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Article

Nucleophilic Degradation of a *β*-Diketiminato Ancillary by a Transient Scandium Hydride Intermediate

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Reactions of a β-diketiminato-supported scandium dichloride $LScCl_2$ (L = (Ar)NC(^{t}Bu)CHC(^{t}Bu)N(Ar); Ar = 2,6-^{i}Pr$_2$-C_6H_3) with boro- and aluminohydride reagents result in transient scandium hydrides, which undergo hydride transfer to the ligand backbone, inducing fragmentation of the ancillary. The products of this fragmentation have been characterized and include an organic enamine (**2**) and scandium imido containing clusters. One such product, formed via reaction with $LiBEt_3H$ and $LScCl_2$, is the trimer [ArNScCl(THF)]$_3$[LiH(THF)], **1**, which includes an occluded molecule of lithium hydride. The reactions involving $LiAlH_4$, along with labeling studies, helped to clarify the fragmentation pathway and account for the observed products.

Introduction

Well-defined, monomeric hydrides of the group 3 metals are rare,[1] but potentially useful as mediators of catalytic cycles dominated by σ-bond metathesis and migratory insertion reactions.[2] For example, Cp*$_2$Sc-H[1a] has been shown by Tilley to mediate hydromethylation of olefins[3] and dehydrosilylation of alkanes,[4] albeit with low turnovers. Aside from Cp*$_2$Sc-H and Ind*$_2$YH(THF),[1b] group 3 hydrides are typically dimeric,[5] oligomeric,[6] or heteromultimetallic,[7] although reactivity may be funneled through highly active monomeric species. Most of the known examples of group 3 hydrides are stabilized by cyclopentadienyl-type donors;[8] given their demonstrated potential for hydrocarbon functionalization, new examples supported by other ancillary ligand frameworks[9] are of considerable interest.

We,[10] and others,[11] have utilized the β-diketiminato ligand framework to develop the chemistry of dialkyl organo group 3 compounds, and a logical extension of this work is to explore the suitability of this ancillary for supporting reactive scandium hydrides. Typically, early transition metal hydrides are generated from alkyl precursors via hydrogenolysis; in early studies, we found the dialkyl complexes **I** (R = Me, CH_2SiMe_3) to react only slowly with H_2 (4 atm) and generate a complex mixture of products. Thus, we turned to another more classical method,[12] that of treatment of scandium chloride antecedents with $LiMH_4$ (M = B, Al), to generate the desired hydride derivatives. While this technique has been utilized extensively to generate hydrides for most metals in the d-block,[13] typically group 3 hydridoborate or hydridoaluminate complexes arise from such reactions. For

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Scheme 1

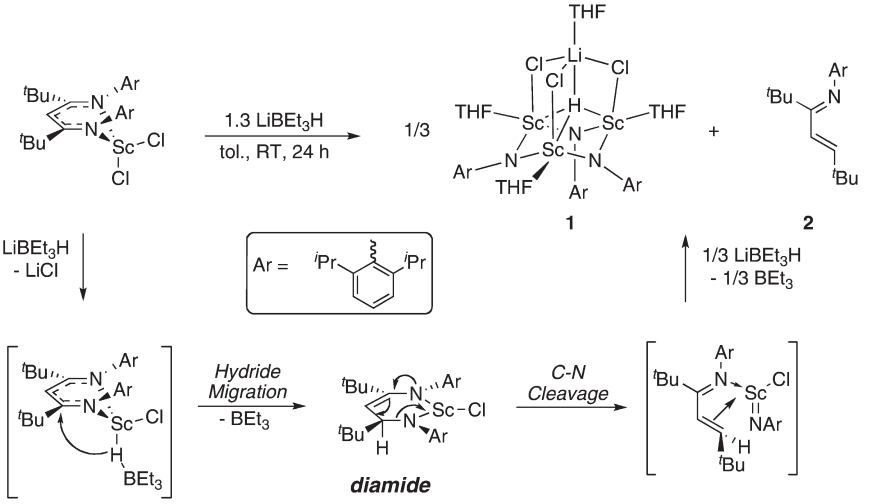
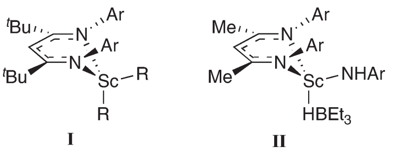


Chart 1



example, Morris and Smith reported the preparation of $\mathrm{Sc(BH_4)_3 \cdot THF}_n$[14] via reaction of anhydrous $\mathrm{ScCl_3}$ with a slight excess of $\mathrm{LiBH_4}$ in THF. The first structurally characterized borohydride of scandium, $[\mathrm{Sc}\{\eta^5\text{-}\mathrm{C_5H_3(SiMe_3)_2}\}_2(\mathrm{BH_4})]$, was prepared a decade later by Lappert and co-workers,[15] and several other examples of scandium $\mathrm{BH_4}$ compounds have been subsequently identified.[16] These compounds can be viewed as masked scandium hydrides, protected by "$\mathrm{BH_3}$"; removal by treatment with a Lewis base could potentially liberate a reactive scandium hydride. Indeed, this was apparently observed by Fryzuk et al. in the reaction of a PNP pincer ligand stabilized scandium borohydride with $\mathrm{PMe_3}$, although the chemistry was not clean enough to allow for exploration of the chemistry of the resulting scandium hydride.[16c] Furthermore, Mindiola et al. have demonstrated that $\mathrm{BEt_3}$ is labile in the complex **II**, prepared via reaction of LSc(NHAr)Cl (Ar = 2,6-diisopropylphenyl) with $\mathrm{NaHBEt_3}$, liberating a putative Sc-H species, which was trapped with a series of oxygen-containing substrates.[11]

With these precedents in mind, we report the reactions of the well-defined, monomeric, and base-free scandium dichloride precursor to dialkyls **I**, in which the nacnac ligand bears *tert*-butyl substituents, with the boro- and aluminohydride reagents $\mathrm{LiHBEt_3}$ and $\mathrm{LiAlH_4}$. These studies show that this nacnac ligand framework does not support scandium hydrides but undergoes fragmentation to yield imide-containing clusters.

Results and Discussion

Clean reaction of the β-diketiminato scandium dichloride ($\mathrm{LScCl_2}$) depicted in Scheme 1 with $\mathrm{LiBEt_3H}$ occurs when carried out with 1.3 equiv of the borohydride reagent in toluene over the course of 12 h, yielding the scandium-containing product **1** and the organic ene-amine **2**. Initial experiments utilized equimolar amounts of $\mathrm{LScCl_2}$ and $\mathrm{LiBEt_3H}$ led to more complex product mixtures from which the unusual cluster **1** was isolated and characterized by X-ray crystallography (see below). The occluded LiH evident in this structure, present in a 1/3 ratio with scandium, suggested that its clean production required an extra 0.33 equiv of $\mathrm{LiBEt_3H}$, which was experimentally borne out in subsequent preparations.

The ene-amine product **2** arises from the β-diketiminate scaffold and was identified by GC/MS (m/z = 327 g/mol) and ^{1}H NMR spectroscopy. Characteristic resonances in $\mathrm{C_6D_6}$ include a well-resolved AB quartet centered at 5.80 ppm corresponding to the *trans*-coupled olefinic protons ($^3J_{\mathrm{HH}}$ = 16.7 Hz) and two signals at 1.40 and 0.77 ppm for the inequivalent ^{t}Bu groups. Loss of this fragment necessarily leaves "ArN=ScCl", which apparently assembles into the trinuclear cluster **1**, templated around LiH and stabilized by THF molecules present since $\mathrm{LiBEt_3H}$ is administered as a 1.0 M solution in THF. Product **1** is isolated by precipitation and washing with cold pentane; its ^{1}H NMR spectrum indicates the presence of two types of coordinated THF ligands in a 3:1 ratio, assignable to the THF ligated to scandium and lithium, respectively. In addition, signals for one *N*Ar group with diastereotopic isopropyl groups are present in this C_{3v} symmetric molecule. A singlet at -1.7 ppm in the $^7\mathrm{Li}\{^1\mathrm{H}\}$ NMR spectrum is suggestive of an anionic scandium "ate" complex[9a] and confirms the presence of lithium in the cluster. No spectroscopic signature for the central $\mathrm{Sc_3}H\mathrm{Li}$ hydride was observed, presumable due to severe quadrupolar broadening.

As alluded to above, the nature of complex **1** was confirmed initially via X-ray crystallography. The compound is highly soluble in aromatic and coordinating solvents and moderately soluble in aliphatic solvents; thus, X-ray quality crystals were grown by slow evaporation from concentrated pentane solutions. The solid-state structure of **1** is shown in Figure 1 along with selected metrical data. The $\mathrm{Sc_3N_3}$ core

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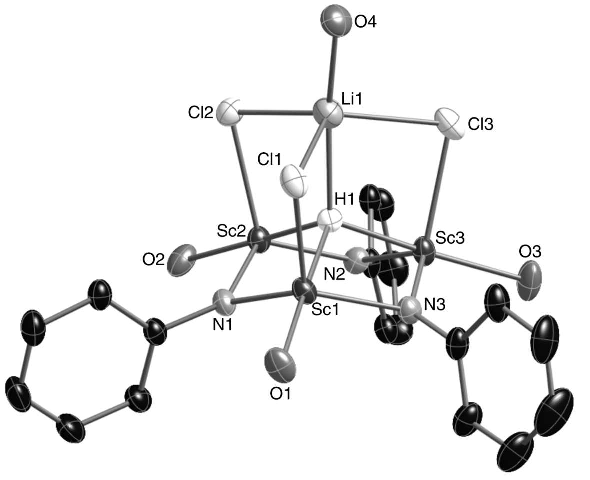

Figure 1. Thermal ellipsoid diagram of **1** at 50% probability. All isopropyl groups, carbons of THF groups, and hydrogen atoms except H1 are removed for clarity. Selected bond lengths (Å): Sc1−N1, 2.037(2); Sc1−N2, 2.046(2); Sc1−O1, 2.166(2); Sc1−Cl1, 2.443(1); Sc1−H1, 2.02(2); Sc2−N2, 2.038(2); Sc2−N1, 2.040(2); Sc2−O2, 2.157(2); Sc2−Cl2, 2.485(1); Sc2−H1, 2.00(2); Sc3−N3, 2.028(2); Sc3−N2, 2.037(2); Sc3−O3, 2.157(2); Sc3−Cl3, 2.460(1); Sc3−H1, 1.98(2); Li1−Cl1, 2.528(5); Li1−Cl2, 2.494(5); Li1−Cl3, 2.476(5); Li1−O4, 1.963(5); Li1−H1, 2.11(3). Selected bond angles (deg): N1−Sc1−N3, 122.05(8); N2−Sc2−N1, 118.78(8); N3−Sc3−N2, 121.11(8); Sc1−N1−Sc2, 102.24(8); Sc2−N2−Sc3, 102.57(9); Sc3−N3−Sc1, 102.80(9).

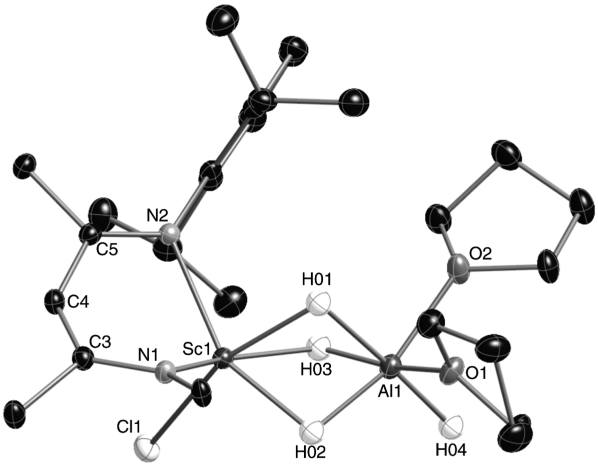

Figure 2. Thermal ellipsoid diagram of **3** at 50% probability. All hydrogen atoms except those associated with Al1 and most of the carbon atoms of the aryl group attached to N1 are removed for clarity. Selected bond lengths (Å): Sc1−N1, 2.122(2); Sc1−N2, 2.208(1); Sc1−Cl1, 2.416(1); Sc1−H01, 1.94(2); Sc1−H02, 1.92(2); Sc1−H03, 1.97(2); Al1−O1, 1.978(1); Al1−O2, 1.985(1); Al1−H01, 1.70(2); Al1−H02, 1.70(2); Al1−H(03), 1.71(2); Al1−H(04), 1.54(2). Selected bond angles (deg): N1−Sc1−N2, 92.95(5); N1−Sc1−Cl1, 105.24(4); N2−Sc1−Cl1, 104.79(4); Cl1−Sc1−H03, 157.0(5); O2−Al1−H02, 164.9(6). Selected torsion angles (deg): N1−C3−C4−C5, 15.9(3); N2−C5−C4−C3, 29.6(3).

adopts a six-membered chair conformation with the three scandium-bound chlorine atoms ($\text{Sc}-\text{Cl}_{\text{av}} = 2.464(1)$ Å) all occupying axial positions in a *cis* arrangement. This positions each chloride to effectively bind to Li(1) with average Cl−Li contacts of 2.499(5) Å. Each scandium adopts a distorted trigonal-bipyramidal geometry, with the encapsulated hydride and oxygen from THF occupying the apical positions. The hydride was crystallographically located and is symmetrically bound to the three scandium centers with an average Sc−H bond length of 2.00(2) Å. The tetrahedral coordination sphere of H(1) is completed with a lithium ion, which features a Li(1)−H(1) distance of 2.11(3) Å. All three imide nitrogens are trigonal planar, and the Dipp groups align essentially orthogonal to the Sc−N−Sc planes. The structural rigidity imposes asymmetry on the top and bottom isopropyl groups, which is borne out in the ^{1}H NMR spectrum of **1**. The Sc−N bond lengths average 2.038(2) Å, which are in good agreement with other bridging scandium imides.[17] The average N−Sc−N bond angles are larger than the corresponding Sc−N−Sc angles by almost 15° presumably due to the greater steric bulk at scandium versus nitrogen. The encapsulated Li-H moiety is an unusual structural motif; direct analogues appear to be absent from the literature, but related examples in which the Li-H participates in three-center−two-electron bonding arrangements with other metals are known.[18]

A plausible sequence for the production of products **1** and **2** is shown in Scheme 1. The reaction likely proceeds through initial salt metathesis to form a scandium borohydride intermediate akin to **II** as observed by Mindiola et al.[11] Since **II** is an isolable species, it is likely that liberation of BEt_3 is facile in the present system; the greater steric demands of the nacnac ligand featuring *tert*-butyl substituents may encourage loss of triethylborane. In any event, the resulting scandium hydrido chloride rapidly converts to the diamide intermediate proposed via hydride transfer to the imine carbon of the nacnac ligand. This intermediate undergoes fragmentation via C−N bond cleavage to form **2** and a scandium imide, which assembles into **1** in the presence of a slight excess of $LiBEt_3H$. Although unanticipated, related fragmentations in titanium β-diketiminato complexes resulting in d^0 imide[19] and phosphinidene[20] complexes provide precedence for such behavior.

Further support for this proposal, in the form of spectroscopic observation of the diamide intermediate of Scheme 1, was found in studying the reactions of $LScCl_2$ with lithium aluminum hydride. Reaction with 1 equiv of purified $LiAlH_4$ in THF at −35 °C produces a new C_s symmetric β-diketiminato-ligated scandium complex with no evidence for ligand degradation, assigned as the aluminohydride adduct, **3** (Scheme 2). The effective C_{2v} ligand symmetry present in

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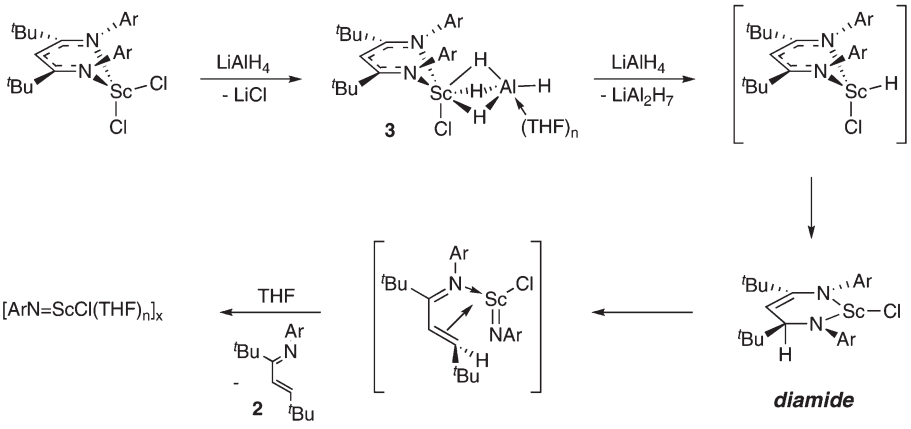
Scheme 2



$LScCl_2$[10] is disrupted in **3**, indicating replacement of one scandium chloride with a new ligand. In addition to two new isopropyl septets at 3.80 and 3.27 ppm signaling the lowered symmetry, a broad resonance at 3.07 ppm integrating to four hydrogens was observed. The concomitant presence of a broad singlet at 99.1 ppm[12] in the $^{27}Al\{^1H\}$ NMR spectrum is fully consistent with a scandium aluminohydride complex.

X-ray quality crystals of **3** were obtained by slow evaporation of THF solutions at −35 °C, and the molecular structure is shown in Figure 2 along with selected metrical data. The four aluminum hydride atoms were located in the difference map and refined in the solid-state structure, and the AlH_4 unit is coordinated to scandium in the *exo* position[10] through three bridging hydrides with average Sc−H bond lengths of 1.94(2) Å, which are slightly shorter than the analogous distances in the solid-state structure of **1**. The trio of three-center−two-electron bonds serve to elongate the $Al-H_{01-03}$ bonds by 0.16 Å relative to the nonbridging $Al-H_{04}$, which is 1.54(2) Å. Two THF molecules complete the coordination sphere of aluminum with Al−O bond lengths of 1.978(1) and 1.985(1) Å. The β-diketiminato ligand deviates noticeably from planarity, with backbone torsion angles of 15.9(3)° and 29.6(3)°, with the backbone C4 residing below the plane formed by N1−C3−C5−N2. The Sc−N contacts (Sc1−N1 = 2.122(2) Å; Sc1−N2 = 2.208(1) Å) are also asymmetric, differing by almost 0.1 Å. A weak interaction appears present between C4 and Cl1, as the *endo* chloride is canted further under the ancillary than in $LScCl_2$[10] The N−Sc−Cl bond angles at 105.24(4)° and 104.79(4)° are significantly smaller in **3** than in the dichloride precursor (cf. 113.5(2)° and 116.0°),[10] which supports this weak intramolecular interaction.

Although stable indefinitely at −35 °C in solution, **3** does decompose when warmed to room temperature to a mixture of products, including a small amount of the ene-imine ligand fragment **2**; this, in addition to the high solubility of the compound, contributes to its low isolated yield of 47%. In an effort to study the decomposition, $LScCl_2$ was treated with an excess (2.5 equiv) of $LiAlH_4$ at −35 °C in a J-Young NMR tube and slowly warmed to room temperature in the NMR probe. Monitoring the reaction over 24 h reveals clean, quantitative conversion of $LScCl_2$ through **3** en route to a new scandium imide product and loss of the ene-imine fragment **2** (Scheme 2). Interestingly, in this system signals for an intermediate assignable to the proposed diamide intermediate formed as a result of hydride transfer to the imine carbon of the β-diketiminato framework are observed during the course of the reaction (Figure 3). Excess $LiAlH_4$ liberates the scandium hydrido chloride through the formation of $LiAl_2H_7$ (observed in the ^{27}Al NMR spectrum $\delta = 87$ ppm),[21] which leads to diamide production. The presence of the intermediate is indicated by two characteristic upfield doublets at 4.91 and 4.53 ppm ($^3J_{HH} = 5.6$ Hz) corresponding to the olefinic and aliphatic protons of the ligand backbone, respectively. When the analogous reaction is performed with $LiAlD_4$, the furthest upfield doublet is no longer observed and the downfield signal becomes a 1:1:1 triplet ($^3J_{H-D} = 1.3$ Hz). On the basis of the NMR data, it appears that C−N cleavage is rate limiting in this system, as the concentration of the diamide increases over time at the expense of **3**, reaching a maximum before eventually converting entirely to a new scandium-containing product concomitant with production of **2**. Stoichiometry dictates that this new scandium product is "ArN=ScCl", which in the absence of $LiBEt_3H$ forms a cluster of undefined nuclearity and THF incorporation. ^1H NMR spectroscopy indicates a symmetrical product on the basis of a single isopropyl group, but all attempts to obtain X-ray quality crystals from the product mixture were unsuccessful, as the material consistently forms extremely thin crystalline plates that were not suitable for diffraction. Efforts are continuing to characterize this potentially useful synthon for scandium imido derivatives.

Conclusions

While scandium alkyls are tolerated by β-diketiminato ligands, hydrides rapidly transfer from the metal to the imine carbon of the ligand. This results in a transiently observed intermediate in which the nacnac ligand is transformed to a chelate of amide-enamide character; this species fragments via C−N bond cleavage to yield an enamine organic product (**2**) and a scandium imido fragment that assembles into higher nuclearity products. Thus, although the nacnac ligand proves unsuitable for supporting scandium hydrides, their transient generation here points to their potentially high reactivity. With ligands less prone to nucleophilic reduction, perhaps this reactivity can be harnessed. Another avenue for investigation that arises from these studies is the possibility

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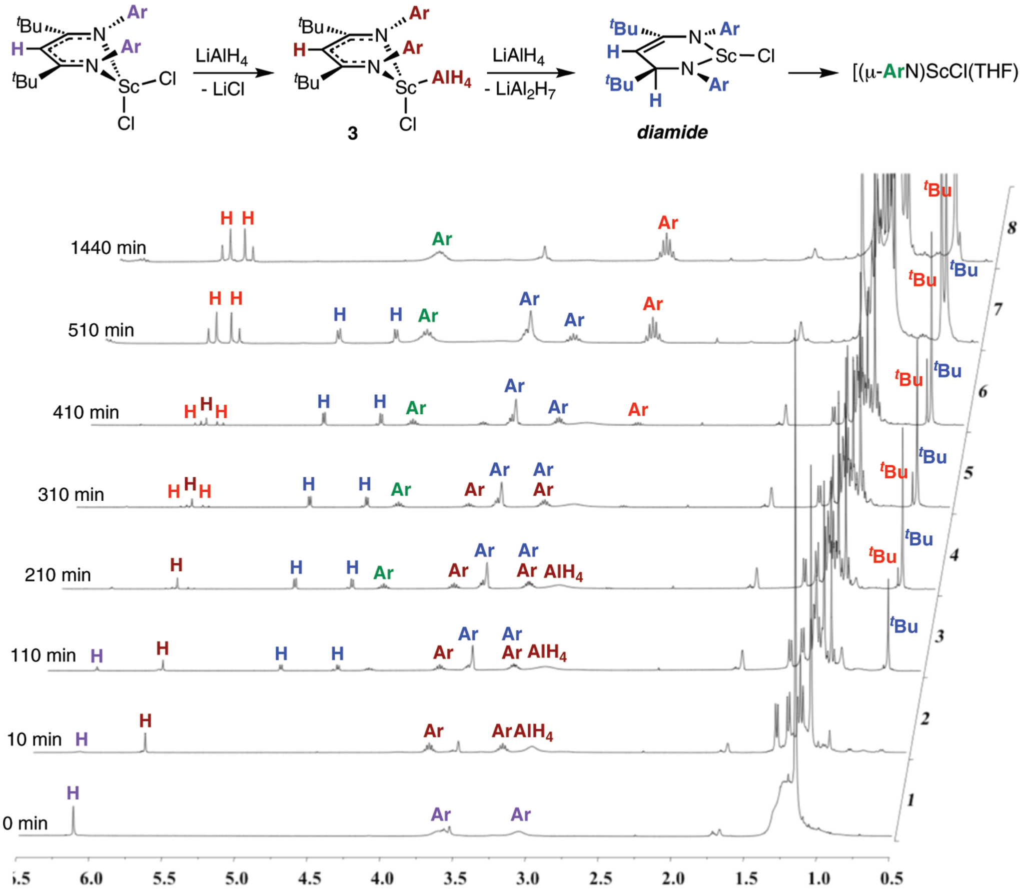

Figure 3. Series of 400 MHz ^{1}H NMR spectra monitoring reaction of $LScCl_2$ with 2.5 equiv of $LiAlH_4$ in d_8-THF at 25 °C.

of using the scandium-containing imido cluster products as synthons for well-defined, monomeric scandium imides.[22]

Experimental Section

General Procedures. All manipulations were performed either in an Innovative Technologies System One inert atmosphere glovebox or on greaseless vacuum lines equipped with Teflon needle valves (Kontes) using swivel-frit-type glassware. Toluene, THF, and hexanes were dried and purified using the Grubbs/Dow purification system[23] and stored in evacuated bombs. Bromobenzene and d_5-bromobenzene were predried over CaH_2, and d_8-THF, d_6-benzene, and d_8-toluene were dried and stored over sodium/benzophenone. All were distilled prior to use. **I-Cl** was synthesized using a literature procedure.[9] $LiAlH_4$ was extracted into anhydrous ether and recrystallized prior to use, and $LiBEt_3H$ was used as a 1.0 M solution in THF from Aldrich, and the ^{1}H and ^{11}B NMR spectra were obtained to assess purity; no evidence for $LiBEt_4$ or $LiBEt_2H_2$ was found.[24]

Samples were analyzed by NMR spectroscopy on Bruker AMX-300 and DRX-400 spectrometers at room temperature unless otherwise specified. ^{1}H and ^{13}C were referenced to $Si(CH_3)_4$ through the residual peaks of the employed solvent, ^{11}B spectra to external $BF_3 \cdot OEt_2$ at 0.0 ppm, and ^{19}F spectra to $CFCl_3$ using an external standard of hexafluorobenzene (δ −163.0 ppm) in C_6D_6. NMR data are provided in ppm. The coupling constants (i.e., $^3J_{H-H}$) for the isopropyl groups on the ligand range between 6.4 and 7.2 Hz and, thus, are not reported in the NMR analysis of the compounds. Elemental analyses were performed by Mrs. Dorothy Fox and Mr. Johnson Li in the microanalytical laboratory at the University of Calgary. Complexes containing scandium have been routinely found to be low in carbon, possibly as a result of metal-catalyzed carbide formation, leading to incomplete combustion.[25] X-ray data were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer using Mo Kα radiation at −100 °C.

Synthesis of [ClScNDipp(THF)]$_3$[LiH(THF)], 1. A 100 mL two-neck flask was charged with $LScCl_2$ (1.510 g, 2.44 mmol) dissolved in 60 mL of toluene added *in vacuo* at −78 °C. The solution was warmed to room temperature, and $LiBEt_3H$ (1.0 M in THF, 3.66 mL) was added dropwise via syringe through a rubber septum. The reaction mixture was stirred overnight, whereupon a cloudy dark yellow solution was obtained. Toluene was removed *in vacuo*, and the flask was attached to a swivel frit apparatus in the glovebox. The assemblage was evacuated, and fresh toluene (50 mL) was vacuum distilled into the flask. The mixture was sonicated for 30 min at room temperature and filtered, and solvent removed under vacuum to afford a dark orange oil. Pentane (25 mL) was added and the mixture sonicated for 20 min, then cooled to −35 °C and back-filtered. The off-white solid was washed with 3 × 5 mL of pentane and evacuated to dryness. X-ray quality crystals were grown from concentrated pentane solutions at −35 °C (0.620 g, 1.76 mmol, 72%). ^{1}H NMR (C_6D_6): δ 7.24 (d, 3H; C_6H_3), 7.12 (d, 3H; C_6H_3), 6.83 (t, 3H; C_6H_3), 4.71 (sp, 3H; $CHMe_2$), 4.05

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Table 1. Data Collection and Refinement Details for 1 and 3

	1	3
formula	$C_{52}H_{84}Cl_3LiN_3O_4Sc_3$	$C_{43}H_{73}AlClN_2$-$O_2Sc\cdot 0.5C_4H_8O$
fw	1063.39	793.48
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	14.195(1)	9.698(1)
b, Å	14.779(3)	13.072(3)
c, Å	27.634(4)	19.616(4)
α, deg	90	82.282(10)
β, deg	100.489(9)	79.336(14)
γ, deg	90	68.963(13)
V, Å^3	5700.4(15)	2274.7(7)
Z	4	2
T, K	173(2)	173(2)
λ, Å	0.71073	0.71073
ρ_{calc}, g/cm^3	1.239	1.158
F(000)	2264	864
μ, mm^{-1}	0.530	0.277
cryst size, mm^3	0.22 × 0.20 × 0.10	0.22 × 0.07 × 0.06
transmn factors	0.9489−0.8923	0.9836−0.9415
θ range, deg	2.66−27.46	2.60−27.49
no. of data/restraints/ params	12 871/0/602	10 365/6/542
GoF	1.013	1.019
R_1 ($I > 2\sigma(I)$)	0.0476	0.0416
wR_2 (all data)	0.0729	0.0697
residual density, e/Å^3	0.492 and −0.440	0.392 and −0.361

(sp, 3H; C*H*Me$_2$), 3.98 (br s, 4H; THF$_{Li}$), 3.27 (br m, 12H; THF$_{Sc}$), 1.58 (d, 18H; CH*Me*$_2$), 1.42 (d, 18H; CH*Me*$_2$), 1.25 (m, 4H; THF$_{Li}$), 0.88 (m, 12H; THF$_{Sc}$), Li−H not observed. ^{13}C{^{1}H} NMR (C_7D_8): *δ* 153.8, 137.6, 134.4, 124.1, 122.1, 117.3 (*C*$_6$H$_3$), 71.1 (THF$_{Sc}$), 33.4 (THF$_{Li}$), 28.3 (CH*Me*$_2$), 26.5 (THF$_{Sc}$), 25.2, 24.5 (CH*Me*$_2$), 22.4 (THF$_{Li}$), 13.9 (CH*Me*$_2$). ^{7}Li NMR (C_6D_6): *δ* −1.7. Anal. Calcd for $C_{52}H_{84}Cl_3LiN_3O_4Sc_3$: C, 58.73; H, 7.96; N, 3.95. Found: C, 58.25; H, 8.20; N, 4.19.

Characterization of DippNC(^{t}Bu)CHCH(^{t}Bu), 2. ^{1}H NMR (C_6D_6): *δ* 7.19 (d, 2H; C$_6$*H*$_3$), 7.04 (t, 1H; C$_6$*H*$_3$) 5.80 (dd, 2H; C*H*=C*H*^{t}Bu), 3.02 (sp, 2H; C*H*Me$_2$), 1.40 (s, 9H; NCC*Me*$_3$), 1.28 (ov d, 12H; CH*Me*$_2$), 0.77 (s, 9H; NCC*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): *δ* 172.4 (N*C*CMe$_3$), 150.3 (Me$_3$C*C*H), 148.4, 133.9, 122.7, 122.6 (*C*$_6$H$_3$), Me$_3$CH*C*HCCMe$_3$) 41.3, 37.1 (*C*Me$_3$), 28.5, 28.4 (C*Me*$_3$), 28.2 (*C*HMe$_2$) 23.2, 22.1 (CH*Me*$_2$). GC-MS (*m*/*z*): 327 g/mol.

Synthesis of [LScCl][AlH$_4$(THF)$_2$], 3. A 20 mL vial was charged with LScCl$_2$ (0.250 g, 0.405 mmol) and LiAlH$_4$ (0.017 g, 0.445 mmol), and 5 mL of THF was added. The vessel was shaken vigorously for 5 min and then cooled to −35 °C for 7 days, over which time large colorless needles were obtained. The supernatant was removed, and the solid was dried *in vacuo* to afford pure **3** (0.144 g, 0.190 mmol, 47%). ^{1}H NMR (*d*$_8$-THF): *δ* 6.95 (m, 6H; C$_6$*H*$_3$), 5.73 (s, 1H; C*H*), 3.78 (sp, 2H; C*H*Me$_2$), 3.27 (sp, 2H; C*H*Me$_2$), 3.07 (br s, 4H; Al*H*$_4$), 1.39 (d, 6H; CH*Me*$_2$), 1.31 (d, 6H; CH*Me*$_2$), 1.24 (ov d, 12H; CH*Me*$_2$), 1.16 (s, 18H; NCC*Me*$_3$), THF$_{Al}$ resonances were not observed due to scrambling with *d*$_8$-THF. ^{13}C{^{1}H} NMR (*d*$_8$-THF): *δ* 173.7 (N*C*CMe$_3$), 148.0 (*C*$_{ipso}$), 146.5, 143.0, 141.6 (*C*$_6$H$_3$), 140.4 (*C*$_{ipso}$), 124.3, 123.5, 123.1 (*C*$_6$H$_3$), 94.3 (*C*H), 44.4 (*C*Me$_3$), 32.2 (*C*HMe$_2$), 32.0 (C*Me*$_3$), 29.8 (*C*HMe$_2$), 27.9, 27.7, 26.3, 25.2 (CH*Me*$_2$). ^{27}Al NMR (*d*$_8$-THF): 99.1. Anal. Calcd for $C_{43}H_{73}AlClN_2O_2Sc$: C, 68.18; H, 9.71; N, 3.70. Found: C, 67.23; H, 10.02; N, 3.58.

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Supporting Information Available: Crystallographic data (CIF) for **1** and **3**. This information is available free of charge via the Internet at http://pubs.acs.org.