

# Synthesis, Characterization, and Heterobimetallic Cooperation in a Titanium–Chromium Catalyst for Highly Branched Polyethylenes

Shaofeng Liu,<sup>†</sup> Alessandro Motta,<sup>†,‡</sup> Massimiliano Delferro,<sup>\*,†</sup> and Tobin J. Marks<sup>\*,†</sup>

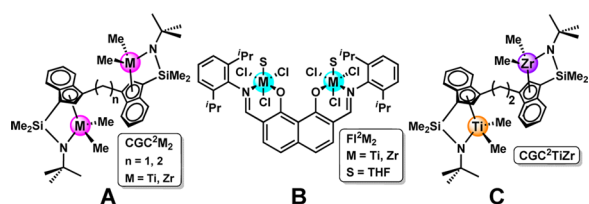
<sup>†</sup>Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, United States

<sup>‡</sup>Dipartimento di Scienze Chimiche, Università di Catania and INSTM, UdR Catania, 95125 Catania, Italy

**S** Supporting Information

**ABSTRACT:** A heterobimetallic catalyst, {Ti–Cr}, consisting of a constrained-geometry titanium olefin polymerization center (CGC<sup>Et</sup>Ti) covalently linked to a chromium bis(thioether)amine ethylene trimerization center (SNSCr) was synthesized and fully characterized. In ethylene homopolymerizations it affords linear low-density polyethylene with molecular weights as high as 460 kg·mol<sup>-1</sup> and exclusively *n*-butyl branches in conversion-insensitive densities of ~18 branches/1000 carbon atoms, which are ~17 and ~3 times (conversion-dependent), respectively, those achieved by tandem mononuclear CGC<sup>Et</sup>Ti and SNSCr catalysts under identical reaction conditions.

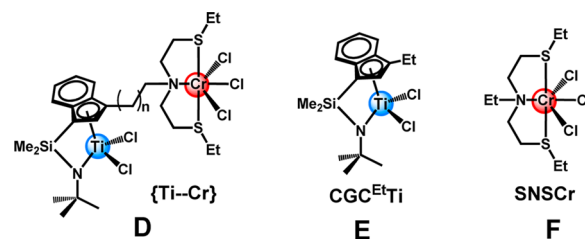
Group 4 homobimetallic polymerization catalysts based on bisconstrained-geometry catalyst (CGC)<sup>1</sup> or bis(phenoxyiminato)<sup>2</sup> scaffolds [e.g., CGC<sup>2</sup>M<sub>2</sub> (A), FI<sup>2</sup>M<sub>2</sub> (B), M = Ti, Zr] have been characterized, and cooperativity effects between adjacent catalytic centers shown to induce significant molecular mass and enchainment selectivity enhancements in ethylene homopolymerizations and ethylene +  $\alpha$ -olefin copolymerizations versus the analogous mononuclear catalysts.<sup>3</sup>



In contrast to this homobimetallic approach, heterobimetallic polymerization catalysts in principle offer new pathways for comonomer introduction and copolymer synthesis.<sup>4</sup> In the only example to date, modest but distinctive cooperative effects were observed in CGC<sup>2</sup>TiZr-mediated polymerizations (C).<sup>5</sup> Whereas the isolated mononuclear Ti centers afford narrow-polydispersity index (PDI), high-*M<sub>w</sub>* polyethylenes (PEs) with moderate comonomer enchainment activity and the isolated Zr centers produce low-*M<sub>w</sub>*, larger-PDI PEs with vinylene end groups, CGC<sup>2</sup>TiZr produces monomodal, significantly higher *M<sub>w</sub>* PEs than simple mononuclear catalyst mixtures but with only ~2 branches ( $\geq C_6$ ) per 1000 C atoms, reflecting the limited activity and chain-transfer characteristics of CGCZr centers.<sup>3c</sup>

Mixtures of homogeneous oligomerization and polymerization catalysts (tandem catalysts) are of interest for copolymer

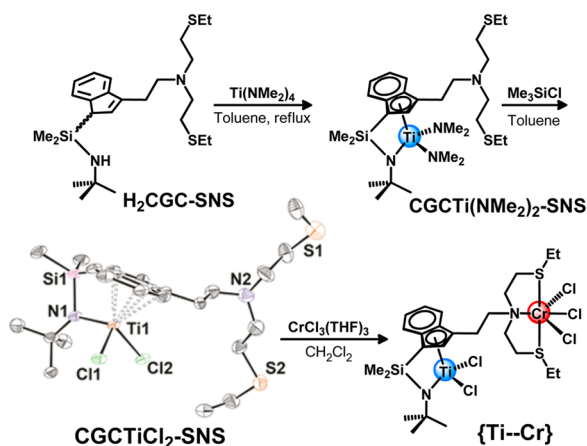
synthesis since they utilize ethylene as the only feed.<sup>6</sup> However, coupling of intermolecular elimination with re-enchainment sequences is typically challenged by the low probability that the product of one catalytic center can be efficiently captured by the other in dilute solutions. In principle, multimetallic catalysts<sup>3,7</sup> could provide such products if centers having significantly different catalytic characteristics were held proximate. To explore modes of delivering significant quantities of precisely defined short-chain oligomers to nearby CGCTi polymerization centers via mechanisms different from group 4,<sup>8</sup> we envisioned heterobimetallic catalyst **D** that combines the aforementioned properties of CGCTi-type catalysts (**E**) with a selective ethylene trimerization catalyst<sup>6a,9</sup> such as the Cr(III) catalyst SNSCr (**F**).<sup>10</sup> Here we report on the cooperative properties of the first group 4–group 6 heterobimetallic olefin polymerization catalyst, {Ti–Cr} (**D**, *n* = 1), which covalently joins CGC<sup>Et</sup>Ti and SNSCr centers. It is shown that {Ti–Cr} affords high-*M<sub>w</sub>* PEs with selective, conversion-insensitive, enhanced intramolecular *n*-butyl (>99% C<sub>4</sub>) branch introduction, in contrast to the E + F tandem system, which under identical conditions yields lower-*M<sub>w</sub>* PEs with conversion-sensitive introduction of significantly less dense intermolecular branching.



The synthesis of the binuclear ligand H<sub>2</sub>CGC–SNS is shown in Scheme S1 in the Supporting Information (SI). Condensation of 3-(2-aminoethyl)indene hydrobromide (**1**) with 2.0 equiv of 1-(ethylthio)-2-bromoethane yielded 3-[(EtSCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>]indene (**2**). H<sub>2</sub>CGC–SNS was then synthesized by <sup>n</sup>BuLi deprotonation of **2** followed by sequential addition of Me<sub>2</sub>SiCl<sub>2</sub> and <sup>t</sup>BuNH<sub>2</sub>. All of the products were characterized by conventional spectroscopic/analytical methodologies (see the SI). {Ti–Cr} was synthesized as shown in Scheme 1. The monometallic amido complex CGCTi(NMe<sub>2</sub>)<sub>2</sub>–SNS was prepared by protodeamination of Ti(NMe<sub>2</sub>)<sub>4</sub> with H<sub>2</sub>CGC–SNS in refluxing toluene with

Received: April 21, 2013

Scheme 1. Synthesis of the Heterobimetallic Catalyst {Ti--Cr}



constant removal of the byproduct  $\text{HNMe}_2$  (Figures S5 and S6).<sup>11</sup> The reaction of  $\text{CGCTi}(\text{NMe}_2)_2\text{-SNS}$  with excess  $\text{Me}_3\text{SiCl}$  gave  $\text{CGCTiCl}_2\text{-SNS}$  (Figures S7 and S8).  $\text{CGCTiCl}_2\text{-SNS}$  crystals were obtained from hexane solution, and an ORTEP plot is shown in Scheme 1 (also see Figure S1). Subsequent reaction with  $\text{CrCl}_3(\text{THF})_3$  afforded dark-red paramagnetic {Ti--Cr}, the constitution of which was confirmed by elemental analysis (Ti, Cr, C, H, N),  $^1\text{H}$  NMR spectroscopy (very broad), and MALDI-TOF mass spectrometry (Figure S9). {Ti--Cr} exhibits stability in coordinating solvents, as confirmed by  $^1\text{H}$  NMR analysis in  $\text{THF-}d_8$ , where the  $\text{CrCl}_3$  moiety is not displaced by the solvent (Figure S10).

In initial experiments, ethylene polymerizations/oligomerizations were carried out with a suite of controls to probe cooperative enchainment effects, using a conventional methylaluminoxane (MAO) cocatalyst/activator under rigorously anhydrous/anaerobic conditions, and attending to exothermic and mass-transfer effects.<sup>3,12</sup> Catalysts were investigated under varied reaction conditions, including the Al:M ratio ( $M = \text{Ti, Cr}$ ), reaction temperature (25, 80 °C; Table S3), ethylene pressure (1, 3, 5, 8 atm; Table S3), and reaction time (5, 10, 20, 60 min). The overall optimum catalytic performance (activity, branches per 1000 C atoms,  $M_w$ , PDI, cooperative effects) was achieved with Al:M = 500 at 80 °C under a constant ethylene pressure of 8.0 atm. The data in Table 1 indicate that ethylene homopolymerizations mediated by mononuclear  $\text{CGC}^{\text{Et}}\text{Ti}$  and

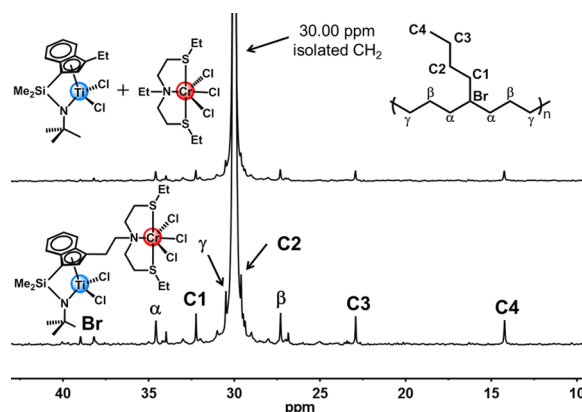


Figure 1.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 120 °C) of PEs produced by the  $\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$  and {Ti--Cr} catalysts (Table 1, entries 4 and 7), scaled to the PE  $\text{CH}_2$  backbone resonance at 30 ppm.

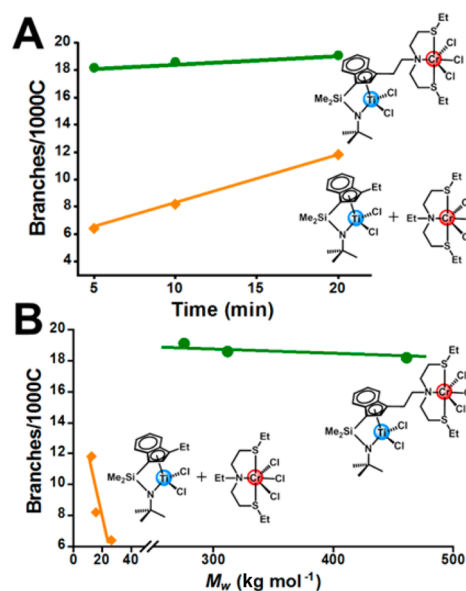


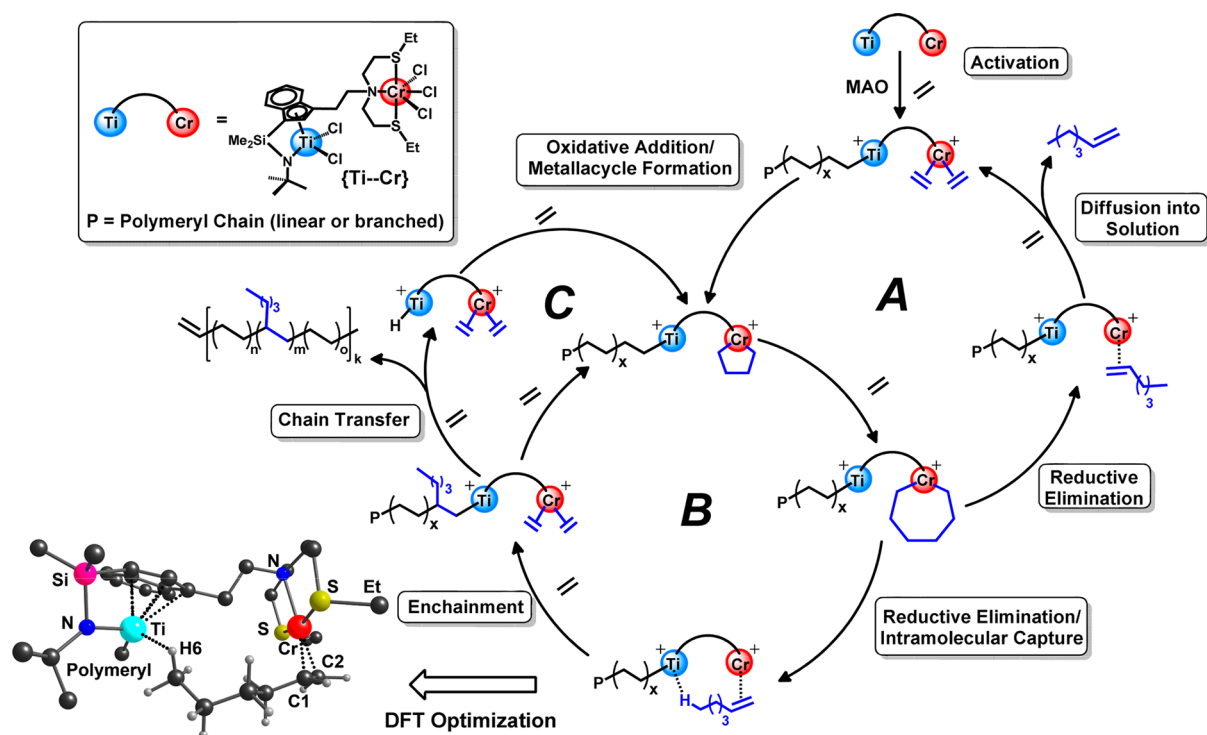
Figure 2. (A) PE branch densities ( $\rho_{\text{br}}$ ) introduced by  $\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$  and {Ti--Cr} as functions of reaction time at  $P_{\text{ethylene}} = 8.0$  atm (Table 1, entries 4–9). (B) Relationship of  $\rho_{\text{br}}$  and  $M_w$  for  $\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$  and {Ti--Cr} in the same reactions.

Table 1. Ethylene Polymerization Data for Catalysts  $\text{CGC}^{\text{Et}}\text{Ti}$ ,  $\text{CGCTiCl}_2\text{-SNS}$ ,  $\text{SNSCr}$ , 1:1  $\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$ , and {Ti--Cr}<sup>a</sup>

entry	catalyst	$t$ (min)	PE (g)	activity (PE) <sup>b</sup>	oligomers (g) <sup>c</sup>	activity (oligomers) <sup>d</sup>	$\rho_{\text{br}}^e$	$M_w$ (kg·mol <sup>-1</sup> ) <sup>f</sup>	PDI <sup>f</sup>	$T_m$ (°C) <sup>g</sup>
1	$\text{CGC}^{\text{Et}}\text{Ti}$	5	6.500	975.0	—	—	0	42.0	2.5	128.4
2	$\text{CGCTiCl}_2\text{-SNS}$	5	0.054	8.1	—	—	0	76.9	3.2	136.8
3	$\text{SNSCr}$	5	0.045	6.7	0.490	73.5	0	143.7	2.2	133.6
4	$\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$	5	3.200	480.0	0.204	30.6	6.4	26.2	2.3	125.9
5	$\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$	10	5.950	446.0	0.382	28.6	8.2	15.3	2.5	123.2
6	$\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$	20	10.80	405.0	0.720	27.0	11.8	12.5	2.3	121.9
7	{Ti--Cr}	5	0.184	27.6	0.075	11.3	18.2	461.3	2.5	123.5
8	{Ti--Cr}	10	0.359	26.9	0.138	10.4	18.6	312.1	2.5	119.2
9	{Ti--Cr}	20	0.672	25.2	0.272	10.2	19.1	276.4	3.2	117.5
10	{Ti--Cr}	60	1.440	18.0	0.474	5.9	18.9	365.5	1.9	121.6

<sup>a</sup>Conditions: 10  $\mu\text{mol}$  of catalyst (10  $\mu\text{mol}$  of each component for  $\text{CGC}^{\text{Et}}\text{Ti} + \text{SNSCr}$ ) with MAO/catalyst = 500 in 50 mL of toluene at 80 °C with  $P_{\text{ethylene}} = 8$  atm. Each entry was performed in duplicate. <sup>b</sup>In units of (kg of PE)·(mol of catalyst)<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup>. <sup>c</sup>As determined by GC-TOF with mesitylene added as an internal standard. The selectivity for 1-hexene ranged from 53% (entry 3) to 98% (entries 7–9). <sup>d</sup>In units of (kg of oligomer)·(mol of catalyst)<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup>. <sup>e</sup>Branch density (number of branches per 1000 C atoms) as determined by  $^{13}\text{C}$  NMR analysis.<sup>19f</sup>As determined by triple-detection GPC. <sup>g</sup>Melting temperature as determined by differential scanning calorimetry.

Scheme 2. Scenario for Altered Ethylene Polymerization Propagation and Chain-Transfer Processes at the Heterobimetallic {Ti--Cr} Catalyst



CGCTiCl<sub>2</sub>–SNS afforded relatively high-*M<sub>w</sub>*, high-melting PEs with negligible chain branching (Table 1, entries 1 and 2). For all of the polymerizations, the monomodal gel-permeation chromatography (GPC) traces and product PDIs are consistent with single-site processes (Figure S11)<sup>3a,13</sup> and catalyst deactivation processes that are minor under the conditions examined, even at longer polymerization times (Table 1, entry 10 and Figures S12 and S13). Furthermore, the <sup>1</sup>H NMR spectra of the PEs produced by both the CGC<sup>Et</sup>Ti + SNSCr tandem catalyst and the {Ti--Cr} heterobimetallic catalyst exhibit vinylene (–CH<sub>2</sub>CH=CH<sub>2</sub>) and vinylidene [–CH<sub>2</sub>C(R)=CH<sub>2</sub>] end-group distributions, with the former predominating (Figure S14). This indicates that β-hydride elimination is the dominant chain-transfer pathway<sup>14</sup> and that chain transfer to alkyl-Al is negligible.<sup>15</sup>

Under the present polymerization conditions, the Cr catalysts in either the tandem or bimetallic systems display good selectivity for ethylene trimerization (72–98% 1-hexene as determined by NMR spectroscopy and GC–TOF; Table S4). Under these conditions, monometallic SNSCr is known to be somewhat less selective for 1-hexene (53% in our hands) and also to produce small amounts (~9%) of high-*M<sub>w</sub>* PE.<sup>6,16,17</sup> More importantly, comparison of the tandem and heterobimetallic polymerization data (Table 1 entries 4–6 vs 7–9) shows that {Ti--Cr} consistently produces higher-*M<sub>w</sub>* products under all conditions by a factor of ~20 but with ~18-fold lower activity; the latter is likely due to steric constraints and competition by 1-hexene (vide infra), both of which should retard the polymerization rate.<sup>1,18</sup> Furthermore, the very different polymerization characteristics of the {Ti--Cr} and CGCTiCl<sub>2</sub>–SNS catalysts (e.g., entry 7 vs 2) argue that the SNSCr center remains intact during the polymerization. In regard to the copolymerization selectivity, Table 1 (entries 4–6 vs 7–9) and the PE <sup>13</sup>C NMR spectra (Figure 1) show that {Ti--Cr} enchainment ~18.6 *n*-butyl

branches/1000 C atoms, with a <1% yield of branches of any other length. Also, the branch density ( $\rho_{br}$ ) is essentially independent of reaction time and conversion despite increasing concentrations of available “free” oligomer (Tables 1 and S5 and Figure S16). In contrast, the tandem CGC<sup>Et</sup>Ti + SNSCr system introduces far lower  $\rho_{br}$  under identical reaction conditions (e.g., 6.4 *n*-butyl branches/1000 C atoms; Table 1, entry 4 and Figure 1) despite the far higher “free” oligomer concentrations. Also, the  $\rho_{br}$  values obtained with the tandem system are far more conversion-sensitive (Table 1, entries 4–6; Table S5; and Figure S16), and differences in product microstructure are also evident in the product melting points (Table 1 and Figure S15).

Taken together, these results argue that covalently linking the metallic sites in {Ti--Cr} spatially confined the catalytic centers in such a way that the efficiency of intramolecular comonomer transfer to the CGCTi center is significantly increased, with high selectivity for the C<sub>6</sub> comonomer. The fact that the PE  $\rho_{br}$  introduced by {Ti--Cr} remains essentially constant with increasing reaction time (Table 1, entries 7–9; Figure 2A; Table S5 and Figure S16) argues that the “local concentration” of  $\alpha$ -olefin remains nearly constant. Also, even though increasing the “free” oligomer concentration/reaction time depresses the copolymer *M<sub>w</sub>* and activity in the tandem system, as is typical for CGCTi catalysts,<sup>20</sup> this has little effect on the heterobimetallic catalyst (Figure 2B). Clearly, the presence of the tethered SNSCr oligomerization center dramatically alters both the propagation and chain-transfer characteristics of the mononuclear CGCTi catalyst, producing higher-*M<sub>w</sub>* copolymers with higher C<sub>4</sub>-only branching densities. To probe further the integrity of 1-hexene transfer at {Ti--Cr}, 0.10 M 1-pentene was added to the polymerization and allowed to compete with the 1-hexene produced by the Cr catalytic center (see the SI). In these experiments, the CGC<sup>Et</sup>Ti + SNSCr tandem catalyst yields PEs with 68.0 branches/1000 C atoms, of which 91% were *n*-propyl



(Figure S17), consistent with intermolecular  $\alpha$ -olefin capture. In contrast, under identical conditions, {Ti--Cr} produces PE with 26.4 branches/1000 C atoms, of which only 35% were *n*-propyl (Figure S13), and the 1-hexene enchainment density is nearly unchanged from the experiments without pentene (17.4 *n*-butyl/1000 C atoms; Figure S17 and Table 1, entries 7–9).

Scheme 2 presents a tentative scenario to accommodate the above observations. C<sub>6</sub> fragments are produced by established sequences<sup>8</sup> of reductive ethylene coupling and metallocyclopentane expansion to a metallocycloheptane followed by reductive elimination (cycle A → B), yielding 1-hexene, which can either “leak” from the immediate {Ti--Cr} environment or be captured/enchained at the CGCTi center. The present data do not distinguish between concerted or stepwise reductive elimination and 1-hexene capture or even Ti-mediated metallocycloheptane opening. However, preliminary density functional theory (DFT) calculations<sup>21</sup> identify an energetic minimum in which 1-hexene is  $\pi$ -bound to the Cr center while engaging in a –CH<sub>3</sub>...M agostic interaction with Ti (Ti...Cr distance = 6.35 Å, Scheme 2 inset). This transfer process is efficient enough to limit enchainment of exogenous  $\alpha$ -olefin, as evidenced by the near-constant *n*-butyl branch content and PE *M<sub>w</sub>* as conversion progresses and by the 1-pentene competition results.

In summary, we report a heterobimetallic catalyst linking single-site Ti constrained-geometry and Cr bis(thioether)amine centers. This catalyst selectively produces *n*-butyl-branched polyethylenes from ethylene as the only feed with conversion-insensitive *M<sub>w</sub>*'s and branch densities that are ~17 and ~3 times, respectively, those achieved using the analogous tandem catalyst. The results argue that proximity of the catalytic centers dramatically alters the propagation and chain-transfer characteristics of the heterobimetallic catalyst.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental details and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

m-delferro@northwestern.edu; t-marks@northwestern.edu

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support by NSF (CHE-1213235) is gratefully acknowledged. Purchases of the NMR and GC–TOF instrumentation at IMSERC were supported by NSF (CHE-1048773 and CHE-0923236, respectively). We acknowledge CINECA Award HP10CPZK0T 2012 for the availability of high-performance computing resources and support.

## ■ REFERENCES

- (1) (a) Nomura, K.; Liu, J.-Y. *Dalton Trans.* **2011**, 40, 7666. (b) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, 250, 2691.
- (2) (a) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem. Rev.* **2011**, 111, 2363. (b) Makio, H.; Fujita, T. *Acc. Chem. Res.* **2009**, 42, 1532.
- (3) (a) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, 111, 2450. (b) Li, H.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, 103, 15295. (c) Li, H.; Stern, C. L.; Marks, T. J. *Macromolecules* **2005**, 38, 9015.

(4) Conventionally, LLDPE is produced via copolymerization of ethylene with  $\alpha$ -olefin comonomers. Single-site homogeneous CGCs are particularly well-suited for this purpose because the open coordination spheres afford enhanced  $\alpha$ -olefin selectivity. See: Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Y. *Eur. Pat. Appl. EP416815A2*, 1991.

(5) Wang, J.; Li, H. B.; Guo, N.; Li, L. T.; Stern, C. L.; Marks, T. J. *Organometallics* **2004**, 23, 5112.

(6) (a) McGuinness, D. S. *Chem. Rev.* **2010**, 111, 2321. (b) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, 105, 1001.

(c) Schwerdtfeger, E. D.; Price, C. J.; Chai, J. F.; Miller, S. A. *Macromolecules* **2010**, 43, 4838.

(7) (a) Mandal, S. K.; Roesky, H. W. *Acc. Chem. Res.* **2010**, 43, 248. (b) Mitić, N.; Smith, S. J.; Neves, A.; Guddat, L. W.; Gahan, L. R.; Schenk, G. *Chem. Rev.* **2006**, 106, 3338.

(8) (a) Yang, Y.; Liu, Z.; Zhong, L.; Qiu, P. Y.; Dong, Q.; Cheng, R. H.; Vanderbilt, J.; Liu, B. P. *Organometallics* **2011**, 30, 5297. (b) Arteaga-Muller, R.; Tsurugi, H.; Saito, T.; Yanagawa, M.; Oda, S.; Mashima, K. *J. Am. Chem. Soc.* **2009**, 131, 5370. (c) McGuinness, D. S.; Suttill, J. A.; Gardiner, M. G.; Davies, N. W. *Organometallics* **2008**, 27, 4238. (d) Agapie, T.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2007**, 129, 14281. (e) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Haasbroek, D.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H. *J. Am. Chem. Soc.* **2005**, 127, 10723. (f) Blok, A. N. J.; Budzelaar, P. H. M.; Gal, A. W. *Organometallics* **2003**, 22, 2564.

(9) (a) Agapie, T. *Coord. Chem. Rev.* **2011**, 255, 861. (b) Wass, D. F. *Dalton Trans.* **2007**, 816. (c) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, 689, 3641.

(10) (a) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *J. Am. Chem. Soc.* **2006**, 128, 9238. (b) McGuinness, D. S.; Brown, D. B.; Toozee, R. P.; Hess, F. M.; Dixon, J. T.; Slawin, A. M. Z. *Organometallics* **2006**, 25, 3605. (c) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *J. Am. Chem. Soc.* **2003**, 125, 5272.

(11) Li, H.; Li, L.; Marks, T. J.; Liable-Sands, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, 125, 10788.

(12) (a) Weberski, M. P.; Chen, C.; Delferro, M.; Marks, T. J. *Chem.—Eur. J.* **2012**, 18, 10715. (b) Weberski, M. P.; Chen, C.; Delferro, M.; Zuccaccia, C.; Macchioni, A.; Marks, T. J. *Organometallics* **2012**, 31, 3773.

(13) (a) Kaminsky, W. *Macromolecules* **2012**, 45, 3289. (b) Chen, E. Y.-X. *Chem. Rev.* **2009**, 109, 5157. (c) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, 100, 1391.

(14) Liu, Z.; Somsok, E.; White, C. B.; Rosaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, 123, 11193.

(15) Bochmann, M. *Organometallics* **2010**, 29, 4711.

(16) The characteristics of the PE produced by the SNSCr catalyst (*M<sub>w</sub>*,  $\rho_{br}$ , *T<sub>m</sub>*) are completely different from those obtained using the tandem and bimetallic systems.

(17) (a) Bowen, L. E.; Charernsuk, M.; Hey, T. W.; McMullin, C. L.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2010**, 39, 560. (b) Wohl, A.; Muller, W.; Peitz, S.; Peulecke, N.; Aluri, B. R.; Muller, B. H.; Heller, D.; Rosenthal, U.; Al-Hazmi, M. H.; Mosa, F. M. *Chem.—Eur. J.* **2010**, 16, 7833. (c) Walsh, R.; Morgan, D. H.; Bollmann, A.; Dixon, J. T. *Appl. Catal., A* **2006**, 306, 184.

(18) Möhring, P. C.; Coville, N. J. *Coord. Chem. Rev.* **2006**, 250, 18.

(19) Seger, M. R.; Maciel, G. E. *Anal. Chem.* **2004**, 76, 5734.

(20) Copolymerization of ethylene with 1-hexene (~0.5 M) catalyzed by CGC<sup>Et</sup>Ti/MAO exhibits behavior similar to the tandem system: decreased activity [360 (kg of PE)·(mol of catalyst)<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup>] and *M<sub>w</sub>* (18.5 kg·mol<sup>-1</sup>, PDI = 1.94) vs ethylene homopolymerizations, along with C<sub>4</sub> branch introduction (46.1 branches/1000 C atoms).

(21) Motta, A.; Fragala, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, 131, 3974.