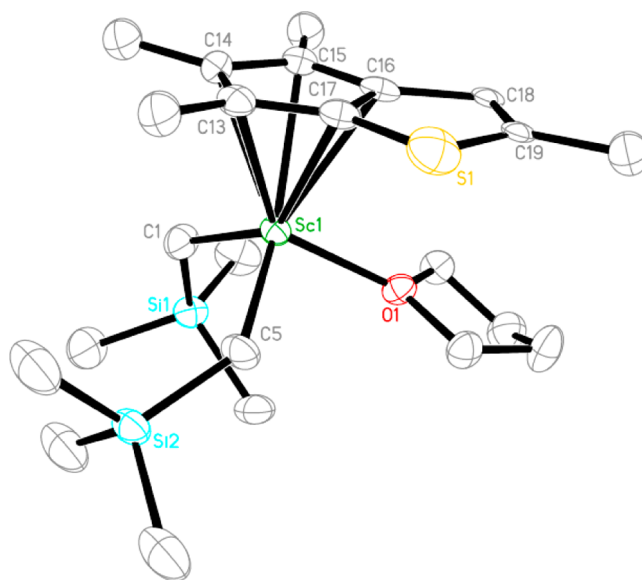


**Figure 1.** Molecular structure of complex **1** with 35% probability thermal ellipsoids; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sc(1)–O(1) 2.164(2), Sc(1)–C(1) 2.211(4), Sc(1)–C(5) 2.223(4), O(1)–Sc(1)–C(1) 96.48(12), O(1)–Sc(1)–C(5) 97.69(13), C(1)–Sc(1)–C(5) 109.32(15), Cp<sub>cent</sub>–Sc(1) 2.204, Cp<sub>cent</sub>–Sc(1)–O(1) 115.45, Cp<sub>cent</sub>–Sc(1)–C(5) 121.22, Cp<sub>cent</sub>–Sc(1)–C(1) 113.15.



**Figure 2.** Molecular structure of complex **2** with 35% probability thermal ellipsoids; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sc(1)–O(1) 2.141(3), Sc(1)–C(1) 2.210(4), Sc(1)–C(5) 2.222(4), O(1)–Sc(1)–C(1) 97.41(12), O(1)–Sc(1)–C(5) 97.64(14), C(1)–Sc(1)–C(5) 110.01(17), Cp<sub>cent</sub>–Sc(1) 2.210, Cp<sub>cent</sub>–Sc(1)–O(1) 112.71, Cp<sub>cent</sub>–Sc(1)–C(5) 117.74, Cp<sub>cent</sub>–Sc(1)–C(1) 117.72.

same geometry model in which the central metal Sc<sup>3+</sup> is coordinated by one η<sup>5</sup>-Cp ring and two alkyl groups and a THF molecule, adopting a pseudotetrahedral geometry in a typical three-legged piano-stool configuration. The heterocyclic-fused cyclopentadienyl ligands hardly influence the interaction between Sc metal and Cp, and the distances from Sc<sup>3+</sup> to the Cp center in the three complexes are around 2.20 Å, comparable to those in cyclopentadienyl ligated Sc complexes (2.177–2.189 Å).<sup>16</sup> However, the phenyl substituents in **1** and



**Figure 3.** Molecular structure of complex **3** with 35% probability thermal ellipsoids; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sc(1)–O(1) 2.160(4), Sc(1)–C(5) 2.219(6), Sc(1)–C(1) 2.225(6), O(1)–Sc(1)–C(5) 95.1(2), O(1)–Sc(1)–C(1) 105.3(2), C(5)–Sc(1)–C(1) 105.9(3), Cp<sub>cent</sub>–Sc 2.202, Cp<sub>cent</sub>–Sc(1)–O(1) 112.89, Cp<sub>cent</sub>–Sc(1)–C(1) 114.94, Cp<sub>cent</sub>–Sc(1)–C(5) 120.16.

**2** are out of the Cp plane relative to those methyl groups, which might arouse steric hindrance for the bulky DCPD monomer coordination to the active metal center, resulting in reduced DCPD incorporation in the copolymer (*vide infra*).

**Copolymerization of Ethylene and Dicyclopentadiene.** As expected, all catalytic systems based on Sc precursors **1**–**4** were low active for the homopolymerization of DCPD to give trace amounts of products (Table 1, entry 1). Meanwhile they could polymerize ethylene to produce low-molecular-weight linear products with moderate activities ( $T_m = 130\text{ }^{\circ}\text{C}$ ) (Table 1, entries 2–5).

To our delight, the copolymerizations of ethylene and DCPD with these catalysts (Scheme 1) under the same polymerization conditions showed much higher activities than both homopolymerizations, consistent with the previously reported “comonomer effect” (entries 7, 10–12),<sup>17</sup> which was partly attributed to the coordination of the cyclic DCPD comonomer to the polyethylene active species, reducing the transition-state energy rather than that of the ethylene monomer.<sup>17c</sup> Molecular weight distributions ( $M_w/M_n$ ) of the obtained copolymers appeared as monomodal in GPC traces ranging from 1.41 to 2.05, indicating the single-site nature of the active species and that the polymerization products are true copolymers not mixtures of the homopolymers.

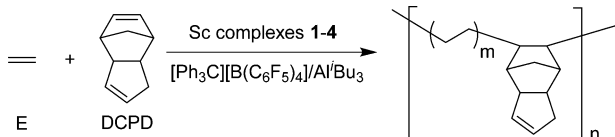
The type of heterocyclic ring slightly affected the catalytic activity. Complex **1**, bearing the pyrrole-fused cyclopentadienyl ligand (**L1**), exhibited a higher activity ( $2.8 \times 10^6\text{ g/mol}_{\text{Sc}}\cdot\text{h}\cdot\text{bar}$ ) than complex **2** ( $1.4 \times 10^6\text{ g/mol}_{\text{Sc}}\cdot\text{h}\cdot\text{bar}$ ), supported by the thiophene-fused cyclopentadienyl ligand (**L2**), which is consistent with the energy levels of HOMOs (highest occupied molecular orbitals) of  $-0.46\text{ eV}$  for **L2** and  $-0.34\text{ eV}$  for **L1** calculated by DFT (see Supporting Information). For the thiophene-fused cyclopentadienyl complexes, an increasing copolymerization activity from  $1.4 \times 10^6\text{ g/mol}_{\text{Sc}}\cdot\text{h}\cdot\text{bar}$  for **2** and  $2.2 \times 10^6\text{ g/mol}_{\text{Sc}}\cdot\text{h}\cdot\text{bar}$  for **3** to  $2.9 \times 10^6\text{ g/mol}_{\text{Sc}}\cdot\text{h}\cdot\text{bar}$  for

**Table 1.** Copolymerization of Ethylene and DCPD by Complexes 1–4/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Al<sup>i</sup>Bu<sub>3</sub><sup>a</sup>

entry	catalyst	$f_{\text{DCPD}}^b$ (mmol)	activity <sup>b</sup>	$F_{\text{DCPD}}^c$ (mol %)	$M_n^d$ (kg/mol)	$M_w/M_n^d$	$T_g^e/T_m^f$
1	1–4	10	trace	100			
2	1	0	0.7	0	1.7	2.42	130 <sup>h</sup>
3	2	0	0.4	0	3.6	2.94	130 <sup>h</sup>
4	3	0	0.8	0	4.2	2.85	130 <sup>h</sup>
5	4	0	0.9	0	5.0	3.10	130 <sup>h</sup>
6	1	10	2.4	14.6	14.0	1.50	32
7	1	20	2.8	27.7	23.1	1.70	86
8	1	40	2.3	32.8	27.4	1.90	111
9	1	60	2.3	34.2	46.6	2.05	124
10	2	20	1.4	29.1	30.2	1.71	95
11	3	20	2.2	38.0	14.4	1.67	112
12	4	20	2.9	37.8	13.7	1.56	123
13	4	10	2.2	28.0	9.1	1.65	94
14	4	40	2.5	45.7	24.6	1.51	162
15	4	60	2.5	46.1	29.8	1.81	166
16 <sup>e</sup>	4	20	2.2	41.5	12.2	1.53	139
17 <sup>f</sup>	4	20	1.8	44.2	7.6	1.70	151

<sup>a</sup>Polymerization conditions: 30 mL of toluene, 10  $\mu$ mol of Sc, 10  $\mu$ mol of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], 100  $\mu$ mol of Al<sup>i</sup>Bu<sub>3</sub>, 1 atm of ethylene, 40  $^{\circ}$ C, polymerization time 5 min. <sup>b</sup>In unit of 10<sup>6</sup> g/mol<sub>Sc</sub>·h·bar. <sup>c</sup>Determined by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> at 25  $^{\circ}$ C. <sup>d</sup>Measured by GPC in THF at 40  $^{\circ}$ C using the polystyrene standard. <sup>e</sup>Polymerization temperature 60  $^{\circ}$ C. <sup>f</sup>Polymerization temperature 80  $^{\circ}$ C. <sup>g</sup>Determined by DSC. <sup>h</sup>Melting point for PE.

#### Scheme 1. Copolymerization of Ethylene and Dicyclopentadiene with Sc Catalysts 1–4

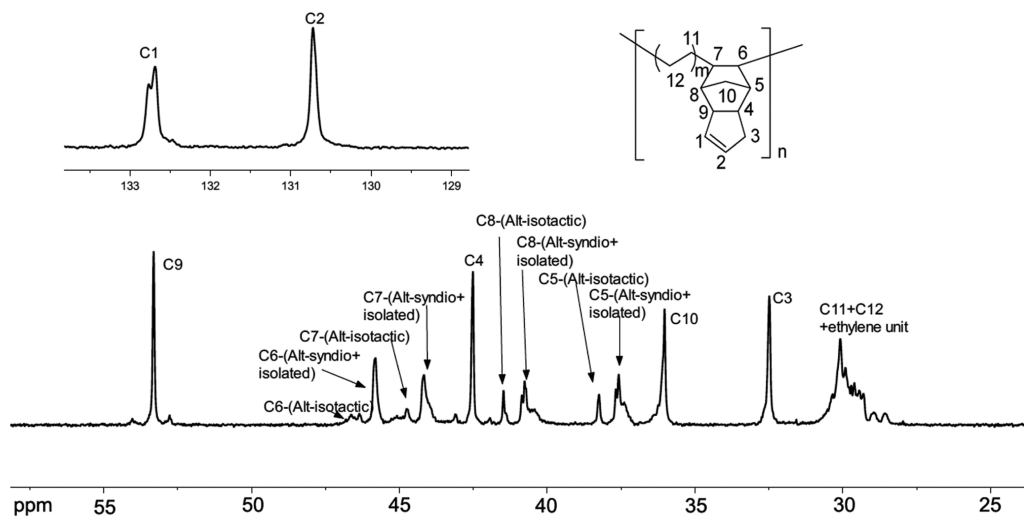


4 is observed due to the increasing ligand electron-donating ability of thiophene-fused cyclopentadienyl rings (see Supporting Information). Such an electronic effect has also been observed in the previous reports that the electron-donating ligands facilitate propylene insertion.<sup>14d</sup> DCPD incorporation

in copolymer is also affected by catalyst structure. Complexes 3 and 4 afforded the copolymers with higher comonomer incorporation (38.0 mol % for 3 and 37.8 mol % for 4) relative to 1 (27.7 mol %) and 2 (29.1 mol %) under the same conditions. The enhancement of DCPD incorporation for catalysts 3 and 4 may be caused by the methyl-substituted heterocyclic Cp ligands that are planar and provide a more opened coordination sphere as compared with the phenyl-substituted heterocyclic Cp ligands, where the phenyl group deviates from the Cp plane to create a more crowded environment for the coordination and insertion of the bulky DCPD monomer (*vide supra*). A similar observation has been reported in copolymerization of ethylene and DCPD using non-cyclopentadienyl titanium catalysts.<sup>5e</sup>

Besides the structural factors, polymerization conditions also affected the catalytic performances. It seemed that increasing the DCPD feed amount from 10 to 20 mmol would arouse rapid polymerization for both complexes 1 and 4 (Table 1, entries 6–9 vs entries 12–15), whereas the activity remained unchanged with further loading of DCPD. In contrast, the content of DCPD in the copolymer continuously increased despite the ligand frameworks, which reached up to 34.2 mol % and 46.1 mol % when 60 mmol of DCPD was added into 1 and 4 catalytic systems, respectively. At elevated temperatures, the catalytic activity decreased while the incorporation of DCPD in copolymer increased (entries 16, 17), which might be ascribed to low ethylene solubility in the reaction media, while the molecular weight of the copolymer dropped significantly as chain transfer/termination reactions became active at high temperature.

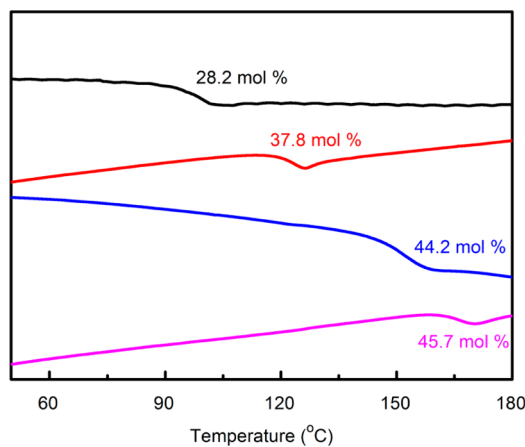
It is found that the NMR spectra of the polymer samples obtained from the four catalyst systems were similar. In the <sup>1</sup>H NMR spectrum, two double-bond resonances at  $\delta$  5.5–5.8 ppm are clearly observed arising from the cyclopentene units (Figure S7 in the Supporting Information), indicating that the vinyl-polymerization reaction of DCPD occurred regioselectively. It is seen virtually that no broad alkyl group signal at  $\delta$  0.6–3.4 ppm and deep valley around  $\delta$  1.75 ppm are observed, suggesting that no continuous DCPD–DCPD units are present in the copolymer chains.<sup>18</sup> This is consistent with the fact that the present catalyst systems are active for E–DCPD copolymerization but show very low activity toward DCPD

**Figure 4.** <sup>13</sup>C NMR spectrum of poly(E-*alt*-DCPD) copolymer (entry 12).



homopolymerization. The resonances at  $\delta$  130.7 and 132.7 ppm in the  $^{13}\text{C}$  NMR spectrum further prove the DCPD incorporation into the ethylene chain with the *endo*-configuration, as shown in Figure 4.<sup>19</sup> In addition, the peak at  $\delta$  1.3 ppm in the  $^1\text{H}$  NMR and a strong resonance at  $\delta$  30 ppm in the  $^{13}\text{C}$  NMR spectrum of the copolymer were assigned to the continuous ethylene units.<sup>18</sup> On the basis of the above NMR spectroscopy analysis, it can be safely concluded that the obtained poly(E-*co*-DCPD) comprises discrete DCPD units separated by polyethylene units. Therefore, when the DCPD content in the copolymer was close to 50 mol % (46.1 mol %), the alternating microstructure was formed.

All the copolymer products are amorphous without melting temperature, and glass transition temperature ( $T_g$ ) values fall in the range 86–166 °C (Figure 5). The higher the incorporation



**Figure 5.** DSC curves of the poly(E-*alt*-DCPD)s with various DCPD incorporations.

of DCPD in the copolymers, the higher the  $T_g$  of the resulting copolymer. The highest  $T_g$  of 166 °C was observed from the sample with the 46.1 mol % DCPD content, which is comparable to the value reported in a patent but much higher than those found in the poly(E-*alt*-DCPD) isolated from the catalyst system composed of the half-sandwich scandium complex bearing a  $\text{SiMe}_3$ -substituted cyclopentadienyl ligand (125 °C).<sup>6</sup> The high  $T_g$  value of the obtained poly(E-*alt*-DCPD) could be mainly attributed to the stereorestructures (the high tacticity) of the copolymer; however, a quantitative assignment of the tacticity of the copolymer is difficult. With respect to the previous work on copolymerization of ethylene and DCPD catalyzed by a silylmethyl-substituted Cp-supported scandium system,<sup>6</sup> we demonstrated in this work that by designing new rare-earth metal catalysts bearing modified heterocyclic-fused Cp rings, the competitive high catalytic activity and DCPD incorporation in the copolymer could be realized and, particularly, the more a stereoregular alternating structure in the poly(E-*co*-DCPD) might be generated; thus the poly(E-*alt*-DCPD) with higher  $T_g$  even at the same DCPD incorporation can be obtained.

## CONCLUSIONS

In summary, we have successfully synthesized and characterized new half-sandwich scandium complexes **1–4** bearing pyrrole- and thiophene-fused cyclopentadienyl rings to achieve the controlled and regioselective copolymerization of ethylene and dicyclopentadiene by giving linear products. Introduction of

methyl groups on the heterocyclic rings is crucial to establish an effective catalyst system having high activity ( $2.9 \times 10^6$  g/mol $_{\text{Sc}}$ ·h-bar) and a high comonomer insertion ratio (45.7 mol %). Therefore, the alternating poly(E-*alt*-DCPD) copolymer with a high  $T_g$  of 166 °C can be achieved under high DCPD feeding. We present here a strategy for designing new half-sandwich rare-earth metal catalysts by modification of the Cp ring with heterocyclic fusion, and the resultant catalytic precursors may be used in a broad spectrum of applications in the catalytic polymerizations.

## EXPERIMENTAL SECTION

**General Methods.** All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. All solvents were purified with an MBraun SPS system. DCPD used for the polymerization reaction was purchased from Aldrich and purified over a Na/K alloy.  $\text{Al}^i\text{Bu}_3$  (1.0 M in hexane) and  $\text{LiCH}_2\text{SiMe}_3$  solution (1.0 M in pentane) were purchased from Aldrich. Polymerization grade ethylene was donated by the China Petroleum & Chemical Corporation.  $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$  was prepared according to the literature.<sup>20</sup>  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  was synthesized following the literature procedure.<sup>21</sup> Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ) spectrometer. Variable-temperature  $^1\text{H}$  NMR spectra of complex **4** in  $\text{C}_7\text{D}_8$  were performed on a Bruker AV400 over a temperature range from –60 to 50 °C. Elemental analyses were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). The molecular weight and molecular weight distribution of the polymers were measured by a TOSOH HLC-8220 GPC. Differential scanning calorimetry (DSC) analyses were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10 °C/min.

**X-ray Crystallographic Studies.** Crystals for X-ray analysis were obtained by recrystallization in hexane at low temperature. The crystals were manipulated in a glovebox. Data collections were performed at –88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on  $F^2$  anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The methyl carbon atoms (C2, C3, C4, C6, C7, and C8 in **2**) of  $\text{SiMe}_3$  groups were disordered and were refined with 50% occupancy anisotropically for all the atoms in complex **2**.

**Synthesis of Complexes.** **Complex 1.** Under a nitrogen atmosphere, to a hexane solution (10 mL) of  $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$  (0.90 g, 2.0 mmol) was added slowly at room temperature 1 equiv of HL1 (0.39 g, 2.0 mmol). The mixture was stirred overnight to afford a yellow solution. Removal of solvent gave the yellow solid, and the analytically pure compound was obtained through recrystallization in hexane at –30 °C in 95% (0.92 g) yield.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.28 (d,  $J = 8.4$  Hz, 2H, Ph-*H*), 7.14 (t,  $J = 8.8$  Hz, 2H, Ph-*H*), 6.92 (d,  $J = 3.2$  Hz, 1H, pyrrole-*H*), 6.87 (t,  $J = 7.6$  Hz, 1H, Ph-*H*), 6.20 (d,  $J = 3.2$  Hz, 1H, pyrrole-*H*), 6.12 (s, 1H, Cp-*H*), 6.04 (s, 1H, Cp-*H*), 3.47 (br s, 4H, THF), 2.44 (s, 3H,  $\text{CH}_3$ ), 1.11 (br s, 4H, THF), 0.30 (s, 18H,  $\text{CH}_2\text{SiMe}_3$ ), –0.27 and –0.37 (AB,  $J_{\text{H-H}} = 11.2$  Hz, 4H,  $\text{ScCH}_2\text{SiMe}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  141.30, 131.69, 129.75, 126.06, 124.81, 123.38, 122.47, 117.80, 102.31, 95.21, 90.63, 71.31 (s, THF), 40.54 (1C,  $\text{Sc-CH}_2\text{SiMe}_3$ ), 24.79 (s, THF), 16.74, 4.15 (s, 3C,  $\text{CH}_2\text{SiMe}_3$ ) ppm. Anal. Calcd for

$C_{26}H_{41}NOScSi_2$  (%): C, 64.42; H, 8.53; N, 2.89. Found: C, 64.68; H, 8.52; N, 3.04.

**Complex 2.** Under a nitrogen atmosphere, to a hexane solution (10 mL) of  $Sc(CH_2SiMe_3)_3(THF)_2$  (0.90 g, 2.0 mmol) was added slowly at room temperature 1 equiv of HL2 (0.45 g, 2.0 mmol). The mixture was stirred 1 day to afford a light yellow solution. Removal of solvent gave a light yellow solid, and analytically pure compound was obtained through recrystallization in hexane at  $-30\text{ }^\circ\text{C}$  (0.81 g, 78%).  $^1H$  NMR (400 MHz,  $C_6D_6$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  7.50 (dd,  $J = 8.0, 1.2\text{ Hz}$ , 2H, Ph-H), 7.26 (td,  $J = 8.0, 1.6\text{ Hz}$ , 2H, Ph-H), 7.11 (tt,  $J = 8.0, 1.6\text{ Hz}$ , 1H, Ph-H), 6.32 (d,  $J = 1.6\text{ Hz}$ , 1H, Cp-H), 6.24 (d,  $J = 1.6\text{ Hz}$ , 1H, Cp-H), 3.43 (br s, 4H, THF), 2.36 (s, 3H,  $CH_3$ ), 2.25 (s, 3H,  $CH_3$ ), 1.07 (br s, 4H, THF), 0.28 (s, 18H,  $CH_2SiMe_3$ ),  $-0.21$  and  $-0.26$  (AB,  $^2J_{H-H} = 12.0\text{ Hz}$ , 4H,  $ScCH_2SiMe_3$ ) ppm.  $^{13}C$  NMR (100 MHz,  $C_6D_6$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  136.50, 135.38, 135.08, 129.21, 129.06, 128.79, 127.06, 123.13, 101.15, 100.33, 71.64 (s, THF), 41.86 (1C,  $Sc-CH_2SiMe_3$ ), 24.82 (s, THF), 16.51, 15.29, 4.04 (s, 3C,  $CH_2SiMe_3$ ) ppm. Anal. Calcd for  $C_{27}H_{42}OSScSi_2$  (%): C, 62.87; H, 8.21. Found: C, 62.68; H, 8.52.

**Complex 3.** The complex was synthesized using the same conditions and procedure as for complex 2 using HL3. The product was obtained as a yellow solid in 78% yield.  $^1H$  NMR (400 MHz,  $C_6D_6$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  6.32 (s, 1H, Cp-H), 3.53 (br s, 4H, THF), 2.30 (s, 3H,  $CH_3$ ), 2.17 (s, 3H,  $CH_3$ ), 2.16 (s, 3H,  $CH_3$ ), 2.15 (s, 3H,  $CH_3$ ), 1.18 (br s, 4H, THF), 0.29 (s, 18H,  $CH_2SiMe_3$ ),  $-0.29$  (s, 4H,  $ScCH_2SiMe_3$ ) ppm.  $^{13}C$  NMR (100 MHz,  $C_6D_6$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  138.05, 132.61, 125.94, 123.86, 116.28, 109.68, 109.13, 71.16 (s, THF), 41.14 (s, 1C,  $Sc-CH_2SiMe_3$ ), 24.94 (s, THF), 16.54, 13.40, 13.12, 12.56, 4.29 (s, 3C,  $CH_2SiMe_3$ ) ppm. Anal. Calcd for  $C_{23}H_{42}OSScSi_2$  (%): C, 59.06; H, 9.05. Found: C, 59.33; H, 8.79.

**Complex 4.** The complex was synthesized using the same conditions and procedure as for complex 3 using HL4. The product was obtained as a pale yellow solid in 85% yield.  $^1H$  NMR (400 MHz,  $C_6D_6$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  3.59 (d, 2H,  $J = 8.0\text{ Hz}$ , THF), 3.50 (d, 2H,  $J = 8.0\text{ Hz}$ , THF), 2.41 (s, 3H,  $CH_3$ ), 2.19 (s, 3H,  $CH_3$ ), 2.15 (s, 3H,  $CH_3$ ), 2.09 (s, 3H,  $CH_3$ ), 2.02 (s, 3H,  $CH_3$ ), 1.19 (br s, 4H, THF), 0.29 (s, 18H,  $CH_2SiMe_3$ ),  $-0.23$  (s, 2H,  $ScCH_2SiMe_3$ ),  $-0.25$  and  $-0.38$  (AB,  $^2J_{H-H} = 12.0\text{ Hz}$ , 2H,  $ScCH_2SiMe_3$ ) ppm.  $^{13}C$  NMR (100 MHz,  $C_6D_6$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  133.31, 130.43, 126.24, 124.77, 121.75, 110.13, 109.28, 71.53 (s, THF), 41.14 (s,  $CH_2SiMe_3$ ), 39.68 (s,  $CH_2SiMe_3$ ), 24.96 (s, THF), 13.87, 13.30, 12.95, 12.68, 12.33, 4.34 (s, 3C,  $CH_2SiMe_3$ ) ppm. Anal. Calcd for  $C_{24}H_{44}OSScSi_2$  (%): C, 59.83; H, 9.21. Found: C, 60.14; H, 8.95.

**Ethylene/DCPD Copolymerization Procedure.** A detailed polymerization procedure is described as a typical example (run 7 in Table 1). In the glovebox, a Schlenk bottle containing a magnetic stirring bar was charged with a toluene solution (30 mL) of DCPD (2.64 g, 20 mmol) and  $Al^iBu_3$  (0.05 mL, 50  $\mu\text{mol}$ , 1.0 M in hexane). The reactor was equipped with an ampule bottle filled with 2 mL of a toluene solution of complex 1 (4.9 mg, 10  $\mu\text{mol}$ ),  $Al^iBu_3$  (0.05 mL, 50  $\mu\text{mol}$ , 1.0 M in hexane), and  $[Ph_3C][B(C_6F_5)_4]$  (9.2 mg, 10  $\mu\text{mol}$ ). The reactor was taken out of the glovebox, connected to the Schlenk line, and set in the thermostated oil bath ( $40\text{ }^\circ\text{C}$ ). The solution was degassed and then saturated with ethylene (1 atm) three times under vigorous stirring. The solution of the catalyst system was quickly transferred to the polymerization bottle to initiate the polymerization. The polymerization was quenched after 5 min by addition of acidified ethanol (200 mL). The precipitated polymer was filtered and washed with ethanol and then dried under vacuum at  $40\text{ }^\circ\text{C}$  for several hours.

## ■ ASSOCIATED CONTENT

### Supporting Information

CIF files, crystal data and structure refinement for Sc complexes 1–3,  $^1H$  NMR of Sc complexes 1–4, synthesis and characterization of ligands, NMR spectra of representative polymers, and DFT calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*(C. Wu) E-mail: wuchunji@ciac.ac.cn.

\*(D. Cui) Fax: +86-431-85262774. E-mail: dmcui@ciac.ac.cn.

### Notes

The authors declare no competing financial interest.

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