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Scandium Alkyl Complexes Supported by a Ferrocene Diamide Ligand

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Synthesis of a scandium dimethylbenzyl complex supported by a ferrocene diamide ligand was accomplished by alkane elimination from Sc(CH$_2$Xy-3,5)$_3$(THF)$_2$. The scandium dimethylbenzyl complex Sc(fc[NSi(*t*-Bu)Me$_2$]$_2$)(CH$_2$Xy-3,5)(THF), **2-(CH$_2$Xy-3,5)(THF)**, was used as a starting material for the synthesis of the corresponding chloride-bridged dimer, **(2-Cl)$_2$**, which, in turn, led to a scandium bis(*neo*-pentyl) ate salt, **Li[2-Np$_2$]**. Attempts to remove the coordinated THF molecule from **2-(CH$_2$Xy-3,5)(THF)** with AlMe$_3$ led to the isolation of a scandium methyl complex with two coordinated AlMe$_3$ molecules, **2-Me(AlMe$_3$)$_2$**. Compound **2-Me(AlMe$_3$)$_2$** led to a scandium methyl complex, **2-Me(THF)$_2$**, by stirring in THF. All ferrocene diamido compounds were characterized by X-ray crystallography. DFT calculations on model compounds were used to explain the stability of the compounds synthesized and to probe the existence of an iron−scandium interaction. Compounds **2-(CH$_2$Xy-3,5)(THF)** and **2-Me(AlMe$_3$)$_2$** polymerize L-lactide.

Introduction

Cyclopentadienyl complexes have dominated group 3 organometallic chemistry for a long time.[1–6] While astonishing results have been achieved with this class of ligands, interest in noncyclopentadienyl complexes is increasing,[7–10] with the goal of expanding the reactivity of the metal centers toward challenging substrates, such as saturated[11] or unsaturated[3,12] hydrocarbons and polar substrates.[13–15] Since the metal center is very electrophilic even in neutral alkyl complexes, design of complexes with the goal of σ-bond metathesis reactions in mind has focused on dianionic ancillary ligand, monoalkyl complexes.[16–23] Architectures such as bis-cyclopentadienyl, *ansa*-metallocene, bis-amide have been explored[2] and good reactivity in C−H bond activation[24–27] has been observed in a number of cases. In practice, a fine balance between electronic and steric factors needs to be maintained in order to be able to evaluate the reactivity observed and explore the electrophilicity of the metal center.[7]

Our goal is to synthesize scandium alkyl complexes that display reactivity behavior complementary to existing ones. We are interested in exploiting ferrocene 1,1′-diamides as versatile frameworks in supporting highly electrophilic group 3 metal centers. Such ligands have a number of desirable characteristics: (i) the 1,1′-disubstituted ferrocene enforces *cis*-coordination of the two donors; thus only one side of the metal center is blocked; (ii) the ferrocene backbone has the ability to accommodate changes in the electronic density at the metal center, by varying the geometry around iron; (iii) the other ligands and incoming substrates coordinate in a plane perpendicular to the plane formed by the two donors, iron, and the metal; thus the access to the electrophilic center is unrestricted; (iv) a weak interaction of donor–acceptor type could occur between iron and the metal, possibly influencing the reactivity of the complex.[28]

Results and Discussion

Synthesis and Characterization of Scandium Alkyl Complexes. The ligand fc[NHSi(*t*-Bu)Me$_2$]$_2$ (fc = 1,1′-ferrocenylene)[29] has been chosen for initial studies because the

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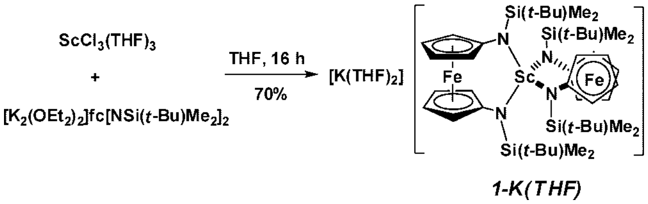
Scheme 1. Synthesis of Scandium ate Complex 1-K(THF)



synthesis of a close analogue has already been reported[30] and it is amenable to alteration of the nitrogen substituent. Salt metathesis reactions between $ScCl_3(THF)_3$ and the potassium salt of the ferrocene diamide ligand, $[K(OEt_2)]_2fc[NSi(t\text{-}Bu)Me_2]_2$ (Scheme 1), were initially carried out. Regardless of the conditions used, a potassium ate complex, $[K(solvent)_x][Sc(fc[NSi(t\text{-}Bu)Me_2]_2)_2]$, **1-K(solvent)** (solvent = THF, $x = 2$ and solvent = toluene, $x = 1$), was always isolated; two ligands are coordinated to the metal (Figure 1). The single-crystal X-ray structures are informative with respect to the relative orientation of the two ligands: the N−Sc−N angles are 108° regardless of whether the nitrogen atoms belong to the same ligand, indicating a tetrahedral geometry around the scandium center. The ferrocene backbones adopt an eclipsed conformation and the scandium−nitrogen distances are ca. 2.14 Å, similar to other scandium−amide distances reported.[31–35]

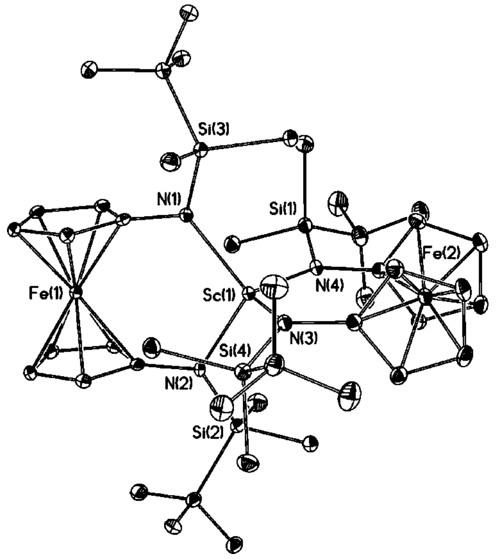
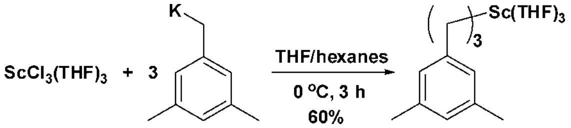


Figure 1. Thermal ellipsoid (35% probability) representation of $[K(THF)_2][Sc(fc[NSi(t\text{-}Bu)Me_2]_2)_2]$, **1-K(THF)**. The potassium cation is not shown. Hydrogen atoms were omitted for clarity.

Scheme 2. Synthesis of Scandium Tris(dimethylbenzyl) Complex $Sc(CH_2Xy\text{-}3,5)_3(THF)_3$



Since salt metathesis reactions resulted in ate complex formation, a common occurrence[7] in the chemistry of group 3 and lanthanide elements, we decided to carry out acid–base reactions. Inspired by a recent report[36] by Hessen et al. on the synthesis of $LaBz_3(THF)_3$ (Bz = benzyl) we set out to isolate the analogous scandium benzyl complex. Although $ScBz_3(THF)_3$ did form when employing a procedure similar to the one for $LaBz_3(THF)_3$, its isolation was not trivial because of its limited solubility in hydrocarbon solvents. It was reasoned that increasing the hydrophobicity of the benzyl substituent might solve this problem. Indeed, the isolation of $Sc(CH_2Xy\text{-}3,5)_3(THF)_2$ (Scheme 2) was facile, and the desired compound could be purified by recrystallization from toluene/hexanes. The yield of the pure product is consistently 60%. During the preparation of the manuscript, the synthesis of a scandium tris(dimethylaminobenzyl) complex was reported;[37,38] this complex features dimethylamine coordinated as an internal Lewis base. Other scandium tris(alkyl) starting materials[39] have been known and used in syntheses of scandium alkyl complexes; in most cases, the alkyl chlorides used to prepare the alkali/alkaline earth alkyl compound are expensive. Additionally, in acid–base reactions, 1 or 2 equiv of the corresponding alkane is eliminated and therefore lost during the preparation of the final scandium complex. It is advantageous that the byproduct of the alkane elimination reactions is mesitylene since it is volatile; contamination of the desired product with mesitylene is not likely. When all these factors are considered, $Sc(CH_2Xy\text{-}3,5)_3(THF)_2$ is a practical entry into scandium organometallic chemistry.

With $Sc(CH_2Xy\text{-}3,5)_3(THF)_2$ in our hands, we carried out its reaction with $fc[NHSi(t\text{-}Bu)Me_2]_2$ and isolated $Sc(fc[NSi(t\text{-}Bu)Me_2]_2)(CH_2Xy\text{-}3,5)(THF)$, **2-(CH$_2$Xy-3,5)(THF)**, in 80% yield after crystallization from pentane/Et_2O (Scheme 3). Single crystals were grown from pentane/toluene, and the crystal structure of **2-(CH$_2$Xy-3,5)(THF)** (Figure 2) was determined. The solid-state structure of **2-(CH$_2$Xy-3,5)(THF)** is informative with respect to the scandium−iron distance of 3.16 Å. This distance is longer than the titanium−iron distance in $[Ti(fc[NSiMe_3]_2)Me][MeBPh_3]$ (3.07 Å),[40] but it is shorter than in the corresponding titanium dimethyl compound (3.32 Å), consistent with an electrophilic scandium center in a neutral compound (Sc(III) ionic radius is 0.87 Å, Ti(IV) ionic radius is 0.74 Å).[41] The benzyl ligand coordinates in an η^2-fashion: the distance to the aryl carbon is 2.74 Å and the Sc−C−C angle is 92.1°. The THF molecule and the benzyl ligand coordinate in a plane perpendicular to the one formed by scandium and the nitrogen atoms. Although the O−Sc−C angle is 111.3°, the O−Sc−N angles are 96.3° and the N−Sc−N angle is 140.9°, indicating a relatively distorted tetrahedral environment around scandium.

Thermal Decomposition of Scandium Benzyl Complex. The thermal stability of **2-(CH$_2$Xy-3,5)(THF)** was investigated by heating a C_6D_6 solution gradually to 60 °C for 24 h; under these conditions, **2-(CH$_2$Xy-3,5)(THF)** was relatively robust.

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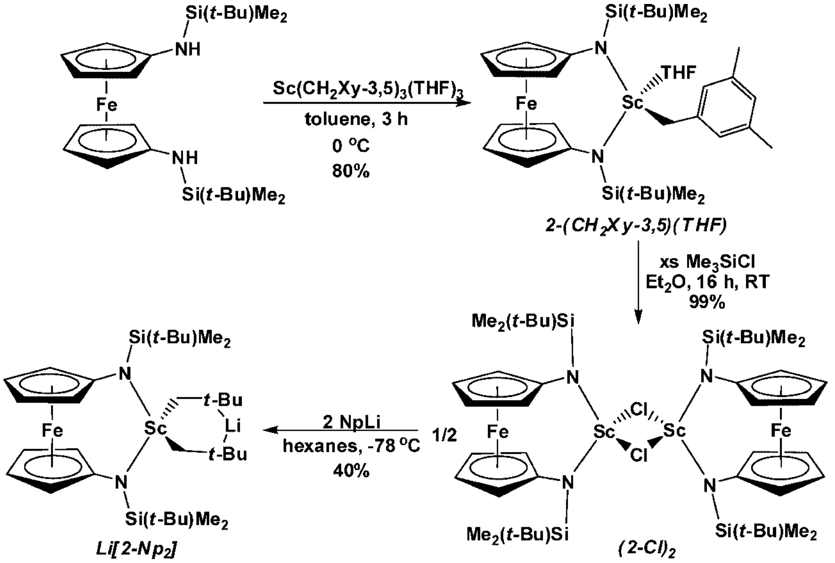
Scheme 3



Decomposition was observed upon prolonged heating at 80 °C, but the products could not be identified. Heating a C_7D_8 solution of **2-(CH_2Xy-3,5)(THF)** at 120 °C for 45 min also led to decomposition and intractable mixtures. Since aromatic hydrocarbons might be involved in C−H activation reactions with alkyl groups, a control experiment was carried out, in which **2-(CH_2Xy-3,5)(THF)** was heated at 95 °C for 16 h in *c*-C_6D_{12}; a similar reaction mixture was obtained during the experiment. On the basis of the results of the thermal decomposition experiments we can conclude that complex **2-(CH_2Xy-3,5)(THF)** is relatively stable at moderate temperatures (60–80 °C); at higher temperatures its thermal decomposition is too complicated, but it is not solvent dependent.

Synthesis of THF-Free Chloride Scandium Complex. The stability of **2-(CH_2Xy-3,5)(THF)** was not unexpected considering that Lewis base coordination (THF) to an electrophilic metal center is known to increase the stability of the complex and decrease its reactivity. We reasoned that the transformation of **2-(CH_2Xy-3,5)(THF)** in a scandium chloride complex would allow the isolation of a THF-free compound since the chloride ion is a small ligand, biasing the metal center toward dimer formation. If a dimer were formed, then the steric crowding around the metal centers would prevent THF coordination. Indeed, the reaction[42] between **2-(CH_2Xy-3,5)(THF)** and excess Me_3SiCl (Scheme 3) resulted in the isolation of [Sc(fc[NSi(*t*-Bu)Me_2]$_2$)(μ-Cl)]$_2$, **(2-Cl)$_2$**, a chloride-bridged dimer without THF coordinated to the scandium center, as evidenced by its X-ray crystal structure (Figure 3). The scandium−iron distance in **(2-Cl)$_2$** (2.80 Å) is significantly shorter than in **2-(CH_2Xy-3,5)(THF)** (3.16 Å), a trend similar to that observed when comparing titanium−iron distances in [Ti(fc[NSiMe_3]$_2$)Me]-[MeBPh_3] and [Ti(fc[NSiMe_3]$_2$)Cl]$_2$[B(C_6F_5)$_4$] (3.07 vs 2.49 Å). Unlike in the ate complex **1-K(THF)**, the two ferrocene ligands are not tilted with respect to each other. One interesting feature is the fact that the scandium atom sits out of the plane formed by the two nitrogens and the two carbons connected to them; such a geometrical characteristic has been correlated to π-bonding involving the nitrogen atoms in other chelating diamide complexes.[43,44]

With **(2-Cl)$_2$** isolated, the formation of a scandium alkyl, THF-free complex was investigated. The reaction between **(2-Cl)$_2$** and 2 equiv of LiNp (Np = CH_2-*t*-Bu) carried out in hexanes gave Li[Sc(fc[NSi(*t*-Bu)Me_2]$_2$)Np_2], **Li[2-Np$_2$]**, in which two *neo*-pentyl ligands coordinate to scandium (Scheme 3). The Fe−Sc distance of 3.19 Å is only slightly longer than in **2-(CH_2Xy-3,5)(THF)** (3.16 Å). The X-ray crystal structure of **Li[2-Np$_2$]** (Figure 4) features a lithium center disordered over two equivalent positions. This symmetrical structure is supported by the solution structure of **Li[2-Np$_2$]**, since the ^{1}H NMR spectrum is consistent with a C_{2v} arrangement of the ligands (see Supporting Information). Compound **Li[2-Np$_2$]** decomposes when heated at 60 °C in C_6D_6, but it is relatively stable to 40 °C. Other attempts to synthesize a scandium monoalkyl complex supported by the ferrocene diamide ligand discussed here from

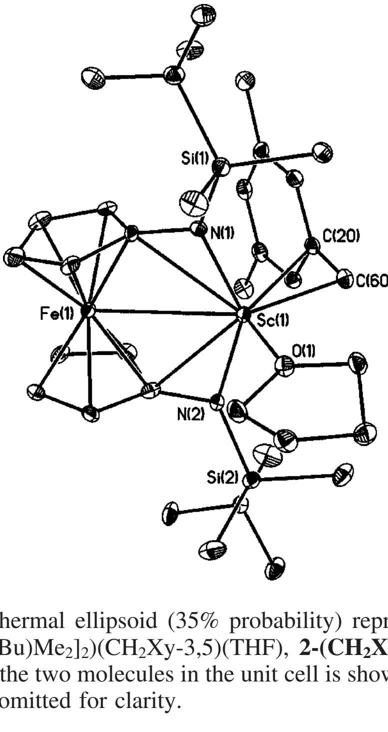


Figure 2. Thermal ellipsoid (35% probability) representation of Sc(fc[NSi(*t*-Bu)Me_2]$_2$)(CH_2Xy-3,5)(THF), **2-(CH_2Xy-3,5)(THF)**. Only one of the two molecules in the unit cell is shown. Hydrogen atoms were omitted for clarity.

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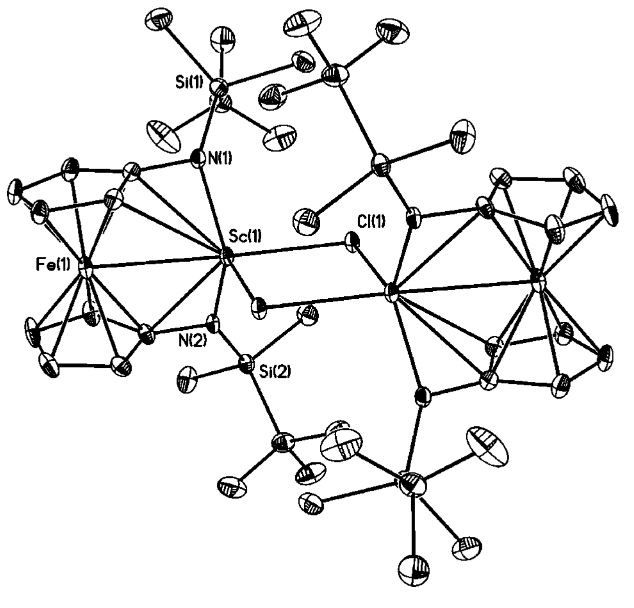

Figure 3. Thermal ellipsoid (35%) representation of [Sc(fc[NSi(*t*-Bu)Me_2]$_2$)(μ-Cl)]$_2$, **(2-Cl)$_2$**. Hydrogen atoms were omitted for clarity.

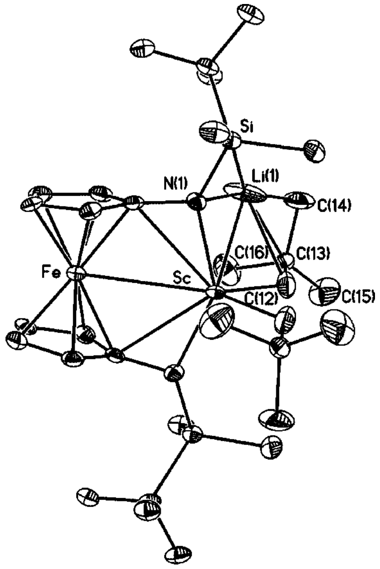

Figure 4. Thermal ellipsoid (35% probability) representation of Li[Sc(fc[NSi(*t*-Bu)Me_2]$_2$)Np_2], **Li[2-Np$_2$]**. Hydrogen atoms and atoms obtained from modeling thermal disorder were omitted for clarity.

the scandium chloride dimer **(2-Cl)$_2$** failed when starting with the most common Grignard or lithium reagents, regardless of reaction conditions.

Attempts to Remove the Coordinated THF Molecule. Since the chloride route did not lead to a monoalkyl scandium complex, other avenues for the removal of coordinated THF were considered. Trimethyl aluminum has been used to abstract coordinated THF molecules.[45] The reaction between **2-(CH$_2$Xy-3,5)(THF)** and an excess of $AlMe_3$ (Scheme 4) led to the isolation of a scandium methyl complex, Sc(fc[NSi(*t*-Bu)Me_2]$_2$)Me($AlMe_3$)$_2$, **2-Me(AlMe$_3$)$_2$**, in which two molecules of $AlMe_3$ are present (Figure 5): one molecule is connected to scandium through two bridging methyl groups, the other through one methyl group and one amide nitrogen. The ^{1}H NMR spectrum shows broad peaks for the ancillary ligand protons and the coordinated $AlMe_3$ protons, and it is consistent with interchange of the methyl groups on the NMR spectroscopy time scale.

When the stoichiometry for the formation of the bis(trimethyl aluminum) adduct was 3 equiv of $AlMe_3$ to 1 equiv of **2-(CH$_2$Xy-3,5)(THF)**, the yield of the desired product increased as expected. We propose that 1 equiv of $AlMe_3$ is necessary for the transmetalation of the benzyl group since $AlMe_3$ is a known alkylation reagent;[46–48] it is likely that $AlMe_2$(CH_2Xy-3,5)(THF) is formed and eliminated during the work up of the reaction mixture. If less than 3 equiv of $AlMe_3$ is used, then starting material is still present at the end of the reaction. Compound **2-Me(AlMe$_3$)$_2$** is thermally stable, as indicated by heating it in C_6D_6 at 82 °C, which led to no decomposition after several hours.

When **2-Me(AlMe$_3$)$_2$** was stirred in THF (Scheme 4), a new compound formed after 1 h at room temperature. On the basis of its ^{1}H NMR spectrum, we assigned this product to be the scandium methyl THF compound Sc(fc[NSi(*t*-Bu)Me_2]$_2$)-Me(THF)$_2$, **2-Me(THF)$_2$**. This assignment is supported by an X-ray crystal structure determination (Figure 6). The iron–scandium distance in **2-Me(THF)$_2$** is 3.26 Å, longer by 0.1 Å than in **2-(CH$_2$Xy-3,5)(THF)**, consistent with the presence of two coordinated THF molecules and decreased electrophilicity of the scandium center. The geometry around scandium is best described as a distorted trigonal bipyramid; although the N–Sc–C_{Me} angles deviate from 120° (108° and 113°), the other angles around scandium are consistent with this interpretation: O–Sc–C_{Me} angles are 85° and 88° and the O–Sc–O angle is 173°. The scandium–carbon distance, Sc–C_{Me}, of 2.28 Å is similar to that found in Cp*$_2$ScMe (2.24 Å).[16]

DFT Calculations. In order to understand the stability of the scandium alkyl complexes reported here and to probe the scandium–iron interaction, we set out to investigate computationally models for the various scandium ferrocene diamido complexes synthesized (Table 1, see Supporting Information for further details). Calculations were also performed on a model featuring a THF-free scandium center; such calculations could point to the preferred geometry of the scandium center in this THF-free complex and might suggest explanations for the observed coordination of more than one ligand besides the ancillary ligand.

The agreement between the scandium–iron distances in the model complexes and those obtained from crystal structure data was good. In the case of [fc($NSiH_3$)$_2$]Sc(CH_3)$_2^-$, the Fe–Sc calculated distance is larger by 0.08 Å than that observed in the X-ray crystal structure of **Li[2-Np$_2$]**; this difference might arise from the fact that the calculations were carried out on an anionic compound, with no contribution from the corresponding cation. As can be seen in Figure 7 and Table 1, the compound for which the molecular orbital shows the greatest contribution from scandium to the interaction between iron and scandium is [fc($NSiH_3$)$_2$]Sc(CH_3)(OMe_2)$_2$. In this model the alkyl group is methyl and the coordinated THF molecules were replaced by Me_2O. The contribution from the iron orbital though is around 10%, much smaller than the iron contribution for the benzyl

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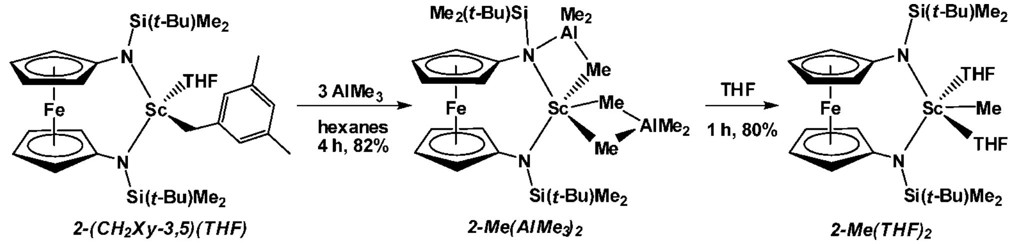
Scheme 4



model, $[fc(NSiH_3)_2]Sc(CH_2Ph)(OMe_2)$. In an analogous complex, $[fc(NSiH_3)_2]Sc(CH_3)(OMe_2)$, in which the benzyl group was replaced with a methyl group, the contributions from both iron and scandium to the molecular orbital with the iron−scandium interaction are reduced. These contributions increase slightly when the coordinated ether fragment is omitted and decrease again for the bis(methyl) scandium anion $[fc(NSiH_3)_2]Sc(CH_3)_2^-$.

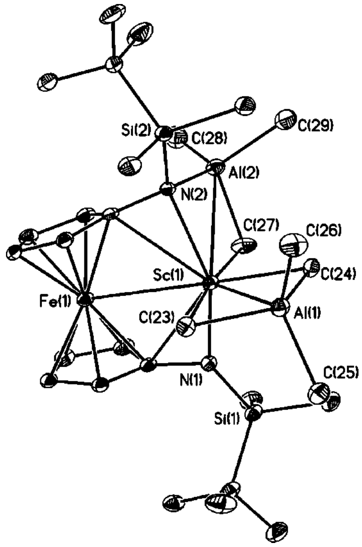


Figure 5. Thermal ellipsoid (35% probability) representation of $Sc(fc[NSi(t\text{-}Bu)Me_2]_2)Me(AlMe_3)_2$, **2-Me(AlMe$_3$)$_2$**. Hydrogen atoms were omitted for clarity.

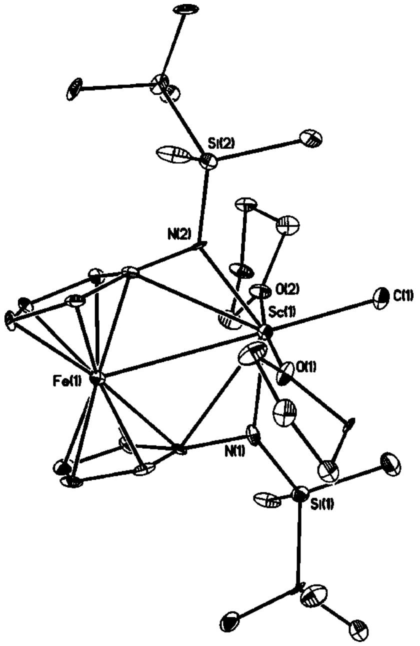


Figure 6. Thermal ellipsoid (35% probability) representation of $Sc(fc[NSi(t\text{-}Bu)Me_2]_2)Me(THF)_2$, **2-Me(THF)$_2$**. Hydrogen atoms were omitted for clarity.

Since we could not correlate conclusively the calculated iron−scandium distance and the iron−scandium interaction, NBO (natural bond order) charges were investigated (Table 1). These charges might be used as an indication of the electrophilicity of the metal center.[49] The charge of the scandium center (1.35) in $[fc(NSiH_3)_2]Sc(CH_2Ph)(OMe_2)$ is slightly smaller than the one in Cp_2ScMe (1.39) and in $[fc(NSiH_3)_2]Sc(CH_3)(OMe_2)_2$ (1.41). The methyl complexes with no or one coordinated ether molecule, $[fc(NSiH_3)_2]Sc(CH_3)$ and $[fc(NSiH_3)_2]Sc(CH_3)(OMe_2)$, show even higher scandium charges (1.57 and 1.51, respectively). Based on this data, some conclusions can be drawn: (1) the scandium charge (indicative of electrophilicity) can be correlated with the iron−scandium distance in complexes where the alkyl ligand is the same and (2) the scandium center in ferrocene diamide alkyl complexes is highly electrophilic, so the stability of these complexes is probably a consequence of Lewis base coordination.

An explanation for the fact that an alkyl complex with no additional ligand coordinating the scandium center has not been synthesized can be advanced based on the geometry optimization results for $[fc(NSiH_3)_2]Sc(CH_3)$; regardless of the geometry of the starting complex, the final geometry showed an Fe−Sc−C_{Me} angle of ~135°; the methyl group does not sit in the plane that bisects the Cp rings, as observed for Cp_2ScMe.[50] As a consequence, the unoccupied d orbitals of π symmetry for $[fc(NSiH_3)_2]Sc(CH_3)$ point away from the methyl group, while for Cp_2ScMe they point toward the methyl group. The availability of multiple d orbitals for interaction with an incoming ligand as opposed to just one for Cp_2ScMe (the orbital of σ symmetry) might explain the facility with which additional ligands coordinate to the scandium center in ferrocene diamide complexes.

It is difficult to understand the contribution of the scandium−iron interaction to the stability and/or electrophilicity of the scandium center. Such donor–acceptor interactions[51] have been identified in zirconium or thorium−platinum complexes.[52–54] In those cases, contributions from different metal orbitals were taken as an indication of the strength of the interaction. If the same criterion is applied to the present complexes, then $[fc(NSiH_3)_2]Sc(CH_2Ph)(OMe_2)$ and $[fc(NSiH_3)_2]Sc(CH_3)(OMe_2)_2$ show the strongest iron−scandium interaction. As a consequence, the electrophilicity of the scandium center in these complexes is lower than in the other scandium ferrocene diamide complexes modeled by DFT.

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Table 1. Orbital Contributions of Fe and Sc to the Fe−Sc Interaction and Charges of Scandium Determined by NBO Analysis

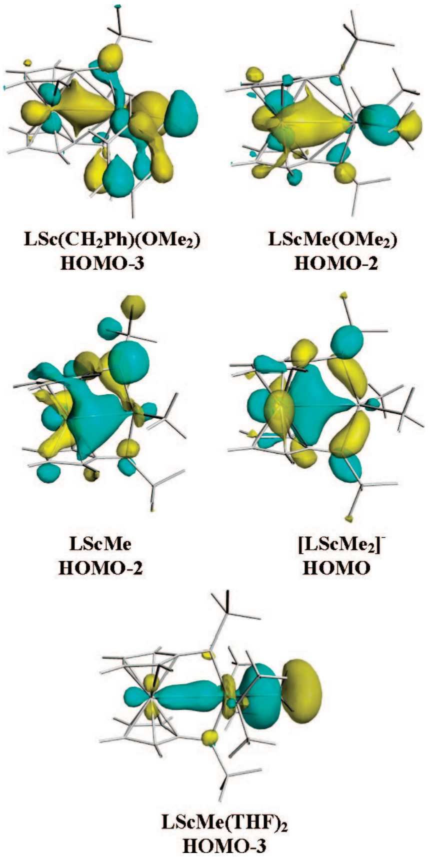
compound	Sc−Fe distance (Å) calcd (exptl)	orbital	Sc + Fe (%)	Sc charge
[fc(NSiH$_3$)$_2$]ScBz(OMe$_2$)	3.13 (3.16)	HOMO-3	8.8 + 27.2	1.35
[fc(NSiH$_3$)$_2$]ScMe(OMe$_2$)$_2$	3.23 (3.26)	HOMO-3	13.9 + 9.44	1.41
[fc(NSiH$_3$)$_2$]ScMe(OMe$_2$)	3.09	HOMO-2	3.4 + 5.6	1.51
[fc(NSiH$_3$)$_2$]ScMe	2.76	HOMO-2	5.0 + 10.0	1.57
[fc(NSiH$_3$)$_2$]ScMe$_2^-$	3.27 (3.19)	HOMO	2.8 + 44.5	

Ring-Opening Polymerization of L-Lactide. Although lanthanide complexes are widely used in the ring-opening polymerization of cyclic esters,[14,55] reports of active scandium catalysts are scarce.[56,57] On the basis of studies performed with the lanthanides and extension to scandium, the decreased reactivity of its complexes is attributed to its smaller size compared to those of the lanthanides.[57] Given the results of the DFT calculations that indicate electrophilic metal centers in **2-(CH$_2$Xy-3,5)(THF)** and **2-Me(THF)$_2$** and the fact that access to the scandium center is relatively unrestricted (coordination of additional ligands/substrates happens in a plane perpendicular to the plane bisecting the ferrocene ligand), we decided to investigate whether these characteristics translate into good activity for the ring-opening polymerization of cyclic esters. We have chosen L-lactide because of its cost and availability and the fact that it is more difficult to polymerize than other cyclic esters (ϵ-caprolactone, for example).[55] Reactions with 1 mol % **2-(CH$_2$Xy-3,5)(THF)** or **2-Me(THF)$_2$** were conducted both in toluene and in THF. Surprisingly, the reaction in THF mediated by **2-(CH$_2$Xy-3,5)(THF)** gave no polymer after 15 h at 60 °C, although THF was reported to have a beneficial effect on scandium lactide ring-opening reactions.[56] On the other hand, the reaction in C_6D_6 reached 91% completion after 6 h at 60 °C and 88% after 15 h at room temperature for **2-(CH$_2$Xy-3,5)(THF)**. The polymer obtained had a PDI (polydispersity index, M_w/M_n) of 1.4, but the value of M_n was 3 times that of the calculated molecular weight, indicating possible decomposition of the active species during polymerization. When **2-Me(THF)$_2$** was used as an initiator, the conversion was 92% in C_6D_6 after only 1 h at 70 °C. Again, experimental molecular weights were larger than those calculated (Table 2, 1.2 to 3.8 times larger) although the PDI values were around 1.5. Catalyst decomposition was confirmed by the presence of free ligand in ^{1}H NMR spectra. Although the polymerization seems somewhat controlled, it obviates a kinetic analysis, since no comparison with living-polymerization processes can be undertaken. In order to understand the cause for this phenomenon, the following experiment was performed: a polymerization reaction was carried out with a 100:1 monomer to catalyst ratio; at the end of this first polymerization, the reaction was sampled and a second 100 equiv of L-lactide (with respect to initial catalyst amount) was added. The polymers from the sample and at the end of the second reaction were analyzed by GPC. The ratio between the molecular weights (M_n) of the two polymer samples was 1.5 and a unimodal molecular weight distribution was found for the second polymer. We reasoned that if impurities are the cause of the higher molecular weights obtained, then the same amount of catalyst destroyed at the end of the first reaction will be destroyed at the end of the second reaction and the M_n of the second polymer will be higher than twice the M_n of the first polymer. Since the molecular weight of the second polymer is less (and not more) than twice as high as the molecular weight of the first polymer, we propose that the catalyst decomposition observed is related to the reaction progress and not to the presence of adventitious impurities. It is likely that the process by which an active catalyst is generated from the scandium alkyl complexes is complicated; once the active species is generated, polymerization proceeds in a rather controllable manner, explaining the relatively low PDIs observed.

Table 2. L-Lactide Polymerization Data for Reactions Catalyzed by 2-Me(THF)$_2$[a]

L-lactide:2-Me(THF)$_2$	M_c[b]	M_n	PDI
100	13 724	52 583	1.33
200	27 448	43 655	1.63
300	41 171	52 151	1.59
400	54 895[c]	69 0828[c]	1.46[c]
500	68 619	80 012	1.52

[a] All reactions were carried out in toluene at 70 °C and allowed to reach 95.2% conversion before workup. [b] M_c was calculated based on 95.2% conversion. [c] A high molecular weight peak was also found: M_n = 1 062 853; PDI = 1.03.



LSc(CH$_2$Ph)(OMe$_2$) HOMO-3

LScMe(OMe$_2$) HOMO-2

LScMe HOMO-2

[LScMe$_2$]$^-$ HOMO

LScMe(THF)$_2$ HOMO-3

Figure 7. Various computational models and molecular orbitals that show a scandium−iron interaction for scandium alkyl complexes (L = fc(NSiH$_3$)$_2$).

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Although there are two THF molecules coordinated to scandium in **2-Me(THF)$_2$** and only one in **2-(CH$_2$Xy-3,5)(THF)**, the first compound is a more active mediator for L-lactide polymerization. Given the different coordination geometries in the two compounds, it is difficult to interpret the role that steric factors play. If only the electrophilicity of the scandium center is considered, then the polymerization results follow the DFT findings of scandium charges.

In conclusion, we have shown that Sc(CH$_2$Xy-3,5)$_3$(THF)$_2$ is a useful starting material for the synthesis of ferrocene diamide scandium complexes. In addition, a scandium dimethylbenzyl compound was transformed into the corresponding THF-free scandium chloride-bridged dimer, which was used subsequently as a precursor in a reaction with *neo*-pentyl lithium. As a consequence of the ligand architecture, the isolation of a salt-free scandium *neo*-pentyl complex was not possible. Attempts to remove the coordinated THF molecule from **2-(CH$_2$Xy-3,5)(THF)** with AlMe$_3$ led to the isolation of a scandium methyl complex with two coordinated AlMe$_3$ molecules; the formation of a scandium methyl complex with two THF molecules coordinated was observed when the trimethyl aluminum complex was stirred in THF. DFT calculations indicate that if the iron−scandium interaction becomes stronger, then the electrophilicity of the scandium center decreases. We are currently exploring ligand frameworks that are more conducive to the formation of scandium monoalkyl, Lewis base-free complexes, which would complement existing scandocene examples.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[58] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. Scandium oxide was purchased from Stanford Materials Corporation (Aliso Viejo, CA) and used as received. KBz[59] and fc[NHSi(*t*-Bu)Me$_2$]$_2$ (fc = 1,1′-ferrocenylene)[29] were prepared following published procedures. Other chemicals were used as received. ^{1}H NMR spectra (this material is based on work supported by NSF grant CHE-9974928) were recorded on Bruker 300 or Bruker 500 spectrometers at room temperature in C$_6$D$_6$ or CDCl$_3$ unless otherwise specified. Chemical shifts are reported with respect to internal solvent, 7.16 ppm (C$_6$D$_6$). CHN analyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY), Desert Analytics (Tucson, AZ), and UC Berkeley Micro-Mass Facility (Berkeley, CA).

Synthesis of [K(solvent)][Sc(fc[NSi(*t*-Bu)Me$_2$]$_2$)$_2$], 1-K(solvent) (solvent = THF or toluene). ScCl$_3$(THF)$_3$ (50.8 mg, 0.1382 mmol) and K$_2$fc[NSi(*t*-Bu)Me$_2$]$_2$(OEt$_2$)$_2$ (185 mg, 0.276 mmol) were each dissolved in ca. 2 mL of THF and cooled to freezing. The solutions were combined slowly, and the resulting mixture was stirred for 3 h. The reaction mixture was filtered through Celite, and the THF was removed by vacuum. The remaining solid was dissolved in toluene, layered with pentane, and cooled to −35 °C. Crystals were isolated after 2 days. Yield: 0.080 g, 56%.

^{1}H NMR (500 MHz, C$_4$D$_8$O): δ, ppm: 3.94 (br s, 8H, fc-C*H*), 3.65 (br s, 8H, fc-C*H*), 0.643 (s, 36H, SiC(C*H*$_3$)$_3$), 0.416 (s, 24H, SiC*H*$_3$). ^{13}C NMR (126 MHz, C$_4$D$_8$O): δ 106.5, 69.1, 63.8, 29.1, 26.9, 0.65, −3.95.

Synthesis of Sc(CH$_2$Xy-3,5)$_3$(THF)$_2$. ScBr$_3$(THF)$_3$ (1.5 g, 2.99 mmol) was placed in a 100 mL round-bottom flask along with 80 mL of 2:1 THF/hexanes; this mixture was cooled to near freezing. K(CH$_2$Xy-3,5) (1.42 g, 8.98 mmol) was divided into two equal portions; the first portion was added immediately and the solution was warmed to 0 °C. After the orange color of the K(CH$_2$Xy-3,5) had faded to pale yellow (ca. 1 h), the second portion of K(CH$_2$Xy-3,5) was added and the mixture was stirred a further 2 h at 0 °C. After this time the reaction mixture was filtered through Celite and the solvent was removed. The resulting tan solid was dissolved in toluene (20 mL), and hexanes (20 mL) was added. The solution was cooled to −35 °C overnight, and feathery crystals were observed in the morning. Yield: 0.962 g, 59%. *Note*: this reaction does not scale up well, but reactions run in parallel can be combined at the filtration step with no decrease in yield. When precipitated from toluene with hexanes, ^{1}H NMR spectroscopy shows that the product is Sc(CH$_2$Xy-3,5)$_3$(THF)$_2$.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ, ppm 6.52 (s, 6H, *o*-Ar-C*H*), 6.45 (s, 3H, *p*-Ar-C*H*), 3.49 (br s, 8H, OC*H*$_2$CH$_2$), 2.22 (s, 18H, Ar-C*H*$_3$), 2.10 (s, 6H, Ar-C*H*$_2$), 1.16 (br s, 8H, OCH$_2$C*H*$_2$). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ, ppm 151.3, 123.2, 120.9, 70.3, 25.4, 21.8. Anal. Calcd for C$_{35}$H$_{49}$O$_2$Sc: C, 76.89; H, 9.03. Found: C, 76.70, H, 8.73.

Synthesis of Sc(fc[NSi(*t*-Bu)Me$_2$]$_2$)(CH$_2$Xy-3,5)(THF), 2-(CH$_2$Xy-3,5)(THF). Sc(CH$_2$Xy-3,5)$_3$(THF)$_2$ (285 mg 0.521 mmol) and fc[NHSi(*t*-Bu)Me$_2$]$_2$ (232 mg, 0.521 mmol) were each dissolved in 5 mL of toluene and cooled to −35 °C. The solutions were combined and stirred for 3 h at 0 °C. The solvent was removed, hexanes was added, and the mixture was filtered through Celite. After solvent removal the resulting solid was recrystallized from Et$_2$O/pentane. Yield: 283 mg, 80%.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.94 (s, 2H, *o*-Ar-C*H*), 6.49 (s, 1H, *p*-Ar-C*H*), 4.09 (s, br, 2H, fc-C*H*), 3.85 (s, br, 2H, fc-C*H*), 3.76 (br, 4H, OC*H*$_2$CH$_2$), 3.29 (s, br, 2H, fc-C*H*), 3.15 (s, br, 2H, fc-C*H*), 2.51 (s, 2H, benzyl), 2.32 (s, 6H, Ar-C*H*$_3$), 1.32 (br, 4H, OCH$_2$C*H*$_2$), 1.03 (s, 18H, SiC(C*H*$_3$)$_3$), 0.34–0.21 (br, 12H SiC*H*$_3$). ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 149.2, 121.7, 103.6, 70.9, 69.9, 68.0, 67.8, 66.7, 55.6, 27.9, 25.1, 20.3, −1.8, −3.0. Anal. Calcd for C$_{35}$H$_{57}$FeN$_2$OScSi$_2$: C, 61.93; H, 8.46. Found: C, 61.83, H, 8.15.

Synthesis of [Sc(fc[NSi(*t*-Bu)Me$_2$]$_2$)(μ-Cl)]$_2$, (2-Cl)$_2$. Compound **2-(CH$_2$Xy-3,5)(THF)** (415 mg, 0.611 mmol) and Me$_3$SiCl (332 mg, 3.06 mmol) were each dissolved in 5 mL of toluene and cooled to −78 °C. The two solutions were combined and stirred for 16 h at room temperature. The solvent was removed by vacuum and the resulting oily mixture was washed with hexanes, yielding a yellow solid, which was toluene soluble. This solid was dissolved in toluene:pentane and crystals were observed after 3 days. Yield: crude, 315 mg, 99%; crystals, 197 mg, 61%.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 4.06 (s, br, 8H, fc-C*H*), 3.87 (s, 4H, fc-C*H*), 1.09 (s, 36H, SiC(C*H*$_3$)$_3$), 0.41 (s, 24H, SiC*H*$_3$). ^{13}C NMR (126 MHz, C$_7$D$_8$): δ 136.8, 106.7, 70.2, 27.8, 20.0, −2.1. Anal. Calcd for C$_{30}$H$_{54}$FeN$_2$O$_2$ScClSi$_2$ (this compound was submitted for analysis as the THF adduct, since the adduct is more thermally stable than the chloride dimer): C, 54.00; H, 8.16. Found: C, 54.00, H, 7.88.

Synthesis of Li[Sc(fc[NSi(*t*-Bu)Me$_2$]$_2$)(Np)$_2$], Li[2-Np$_2$]. NpLi (11.5 mg, 0.147 mmol) and **(2-Cl)$_2$** (70.0 mg, 0.067 mmol) were each cooled to freezing in 2 mL of hexanes and combined immediately upon thawing. The mixture was stirred at −78 °C for 3 h. The solution was filtered in hexanes and crystals were grown from a concentrated pentane solution. Yield: 15 mg, 32%. Reactions run with freshly recrystalized **(2-Cl)$_2$** at −78 °C constantly yielded one major product.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 3.95 (s, 4H, fc-C*H*), 3.23 (s, 4H, fc-C*H*), 1.19 (s, 18H, SiC(C*H*$_3$)$_3$), 0.92 (s, 18H, CH$_2$C(C*H*$_3$)$_3$), 0.89

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(s, 4H, $CH_2C(CH_3)_3$), 0.51 (s, 12H, $SiCH_3$). ^{13}C NMR (75 MHz, C_6D_6): δ 104.3, 68.3, 67.2, 35.9, 31.6, 27.7, 20.7, −1.9.

Synthesis of Sc(fc[NSi(*t*-Bu)Me$_2$]$_2$)Me(AlMe$_3$)$_2$, 2-Me(AlMe$_3$)$_2$. Compound **2-(CH$_2$Xy-3,5)(THF)** (400 mg, 0.589 mmol) was divided into two equal portions and each portion was dissolved in hexanes (10 mL). To each portion was added $AlMe_3$ (100 mg, 1.38 mmol, 4.68 equiv). The reaction mixture was stirred 3 h at room temperature. The solutions were combined, reduced in volume until precipitate began to form, and filtered through Celite. The filtrate was cooled to −35 °C overnight, and yellow crystals were observed in the morning. Yield: 314 mg, 82%.

^{1}H NMR (300 MHz, C_6D_6): δ 3.91 (br, 4H, fc-CH), 3.58 (br, 4H, fc-CH), 0.95 (s, br, 18H, $SiC(CH_3)_3$), 0.30–0.50 (br, 21H), 0.25 (s, br, 12H, $SiCH_3$). Anal. Calcd for $C_{29}H_{59}Al_2FeN_2Si_2Sc$.: C, 53.85; H, 9.19; N, 4.33. Found: C, 53.47; H, 9.49%; N, 4.26.

Synthesis of Sc(fc[NSi(*t*-Bu)Me$_2$]$_2$)Me(THF)$_2$, 2-Me(THF)$_2$. Compound **2-Me(AlMe$_3$)$_2$** (289.2 mg, 0.4471 mmol) was dissolved in THF (5 mL) and stirred 1 h at room temperature. The solvent was removed and the reaction mixture was extracted with pentane and filtered through Celite. Crystals were grown from Et_2O/pentane. Yield: 232.8 mg, 80%.

^{1}H NMR (300 MHz, C_6D_6): δ 4.02 (s, 4H, fc-CH), 3.69 (s, br, 8H, OCH_2CH_2), 0.95 (s, 4H, fc-CH), 1.24 (s, br, 8H, OCH_2CH_2), 1.06 (s, 18H, $SiC(CH_3)_3$), 0.31 (s, 12H, $SiCH_3$), −0.38 (s, 3H, $ScCH_3$). Anal. Calcd for $C_{31}H_{57}FeN_2O_2Si_2Sc$: C, 57.56; H, 8.88; N, 4.33. Found: C, 57.72; H, 8.78; N, 4.60.

X-ray Crystal Structures. General Considerations. X-ray quality crystals were obtained from various concentrated solutions placed in a −35 °C freezer in the glovebox. Inside the glovebox, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glovebox. The X-ray data collections were carried out on a Bruker AXS single-crystal X-ray diffractometer using MoKα radiation and a SMART APEX CCD detector. The data are reduced by SAINTPLUS and an empirical absorption correction is applied using the package SADABS. The structure was solved and refined using SHELXTL (Brucker 1998, SMART, SAINT, XPREP, and SHELXTL, Brucker AXS Inc., Madison, WI). Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the bond lengths and angles, and with anisotropic displacement parameters are listed in the cif files.

Computational Details. The Amsterdam Density Functional (ADF) package (version ADF2006.01) was used to do a full geometry optimization on Cartesian coordinates of the model compounds specified in the text. For the scandium, iron, and silicon atoms, standard triple-ζ STA basis sets from the ADF database TZP were employed with 1s-3p (Sc, Fe) and 1s-2s (Si) electrons treated as frozen cores. For all the other elements, standard double-ζ STA basis sets from the ADF database DZP were used, with the 1s electrons treated as frozen core for non-hydrogen atoms. The local density approximation (LDA) by Vosko, Wilk, and Nusair (VWN) was used together with the exchange and correlation corrections that are used by default by the ADF2006.01 program suite.

For the complex $[fc(NSiH_3)_2]ScMe$ two different geometry optimizations gave the same result: in the first one, the coordinates were imported from the optimization of $[fc(NSiH_3)_2]ScMe(OMe_2)$ geometry and then the OMe_2 fragment was removed; for the latter, the CScFe angle was modified to start at 90°.

L-Lactide Polymerization Details. In the glovebox, L-lactide (0.2506 g, recrystallized from toluene) was transferred into a 25 mL Schlenk tube equipped with a magnetic stirrer. The L-lactide was dissolved in the proper volume of benzene to make the final L-lactide concentration 0.223 M and the final volume 7.8 mL. Then, the proper amount of catalyst (in a benzene solution) was rapidly added and the Schlenk tube was removed from the glovebox and placed in a vigorously stirring 70 °C bath. After the reaction was completed, the polymer was precipitated twice from dichloromethane with cold methanol and dried overnight under vacuum.

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Supporting Information Available: Experimental details for compound syntheses, full crystallographic descriptions (as cif), and computational details are available free of charge via the Internet at http://pubs.acs.org.

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