ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

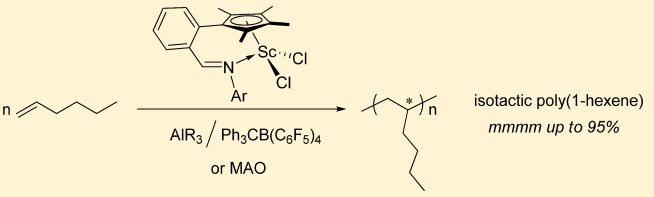
Achiral C_s-Symmetric Half-Sandwich Scandium(III) Complexes with Imine−Cyclopentadienyl Ligands Catalyze Isotactic Polymerization of 1-Hexene

Xin Tao, Wei Gao, Hang Huo, and Ying Mu*

The State Key Laboratory for Supramolecular Structure and Materials, School of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

Supporting Information

ABSTRACT: Unchelated scandium(III) trichloride complexes, 2-(ArN=CH)$C_6H_4Me_4CpScCl_3Li(THF)_4$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1a**), 2,6-Et$_2$C$_6$H$_3$ (**1b**), 2,6-Me$_2$C$_6$H$_3$ (**1c**)), were obtained from the reaction of $ScCl_3(THF)_3$ with the lithium salt of the corresponding ligand, 2-(ArC$_6$H$_3$N=CH)$C_6H_4Me_4CpLi$, in THF. After heating at 120 °C under vacuum for 30 min, the attached LiCl and THF were removed from complexes **1** to give the chelated scandium(III) dichloride complexes 2-(ArN=CH)$C_6H_4Me_4CpScCl_2$ ([Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2a**), 2,6-Et$_2$C$_6$H$_3$ (**2b**), 2,6-Me$_2$C$_6$H$_3$ (**2c**)). Attempts to synthesize dialkyl scandium(III) complexes by the reaction of $Sc(CH_2SiMe_3)_3(THF)_2$ with the corresponding free ligands were not successful. The scandium(III) trialkyl complex 2-[Li(THF)$_3$(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH]$C_6H_4Me_4CpSc(CH_2SiMe_3)_3$ (**3**) was synthesized by a one-pot reaction of $ScCl_3(THF)_3$ with 2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)$C_6H_4Me_4CpLi$ and 3 equiv of Me_3SiCH_2Li in THF sequentially. The scandium(III) dialkyl complex 2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)$C_6H_4Me_4CpSc(CH_2SiMe_3)_2$ (**4**) was obtained from the reaction of the dichloride complex **2a** with 2 equiv of Me_3SiCH_2Li in hexane. Complexes **1b,c** were directly converted to complexes **2b,c** without purification and characterization. All other scandium(III) complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analyses. The structures of complexes **1a**, **2c**, **3**, and **4** were determined by single-crystal X-ray crystallography, which indicates that the imine N atoms in complexes **1a** and **3** do not coordinate to the central scandium atoms. Complexes **2a−c** and **4** were found to exhibit moderate catalytic activity for propylene and 1-hexene polymerization upon activation with $AlR_3/Ph_3CB(C_6F_5)_4$ or methylaluminoxane (MAO) and produce atactic polypropylene and isotactic poly(1-hexene). The effects of molecular structures and reaction conditions on the catalytic behavior of these complexes were examined and the possible catalytic mechanism was discussed.



INTRODUCTION

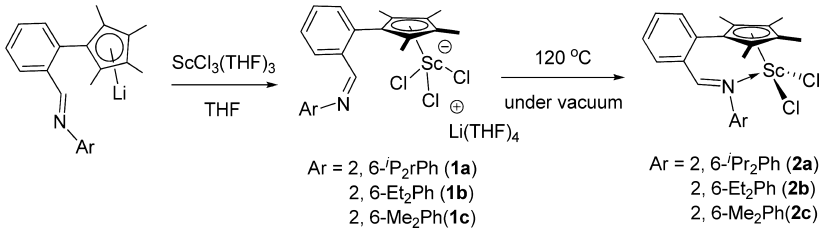
The development of stereospecific homogeneous α-olefin polymerization catalysts has been a major research field involving many academic and industrial research groups in the past two decades.[1−14] Although most of the research efforts have been focused on the development of new catalysts for propylene polymerization,[1] the design and synthesis of efficient catalysts for the stereospecific polymerization of long-chain α-olefins have also attracted extensive research interests.[2−14] The first single-component C_2-symmetric catalyst system for the stereospecific polymerization of long chain α-olefins, *rac*-Me$_2$Si(2-SiMe$_3$-4-^{t}Bu-C$_5$H$_2$)$_2$YR, was reported by Bercaw's group in 1992.[2] These C_2-symmetric yttrium catalysts show remarkably high stereospecificities for the polymerization of α-olefins. The *rac*-ethylene-1,2-bis(1-indenyl)$ZrCl_2$/MAO catalyst system was studied for the polymerization of α-olefins and found to be able to polymerize 1-hexene to yield highly isotactic poly(1-hexene) in various solvents.[3,4] The polymers of long-chain α-olefins obtained with these catalysts have low molecular weight. High-molecular-weight poly(1-hexene) was obtained under high pressures (over 100 MPa) with achiral zirconocene and hafnocene/MAO catalysts.[5] Stereospecific polymerization of 1-hexene under high pressures (up to 1000 MPa) with chiral metallocene/MAO catalysts was reported to produce high-molecular-weight stereospecific poly(1-hexene).[6] Polymerization of α-olefins initiated by the relatively bulky *rac*-Me$_2$Si(1-C$_5$H$_2$-2-CH$_3$-4-^{t}Bu)$_2$Zr(NMe$_2$)$_2$/Al(^{i}Bu)$_3$/$Ph_3CB(C_6F_5)_4$ catalyst was found to yield high-molecular-weight polymers without the need for high pressures.[7] In 2000, it was reported that a class of bulky C_1-symmetric cyclopentadienylzirconium acetamidinate complexes, Cp*ZrMe$_2$[NR^{1}C(Me)NR^2], catalyze the isospecific living polymerization of 1-hexene and produce highly isotactic, high-molecular-weight polymers with low polydispersities.[8] In the same year, C_2-symmetric non-metallocene zirconium complexes with [ONNO] ligands were also reported as good catalysts for the isospecific living polymerization of 1-hexene.[9] These two classes of catalysts were further investigated for their catalytic performance in the stereospecific polymerizations of α-olefins in the following years.[10] In recent

Special Issue: Recent Advances in Organo-f-Element Chemistry

Received: October 30, 2012
Published: February 6, 2013

   dx.doi.org/10.1021/om301026e | *Organometallics* 2013, 32, 1287−1294

Scheme 1. Synthetic Route for Complexes 1 and 2



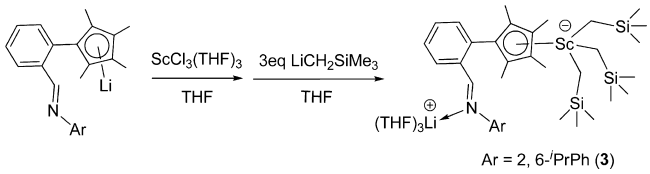
years, types of C_1-symmetric zirconium complexes with [NNN] ligands[11] and types of C_2-symmetric zirconium complexes with [OSSO] ligands[12] were also reported to be good catalysts for the isospecific polymerization of 1-hexene. In addition, isotactic polymerization of 1-hexene catalyzed by C_3-symmectric dicationic Sc alkyl species was reported, and the stereoselectivity was believed to result from a *chain-end control* mechanism according to a computational study.[13] Although most of the complexes that show good catalytic performance for the stereospecific polymerizations of α-olefins possess C_1 or C_2 symmetry, a few C_s-symmetric zirconium and hafnium complexes with a pyridylamido ligand[14a,b] or a phenylthiomethyl-substituted phenoxy ligand[14c] have been reported to catalyze the isospecific polymerization of α-olefins, and the stereoselectivity has been found to follow the *enantiomorphic site control* mechanism[14a,b] in spite of the fact that the origin of the chirality is unclear. Half-sandwich rare-earth complexes have been studied as good catalysts for the stereo- and regioselective (co)polymerizations of olefins.[15] In particular, it was found that a side arm on the Cp ring of the half-sandwich rare-earth complexes significantly affects their catalytic activity[15b,g,h] and stereoselectivity.[15a,16] Inspired by these aforementioned results, we have developed a number of new C_s-symmetric imino−cyclopentadienyl scandium(III) complexes and found that they can catalyze the isospecific polymerization of 1-hexene upon activation with AlR_3/$Ph_3CB(C_6F_5)_4$ or methylaluminoxane (MAO) and produce isotactic poly(1-hexene) with ultrahigh molecular weight at room temperature. In this paper, we report the synthesis and characterization of these complexes as well as their catalytic properties for 1-hexene and propylene polymerization.

RESULTS AND DISCUSSION

Synthesis of Complexes. The free ligands 2-(ArN=CH)$C_6H_4Me_4CpH$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**La**H), 2,6-Et$_2$C$_6$H$_3$ (**Lb**H), 2,6-Me$_2$C$_6$H$_3$ (**Lc**H)) were synthesized as reported previously.[17] They can be deprotonated by treatment with BuLi to give the corresponding lithium salts 2-(ArN=CH)-$C_6H_4Me_4CpLi$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**La**Li), 2,6-Et$_2$C$_6$H$_3$ (**Lb**Li), 2,6-Me$_2$C$_6$H$_3$ (**Lc**Li)). The new scandium(III) chloride complexes were synthesized by the reactions of $ScCl_3(THF)_3$ with the corresponding lithium salts of the ligands in THF at room temperature, as illustrated in Scheme 1. The scandium-(III) trichloride complexes 2-(ArN=CH)$C_6H_4Me_4CpScCl_3Li$-$(THF)_4$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1a**), 2,6-Et$_2$C$_6$H$_3$ (**1b**), 2,6-Me$_2$C$_6$H$_3$ (**1c**)) were obtained directly from reactions in about 60% yields. After heating at 120 °C under vacuum for several hours, the attached LiCl and THF were removed from complexes **1** to give the chelated scandium(III) dichloride complexes 2-(ArN=CH)$C_6H_4Me_4CpScCl_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2a**), 2,6-Et$_2$C$_6$H$_3$ (**2b**), 2,6-Me$_2$C$_6$H$_3$ (**2c**)). Pure complexes **2** were obtained in 60−65% isolated yields by extraction with CH_2Cl_2 to remove insoluble impurities and recrystallization in a CH_2Cl_2/hexane mixed solvent system.

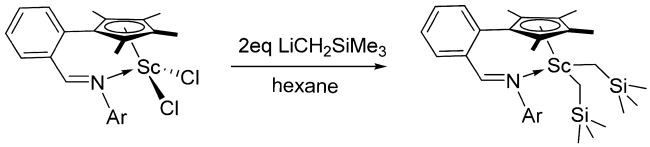
Attempts to synthesize scandium(III) dialkyl complexes by reactions of $Sc(CH_2SiMe_3)_3(THF)_2$ with the corresponding free ligands or reactions of $ScCl_3(THF)_3$ with the corresponding lithium salts of the ligands and 2 equiv of Me_3SiCH_2Li sequentially in THF as reported in the literature[15g,18] were unsuccessful. No distinguishable product has been isolated from these reactions. However, the scandium(III) trialkyl complex 2-[Li(THF)$_3$(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH]$C_6H_4Me_4CpSc$-$(CH_2SiMe_3)_3$ (**3**) was obtained from a one-pot reaction of $ScCl_3(THF)_3$ with **La**Li and 3 equiv of Me_3SiCH_2Li in THF, as shown in Scheme 2. Finally, the scandium(III) dialkyl complex

Scheme 2. Synthetic Route for Complex 3



2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)$C_6H_4Me_4CpSc(CH_2SiMe_3)_2$ (**4**) was successfully synthesized by the reaction of the scandium(III) dichloride complex **2a** with 2 equiv of Me_3SiCH_2Li in hexane, as seen in Scheme 3. On the basis of the above results, it seems

Scheme 3. Synthetic Route for Complex 4



that the formation of the anionic half-sandwich scandium(III) trialkyl or trichloride complexes with their imine N atom uncoordinated to the central scandium atom is favorable for this ligand system when the reactions are carried out in THF. The structures of complexes **2c**, **3**, and **4** were also confirmed by X-ray crystallography.

The new scandium(III) complexes **1a**, **2a**−**c**, **3**, and **4** were characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses. The structures of complexes **1a**, **2c**, **3**, and **4** were determined by single -crystal X-ray crystallography, which confirms that the imine N atom in complexes **1a** and **3** does not coordinate to the central scandium atom. The anionic trichloride complexes **1b,c** were directly converted to the neutral dichloride complexes **2b,c** without purification and characterization. The ^{1}H NMR spectra of these complexes all show two sets of singlets for the CpCH_3 protons and one set of

dx.doi.org/10.1021/om301026e | *Organometallics* 2013, 32, 1287−1294

singlets for the C*H*═N protons. Complexes **1a** and **3** show one set of doublets for the methyl protons of the CH(CH_3)$_2$ group (1.06 ppm for **1a** and 1.16 ppm for **3**) in their ligands, while complexes **2a** and **4** show two sets of doublets for the methyl protons of the CH(CH_3)$_2$ group (1.04 and 1.36 ppm for **2a**, 0.85 and 1.37 ppm for **4**). On the other hand, the ^{13}C NMR spectra of complexes **2a** and **4** show two signals for the two methyl carbons (22.0 and 26.2 ppm for **2a**, 22.5 and 26.4 ppm for **4**) of the ^{i}Pr group. A similar phenomenon was also observed for the resonances of the CH_2CH_3 protons in complex **2b**, which has two sets of multiplets for the methylene protons (2.75−2.62 and 2.48−2.33 ppm). These observations indicate that the rotation of the 2,6-$R_2C_6H_3$ group about the N−C (Ar group) bond is restricted in complexes **2** and **4**, with the imine N atom coordinating to the central scandium atom. The ^{1}H NMR spectrum of complex **3** shows a broad singlet for the methylene protons of the CH_2SiMe_3 group at −0.16 ppm. In contrast, the methylene protons of the same CH_2SiMe_3 group in complex **4** give a doublet of doublets (−0.48, −0.21 ppm, J_{H-H} = 10.5 Hz). These results demonstrate that the imine N atom in the ligand of complex **4** coordinates to the central scandium atom, while that in complex **3** does not in solution. In addition, the ^{1}H NMR spectroscopic analysis on complexes **1a** and **3** reveals that these anionic complexes convert to the neutral complexes **2a** and **4** slowly in solution with the resonance of the methyl protons in the ^{i}Pr group changing from one set of doublets to two sets of doublets over several hours. As a result, the ^{13}C NMR spectra of complexes **1a** and **3** could not be obtained.

X-ray Crystallography Studies. Single crystals of complexes **1a**, **2c**, **3**, and **4** suitable for X-ray crystallographic analysis were obtained and their structures were determined. The molecular structures (in ORTEP form) of complexes **1a**, **2c**, **3** and **4**, together with selected bond distances and angles of them, are shown in Figures 1−4, respectively. The X-ray diffraction analysis reveals that the central scandium atom in these scandium complexes is coordinated by one Cp ring and

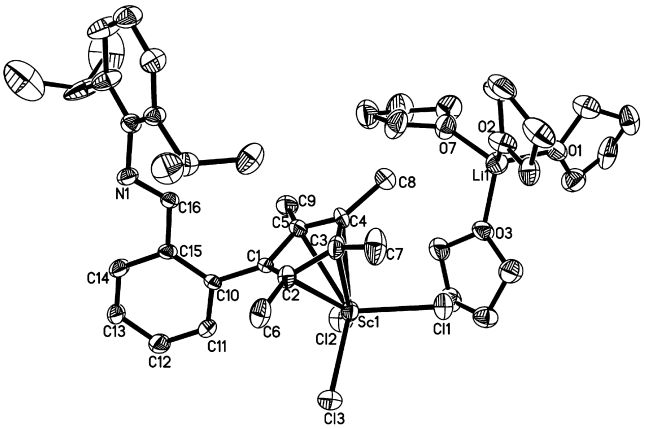


Figure 1. Perspective view of **1a** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sc(1)−C_{Cp}(range) = 2.438(7)−2.504(6), Sc(1)−C_{Cp}(av) = 2.475, Sc(1)−Cp(ct) = 2.165, Sc(1)−Cl(1) = 2.392(2), Sc(1)−Cl(2) = 2.370(2), Sc(1)−Cl(3) = 2.384(2), C(16)−N(1) = 1.268(7); Cl(1)−Sc(1)−Cl(2) = 103.18(8), Cl(1)−Sc(1)−Cl(3) = 102.48(8), Cl(2)−Sc(1)−Cl(3) = 101.97(9), C(16)−N(1)−C(17) = 120.7(6), N(1)−C(16)−C(15) = 122.6(6), Cp(ct)−C(1)−C(10) = 172.80, Cp(ct)−Sc(1)−Cl(1) = 114.44, Cp(ct)−Sc(1)−Cl(2) = 116.07, Cp(ct)−Sc(1)−Cl(3) = 116.71.

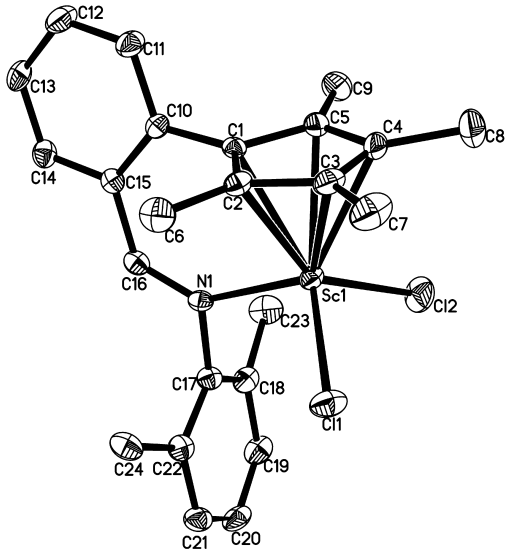


Figure 2. Perspective view of **2c** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sc(1)−C_{Cp}(range) = 2.412(4)−2.459(5), Sc(1)−C_{Cp}(av) = 2.438, Sc(1)−N(1) = 2.254(2), Sc(1)−Cp(ct) = 2.118, Sc(1)−Cl(1) = 2.3804(16), Sc(1)−Cl(2) = 2.3776(17), C(16)−N(1) = 1.285(6); Cl(1)−Sc(1)−Cl(2) = 101.72(6), Cl(1)−Sc(1)−N(1) = 105.99(11), Cl(2)−Sc(1)−N(1) = 104.00(6), C(16)−N(1)−Sc(1) = 135.9(3), C(17)−N(1)−Sc(1) = 108.7(3), C(16)−N(1)−C(17) = 115.3(4), N(1)−C(16)−C(15) = 127.9(4), Cp(ct)−C(1)−C(10) = 171.87, Cp(ct)−Sc(1)−Cl(1) = 117.24, Cp(ct)−Sc(1)−Cl(2) = 117.79, Cp(ct)−Sc(1)−N(1) = 108.75.

three other ligands in a three-legged piano-stool geometry with a distorted-octahedral coordinating environment. Complexes **1a** and **3** exist in an anionic form with an additional chloride or alkyl ligand instead of the neutral imine N atom in their ligand coordinating to the central metal atom. The lithium counterions attached to **1a** and **3** are coordinated by four THF molecules or three THF molecules plus the imine N atom in a distorted-tetrahedral geometry. In complexes **2c** and **4**, the imine N atom coordinates to the central scandium atom to form a six-membered chelating ring in a vertical position to the cyclopentadienyl ring with the aryl group at the imine N atom being placed close to the metal center, which constructs a relatively crowded coordinating environment surrounding the central scandium atom.

The Sc−Cp(ct) (ct = centroid) distances in the neutral chelating complexes **2c** (2.118 Å) and **4** (2.201 Å) are shorter than those in their corresponding anionic complexes **1a** (2.165 Å) and **3** (2.262 Å). These parameters are in agreement with those reported for similar N-functionalized scandium cyclopentadienyl complexes.[15g,h,18,19] The Sc−C_{Cp}(av) (av = average) distances are 2.475 Å for **1a**, 2.438 Å for **2c**, 2.564 Å for **3**, and 2.510 Å for **4**. In complex **1a**, the Sc−C3 (2.438(7) Å) and Sc−C4 (2.458(7) Å) distances are obviously shorter than the remaining Sc−C_{Cp} distances (2.480(6), 2.494(6), and 2.504(6) Å), indicating that the central scandium atom is located away from the position below the center of the Cp ring due to the steric hindrance of the uncoordinated bulky side arm. The Sc−Cl bond distances of complex **1a** (2.392(2), 2.370(2), and 2.384(2) Å) are close to those of complex **2c** (2.3804(16) and 2.3776(17) Å). The Sc−C1 distances in complexes **2c** (2.412(4) Å) and **4** (2.443(2) Å) are shorter than

dx.doi.org/10.1021/om301026e | *Organometallics* 2013, 32, 1287−1294

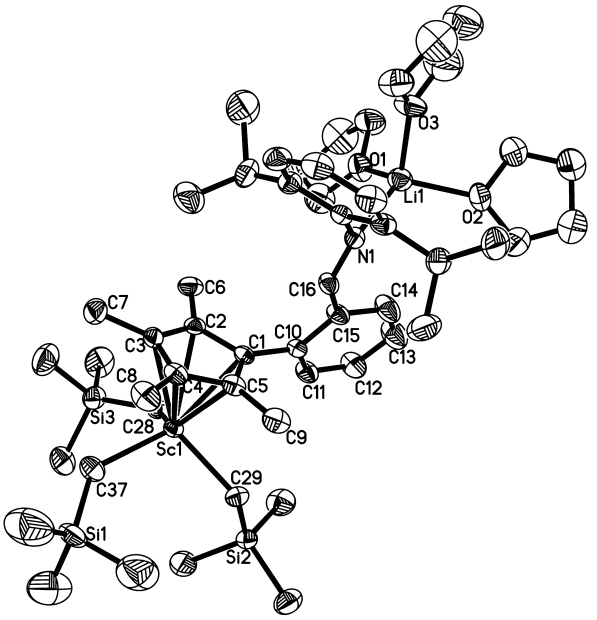


Figure 3. Perspective view of **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sc(1)−C_{Cp}(range) = 2.555(5)−2.570(5), Sc(1)−C_{Cp}(av) = 2.564, Sc(1)−Cp(ct) = 2.262, Sc(1)−C(28) = 2.259(5), Sc(1)−C(29) = 2.287(6), Sc(1)−C(37) = 2.262(6), C(16)−N(1) = 1.277(7), Li(1)−N(1) = 2.138(11); C(28)−Sc(1)−C(29) = 103.3(2), C(28)−Sc(1)−C(37) = 101.6(2), C(29)−Sc(1)−C(37) = 106.6(2), C(16)−N(1)−Li(1) = 132.7(5), C(17)−N(1)−Li(1) = 111.9(4), N(1)−C(16)−C(15) = 124.1(5), Cp(ct)−C(1)−C(10) = 173.35, Cp(ct)−Sc(1)−C(28) = 116.83, Cp(ct)−Sc(1)−C(29) = 113.68, Cp(ct)−Sc(1)−C(37) = 114.56.

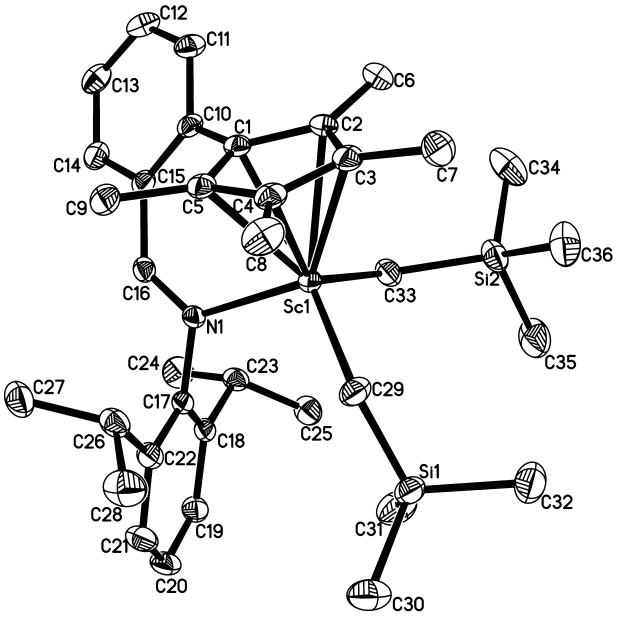


Figure 4. Perspective view of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sc(1)−C_{Cp}(range) = 2.443(2)−2.558(2), Sc(1)−C_{Cp}(av) = 2.510, Sc(1)−N(1) = 2.3125(17), Sc(1)−Cp(ct) = 2.201, Sc(1)−C(29) = 2.229(2), Sc(1)−C(33) = 2.211(2), C(16)−N(1) = 1.288(6); C(29)−Sc(1)−C(33) = 108.66(9), C(29)−Sc(1)−N(1) = 110.34(8), C(33)−Sc(1)−N(1) = 96.09(8), C(16)−N(1)−Sc(1) = 127.64(14), C(17)−N(1)−Sc(1) = 116.46(12), C(16)−N(1)−C(17) = 115.62(17), N(1)−C(16)−C(15) = 129.58(19), Cp(ct)−C(1)−C(10) = 177.73, Cp(ct)−Sc(1)−C(29) = 115.37, Cp(ct)−Sc(1)−C(33) = 118.97, Cp(ct)−Sc(1)−N(1) = 105.42.

the remaining Sc−C_{Cp} bond lengths (average 2.445 Å for **2c** and 2.515 Å for **4**) due to the coordination of the imine N atom. The Sc−N distance in the dichloride complex **2c** (2.254(4) Å) is shorter than that in the dialkyl complex **4** (2.3125(17) Å). They are longer than the Sc−N coordination bonds found in related CpPN-Sc type complexes (2.188(2)−2.214(3) Å).[15i] In addition, the Sc−C_{alkyl}(av) bond length in the trialkyl complex **3** (2.269 Å) is longer than that in complex **4** (2.220 Å). The imino C═N bonds in these complexes retain their double-bond character, being 1.268(7) Å for **1a**, 1.285(6) Å for **2c**, 1.277(7) Å for **3**, and 1.288(3) Å for **4**.

In the chelated complexes **2c** and **4**, the Cp(ct)−Sc−N angles (108.75° for **2c** and 105.42° for **4**) are obviously influenced by the bulkiness of the aryl groups at the imine N atoms, while little similar effect on the Cp(ct)−Sc−Cl (C_{alkyl}) angles (117.24 and 117.79° for **2c**, 115.37 and 118.97° for **4**) can be seen. The Sc−N−C(17) (108.70°) and N−Sc−Cp(ct) angles (108.75°) in complex **2c** are almost the same, which locates the aryl group at the imine N atom in a nearly vertical direction to the cyclopentadienyl ring. In contrast, the Sc−N−C(17) bond angle (116.46°) in complex **4** is obviously larger than the N−Sc−Cp(ct) angle (105.42°) due to the relatively large repulsion between the $^{i}Pr_2C_6H_3$ aryl group and the two Me_3SiCH_2 alkyl groups. The dihedral angles between the Cp plane and the attached phenyl plane (79.97° for **2c** and 52.40° for **4**) are less than 90°, indicating that the six-membered chelating rings in these complexes are somewhat distorted in their solid-state structures.

Polymerization of 1-Hexene and Propylene. The scandium(III) dichloride complexes **2a−c** have been tested as precatalysts for the polymerization of propylene and 1-hexene under different conditions. It was found that these complexes show moderate catalytic activity for propylene and 1-hexene polymerization upon activation with $AlR_3/Ph_3CB(C_6F_5)_4$ (R = Me, Et, ^{i}Bu) or MAO. The polymerization results of propylene and 1-hexene with **2a−c**/$AlR_3/Ph_3CB(C_6F_5)_4$ catalyst systems are summarized in Table 1. Atactic polypropylene was obtained from the propylene polymerization, as indicated by the ^{13}C NMR spectrum of a typical polypropylene sample shown in Figure 5. It is expected for these catalyst systems to produce syndiotactic or atactic polypropylene on the basis of their C_s-symmetric structural feature. Similar C_s-symmetric constrained geometry catalysts of group 4 metals have usually been reported to produce atactic polypropylene.[1b,20,21] It is very interesting that ultrahigh-molecular-weight isotactic poly(1-hexene) was obtained from the polymerization reactions of 1-hexene catalyzed by **2a−c**/$AlR_3/Ph_3CB(C_6F_5)_4$ and **4**/$Al^{i}Bu_3/Ph_3CB(C_6F_5)_4$ catalyst systems under conditions similar to those for the propylene polymerization. The ^{1}H NMR spectrum of a typical poly(1-hexene) sample shows no resonance for terminal olefinic groups, demonstrating that either the obtained poly(1-hexene) is of high molecular weight or the main polymer chain termination step of the polymerization reaction is not the β-hydride elimination process. GPC analysis indicates that the obtained poly(1-hexene) samples indeed possess high molecular weight with a weight-averaged molecular weight (M_w) up to 1.48×10^6. On the basis of the yields of the poly(1-hexenes) and their molecular weights, it can be seen that the precatalysts are only partially activated (10% or lower) in these system. ^{13}C

dx.doi.org/10.1021/om301026e | Organometallics 2013, 32, 1287−1294

Table 1. Polymerization Results Catalyzed by Complexes 2 and 4/AlR_3/$Ph_3CB(C_6F_5)_4$ Systems[a]

entry	monomer	procatalyst	AlR_3	temp (°C)	yield (g)	[*mmmm*] (%)	M_w[b]	M_w/M_n[b]
1	1-hexene	**2a**	Al^iBu_3	20	0.61	90	1337	1.38
2	1-hexene	**2b**	Al^iBu_3	20	0.33	51	1268	1.59
3	1-hexene	**2c**	Al^iBu_3	20	0.25	39	1153	1.56
4	1-hexene	**2a**	$AlEt_3$	20	0.32	21	1214	1.47
5	1-hexene	**2a**	$AlMe_3$	20	0.21	13	1136	1.78
6	1-hexene	**2a**	Al^iBu_3	40	0.82	41	1195	4.13
7	1-hexene	**2a**	Al^iBu_3	0	0.16	95	1479	2.15
8	1-hexene	**4**	Al^iBu_3	20	0.56	88	1315	1.42
9[c]	1-hexene	**2a**		20	0.58	95	755	5.08
10[d]	propylene	**2a**	Al^iBu_3	20	0.54	atactic	159	2.17
11[d]	propylene	**2b**	Al^iBu_3	20	0.45	atactic	126	2.24
12[d]	propylene	**2c**	Al^iBu_3	20	0.38	atactic	104	2.35

[a]Polymerization of 1-hexene was carried out with 5 μmol of precatalyst, 60 equiv of AlR_3, and 1.1 equiv of $Ph_3CB(C_6F_5)_4$ in a mixture of 2 mL of toluene and 5 mL of monomer for 48 h. [b]IN units of kg/mol of polymer, determined by GPC analysis at 40 °C using polystyrene standards and THF as the eluant. [c]Activated by 500 equiv of MAO. [d]Polymerization of propylene was carried out with 5 μmol of procatalyst, 60 equiv of Al^iBu_3, and 1.1 equiv of $Ph_3CB(C_6F_5)_4$ in 20 mL of toluene under 0.5 MPa propylene pressure at 20 °C for 48 h.

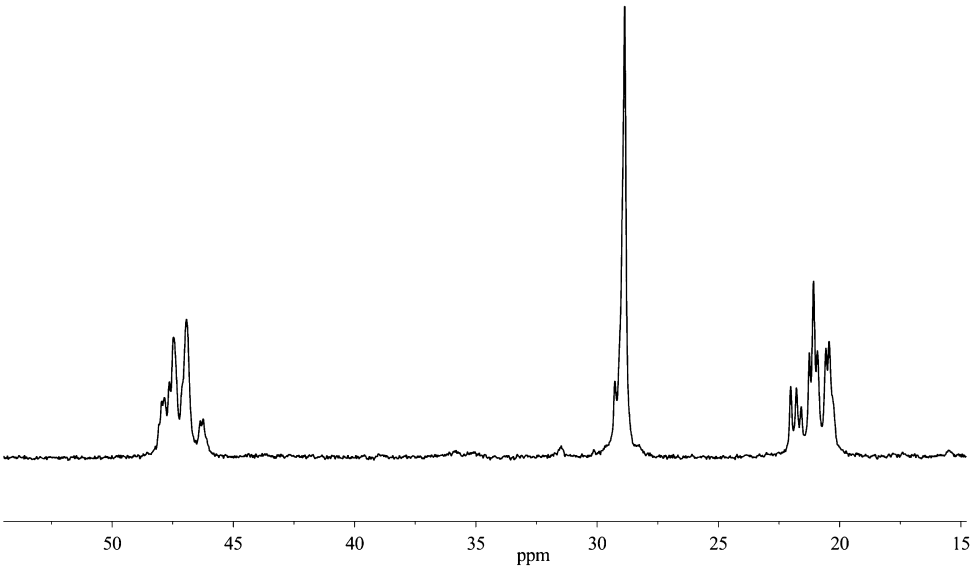


Figure 5. ^{13}C NMR (100 MHz, *o*-$C_6D_4Cl_2$, 130 °C) spectrum for polypropylene produced from entry 10 (Table 1).

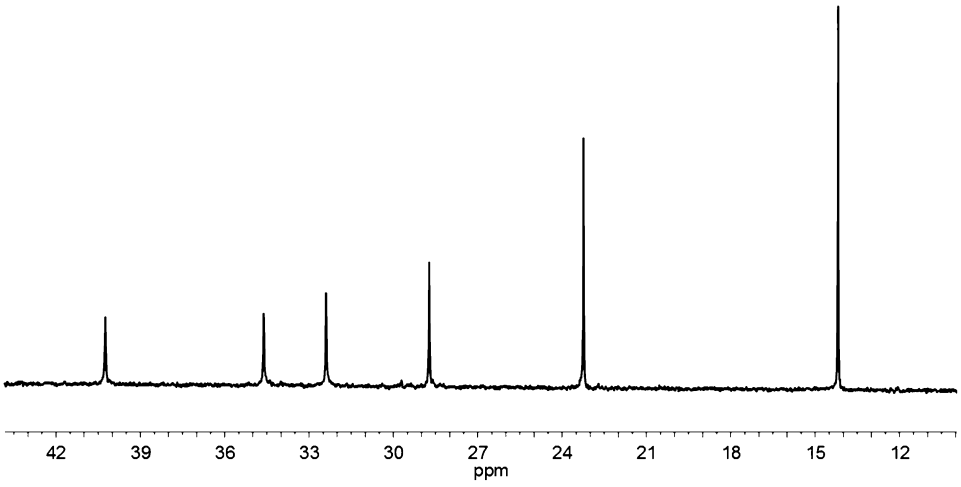


Figure 6. ^{13}C NMR (125 MHz, CDCl3, 25 °C) spectrum for poly(1-hexene) produced from entry 7 (Table 1).

NMR spectroscopic analysis of the obtained poly(1-hexenes)[22] as shown in Figures 6 and 7 reveals that isotactic poly(1-hexenes) with [*mmmm*] up to 95% can been produced by these C_s-symmetric half-sandwich scandium(III) complexes. It has

dx.doi.org/10.1021/om301026e | *Organometallics* 2013, 32, 1287−1294

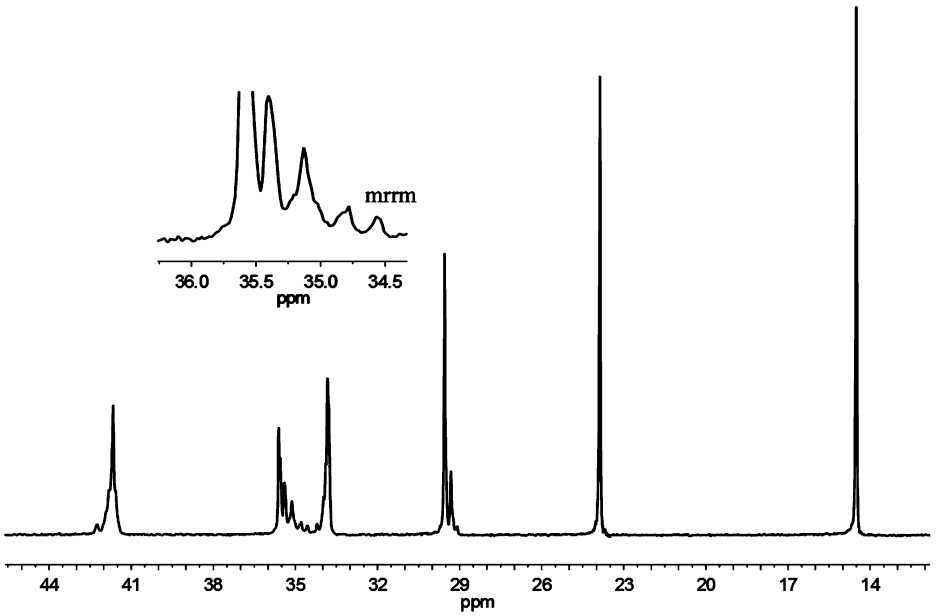


Figure 7. ^{13}C NMR (100 MHz, *o*-$C_6D_4Cl_2$, 130 °C) spectrum for poly(1-hexene) produced from entry 3 (Table 1).

been reported that atactic poly(1-hexenes) were obtained with half-sandwich scandium(III) catalysts without a side arm.[15a,16] By comparison of the polymerization results obtained under similar conditions, it can be seen that the steric effect of the Ar group at the imine N atom of these complexes on the isotacticity of the produced poly(1-hexenes) is remarkable. The stereoselectivity of complexes **2a**−**c** decreases in the order **2a** > **2b** > **2c** under similar conditions, which may be attributed to the fact that a bulkier aryl group at the imine N atom would make the coordination sphere of the catalytic active species more crowded and therefore have more impact on the direction of the coordinated 1-hexene. On the other hand, the stereoselectivity of these catalyst systems also depends on the type of AlR_3 used and decreases in the order Al^iBu_3 > $AlEt_3$ > $AlMe_3$ with complex **2a** as the precatalyst. In addition, the MAO activated **2a** catalyst system was found to produce poly(1-hexene) with the highest isotacticity under similar conditions.

The detailed mechanism for these catalyst systems in promoting the isospecific polymerization of 1-hexene is not clear. In principle, isotactic poly(1-hexene) can be formed by either an *enantiomorphic site control* mechanism or a *chain end control* mechanism.[1b] For the isotactic poly(1-hexenes) produced by the *enantiomorphic site control* mechanism, ^{13}C NMR signals for the *mrrm* pentads caused by misinsertion can usually be observed from samples with adequate isotacticity.[1b,13,22] We have clearly observed the *mrrm* pentads in ^{13}C NMR spectra of some isotactic poly(1-hexene) samples produced by these C_s-symmetric half-sandwich scandium(III) complexes, as shown in Figure 7 for a typical sample, implying that the isotactic poly(1-hexene) may be produced by the *enantiomorphic site control* mechanism for our present catalyst systems. On the basis of the widely accepted olefin polymerization mechanism, the chain migratory insertion entailing the site isomerization was essential feature of C_s-symmetric metallocene catalysts to produce atactic or syndiotactic polymer.[1b,20c,d] Something must happen in our present catalyst systems to cause the C_s-symmetric precatalysts to be transformed into chiral active catalysts. Considering the fact that the isotacticity of the produced poly(1-hexenes) is significantly affected by the size of both the aryl group at the imine N atom and the AlR_3 (or MAO) cocatalyst, it is possible that a strong interaction[23] between the catalyst and the cocatalyst AlR_3 or MAO may exist in our catalyst systems, which creates a catalyst having a C_1-symmetric environment for the coordination and insertion of the 1-hexene molecule and leads to the formation of the isotactic poly(1-hexene).

■ CONCLUSION

A number of new half-sandwich scandium(III) dichloride, 2-(ArN═CH)$C_6H_4Me_4CpScCl_2$ (**2a**−**c**), and trichloride complexes, 2-(ArN═CH)$C_6H_4Me_4CpScCl_3Li(THF)_4$ (**1a**−**c**), have been synthesized in good yields. The dichloride complexes were obtained by heating the corresponding trichloride complexes at 120 °C under vacuum to remove the attached LiCl and THF. The scandium(III) trialkyl complex 2-[$Li(THF)_3$(2,6-$^iPr_2C_6H_3$)N═CH]$C_6H_4Me_4CpSc(CH_2SiMe_3)_3$ (**3**) was synthesized by a one-pot reaction of $ScCl_3(THF)_3$ with 2-(2,6-$^iPr_2C_6H_3N$═CH)$C_6H_4Me_4CpLi$ and 3 equiv of Me_3SiCH_2Li in THF sequentially, while the scandium(III) dialkyl complex 2-(2,6-$^iPr_2C_6H_3N$═CH)$C_6H_4Me_4CpSc(CH_2SiMe_3)_2$ (**4**) was obtained from the reaction of the dichloride complex **2a** with 2 equiv of Me_3SiCH_2Li in hexane. X-ray crystallographic analysis of complexes **1a**, **2c**, **3** and **4** indicates that these half-sandwich scandium(III) complexes adopt a three-legged piano-stool geometry with a distorted-octahedral coordinating environment. Upon activation with $Al^iBu_3/Ph_3CB(C_6F_5)_4$ or MAO, the C_s-symmetric half-sandwich scandium(III) dichloride complexes exhibit moderate catalytic activity for propylene and 1-hexene polymerization and produce atactic polypropylene and high-molecular-weight isotactic poly(1-hexene).

■ EXPERIMENTAL SECTION

General Considerations. All manipulations for air- and water-sensitive compounds were performed under an inert atmosphere of nitrogen using standard Schlenk or glovebox techniques.[24] Solvents and 1-hexene were purified and dried by known procedures and

distilled under nitrogen prior to use.[25] Polymerization grade proylene was further purified by passage through columns of 5 Å molecular sieves and MnO. $ScCl_3(THF)_3$, $Ph_3CB(C_6F_5)_4$,[26] and 2-(aryliminomethyl)phenyltetramethylcyclopentadiene[17] ligands were prepared according to published procedures. MAO, $AlMe_3$, $AlEt_3$, Al^iBu_3, 2,6-dimethylaniline, 2,6-diethylaniline, and 2,6-diisopropylaniline were purchased from Aldrich or Acros and used as received. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer, and elemental analyses were performed on a Perkin-Elmer 2400 analyzer. ^{13}C NMR spectra of polypropylene and poly(1-hexene) samples were measured on a Varian Unity 400 MHz spectrometer at 130 °C in *o*-$C_6D_4Cl_2$ or on a Bruker AVANCEIII500 spectrometer at 25 °C in $CDCl_3$. The molecular weights and molecular weight distributions of the polymer samples were determined by gel permeation chromatography on a Waters Breeze HPLC with a Waters 2414 refractive index detector at 40 °C using THF as an eluent at a flow rate of 1.00 mL/min against polystyrene standards.

Synthesis of Complex 1a. To a solution of the free ligand 2-(2,6-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$Me$_4$CpH (750 mg, 1.95 mmol) in 10 mL of THF was added dropwise a solution of butyllithium (1.15 mL, 1.95 mmol) in THF at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The resulting solution was then added to a suspension of $ScCl_3(THF)_3$ (717 mg, 1.95 mmol) in 30 mL of THF at room temperature, and then the reaction mixture was stirred for another 12 h. During the reaction period, the color of the reaction mixture changed from white to yellow. After the solvent was removed under vacuum, the residue was extracted with 15 mL of toluene to remove the insoluble impurities. Oily product was obtained by removing the toluene. Pure product **1a** was obtained by recrystallization from THF/*n*-hexane ((1−2)/10 v/v) as yellow crystals (989 mg, 1.19 mmol, 61.1%). Anal. Calcd for $C_{44}H_{66}Cl_3LiNO_4Sc$ (831.26): C, 63.58; H, 8.00; N, 1.69. Found: C, 63.61; H, 8.04; N, 1.72. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.35 (d, J = 7.5 Hz, 1H, Ar*H*), 7.82 (d, J = 7.5 Hz, 1H, Ar*H*), 7.59 (s, 1H, C*H*═N), 7.56−7.39 (m, 2H, Ar*H*), 7.15−7.00 (m, 3H, Ar*H*), 3.81 (b, 12H, THF), 2.87 (m, 2H, C*H*(CH$_3$)$_2$), 2.10 (s, 6H, CpC*H*$_3$), 2.00 (s, 6H, CpC*H*$_3$), 1.90 (b, 12H, THF), 1.06 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$).

Synthesis of Complex 2a. To a solution of the free ligand 2-(2,6-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$Me$_4$CpH (750 mg, 1.95 mmol) in 10 mL of THF was added dropwise a solution of butyllithium (1.15 mL, 1.95 mmol) in THF at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The resulting solution was added to a suspension of $ScCl_3(THF)_3$ (717 mg, 1.95 mmol) in 30 mL of THF at room temperature, and then the reaction mixture was stirred for another 3 h. During the reaction period, the color of the reaction mixture changed from white to yellow. After the solvent was removed under vacuum, the oily crude product was heated to 120 °C to remove the THF which coordinated to the Li atom. The residue was extracted with 15 mL of CH_2Cl_2 to remove the insoluble impurities. A yellow powder was obtained by removing the CH_2Cl_2 and washing with hexane (641 mg, 1.28 mmol, 65.4%). Anal. Calcd for $C_{28}H_{34}Cl_2NSc$ (500.44): C, 67.20; H, 6.85; N, 2.80. Found: C, 67.25; H, 6.90; N, 2.75. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.29 (s, 1H, C*H*═N), 7.76 (t, J = 7.5 Hz, 1H, Ar*H*), 7.68 (d, J = 7.7 Hz, 1H, Ar*H*), 7.58 (t, J = 7.5 Hz, 1H, Ar*H*), 7.40−7.20 (m, 4H, Ar*H*), 2.86 (m, 2H, CH(CH$_3$)$_2$), 2.27 (s, 6H, CpC*H*$_3$), 2.06 (s, 6H, CpC*H*$_3$), 1.36 (d, J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 175.7, 144.4, 142.0, 138.2, 137.7, 135.4, 134.4, 131.0, 128.9, 128.5, 127.5, 125.0, 124.84, 124.5, 29.4, 26.2, 22.0, 12.5, 12.3 ppm.

Synthesis of Complex 2b. Complex **2b** was synthesized in the same manner as for complex **2a** with 2-(2,6-Et$_2$C$_6$H$_3$N═CH)-C$_6$H$_4$Me$_4$CpH (697 mg, 1.95 mmol), *n*-BuLi (1.15 mL, 1.95 mmol), and $ScCl_3(THF)_3$ (717 mg, 1.95 mmol) as starting materials. Pure product **2b** (577 mg, 1.22 mmol, 62.6%) was obtained as a yellow powder. Anal. Calcd for $C_{26}H_{30}Cl_2NSc$ (472.39): C, 66.11; H, 6.40; N, 2.97. Found: C, 66.14; H, 6.45; N, 2.92. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.29 (s, 1H, C*H*═N), 7.75 (td, J = 7.5, 1.5 Hz, 1H, Ar*H*), 7.70 (dd, J = 7.7, 1.5 Hz, 1H, Ar*H*), 7.58 (td, J = 7.6, 1.3 Hz, 1H, Ar*H*), 7.35−7.13 (m, 4H, Ar*H*), 2.75−2.62 (m, 2H, C*H*$_2$CH$_3$), 2.48−2.33 (m, 2H, C*H*$_2$CH$_3$), 2.27 (s, 6H, CpC*H*$_3$), 2.03 (s, 6H, CpC*H*$_3$), 1.14 (t, J = 7.5 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 175.8, 144.5, 138.3, 137.8, 137.2, 135.5, 134.4, 131.1, 129.1, 128.6, 127.3, 127.0, 125.4, 125.2, 25.8, 15.1, 12.3 (2C) ppm.

Synthesis of Complex 2c. Complex **2c** was synthesized in the same manner as for complex **2a** with 2-(2,6-Me$_2$C$_6$H$_3$N═CH)-C$_6$H$_4$Me$_4$CpH (643 mg, 1.95 mmol), *n*-BuLi (1.15 mL, 1.95 mmol), and $ScCl_3(THF)_3$ (717 mg, 1.95 mmol) as starting materials. Pure product **2c** (533 mg, 1.20 mmol, 61.5%) was obtained as a yellow powder. A single crystal suitable for X-ray crystallographic analysis was obtained from a CH_2Cl_2/*n*-hexane solution ((1−2)/10 v/v). Anal. Calcd for $C_{24}H_{26}Cl_2NSc$ (444.33): C, 64.87; H, 5.90; N, 3.15. Found: C, 64.90; H, 5.95; N, 3.10. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.28 (s, 1H, C*H*═N), 7.79−7.68 (m, 2H, Ar*H*), 7.62−7.55 (m, 1H, Ar*H*), 7.35 (d, J = 7.6 Hz, 1H, Ar*H*), 7.18−7.07 (m, 3H, Ar*H*), 2.28 (s, 6H, CpC*H*$_3$), 2.24 (s, 6H, ArC*H*$_3$), 2.03 (s, 6H, CpC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 176.8, 145.9, 138.2, 137.9, 135.5, 134.3, 131.4, 131.3, 129.3, 128.7, 128.5, 128.0, 127.3, 125.3, 19.7, 12.3 (2C) ppm.

Synthesis of Complex 3. To a solution of free ligand 2-(2,6-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$Me$_4$CpH (750 mg, 1.95 mmol) in 10 mL of THF was added dropwise a solution of butyllithium (1.15 mL, 2.40 mmol) in THF at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The resulting solution was then added to a suspension of $ScCl_3(THF)_3$ (717 mg, 1.95 mmol) in 30 mL of THF at room temperature. The reaction mixture was stirred for another 1 h, and the color of the reaction mixture changed from white to yellow. To the reaction mixture was slowly added $LiCH_2SiMe_3$ (551 mg, 5.85 mmol) at −40 °C. After the mixture was stirred at room temperature for 30 min, the color of the reaction mixture changed from yellow to red. The solvent was removed under vacuum, and the residue was extracted with 15 mL of toluene to remove the insoluble impurities. An oily product was obtained by removing the toluene. Single crystals suitable for X-ray analysis were grown from a hexane solution at −30 °C (822 mg, 0.90 mmol, 46.4%). Anal. Calcd for $C_{52}H_{91}LiNO_3ScSi_3$ (914.44): C, 68.30; H, 10.03; N, 1.53. Found: C, 68.35; H, 10.08; N, 1.50. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 8.78 (d, J = 7.7 Hz, 1H, Ar*H*), 8.05 (s, 1H, C*H*═N), 7.62 (d, J = 6.4 Hz, 1H, Ar*H*), 7.36−6.99 (m, 5H, Ar*H*), 3.56 (b, 12H, THF), 3.31−3.09 (m, 2H, C*H*(CH$_3$)$_2$), 1.98 (s, 6H, CpC*H*$_3$), 1.85 (s, 6H, CpC*H*$_3$), 1.40 (b, 12H, THF), 1.16 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.30 (s, 27H, CH$_2$Si(C*H*$_3$)$_3$), −0.16 (broad, 6H, C*H*$_2$SiMe$_3$).

Synthesis of Complex 4. To a suspention of complex **2a** (500 mg, 1.00 mmol) in 10 mL of *n*-hexane was slowly added $LiCH_2SiMe_3$ (188 mg, 2.00 mmol) powder at room temperature. The orange mixture was stirred at room temperature for 3 h, and then the LiCl was removed by filtration. After reduction of the residual solution volume to about 2 mL under reduced pressure, the oily residue was cooled at −30 °C overnight to give **4** as red crystals (331 mg, 0.55 mmol, 54.7% yield). Anal. Calcd for $C_{36}H_{55}NScSi_2$ (603.96): C, 71.59; H, 9.35; N, 2.32. Found: C, 71.73; H, 9.22; N, 2.34. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.90 (s, 1H, C*H*═N), 7.17−6.78 (m, 7H, Ar*H*), 2.92 (m, 2H, C*H*(CH$_3$)$_2$), 2.32 (s, 6H, CpC*H*$_3$), 2.09 (s, 6H, CpC*H*$_3$), 1.37 (d, J = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.85 (d, J = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.25 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), −0.21 (d, J = 10.5 Hz, 2H, C*H*$_2$Si(CH$_3$)$_3$), −0.48 (d, J = 10.5 Hz, 2H, C*H*$_2$Si(CH$_3$)$_3$). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 175.9, 147.5, 141.7, 139.7, 137.2, 134.7, 134.1, 131.2, 128.6, 127.1, 124.8, 123.2, 120.4, 119.2, 45.9, 29.1, 26.4, 22.5, 13.1, 12.4, 4.5 ppm.

Propylene Polymerization Procedures. A dry 250 mL steel autoclave with a magnetic stirrer was charged with 18 mL of toluene and saturated with propylene (1.0 bar) at 20 °C. The polymerization reaction was started by injection of a mixture of AlR_3 and a catalyst in toluene (1 mL) together with a solution of $Ph_3CB(C_6F_5)_4$ in toluene (1 mL). The vessel was repressurized to the desired pressure with propylene immediately, and the pressure was maintained by continuous feeding of propylene. After a certain period of time, the polymerization was quenched by injecting acidified methanol (HCl (3 M)/methanol = 1/1). Then the polymer was collected by filtration,

dx.doi.org/10.1021/om301026e | *Organometallics* 2013, 32, 1287−1294

washed with water and methanol, and dried at 40 °C under vacuum to a constant weight.

1-Hexene Polymerization Procedures. In the glovebox, to a mixture of toluene, 1-hexene, and procatalyst was added MAO (500 equiv) or a mixture of AlR_3 (60 equiv)/$Ph_3CB(C_6F_5)_4$ (1.1 equiv) at polymerization temperature. After it was stirred for about 48 h, the reaction mixture was quenched by addition of acidified methanol and the polymer was collected, washed with water and methanol, and dried at 40 °C under vacuum to a constant weight.

Crystal Structure Determination. The crystals were mounted on a glass fiber using an oil drop. Data obtained with the $\omega-2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods,[27] and further refinements with full-matrix least squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages.[28]

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data for complexes **1a**, **2c**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: (86)-431-85168376. Fax: (86)-431-85193421. E-mail: ymu@jlu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research work was supported by the National Natural Science Foundation of China (Nos. 51173061, 21074043, and 21274050).

■ REFERENCES

(1) (a) Brintzinger, H. H.; Fischer, D.; Müllhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (c) Müller, G.; Rieger, B. *Prog. Polym. Sci.* **2002**, *27*, 815. (d) De Rosa, C.; Auriemma, F.; Di Capua, A.; Resconi, L.; Guidotti, S.; Camurati, I.; NifantGev, I. E.; Lashevtsev, I. P. *J. Am. Chem. Soc.* **2004**, *126*, 17040. (e) Harney, M. B.; Zhang, Y.; Sita, L. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6140. (f) Harney, M. B.; Zhang, Y.; Sita, L. R. *Angew. Chem.* **2006**, *118*, 2460; *Angew. Chem., Int. Ed.* **2006**, *45*, 2400. (g) Sita, L. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 2464. (h) Cohen, A.; Kopilov, J.; Lamberti, M.; Venditto, V.; Kol, M. *Macromolecules* **2010**, *43*, 1689. (i) Press, K.; Cohen, A.; Goldberg, I.; Venditto, V.; Mazzeo, M.; Kol, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 3529. (j) Li, G.; Lamberti, M.; Roviello, G.; Pellecchia, C. *Organometallics* **2012**, *31*, 6772.

(2) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606.

(3) Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1996**, *197*, 855.

(4) Babu, G. D.; Newmark, R. A.; Chien, J. C. W. *Macromolecules* **1994**, *27*, 3383.

(5) Fries, A.; Mise, T.; Matsumoto, A.; Ohmori, H.; Wakatsuki, Y. *Chem. Commun.* **1996**, 783.

(6) Yamaguchi, Y.; Suzuki, N.; Fries, A.; Mise, T.; Koshino, H.; Ikegami, Y.; Ohmori, H.; Matsumoto, A. *J. Polym. Sci. A: Polym. Chem.* **1999**, *37*, 283.

(7) Kim, I.; Zhou, J.; Chung, H. *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 1687.

(8) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958.

(9) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706.

(10) (a) Zhang, Y.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 9062. (b) Zhang, Y.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 7776. (c) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200. (f) Yeori, A.; Goldberg, I.; Shuster, M.; Kol, M. *J. Am. Chem. Soc.* **2006**, *128*, 13062.

(11) Li, G.; Lamberti, M.; D'Amora, S.; Pellecchia, C. *Macromolecules* **2010**, *43*, 8887.

(12) (a) Ishii, A.; Toda, T.; Nakata, N.; Matsuo, T. *J. Am. Chem. Soc.* **2009**, *131*, 13566. (b) Ishii, A.; Asajima, K.; Toda, T.; Nakata, N. *Organometallics* **2011**, *30*, 2947. (c) Nakata, N.; Toda, T.; Matsuo, T.; Ishii, A. *Inorg. Chem.* **2012**, *51*, 274.

(13) (a) Ward, B. D.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1668. (b) Kang, X.; Song, Y.; Luo, Y.; Li, G.; Hou, Z.; Qu, J. *Macromolecules* **2012**, *45*, 640.

(14) (a) Annunziata, L.; Pappalardo, D.; Tedesco, C.; Pellecchia, C. *Macromolecules* **2009**, *42*, 5572. (b) Domski, G. J.; Lobkovsky, E. B.; Coates, G. W. *Macromolecules* **2007**, *40*, 3510. (c) Lian, B.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2009**, 311.

(15) (a) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114. (b) Jian, Z.; Cui, D.; Hou, Z. *Chem. Eur. J.* **2012**, *18*, 2674. (c) Jian, Z.; Tang, S.; Cui, D. *Chem. Eur. J.* **2010**, *16*, 14007. (d) Jian, Z.; Cui, D.; Hou, Z.; Li, X. *Chem. Commun.* **2010**, *46*, 3022. (e) Pan, Y.; Rong, W.; Jian, Z.; Cui, D. *Macromolecules* **2012**, *45*, 1248. (f) Jian, Z.; Tang, S.; Cui, D. *Macromolecules* **2011**, *44*, 7675. (g) Li, X.; Nishiura, M.; Hu, L.; Mori, K.; Hou, Z. *J. Am. Chem. Soc.* **2009**, *131*, 13870. (h) Jian, Z.; Cui, D. *Chem. Eur. J.* **2011**, *17*, 14578. (i) Jian, Z.; Petrov, A. R.; Hangaly, N. K.; Li, S.; Rong, W.; Mou, Z.; Rufanov, K. A.; Harms, K.; Sundermeyer, J.; Cui, D. *Organometallics* **2012**, *31*, 4267.

(16) Luo, Y.; Hou, Z. *Stud. Surf. Sci. Catal.* **2006**, *161*, 95.

(17) Zhang, L.; Gao, W.; Tao, X.; Wu, Q.; Mu, Y.; Ye, L. *Organometallics* **2011**, *30*, 433.

(18) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720.

(19) (a) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (b) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

(20) (a) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649. (b) Chen, Y.-X.; Fu, P.-F.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 5958. (c) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (d) Chen, M.-C.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 11803. (e) Shiomura, T.; Asanuma, T.; Inoue, N. *Macromol. Rapid Commun.* **1996**, *17*, 9.

(21) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.

(22) (a) Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334. (b) Babu, G. N.; Newmark, R. A.; Chien, J. C. W. *Macromolecules* **1994**, *27*, 3383.

(23) (a) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908. (b) Carr, A. G.; Dawson, D. M.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1999**, *18*, 2933. (c) Bryliakov, K. P.; Talsi, E. P.; Voskoboynikov, A. Z.; Lancaster, S. J.; Bochmann, M. *Organometallics* **2008**, *27*, 6333. (d) Lv, K.; Cui, D.-M. *Organometallics* **2010**, *29*, 2987.

(24) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(25) Perrin, D. D.; Armarego,W. L. F.; Perrin, D. R. *The Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

(26) (a) Massey, A. G.; Park, A. J. *J. Org. Chem.* **1962**, *2*, 245. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218. (c) Chein, J. C. W.; Tsai, W. M.; Rasch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

(27) *SHELXTL PC*; Siemens Analytical X-ray Instruments, Madison, WI, 1993.

(28) Sheldrick, G. M. *SHELXTL Structure Determination Programs, Version 5.0, PC*; Siemens Analytical Systems, Madison, WI, 1994.