

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230661712>

A Bis(1,2-Azaboroly)yttrium Alkyl Complex: Synthesis, Structure, and Polymerization Study

ARTICLE in ORGANOMETALLICS · JANUARY 2008

Impact Factor: 4.13 · DOI: 10.1021/om800073s

CITATIONS

12

READS

38

4 AUTHORS, INCLUDING:



Yuanfu Deng

South China University of Technology

44 PUBLICATIONS 573 CITATIONS

SEE PROFILE



Firmin Moingeon

University of Waterloo

9 PUBLICATIONS 76 CITATIONS

SEE PROFILE

Communications

A Bis(1,2-Azaborolyl)yttrium Alkyl Complex: Synthesis, Structure, and Polymerization Study

Xiangdong Fang,* Yuanfu Deng, Qinxing Xie, and Firmin Moingeon

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received January 26, 2008

Summary: Yttrium complex **3**, the first example of a group III metal alkyl complex with an ancillary 1,2-azaborolyl ligand, was prepared and characterized; complex **3** initiates methyl methacrylate (MMA) polymerization with living character to afford syndiotactic-rich poly(methyl methacrylate) (PMMA).

The omnipresence of the cyclopentadienyl (Cp) group in organometallic chemistry is best demonstrated by its successful utilization in various metal catalysts or catalyst precursors for olefin polymerization¹ and selective organic synthesis.² The participation of the Cp ligand in metal catalysis is mainly as a spectator ligand that remains tightly bound to the metal center during the entire catalytic process. Thus, by interacting sterically and electronically with the metal atom, the Cp ligand can both control the number of open coordination sites around the metal center and influence the reactivity of the metal center. It is not surprising to see that one of the major themes in organometallic chemistry is to modulate the reactivity and selectivity of the catalysts, which in turn has spurred the design and syntheses of numerous Cp analogues.³ In this regard, the 1,2-azaborolyl (Ab) group has been investigated as a potential isoelectronic and isolobal surrogate for the Cp ligand in many metal complexes such as the Ab derivatives of group IV and VIII transition metals.⁴ One of the advantages offered by the Ab systems is that the electronic nature of the metal center can be easily modulated by judicious choices of the exocyclic substituent at boron, as demonstrated in the electrochemical study of the iron complexes by Fu and co-workers.⁵ Another merit of the Ab ligands lies in their different ring geometry relative to the Cp counterparts, which might provide a unique steric

environment around the metal center.⁶ As we are interested in their prominent features, it is to our major surprise to find that group III rare-earth-metal complexes based on the Ab ligand have never been reported, since Schmid's pioneering synthesis of the anionic 1,2-azaborolyl ligand.^{4a} In this communication, we present the first synthesis and characterization of a THF-coordinated bis-Ab yttrium alkyl complex (YL₂(CH₂SiMe₃)(THF) (**3**, L = 1-methyl-2-phenyl-1,2-azaborolyl). In addition, we have found that this novel yttrium complex can serve as a single-component initiator for the polymerization of methyl methacrylate (MMA) in a living fashion.

The synthesis of complex **3** is outlined in Scheme 1. Reaction of YCl₃(THF)₃ with 2 equiv of the Ab lithium species **1**^{4c} in THF affords complex **2**, a THF-coordinated bis(1-methyl-2-phenyl-1,2-azaborolyl)yttrium chloride complex, which has been determined as a mixture of meso and racemic isomers in a 1:3 molar ratio by ¹H NMR spectroscopy. Attempts to isolate the racemic isomer from the above mixture in toluene were unsuccessful, due to the tenacious formation of insoluble white solids, presumably oligomeric or polymeric yttrium chloride compounds. The results of elemental analysis and the ⁷Li NMR spectrum are consistent with the formation of the expected yttrium chloride complex **2** and hence exclude the possibility of **2** forming the "ate"-type complexes with LiCl.⁷ The subsequent alkylation step was carried out by treating yttrium compound **2** with 1 equiv of LiCH₂Si(CH₃)₃ at −78 °C, which gave rise to complex **3** (meso:racemic = 1:3) as the final product. In contrast to **2**, a pure racemic isomer of **3** can be

(6) Fang, X. D.; Assoud, J. *Organometallics* **2008**, *27*, 2408.

(7) Preparation of **2**: the Ab lithium species **1** (0.98 g, 6.0 mmol) and YCl₃(THF)₃ (1.23 g, 3.0 mmol) in a Schlenk flask with a stir bar were treated with 20 mL of THF at 0 °C. The mixture was refluxed at 70 °C for 3 h. After solvent removal, the oily residue was dissolved in 15 mL of toluene to give a clear solution, which was concentrated and crystallized at −30 °C. After it was rinsed with pentane and dried in vacuo, the product was obtained as white crystals (0.94 g, 60% yield). ¹H NMR (300 MHz, C₆D₆): δ 7.83 (d, *J* = 8.0 Hz), 7.73 (d, *J* = 8.0 Hz), 7.26 (t, *J* = 7.6 Hz), 7.20–7.03 (m), 6.60 (dd, *J* = 5.4, 2.3 Hz), 6.30 (dd, *J* = 5.3, 2.2 Hz), 5.95–6.00 (m), 5.18 (dd, *J* = 5.3, 2.2 Hz), 5.10 (dd, *J* = 5.4, 2.3 Hz), 3.44 (s), 3.38 (s), 3.17 (b, THF), 0.64 (b, THF). ¹³C NMR (75.45 MHz, C₆D₆): δ 134.3, 127.7, 127.4, 127.2, 120.7, 120.3, 118.6, 96.2 (b), 71.8, 37.3, 37.0, 24.7. ¹¹B NMR (96.3 MHz, C₆D₆): δ 31.3. ⁷Li NMR (116.6 MHz, C₆H₆): no signal. Anal. Calcd for C₂₄H₃₀B₂ClN₂OY: C, 56.69; H, 5.95; N, 5.51. Found: C, 56.82; H, 5.75; N, 5.49. On the basis of the ¹H NMR spectrum, the product **2** has been determined as a mixture of meso and racemic isomers (meso:racemic = 1:3; see the Supporting Information). Structural determination by X-ray diffraction was performed, but the structural parameters could not be refined.

*To whom correspondence should be addressed. E-mail: xdfang@uwaterloo.ca. Tel: 01-519-888-4567, ext. 36229. Fax: 01-519-746-0435.

(1) (a) Brintzinger, H. H.; Fischer, D.; Mühlaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

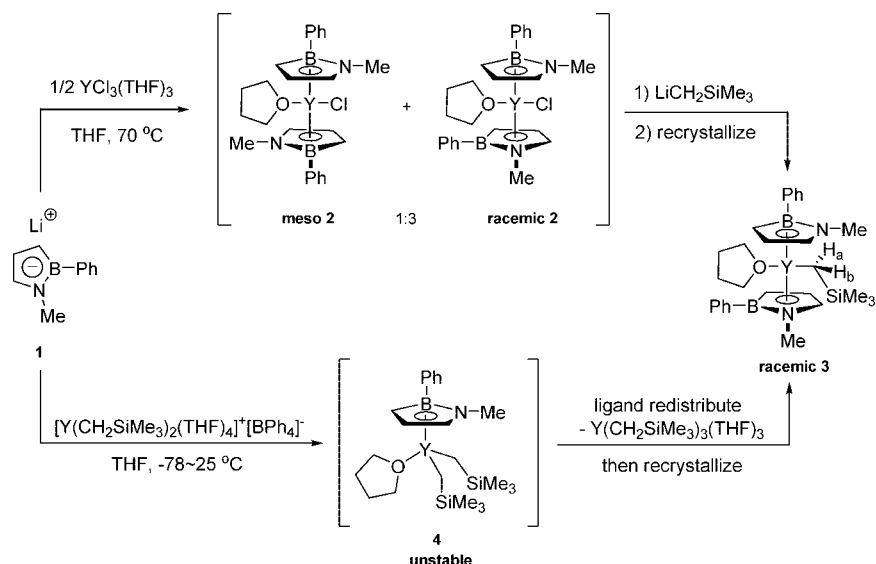
(2) (a) *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley: New York, 2002. (b) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673.

(3) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (c) Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, *347*, 355.

(4) (a) Schmid, G. In *Comprehensive Heterocyclic Chemistry II*; Shinkai, I., Ed.; Elsevier: Oxford, U.K., 1996; Vol. 3, Chapter 3.17. (b) Liu, S. Y.; Hills, I. D.; Fu, G. C. *Organometallics* **2002**, *21*, 4323. (c) Ashe, A. J. III.; Fang, X. D. *Org. Lett.* **2000**, *2*, 2089.

(5) Liu, S. Y.; Lo, M. M. C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 174.

Scheme 1. Synthesis of Racemic 3



obtained by repeated recrystallization in a hydrocarbon solvent such as toluene or hexane.⁸

Another route for the preparation of **3** was discovered unexpectedly in the synthesis of the half-sandwich yttrium bis(alkyl) complex with supporting ancillary Ab ligand (Scheme 1). Okuda et al. have reported a facile synthesis of an interesting monocationic THF-coordinated yttrium bis(alkyl) species and its crown ether adduct.⁹ We anticipated that the reaction of this monocationic yttrium species with lithium salt **1** would lead to the half-sandwich yttrium bis(alkyl) complex **4**. However, instead of the much desired **4**, only the bis-Ab yttrium complex **3** and $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_3$ were isolated as the final products.

(8) Preparation of racemic **3**: a solution of $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$ (96 mg, 1.0 mmol) in 5 mL of THF was added dropwise into a solution of **2** (0.52 g, 1.0 mmol) in 5 mL of THF at -78°C . The mixture was stirred for 2 h at -78°C and then 20 min at 25°C . After solvent removal, the oily residue was extracted with 25 mL of toluene and the mixture was filtered. The filtrate was concentrated and layered with hexane. The mixture was crystallized at -30°C for 2 days to afford pale yellow solids, which could be recrystallized by slow diffusion of hexane into its toluene solution. The product **3** was obtained as white crystals (0.30 g, 53% yield). On the basis of the ^1H NMR spectrum, the product **3** has been determined to be a mixture of meso and racemic isomers (meso:racemic = 1:3; see the Supporting Information). Pure racemic **3** was obtained as colorless crystals by performing recrystallization (3 \times) in hexane/toluene (0.15 g, 27% yield). Attempts to isolate meso **3** were unsuccessful. Another route leading to **3**: a solution of the Ab lithium species **1** (0.11 g, 1.1 mmol) in 10 mL of THF was added dropwise into a solution of $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_4]^+[\text{BPh}_4]^-$ (1.0 g, 1.1 mmol) in 7 mL of THF at -78°C . The clear yellow solution gradually turned cloudy, and the mixture was warmed to 25°C and stirred for 15 min. After solvent removal, the residue was extracted with pentane (20 mL) and the mixture was filtered. The filtrate was further concentrated and crystallized at -35°C to remove $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_3$ which came out first. Complex **3** (meso:racemic = 1:4) was obtained as white crystalline solids after recrystallization. (0.31 g, 50% yield). ^1H NMR (300 MHz, C_6D_6): δ 7.82 (d, J = 7.0 Hz, 2H, Ar H), 7.58 (d, J = 6.8 Hz, 2H, Ar H), 7.30 (t, J = 7.3 Hz, 2H, Ar H), 7.20–7.06 (m, 4H, Ar H), 6.66 (d, J = 3.0 Hz, 1H, Ab H), 6.31 (m, 1H, Ab H), 6.16–6.13 (m, 2H, Ab H), 5.22 (d, J = 3.0 Hz, 1H, Ab H), 5.11 (d, J = 3.0 Hz, 1H, Ab H), 3.31 (s, 3H, NCH_3), 3.19 (s, 3H, NCH_3), 2.91 (b, 4H, THF), 0.57 (b, 4H, THF), 0.40 (s, 9H, SiMe_3), -0.71 (dd, $^2J_{\text{Y-C-H}}$ = 3.24 Hz, $^2J_{\text{H-C-H}}$ = 10.4 Hz, 1H, CH_2SiMe_3), -0.89 (dd, $^2J_{\text{Y-C-H}}$ = 3.24 Hz, $^2J_{\text{H-C-H}}$ = 10.4 Hz, 1H, CH_2SiMe_3). ^{13}C NMR (75.45 MHz, C_6D_6): δ 134.0, 133.9, 127.2, 126.9, 120.2, 119.1, 116.7, 115.3, 71.7, 36.9, 30.3 (d, $^1J_{\text{Y-C}}$ = 43.4 Hz), 24.4, 5.4. ^{11}B NMR (96.3 MHz, C_6D_6): δ 30.4. Anal. Calcd for $\text{C}_{28}\text{H}_{41}\text{B}_2\text{N}_2\text{OSiY}$: C, 59.97; H, 7.37; N, 5.00. Found: C, 58.08; H, 7.33; N, 4.90. The combustion carbon analysis for organolanthanide complexes is difficult, due to their extreme sensitivity toward air and moisture, which has been repeatedly observed in the literature. For example, see: (a) Arndt, S.; Beckerle, K.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7473. (b) Cameron, T. M.; Gordon, J. C.; Scott, B. L. *Organometallics* **2004**, *23*, 2995.

Similarly, complex **3** from the above reaction was a mixture of meso and racemic isomers (meso:racemic = 1:4), and racemic **3** could be separated from the above mixture by repetitive recrystallization. Clearly, the facile formation of the thermodynamically more stabilized **3**, relative to the less stabilized **4**, is the result of an intermolecular ligand redistribution reaction, also commonly observed in group III metal and lanthanide Cp chemistry.¹⁰ This result suggests that ligand **1** is not sizable enough to prevent the occurrence of ligand redistribution in the above reaction. Therefore, we expect that using more sterically demanding Ab ligands may be helpful in isolating the corresponding half-sandwich yttrium Ab complex by making the system kinetically sufficiently inert with respect to ligand distribution.

A single crystal of racemic **3** suitable for X-ray diffractometry was grown by slow diffusion of hexanes into the saturated toluene solution of **3** at -30°C . The solid-state molecular structure of **3**, as illustrated in Figure 1,¹¹ shows a typical bent metallocene sandwich complex, in which the Y atom has a pseudotetrahedral coordination geometry. Two Ab rings are tilted with a dihedral angle of 53.5° , and the centroid–yttrium–centroid (Ct01–Y1–Ct02) angle is $128.8(1)^\circ$, comparable with those observed in the analogous bis-Cp systems.¹² Notably, the large Y1–C11–Si1 bond angle of $137.5(1)^\circ$ deviates greatly from the ideal tetrahedral angle (109.5°), which may reflect the spatial requirement of the sterically demanding trimethylsilyl group and other ligand groups attached to the Y atom.¹³ As a matter of fact, the Y–C(alkyl) bond distance (2.397(2) Å) is consistent

(9) (a) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5075. (b) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404.

(10) (a) Booiij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H. *Organometallics* **1989**, *8*, 2454. (b) Xu, G. X.; Ren, J. Q.; Huang, C. H.; Wu, J. G. *Pure Appl. Chem.* **1988**, *60*, 1145.

(11) Crystal data for **3**: $\text{C}_{28}\text{H}_{41}\text{B}_2\text{N}_2\text{OSiY}$, $M = 560.25$, triclinic, $P\bar{1}$, $a = 9.8648(5)$ Å, $b = 12.5348(6)$ Å, $c = 13.7472(6)$ Å, $\alpha = 102.128(1)^\circ$, $\beta = 107.478(1)^\circ$, $\gamma = 108.072(1)^\circ$, $V = 1452.6(2)$ Å³, $D_c = 1.281$ g/cm³, $Z = 2$, $R_1 = 0.037$, $wR_2 = 0.089$, for 361 parameters and 7939 reflections ($I > 2\sigma(I)$).

(12) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194.

(13) Haan, K. H. D.; Bore, J. L. D.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *327*, 31.

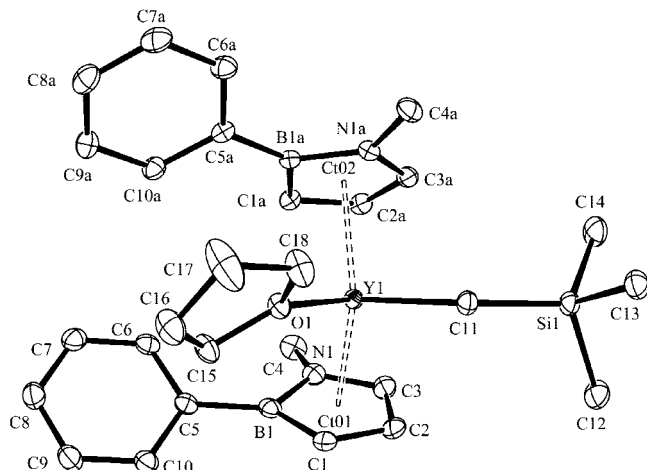


Figure 1. An ORTEP diagram of racemic yttrium complex **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (in Å) and bond angles (in deg): Y1–C1 = 2.656(3), Y1–C2 = 2.622(3), Y1–C3 = 2.633(3), Y1–N1 = 2.699(2), Y1–B1 = 2.795(3), Y1–C11 = 2.394(3), Y1–O1 = 2.395(2), Y1–Ct01 = 2.389(3), Y1–Ct02 = 2.402(3), B1–N1 = 1.466(3), B1–C1 = 1.509(3), B1–C5 = 1.577(3), C1–C2 = 1.428(3), C2–C3 = 1.378(3), C3–N1 = 1.399(3), N1–C4 = 1.462(3); \angle Ct01–Y1–Ct02 = 128.8(1), \angle O1–Y1–C11 = 89.0(1), \angle C11–Y1–Ct01 = 111.2(1), \angle C11–Y1–Ct02 = 128.9(1), \angle Y1–C11–Si1 = 137.5(1).

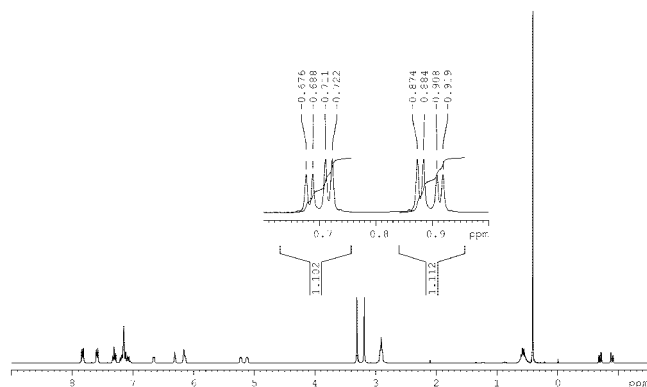


Figure 2. ^1H NMR spectrum of racemic yttrium complex **3** (300 MHz, C_6D_6 , 20 °C).

with a single covalent bond length between Y and C atoms.¹⁴ The two Ab rings are almost planar (0.018 and 0.024 Å deviation out of the mean planes, respectively) but are unsymmetrically coordinated to the Y atom in such a manner that Y is closer to C and N (2.62–2.70 Å) and farther away from B (2.80 Å). Thus, the coordination of the Ab rings to the Y atom can be best described as η^4 .

The NMR spectral data of racemic **3** in the solution phase are in agreement with its monomeric solid-state molecular structure. At the beginning of the study, we anticipated that the (trimethylsilyl)methyl group attached to the Y atom could serve as an indicator for the relative ratio of the meso and racemic isomers in the final product. In racemic **3**, two H groups (H_a and H_b) of CH_2SiMe_3 are expected to be prochiral and inequivalent, while those of meso **3** will become identical. In fact, this inequivalence of two hydrogen groups at the methylene

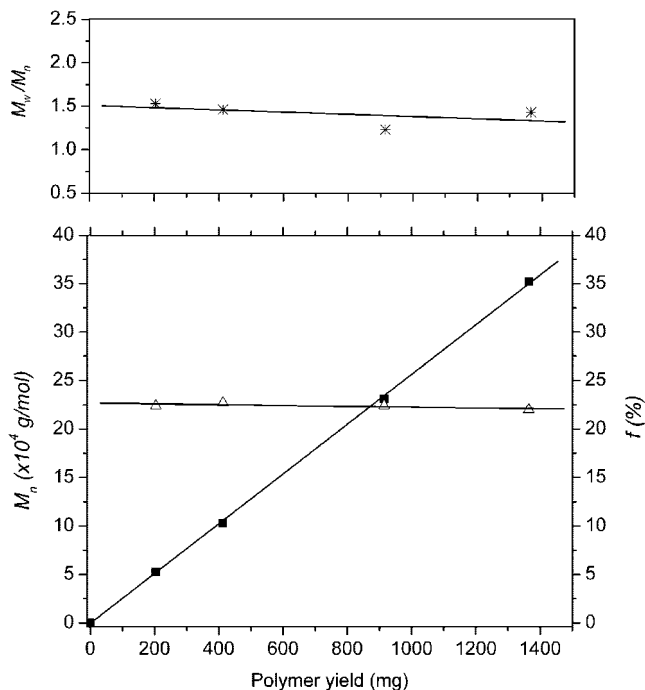


Figure 3. Time course plots of M_n , M_w/M_n , and f vs polymer yields in MMA polymerization by initiator **3** at –20 °C (17.8 μmol of **3**, solvent toluene, $[\text{sol}]/[\text{M}] = 20:1$ (v/v), 20 min (■, runs 1–4); M_n = number-average molecular weight, M_w = weight-average molecular weight, M_w/M_n = molecular weight distribution (polydispersity, PDI) (*); f = initiator efficiency (Δ)).

carbon atom has been confirmed by the presence of two sets of signals at –0.71 and –0.89 ppm ($^2J_{\text{Y-C-H}} = 3.2$ Hz,^{13,15} $^2J_{\text{H-C-H}} = 10.4$ Hz^{14a}), as illustrated in Figure 2. Similarly, two Ab rings give rise to six distinctive H signals in racemic **3**, indicating a chiral environment lack of symmetry around the Y metal center. In addition, a doublet signal at 30.3 ppm with $^1J_{\text{Y-C}} = 43.4$ Hz is attributed to the methylene carbon atom in the ^{13}C NMR spectrum of racemic **3**, which is comparable with the values found for the corresponding bis-Cp yttrium alkyl THF complexes.¹³ Therefore, it is highly possible that the racemic complex **3** exists monomerically in solution. The conversion between the meso and racemic isomers of **3** must not take place appreciably in solution, because racemic **3** did not transform into its meso isomer, as monitored by ^1H NMR spectroscopy at 25 °C for 24 h.

Lanthanide complexes, in particular Cp derivatives, have been utilized as highly efficient initiators to prepare poly(methyl methacrylate) (PMMA).^{16,17} Among these lanthanide Cp derivatives, living systems are of the greatest interest, as they confer control over molecular weight and polydispersity (PDI) as well

(15) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, 5, 263.

(16) Because there are extensive literature precedents concerning organolanthanide-initiated MMA polymerization, only some representative examples are given here: (a) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, M.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, 114, 4908. (b) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, 26, 7134. (c) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, 117, 3276. (d) Boffa, L. S.; Novak, M. *Macromolecules* **1994**, 27, 6993. (e) Qian, Y. L.; Bala, M.; Yousef, M.; Zhang, H.; Huang, J. L.; Sun, J. Q.; Liang, C. F. *J. Organomet. Chem.* **2002**, 188, 1. (f) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2004**, 23, 2972. (g) Gamer, M. T.; Rastätter, M.; Roesky, P. W.; Steffens, A.; Glanz, M. *Chem. Eur. J.* **2005**, 11, 3165. (h) Cui, P.; Chen, Y. F.; Zeng, X.; Sun, J.; Li, G.; Xia, W. *Organometallics* **2007**, 26, 6519.

(14) (a) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985. (b) Sum of the covalent radii: $r(\text{Y}) + r(\text{C}) = 1.62 + 0.77 = 2.39$ Å.

as microstructure in the polymerization process.¹⁷ However, examples of yttrium Cp complexes that could initiate living MMA polymerization are few in number.^{16b,17b,e} Fortunately, our preliminary results indicate that yttrium complex **3** initiates MMA polymerization in a living manner in toluene at $-20\text{ }^{\circ}\text{C}$, as evidenced by the fact that the number-average molecular weight (M_n) of PMMA grows linearly with the amount of monomer consumed (Figure 3). In all runs, over 97% yields of PMMA have been obtained in 20 min using a small load of initiator (17.8 μmol of **3**) and the M_n values of PMMA reach up to 3.5×10^5 with relatively low PDI values (1.2–1.5). Notably, all gel permeation chromatography (GPC) curves possess bimodal molecular weight distributions, plagued with a small peak attributed to a higher molecular weight fraction of PMMA (see the Supporting Information). It is unlikely that the small fraction of high-molecular-weight PMMA is generated via O_2 -mediated coupling of two polymer chains,¹⁸ because this small high-molecular-weight fraction remained in the GPC chromatogram even after the O_2 -free methanol had been used to terminate the growing centers at the end of the polymerization process. Therefore, it is our current thinking that this small fraction peak more likely originates from a second species formed during the polymerization with a low concentration.^{16e} Low-molecular-weight tailing responsible for increasing the polydispersity is also observed in the main GPC peak. The exact origin of the tailing is still uncertain, but it seems likely that the tailing may be the result of slow initiation and/or chain termination by a small amount of impurity at the early stage of the polymerization process. Microstructural analysis indicates that the PMMA produced with racemic **3** is a syndiotactic-rich polymer ($mm:mr:rr = 10.0:27.4:62.6$),¹⁹ which is more consistent with a site-control mechanism as predicted by the Bernoulli model ($2[mm]/[mr] = 1$).²⁰ It is worth noting that this triad ratio is somewhat unexpected and is different from

the chain-end control of tacticity commonly observed in the MMA polymerization initiated by group III metal and lanthanide Cp derivatives.¹⁶ In comparison, blank MMA polymerization experiments using the corresponding Ab lithium salt as initiator did not afford PMMA, which rules out the possibility that the observed polymerization is initiated by a free anionic Ab ligand.

In summary, the THF-coordinated yttrium alkyl complex **3** is the first example of a group III metal complex with a supporting ancillary Ab ligand. X-ray diffraction revealed η^4 -coordinated Ab rings in the racemic yttrium complex **3**. Complex **3** serves as an efficient single-component initiator to initiate MMA polymerization with living character, and the polymerization is more consistent with a site-control mechanism. Further effort will be directed to extend this synthetic approach to other lanthanide complexes based on 1,2-azaborolyls, in particular multisubstituted Ab ligands, and to prepare their THF-free lanthanide analogues by ligand modification that will promote rapid initiation and exhibit higher stereospecificity in the polymerization process.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI), and the Ontario Innovation Trust (OIT) for their generous financial support. We also thank Prof. Dr. Mario Gauthier (University of Waterloo) for a helpful discussion.

Supporting Information Available: Text, figures, and a table providing general remarks on the experiments and characterization data for all complexes and PMMA, NMR spectroscopic data for **2** and **3**, GPC chromatograms of the PMMA prepared, and polymerization results and a CIF file giving X-ray crystallographic data for yttrium complex **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM800073S

(17) For reviews, see: (a) Hou, Z. M.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, 231, 1. (b) Yasuda, H. *J. Organomet. Chem.* **2002**, 647, 128. (c) Okuda, J. *Dalton Trans.* **2003**, 2367. (d) Edelmann, F. T.; Lorenz, V. *Coord. Chem. Rev.* **2000**, 209, 99. (e) Nakayama, Y.; Yasuda, H. *J. Organomet. Chem.* **2004**, 689, 4489.

(18) (a) *The Chemistry of Organolithium Compounds*; Wakefield, B. J., Ed.; Pergamon Press: New York, 1974. (b) Panek, E. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1972**, 94, 8768.

(19) (a) Bovey, F. A. *J. Polym. Sci.* **1960**, 46, 59. (b) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, 44, 173.

(20) Typical procedure for MMA polymerization using **3** as the initiator: toluene (3.0 mL) and MMA (0.210 g, 118 equiv) were added in a Schlenk flask in the glovebox. The temperature of the flask was kept at $-20\text{ }^{\circ}\text{C}$, and a toluene solution (1.0 mL) containing complex **3** (10.0 mg, 17.8 μmol) was then added into the flask via a syringe. The mixture was magnetically stirred for 20 min and was then poured into excess MeOH. The resultant polymer was collected on a filter paper by filtration, washed with MeOH, and then dried in vacuo. MeOH was obtained by purging commercial MeOH with N_2 for 30 min to ensure that it was O_2 -free prior to use.