JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Synthesis, Characterization, and Heterobimetallic Cooperation in a Titanium–Chromium Catalyst for Highly Branched Polyethylenes

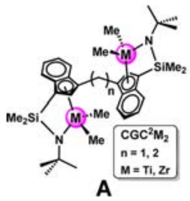
Shaofeng Liu,[†] Alessandro Motta,[†,‡] Massimiliano Delferro,*[,†] and Tobin J. Marks*[,†]

[†]Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, United States
[‡]Dipartimento di Scienze Chimiche, Università di Catania and INSTM, UdR Catania, 95125 Catania, Italy

Supporting Information

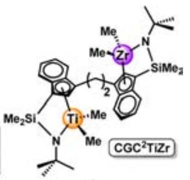
ABSTRACT: A heterobimetallic catalyst, **{Ti--Cr}**, consisting of a constrained-geometry titanium olefin polymerization center (**CGC^{Et}Ti**) covalently linked to a chromium bis(thioether)amine ethylene trimerization center (**SNSCr**) was synthesized and fully characterized. In ethylene homopolymerizations it affords linear low-density polyethylene with molecular weights as high as 460 kg·mol^{-1} 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^{Et}Ti** and **SNSCr** catalysts under identical reaction conditions.

Group 4 *homobinuclear* polymerization catalysts based on bisconstrained-geometry catalyst (CGC)[1] or bis(phenoxyiminato)[2] scaffolds [e.g., **CGC^{2}M$_2$** (**A**), **FI^{2}M$_2$** (**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 + α-olefin copolymerizations versus the analogous mononuclear catalysts.[3]



A

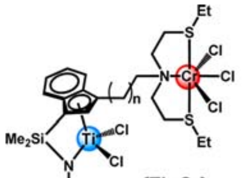
B



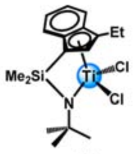
C

In contrast to this homobimetallic approach, *heterobimetallic* polymerization catalysts in principle offer new pathways for comonomer introduction and copolymer synthesis.[4] In the only example to date, modest but distinctive cooperative effects were observed in **CGC^{2}TiZr**-mediated polymerizations (**C**).[5] Whereas the isolated mononuclear Ti centers afford narrow-polydispersity index (PDI), high-M_w polyethylenes (PEs) with moderate comonomer enchainment activity and the isolated Zr centers produce low-M_w, larger-PDI PEs with vinylene end groups, **CGC^{2}TiZr** produces monomodal, significantly higher M_w PEs than simple mononuclear catalyst mixtures but with only ∼2 branches (≥C$_6$) per 1000 C atoms, reflecting the limited activity and chain-transfer characteristics of **CGCZr** centers.[3c]

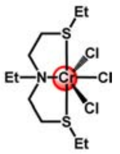
Mixtures of homogeneous oligomerization and polymerization catalysts (tandem catalysts) are of interest for copolymer synthesis since they utilize ethylene as the only feed.[6] However, coupling of intermolecular elimination with re-enchainment sequences is typically challenged by the low probability that the product of one catalytic center can be efficiently captured by the other in dilute solutions. In principle, multimetallic catalysts[3,7] 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,[8] we envisioned heterobimetallic catalyst **D** that combines the aforementioned properties of **CGCTi**-type catalysts (**E**) with a selective ethylene trimerization catalyst[6a,9] such as the Cr(III) catalyst **SNSCr** (**F**).[10] 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^{Et}Ti** and **SNSCr** centers. It is shown that **{Ti--Cr}** affords high-M_w PEs with selective, conversion-insensitive, enhanced intramolecular *n*-butyl (>99% C$_4$) branch introduction, in contrast to the **E** + **F** tandem system, which under identical conditions yields lower-M_w PEs with conversion-sensitive introduction of significantly less dense intermolecular branching.



{Ti--Cr}
D



CGC^{Et}Ti
E

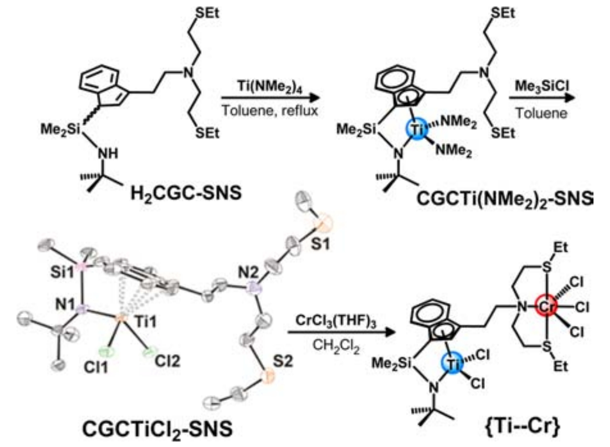


SNSCr
F

The synthesis of the binuclear ligand **H$_2$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$_2$CH$_2$)$_2$NCH$_2$CH$_2$]indene (**2**). **H$_2$CGC–SNS** was then synthesized by ^{n}BuLi deprotonation of **2** followed by sequential addition of Me$_2$SiCl$_2$ and ^{t}BuNH$_2$. 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$_2$)$_2$–SNS** was prepared by protodeamination of Ti(NMe$_2$)$_4$ with **H$_2$CGC–SNS** in refluxing toluene with

Received: April 21, 2013
Published: May 27, 2013

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



constant removal of the byproduct $HNMe_2$ (Figures S5 and S6).[11] The reaction of **CGCTi(NMe$_2$)$_2$−SNS** with excess Me_3SiCl gave **CGCTiCl$_2$−SNS** (Figures S7 and S8). **CGCTiCl$_2$−SNS** crystals were obtained from hexane solution, and an ORTEP plot is shown in Scheme 1 (also see Figure S1). Subsequent reaction with $CrCl_3(THF)_3$ afforded dark-red paramagnetic **{Ti--Cr}**, the constitution of which was confirmed by elemental analysis (Ti, Cr, C, H, N), ^{1}H NMR spectroscopy (very broad), and MALDI−TOF mass spectrometry (Figure S9). **{Ti--Cr}** exhibits stability in coordinating solvents, as confirmed by ^{1}H NMR analysis in THF-d_8, where the $CrCl_3$ 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.[3,12] Catalysts were investigated under varied reaction conditions, including the Al:M ratio (M = 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 **CGC^{Et}Ti** and

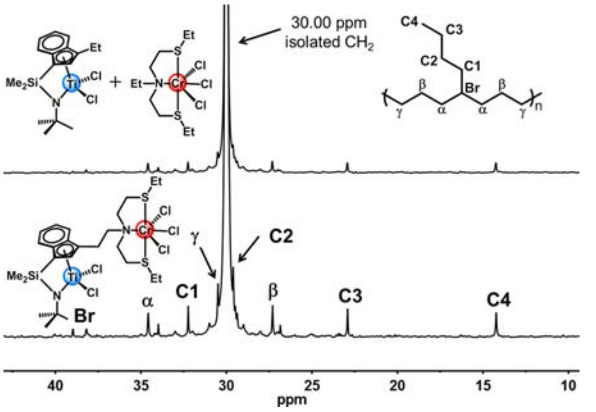


Figure 1. $^{13}C\{^1H\}$ NMR spectra (100 MHz, $C_2D_2Cl_4$, 120 °C) of PEs produced by the **CGC^{Et}Ti** + **SNSCr** and **{Ti--Cr}** catalysts (Table 1, entries 4 and 7), scaled to the PE CH_2 backbone resonance at 30 ppm.

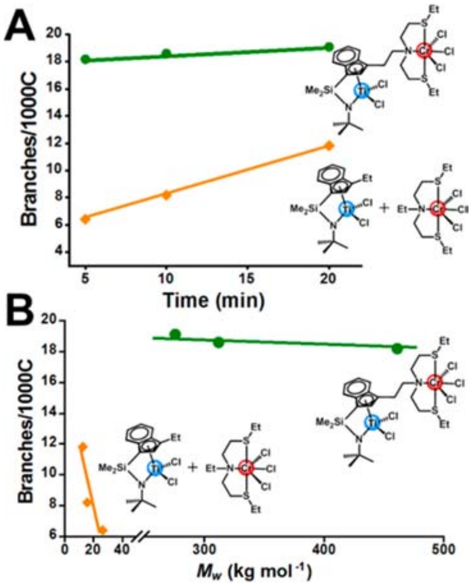


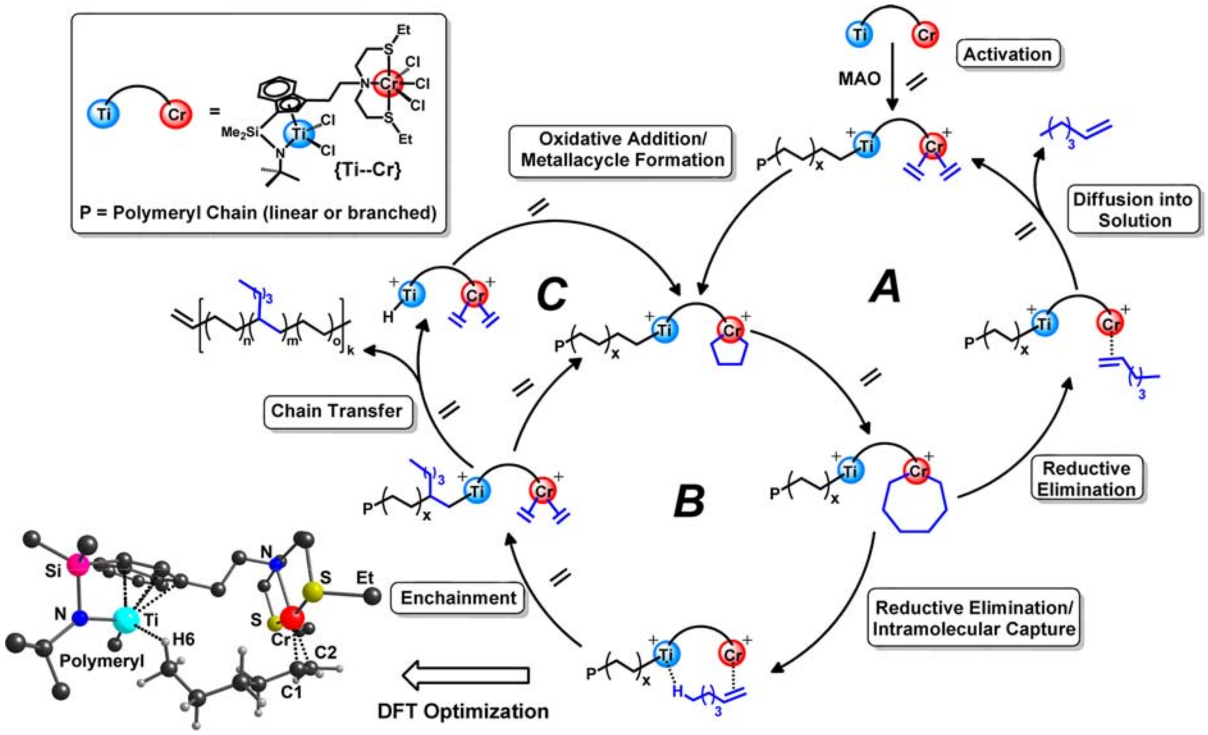
Figure 2. (A) PE branch densities (ρ_{br}) introduced by **CGC^{Et}Ti** + **SNSCr** and **{Ti--Cr}** as functions of reaction time at $P_{ethylene}$ = 8.0 atm (Table 1, entries 4−9). (B) Relationship of ρ_{br} and M_w for **CGC^{Et}Ti** + **SNSCr** and **{Ti--Cr}** in the same reactions.

Table 1. Ethylene Polymerization Data for Catalysts CGC^{Et}Ti, CGCTiCl$_2$−SNS, SNSCr, 1:1 CGC^{Et}Ti + SNSCr, and {Ti--Cr}[a]

entry	catalyst	t (min)	PE (g)	activity (PE)[b]	oligomers (g)[c]	activity (oligomers)[d]	ρ_{br}[e]	M_w (kg·mol^{-1})[f]	PDI[f]	T_m (°C)[g]
1	**CGC^{Et}Ti**	5	6.500	975.0	–	–	0	42.0	2.5	128.4
2	**CGCTiCl$_2$−SNS**	5	0.054	8.1	–	–	0	76.9	3.2	136.8
3	**SNSCr**	5	0.045	6.7	0.490	73.5	0	143.7	2.2	133.6
4	**CGC^{Et}Ti + SNSCr**	5	3.200	480.0	0.204	30.6	6.4	26.2	2.3	125.9
5	**CGC^{Et}Ti + SNSCr**	10	5.950	446.0	0.382	28.6	8.2	15.3	2.5	123.2
6	**CGC^{Et}Ti + 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

[a]Conditions: 10 μmol of catalyst (10 μmol of each component for **CGC^{Et}Ti + SNSCr**) with MAO/catalyst = 500 in 50 mL of toluene at 80 °C with $P_{ethylene}$ = 8 atm. Each entry was performed in duplicate. [b]In units of (kg of PE)·(mol of catalyst)$^{-1}$·h^{-1}·atm^{-1}. [c]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). [d]In units of (kg of oligomer)·(mol of catalyst)$^{-1}$·h^{-1}·atm^{-1}. [e]Branch density (number of branches per 1000 C atoms) as determined by ^{13}C NMR analysis.[19] [f]As determined by triple-detection GPC. [g]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$_2$−SNS afforded relatively high-M_w, 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)[3a,13] 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 ^{1}H NMR spectra of the PEs produced by both the **CGC^{Et}Ti + SNSCr** tandem catalyst and the **{Ti--Cr}** heterobimetallic catalyst exhibit vinylene ($-CH_2CH{=}CH_2$) and vinylidene [$-CH_2C(R){=}CH_2$] end-group distributions, with the former predominating (Figure S14). This indicates that β-hydride elimination is the dominant chain-transfer pathway[14] and that chain transfer to alkyl-Al is negligible.[15]

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_w PE.[6,16,17] 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_w 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.[1,18] Furthermore, the very different polymerization characteristics of the **{Ti--Cr}** and **CGCTiCl$_2$−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 ^{13}C NMR spectra (Figure 1) show that **{Ti--Cr}** enchained ~18.6 *n*-butyl branches/1000 C atoms, with a <1% yield of branches of any other length. Also, the branch density (ρ_{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^{Et}Ti + SNSCr** system introduces far lower ρ_{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 ρ_{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_6 comonomer. The fact that the PE ρ_{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 α-olefin remains nearly constant. Also, even though increasing the "free" oligomer concentration/reaction time depresses the copolymer M_w and activity in the tandem system, as is typical for **CGCTi** catalysts,[20] 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_w copolymers with higher C_4-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^{Et}Ti + SNSCr** tandem catalyst yields PEs with 68.0 branches/1000 C atoms, of which 91% were *n*-propyl

(Figure S17), consistent with intermolecular α-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_6 fragments are produced by established sequences[8] of reductive ethylene coupling and metallacyclopentane expansion to a metallacycloheptane 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 metallacycloheptane opening. However, preliminary density functional theory (DFT) calculations[21] identify an energetic minimum in which 1-hexene is π-bound to the Cr center while engaging in a $-CH_3\cdots M$ agostic interaction with Ti ($Ti\cdots Cr$ distance = 6.35 Å, Scheme 2 inset). This transfer process is efficient enough to limit enchainment of exogenous α-olefin, as evidenced by the near-constant *n*-butyl branch content and PE M_w 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_w's and branch densities that are $\sim$17 and $\sim$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@nortwestern.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.

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