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Carbon−Oxygen Bond Cleavage Promoted by a Scandium Borohydride Complex

Falguni Basuli, John Tomaszewski, John C. Huffman, and Daniel J. Mindiola*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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Treatment of (Nacnac)$ScCl_2$(THF) ($Nacnac^-$ = ArNC(CH_3)CHC(CH_3)NAr, Ar = 2,6-(CH(CH_3)$_2$)$_2C_6H_3$) with KNHAr in THF affords in 83% yield the chloro−anilide complex (Nacnac)ScCl(NHAr)(THF) (**1-Cl(THF)**). **1-Cl(THF)** was fully characterized, and a single-crystal X-ray diffraction study reveals the complex to be a five-coordinate scandium complex containing a bound THF ligand. The complex **1-Cl(THF)** reacts cleanly with $NaBHEt_3$ in toluene to yield the triethylborohydride adduct (Nacnac)Sc(NHAr)($HBEt_3$) (**1-HBEt$_3$**) in 78% yield. The molecular structure of **1-HBEt$_3$** indicated a bridged hydride ligand confined between the scandium and boron atoms. The coordination environment of scandium was that of an octahedron, with the two remaining coordination sites being occupied by one hydrogen from each methylene group on the borane interacting with the scandium center through agostic interactions. Variable-temperature ^{11}B NMR spectroscopy indicated a doublet with J_{BH} = 53 Hz (70 °C). Borane extrusion in the complex **1-HBEt$_3$** in Et_2O affords the ethoxide (Nacnac)Sc(NHAr)(OEt) (**1-OEt**), which was structurally characterized. Tetrahydrofuran also reacts cleanly with **1-HBEt$_3$** to yield the enolate complex (Nacnac)Sc(NHAr)($OCH{=}CH_2$) (**1-OCH═CH$_2$**) in 70% yield. The molecular structure of **1-OCH═CH$_2$** was also determined by single-crystal X-ray diffraction methods. In the absence of Lewis bases such as Et_2O or THF, **1-HBEt$_3$** was found to thermally decompose to a mixture of products. When 1 equiv of benzophenone was added to **1-HBEt$_3$**, the putative hydride "**1-H**" was trapped to yield the diphenylmethoxide complex (Nacnac)Sc(NHAr)($OCHPh_2$) (**1-OCHPh$_2$**) in 80% yield. As an alternative to **1-HBEt$_3$** cleaving C−O bonds, the stable *tert*-butyl complex (Nacnac)Sc(NHAr)(^tBu) (**1-^{t}Bu**), prepared in 94% yield from **1-Cl(THF)** and solid Li^tBu, was also found to react with Et_2O to yield **1-OEt**. The complex **1-^{t}Bu** was fully characterized, and the molecular structure was established by single-crystal X-ray diffraction methods. **1-^{t}Bu** was thermally stable in the absence of Et_2O and THF.

Introduction

The use of β-diketiminates as supporting ligands for reactive organometallic complexes has undergone a revival of interest.[1−7] Such a renaissance in the usage of this ligand is remarkable, since this class of molecules has been known for a long time.[8] β-Diketiminate ligands are particularly attractive ligands, since the aryl derivatives are easy to prepare in large scale starting from commercially available reagents.[1,2,5] These ligands also lack β-hydrogens and are easy to modify at both the β-carbon and the nitrogen positions.[1,2,5] Modification of the β-carbon backbone and aryl flanking groups allows for control of both electronic and steric factors governing the system of interest. In addition, Tolman and coauthors reported recently a new class of β-diketiminates in which the γ-position of the backbone could be easily modified to alter the electronic properties of the ligand.[9] Budzelaar,[5] Piers,[10−14] Theopold,[15] and others[1b] have

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* To whom correspondence should be addressed. Phone: 812-855-2399. Fax: 812-855-8300. E-mail: mindiola@indiana.edu.

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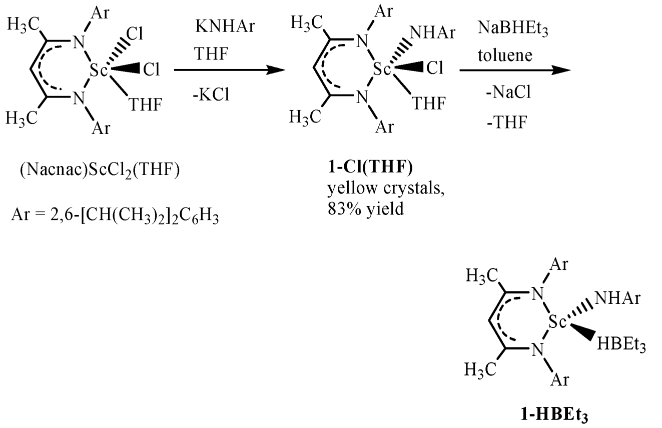
Scheme 1



(Nacnac)ScCl$_2$(THF)

Ar = 2,6-[CH(CH$_3$)$_2$]$_2$C$_6$H$_3$

1-Cl(THF)
yellow crystals,
83% yield

1-HBEt$_3$
yellow blocks,
78% yield

demonstrated that bulky and chelating ligands such as β-diketiminates (referred to as Nacnac$^-$) can stabilize neutral as well as cationic group 3 and 4 alkyl complexes. These systems have been shown to be active olefin polymerization catalysts,[5,10−15] as well as excellent ligand scaffolds for the stabilization of metal hydrides.[16] β-Diketiminates have also been incorporated into the heavier lanthanides.[1b,17] Whereas metallocene-based hydride systems of scandium have been studied,[18,19] reports of nonmetallocene scandium hydrides are surprisingly scarce and have received far less attention.[20,21]

In view of the ability of the β-diketiminate ligand to support reactive metal complexes, we turned our attention to the precursor complex prepared by Piers and co-workers[10] in pursuit of a reactive scandium hydride. Our goal was to assemble a useful scandium template composed of both a robust Nacnac$^-$ and a π-donor monoanionic amide ligand lacking β-hydrogens. Herein we report a series of reactions containing the (Nacnac)Sc(NHAr) (Nacnac$^-$ = ArNC(CH$_3$)CHC(CH$_3$)NAr, Ar = 2,6-CH(CH$_3$)$_2$C$_6$H$_3$) skeleton (defined as **1**). Such a framework has allowed us to prepare a reactive scandium triethylborohydride complex and observe facile C−O bond cleavage of Et$_2$O and THF. The putative scandium hydride intermediate was trapped with benzophenone to afford the corresponding alkoxide, the consequence of ketone insertion into the Sc−hydride bond. In addition, a stable and rare *tert*-butyl complex of scandium has been prepared and has been shown to also engage in C−O bond cleavage. The present work describes the synthesis and characterization of the products generated from C−O bond rupture of ethers as well as reduction of benzophenone by a scandium triethylborohydride complex.

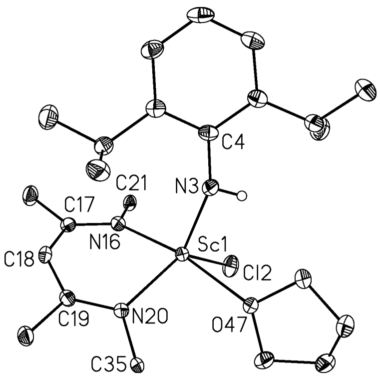


Figure 1. Perspective view of **1-Cl(THF)** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the α-hydrogen have been omitted for clarity. Aryl groups on the β-diketiminate nitrogens, with the exception of ipso carbons have also been omitted for the purpose of clarity. Selected bond lengths (Å): Sc(1)−N(3), 2.0453(13); Sc(1)−N(20), 2.1763(11); Sc(1)−N(16), 2.2281(11); Sc(1)−O(47), 2.2844(10); Sc(1)−Cl(2), 2.3778(5); N(3)−C(4), 1.3935(19); N(16)−C(17), 1.3318(17); C(17)−C(18), 1.4073(19); C(18)−C(19), 1.3952(19); C(19)−N(20), 1.3472(17). Selected angles (deg): N(20)−Sc(1)−N(16), 85.12(4); N(3)−Sc(1)−N(20), 122.88(5); N(3)−Sc(1)−N(16), 104.66(5); N(3)−Sc(1)−O(47), 88.60(4); N(20)−Sc(1)−O(47), 90.24(4); N(16)−Sc(1)−O(47), 166.40(4); N(3)−Sc(1)−Cl(2), 109.91(4); N(20)−Sc(1)−Cl(2), 126.43(3); N(16)−Sc(1)−Cl(2), 90.37(3); O(47)−Sc(1)−Cl(2), 82.10(3); Sc(1)−N(3)−C(4), 155.70(11); Sc(1)−N(16)−C(17), 122.94(9); Sc(1)−N(20)−C(19), 123.43(9); N(20)−C(19)−C(18), 124.46(12); C(19)−C(18)−C(17), 128.18(13); C(18)−C(17)−N(16), 124.25(12).

Results and Discussion

When a cold THF solution of Piers' complex (Nacnac)ScCl$_2$(THF)[10] is treated with 1 equiv of KNHAr, the monoanilide complex (Nacnac)ScCl(NHAr)(THF) (**1-Cl(THF)**) is formed in good yield (83%) as pale yellow crystals (Scheme 1). The use of the potassium anilide salt leads to formation of **1-Cl(THF)** without any contamination of "ate" complexes.[1a,17] **1-Cl(THF)** was fully characterized, and ^{1}H and ^{13}C solution NMR spectroscopy in addition to solid-state characterization (elemental analysis and X-ray) are consistent with the molecule coordinating one THF per metal center. NMR spectra are in accordance with the molecule retaining C_s symmetry in solution (equivalent methyl groups on the β-diketiminate β-carbons), thus suggesting that THF is dissociating from the metal center. In fact, mild heating of **1-Cl(THF)** under dynamic vacuum generates the desolvated complex **1-Cl**, thus indicating that the THF is labile. This characteristic has been observed for the corresponding bis(alkyl) complexes studied by Piers and co-workers.[14] Single crystals of **1-Cl(THF)** were grown from Et$_2$O, and the molecular structure is depicted in Figure 1. The structure of **1-Cl(THF)** reveals

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Table 1. Summary of Crystallographic Data and Structure Refinement Details for 1-Cl(THF), 1-HBEt$_3$, and 1-OEt

	1-Cl(THF)	**1-HBEt$_3$**	**1-OEt**
formula	$C_{45}H_{67}ClN_3OSc$	$C_{47}H_{75}BN_3Sc$	$C_{43}H_{64}N_3OSc$
fw	746.43	737.87	683.93
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	12.1239(5)	11.3666(6)	10.0234(11)
b (Å)	17.0782(7)	17.6914(9)	11.1852(12)
c (Å)	20.3922(8)	22.4483(12)	19.658(2)
α (deg)			84.590(3)
β (deg)	93.4750(10)	91.6940(10)	83.677(3)
γ (deg)			70.261(3)
V (Å^3)	4214.3	4512.2(4)	2058.0(4)
Z	4	4	2
D_{calcd}	1.176	1.086	1.104
μ (mm^{-1})	2.740	1.960	2.120
F(000)	1616	1616	744
cryst color	pale yellow	yellow	pale yellow
cryst form	plate	block	diamondlike
cryst size (μm)	300 × 100 × 100	350 × 350 × 250	230 × 180 × 50
θ range (lattice, deg)	2.06−30.02	2.13−30.03	2.09−27.61
index ranges	$-17 \le h \le 12, -24 \le k \le 24, -28 \le l \le 28$	$-15 \le h \le 16, -24 \le k \le 24, -30 \le l \le 31$	$-12 \le h \le 12, -14 \le k \le 14, -25 \le l \le 25$
no. of rflns collected	50 854	73 003	22 418
no. of indep rflns	12 298	13 163	9440
no. of obsd rflns	8002	8496	5791
R_{int}	0.0626	0.0840	0.1394
final R indices ($I > 2\sigma(I)$)	R1 = 0.0715, wR2 = 0.0797	R1 = 0.0932, wR2 = 0.0956	R1 = 0.1185, wR2 = 0.1722
R indices (all data)	R1 = 0.0390, wR2 = 0.0902	R1 = 0.0454, wR2 = 0.1232	R1 = 0.0744, wR2 = 0.1899
GOF on F^2	0.913	1.020	0.978

a scandium center in a pseudo-trigonal-bipyramidal geometry, with the Nacnac$^-$ ligand occupying both the axial and equatorial positions. The geometrical parameters are nearly identical with those of the precursor complex (Nacnac)ScCl$_2$(THF).[10,14] Selected metrical parameters are displayed with Figure 1, and structural parameters for **1-Cl(THF)** are shown in Table 1. The anilido nitrogen N(3) is nearly planar, and the Sc−N$_{anilido}$ bond length of 2.0453(13) Å is considerably shorter than the Sc−N$_{Nacnac}$ bonds (N(16)−Sc(1), 2.2281(11) Å; N(20)−Sc(1), 2.1763(11) Å). The molecular structure of **1-Cl(THF)** displays no other exceptional features.

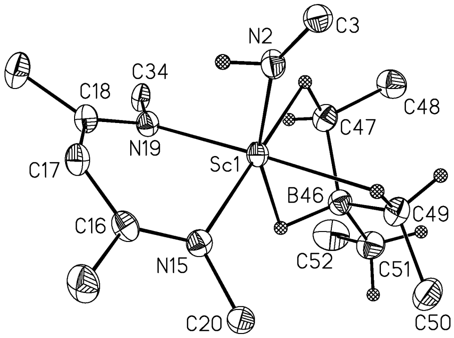

Figure 2. Perspective view of **1-HBEt$_3$** with thermal ellipsoids at the 50% probability level. The hydrogen atoms on the borane ethyl groups were located in the Fourier map and refined isotropically. Hydrogen atoms, with the exception of the hydride and the methylene groups on the borane, have been omitted for clarity. Aryl groups on nitrogens, with the exception of ipso carbons, have also been omitted for clarity. Selected bond lengths (Å): Sc(1)−N(2), 2.0280(15); Sc(1)−N(19), 2.1509(14); Sc(1)−N(15), 2.1538(14); N(19)−C(18), 1.337(2); C(18)−C(17), 1.401(2); C(17)−C(16), 1.408(2); C(16)−N(15), 1.327(2); B(46)−C(47), 1.672(3); B(46)−C(49), 1.659(3); B(46)−C(51), 1.617(3); N(2)−C(3), 1.407(2); N(19)−C(34), 1.452(2); N(15)−C(20), 1.448(2). Selected angles (deg): N(2)−Sc(1)−N(19), 98.59(6); N(2)−Sc(1)−N(15), 98.05(6); N(19)−Sc(1)−N(15), 87.57(5); Sc(1)−N(3)−C(3), 153.73(12); Sc(1)−N(15)−C(16), 119.14(11); Sc(1)−N(15)−C(20), 121.33(10); N(15)−C(16)−C(17), 123.48(15); C(16)−C(17)−C(18), 129.80(15); C(17)−C(18)−N(19), 123.83(16); Sc(1)−N(19)−C(18), 117.63(11).

Having the "(Nacnac)Sc(NHAr)" framework assembled, we reasoned that metathesis of **1-Cl(THF)** with a hydride source would generate a reactive scandium hydride complex. Accordingly, treatment of **1-Cl(THF)** with NaHBEt$_3$, in toluene, generates in 78% yield the triethylborohydride complex (Nacnac)Sc(NHAr)(HBEt$_3$) (**1-HBEt$_3$**) (Scheme 1). **1-HBEt$_3$** is thermally stable both in solution and in the solid state, but in the presence of Lewis bases it transforms into a new product (depending on the Lewis base, vide infra). Indicative of a hydride being present was the variable-temperature ^{11}B NMR spectrum of **1-HBEt$_3$**, displaying a resonance at −8.70 ppm with J_{B-H} = 53 Hz (70 °C, C_6D_6). We have not been able to locate the hydride resonance in the ^{1}H NMR spectrum, presumably due to broadening of the signal by coupling of the hydride to both ^{45}Sc ($I = ^7/_2$, 100%) and ^{11}B ($I = ^3/_2$, 80%) quadrupolar nuclei.[22] This phenomenon has been inferred with related hydrido complexes of scandium.[18] Varying the temperature of NMR samples containing **1-HBEt$_3$** did not alleviate the quadrupolar broadening.[22b] Attempts to make the corresponding deuterium analogue were hampered by the formation of side products generated from the reaction of **1-Cl(THF)** with LiDBEt$_3$. Single crystals of **1-HBEt$_3$** were grown from hexane at −35 °C, and the molecular structure is displayed in Figure 2. Geometrical and crystal structure parameters are shown in Figure 2 and Table 1, respectively. The structure of **1-HBEt$_3$** reveals a scandium center confined in a pseudo-octahedral

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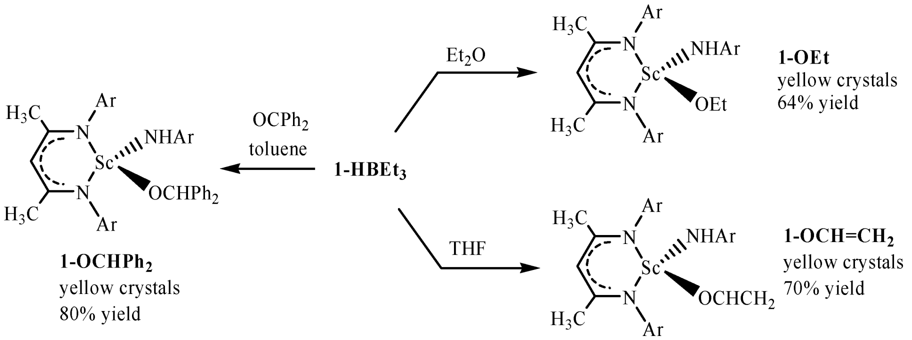
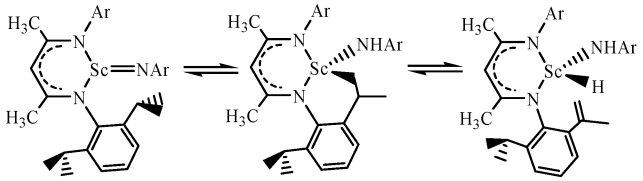
Scheme 2



Scheme 3



environment and represents the first structurally characterized triethylborohydride complex of scandium. In fact, structurally characterized examples of scandium borohydride complexes are scarce.[23] In addition to the Nacnac$^-$ and anilide occupying three coordination positions, the hydride and two methylene hydrogens from the ethyl groups of the borane complete the additional three coordination sites in the pseudo-octahedron. Although there is a systematic error in detection of hydrogens by X-ray diffraction,[24] the location of the hydrogens in the Fourier map leaves little uncertainty about their presence. Unfortunately, the room-temperature ^{1}H NMR spectrum of **1-HBEt$_3$** did not suggest any evidence for such an agostic interaction. Variable-temperature ^{1}H NMR (−65 °C, CD_2Cl_2) only led to broadening of the ethyl groups on the borane. However, high-temperature ^{11}B NMR was consistent with fluxionality of the $HBEt_3$ unit in solution (vide supra).

Although stable as a solid, **1-HBEt$_3$** extrudes BEt_3 in solution and in the presence of a Lewis base, transforming into a new product. Hence, mild heating of **1-HBEt$_3$** with Et_2O leads to C−O bond cleavage and subsequent formation of the ethoxide complex (Nacnac)Sc(NHAr)(OEt) (**1-OEt**) in 64% isolated yield (Scheme 2). The ethoxide resonances were located at 3.86 and 0.84 ppm in the ^{1}H NMR spectrum of **1-OEt**. This transformation led us to speculate that the putative hydride (Nacnac)Sc(NHAr)(H) (**1-H**) is generated upon extrusion of the borane. Lewis bases such as Et_2O can promote elimination of the borane ($Et_2O \rightarrow BEt_3$ elimination), which would accompany production of the reactive hydride species. Preparation of the corresponding d_5 isotopomer of **1-OEt** (using Et_2O-d_{10}) led to washing of deuterium into the isopropyl methyls and methine hydrogens, as suggested by ^{2}H NMR spectra. We observed deuteration of the γ-CH backbone of the Nacnac as well as the NH proton for the supporting anilide ligand. This suggests that formation of **1-OEt** likely occurs by C−H and N−H hydrogen abstraction reactions. Piers and co-workers observed C−H bond cleavage of the isopropyl methyl on the aryl in Nacnac$^-$ via thermolysis of the bis(alkyl) species to make the corresponding scandium metallacycle.[10] In our case, deuterium scrambling into the methine positions suggests that β-hydride elimination of a putative scandium metallacycle and reinsertion of the pendant olefin fragment might be taking place during the reaction (Scheme 3). Goldberg and coworkers have reported reversible β-hydride elimination and reinsertion reactions in platinum complexes supported by the Nacnac$^-$ ligand derivative used in the present study.[25] One possible explanation for scrambling of deuterium into these positions is depicted in Scheme 3. Scheme 3 suggests that a reactive scandium imide[26,27] and scandium hydride could be formed during the course of the reaction. Examination of the volatiles from the reaction mixture by ^{1}H NMR spectroscopy did not indicate formation of $CH_2{=}CH_2$ or H_2 but, rather, a complex mixture of products with multiple resonances in the aliphatic region. We are not certain which of these likely intermediates is involved in the C−O cleavage process, and at this point our mechanism is merely speculative. Scrambling of deuterium into the γ-C of the Nacnac$^-$ backbone is intriguing, and this result could suggest that electrophilic activation of this site[1b] by another scandium center could be responsible for this occurrence.

Single crystals of **1-OEt** were grown from hexane, and the molecular structure is shown in Figure 3. Relevant crystal parameters are displayed in Table 1. Salient features in the structure of **1-OEt** include the Sc−$O_{alkoxide}$ bond length of 1.882(3) Å. The Sc(1)−O(46)−C(47) angle of 156.2(3)° is indicative of substantial π-donation from the alkoxide oxygen. In fact, structurally characterized terminal or bridging ethoxide com-

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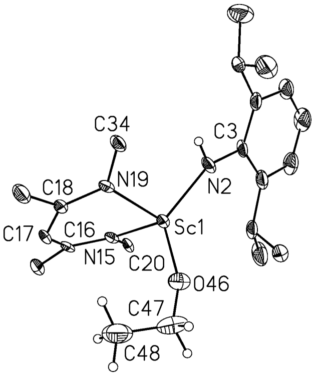

Figure 3. Perspective view of **1-OEt** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the anilido N(2) and the ethoxide ligands, have been omitted for clarity. Hydrogen atoms were located in the Fourier map and refined isotropically. Aryl groups on the β-diketiminate nitrogens, with the exception of ipso carbons, have been also omitted for clarity. Selected bond lengths (Å): Sc(1)−O(46), 1.882(3); Sc(1)−N(2), 2.059(2); Sc(1)−N(19), 2.122(2); Sc(1)−N(15), 2.148(2), N(15)−C(16), 1.334(4); C(16)−C(17), 1.418(4); C(17)−C(18), 1.397(4); C(18)−N(19), 1.342(3); N(19)−C(34), 1.440(4); N(15)−C(20), 1.436(4); O(46)−C(47), 1.411(5); C(47)−C(48), 1.495(7). Selected angles (deg): N(19)−Sc(1)−N(2), 100.2(2); N(15)−Sc(1)−N(2), 121.2(1); N(19)−Sc(1)−N(15), 88.12(9); N(19)−Sc(1)−O(46), 108.2(2); N(2)−Sc(1)−O(46), 125.5(1); Sc(1)−N(2)−C(3), 144.4(2); Sc(1)−O(46)−C(47), 156.2(3); O(46)−C(47)−C(48), 112.3(4); Sc(1)−N(19)−C(18), 119.7(9); Sc(1)−N(15)−C(16), 120.6(2); N(19)−C(18)−C(17), 123.6(3); C(18)−C(17)−C(16), 129.9(3); C(17)−C(16)−N(15), 123.4(3); Sc(1)−N(19)−C(34), 119.3(7); Sc(1)−N(15)−C(20), 117.8(7).

plexes of group 3 metals are rare, and to our knowledge the structure of **1-OEt** is a unique example.[28]

THF also reacts with **1-HBEt$_3$** to afford the corresponding enolate complex (Nacnac)Sc(NHAr)(OCH=CH$_2$) (**1-OCH=CH$_2$**) in 70% isolated yield (Scheme 2). Diagnostic features for **1-OCH=CH$_2$** include the presence of three inequivalent ^{1}H NMR resonances for the enolate hydrogens centered at 6.65 (dd, $J_{\mathrm{H-Htrans}} = 14$ and $J_{\mathrm{H-Hcis}} = 6$ Hz), 4.16 (d, $J_{\mathrm{H-Htrans}} = 14$ Hz), and 3.92 ppm (d, $J_{\mathrm{H-Hcis}} = 6$ Hz). In general, lanthanide complexes containing a terminal enolate ligand with only hydrogens in both the β- and γ-positions are exceedingly rare, and such complexes are typically prepared from analogous metalation or reduction of THF,[29a,b] or by direct salt metathesis of the metal halide with LiOCH=CH$_2$.[29c,d] Examination of the volatiles revealed CH$_2$=CH$_2$ to be one of the main products formed in the reaction. Preparation of the deuterio complex **1-OCH=CH$_2$**-d_3 from THF-d_8 revealed scrambling of deuterium into the methine and methyl positions of the isopropyl groups as well as into the NH position. As suggested for the formation of **1-OEt** (vide supra), **1-OCH=CH$_2$** appears to also form via C−H and N−H hydrogen atom abstraction processes. We do not, however, observe incorporation of deuterium into the γ-CH backbone of the Nacnac$^-$ ligand, thus hinting as to whether formation of **1-OEt** and **1-OCH=CH$_2$** might involve different mechanistic pathways. In the absence of Lewis bases (e.g. Et$_2$O or THF), prolonged thermolysis of **1-HBEt$_3$** in C$_6$D$_6$ leads to decomposition and formation of a myriad of products.

Single crystals of the enolate **1-OCH=CH$_2$** were grown from a saturated hexane solution cooled to −35 °C. Crystal structure parameters are listed in Table 2, and a molecular structure representation of one of the two crystallographically independent molecules present in the asymmetric unit is displayed in Figure 4. Salient features for the structure of **1-OCH=CH$_2$** include a short C−C bond for the enolate ligand (1.298(5) Å), in comparison to the ethoxide derivative (vide supra, 1.495(7) Å). The molecular structure of **1-OCH=CH$_2$** represents a rare example of a terminal and parent enolate complex of scandium.[29]

Precedent in the literature suggests substrates such as benzophenone to be ideal reagents for trapping transient and reactive hydride complexes generated from their corresponding borohydride precursors.[30,31] Accordingly, treatment of **1-HBEt$_3$** with an equimolar amount of OCPh$_2$ in toluene afforded the diphenylmethoxide complex **1-OCHPh$_2$** in 80% isolated yield (Scheme 2). Formation of **1-OCHPh$_2$** entails insertion of the carbonyl functionality into the Sc−H bond. Our data, however, cannot indicate whether reduction of benzophenone occurs before or after borane extrusion. Exhibited features of **1-OCHPh$_2$** include the β-hydrogen of the alkoxide ligand, which was located at 5.96 ppm in the ^{1}H NMR spectrum using HMQC methods.[32] The downfield shift for the proton in the OC*H*Ph$_2$ ligand is similar to that for previously reported benzophenone insertion reactions into Nb−H[30] and Mo−H[31] bonds. ^{1}H NMR resonances for the anilido nitrogen (4.46 ppm, N*H*) and γ-carbon of the Nacnac$^-$ ligand (5.15 ppm, C*H*) were also assigned unambiguously. Crystals of **1-OCHPh$_2$** suitable for X-ray analysis were obtained from a saturated Et$_2$O solution cooled to −35 °C. The molecular structure of **1-OCHPh$_2$** is shown in Figure 5, and crystal structure parameters are displayed in Table 2. The structure of **1-OCHPh$_2$** reveals an intact "(Nacnac)-Sc(NHAr)" frame containing the diphenylmethoxide ligand. Relevant bond lengths and angles are listed in Figure 5. The β-hydrogen of the alkoxide (C(47)) was located and refined isotropically. Judging from the angles, the β-carbon of the diphenylmethoxide ligand is clearly sp^3 hybridized, and the elongation of the O−C bond (1.405(5) Å) is substantial relative to free benzophenone (1.224−1.238 Å).[33]

tert-Butyl alkyl groups attached directly to early-transition-metal complexes are rare.[34−36] The instability

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Table 2. Summary of Crystallographic Data and Structure Refinement Details for 1-OCH=CH_2, 1-$OCHPh_2$·0.5Et_2O, and 1-^{t}Bu·0.5Et_2O

	1-OCH=CH_2	**1-$OCHPh_2$**	**1-^{t}Bu**
formula	$C_{43}H_{62}N_3OSc$	$C_{56}H_{75}N_3O_{1.5}Sc$	$C_{47}H_{73}N_3O_{0.5}Sc$
fw	681.92	859.15	733.04
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	40.771(5)	10.2169(3)	20.2074(19)
b (Å)	9.7758(15)	11.5960(4)	10.7832(10)
c (Å)	20.661(4)	22.0076(7)	20.592(2)
α (deg)		97.9060(10)	
β (deg)	101.259(8)	95.6130(10)	91.364(2)
γ (deg)		105.8220(10)	
V (Å^3)	8077(2)	2459.55(14)	4485.7(7)
Z	8	2	4
D_{calcd}	1.122	1.160	1.085
μ (mm^{-1})	2.160	1.920	1.920
F(000)	2960	930	1604
cryst color	pale yellow	pale yellow	pale yellow
cryst form	plate	plate	block
cryst size (μm)	120 × 80 × 60	250 × 250 × 130	200 × 180 × 180
θ range (lattice, deg)	2.01−27.57	2.17−30.02	2.13−30.02
index ranges	$-52 \le h \le 53$, $-12 \le k \le 12$, $-26 \le l \le 26$	$-14 \le h \le 14$, $-16 \le k \le 16$, $-30 \le l \le 30$	$-28 \le h \le 28$, $-15 \le k \le 15$, $-28 \le l \le 28$
no. of rflns collected	87 693	78 828	138 820
no. of indep rflns	18 584	14 367	13 092
no. of obsd rflns	7302	10 091	9129
R_{int}	0.2009	0.0719	0.0834
final R indices ($I > 2\sigma(I)$)	R1 = 0.655, wR2 = 0.1714	R1 = 0.0692, wR2 = 0.1027	R1 = 0.0739, wR2 = 0.0943
R indices (all data)	R1 = 0.0561, wR2 = 0.0825	R1 = 0.0423, wR2 = 0.1164	R1 = 0.0383, wR2 = 0.1141
GOF on F^2	0.780	0.997	1.011

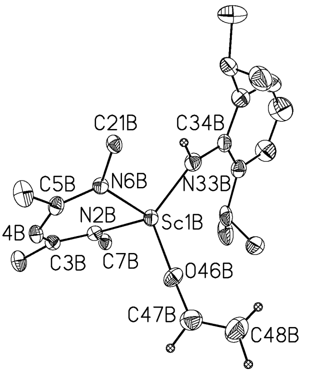

Figure 4. Perspective view of **1-OCH=CH_2** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the anilido N33B and the enolate, have been omitted for clarity. Hydrogen atoms were located in the Fourier map and refined isotropically. Aryl groups on the β-diketiminate nitrogens, with the exception of ipso carbons, have been also omitted for clarity. Selected bond lengths (Å): Sc(1B)−N(33B), 2.045(3); Sc(1B)−N(6B), 2.110(2); Sc(1B)−N(2B), 2.159(2); Sc(1B)−O(46B), 1.904(2); O(46B)−C(47B), 1.339(4); C(47B)−C(48B), 1.298(5); N(33B)−C(34B), 1.393(4); N(6B)−C(5B), 1.341(3); C(5B)−C(4B), 1.390(4); C(4B)−C(3B), 1.412(4); C(3B)−N(2B), 1.340(3). Selected angles (deg): N(6B)−Sc(1B)−N(33B), 98.44(10); N(6B)−Sc(1B)−O(46B), 111.5(1); N(6B)−Sc(1B)−N(2B), 87.27(9); N(33B)−Sc(1B)−O(46B), 122.9(2); N(2B)−Sc(1B)−O(46B), 106.1(1); O(46B)−C(47B)−C(48B), 126.1(4); Sc(1B)−N(33B)−C(34B), 146.5(2); Sc(1B)−O(46B)−C(47B), 178.0(2); Sc(1B)−N(6B)−C(5B), 120.7(9); Sc(1B)−N(2B)−C(3B), 120.8(9); N(6B)−C(5B)−C(4B), 123.5(3); C(5B)−C(4B)−C(3B), 129.6(3); C(4B)−C(3B)−N(2B), 123.6(3).

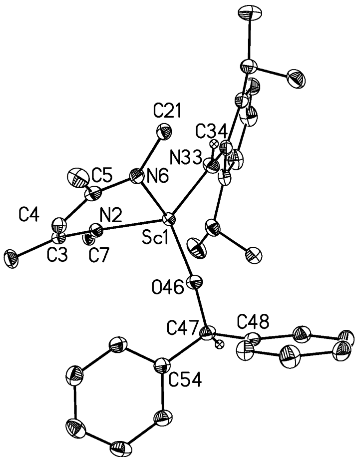

Figure 5. Perspective view of **1-$OCHPh_2$** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the anilido nitrogen N(33) and carbon C(47), have been omitted for clarity. Hydrogen atoms were located in the Fourier map and refined isotropically. Aryl groups on the β-diketiminate nitrogens, with the exception of ipso carbons, and a solvent molecule have been also omitted for clarity. Selected bond lengths (Å): Sc(1)−O(46), 1.8941(9); Sc(1)−N(33), 2.048(2); Sc(1)−N(6), 2.122(1); Sc(1)−N(2), 2.162(1); O(46)−C(47), 1.405(5); N(33)−C(34), 1.389(7); C(47)−C(48), 1.531(8); C(47)−C(54), 1.532(9); N(6)−C(5), 1.342(7); C(5)−C(4), 1.395(8); C(4)−C(3), 1.418(9); C(3)−N(2), 1.331(7). Selected angles (deg): N(6)−Sc(1)−N(33), 97.81(5); N(6)−Sc(1)−O(46), 113.05(4); N(6)−Sc(1)−N(2), 87.93(4); N(2)−Sc(1)−O(46), 107.91(4); N(2)−Sc(1)−N(33), 120.36(5); Sc(1)−O(46)−C(47), 170.42(8); Sc(1)−N(33)−C(34), 143.6(1); Sc(1)−N(6)−C(5), 118.45(9); Sc(1)−N(2)−C(3), 118.09(9); N(6)−C(5)−C(4), 112.8(2); C(5)−C(4)−C(3), 130.1(2); C(4)−C(3)−N(2), 124.0(2); C(54)−C(47)−O(46), 111.5(1); C(48)−C(47)−O(46), 111.1(1); C(54)−C(47)−C(48), 111.9(1).

of these systems arises from the presence of nine β-hydrogens, often leading to β-hydride elimination concomitant with formation of the metal hydride species.[37] Isobutene, the olefin generated from β-hydride elimination, can engage in further reactions such as reinsertion into the metal−hydride bond to form the corresponding isobutyl isomer.[37] In fact, early-transition-metal complexes bearing any alkyl groups with

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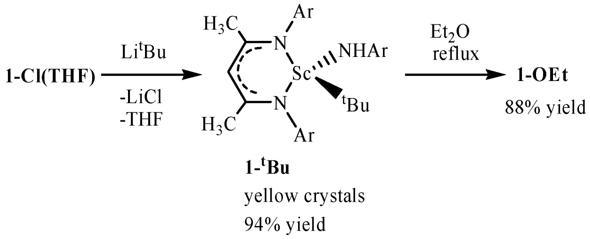
Scheme 4



β-hydrogens are relatively rare.[5,10,38] Hence, we thought that preparation of the scandium *tert*-butyl derivative would serve as a precursor to a scandium hydride complex via β-hydride elimination. Accordingly, treatment of cold ethereal solutions of **1-Cl(THF)** with Li^{t}Bu afforded in good yield (94% isolated yield) the *tert*-butyl complex (Nacnac)Sc(NHAr)(^{t}Bu) (**1-^{t}Bu**) (Scheme 4). **1-^{t}Bu** is stable both in solution and in the solid state and represents a rare case of a ^{t}Bu complex in the context of group 3 metal alkyls.[34] The room-temperature ^{1}H NMR spectrum of **1-^{t}Bu** reveals one singlet for the ^{t}Bu group at an unexceptional chemical shift, thus suggesting no evidence of the scandium engaging in β-hydrogen agostic interactions. When ethereal solutions of **1-^{t}Bu** are refluxed, the ethoxide **1-OEt** is formed in good yield (≥88% isolated yield, Scheme 4). Isobutene is not observed in the reaction mixture, inasmuch as β-hydride elimination does not occur upon formation of **1-OEt**. In fact, examination of the volatiles reveals only formation of ^{t}Bu-H. This result is consistent with ^{t}Bu$^\bullet$ radical loss and subsequent C−H abstraction reactions in the formation of **1-OEt** from **1-^{t}Bu**. Surprisingly, heating **1-^{t}Bu** in C_6D_6 (60 °C, 16 h) leads to no decomposition, thus suggesting that binding of the Lewis base might be the promoter in the C−O bond cleavage reaction. The highly congested structure of **1-^{t}Bu** was confirmed by single-crystal X-ray diffraction (Figure 6 and Table 2), and from direct inspection the scandium metal lies in a pseudo-tetrahedral environment, where one of the positions is occupied by the bulky ^{t}Bu alkyl ligand. The Sc−C$_{^t\mathrm{Bu}}$ bond distance (Sc(1)−C(46), 2.228(3) Å) is in accordance with typical scandium alkyl complexes supported by the Nacnac$^-$ ligand (with or without β-hydrogens).[10]

In summary, we have shown that the skeleton "(Nacnac)Sc(NHAr)" is compatible with halide, triethylborohydride, alkoxides, enolate, and a bulky alkyl having β-hydrogens. Synthesis and characterization of an amazingly stable scandium *tert*-butyl complex is surprising (even at elevated temperatures), despite the presence of nine β-hydrogens. Most notably, we do not observe dehydrohalogenation of the scandium chloro−anilide precursor with Li^{t}Bu to generate the corresponding scandium imide complex. Such a result is remarkable, since lanthanide complexes possessing the imido functionality have been reported.[39] The present work establishes that a scandium borohydride in combination with the supporting Nacnac$^-$ and anilide ligand N[2,6-(CH(CH$_3$)$_2$)$_2$C$_6$H$_3$] is capable of performing both C−O bond cleavage and reduction reactions. Hence, the scandium triethylborohydride or scandium *tert*-butyl complexes described in this paper are close analogues of LiH or Li^{t}Bu in the context of C−O bond cleavage reactions.[40] Terminal and stable scandium hydrides systems remain attractive as synthetic targets.

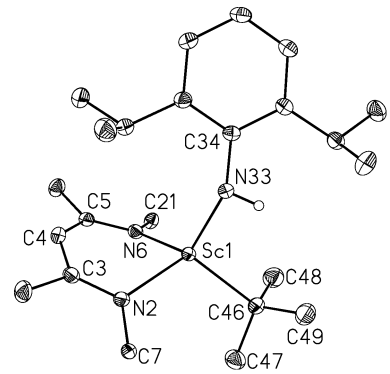


Figure 6. Perspective view of **1-^{t}Bu** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the α-anilido nitrogen N(33), have been omitted for clarity. The hydrogen atom was located in the Fourier map and refined isotropically. Aryl groups on the β-diketiminate nitrogens, with the exception of ipso carbons, and a solvent molecule have been also omitted for clarity. Selected bond lengths (Å): Sc(1)−N(33), 2.024(1); Sc(1)−N(6), 2.160(1); Sc(1)−N(2), 2.155(1); Sc(1)−C(46), 2.228(3); N(33)−C(34), 1.406(6); N(6)−C(5), 1.338(7); C(5)−C(4), 1.408(8); C(4)−C(3), 1.402(8); C(3)−N(2), 1.337(6). Selected angles (deg): N(6)−Sc(1)−N(2), 88.19(4); N(6)−Sc(1)−N(33), 115.42(4); N(6)−Sc(1)−C(46), 118.39(5); N(2)−Sc(1)−N(33), 119.87(5); N(2)−Sc(1)−C(46), 112.74(5); N(33)−Sc(1)−C(46), 102.91(5); Sc(1)−N(6)−C(5), 117.36(8); Sc(1)−N(2)−C(3), 117.46(8); Sc(1)−N(33)−C(34), 150.78(9); N(6)−C(5)−C(4), 124.3(2); C(5)−C(4)−C(3), 130.4(2); C(4)−C(3)−N(2), 123.9(2).

Experimental Procedures

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun LabMaster drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.[41] Hexane, pentane, toluene, and benzene were dried by passage through activated alumina and Q-5 columns.[42] Diethyl ether and CH_2Cl_2 were dried by passage through two activated alumina columns. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a drybox. C_6D_6, THF-d_8, Et$_2$O-d_{10}, and CD_2Cl_2 were purchased from Cambridge Isotope Laboratory (CIL). C_6D_6 was degassed and dried over activated 4 Å molecular sieves, and CD_2Cl_2 was dried over CaH_2 and vacuum-transferred into 4 Å molecular sieves. THF-d_8 and

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(37) For references describing the use of *tert*-butyl as a hydrido source in early-transition-metal chemistry see: (a) Pool, J. A.; Bradley, C. A.; Chirik, P. J. *Organometallics* **2002**, *21*, 1271. (b) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241.

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(39) Synthesis of lanthanide complexes containing metal−ligand multiple bonds are exceedingly rare: (a) Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652. (b) Asparna, K.; Ferguson, M.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 726.

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(41) For a general description of the equipment and techniques used in carrying out this chemistry see: Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society; Washington, DC, 1987; pp 79−98.

(42) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Et$_2$O-*d*$_{10}$ were degassed and stored over sodium metal. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Li(Nacnac)[2] (Nacnac$^-$ = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$) and (Nacnac)ScCl$_2$(THF)[10] were prepared according to the literature. 2,6-Diisopropylaniline was distilled prior to usage and deprotonated in Et$_2$O at −35 °C with KCH$_2$Ph[43] to give the potassium salt KNHAr. Solid Li^{t}Bu was collected by cooling a saturated pentane solution to −78 °C, followed by rapid filtration. All other chemical were used as received. In all reported reactions percentage yields are based on the scandium precursor. Infrared data (CaF$_2$ plates) were measured by using a Nicolet 510P FTIR spectrometer. CHN elemental analyses were performed by Desert Analytics (Tucson, AZ). ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on Varian 400 and 300 MHz NMR spectrometers. ^{1}H and ^{13}C NMR are reported with reference to solvent resonances (for ^{1}H and ^{13}C, respectively: residual C$_6$D$_5$H in C$_6$D$_6$, 7.16 ppm and 128.0 ppm; residual CHDCl$_2$ in CD$_2$Cl$_2$, 5.32 ppm and 53.8 ppm; residual protio THF in THF-*d*$_8$, 1.73 and 3.58 ppm and 65.6 and 23.5 ppm). ^{11}B NMR spectra were reported with respect to external BF$_3$·OEt$_2$ (δ 0.0 ppm). X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N$_2$(g) at low temperatures.

Synthesis of 1-Cl(THF). In a vial was dissolved (Nacnac)ScCl$_2$(THF) (300 mg, 0.49 mmol) in 10 mL of THF and the solution cooled to −35 °C. To the pale yellow solution was added a cold THF solution (5 mL) of KNHAr (104 mg, 0.48 mmol), causing a color change to yellow. After the reaction was stirred, for 24 h, the solution was filtered, and the filtrate dried under reduced pressure. The yellow powder was extracted with Et$_2$O, and the extracts were filtered, concentrated, and cooled for 2 days at −35 °C to afford in two crops yellow crystals of **1-Cl(THF)** (306 mg, 0.41 mmol, 83% yield). ^{1}H NMR (20 °C, 399.8 MHz, C$_6$D$_6$): δ 7.06 (m, aryl, 4H), 7.00 (m, aryl, 2H), 6.93 (d, aryl, 2H), 6.77 (t, aryl, 1H), 6.20 (bs, N*H*, 1H), 5.06 (s, ArNC(CH$_3$)C*H*C(CH$_3$)NAr, 1H), 3.52 (m, THF, 4H), 3.50 (septet, C*H*(CH$_3$)$_2$, 2H), 3.18 (septet, C*H*(CH$_3$)$_2$, 2H), 2.36 (septet, C*H*(CH$_3$)$_2$, 2H), 1.53 (s, ArNC(C*H*$_3$)CHC(C*H*$_3$)NAr, 6H), 1.42 (d, CH(C*H*$_3$)$_2$, 6H), 1.33 (m, THF, 4H), 1.12 (d, CH(C*H*$_3$)$_2$, 6H), 1.08 (d, CH(C*H*$_3$)$_2$, 6H), 1.02 (d, CH(C*H*$_3$)$_2$, 12H), 0.97 (d, CH(C*H*$_3$)$_2$, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 168.8 (ArN*C*(CH$_3$)CH*C*(CH$_3$)NAr), 148.9 (aryl), 143.8 (aryl), 142.3 (aryl), 141.7 (aryl), 133.9 (aryl), 127.4 (aryl), 125.2 (aryl), 124.6 (aryl), 122.9 (aryl), 118.4 (aryl), 98.25 (ArNC(CH$_3$)*C*HC(CH$_3$)NAr), 68.18 (THF), 31.15 (*C*H(CH$_3$)$_2$), 28.86 (*C*H(CH$_3$)$_2$), 28.67 (*C*H(CH$_3$)$_2$), 26.19 (CH(*C*H$_3$)$_2$), 25.62 (THF), 24.79 (CH(*C*H$_3$)$_2$), 24.59 (CH(*C*H$_3$)$_2$), 23.99 (CH(*C*H$_3$)$_2$), 23.87 (ArNC(*C*H$_3$)CHC(*C*H$_3$)NAr). IR (C$_6$H$_6$, CaF$_2$): 3300 (w), 3071 (s), 3044 (s), 3028 (s), 2964 (s), 2868 (m), 1959 (w), 1815 (w), 1528 (w), 1483 (s), 1433 (m), 1378 (s), 1319 (m), 1259 (m), 1171 (w) cm^{-1}. Anal. Calcd for C$_{45}$H$_{67}$N$_3$OClSc: C, 72.40; H, 9.05; N, 5.63. Found: C, 72.02; H, 8.86; N, 5.62.

Synthesis of 1-HBEt$_3$. In a vial was dissolved **1-Cl(THF)** (300 mg, 0.40 mmol) in 15 mL of toluene and the solution cooled to −35 °C. To the cold solution was added a cold NaHBEt$_3$ solution (0.43 mmol, 1 M solution in toluene), causing a rapid color change to a darker yellow. After the reaction was stirred for 6 h, the solution was filtered, and the filtrate dried under reduced pressure. The yellow powder was extracted with hexane, and the extracts were filtered, concentrated, and cooled for 3 days at −35 °C to afford in three crops large yellow blocks of **1-HBEt$_3$** (232 mg, 0.31 mmol, 78% yield). ^{1}H NMR (20 °C, 399.8 MHz, C$_6$D$_6$): δ 7.10 (m, aryl, 8H), 6.88 (t, aryl, 1H), 5.94 (s, N*H*, 1H), 5.18 (s, ArNC(CH$_3$)C*H*C(CH$_3$)NAr, 1H), 3.51 (septet, C*H*(CH$_3$)$_2$, 1H), 3.37 (septet, C*H*(CH$_3$)$_2$, 2H), 3.29 (septet, C*H*(CH$_3$)$_2$, 1H), 3.14 (septet, C*H*(CH$_3$)$_2$, 2H), 1.60 (s, ArNC(C*H*$_3$)CHC(C*H*$_3$)NAr, 6H), 1.36 (d, CH(C*H*$_3$)$_2$, 6H), 1.29 (d, CH(C*H*$_3$)$_2$, 6H), 1.26 (d, CH(C*H*$_3$)$_2$, 6H), 1.01 (d, CH(C*H*$_3$)$_2$, 18H), 0.63 (t, BCH$_2$C*H*$_3$, 9H), 0.51 (br, BC*H*$_2$CH$_3$, 6H). The hydride was not located in the ^{1}H NMR spectrum of **1-HBEt$_3$**. ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 168.6 (ArN*C*(CH$_3$)CH*C*(CH$_3$)NAr), 150.1 (aryl), 143.9 (aryl), 143.2 (aryl), 142.5 (aryl), 137.3 (aryl), 133.4 (aryl), 125.2 (aryl), 127.2 (aryl), 125.2 (aryl), 124.6 (aryl), 123.7 (aryl), 122.3 (aryl), 118.8 (aryl), 98.64 (ArNC(CH$_3$)*C*HC(CH$_3$)NAr), 29.00 (*C*H(CH$_3$)$_2$), 28.91 (*C*H(CH$_3$)$_2$), 28.39 (*C*H(CH$_3$)$_2$), 28.16 (*C*H(CH$_3$)$_2$), 25.58 (*C*H$_3$), 25.04 (*C*H$_3$), 24.85 (*C*H$_3$), 24.67 (*C*H$_3$), 24.52 (*C*H$_3$), 24.25 (*C*H$_3$), 24.16 (*C*H$_3$), 17.67 (br, B*C*H$_2$CH$_3$), 10.80 (BCH$_2$*C*H$_3$). ^{11}B NMR (70 °C, 128.37 MHz, C$_6$D$_6$): δ −8.70 (d, B*H*, $J_{\mathrm{B-H}}$ = 53 Hz). IR (C$_6$H$_6$, CaF$_2$): 3097 (w), 3076 (m), 2963 (s), 2869 (m), 1957 (m), 1813 (m), 1590 (w), 1523 (s), 1487 (s), 1463 (s), 1386 (s), 1315 (s), 1256 (s), 1170 (w), 1117 (w), 1042 (w) cm^{-1}. Anal. Calcd for C$_{47}$H$_{75}$N$_3$BSc: C, 76.50; H, 10.24; N, 5.696. Found: C, 76.16; H, 10.16; N, 5.84.

Synthesis of 1-OEt. In a vial was dissolved **1-HBEt$_3$** (300 mg, 0.41 mmol) in 20 mL of Et$_2$O. The solution was transferred to a reaction vessel and the mixture heated for 28 h, the color changing to pale yellow. The solution was dried under reduced pressure, the yellow powder was extracted with hexane, and the extracts were filtered. The filtrate was concentrated, and cooled for 2 days at −35 °C to afford in two crops pale yellow crystals of **1-OEt** (178 mg, 0.26 mmol, 64% yield). ^{1}H NMR (20 °C, 399.8 MHz, C$_6$D$_6$): δ 7.16−7.02 (m, aryl, 8H), 6.77 (t, aryl, 1H), 5.22 (s, N*H*, 1H), 4.96 (s, ArNC(CH$_3$)C*H*C(CH$_3$)NAr, 1H), 3.86 (q, OC*H*$_2$CH$_3$, 2H), 3.42 (septet, C*H*(CH$_3$)$_2$, 2H), 3.23 (septet, C*H*(CH$_3$)$_2$, 2H), 2.46 (br, C*H*(CH$_3$)$_2$, 2H), 1.54 (s, ArNC(C*H*$_3$)CHC(C*H*$_3$)NAr, 6H), 1.34 (d, CH(C*H*$_3$)$_2$, 12H), 1.17 (d, CH(C*H*$_3$)$_2$, 6H), 1.06 (d, CH(C*H*$_3$)$_2$, 12H), 1.04 (d, CH(C*H*$_3$)$_2$, 12H), 0.84 (t, OCH$_2$C*H*$_3$, 3H). ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 168.6 (ArN*C*(CH$_3$)CH*C*(CH$_3$)NAr), 149.9 (aryl), 143.3 (aryl), 142.7 (aryl), 142.0 (aryl), 133.4 (aryl), 126.9 (aryl), 124.6 (aryl), 122.7 (aryl), 116.7 (aryl), 97.24 (ArNC(CH$_3$)*C*HC(CH$_3$)NAr), 65.40 (O*C*H$_2$CH$_3$), 30.08, 28.71, 28.37, 25.23 (*C*H$_3$), 24.63 (*C*H$_3$), 24.56 (*C*H$_3$), 23.87 (*C*H$_3$), 23.76 (*C*H$_3$), 21.16 (OCH$_2$*C*H$_3$). IR (C$_6$H$_6$, CaF$_2$): 3098 (w), 3088 (s), 2962 (s), 2926 (m), 2868 (m), 1958 (m), 1814 (m), 1590 (w), 1512 (s), 1462 (s), 1430 (s), 1386 (s), 1319 (s), 1262 (s), 1153 (s), 1104 (w), 1074 (w), 1041 (w) cm^{-1}. Anal. Calcd for C$_{43}$H$_{64}$N$_3$OSc: C, 75.51; H, 9.43; N, 6.17. Found: C, 75.13; H, 9.82; N, 5.98.

Synthesis of 1-OCH=CH$_2$. In a vial was dissolved **1-HBEt$_3$** (300 mg, 0.41 mmol) in 20 mL of THF. The solution was transferred to a reaction vessel and the mixture heated for 28 h, the color changing to pale yellow. The solution was dried under reduced pressure and the vessel taken into the glovebox. The yellow powder was extracted with hexane, and the extracts were filtered. The filtrate was concentrated, and cooled for 2 days at −35 °C to afford in two crops pale yellow crystals of **1-OCH=CH$_2$** (195 mg, 0.28 mmol, 70% yield). ^{1}H NMR (20 °C, 399.8 MHz, C$_6$D$_6$): δ 7.08−6.99 (m, aryl, 6H), 6.96 (d, aryl, 2H), 6.76 (t, aryl, 1H), 6.67−6.63 (dd, OC*H*=CH$_2$, $J_{\mathrm{H-Htrans}}$ = 14 Hz, $J_{\mathrm{H-Hcis}}$ = 6 Hz, 1H), 5.49 (s, N*H*, 1H), 4.99 (s, ArNC(CH$_3$)C*H*C(CH$_3$)NAr, 1H), 4.16 (broad d, OCH=C*H*$_2$, $J_{\mathrm{H-Htrans}}$ = 14 Hz, 1H), 3.92 (d, OCH=C*H*$_2$, $J_{\mathrm{H-Hcis}}$ = 6 Hz, 1H), 3.32 (septet, C*H*(CH$_3$)$_2$, 2H), 3.23 (septet, C*H*(CH$_3$)$_2$, 2H), 2.36 (br, C*H*(CH$_3$)$_2$, 2H), 1.54 (s, ArNC(C*H*$_3$)CHC(C*H*$_3$)NAr, 6H), 1.36 (d, CH(C*H*$_3$)$_2$, 6H), 1.34 (d, CH(C*H*$_3$)$_2$, 6H), 1.17 (d, CH(C*H*$_3$)$_2$, 6H), 1.12 (d, CH(C*H*$_3$)$_2$, 6H), 1.04 (d, CH(C*H*$_3$)$_2$, 12H). ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 168.4 (ArN*C*(CH$_3$)CH*C*(CH$_3$)NAr), 154.7 (aryl), 149.4 (aryl), 143.6 (aryl), 142.6 (aryl), 142.0 (aryl), 133.6 (aryl), 127.0 (aryl), 124.8 (aryl), 124.7 (aryl), 122.7 (aryl), 117.4 (aryl), 97.75 (ArNC(CH$_3$)*C*HC(CH$_3$)NAr), 90.48 (O*C*H=CH$_2$), 68.06 (OCH=*C*H$_2$), 30.45 (*C*H(CH$_3$)$_2$), 28.80 (*C*H(CH$_3$)$_2$), 28.41 (*C*H(CH$_3$)$_2$), 25.67 (*C*H$_3$), 25.20 (*C*H$_3$), 24.68 (*C*H$_3$), 24.27 (*C*H$_3$), 23.90 (*C*H$_3$), 23.78 (*C*H$_3$), 22.53. IR (C$_6$H$_6$, CaF$_2$): 3097 (w), 3088 (s), 3061 (m), 3029 (s), 2963 (s), 2926 (m), 2868 (m), 1957 (m), 1814 (m), 1591 (m), 1524 (s), 1476 (s), 1462 (s), 1431 (s), 1386 (s), 1317 (s), 1261 (s), 1214

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(43) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed., Engl.* **1973**, *12*, 508.

(s), 1173 (w), 1152 (w), 1103 (w) cm^{-1}. Anal. Calcd for $C_{43}H_{62}N_3OSc$: C, 75.73; H, 9.16; N, 6.16. Found: C, 75.62; H, 8.55; N, 5.77.

Synthesis of 1-OCHPh$_2$. In a vial was dissolved **1-HBEt$_3$** (100 mg, 0.13 mmol) in 10 mL of toluene and the solution cooled to −35 °C. To the solution was added solid Ph_2CO (25 mg, 0.14 mmol), causing a rapid color change to light yellow. After it was stirred for 2 h, the solution was filtered and the filtrate dried under reduced pressure. The light yellow powder was extracted with Et_2O, and the extracts were filtered, the filtrate concentrated, and cooled for 2 days at −35 °C to afford in three crops light yellow crystals of **1-OCHPh$_2$** (89 mg, 0.11 mmol, 80% yield). HMQC experiments was performed on **1-OCHPh$_2$** in order to assign some of the ^{1}H and ^{13}C NMR resonances.[32] ^{1}H NMR (20 °C, 399.8 MHz, C_6D_6): δ 7.38 (br, aryl, 1H), 7.19−6.80 (m, aryl, 18H), 5.96 (s, OC*H*Ph$_2$, 1H), 5.46 (s, N*H*, 1H), 5.15 (s, ArNC(CH$_3$)C*H*C(CH$_3$)NAr, 1H), 3.31 (br, C*H*(CH$_3$)$_2$, 2H), 3.07 (br, C*H*(CH$_3$)$_2$, 2H), 2.70 (br, C*H*(CH$_3$)$_2$, 1H), 2.24 (br, C*H*(CH$_3$)$_2$, 1H), 1.64 (s, ArNC(C*H*$_3$)CHC(C*H*$_3$)NAr, 6H), 1.38 (br, CH(C*H*$_3$)$_2$, 6H), 1.06 (br, CH(C*H*$_3$)$_2$, 24H), 0.92 (br, CH(C*H*$_3$)$_2$, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.8 (ArN*C*(CH$_3$)CH*C*(CH$_3$)NAr), 149.9 (aryl), 146.7 (aryl), 143.8 (aryl), 142.5 (aryl), 141.7 (aryl), 134.2 (aryl), 133.5 (aryl), 127.0 (aryl), 126.8 (aryl), 126.7 (aryl), 126.5 (aryl), 124.7 (aryl), 124.5 (aryl), 122.9 (aryl), 122.8 (aryl), 116.9 (aryl), 97.56 (ArNC(CH$_3$)*C*HC(CH$_3$)NAr), 83.23 (O*C*HPh$_2$), 31.24 (*C*H(CH$_3$)$_2$), 28.65 (*C*H(CH$_3$)$_2$), 28.39 (*C*H(CH$_3$)$_2$), 28.19 (*C*H(CH$_3$)$_2$), 25.24 (*C*H$_3$), 25.04 (*C*H$_3$), 24.64 (*C*H$_3$), 24.50 (*C*H$_3$), 24.21 (*C*H$_3$), 23.56 (*C*H$_3$), 22.67, 14.24. IR (C_6H_6, CaF_2): 3097 (m), 3071 (s), 3029 (s), 3023 (m), 2962 (s), 2926 (m), 2868 (m), 1960 (m), 1815 (m), 1575 (m), 1558 (m), 1539 (m), 1506 (s), 1476 (s), 1457 (s), 1430 (s), 1386 (s), 1318 (s), 1261 (s), 1173 (m), 1122 (m), 1070 (w) cm^{-1}. Anal. Calcd for $C_{43}H_{64}N_3OSc\cdot 0.5Et_2O$: C, 78.28; H, 8.80; N, 4.89. Found: C, 78.52; H, 8.95; N, 5.03.

Synthesis of 1-^{t}Bu. In a vial was dissolved **1-Cl(THF)** (100 mg, 0.13 mmol) in 10 mL of Et_2O and the solution cooled to −35 °C. To the solution was added a cold Et_2O (5 mL) solution containing Li^{t}Bu (9.01 mg, 0.14 mmol), causing a color change to darker yellow. After it was stirred for 2 h, the solution was filtered and the filtrate dried under reduced pressure. The yellow powder was extracted with hexane, and the extracts were filtered. The filtrate was concentrated, and cooled for 2 days at −35 °C to afford in three crops yellow crystals of **1-^{t}Bu** (87.6 mg, 0.12 mmol, 94% yield). ^{1}H NMR (20 °C, 399.8 MHz, C_6D_6): δ 7.20−7.10 (m, aryl, 8H), 6.94 (t, aryl, 1H), 5.87 (s, N*H*, 1H), 5.16 (s, ArNC(CH$_3$)C*H*C(CH$_3$)NAr, 1H), 3.49 (septet, C*H*(CH$_3$)$_2$, 2H), 3.41 (septet, C*H*(CH$_3$)$_2$, 1H), 3.16 (septet, C*H*(CH$_3$)$_2$, 2H), 2.86 (septet, C*H*(CH$_3$)$_2$, 1H), 1.69 (s, ArNC(C*H*$_3$)CHC(C*H*$_3$)NAr, 6H), 1.36 (d, CH(C*H*$_3$)$_2$, 6H), 1.33 (d, CH(C*H*$_3$)$_2$, 6H), 1.31 (d, CH(C*H*$_3$)$_2$, 6H), 1.22 (d, CH(C*H*$_3$)$_2$, 6H), 1.10 (d, CH(C*H*$_3$)$_2$, 6H), 1.06 (d, CH(C*H*$_3$)$_2$, 6H), 0.92 (s, C(C*H*$_3$)$_3$, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.6 (ArN*C*(CH$_3$)CH*C*(CH$_3$)NAr), 150.6 (aryl), 143.7 (aryl), 142.7 (aryl), 142.3 (aryl), 135.5 (aryl), 132.9 (aryl), 127.0 (aryl), 124.9 (aryl), 124.5 (aryl), 122.9 (aryl), 122.8 (aryl), 117.4 (aryl), 97.97 (ArNC(CH$_3$)*C*HC(CH$_3$)NAr), 31.91 (*C*H(CH$_3$)$_2$), 31.08 (*C*H(CH$_3$)$_2$), 30.18 (ArNC(*C*H$_3$)CHC(*C*H$_3$)NAr), 28.87 (CH(*C*H$_3$)$_2$), 28.52 (*C*H(CH$_3$)$_2$), 28.41 (CH(*C*H$_3$)$_2$), 25.67 (CH(*C*H$_3$)$_2$), 25.10 (C(*C*H$_3$)$_3$), 24.73 (CH(*C*H$_3$)$_2$), 24.42 (CH(*C*H$_3$)$_2$), 23.52 (CH(*C*H$_3$)$_2$), 23.00, 14.30 (*C*(CH$_3$)$_3$). IR (C_6H_6, CaF_2): 3200 (w), 3097 (w), 3077 (s), 3044 (s), 2962 (s), 2927 (m), 2869 (m), 2798 (m), 1957 (m), 1812 (w), 1591 (w), 1517 (s), 1461 (s), 1430 (s), 1386 (s), 1315 (s), 1260 (s), 1171 (w), 1107 (w), 1041 (w), 1019 (w) cm^{-1}. Anal. Calcd for $C_{45}H_{68}N_3Sc$: C, 77.65; H, 9.85; N, 6.04. Found: C, 77.60; H, 9.88; N, 6.18.

Thermolysis of 1-^{t}Bu in Et$_2$O To Prepare 1-OEt. In an NMR tube was dissolved **1-^{t}Bu** (47 mg, 0.067 mmol) in 0.6 mL of C_6D_6, and ∼3 drops of Et_2O were added. The solution was heated at 60 °C for 44 h. The volatile materials were vacuum-transferred into another NMR tube, leaving behind a yellow residue, which was extracted with hexane; the extracts were filtered, the filtrate concentrated, and cooled overnight at −35 °C to afford yellow crystals of **1-OEt** (40.9 mg, 0.59 mmol, 88% yield). Examination by ^{1}H NMR spectrum of the volatiles revealed the major product to be 2-methylpropane (^{t}Bu−H), as evidenced by ^{1}H NMR spectroscopy.

Thermolysis of 1-HBEt$_3$ in the Absence of Lewis Bases. In a vial was dissolved **1-HBEt$_3$** (50 mg, 0.068 mmol) in 10 mL of benzene. The solution was transferred to a reaction vessel and heated at 80 °C for 12 h, causing a color change to pale yellow. The solution was then dried under reduced pressure, and the vessel was taken into the glovebox. Examination of the crude mixture by ^{1}H NMR spectroscopy revealed formation of a myriad of products.

Thermolysis of 1-^{t}Bu in the Absence of Lewis Bases. In a vial was dissolved **1-^{t}Bu** (72.4 mg, 0.104 mmol) in 15 mL of benzene. The solution was transferred to a reaction vessel and was heated at 60 °C for 16 h. The solution was dried under reduced pressure, and the vessel was taken into the glovebox. The yellow powder was extracted with hexane, and the extracts were filtered, concentrated, and cooled overnight at −35 °C to afford yellow crystals. The ^{1}H NMR spectrum revealed that no reaction had occurred.

Structure Solution and Refinement. A summary of crystal data and refinement details for all structures are given in Tables 1 and 2.

General Parameters for Data Collection and Refinement. Single crystals of **1-Cl(THF)**, **1-OCHPh$_2$·**0.5Et$_2$O, and **1-^{t}Bu·**0.5Et$_2$O were grown from Et_2O at −35 °C. Single crystals of **1-HBEt$_3$**, **1-OEt**, and **1-OCH═CH$_2$** were grown from hexane at −35 °C. Inert-atmosphere techniques were used to place the crystal onto the tip of a diameter glass capillary (0.06−0.20 mm), which was mounted on a SMART-6000 instrument (Bruker) at 127−140(2) K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20−30 frames. The data collection was carried out using graphite-monochromated Mo Kα radiation with a frame time of 3 s and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at −43° in 2θ. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT).[44] The structure was solved by using SHELXS-97 and refined with SHELXL-97.[45] A direct-methods solution was calculated which provided most non-hydrogen atoms from the *E* map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined with isotropic displacement parameters.

For **1-HBEt$_3$**, the structure is unique in that the HBEt$_3$ anion is bound to the Sc atom through three hydrogen atoms. The bonds are weak (d[Sc−H] = 1.98−2.18 Å) but are located such that the coordination about the Sc atom is pseudo-octrahedral. These values are longer than estimated values calculated with the Pauling and Schomaker-Stevenson covalent radii, with corrections for electronegativity differences (d[Sc−H] = 1.68 Å).[46]

For **1-OCHPh$_2$·**0.5Et$_2$O, in addition to the molecule of interest a disordered Et_2O solvent was located. All non-hydrogen atoms were refined with anisotropic displacement parameters, with the exception of that particular solvent. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. One of the solvent hydrogen atoms was not located.

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(44) SAINT 6.1; Bruker Analytical X-ray Systems, Madison, WI.

(45) SHELXTL-Plus V5.10; Bruker Analytical X-ray Systems, Madison, WI.

(46) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

For **1-^{t}Bu**·0.5Et$_2$O, in addition to the molecule of interest a disordered Et$_2$O solvent was located and modeled. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located and refined with isotropic displacement parameters. The only exception is the absence of two of the hydrogen atoms associated with one of the terminal methyl groups of the solvent.

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Supporting Information Available: Complete details for data sets including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and structural diagrams for **1-Cl(THF)**, **1-HBEt$_3$**, **1-OEt**, **1-OCH═CH$_2$**, **1-OCHPh$_2$**·0.5Et$_2$O, and **1-^{t}Bu**·0.5Et$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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