β-Diketiminato Scandium Chemistry: Attempted Deprotonation of Cationic Amido Complexes

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Summary: Treatment of the β-diketiminato-supported scandium amido methyl derivatives [ArNC(tBu)CHC(tBu)NAr]Sc(Me)-(NHR) (Ar = 2,6-iPr2-C6H3; R = tBu, 2,6-iPr2-C6H3) with 1 equiv of tris(pentafluorophenyl)borane resulted in the formation of scandium amido ion pairs, ***1a*** *and* ***1b****, respectively, in good yields. A single-crystal X-ray analysis of* ***1a*** *was undertaken, and two crystallographically independent molecules were observed in which one contains an N−H···F−C hydrogen bond while the other does not. Several attempts to deprotonate the amido ligand to yield a neutral imido species resulted in either attack of the base at the metal center or deprotonation of the β-diketiminato ligand. For example, treatment of* ***1a*** *with tert-butyllithium gave [ArNC(tBu)CHC(tBu)NAr]Sc(CMe3)(NHtBu)* ***(2)****, while treatment with the phosphazene base [(Me2N)3-P═N]3P═NtBu gave the previously characterized metalated complex* ***3****.*

Introduction

Terminal imido ligands (═NR) are playing an increasingly important role in early-transition-metal chemistry as reactive intermediates or spectator ligands. As bulky imido ligands are isoelectronic with Cp ligands, they have been employed as ancillary ligands with group 5 and 6 metals for metal-based olefin polymerization, resulting in molecular fragments that are isolobal with group 4 metallocenes.[1] In addition, highly reactive group 4 L_nM═NR species are known to activate C−H bonds of alkanes via a 1,2-addition across the M═N functionality.[2] Also, these kinds of species are considered to be key intermediates in the catalytic hydroamination of allenes and alkynes by titanium- and zirconium-based catalyst precursors.[3] Experimental and kinetic evidence suggests that the first step of the catalytic cycle is the generation of the L_nM═NR species from the metal amido precursors, followed by 2 + 2 cycloaddition with substrate, resulting in the formation of the C−N bond.

Given the well-developed imido chemistry of the metals in groups 4−6, it is surprising that the imido chemistry of the group 3 metals (and indeed the lanthanides) is still rather limited. To the best of our knowledge, a monomeric, discrete L_nM═NR complex for group 3 has not yet been prepared.[4] However, Hessen et al. recently reported[5] a dimeric scandium imido complex that implied the intermediacy of a monomeric scandium imido species and suggests that, with the appropriate level of steric support, such species might be prevented from dimerizing.[6]

Recently, bulky N-aryl β-diketiminato[7] and related[8] ligands have been demonstrably effective at stabilizing low-coordinate environments.[9] In particular, monomeric imides for the group 13 metals aluminum[10] and gallium[11] as supported by these ligands have been prepared. For this reason, we felt it would be a useful template from which to develop the chemistry of terminal scandium imido complexes. However, despite the availability of a wide variety of β-diketiminato ("nacnac")-supported scandium bis(alkyl),[12] bis(amido)[13,14] and mixed alkyl−amido complexes, [ArNC(R)CH(R)CNAr]ScR′(R″) (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$; R = Me, ^{t}Bu; R′ = R″ = Me, Et, Bn, CH_2SiMe_3, CH_2CMe_3 or R′ ≠ R″, R′ = Me and R″ = NH^{t}Bu, NHAr), we could not induce formation of "LSc═NR" by the classical thermal pathways developed by Bergman[2a] and Wolczanski[2b] for group 4 congeners. In all instances, metalation of the *o*-isopropyl groups was observed rather than loss of alkane or amine, and labeling studies negated the possibility of the

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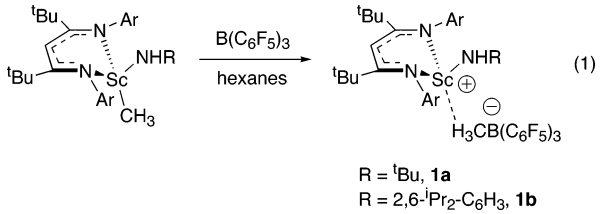
involvement of a terminal imide in the metalation product-forming process.[13]

Another strategy involves the deprotonation of primary amido complexes,[6,15] a process that should be thermodynamically more favorable if the amido starting material is cationic. Given that the nacnac scandium bis(alkyl) compounds readily undergo alkide abstraction to form well-defined organoscandium cations,[16] we surmised that nacnac amido cations should be accessible from mixed alkyl−amido complexes. Herein we describe the synthesis of such cations and their reaction with various bases in attempts to uncover deprotonative routes to terminal scandium imido complexes.

Results and Discussion

The amido methyl complexes [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]Sc(Me)(NHR) (R = ^{t}Bu, 2,6-^{i}Pr$_2$-C$_6$H$_3$) were prepared as described previously and treated with 1 equiv of the strong organometallic Lewis acid B(C$_6$F$_5$)$_3$[17] in order to effect abstraction of the methide anion.[18] When it is carried out in hexanes, this reaction results in nearly quantitative precipitation of the contact ion pairs [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]Sc(NHR)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$; R = ^{t}Bu (**1a**), 2,6-^{i}Pr$_2$-C$_6$H$_3$ (**1b**)) as pale yellow microcrystalline solids, as shown in eq 1. Cation formation is



(1)

R = ^{t}Bu, **1a**
R = 2,6-^{i}Pr$_2$-C$_6$H$_3$, **1b**

signaled by several spectroscopic features present in the NMR spectra of compounds **1** obtained in d_8-toluene. The ^{11}B NMR resonances appear at −15.1 and −14.9 ppm for **1a** and **1b**, respectively, typical of anionic four-coordinate borate centers.[19] This is supported by ^{19}F NMR spectroscopic data, which show the separation between the resonances for the meta and para fluorines as being 4.6 ppm (**1a**) and 4.1 ppm (**1b**), values typical of the weakly coordinating methyl borate counteranion.[20] In the ^{1}H NMR spectra, the resonances for the N−H protons shift significantly downfield (5.39 ppm for **1a** and 7.54 ppm for the anilido cation **1b**) relative to the positions of these signals in the neutral methyl amido starting materials (3.54 and 5.44 ppm). Additionally, the resonances for the Sc−CH$_3$ protons broaden and shift to the region characteristic of methyl borate anions engaged in bridging interactions with the scandium center.[16]

Previously, we have shown that a variety of (nacnac)ScX$_2$ species are fluxional in solution,[12,13,21] manifested by exchange between the diastereotopic endo (underneath the N$_2$C$_3$ ligand plane) and exo positions; this process can be studied via variable-temperature NMR experiments. The exchange process

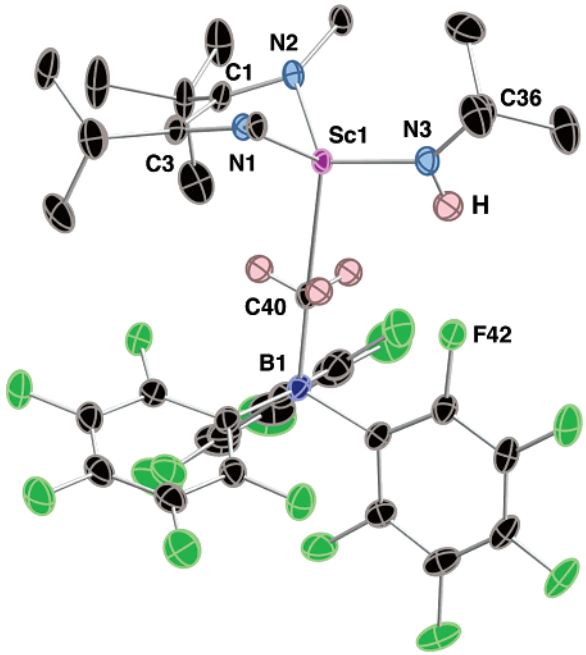


Figure 1. Crystalmaker thermal ellipsoid diagram (50%) of molecule A of **1a**. all but the ipso carbons of the N-aryl 2,6-diisopropyl groups have been removed for clarity. For all of the following data, analogous values for molecule B are given in italics. Selected bond distances (Å): Sc−N(1), 2.121(2), *2.095(3)*; Sc−N(2), 2.078(2), *2.112(2)*; Sc−N(3), 1.969(3), *1.943(3)*; Sc−C(40), 2.521(3), *2.537(3)*; C(40)−B, 1.675(4), *1.679(4)*. Nonbonded distance (Å): F(42)−N(3), 3.162. Closest N(3)−F contact in molecule B: *3.996* Å. Distance of Sc from N(1)−C(3)−C(2)−C(1)−N(2) mean plane (Å); 1.257(3), *1.234(3)*. Selected bond angles (deg): N(1)−Sc−N(2), 94.8(1), *95.0(1)*; C(40)−Sc−N(3), 103.3(1), *96.6(2)*; Sc−N(3)−C(36), 141.2(2), *152.9(4)*.

occurs via a C_{2v}-symmetric transition state wherein the Sc passes through the N$_2$C$_3$ plane. In systems where the groups on scandium are chemically distinct, as in compounds **1**, two diastereomers are potentially in exchange via this process.[16b] Variable-temperature ^{1}H NMR studies on both **1a** and **1b**, however, indicated that only one isomer is present over the accessible temperature range (200−360 K). By analogy to our more detailed analysis of the neutral alkyl amido precursors,[13] the isomer present is likely that in which the amido group occupies the exo site, which is both sterically preferred and electronically favorable for π-donating ligands.[13]

This assignment is borne out in the molecular structure of **1a**, determined by X-ray crystallography on single crystals of this derivative. There are two crystallographically independent molecules in the unit cell; a diagram of molecule A is shown in Figure 1, along with selected metrical data for both, and crystal data and refinement details are given in Table 1. In both molecules, the amide ligand occupies the exo site, while the more sterically hindered endo site accommodates the methyl borate anion, whose steric bulk is farther removed from the scandium center. The two molecules differ mainly in the orientation of the borate counteranion with respect to the amide ligand. In molecule A, one of the C$_6$F$_5$ rings is oriented such that the C(42)−F(42) axis is aligned with the N−H moiety of the amide, forming a weak N−H′···F hydrogen bond (the N(3)−F(42) distance is 3.162 Å, which is close to the sum of the van der Waals radii for N−F of 3.15 Å[22]). In molecule B, this ring

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Table 1. Summary of Data Collection and Structure Refinement Details for 1a

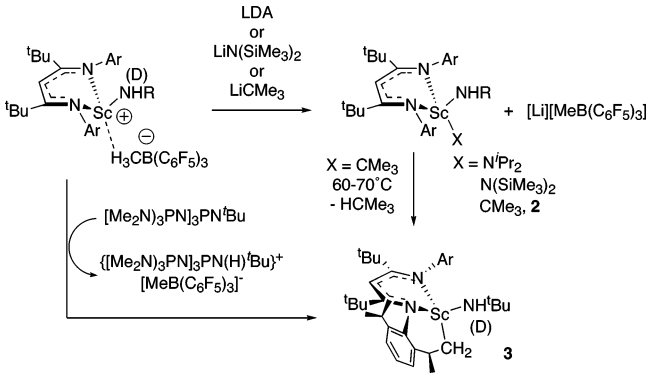
formula	$C_{58.75}H_{67.75}N_3ScBF_{15}$
fw	1156.68
temp, °C	−80
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	13.525(4)
b, Å	22.096
c, Å	22.507
α, deg	65.395(5)
β, deg	78.125(5)
γ, deg	87.470(5)
V, Å^3	5978(3)
Z	4
d_{calcd}, g cm^{-3}	1.285
μ, mm^{-1}	0.208
no. of rflns measd	36364
no. of unique rflns	15328
R1/wR2	0.0714/0.2136
GOF	0.986
resid density, e/Å^3	+0.911/ −0.831

is twisted out of this alignment, such that the closest N(3)−F contact is 3.996 Å. This change in orientation also has an impact on the Sc−N(3)−C(36) and C(40)−Sc−N(3) angles, which differ by several degrees in the two molecules. For the rest, the metrical data is quite similar between the two molecules and we will refer only to that for molecule A for the remainder of the discussion. The abstracted methyl group is now 2.521(3) Å away from the scandium center, as opposed to 2.229(2) Å in the starting methyl amide.[13] The B(1)−C(40) distance of 1.675(4) Å is typical of such anions;[18] the hydrogens of this methyl group are placed in idealized positions based on C(40). The Sc−N(3) distance of 1.969(3) Å is only slightly contracted from the observed length of 2.000(2) Å in the neutral precursor complex [ArNC(ᵗBu)CHC(ᵗBu)NAr]Sc(Me)(NHᵗBu), indicating that cation formation does not significantly impact the extent of π bonding between Sc and N,[23] and is consistent with the notion that π bonding is already quite significant in the neutral amido alkyl compounds.[13]

Our interest in these compounds stems from their potential as precursors to heretofore unknown group 3 metal imido complexes via deprotonation. While several strategies to deprotonate the neutral precursors to cations **1** failed to yield imido-containing products, we felt that deprotonation of the presumably more acidic cationic primary amido ligand would be more thermodynamically favored if a suitable base could be found to favor this pathway kinetically. Selective deprotonation of a cationic zirconium amide has recently been realized, but these reactions are extremely sensitive to the nature of the base and the ligand environments employed.[15]

Treatment of **1a** or **1b** with various anionic bases (LDA, LiN(TMS)$_2$, LiCMe$_3$) at ambient or low temperature and in the presence or absence of coordinating bases (THF, pyridine) invariably resulted in attack of the nucleophile at the scandium center and elimination of [Li][MeB(C$_6$F$_5$)$_3$] (Scheme 1). The latter product was identified by matching ^{19}F NMR signals with an authentic sample, prepared in situ from B(C$_6$F$_5$)$_3$ and MeLi.[24] In the case of the *tert*-butyllithium reaction, preparative-scale experiments allowed for isolation of [ArNC(ᵗBu)CHC(ᵗBu)NAr]Sc(CMe$_3$)(NHᵗBu) (**2**), which was fully characterized by NMR

Scheme 1



spectroscopy and elemental analysis (see Experimental Section). A related compound, [ArNC(Me)CHC(Me)NAr]Sc(CMe$_3$)(NHAr), was recently reported by Mindiola et al.,[14] and **2** has spectroscopic properties similar to those of this derivative. Compound **2** is also the major product when **1a** is first treated with 1 equiv of pyridine to block the scandium center, although the reaction in this case is both slower and less selective. Further heating of **2** resulted in loss of isobutane and formation of the previously characterized metalated complex **3**,[13] likely formed by prior isomerization of the *tert*-butyl to the *sec*-butyl derivative before σ-bond metathetical loss of the alkyl group. Thus, it appears that even with these nonnucleophilic or sterically bulky bases, attack at the electrophilic and relatively accessible metal center is kinetically (and perhaps even thermodynamically) favored.

We therefore turned to the commercially available phosphazene superbase [(Me$_2$N)$_3$P═N]$_3$P═Nᵗ Bu as a base that has great thermodynamic strength but poor nucleophilicity.[25] Sita et al. have had success with the deprotonation of a cationic zirconium amido species with a similar base.[15] Unfortunately, reaction of **1a** with 1 equiv of [(Me$_2$N)$_3$P═N]$_3$P═Nᵗ Bu led rapidly to the metalated product **3** (Scheme 1). The reaction was also performed with *d*-**1a**, selectively deuterated in the amido NH position, and the product was *d*-**3**, indicating that **3** is produced via direct deprotonation of the aryl isopropyl group and not via a transient scandium imido derivative.[26] Since it is difficult to see how the isopropyl methyl protons could be more acidic than the amido proton, this pathway must be kinetically and statistically favored. Thus, while the deprotonation of a cationic primary amido species is perhaps yet a potentially viable route to the elusive scandium imido function, the search for a suitable supporting ligand framework and base continues.

Experimental Section

General procedures and the syntheses of compounds **1** and their precursors have been described in detail elsewhere.[13] *tert*-Butyllithium was purified by filtering commercial 1.7 M solutions in pentane and removing the solvent in vacuo and was used as a solid.[27] Solvent was removed under reduced pressures from the 1.0 M hexane solution of [(Me$_2$N)$_3$P═N]$_3$P═Nᵗ Bu (Aldrich-Sigma),

(23) Interestingly, the analogous distance in molecule B, which does not feature the N−H···F hydrogen bond, is slightly more contracted, to 1.943(3) Å, consistent with the expectation that hydrogen bonding would render the amide a poorer π donor to scandium.

(24) *Caution*! Dry [Li][MeB(C$_6$F$_5$)$_3$] is prone to detonation: Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2001**, *123*, 1483.

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(26) No evidence for the scrambling of the N−D deuteron into the isopropyl groups of the nacnac N-aryl groups was observed, suggesting that **3** is not in equilibrium with the elusive scandium imido isomer.

which was then utilized as a solid without further purification. Tris(pentafluorophenyl)borane was purchased from Boulder Scientific, purified by treatment with $Me_2SiH(Cl)$ in hexanes to remove water, and sublimed (120 °C, dynamic vacuum). In the following, Ar = 2,6-diisopropylphenyl.

Synthesis of 1a. The *tert*-butylamido methyl complex [ArNC(ᵗBu)CHC(ᵗBu)NAr]Sc(Me)(NHᵗBu) (0.152 g, 0.240 mmol) and $B(C_6F_5)_3$ (0.123 g, 0.240 mmol) were weighed out separately and dissolved in hexane. A solution of $B(C_6F_5)_3$ was added dropwise to the stirred solution of the amido methyl reagent. The reaction mixture was stirred for 2 h at room temperature, and then it was left overnight at −36 °C. The supernatant was decanted off of the pale yellow precipitate of **1a**, and the solid was dried in vacuo. Yield: 0.267 g, 97%. ^{1}H NMR (T = 248 K, toluene-d_8): δ 6.96 and 6.82 (m, 6H, C_6H_3), 5.54 (s, 1H, C*H*), 5.39 (br s, 1H, N*H*), 2.56 (m, 4H, C*H*$(CH_3)_2$), 1.53 (br s, 3H, C*H*$_3$B$(C_6F_5)_3$), 1.41, 1.17, 1.10, and 1.02 (d, 4 × 6H, CH(C*H*$_3)_2$, J_{H-H} = 6.5 or 6.6 Hz), 0.85 (s, 18H, NCC(C*H*$_3)_3$), 0.58 (s, 9H, NHC(C*H*$_3)_3$). ^{13}C{^{1}H} NMR (T = 239 K, toluene-d_8): δ = 175.7 (N*C*C(CH$_3)_3$), 149.9, 147.5, 140.4, 136.1, 123.0, and 122.8 (C_6F_5), 143.1, 140.3, 139.0, 127.2, 124.6, 124.3 (C_6H_3), 86.4 (*C*H), 55.9 (NH*C*$(CH_3)_3$), 44.9 (NC*C*$(CH_3)_3$), 32.6 (NHC(*C*H$_3)_3$), 31.0 (NCC(*C*H$_3)_3$), 28.7 and 25.5 (*C*H$(CH_3)_2$), 25.2, 24.2, 24.1, and 23.2 (CH(*C*H$_3)_2$), 24.9 (*C*H$_3$B). ^{19}F NMR: δ −132.6 (d, 6F, *o*-F, J_{F-F} = 23.3 Hz), −159.8 (br s, 3F, *p*-F), −164.4 (br s, 6F, *m*-F). ^{11}B NMR: δ −15.1 (s, CH$_3$*B*). Anal. Calcd for $C_{58}H_{66}N_3F_{15}BSc$: C, 60.79; H, 5.81; N, 3.67. Found: C, 60.70; H, 5.75; N, 3.55.

Synthesis of 1b. The compound [ArNC(ᵗBu)CHC(ᵗBu)NAr]Sc(Me)(NHAr) (0.074 g, 0.100 mmol) and $B(C_6F_5)_3$ (0.051 g, 0.100 mmol) were combined to synthesize **1b** using the same method as that employed to produce **1a**. Yield: 0.103 g, 82%. ^{1}H NMR (T = 228 K, toluene-d_8): δ 7.65 (br s, 1H, N*H*), 6.85 (t, 2H, 3 × C_6H_3, J_{H-H} = 7.7 Hz), 6.68 (m, 7H, 3 × C_6H_3), 6.10 (s, 1H, C*H*), 2.97 and 2.71 (m, 2 × 2H, C*H*$(CH_3)_2$, J_{H-H} = 6.4 Hz), 1.39 (br m, 5H, NH-2,6-(C*H*$(CH_3)_2)_2C_6H_3$ and C*H*$_3$B$(C_6F_5)_3$), 1.15, 1.09, 1.01, and 0.78 (d, 4 × 6H, CH(C*H*$_3)_2$, J_{H-H} = 6.4 Hz), 0.98 (s, 18H, NCC(C*H*$_3)_3$), 0.63 (d, 12H, NH-2,6-(CH(C*H*$_3)_2)_2C_6H_3$, J_{H-H} = 6.4 Hz). ^{13}C{^{1}H} NMR (T = 228 K, toluene-d_8): δ 178.4 (N*C*C(CH$_3)_3$), 150.0, 147.7, 138.5, 138.1, and 136.0 (1 signals was unobserved for C_6F_5), 147.5, 144.4, 141.9, 141.2, 141.1, 133.9, 133.8, 124.8, 123.4, and 120.5 (10 of 12 signals were observed for 3 × C_6H_3), 93.0 (*C*H), 44.5 (NC*C*$(CH_3)_3$), 32.2 (NH-2,6-(*C*H$(CH_3)_2)_2C_6H_3$), 31.1 (NCC(*C*H$_3)_3$), 29.1 and 28.4 (*C*H$(CH_3)_2$), 28.6, 25.64, 25.59, and 24.1 (CH(*C*H$_3)_2$), 23.9 (NH-2,6-(CH(*C*H$_3)_2)_2C_6H_3$), 19.4 (*C*H$_3$B$(C_6F_5)_3$). ^{19}F NMR: δ −131.7 (d, 6F, *o*-F, J_{F-F} = 21.2 Hz), −160.5 (t, 3F, *p*-F, J_{F-F} = 20.7 Hz), −164.6 (t, 6F, *m*-F, J_{F-F} = 20.7 Hz). ^{11}B NMR (C_6D_5Br): δ −14.9 (s, CH$_3$B). Anal. Calcd for $C_{66}H_{74}N_3ScF_{15}B$: C, 63.42; H, 5.97; N, 3.36. Found: C, 63.03; H, 6.01; N, 3.30.

Synthesis of 2. 1a (0.107 g, 0.0934 mmol) and ᵗBuLi (0.007 g, 0.109 mmol) were weighed into a vial and dissolved in hexane (5 mL). The reaction mixture consisted of a yellow solution with yellow-orange powder, and it was stirred overnight at room temperature. The light orange precipitate was filtered off, and the precipitate was washed with hexane (4 × 1 mL). (*Caution!* Dry [Li][MeB$(C_6F_5)_3$] has been known to detonate.) Following filtration, the light orange precipitate of [Li][MeB$(C_6F_5)_3$] was immediately dissolved in toluene and water was added to the solution to deactivate any remaining [Li][MeB$(C_6F_5)_3$]. The four hexane fractions and the filtrate were combined, and the solvent was removed under reduced pressure, producing a yellow powder of **2**. Yield: 0.054 g, 87%. ^{1}H NMR: δ 7.13−7.00 (m, 6H, C_6H_3), 5.55 (s, 1H, C*H*), 4.30 and 3.03 (m, 2 × 2H, C*H*$(CH_3)_2$, J_{H-H} = 6.8 or 7.2 Hz), 3.51 (br s, 1H, N*H*), 1.62, 1.45, 1.28, and 1.24 (d, 4 × 6H, CH(C*H*$_3)_2$, J_{H-H} = 6.8 or 7.2 Hz), 1.32 (s, 9H, NHC(C*H*$_3)_3$), 1.14 (s, 18H, NCC(C*H*$_3)_3$), 0.75 (s, 9H, ScC(C*H*$_3)_3$). ^{13}C{^{1}H} NMR: δ 175.1 (N*C*C(CH$_3)_3$), 145.4, 143.3, 142.4, 126.7, 125.2, and 124.6 (C_6H_3), 95.1 (*C*H), 54.6 (NH*C*$(CH_3)_3$), 45.2 (NC*C*$(CH_3)_3$), 35.6 (NHC(*C*H$_3)_3$), 33.4 (NCC(*C*H$_3)_3$), 32.2 (ScC(*C*H$_3)_3$), 29.4 and 28.2 (*C*H$(CH_3)_2$), 28.0, 26.4, 25.3, and 25.2 (CH(*C*H$_3)_2$). Note: Sc*C*$(CH_3)_3$ was not visible in the ^{13}C{^{1}H} NMR spectrum, and this phenomenon was most likely due to the quadrupolar nature of scandium, where $I = {}^7/_2$. Anal. Calcd for $C_{40}H_{66}N_3Sc$: C, 75.78; H, 10.49; N, 6.63. Found: C, 75.72; H, 10.31; N, 6.58.

Thermolysis of 2. 2 was dissolved in C_6D_6 and heated to 60 °C for approximately 4 h, and then the temperature was raised to 70 °C for 17 h. At this point, the reaction was about 50% complete and the resonances for the product **3** and HC$(CH_3)_3$ were present in the 400 MHz ^{1}H NMR spectrum.

In Situ Synthesis of the Pyridine Adduct of 1a. The scandium ion pair **1a** (0.020 g, 0.0175 mmol) was dissolved in toluene-d_8 and placed in an NMR tube; pyridine (1.4 μL, 0.0175 mmol) was syringed into the tube. The NMR tube was briefly shaken, and then the reaction mixture was characterized by ^{1}H and ^{19}F NMR spectroscopy. ^{1}H NMR (toluene-d_8): δ 8.40 (m, 2H, NC$_5H_5$), 7.44 (m, 1H, NC$_5H_5$), 6.96 and 6.82 (m, 8H, C_6H_3 and NC$_5H_5$), 5.92 (s, 1H, C*H*), 4.52 (br s, 1H, N*H*), 2.64 and 2.30 (m, 2 × 2H, C*H*$(CH_3)_2$), 1.24 (br s, 6H, CH(C*H*$_3)_2$), 1.20−0.91 (m, 21H, CH(C*H*$_3)_2$ and C*H*$_3$B$(C_6F_5)_3$), 1.01 (s, 18H, NCC(C*H*$_3)_3$), 0.63 (s, 9H, NHC(C*H*$_3)_3$). ^{19}F NMR (toluene-d_8): δ −131.4 (d, 6F, *o*-F, J_{F-F} = 19.1 Hz), −164.3 (t, 3F, *p*-F, J_{F-F} = 20.7 Hz), −166.5 (m, 6F, *m*-F).

Deprotonation of 1a with [(Me$_2$N)$_3$P═N]$_3$P═Nᵗ Bu. Complex **1a** was prepared in situ by dissolving [ArNC(ᵗBu)CHC(ᵗBu)NAr]Sc(Me)(NHᵗBu) (0.006 g, 9.46 × 10^{-6} mol) and $B(C_6F_5)_3$ (0.005 g, 9.77 × 10^{-6} mol) in C_6D_6 in a vial. To ensure the reaction went to completion, the reaction mixture was stirred for 2 min. The phosphazene base (0.006 g, 9.56 × 10^{-6} mol) was dissolved in a separate vial in the same solvent. While the mixture was stirred continuously, the phosphazene base solution was added dropwise to the yellow solution of **1a**. After approximately 10 min, the reaction was complete and the known metalated neutral scandium−amido species **3** and the new ion pair [[(Me$_2$N)$_3$P═N]$_3$P═N(H)ᵗBu][MeB$(C_6F_5)_3$] were present. The reaction went quantitatively to completion, as shown by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy. Compound **3** was never isolated on a large scale by this method. ^{19}F NMR: δ −131.9 (br s, 6F, *o*-F), −165.1 (br s, 3F, *p*-F), −167.3 (br s, 6F, *m*-F). ^{31}P{^{1}H} NMR: δ 10.9 (d, *P*[N(Me$_2$)$_3$], $^2J_{P-P}$ = 47.6 Hz), −25.1 (q, *P*═Nᵗ Bu, $^2J_{P-P}$ = 47.6 Hz).

X-ray Crystallography for 1a. Measurements were made on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα (0.710 73 Å) radiation. Crystal data and refinement details are given in Table 1, and the crystallographic information file is available as Supporting Information and from the Cambridge Database (CCDC 299421).

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Supporting Information Available: A CIF file giving crystallographic data and ORTEP diagrams for both molecules of **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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