Organometallics **2009,** *28,* 517–522

1,2-Azaborolyl-Ligated Half-Sandwich Complexes of Scandium(III) and Lutetium(III): Synthesis, Structures, and Syndiotactic Polymerization of Styrene[†]

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Received July 31, 2008

Half-sandwich Sc(III) and Lu(III) complexes with ancillary trisubstituted 1,2-azaborolyl (Ab) ligands have been conveniently prepared via the reaction of the corresponding anionic Ab ligands with cationic Sc(III) and Lu(III) dialkyl species in good yields and characterized crystallographically. In the solid-state molecular structures of the half-sandwich mono-Ab Sc(III) complexes **5** and **6**, the interaction between the Sc metal center and Ab ligand is strongly influenced by the exocyclic B substituent, whereas in the analogous Lu(III) system **8** this interaction becomes much less prominent, as indicated by a relatively shorter Lu−B bond distance along with an attenuated exocyclic B−N bond interaction. Upon activation, the Sc(III) complexes **5** and **7** were found to be highly active in the syndiospecific polymerization of styrene.

Introduction

Cyclopentadienyl (Cp)-based half-sandwich group III rare-earth metal dialkyl complexes (Figure 1, **A**) have attracted a tremendous amount of current research interest in selective organic transformations and homogeneous polymerization catalysis, due to their unique bonding and structural features.[1] For example, the coordination site in half-sandwich group III metal Cp complexes becomes generally more accessible to the substrate and the metal center is more electronically unsaturated, which furnishes the complexes with significantly higher reactivity with respect to their metallocene analogues (Figure 1, **B**). On the other hand, this sterically and electronically unsaturated character of **A** also hampers its synthesis, mainly because of the thermodynamics-driven ligand redistribution reaction that prefers to yield relatively more stabilized metallocene analogues **B** as the product. Thus, the synthetic strategies used to stabilize these considerably labile half-sandwich group III metal complexes and to avoid the occurrence of ligand redistribution involve either sterically demanding Cp ligands such as pentamethylcyclopentadienyl (Cp*) or Cp derivatives bearing a chelate structure, as utilized in constrained geometry catalysts (CGC). Despite the great success in the Cp chemistry, a myriad of useful Cp surrogate ligands have been synthesized and studied with an aim to provide new possibilities relative to more readily available Cp derivatives.[2] In particular, as the isoelectronic and isolobal Cp analogues,[3,4,6,7] 1,2-azaborolyl (Ab) ligands have been observed to be more electron-donating than the Cp counterparts by Fu and co-workers,[4,7c] which is also supported by the DFT calculation results.[5] One additional advantage of Ab over Cp ligands has been noted for easy modulation of the electronic nature of the Ab ligand in the complexes being studied.[4] Ab ligands also merit from their unique ring geometry, which may provide a coordination environment different from that of Cp.[6] Surprisingly, in sharp contrast to the rapid development of Cp-containing half-sandwich group III metal complexes, no example even exists in the literature concerning analogous Ab-ligated half-sandwich transition-metal alkyl complexes.[7,8] We have recently reported the syntheses and characterization of multiply substituted Ab ligands and demonstrated that these Ab ligands can serve as good supporting ancillary ligands in group IV transition-metal complexes.[6] These results provide further incentives for the study of half-sandwich transition-metal complexes based on Ab ligands in a broad sense. In this contribution we describe a novel synthesis and structural comparison of mono-Ab dialkyl complexes of Sc(III) and Lu(III), the first examples of Ab-ligated half-sandwich group

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[†] The design, syntheses, and structural determination of Sc complexes **5**−**7**, Lu complex **8**, and initial polymerization study were carried out independently at the University of Waterloo; the polymerization study of **5**−**7** and elemental analyses of **5**−**7** were performed at RIKEN.

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[§] RIKEN.

[⊥] X-ray crystallographer.

(1) For reviews on Cp-ligated half-sandwich rare-earth-metal complexes, see: (a) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953. (b) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114. (c) Okuda, J. *Dalton Trans.* **2003**, 2367.

(2) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851.

(3) Ashe, A. J., III; Fang, X. *Org. Lett.* **2000**, *2*, 2089.

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

(5) Orian, L. *Rev. Roum. Chim.* **2007**, *52*, 551.

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

(7) There are a few scattered examples of Ab-ligated half-sandwich late-transition-metal non-alkylated complexes (e.g. Cr/Co/Rh); see: (a) Schmid, G. In *Comprehensive Heterocyclic Chemistry II*; Shinkai, I., Ed.; Elsevier: Oxford, U.K., 1996; Chapter 3.17. (b) Schmid, G.; Schütz, M. *Organometallics* **1992**, *11*, 1789. (c) Liu, S.-Y.; Hills, I. D.; Fu, G. C. *Organometallics* **2002**, *21*, 4323.

(8) Half-sandwich rare-earth-metal dialkyl complexes bearing pyrollyl and phospholyl ligands were reported recently. See: (a) Nishiura, M.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2008**, 2019. (b) Jaroschik, F.; Shima, T.; Li, X.; Mori, K.; Ricard, L.; Le Goff, X.-F.; Nief, F.; Hou, Z. *Organometallics* **2007**, *26*, 5654. (c) Roux, E. L.; Nief, F.; Jaroschik, F.; Törnroos, K. W.; Anwander, R. *Dalton Trans.* **2007**, 4866.

10.1021/om800734v CCC: $40.75

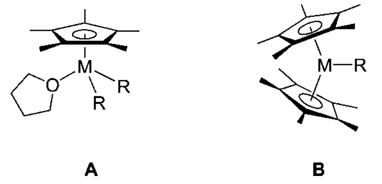
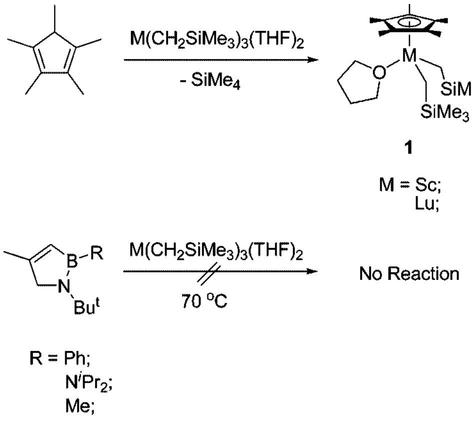


Figure 1. Cp-based rare-earth-metal complexes (M = Sc; Y; lanthanide metals. R = alkyl group).

Scheme 1



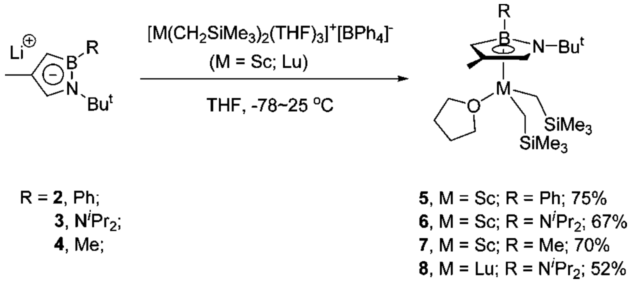
III rare-earth metal complexes. Upon activation with trityl cation and Al^{i}Bu$_3$, these complexes show interesting catalytic activity in the syndiospecific polymerization of styrene.

Results and Discussion

In analogy to the Cp chemistry,[9] our initial synthetic approach involved the reaction of M(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (M = Sc, Lu) with the conjugate acids of the anionic Ab ligands, as shown in Scheme 1. Unfortunately, the expected Sc or Lu adducts such as complexes **5**−**8** were not observed, as monitored by ^{1}H NMR spectroscopy, even after prolonged reaction time at 70 °C. Admittedly, this observation was completely consistent with the fact that the conjugate acids of Ab ligands were less acidic than those of Cp ligands, due to the less aromatic nature of the Ab ligands, relative to their Cp analogues. Therefore, the chemistry of Ab ligands did not necessarily follow that of Cp congeners, which prompted us to find other synthetic routes for the preparation of the intended mono-Ab group III metal dialkyl complexes **5**−**8**.

In 2005, Okuda et al. reported that some THF-coordinated rare-earth-metal (Sc/Y/Lu) dialkyl cations and monoalkyl dications can be conveniently prepared in excellent yields via the reaction of the corresponding trialkyl species with a weak protic acid such as [Ph$_2$NMeH]$^+$[BPh$_4$]$^-$.[10] We reasoned that, unlike lithium halides that might form "ate" types of bimetallic complexes by bridging two electron-deficient metal centers (rare-earth metal and lithium) via a halide group, noncoordinating salts such as Li$^+$[BPh$_4$]$^-$ had no lone pair of electrons to share with the metal centers and thus were ideal candidates for the preparation of salt-free half-sandwich group III metal complexes through a salt elimination pathway. We further envisioned that Okuda's cationic species can serve as the precursors for the direct preparation of THF-coordinated half-sandwich rare-earth-metal dialkyl complexes such that the synthetic difficulty encountered above can be easily resolved (Scheme 2). Thus, a simple reaction of [M(CH$_2$SiMe$_3$)$_2$(THF)$_3$]$^+$[BPh$_4$]$^-$ (M = Sc, Lu) with the corresponding trisubstituted Ab ligands **2**−**4**[6] in THF afforded the desired half-sandwich Sc/Lu complexes as air- and moisture-sensitive colorless crystals in good yields, which appeared to be much more soluble in hydrocarbon solvents such as pentane and hexane. The colorless block single crystals of complexes **5**−**8** suitable for X-ray diffraction experiments were grown slowly in pentane at −35 °C. In contrast, the reaction of less substituted Ab ligands such as 1-*tert*-butyl-2-phenyl-1,2-azaborolyl with the above Sc/Lu cation species yielded uncharacterizable products, and attempts to prepare a yttrium analogue of complexes **5**−**8** with a disubstituted Ab ligand afforded only [(Ab)$_2$Y(CH$_2$SiMe$_3$)(THF)], presumably as a result of facile ligand redistribution.[11] These observations underline the importance of multiply substituted Ab ligands in the synthesis of Ab-ligated half-sandwich metal complexes.

Scheme 2



The solid-state molecular structures of Sc (**5** and **6**) and Lu (**8**) complexes along with the selected bond lengths and angles are summarized in Figures 2−4, respectively. With the exception of Sc complex **7**, whose structural parameters could not be refined, the other two Sc complexes (**5**, *B*-Ph; **6**, *B*-N^{i}Pr$_2$) similarly show a typical three-legged piano-stool coordination geometry around the Sc center. In both cases, the Ab ligands coordinate to the Sc centers in an unsymmetric way such that Sc atoms tend to slip away from boron (Sc−B (Å): **5**, 2.664(2); **6**, 2.715(2))[12] and become more tightly affiliated with intraring C (Sc−C (Å): **5**, 2.443(2)−2.512(2); **6**, 2.411(2)−2.453(2)) and N (Sc−N (Å): **5**, 2.505(2); **6**, 2.459(2)), while the Ab ligands adopt a slight envelope-like structure. Therefore, the Sc coordination modes can be best depicted as η^4. Interestingly, the exocyclic B substituent seems to dictate the coordination mode of the metal center, because this metal slippage away from boron becomes much more intensified when a more electron-donating group such as −N^{i}Pr$_2$ is utilized, as seen in complex **6**. Notably, in the case of complex **6**, this coordination slippage makes the Sc atom even more tightly bound to an intraring N that bears a more sterically demanding *tert*-butyl group. Thus, it is likely that the above slippage is induced electronically by the exocyclic B substituent rather than the steric effect. As a consequence, the Sc−C(Ab) and Sc−N(Ab) bond lengths in **6** are much shorter than those observed in **5** (vide supra). In

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[9] (a) Evans, W. J.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711. (b) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227. (c) Cameron, T. M.; Gordon, J. C.; Scott, B. L. *Organometallics* **2004**, *23*, 2995. (d) Cui, D. M.; Nishiura, M.; Hou, Z. M. *Macromolecules* **2005**, *38*, 4089.

[10] (a) Elvidge, B. R.; Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2005**, *44*, 6777. (b) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339.

[11] Fang, X.; Deng, Y.; Xie, Q.; Moingeon, F. *Organometallics* **2008**, *27*, 2892.

[12] Shorter Sc−B bond distances (1.50−1.55 Å) were recorded in a dinuclear [{Cp*(C$_2$B$_9$H$_{11}$)ScH}$_2$]$_2$ dianionic species; see: Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126.

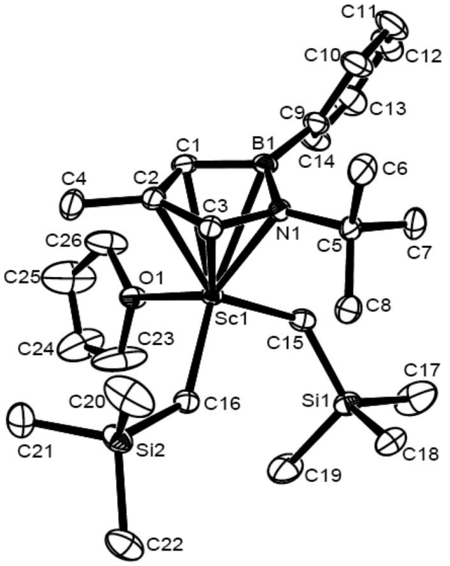

Figure 2. ORTEP drawing of Sc complex **5**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): Sc1−B1 = 2.664(2), Sc1−C1 = 2.512(2), Sc1−C2 = 2.490(2), Sc1−C3 = 2.443(2), Sc1−N1 = 2.505(2), B1−N1 = 1.480(3), B1−C3 = 1.503(3); ∠O1−Sc1−C15 = 98.1(1), ∠O1−Sc1−C16 = 98.2(1), ∠C15−Sc1−C16 = 103.6(1).

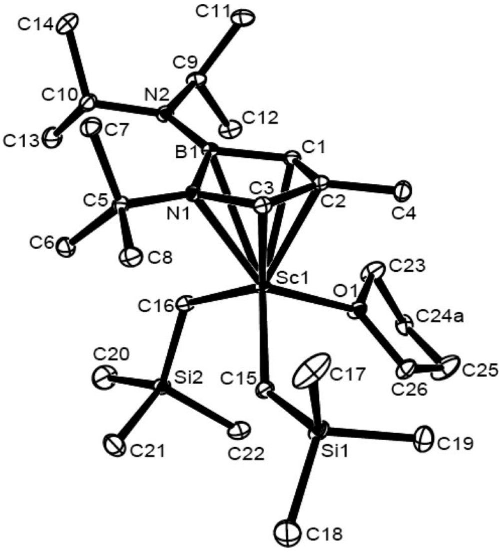

Figure 3. ORTEP drawing of Sc complex **6**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): Sc1−B1 = 2.715(2), Sc1−C1 = 2.453(2), Sc1−C2 = 2.441(2), Sc1−C3 = 2.411(2), Sc1−N1 = 2.459(2), B1−N1 = 1.525(3), B1−N2 = 1.440(3), B1−C1 = 1.532(3); ∠O1−Sc1−C15 = 96.5(1), ∠O1−Sc1−C16 = 97.0(1), ∠C15−Sc1−C16 = 108.0(1).

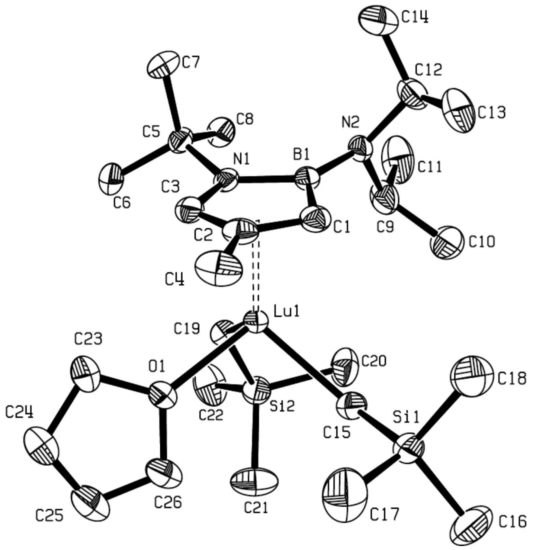

Figure 4. ORTEP drawing of Lu complex **8**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): Lu1−B1 = 2.775(3), Lu1−N1 = 2.643(2), Lu1−C1 = 2.601(3), Lu1−C2 = 2.592(3), Lu1−C3 = 2.567(3), Lu1−O1 = 2.269(2), Lu1−C15 = 2.331(3), Lu1−C19 = 2.323(4), B1−N2 = 1.471(4), B1−C1 = 1.506(4), B1−N1 = 1.498(4), C1−C2 = 1.422(4), C2−C3 = 1.363(4), C3−N1 = 1.414(3); ∠B1−N2−C9 = 116.1(2), ∠B1−N2−C12 = 119.5(2), ∠C9−N2−C12 = 116.2(2), ∠O1−Lu1−C15 = 97.59(10), ∠O1−Lu1−C19 = 94.29(10), ∠C15−Lu1−C19 = 103.09(11).

addition, the Sc−O(THF) and Sc−C(alkyl) bond distances in complex **6** are all relatively longer than the corresponding bond distances in complex **5**, consistent with a weaker interaction between Sc and non-Ab groups in **6**, as a result of the stronger electron-donating character of the *B*-diisopropylamino Ab ligand vs that of the *B*-phenyl Ab ligand. It is also worth noting that the bonding interaction between Sc and the Ab ligand in **6** may be even stronger than that in the comparable $Cp^*Sc(CH_2SiMe_3)_2(THF)$ complex **1**,[13] as evidenced by a relatively shorter average Sc−C(Ab) bond length (**6**: 2.45 Å) vs average Sc−C(Cp*) bond length (**1**: 2.50 Å).

It is of great interest to compare the X-ray structures of **6** and **8**, as they only differ in the metal atoms. First, complexes **6** and **8** share some structural similarities, as the metal centers in both cases are pseudotetrahedrally coordinated to give the complexes a typical three-legged piano-stool geometry, in which only one Ab ring is allowed to ligate the η^4-metal center that is shifted away from B (**6**, vide supra; **8**, Lu−B = 2.775(3) Å, Lu−C/N = 2.567(3)−2.643(3) Å). Second, both **6** and **8** differ from each other. In a closer examination, one can tell that the slippage away from B becomes relatively less prominent in the Lu complex **8**, as the observed metrical difference between Lu−B and Sc−B bond lengths (2.77 vs 2.71 Å) is noticeably smaller than that of normal Lu−B and Sc−B covalent bonds (2.42 vs 2.26 Å).[14] In addition, the exocyclic B−N bond of the Ab ligand in **8** is attenuated with less double bond character. For example, the elongation of the exocyclic B−N bond length in **8** (**6**, 1.441(3) Å; **8**, 1.471(3) Å) has been noted, and the diisopropylamino group is twisted away from being coplanar with the Ab ring such that the diisopropylamino N in **8** turns pyramidal (sum of the three bond angles around N (in deg): **6**, 360; **8**, 352). Another notable structural difference is that upon switching the metal center from Sc to Lu, the metrical values of intraring bond lengths of the Ab ligand in the Lu complex **8** fall short of those of Sc analogue **6**, and the Ab ring in complex **8** is almost planar, in contrast to an η^4-coordinated envelope-like Ab structure of complex **6**. Perhaps this structural discrepancy of complexes **6** and **8** cannot be simply ascribed to the different ionic radii of Sc (0.88 Å) and Lu (1.00 Å),[14] because

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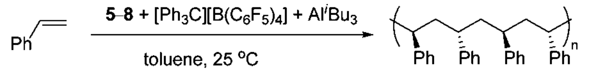
[13] Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962.

[14] *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985.

in analogous bis-Ab yttrium alkyl complexes, the Ab ligands were observed to coordinate to the Y atom with a larger ionic radius (1.04 Å)[14] in a way much similar to that in complex **6**,[15] which clearly does not sustain the above ionic-radius assumption. In view of the electropositive nature and limited radial extension of the 4f orbital configuration generally associated with lanthanide metals,[16] we expect that the electrostatic interaction between the lanthanide metal center (e.g., Lu) and ligand (e.g., Ab) becomes important. As a result, the Lu−Ab interaction possesses more ionic character, which drives the Ab ligand to keep its original aromatic identity. Nonetheless, further studies are needed to provide a conclusive explanation for the above observations.

The ^{1}H and ^{13}C NMR spectroscopic investigations were carried out in benzene-d_6 or toluene-d_8 to gain insight into their solution-phase behavior. The NMR data of all Sc and Lu complexes in hydrocarbon solution are consistent with their monomeric structures. For example, the ring H resonances appeared as two doublets ranging from 3.9 to 6.8 ppm in all four cases. In particular, the ambient-temperature NMR spectrum suggests the slow B−N rotation in complexes **6** and **8**, as indicated by diastereotopic ^{i}Pr groups. Upon heating up to 100 °C in toluene-d_8, no coalescence of two signals corresponding to the ^{i}Pr methyl groups (**6**, δ 25.0, 24.8 ppm; **8**, 24.8, 24.7 ppm) in the ^{13}C NMR spectra has been observed, which implies a fairly strong B−N π bond with a rotational barrier of $\Delta G^\ddagger > 19.2 \pm 0.5$ kcal mol^{-1} in both cases.[17] This result agrees well with the strongly electron deficient nature of the metal centers that effectively withdraws electron density away from the Ab ligand and makes boron interact with its electron-rich exocyclic substituent, as evidenced by short exocyclic B−N bond lengths (**6**, 1.440(3) Å; **8**, 1.471(4) Å). It should be pointed out that the presence of a bulky N-^{t}Bu group also helps to increase the free energy of the B−N bond rotational barrier.

Table 1. Syndiospecific Polymerization of Styrene[a]



entry	cat.	amt of Al^{i}Bu$_3$ (equiv)	[M]/[Sc]	yield (%)	sPS[b] (%)	$10^5 M_n$[c]	M_w/M_n[c]	T_m[d] (°C)
1	**5**	2	2000	100	100	6.8	2.2	270
2	**5**	2	2500	100	100	9.1	2.1	270
3	**5**	2	3000	94	100	13.5	1.9	270
4	**6**	2	2000	27	100	31.2/2.2	1.5/2.5	271
5	**7**	2	2000	100	100	5.7	2.5	271
6	**7**	2	2500	100	100	10.5	1.7	271
7	**7**	2	3000	95	100	16.3	1.5	271
8	**7**	5	3000	100	100	4.1	3.1	271
9	**7**	10	3000	100	100	1.9	3.5	270
10	**8**	1	500	20	100	0.38	2.6	270
11	**8**	2	500	16	100	0.30	1.8	271
12	**8**	5	500	10	100	0.10	1.5	270
13	**8**	1	1000	22	100	0.36	2.6	270

[a] Conditions: Sc, 25 μmol; [Sc]/[B] = 1/1 (mol/mol); 30 mL of toluene; t = 10 min, T = 25 °C; Lu, 25 μmol; [Lu]/[B] = 1/1 (mol/mol); 30 mL of toluene; t = 10 h, T = 25 °C. [b] Determined by ^{13}C NMR. Solvent fractionation showed no presence of atactic polystyrene. [c] Determined by Tosoh HLC-8121GPC/HT in 1,2-dichlorobenzene or Varian PL GPC-220 with Wyatt HELEOS MALS in 1,2,4-trichlorobenzene at 145 °C against polystyrene standard. [d] Determined by DSC.

At the beginning of the preliminary polymerization study, we were intrigued by the role of Ab ligand as a strong electron donor in stabilizing electron-deficient cationic metal species, the catalytically active species responsible for the chain growth in syndiospecific styrene polymerization processes.[1b,18] It is expected that this relatively more stabilized cationic Ab-ligated metal species, relative to the Cp analogues, may have an increased life span and essentially contribute to a more efficient catalyst system. In fact, when activated by 1 equiv of $[Ph_3C]^+[B(C_6F_5)_4]^-$ in the presence of Al^{i}Bu$_3$, Sc complexes **5**−**7** showed high activity for the syndiospecific polymerization of styrene to yield polystyrene with syndioselectivity of >99% (*rrrr*). Some representative results are summarized in Table 1. In the case of complexes **5** and **7**, 2000 equiv of styrene monomer could be quantitatively polymerized within 10 min, yielding unimodal syndiotactic polystyrenes with moderate molecular weight distributions (M_w/M_n = 2.2−2.5), consistent with the predominance of a single homogeneous catalytic species (Table 1, entries 1 and 5). Under the same conditions ([M]/[Sc] = 2000), Sc complex **6** showed lower activity and afforded polystyrene with a bimodal molecular weight distribution, suggesting the presence of two active species in this system (Table 1, entry 4). Similarly, Lu complex **8** showed lower yet steady activity that could last at least for 10 h, and its polymerization was unaffected by the relative monomer-to-catalyst ratio (Table 1, entries 10 and 13) but was significantly influenced by the amount of Al^{i}Bu$_3$ added in the polymerization process, as the increase of the Al^{i}Bu$_3$ addition resulted in lower molecular weight and smaller M_w/M_n (Table 1, entries 11 and 12). Complexes **5** and **7** were then further examined under various monomer-to-catalyst ratios (2000−3000) (Table 1, entries 1−3 and 5−7). In both systems, the molecular weight of the resultant polymers has been significantly increased with decreased polydispersity as the monomer-to-catalyst ratio is raised. In the case of [M]/[Sc] = 3000, syndiotactic polystyrene with an M_n value as high as 1.6×10^6 and M_w/M_n controlled at 1.5 can be obtained (Table 1, entries 3 and 7). The addition of Al^{i}Bu$_3$ also showed great influence on the present catalyst system.[19] In the case of $\mathbf{7}/[Ph_3C]^+[B(C_6F_5)_4]^-$, the use of more Al^{i}Bu$_3$ led to a higher yield of polystyrene (Table 1, entries 7 and 8). On the other hand, an increase of the [Al]/[Sc] ratio resulted in lower molecular weight and broader molecular weight distribution of the resulting polymers (Table 1, entries 7−9), suggesting that the chain-transfer reaction to Al^{i}Bu$_3$ could occur more frequently at a higher Al^{i}Bu$_3$ feed. Nevertheless, the present catalyst systems yield syndiotactic polystyrene with molecular weight much higher than that produced in the case of the Cp-ligated analogous systems, albeit in the presence of Al^{i}Bu$_3$.

Conclusions

In summary, we have developed an efficient synthesis for novel half-sandwich Sc and Lu dialkyl complexes **5**−**8**, the first examples of Ab-ligated half-sandwich group III metal complexes. Our synthesis has the advantage of being general. The interaction between the Sc metal center and Ab ligand is strongly

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(15) Two bis-Ab yttrium alkyl complexes with B-substituted diisopropylamino groups have been prepared and crystallographically characterized. In both cases, the diisopropylamino N atoms are sp^2 hybridized and the exocyclic B−N bond lengths are in an appropriate range for a moiety with substantial double-bond character (unpublished work).

(16) Evans, W. J. *Inorg. Chem.* **2007**, *46*, 3435.

(17) Friebolin, H. *Basic One-and Two-Dimentional NMR Spectroscopy*, 3rd ed.; Wiley-VCH: New York, 1998; p 307.

(18) (a) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910. (b) Zhang, H.; Luo, Y.; Hou, Z. *Macromolecules* **2008**, *41*, 1064.

(19) In the absence of Al^{i}Bu$_3$, $\mathbf{7}/[Ph_3C][B(C_6F_5)_4]$ alone showed much lower activity and gave a bimodal polymer under the same conditions, which was in contrast with case for the Cp-ligated analogues.

influenced by the exocyclic B substituent, whereas in the analogous Lu(III) system, this interaction becomes much less prominent, as revealed by the X-ray diffraction experiments. When treated with 1 equiv of $[Ph_3C]^+[B(C_6F_5)_4]^-$ in the presence of Al^iBu_3, these Ab-ligated half-sandwich metal complexes demonstrate moderate-to-high catalytic activity in producing syndiotactic polystyrene with molecular weight higher than that for the corresponding Cp systems. Further studies toward the preparation of the analogous half-sandwich complexes based on other group III rare-earth metals and the copolymerization of CO_2 and epoxides are in progress.

Experimental Section

General Method and Instrumentation. All operations involving organometallic compounds were carried out under an atmosphere of pure dinitrogen by means of standard Schlenk techniques and an MBraun Unilab 1200/780 glovebox. The oxygen and moisture in the atmosphere of the MBraun Unilab glovebox were constantly monitored by both oxygen and moisture analyzers to ensure O_2/H_2O concentrations below 0.1 ppm. Et_2O and THF were distilled under nitrogen prior to use from sodium/benzophenone ketyl and CH_2Cl_2 from CaH_2. Pentane, hexane, and toluene were distilled from Na/K alloy. *n*-BuLi (2.5 M in hexanes) and MeMgBr (3.0 M in Et_2O) were purchased from Sigma-Aldrich and used as received. The deuterated NMR solvents were obtained from Cambridge Isotope Laboratories. THF-d_8 was degassed and dried over Na/K alloy. C_6D_6 and $CDCl_3$ were distilled from CaH_2 and degassed prior to use. 1,2-Azaborolyl ligands[6] and $[M(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ (M = Sc; Lu)[10] were prepared using the literature procedures. Styrene (99%, Sigma-Aldrich) was dried by stirring with CaH_2 for 2 days and was purified by distillation and vacuum transfer prior to use. All other materials were commercially available and used without further purification. All B-containing samples for NMR spectroscopic measurements were prepared in the glovebox. NMR spectra were recorded on a Bruker Avance 300 spectrometer. ^1H and ^{13}C NMR spectra were calibrated using the signals from the solvents referenced to Me_4Si. The ^{11}B NMR spectra were referenced to external $BF_3 \cdot OEt_2$. Chemical shifts (δ) are reported in parts per million (ppm). The combustion, differential scanning calorimeter (DSC), and gel permeation chromatography (GPC) analyses were performed at the facility of Organometallic Chemistry Laboratory of RIKEN (Japan), the University of Michigan, or the University of Waterloo. The X-ray diffraction experiments were carried out at the X-ray facility center, Department of Chemistry, University of Waterloo (Canada).

The GPC analyses were performed using Tosoh HLC-8121GPC/HT or Varian PL GPC-220 with Wyatt HELEOS MALS systems maintained at 145 °C. 1,2-Dichlorobenzene (Tosoh) or 1,2,4-trichlorobenzene (Varian) was used as an eluant with a flow rate at 1.0 mL/min. M_w, M_n, and M_w/M_n values were obtained against polystyrene standard or with MALS. The DSC measurement for the melting temperatures (T_m) of polystyrene samples were obtained with an SII Nanotechnology EXSTAR6220 instrument at a heating rate of 10 °C/min under a helium atmosphere.

Synthesis and Characterization of Scandium Complex 5. A typical procedure for the synthesis of Ab-ligated half-sandwich scandium(III) and lutetium(III) dialkyl complexes is given as follows. A solution of lithium salt **2** (0.350 g, 1.59 mmol) in 5 mL of THF was added dropwise into a colorless solution of $[Sc(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ (1.20 g, 1.59 mmol) in 7 mL of THF at −78 °C. The mixture was stirred for 2 h at −78 °C and then for 20 min at 25 °C. After solvent removal, the pale yellow residue was extracted with 20 mL of hexane. The mixture was filtered to remove $LiBPh_4$. The filtrate was further concentrated and crystallized at −35 °C to give compound **5** as colorless block crystals (0.60 g, 1.18 mmol, 75% yield). Other complexes such as **6** and **7** can be prepared analogously. ^1H NMR (300 MHz, C_6D_6): δ 7.85 (d, $J = 2$ Hz, 2H, Ar*H*), 7.31 (t, $J = 2$ Hz, 2H, Ar*H*), 7.19 (t, $J = 2$ Hz, 1H, Ar*H*), 6.76 (d, $J = 2.6$ Hz, 1H), 4.50 (d, $J = 2.6$ Hz, 1H), 3.65 (br, 4H, THF), 2.00 (s, 3H, Ab*Me*), 1.43 (s, 9H, ^{t}Bu), 1.07 (br, 4H, THF), 0.33 (s, 18 H, Si*Me₃*), 0.16 (dd, $J = 27.2$ and 11.5 Hz, 2H, CH_2Si), −0.13 (s, 2H, CH_2Si). ^{13}C NMR (75.5 MHz, C_6D_6): δ 134.5, 132.7, 127.3, 126.7, 109.9, 72.3, 57.3, 32.4, 24.7, 16.5, 4.2, 4.0. ^{11}B NMR (96.3 MHz, C_6D_6): δ 33.0. Anal. Calcd for $C_{26}H_{49}BNOScSi_2$: C, 62.01; H, 9.81; N, 2.78. Found: C, 62.37; H, 9.68; N, 2.59.

Synthesis and Characterization of Scandium Complex 6. A solution of lithium salt **3** (0.385, 1.59 mmol) in 5 mL of THF was treated with a solution of $[Sc(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ (1.20 g, 1.59 mmol) in 7 mL of THF to yield complex **6** as colorless block crystals (0.56 g, yield 67%). ^1H NMR (300 MHz, C_6D_6): δ 6.40 (d, $J = 2.8$ Hz, 1H, Ab*H*), 3.93 (d, $J = 2.8$ Hz, 1H, Ab*H*), 3.75 (br, 4H, THF), 3.70 (sept, $J = 6.6$ Hz, 2H, NC*H*), 1.87 (s, 3H, C(4)*Me*), 1.59 (s, 9H, ^{t}Bu), 1.27 (d, $J = 6.6$ Hz, 6H, $NCHCH_3$), 1.17 (br, 4H, THF), 0.33 (s, 18 H, Si*Me₃*), 0.24 (d, $J = 11.2$ Hz, 1H, CH_2SiMe_3), −0.20 (dd, $J = 26.2$, 11.5 Hz, 2H, CH_2SiMe_3), −0.32 (s, $J = 11.2$ Hz, 1H, CH_2SiMe_3). ^{13}C NMR (75.5 MHz, C_6D_6): δ 131.0, 125.6, 106.1, 72.4, 55.7, 47.8, 32.2, 24.8($CH(CH_3)_2$), 24.7($CH(CH_3)_2$), 23.9, 16.1, 4.31, 4.08. ^{11}B NMR (96.3 MHz, C_6D_6): δ 31.8. Anal. Calcd for $C_{26}H_{58}BN_2OScSi_2$: C, 59.29; H, 11.10; N, 5.32. Found: C, 59.54; H, 10.90; N, 5.68.

Synthesis and Characterization of Scandium Complex 7. A solution of lithium salt **4** (0.250, 1.59 mmol) in 5 mL of THF was treated with a solution of $[Sc(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ (1.20 g, 1.59 mmol) in 7 mL of THF to yield complex **7** as colorless block crystals (0.50 g, yield 72%). ^1H NMR (300 MHz, C_6D_6): δ 6.65 (d, $J = 2.9$ Hz, 1H, Ab*H*), 4.41 (d, $J = 2.9$ Hz, 1H, Ab*H*), 3.67 (br, 4H, THF), 1.91 (s, 3H, C(4)*Me*), 1.43 (s, 9H, ^{t}Bu), 1.12 (br, 4H, THF), 1.07 (s, 3H, B*Me*), 0.30 (s, 18H, Si*Me₃*), 0.12 (d, $J = 10.2$ Hz, 1H, CH_2SiMe_3), −0.14 (d, $J = 11.2$ Hz, 1H, CH_2SiMe_3), −0.32 (dd, $J = 11.2$ and 10.2 Hz, 2H, CH_2SiMe_3). ^{13}C NMR (75.5 MHz, C_6D_6): δ 130.9, 109.4, 71.9, 56.4, 31.7, 24.8, 15.9, 4.3, 4.1. ^{11}B NMR (96.3 MHz, C_6D_6): δ 33.7. Anal. Calcd for $C_{21}H_{47}BNOScSi_2$: C, 57.12; H, 10.73; N, 3.17. Found: C, 56.72; H, 10.38; N, 3.31.

Synthesis and Characetrization of Lutetium Complex 8. A solution of lithium salt **3** (0.22 g, 0.90 mmol) in 5 mL of THF was treated with a solution of $[Lu(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ (0.80 g, 0.90 mmol) in 7 mL of THF to yield complex **8** as colorless block crystals (0.37 g, yield 52%). ^1H NMR (300 MHz, C_6D_6): δ 6.39 (d, $J = 3.0$ Hz, 1H, Ab*H*), 3.93 (d, $J = 3.0$ Hz, 1H, Ab*H*), 3.79 (b, 4H, THF), 3.74 (sep, $J = 6.0$ Hz, 2H, $NCHMe_2$), 1.86 (s, 3H, CH_3(Ab)), 1.58 (s, 9H, ^{t}Bu), 1.33 (d, $J = 6.0$ Hz, 6H, CH_3(^{i}Pr)), 1.27 (d, $J = 6.0$ Hz, 6H, CH_3(^{i}Pr)), 1.18 (b, 4H, THF), 0.31 (s, 18H, $SiMe_3$), 0.22 (d, $J = 12$ Hz, 1H, CH_2Si), −0.16 (d, $J = 12$ Hz, 1H, CH_2Si), −0.25 (d, $J = 12$ Hz, 1H, CH_2Si), −0.32 (d, $J = 12$ Hz, 1H, CH_2Si).^{13}C NMR (75.5 MHz, C_6D_6): δ 131.0 (C_4(Ab)), 106.1 (C_5(Ab)), 96.1 (b, C_3(Ab)), 72.4, 55.7, 47.8, 41.1 (b), 37.6 (b), 32.2, 24.8 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 23.9, 16.7, 4.3, 4.1, −2.5. ^{11}B NMR (96.3 MHz, C_6D_6): δ 31.6. Anal. Calcd for $C_{26}H_{58}BN_2OSi_2Lu$: C, 47.55; H, 8.90; N, 4.27. Found: C, 47.91; H, 9.12; N, 4.20.

Polymerization Procedures. A typical procedure for styrene polymerization using **7**/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ (Table 1, entry 5) is as follows. In a glovebox, a solution of $[Ph_3C][B(C_6F_5)_4]$ (23 mg, 25 μmol) in 15 mL of toluene was added to a solution of **7** (11 mg, 25 μmol) in 15 mL of toluene in a 100 mL flask. The mixture was stirred at room temperature for a few minutes, and 2 equiv of Al^iBu_3 (50 μL, 50 μmol) was added into the above mixture with stirring, followed by styrene (5.2 g, 50 mmol) within 2 min. The magnetic stirring was stopped within a few seconds due to the increased viscosity. After ca. 10 min, methanol (2 mL) was added to terminate the polymerization. The flask was then taken out from the glovebox and the mixture was poured into methanol (400 mL) to precipitate the polymer. The white polymer powder was collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight (5.2 g, 100%).

Crystallographic Data. The single crystals of complexes **5**, **6** and **8** were immersed in FOMBLIN Y oil (HVAC 140/13, Sigma-Aldrich), mounted on a glass fiber, and examined on a Bruker AXS SMART-CCD 1K detector diffractometer equipped with a Cryostream N_2 cooling device using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 173 K, respectively. The determination of crystal class and unit cell was carried out by the SMART program package.[20] The raw frame data were processed using SAINT[21] and SADABS[22] to yield the reflection data file. The structures were solved using the SHELXTL program.[23] Refinement was performed on F^2 anistropically for all the non-hydrogen atoms by full-matrix least-squares methods. Analytical scattering factors for neutral atoms were used throughout the analysis.

Crystal data for **5**: $C_{26}H_{49}BNOScSi_2$, $M_w = 503.61$, monoclinic, $P2_1/n$, $a = 11.3970(5)$ Å, $b = 18.2738(8)$ Å, $c = 15.0873(7)$ Å, $\alpha = 90°$, $\beta = 95.8040(10)°$, $\gamma = 90°$, $V = 3126.1(2)$ Å^3, $D_c = 1.070$ g/cm^3, $Z = 4$, R1 = 0.0449, wR2 = 0.0979, for 301 parameters and 7567 reflections ($I > 2\sigma(I)$).

Crystal data for **6**: $C_{26}H_{58}BN_2OScSi_2$, $M_w = 526.69$, triclinic, $P\bar{1}$, $a = 10.4194(7)$ Å, $b = 12.5772(8)$ Å, $c = 14.1792(9)$ Å, $\alpha = 75.5220(10)°$, $\beta = 76.1870(10)°$, $\gamma = 66.6320(10)°$, $V = 1631.07(18)$ Å^3, $D_c = 1.072$ g/cm^3, $Z = 2$, R1 = 0.0555, wR2 = 0.0999, for 308 parameters and 9170 reflections ($I > 2\sigma(I)$).

Crystal data for **8**: $C_{26}H_{58}BLuN_2OSi_2$; $M_w = 656.70$, triclinic, $P\bar{1}$, $a = 9.2953(6)$ Å, $b = 10.4744(7)$ Å, $c = 19.1047(12)$ Å, $\alpha = 94.948(1)^o$, $\beta = 97.502(1)^o$, $\gamma = 111.509(1)^o$, $V = 1697.5(2)$ Å^3, $T = 296(2)$ K, $Z = 2$, $D_c = 1.285$, 22 005 measured reflections, 9799 unique reflection ($R_{int} = 0.0186$), 298 refined parameters, R1($I > 2\sigma(I)$) = 0.0288, wR2(F^2) = 0.0611.

Acknowledgment. Financial support to X.F. from the Natural Sciences and Engineering Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI), the Ontario Innovation Trust (OIT), and the University of Waterloo is gratefully acknowledged.

Supporting Information Available: CIF files giving crystallographic data for complexes **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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