

# Redox-Active Ligands: An Advanced Tool To Modulate Polyethylene Microstructure

W. Curtis Anderson, Jr.,<sup>†</sup> Jennifer L. Rhinehart,<sup>†</sup> Andrew G. Tennyson,<sup>‡</sup> and Brian K. Long<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

<sup>‡</sup>Department of Chemistry, Clemson University, Clemson, South Carolina 29634, United States

**S** Supporting Information

**ABSTRACT:** The ability to control catalytic activity and selectivity via *in situ* changes in catalyst oxidation-state represents an intriguing tool for enhanced polymerization control. Herein, we report foundational evidence that catalysts bearing redox-active moieties may be used to synthesize high molecular weight polyethylene with tailored microstructure. The ability to modulate branching density and identity is facilitated by ligand-based redox chemistry, and is realized via the addition of chemical reductants into the polymerization reactor. Detailed GPC and NMR analyses demonstrate that branching density may be altered by up to ~30% as a function of *in situ* added reductant.

The development and commercialization of polyolefins has revolutionized modern-day life, providing economical alternatives to natural resources such as wood, glass, and metal. Traditionally, polyolefins are synthesized using heterogeneous titanium-based catalysts that are activated using alkylaluminum reagents;<sup>1,2</sup> however, in an effort to develop deeper insight into the mechanistic details of olefin polymerizations, homogeneous olefin polymerization catalysts have since become extensively studied.<sup>3–5</sup> The evolution of those homogeneous olefin polymerization catalysts has encompassed a vast library of ligand structures ranging from metallocene-based systems<sup>3</sup> to non-metallocene catalysts,<sup>4</sup> and even the utilization of late transition metals, whose popularity grew exponentially after the initial discovery that Ni- and Pd-based catalysts could readily produce high molecular weight polyethylene (PE) and polypropylene (PP).<sup>4–7</sup>

In contrast to most group IV transition metal-based catalysts, late transition metal-based catalysts, namely those of Ni and Pd, have provided unique access to a variety of polyolefin topologies ranging from highly linear to hyperbranched polymer architectures using ethylene as a sole feedstock.<sup>5,8–11</sup> To understand how those branched architectures were formed, mechanistic investigations showed that Ni- and Pd-based catalysts often display a high propensity to undergo a process known as “chain-walking”. Chain-walking occurs via a repeated sequence of  $\beta$ -hydride elimination and re-insertion,<sup>8,9</sup> and enables the catalyst to migrate along the growing polymer backbone and incorporate subsequent monomers, thereby producing branched polymer architectures without the use of more expensive, higher  $\alpha$ -olefin co-monomers.<sup>12</sup>

Enticed by the ability to synthesize lower-density materials from a single inexpensive monomer feedstock (ethylene), researchers quickly discovered that PE topology could be directed via two main methods when using Ni- and Pd-based catalysts: (1) by increasing or decreasing ethylene feed pressures,<sup>8,9,11,13</sup> or (2) by raising or lowering the polymerization temperature.<sup>8,14</sup> Though each of these methods have provided foundational insight toward the development of Ni- and Pd-based catalysts, we hypothesized that a catalytic system could be envisioned in which the resultant polyolefin’s branching content and/or microstructure could be controlled via *in situ* modulations in the electronic nature of the catalyst itself, rather than by altering polymerization conditions/parameters such as ethylene pressure and reaction temperature.

Inspired by a previous report which demonstrated that ligand-based electronics can dramatically influence PE branching density,<sup>15</sup> we chose to investigate olefin polymerization catalysts bearing redox-active ligands to facilitate the synthesis of more than one polymer microstructure via *in situ* changes in the electronic nature of a single catalytically active species. While redox-switchable catalysis has been successfully implemented for a variety of small-molecule transformations<sup>16</sup> and polymerizations,<sup>17</sup> it should be noted that redox-switchable olefin polymerization catalysis has been alluded to and/or attempted previously,<sup>18–21</sup> yet no catalytic differentiation between two or more oxidation states of a single olefin polymerization catalyst has ever been successfully demonstrated for the production of high molecular weight PE.

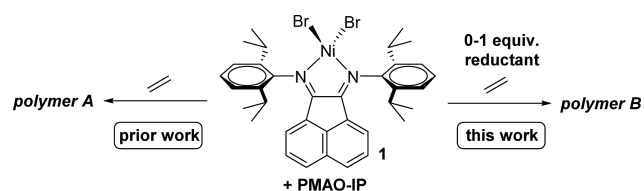
The lack of differentiation in those previously studied redox-active catalysts was attributed to the potential redox chemistry observed between trace amounts of trimethylaluminum (TMA) present in MAO<sup>2</sup> and the ferrocenyl-derived ligands used.<sup>19–22</sup> To avoid these undesirable redox events, we sought to take advantage of catalysts bearing redox-active bis(arylimido)-acenaphthene (BIAN) ligands such as catalyst **1** (Scheme 1). This well-defined catalyst takes advantage of an acenaphthene-quinone-derived, carbon-based redox center that is known to be readily reduced in the presence of appropriate chemical reductants.<sup>23,24</sup>

Initial investigations into the redox behavior of catalyst **1** were performed using cyclic voltammetry (CV) at a scan rate of 100 mV/s. All CV experiments were conducted in dichloromethane (DCM) using [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] (0.1 M) as an electrolyte, and were referenced to a subsequently added ferrocene standard (Fc/Fc<sup>+</sup>).

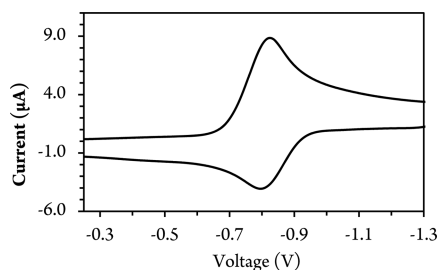
Received: November 24, 2015

Published: January 1, 2016

### Scheme 1. Using Redox-Active Olefin Polymerization Catalyst 1 To Control Polyethylene Microstructure



Under these conditions, catalyst **1** displayed a quasi-reversible one-electron redox couple that was observed at  $E_p^{1/2} = -0.8$  V (vs Fc/Fc<sup>+</sup>) (Figure 1). From this value, cobaltocene was chosen as an appropriate reductant ( $E^{o'} = -1.33$  V in DCM) and quickly proved to be an ideal candidate for subsequent polymerization studies.<sup>25</sup>



**Figure 1.** Cyclic voltammogram of catalyst **1** using 0.1 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] in DCM and referenced to a Fc/Fc<sup>+</sup> standard.

To eliminate the possibility of any competing polymerizations arising from the presence of cobaltocene within the reaction mixture, two control experiments were conducted. First, a polymerization in which cobaltocene and PMAO-IP activator were combined in the absence of catalyst **1** (Table 1, entry 1),

**Table 1. Ethylene Polymerizations Using Catalyst 1 with and without Added Reductant<sup>a</sup>**

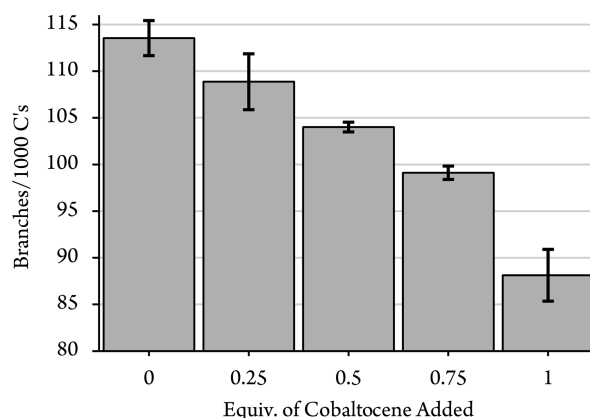
entry	[Co] <sup>b</sup> (µmol)	yield (g)	$M_w^c$ (kg/mol)	$M_w/M_n^c$	$B^d$
1 <sup>e</sup>	10.0	0			
2 <sup>f</sup>	10.0	0			
3	0	1.75	217	1.54	114 (±1.9)
4	2.5	1.94	254	1.65	109 (±3.0)
5	5.0	1.95	271	1.77	104 (±0.5)
6	7.5	2.38	274	1.72	99 (±0.7)
7	10.0	1.78	200	2.04	88 (±2.8)

<sup>a</sup>Polymerization conditions: [**1**] = 10.0 µmol, 148 mL of toluene, 2 mL of DCM, 20 °C, 15 psi ethylene, 30 min, and 92 equiv of PMAO-IP. <sup>b</sup>[Co] = cobaltocene. <sup>c</sup>Determined using triple detection GPC at 140 °C in 1,2,4-trichlorobenzene. <sup>d</sup>Branches per 1000 total C's, determined by <sup>1</sup>H NMR, reported values are averages over multiple trials. <sup>e</sup>No catalyst **1** added. <sup>f</sup>No PMAO-IP added.

and second, a polymerization in which catalyst **1** was reduced using 1 equiv of cobaltocene, but in which no PMAO-IP activator was added (Table 1, entry 2). Each of these control experiments were found to be completely inactive for ethylene polymerization, confirming that both catalyst **1** and PMAO-IP activator are required for polymerization. Likewise, these results confirmed that any polymer obtained in our subsequent polymerization studies would be a direct product of catalyst **1**, or its reduced form, and not from any catalytic chemistry arising from cobaltocene's presence within the reaction mixture.

All ethylene polymerization trials were conducted following established procedures using PMAO-IP as an activator (Table 1, entries 3–7). Polymerizations requiring the reduced catalyst were conducted by adding ≤1 equiv of cobaltocene into the polymerization reactor containing catalyst **1** and toluene prior to injection of PMAO-IP activator. The results of these polymerizations are shown in Table 1 in which each trial proved to yield a highly active catalyst system at low ethylene pressure (15 psi). Analysis of the resultant polymers via gel permeation chromatography (GPC) showed that each polymer sample reached similar molecular weights ( $M_w = 200$ –274 kg/mol), but that their molecular weight distributions were found to increase slightly ( $M_w/M_n = 1.54 \rightarrow 2.04$ ) as the amount of added cobaltocene approached one equivalent relative to catalyst **1**.

Despite their similarities in molecular weight, <sup>1</sup>H NMR analysis revealed a strong and highly reproducible correlation between the amount of cobaltocene added to the polymerization reactor and the microstructure of the resultant PE. For example, polymerizations conducted using catalyst **1** produced PE with ~30% more branches per 1000 total carbons ( $114 \pm 1.9$  branches/1000 C's) (Table 1, entry 3) than polymerizations conducted using catalyst **1** and 1 equiv of added cobaltocene ( $88 \pm 2.8$  branches/1000 C's) (Table 1, entry 7). Furthermore, if the amount of added cobaltocene was varied from 0 to 1 equiv (relative to catalyst **1**), an almost linear relationship with branching density was observed (Figure 2).



**Figure 2.** Plot of branches per 1000 total C's vs amount of cobaltocene added (equivalents relative to catalyst **1**).

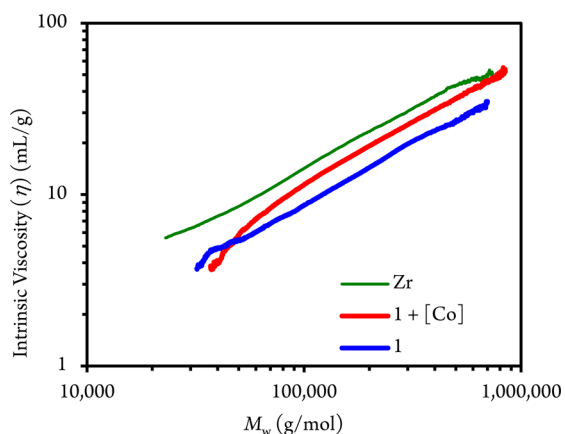
Branching in each PE sample was also measured via size exclusion chromatography (SEC), and their dilute solution parameters/properties are listed in Table 2. The ratio of each

**Table 2. Polyethylene Dilute Solution Parameters for Polymerizations at 20 °C Using Catalyst 1 and Cobaltocene<sup>a</sup>**

	amount of cobaltocene added (equiv)				
	0	0.25	0.5	0.75	1
$M_{w,SEC-LS}$ (kg/mol)	217	254	271	274	200
$R_{g,w}$ (nm)	17.7	21.6	22.8	23.1	19.8
$R_{h,w}$ (nm)	16.7	18.8	19.6	19.6	17.2
$[\eta]_{SEC-\eta}$ (mL/g)	14.9	18.4	19.8	20.3	18.3
$R_g/R_h$	1.06	1.15	1.16	1.18	1.15
$\alpha$	0.73	0.74	0.73	0.73	0.74

<sup>a</sup>Analysis performed using triple detection GPC at 140 °C in 1,2,4-trichlorobenzene.

sample's radius of gyration to hydrodynamic radius ( $R_g/R_h$ ), which reflects the polymer's shape independent of molecular weight, was found to be slightly above unity (1.06–1.18), indicating that that moderately branched PE was formed (note: linear PE samples may produce ratios as high as 2, and highly branched materials frequently display ratios below unity).<sup>26</sup> This result was also supported by the Mark–Houwink  $\alpha$ -parameters observed (0.73–0.74). In similarity to the  $^1\text{H}$  NMR results presented in Table 1, Mark–Houwink log–log plots of  $[\eta]$  vs  $M_w$  unquestionably confirmed differentiation in the degree of branching between polymerizations using catalyst **1** alone, or its cobaltocene reduced form (Figure 3). From that data,



**Figure 3.** Log–log plot of intrinsic viscosity ( $\eta$ ) vs  $M_w$  for polyethylene samples polymerized at 20 °C. Note: only polymers produced using Zr (green trace), catalyst **1** reduced by 1 equiv of cobaltocene (red trace), or only catalyst **1** (blue trace) are shown for clarity.

significantly lower intrinsic viscosities were observed across virtually all molecular weights for PE samples synthesized using catalyst **1** in the absence of added reductant. It should also be noted that in Figure 3, each polymer produced using catalyst **1** or its reduced analogue were compared to a highly linear PE sample synthesized using the commercially available catalyst dimethylbis(indenyl)zirconium (Zr), which as expected, produced highly linear PE with a  $T_m = 130$  °C (see Supporting Information) (perfectly linear PE is typically regarded to have  $T_m = 135$  °C).

In addition to the differences in branching density observed via  $^1\text{H}$  NMR and GPC analyses, quantitative  $^{13}\text{C}$  NMR analysis was used to investigate if the addition of reductant into the polymerization showed any influence over the identity of the PE branches observed (i.e., methyl, ethyl, propyl, etc.) (Table 3). Following the procedures of Galland and co-workers,<sup>27,28</sup> quantitative  $^{13}\text{C}$  NMR analysis was used to determine the identity and abundance of the PE branches within each sample. As shown in Table 3, as the equivalents of added cobaltocene were increased, the polymers produced displayed a greater percentage of methyl branches (54.9%  $\rightarrow$  62.8%) and branches that were six carbons and longer (9.2%  $\rightarrow$  10.4%). In contrast, a corresponding decrease in the percentage of ethyl, propyl, and butyl branches was also observed as a function of increasing equivalents of reductant. Though these differences were admittedly small (relative to the limits of this quantitative  $^{13}\text{C}$  NMR method<sup>27</sup>), they were highly reproducible.

Perhaps an even more intriguing result, was the virtual elimination of *sec*-butyl branching from polymer samples synthesized using catalyst **1** reduced by 1 equiv of cobaltocene.

**Table 3.** Polyethylene Branching Identity Analysis via Quantitative  $^{13}\text{C}$  NMR<sup>a</sup>

	amount of cobaltocene added (equiv)		
	0	0.5	1
methyl	54.9 ( $\pm$ 1.3)	58.5 ( $\pm$ 0.6)	62.8 ( $\pm$ 2.3)
ethyl	9.7 ( $\pm$ 0.5)	9.6 ( $\pm$ 0.4)	8.4 ( $\pm$ 0.3)
propyl	7.3 ( $\pm$ 0.3)	6.4 ( $\pm$ 1.4)	6.2 ( $\pm$ 0.9)
butyl	9.0 ( $\pm$ 1.8)	8.5 ( $\pm$ 0.7)	6.7 ( $\pm$ 1.0)
amyl	4.6 ( $\pm$ 0.7)	4.4 ( $\pm$ 0.5)	4.6 ( $\pm$ 0.1)
long <sup>b</sup>	9.2 ( $\pm$ 1.7)	9.5 ( $\pm$ 0.5)	10.4 ( $\pm$ 1.0)
<i>sec</i> -butyl	5.3 ( $\pm$ 0.7)	3.1 ( $\pm$ 0.1)	0.9 ( $\pm$ 0.2)

<sup>a</sup>The reported values represent their percent of total branching content. <sup>b</sup>Branches six carbons and longer.

*sec*-Butyl branching is the smallest form of a branch-on-branch structure observed for PE and is easily quantitated via integration of its two unique  $^{13}\text{C}$  NMR signals associated with the  $-\text{CH}_3$  groups of a *sec*-butyl branch (see Supporting Information).<sup>26</sup> The observed reduction in *sec*-butyl branching from 5.3% to 0.9% strongly indicates that, while catalyst **1** may readily chain-walk past tertiary carbon centers (or branching points), its ability to chain-walk past those tertiary centers is dramatically hindered when the reduced catalyst **1** is used. This near elimination of branch-on-branch PE structure signifies a small, yet real change in PE branching topology as a result of added reductant.

These observed reduction in PE branching density as a function of added reductant can be directly attributed to a decrease in the rate of  $\beta$ -hydride elimination relative to the overall rate of ethylene coordination and insertion. However, to better understand the origins of this behavior, as well as the near elimination of *sec*-butyl branching, we needed to better understand the electronic structure of reduced catalyst **1**. Previous studies of related BIAN-ligated complexes have shown that the structure of the reduced species could vary based upon the ligand and/or metal used. This suggested that the reduced catalyst **1** could potentially exist as any one of many possibilities that can include (1) a radical anionic ligand form in which the added electron is delocalized over the ligands bisimidoethane bridge, (2) a form in which the transition metal is reduced from Ni(II) to Ni(I), or (3) a structure in which the catalyst complex has been reduced by more than one electron.<sup>23,24</sup>

To probe which of these scenarios might contribute to the polymerization behavior observed, we utilized electron paramagnetic resonance (EPR) spectroscopy, magnetic susceptibility, and UV–vis spectroscopy. EPR experiments indicated that upon reduction of catalyst **1** with 1 equiv of cobaltocene, a formal reduction of Ni(II) to Ni(I) was observed yielding a  $g$ -value of 2.342, which is characteristic of a metal-centered unpaired electron. Addition of Lewis acidic trimethyl aluminum (5 equiv) to this Ni(I) complex resulted in rapid metal-to-ligand electron transfer from the Ni(I) center to the ligand itself, thereby creating a ligand-based, carbon-centered radical ( $g = 2.002$ ) (see Supporting Information). To support these results, magnetic susceptibility measurements were conducted using the Evans NMR method. Catalyst **1** displayed a magnetic moment of 3.2  $\mu_B$ , which agrees with a tetrahedral Ni(II) complex bearing two unpaired electrons, and when reduced using cobaltocene showed a magnetic moment of 2.5  $\mu_B$ . This indicated a reduction from two unpaired electrons to one and agreed with our EPR measurements. Addition of TMA to the reduced Ni(I) complex yielded a magnetic moment of 2.3  $\mu_B$ , and can likely be attributed

to a catalyst in which the unpaired electron is ligand-centered and the reformed Ni(II) center is now in its square-planar geometry. Furthermore, UV-vis spectroscopy of the reduced complex **1** in the presence of TMA showed a strong absorption between 750 and 850 nm, which agrees with other reports of reduced BIAN-ligated species.<sup>23</sup>

These results were similar to the findings of Gao and co-workers, who during the finalization and submission of this work published results regarding a proposed structure of a reduced BIAN-ligated Ni complex.<sup>23</sup> However, in stark contrast, Gao and co-workers demonstrated that their reduced Ni species was highly active for ethylene polymerization in the absence of MAO activators, whereas the reduced catalyst **1** reported herein was completely inactive for all ethylene polymerizations in the absence of MAO-based activators. This result, as well as the preliminary characterizations presented above, strongly suggest that the BIAN ligand of catalyst **1** is reduced in the presence of cobaltocene and TMA to produce a second catalytically active species; however, that species differs from that reported by Gao. Further investigations into the exact structure and electronic nature of reduced catalyst **1** are currently being pursued and include computational methods.

In sum, we have demonstrated that PE branching may be successfully tailored via *in situ* reduction of BIAN-ligated Ni-based olefin polymerization catalysts. This control over branching density was confirmed via <sup>1</sup>H NMR, GPC, and quantitative <sup>13</sup>C NMR analyses, and showed that polymers synthesized using catalyst **1** reproducibly displayed ~30% more branches per 1000 carbons than when using catalyst **1** reduced via cobaltocene addition. To our knowledge, this report represents the first successful example of catalytic differentiation between a reduced and oxidized catalyst for the synthesis of high molecular weight PE. This establishes strong support that redox-active olefin polymerization catalysts may represent an attractive tool for the synthesis of high-molecular-weight polyolefins with targeted microstructure control.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12322.

Detailed experimental procedures, GPC chromatograms, cyclic voltammograms, and <sup>1</sup>H NMR, <sup>13</sup>C NMR, and EPR spectra (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*long@utk.edu

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors acknowledge the Army Research Office (contract no. W911NF-1-0127) for financial support of this work. The authors thank Prof. Lawrence Sita for numerous fruitful discussions and advice regarding this work. The authors thank Dr. Kyle Williams of Malvern Instruments for help obtaining GPC data, and Dr. Jesse Kern for help simulating EPR spectra.

## ■ REFERENCES

- (1) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347.
- (2) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.
- (3) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205.
- (4) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.
- (5) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.
- (6) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem. Rev.* **2011**, *111*, 2363.
- (7) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
- (8) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.
- (9) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059.
- (10) Guan, Z.; Popeney, C. S. *Top. Organometal. Chem.* **2009**, *26*, 179.
- (11) Guan, Z. *Chem. - Asian J.* **2010**, *5*, 1058.
- (12) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686.
- (13) Xu, Y.; Xiang, P.; Ye, Z.; Wang, W.-J. *Macromolecules* **2010**, *43*, 8026.
- (14) (a) Hotta, A.; Cochran, E.; Ruokolainen, J.; Khanna, V.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y. W.; Shimizu, F.; Cherian, A. E.; Hustad, P. D.; Rose, J. M.; Coates, G. W. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15327. (b) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 13770. (c) Rose, J. M.; Cherian, A. E.; Lee, J. H.; Archer, L. A.; Coates, G. W.; Fetters, L. J. *Macromolecules* **2007**, *40*, 6807.
- (15) Popeney, C.; Guan, Z. B. *Organometallics* **2005**, *24*, 1145.
- (16) (a) Lorkovic, I. M.; Duff, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3617. (b) Tennyson, A. G.; Lynch, V. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 9420. (c) Lyaskovskyy, V.; de Bruin, B. *ACS Catal.* **2012**, *2*, 270.
- (17) (a) Gregson, C. K. A.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 7410. (b) Gregson, C. K.; Blackmore, I. J.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; White, A. J. *Dalton Trans.* **2006**, 3134. (c) Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9278. (d) Broderick, E. M.; Diaconescu, P. L. *Inorg. Chem.* **2009**, *48*, 4701. (e) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81.
- (18) Multani, K.; Stanlake, L. J. E.; Stephan, D. W. *Dalton Trans.* **2010**, 39, 8957.
- (19) Shafir, A.; Arnold, J. *Inorg. Chim. Acta* **2003**, *345*, 216.
- (20) Gibson, V. C.; Gregson, C. K. A.; Halliwell, C. M.; Long, N. J.; Oxford, P. J.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2005**, *690*, 6271.
- (21) Gibson, V. C.; Long, N. J.; Oxford, P. J.; White, A. J. P.; Williams, D. J. *Organometallics* **2006**, *25*, 1932.
- (22) Multani, K.; Stanlake, L. J.; Stephan, D. W. *Dalton Trans.* **2010**, 39, 8957.
- (23) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Cherkasov, V. K.; Fukin, G. K.; Lopatin, M. A. *Eur. J. Inorg. Chem.* **2004**, *2004*, 388.
- (24) (a) Khusniyarov, M. M.; Harms, K.; Burghaus, O.; Sundermeyer, J. *Eur. J. Inorg. Chem.* **2006**, *2006*, 2985. (b) van Asselt, R.; Elsevier, C. J.; Amatore, C.; Jutand, A. *Organometallics* **1997**, *16*, 317. (c) Cole, B. E.; Wolbach, J. P.; Dougherty, W. G.; Piro, N. A.; Kassel, W. S.; Graves, C. R. *Inorg. Chem.* **2014**, *53*, 3899. (d) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Fukin, G. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3294. (e) Fedushkin, I. L.; Skatova, A. A.; Lukoyanov, A. N.; Khvoinova, N. M.; Piskunov, A. V.; Nikipelov, A. S.; Fukin, G. K.; Lysenko, K. A.; Irran, E.; Schumann, H. *Dalton Trans* **2009**, 4689.
- (25) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
- (26) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945.
- (27) Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620.
- (28) Azoulay, J. D.; Bazan, G. C.; Galland, G. B. *Macromolecules* **2010**, *43*, 2794.
- (29) Gao, W.; Xin, L.; Hao, Z.; Li, G.; Su, J.-H.; Zhou, L.; Mu, Y. *Chem. Commun.* **2015**, *51*, 7004.