# ORGANOMETALLICS

# New Titanium Catalysts Containing Tetrazole for Cycloaddition of CO<sub>2</sub> to Epoxides

Min Jeong Go,<sup>†</sup> Kang Mun Lee,<sup>‡</sup> Chang Hwa Oh,<sup>†</sup> Yi Young Kang,<sup>†</sup> So Han Kim, <sup>§</sup> Hyoung Ryun Park,<sup>†</sup> Youngjo Kim,<sup>\*, §</sup> and Junseong Lee<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 500-757, Korea

<sup>‡</sup>Department of Chemistry, KAIST, Daejeon 361-763, Korea

<sup>§</sup>Department of Chemistry, Chungbuk National University, 52 Naesudong-ro, Heungdeok-gu, Cheongju, Chungbuk 361-763, Korea

**S** Supporting Information

**ABSTRACT:** A series of new half-sandwich titanocene  $[(\eta^5 C_5H_5$ )TiLCl<sub>2</sub> (1) and nonorganometallic titanium complexes  $[TiLCl_3(THF)]$  (2) and  $[TiL_2Cl_2]$  (3) containing 5-(2hydroxyphenyl)tetrazole (LH) were synthesized in high yield and fully characterized by various spectroscopic methods and X-ray crystallography. In all complexes, the ligand L acted as a monoanionic bidentate ligand and hydrogen bonding between the oxygen of the tetrahydrofuran and hydrogen of the tetrazolyl unit was observed. In the cycloaddition of CO<sub>2</sub> to propylene oxide, complex 3 showed the highest activity among the reported Ti complexes.

vclic carbonate is a source of polycarbonate, which is a / biodegradable polymer, and can be prepared from cycloaddition of CO<sub>2</sub> to epoxides. A variety of metal complexes, including Zn, Al, and Co, have been reported as efficient catalysts for the cycloaddition of CO<sub>2</sub> to epoxides.<sup>1</sup> In the case of Ti, there is only one example of a catalyst which showed limited activity at elevated temperatures (130 °C).<sup>2</sup> In this context, we focused on the development of new Ti catalytic systems containing electron-donating tetrazolyl ligands for the cycloaddition of CO<sub>2</sub> to epoxides.

In recent years, tetrazole has been known as a versatile ligand, due to its application in explosives as well as its diverse coordination ability to late transition metals such as Mn,<sup>3</sup> Cu,<sup>4</sup> and Zn.<sup>5</sup> The tetrazole can act as a mono-, bi-, or tetradentate bridging ligand with transition metals, resulting in the formation of high-dimensional networks.<sup>6</sup> Tetrazole, with a widely spread  $\pi$  conjugation all around the molecule, can promote electron donation toward the metal center and help the stabilization of the cationic metal center during the polymerization process. In addition, its coordinating nature is a convenient [N,O] bidentate type capable of forming a sixmembered chelating ring coordination to the metal. Furthermore, it occupies only a small space of the metal center, reducing the possibility of steric overlapping with other ligands. However, the poor solubility of the tetrazolyl ligand complicates its application. Somewhat surprisingly, the use of tetrazole and its derivatives with early transition metals has been much less studied, and especially there exists only one example of a titanium complex with 5-substituted 1Htetrazoles.<sup>7</sup> In this regard, we chose 5-(2-hydroxyphenyl)-1H-



tetrazole  $(LH)^8$  as a potential ligand for new titanium complexes.

In this paper, we report the synthesis and characterization of novel half-sandwich and nonorganometallic complexes containing one or two *L* ligands, along with their catalytic behavior in the cycloaddition of  $CO_2$  to epoxides. Whereas a large variety of catalytic systems have been reported as effective catalysts, the research of group 4 complexes is an unexplored area. To the best of our knowledge, this is the first example of titanium complexes containing a bidentate tetrazolyl ligand.

# EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk and glovebox techniques.<sup>9</sup> All other chemicals were purchased from Aldrich and used as supplied unless otherwise indicated. CpTiCl<sub>3</sub> was purchased from Strem. *n*-Pentane, toluene, and tetrahydrofuran (THF) were dried with Na/K alloy with benzophenone and stored over activated 3 Å molecular sieves. All deuterium solvents were dried over activated 3 Å molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

Measurements. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at ambient temperature on a Bruker AVANCE 400 NMR spectrometer using standard parameters. All chemical shifts are reported in  $\delta$  units with reference to the residual peaks of CDCl<sub>3</sub> ( $\delta$  7.24, <sup>1</sup>H NMR;  $\delta$ 77.0,  ${}^{13}C{}^{1}H{}$  NMR) or DMSO- $d_6$  ( $\delta$  2.50,  ${}^{1}H{}$  NMR;  $\delta$  39.52, <sup>13</sup>C{<sup>1</sup>H} NMR). Elemental analyses and mass data measurements

Received: June 24, 2013

were performed with EA 1110-FISONS(CE) and ICP-MASS HP-4500 instruments, respectively.

**Synthesis of** *LH*. The tetrazole ligand *LH* was synthesized by the literature procedure.<sup>8</sup>

**Synthesis of [CpTiLCl<sub>2</sub>] (1).** A solution of CpTiCl<sub>3</sub> (1.0 mmol, 0.22 g) in 20 mL of THF was added dropwise to a solution of *LH* (1.0 mmol, 0.16 g) in 20 mL of THF at -78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was then filtered through Celite. All volatiles were removed under vacuum, and the residue was washed with 20 mL of cold *n*-pentane. The desired product 1 was isolated as red crystals after the toluene solution remained at -20 °C in a refrigerator for a few days (0.28 g, 68%). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.63 (d, 1H, *J* = 7.8 Hz), 7.38 (t, 1H, *J* = 7.8 Hz), 7.01 (t, 3H of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 3.74 (t, THF), 1.84 (t, THF). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  150.9, 135.2, 128.9, 123.4, 122.9, 122.7, 122.2, 117.3, 108.8, 68.0 (THF), 25.6 (THF). Anal. Calcd for C<sub>18</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2.5</sub>Ti (1·1.5THF): C, 47.41; H, 4.89; N, 12.36. Found: C, 47.65; H, 4.90; N, 12.63.

**Synthesis of [TiLCl<sub>3</sub>(THF)] (2).** A solution of TiCl<sub>4</sub> (1.0 mmol, 1.0 mL, 1 M solution in CH<sub>2</sub>Cl<sub>2</sub>) in CH<sub>2</sub>Cl<sub>2</sub> was added by syringe over 1 min to a cold (-78 °C) solution of *LH* (1.0 mmol, 0.16 g) in 30 mL of THF. The reaction mixture was warmed to room temperature over 12 h. The reaction mixture was then filtered through Celite. After the solvent was reduced, the crude product was recrystallized by cooling to -20 °C, affording red crystals in a yield of 72% (0.33 g). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, ppm): δ 7.85 (br s, 1H), 7.54 (t, 1H, J = 8.5 Hz), 7.18 (t, 1H, J = 7.6 Hz), 7.00 (d, 1H, J = 8.3 Hz), 4.16 (t, THF), 1.98 (t, THF). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, CDCl<sub>3</sub>, ppm): δ 163.3, 150.3, 134.8, 127.3, 124.7, 116.5, 114.1, 71.6 (THF), 25.6 (THF). Anal. Calcd for C<sub>15</sub>H<sub>21</sub>Cl<sub>3</sub>N<sub>4</sub>O<sub>3</sub>Ti (2·THF): C, 39.20; H, 4.61; N, 12.19. Found: C, 39.28; H, 4.59; N, 12.09.

**Synthesis of [TiL<sub>2</sub>Cl<sub>2</sub>] (3).** In a manner analogous to the procedure for **2**, **3** was prepared from a solution of TiCl<sub>4</sub> (1.0 mmol, 1.0 mL, 1 M solution in CH<sub>2</sub>Cl<sub>2</sub>) in THF and *LH* (2.0 mmol, 0.32 g) in a yield of 71% (0.48 g). <sup>1</sup>H NMR (400.13 MHz, DMSO-*d*<sub>6</sub>, ppm):  $\delta$  10.99 (br s, 2H of NH of tetrazole), 7.95 (d, 2H, *J* = 9.5 Hz), 7.37 (t, 2H, *J* = 8.6 Hz), 7.09 (d, 2H, *J* = 9.1 Hz), 6.96 (t, 2H, *J* = 8.0 Hz), 3.55 (t, THF), 1.72 (t, THF). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  155.4, 151.7, 132.6, 129.0, 119.6, 116.4, 110.4, 67.0 (THF), 25.1 (THF). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>4</sub>Ti (3·2THF): C, 45.15; H, 4.48; N, 19.15. Found: C, 45.33; H, 4.52; N, 18.96.

X-ray Structure Determination for 1-3. Reflection data for 1-3 were collected at 130 K on a Bruker APEX II CCD area diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.7107 Å). Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam by using a video camera. The hemisphere of reflection data was collected as  $\omega$  scan frames with 0.5°/frame and an exposure time of 10 s/frame. Cell parameters were determined and refined by the SMART program.<sup>10</sup> Data reduction was performed using SAINT software.<sup>11</sup> The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.<sup>12</sup> The structures of the compounds were solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms.<sup>13</sup> Further details are given in the Supporting Information. X-ray crystal structures were drawn by the Diamond program, version 2.1e.

**Cycloaddition Tests of CO<sub>2</sub> to Propylene Oxide.** Cycloaddition of CO<sub>2</sub> was carried out by charging a stirring bar, propylene oxide, and titanium catalysts into a 20 mL stainless steel reactor in the glovebox, which was then sealed and removed from the glovebox. The reactor was pressurized to 22 bar of CO<sub>2</sub> and was heated to the reaction temperature (75 or 25 °C). After the contents were stirred for 4.5 h, the reactor was cooled and vented, and a small sample of the mixture was taken for <sup>1</sup>H NMR analysis.

## RESULTS AND DISCUSSION

Synthesis and Characterization. Compound 1 was obtained by adding dropwise a solution of  $CpTiCl_3$  in THF to an equimolar solution of *LH* in THF at -78 °C, as outlined in Scheme 1. Similarly, compounds 2 and 3 were prepared by





adding a solution of TiCl<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> to equimolar and 2 molar amounts of *LH* in THF at -78 °C, respectively. Compounds 1–3 were obtained in high yield (68–72%) and were purified by washing with *n*-hexane and recrystallized in THF. They were remarkably stable in the solid state for a few days. They precipitated out within a couple of hours in chloroform-*d* in capped NMR tubes. Compounds 1–3 are soluble in toluene and polar organic solvents such as THF, CH<sub>2</sub>Cl<sub>2</sub>, and acetone; however, ligand *LH* is insoluble in most solvents such as toluene, THF, water, and acetone.

Compounds 1-3 were characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography. The <sup>1</sup>H NMR spectra of complexes 1-3display well-defined resonances with the expected integrations. Also, well-defined resonances for the aromatic carbons are observed in the  ${}^{13}C{}^{1}H$  NMR spectrum, and there is no indication of the presence of higher oligomers or isomers. In comparison to the free LH ligand, all signals in 1-3 are shifted downfield, a consequence of complexation with the Lewis acidic titanium metal. The most interesting point in the <sup>1</sup>H NMR spectra of complexes 1-3 is the existence of peaks corresponding to the THF molecules. Complexes 1 and 3 have two THF peaks at 3.74 and 1.84 ppm, similar to those of a free THF molecule (free THF: 3.76, 1.85 ppm). In contrast, complex 2 has broad THF peaks at 4.16 and 1.98 ppm that are significantly shifted downfield from the signals for free THF. This indicates that the titanium metal possesses direct and strong bonding with the THF molecule in the structure of complex 2, which was also confirmed by an X-ray structure analysis. These interactions between the THF molecules and tetrazole ligands are likely important main factors in the increased solubility of 1-3. Due to their strong interactions, THF molecules were not removed after evacuation and were thus observed in the <sup>1</sup>H NMR spectra of complexes 1-3. These results are consistent with X-ray structures of 1-3 in the solution phase.

In order to confirm the molecular structure and elucidate the metal-ligand bonding in these titanium complexes, singlecrystal X-ray diffraction studies for 1-3 were performed. Single crystals suitable for X-ray structural determination were obtained by cooling saturated solutions of THF at -20 °C. Complexes 1-3 crystallized in space groups C2/c,  $P\overline{1}$ , and  $P\overline{1}$ , respectively. The X-ray structures, selected bond distances, and selected bond angles for 1-3 are shown in Figures 1-3,



Figure 1. Molecular drawing of compound 1 and atom labeling. H atoms, except for H101, and two THF molecules are omitted for clarity.



Figure 2. Molecular drawing of compound 2 and atom labeling. H atoms, except for H101, are omitted for clarity.



Figure 3. Molecular drawing of compound 3 and atom labeling. H atoms, except for H101 and H102, and two THF molecules are omitted for clarity.

respectively. As shown in Figure 1, the asymmetric unit of the molecular structure in complex 1 contains a molecule of the complex and THF molecules, being consistent with the <sup>1</sup>H NMR spectrum of complex 1. A deprotonated *LH* ligand, cyclopentadienyl (Cp) ring, and two chlorides form a distorted-

square-pyramidal local geometry around the titanium metal center. The average Ti–Cp carbon distance of 2.361(7) Å and the distance between the Cp(centroid) and Ti of 2.045(7) Å fall in the range observed for other known Ti–Cp complexes.<sup>14</sup>

In contrast with the structure of 1, complexes 2 and 3 form a distorted-octahedral geometry around the Ti metal center. The X-ray analysis of 2 reveals that three chloride atoms are located in meridional positions and a THF molecule is placed in the position trans to the oxygen of the LH ligand (see Figure 2). In the case of 3, two chlorides and two nitrogens are located in positions *cis* to each other with angles of 95.8(2), and 82.7(5) $^{\circ}$ , respectively (see Figure 3). The coordination nature of the deprotonated ligand with the Ti leads to several kinds of possible diasteromers for 3, resulting in broad NMR peak widths. The bond lengths of 1.872(4) Å in 1, 1.791(4) Å in 2, and 1.887(14) (average) Å in 3 between Ti and O in the L ligand fall in the range observed for other known Ti-O complexes.<sup>14,15</sup> The bond length of 2.168(5) Å in **2** between Ti and O in THF is relatively longer than the other Ti-O bonds (1.791-1.887 Å). As expected, the bond lengths between Ti and the nitrogen atom of 2.215(5) Å in 1, 2.168(5) Å in 2, and 2.235(18) Å in 3 are in the range observed for other known complexes.<sup>14,15</sup> Also, it is notable that the N-H proton of tetrazole was not deprotonated during the reaction. The hydrogen atom attached to the nitrogen of the tetrazole was easily assigned from the electron density map in the X-ray structure analysis. The  $N(4)_{Tz}$ - $H_{Tz}$  distances (0.790(6) Å in 1, 0.730(7) Å in **2**) are shorter than the calculated value (0.870 Å) of complex 3. The N<sub>ax</sub>-Ti-Cl<sub>ax</sub> angle (176.43(13)°) is quite linear, whereas the  $O_{eq}$ -Ti- $O_{eq}$ (THF) angle (163.09(16)°) and  $Cl_{eq}$ -Ti- $Cl_{eq}$  bond angle (170.42(7)°) are slightly bent.

**Cycloaddition of CO**<sub>2</sub>. Cycloaddition of CO<sub>2</sub> was performed without solvent using the titanium compounds 1-3 as catalysts in the presence of a cocatalyst. The polymerization results are summarized in Table 1. We carried out the

Table 1. Cycloaddition of  $CO_2$  to Propylene Oxide Using Complexes  $1-3^a$ 

entry	cat.	cocat.	amt of cat. (mmol)	amt of cocat. (mmol)	T (°C)	TOF for CPC <sup>b</sup>	conversn (%) <sup>c</sup>
1		n-Bu <sub>4</sub> NI		0.0285	75		
2	1	n-Bu <sub>4</sub> NI	0.0285	0.0285	75	87	39
3	2	n-Bu <sub>4</sub> NI	0.0285	0.0285	75	64	29
4	3	n-Bu <sub>4</sub> NI	0.0285	0.0285	75	191	86
5	3	n-Bu <sub>4</sub> NI	0.0285	0.0285	25	21	9.2
6	3	[PPN] Cl	0.0285	0.0285	75	44	20
7	3	n-Bu <sub>4</sub> NI	0.00285	0.0285	75	422	19
8	3	n-Bu <sub>4</sub> NI	0.00285	0.00285	75	111	5

<sup>*a*</sup>Cycloaddition conditions: propylene oxide (PO, 2.0 mL, 0.0285 mol), CO<sub>2</sub> (22 bar), 4.5 h. <sup>*b*</sup>Turnover frequency (TOF) = (mol of PO consumed)/((mol of Ti center) h). <sup>*c*</sup>Calculated by <sup>1</sup>H NMR spectral integration.

reaction at 75 °C under the conditions of a fixed [Ti]/ [cocatalyst] ratio of 1 and found that complex 3 had highest TOF value (TOF = 191 h<sup>-1</sup>). Propylene oxide was easily converted into the cyclic carbonate with high selectivity (>99%) without any polymerized products (Scheme 2). At low temperature, it showed reduced activity (Table 1. entry 5). Lower conversion was observed when *n*-Bu<sub>4</sub>NI was replaced by [PPN]Cl (Table 1. entry 6). We then investigated the use of Scheme 2. Synthesis of Cyclic Carbonate from CO<sub>2</sub> and Propylene Oxide

$$co_2 + \overset{o}{\searrow} \longrightarrow \overset{o}{\swarrow} o$$

reduced amounts of Ti complex **3** and achieved a considerably increased TOF value, which is highest value among the reported Ti complexes (Table 1, entry 7; TOF = 422 h<sup>-1</sup>). Moreover, catalyst **3** showed somewhat high activity in spite of the use of a reduced amount of cocatalyst (Table 1. entry 8; TOF = 111 h<sup>-1</sup>). Complex **3** hasa longer Ti–N bond than do complexes **1** and **2**. This could increase the Lewis acidity of the metal center and create a vacant site, resulting in high catalytic performance. Detailed studies of the catalytic performance are in progress.

# CONCLUSION

New half-sandwich titanocene and nonmetallocene titanium chloride catalysts with monoanionic bidentate tetrazole ligands were easily prepared, and their catalytic behaviors in the cycloaddition of  $CO_2$  to propylene oxide were investigated. Complex 3 showed the highest activity among reported Ti catalysts.

# ASSOCIATED CONTENT

#### **S** Supporting Information

CIF files giving crystallographic data for the titanium complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

We acknowledge the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0003141 and 2013R1A1A2006317).

# REFERENCES

(1) (a) North, M.; Pasquale, R.; Young, C. Green Chem. 2010, 12, 1514–1539. (b) Li, F.; Xia, C.; Xu, F.; Sun, W.; Chen, G. Chem. Commun. 2003, 4, 2042–2043.

(2) Bai, D.; Jing, H.; Liu, Q.; Zhu, Q.; Zhao, X. Catal. Commun. 2009, 11, 155–157.

(3) (a) Liao, J. H.; Chen, W. T.; Tsai, C. S.; Yang, C. C.; Wang, C. C. *Cryst. Eng. Commun.* **2010**, *12*, 3033–3037. (b) Anwar, M. U.; Lan, Y.; Beltran, L. M. C.; Clerac, R.; Pfirrmann, S.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2009**, *48*, 5177–5186. (c) Hartdegen, V.; Klapotke, T. M.; Sproll, S. M. *Inorg. Chem.* **2009**, *48*, 9549–9556.

(4) (a) Sengupta, O.; Mukherjee, P. S. *Inorg. Chem.* **2010**, *49*, 8583–8590. (b) Zhong, D. C.; Lu, W. G.; Jiang, L.; Feng, X. L.; Lu, T. B. *Cryst. Growth. Des.* **2010**, *10*, 739–746. (c) Li, M. X.; Wang, H.; Liang, S. W.; Shao, M.; He, X.; Wang, Z. X.; Zhu, S. R. *Cryst. Growth. Des.* **2009**, *9*, 4626–4633.

(5) (a) Liu, H. Y.; Wu, H.; Ma, J. F.; Liu, Y. Y.; Liu, B.; Yang, J. Cryst. Growth. Des. 2010, 10, 4795–4805. (b) Tong, X. L.; Wang, D. Z.; Hu, T. L.; Song, W. C.; Tao, Y.; Bu, X. H. Cryst. Growth. Des. 2009, 9, 2280–2286. (c) Li, Y.; Xu, G.; Zou, W. O.; Wang, N. S.; Zheng, F. K.; Wu, M. F.; Zeng, H. Y.; Guo, G. C.; Huang, J. S. Inorg. Chem. 2008, 47, 7945–7947. (d) Fu, D. W.; Zhang, W.; Xiong, R. G. Cryst. Growth. Des. 2008, 8, 3461–3464. (e) Goher, M. A. S.; Sodin, B.; Bitschnau,

- B.; Fuchs, E. C.; Mautner, F. A. *Polyhedron* **2008**, *27*, 1423–1431. (f) Wang, X. S.; Tang, Y. Z.; Huang, X. F.; Qu, Z. R.; Che, C. M.; Chan, P. W. H.; Xiong, R. G. *Inorg. Chem.* **2005**, *44*, 5278–5285.
- (6) (a) Zhang, Z. J.; Xiang, S. C.; Zheng, Q.; Rao, X. T.; Mondal, J. U.; Arman, H. D.; Qian, G. D.; Chen, B. L. *Cryst. Growth. Des.* **2010**, 10, 2372–2375. (b) Wu, T.; Yi, B. H.; Li, D. *Inorg. Chem.* **2005**, 44, 4130–4132.
- (7) Hill, M. S.; Hitchcock, P. B.; Smith, N. Polyhedron 2004, 23, 801-807.
- (8) Koguro, K.; Oga, T.; Mitsui, S.; Orita, R. Synthesis 1998, 910–914.

(9) Armarego, W. L. F.; Chai, C. L. L. In *Purification of Laboratory Chemicals*, 5th ed.; Elsevier: New York, 2003.

(10) (a) Lee, J.; Kim, Y.; Do, Y. Inorg. Chem. 2007, 46, 7701-7703.

(b) Takashima, Y.; Nakayama, Y.; Watanabe, K.; Itono, T.; Ueyama, N.; Nakamura, A.; Yasuda, H.; Harada, A.; Okuda, J. *Macromolecules* **2002**, *35*, 7538–7544.

(11) Takashima, Y.; Nakayama, Y.; Hirao, T.; Yasuda, H.; Harada, A. J. Organomet. Chem. **2004**, 689, 612–619.

(12) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461–6470.

(13) Sheldrick, G. M. SHELXS-97; University of Gottingen, Gottingen, Germany, 1990.

(14) Bott, R. K. J.; Hughes, D. L.; Schormann, M.; Bochmann, M.; Lancaster, S. J. J. Organomet. Chem. **2003**, 665, 135–149.

(15) Pennington, D. A.; Clegg, W.; Coles, S. J.; Harrington, R. W.; Hursthouse, M. B.; Hughes, D. L.; Light, M. E.; Schormann, M.; Bochmann, M.; Lancaster, S. J. *Dalton Trans.* **2005**, 561–571.