

## Thiophene C–H Activation as a Chain-Transfer Mechanism in Ethylene Polymerization: Catalytic Formation of Thienyl-Capped Polyethylene<sup>†</sup>

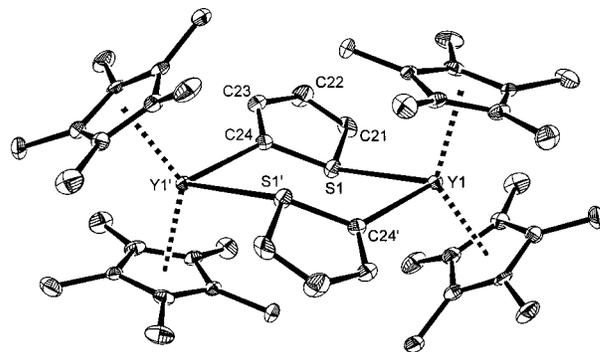
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Metallocene alkyls and hydrides of the group 3 metals and trivalent lanthanides can be considered to be neutral analogues of the cationic group 4 metallocene 14-electron species that are well-known for their efficiency in catalytic olefin polymerization.<sup>1</sup> The bis(pentamethylcyclopentadienyl) lanthanide hydrides [Cp\*<sub>2</sub>-LnH]<sub>2</sub> (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) are highly active species for the polymerization of ethylene to high molecular weight polyethylene,<sup>2</sup> but they (and their related alkyl derivatives) can also readily effect hydrocarbon C–H activation.<sup>2–5</sup> This reduces their efficiency in the polymerization of α-olefins such as propene, as inactive η<sup>3</sup>-allyl species are formed upon chain termination by allylic C–H activation of the substrate.<sup>2,4</sup> In this contribution we show that this ability to perform C–H activation can be used to provide an effective chain-transfer mechanism in the catalytic polymerization of ethylene. The Cp\*<sub>2</sub>La-system was found to be able to combine ethylene polymerization and C–H activation of thiophene to result in catalytic formation of polyethylene with 2-thienyl end-groups. This represents an alternative way to introduce a heteroatom functionality into polyethylene. Functionalized polyethylenes are of interest as a means to improve adhesive properties and dyeability of polyolefin materials.<sup>6</sup>

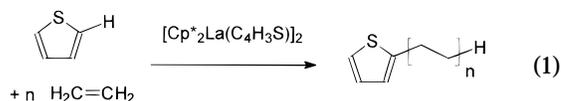
Thiophene is readily metalated on the 2-position by [Cp\*<sub>2</sub>YH]<sub>2</sub>, liberating dihydrogen, and the THF-adduct Cp\*<sub>2</sub>Y(2-C<sub>4</sub>H<sub>3</sub>S)(THF) was reported earlier by our group.<sup>5</sup> In the absence of Lewis bases other than thiophene, the sparingly soluble dimeric [Cp\*<sub>2</sub>Y(μ-C<sub>4</sub>H<sub>3</sub>S)]<sub>2</sub> (**1**) is formed, which was characterized by X-ray diffraction (Figure 1).<sup>7</sup> The thienyl moieties in **1** form C,S bridges between the two metal centers, resulting in a Y<sub>2</sub>C<sub>2</sub>S<sub>2</sub> six-membered ring in a chair conformation. The dimer readily forms



**Figure 1.** Molecular structure of **1**. Selected interatomic distances (Å) and angles (deg): Y(1)–C(24') = 2.452(8), Y(1)–S(1) = 2.951(2), C(21)–C(22) = 1.37(1), C(22)–C(23) = 1.42(1), C(23)–C(24) = 1.38(1), S(1)–Y(1)–C(24') = 78.3(2), Y(1)–C(24)–C(23) = 123.9(6), Y(1)–S(1)–C(24) = 130.8(3), Y(1)–S(1)–C(21) = 111.5(3), C(21)–S(1)–C(24) = 96.8(4).

the monomeric THF adduct on addition of THF, demonstrating that the thiophene/thienyl sulfur can act as a Lewis base toward the group 3 metal center, but that it is considerably more weakly bound than THF. For the larger metal lanthanum it was found that, in a reaction similar to that of yttrium, decamethyl lanthanocene hydride [Cp\*<sub>2</sub>LaH]<sub>2</sub><sup>2c</sup> reacts readily with thiophene in benzene or toluene solvent to give the 2-thienyl complex [Cp\*<sub>2</sub>-La(2-C<sub>4</sub>H<sub>3</sub>S)]<sub>2</sub> (**2**).<sup>8</sup>

The reaction of the yttrium 2-thienyl complex **1** in neat thiophene at 80 °C with 1 bar of ethylene was extremely sluggish, but with the lanthanum 2-thienyl complex **2** this resulted in a clear solution containing a distribution of 2-(*n*-alkyl)-thiophenes of formula H(CH<sub>2</sub>CH<sub>2</sub>)<sub>*n*</sub>(2-C<sub>4</sub>H<sub>3</sub>S) (eq 1). This was seen by GC/



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(6) For recent work on the metal-catalyzed or -mediated preparation of polyolefins containing functionalities, see: (a) Aaltonen, P.; Fink, G.; Löfgren, B.; Seppälä, J. *Macromolecules* **1996**, *29*, 5255. (b) Schneider, M. J.; Schaefer, R.; Mühlaupt, R. *Polymer* **1997**, *38*, 2455. (c) Stehling, U.; Stein, K. M.; Fischer, D.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 14. (d) Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N. *Macromolecules* **1992**, *25*, 5115. (e) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(7) Crystal data: (C<sub>24</sub>H<sub>33</sub>SY)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>; space group C2/c; monoclinic; a = 15.929(1) Å, b = 14.396(1) Å, c = 21.442(1) Å, β = 107.186(6)°, V = 4697.4(5) Å<sup>3</sup> at 130 K, Z = 4. Final refinement on F<sup>2</sup> converged at R<sub>w</sub>(F<sup>2</sup>) = 0.2146 for 5193 reflections with F<sub>o</sub><sup>2</sup> ≥ 0 and 272 parameters, and R(F) = 0.0998 for 4112 reflections with F<sub>o</sub> ≥ 4.0 σ(F<sub>o</sub>). A more accurate structure determination was hampered by the small crystal size and moderate crystal quality.

MS analysis, by comparison with a number of independently prepared 2-(*n*-alkyl)-thiophenes and by quantification through use of an internal standard (cyclooctane). The oligomer distribution follows a Flory–Schultz distribution with [C<sub>*n*+2</sub>]/[C<sub>*n*</sub>] = 0.43(2) for the C<sub>6</sub>–C<sub>14</sub> 2-alkyl substituents, but with a noticeable excess of the 2-ethyl (and to a lesser extent the 2-butyl) thiophene (Figure 2a).

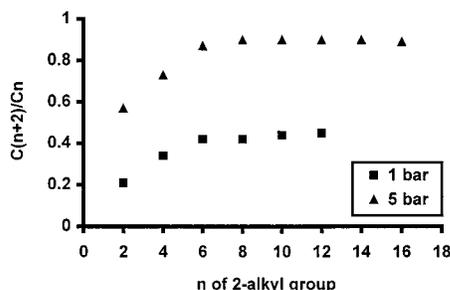
Solid products with higher molecular weights were obtained from autoclave experiments at 80 °C in neat thiophene and at ethylene pressures of 2.5, 5.0, and 7.5 bar. Yields and molecular weight data are listed in Table 1. <sup>1</sup>H and <sup>13</sup>C NMR spectra of these materials (which could be completely dissolved in C<sub>2</sub>D<sub>2</sub>-Cl<sub>4</sub> at 95 °C) are fully consistent with those of CH<sub>3</sub>(CH<sub>2</sub>)<sub>*n*</sub>CH<sub>2</sub>-(2-thienyl) species, and vinylic or internal olefinic end groups were not observed. In the <sup>1</sup>H NMR spectra a good intensity match was found for the 2-alkylthiophene α-CH<sub>2</sub> protons (δ 2.76 ppm) and the methyl protons of the aliphatic end-group (δ 0.93 ppm). These features indicate that C–H activation of thiophene is indeed the only chain-transfer mechanism that is in operation and that

(8) Synthesis of **2**. To a suspension of [Cp\*<sub>2</sub>LaH]<sub>2</sub> (0.979 g, 2.39 mmol La) in 60 mL of toluene, 0.5 mL of thiophene was added at ambient temperature. The solution was stirred for 15 min during which time it was degassed several times. A white solid gradually precipitated. Concentrating the solution and cooling to –70 °C yielded 0.830 g (1.69 mmol La, 71%) of white solid **2**. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 80 °C) δ 7.33 (m, 2H, thienyl CH), 7.22 (m, 1H, thienyl CH), 1.95 (s, 30H, Cp\*). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 80 °C) δ 194.4 (br s, *ipso* thienyl C), 135.86 (d, J<sub>CH</sub> = 158.5 Hz, thienyl CH), 130.60 (d, J<sub>CH</sub> = 158.5 Hz, thienyl CH), 126.37 (d, J<sub>CH</sub> = 180.7 Hz, thienyl CH), 121.17 (Cp\* C), 11.30 (q, J<sub>CH</sub> = 125.6 Hz, Cp\* Me).

**Table 1.** Ethylene Conversion by **2** in the Presence of Thiophene<sup>a</sup>

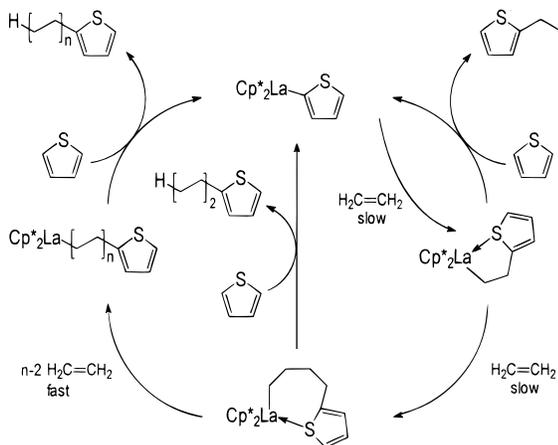
<i>p</i> (ethylene) (atm)	thiophene:toluene (% vol)	run time (h)	yield (g)	productivity (g mmol <sup>-1</sup> h <sup>-1</sup> )	<i>M<sub>n</sub></i> <sup>b</sup>	<i>M<sub>w</sub></i> <sup>b</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>
2.5	100:0	2.0	0.815	5.0	700 <sup>c</sup>		
5.0	100:0	2.0	1.609	10.1	700 <sup>c</sup>		
7.5	100:0	2.0	4.363	27.0	950, <sup>c</sup> 910	1300	1.4 <sup>d</sup>
7.5	100:0	0.2	0.551	34.0			
7.5	20:80	0.2	1.594	98.4	1320	2110	1.6 <sup>d</sup>
7.5	10:90	0.2	1.645	101.5	1630	3330	2.0
7.5	0:100	0.2	1.658	102.3	3430	14500	4.2

<sup>a</sup> Conditions: 81 μmol La, 5 mL of solvent, 80 °C. <sup>b</sup> Determined by GPC (1,2,4-trichlorobenzene, 150 °C) unless mentioned otherwise. <sup>c</sup> Determined by NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 95 °C). <sup>d</sup> Product distribution narrowed due to loss of low molecular weight products upon workup.



**Figure 2.**  $[C_{n+2}]/[C_n]$  as function of *n* for the distributions of 2-*n*-alkylthiophenes formed by **2** in neat thiophene at 80 °C: (■) 1 bar ethylene, (▲) 5 bar ethylene (soluble fraction).

### Scheme 1



all polyethylene chains formed under these conditions are capped on one side by a thienyl group. <sup>1</sup>H NMR also shows that small amounts (up to 5%, by integration) of 2,5-dialkylthiophene products are formed. Lowering the thiophene concentration (by performing reactions in mixtures of toluene and thiophene) resulted in an increase of productivity and of molecular weight (Table 1).

The soluble part of the reaction mixtures obtained in neat thiophene at higher pressures was analyzed by GC, again showing the presence of a clear excess of 2-ethylthiophene (and to a lesser extent of 2-butylthiophene) over that expected for a Flory–Schultz type chain-length distribution (Figure 2b). This suggests that in the first and second ethylene insertion products, intramolecular coordination of the thienyl sulfur gives additional stabilization to the Cp\*<sub>2</sub>La(CH<sub>2</sub>CH<sub>2</sub>)<sub>*n*</sub>(C<sub>4</sub>H<sub>3</sub>S) species over those for *n* > 2. This can lead to an increased ethylene insertion barrier into the La–C bond of these species and the production of a relatively large amount of 2-ethyl and 2-butyl thiophene.

These observations, and the absence of either high molecular weight polyethylene or linear olefins from the reaction mixture, suggest that three elementary reaction steps operate under these conditions. These are (a) insertion of ethylene into the La–thienyl La–C bond (initiation), (b) subsequent insertions of ethylene into the La–alkyl species thus formed (chain growth), and (c) C–H

activation of thiophene by the La–alkyl species, liberating the polymer as alkane and regenerating the La–thienyl species (chain transfer). The initiation step (a) is likely to be the slowest step in the sequence. In an NMR-tube experiment in which **2** was reacted with 1 equiv/La of ethylene in C<sub>6</sub>D<sub>6</sub> in the absence of thiophene, the first insertion product was not observed. Instead, a small amount of insoluble polymer is formed. Due to intramolecular coordination of the thienyl sulfur, the second and third ethylene insertions are noticeably slower than the following ones. This leads to a reaction sequence as shown (slightly simplified) in Scheme 1. The substantial increase of catalyst productivity upon lowering the thiophene concentration suggests that significant inhibition of the ethylene insertion occurs by reversible coordination of thiophene to the La–alkyl species.

The combination of ethylene conversion and C–H activation of another heteroaromatic, pyridine, was reported previously (both with neutral yttrocene<sup>9</sup> and cationic zirconocene species,<sup>10</sup> the latter requiring the presence of a catalytic amount of H<sub>2</sub>), but due to the high stability of the first insertion product of ethylene into the M–pyridyl bond (by intramolecular N-coordination of the pyridyl group) this yields 2-ethyl-pyridine with only traces of higher alkyl products. The weaker and softer Lewis basic characteristics of thiophene readily allow the formation of higher molecular weight products. In that sense the system behaves more like the lanthanide metallocene<sup>11</sup> and Cp–amide titanium<sup>12</sup> catalyzed conversion of olefins and silanes to silyl-terminated polyolefins, where the more active Si–H bond performs the chain-transfer reaction. Notable differences with the system described here are that with the silane chain-transfer the H-atom is transferred to the metal rather than to the alkyl chain and that the silane is unlikely to show a strong inhibition due to reversible coordination to the reaction intermediates.

This reversible coordination, combined with the fact that for the La/thiophene system initiation requires the (relatively slow) initial insertion into the La–C(sp<sup>2</sup>) bond of the thienyl species, makes the activity of the catalytic system presented here modest. Nevertheless, the catalyst seems quite robust under the applied conditions (even in neat thiophene, as seen by comparing the productivities at 7.5 bar over 2 and 0.2 h, Table 1), and good quantities of the thienyl-capped polyethylene can be obtained easily. Although the thienyl functionality is quite apolar, it is amenable to further functionalization, and we are presently exploring the possibilities of using these materials to prepare polyethylene with more polar functional caps.

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**Supporting Information Available:** Synthetic procedures for **1** and **2**, polymerization procedures, and characterization data for the materials produced. Crystal structure data for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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