Low-Coordinate Organoyttrium Complexes Supported by β-Diketiminato Ligands

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Several organoyttrium complexes stabilized by β-diketiminato ligands (Ar)NC(R)CHC(R)N(Ar) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = CH$_3$ (ligand **a**), R = ^{t}Bu (ligand **b**)) have been prepared. Ligand-supported yttrium diiodides LYI$_2$(THF)$_n$ were alkylated with organolithium or potassium reagents, yielding low-coordinate bis-alkyl derivatives. Several of these compounds have been characterized by X-ray crystallography, and a discussion of these structures in comparison to similar scandium complexes is presented. An out-of-plane bonding mode is observed in the solid state, analogous to that seen in scandium bis-alkyls, and spectroscopic studies reveal that fluxional behavior in solution is also comparable to that observed for the scandium species. The bis-alkyls LYR$_2$ are susceptible to metalative alkane elimination at room temperature in solution. Activation of (Lig**a**)YR$_2$ with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] generates alkyl cations stabilized with η^6-arene-bound NMe$_2$Ph. This unique coordination mode was studied via 1D ^{1}H, ^{13}C, and ^{15}N NMR and 2D ROESY spectroscopy and appears to stabilize the alkyl cations against metalative alkane elimination.

Introduction

Low-coordinate, base-free group 3 alkyl complexes are of current interest for their utility as highly active catalysts for olefin polymerization,[1,2] hydroamination,[3−5] and alkyne dimerization.[6] While the bis-cyclopentadienyl framework has been exploited extensively in group 3 chemistry,[3a,7] in recent years there has been considerable focus on the design and use of monoanionic ancillary ligands. The design of sterically bulky and chelating ligands that afford complexes of the type LMR$_2$ (M = Sc, Y) are of particular interest because they provide a synthetic avenue into group 3 alkyl cations that can be compared to metallocenium group 4 cationic polymerization catalysts.[8]

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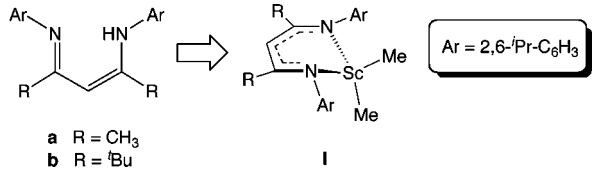
The β-diketiminato, or "nacnac", ligand is an attractive choice for stabilizing numerous transition metal and main group complexes[9] because it exhibits both steric and electronic[10] tunability and its successful application in scandium chemistry,[11] such as in **I**, makes it an obvious choice for investigating analogous yttrium complexes.[12] Given the considerable size differential between scandium and yttrium (ionic radii for Sc^{3+} = 0.745 Å, Y^{3+} = 0.90 Å), the propensity for complex dimerization, ligand redistribution, and the formation of "ate" complexes is typically of greater concern in organoyttrium chemistry, and thus β-diketiminato yttrium complexes of monohapto alkyls have previously eluded isolation.



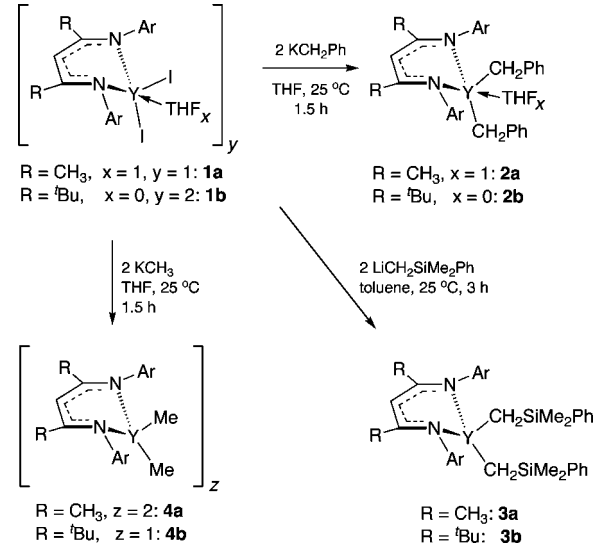
Herein we describe the synthesis of a series of neutral and cationic organoyttrium complexes supported by the bulky β-diketiminate ligands. The two ligands employed have 2,6-$^{i}Pr_2C_6H_3$ aryl groups on nitrogen and either CH_3 (**a** series) or ^{t}Bu (**b** series) as backbone substituents. Although decomposition via ligand metalation has been observed with this ligand ancillary,[10a] many of the complexes reported here exhibit remarkable thermal stability and represent examples of low-coordinate base-free organoyttrium compounds.

Results and Discussion

Neutral Yttrium Bis-alkyls. In order to access yttrium complexes supported by the β-diketiminate ligand framework, a salt metathesis approach was employed for ligand attachment; $YI_3(THF)_{3.5}$ was used exclusively, as it exhibits greater solubility in common organic solvents. Furthermore, in order to avoid complications arising from persistent lithium iodide,[13] potassium salts of two nacnac ligands,[11b] prepared by reaction of proteo-ligands with excess KH, were used as starting materials.

Reaction of the potassium reagent {ArNC(CH_3)CHC(CH_3)-NAr}K, where Ar = 2,6-$^{i}Pr_2C_6H_3$, with a stoichiometric amount of $YI_3(THF)_{3.5}$[14] overnight in THF affords **1a** in 63% yield (Scheme 1), analogous results to those reported by Liddle and Arnold.[11b] In contrast, the bulkier ArNC(^{t}Bu)CHC(^{t}Bu)NAr ligand required more forcing conditions for installation onto yttrium, where reaction of the potassium salt of the ligand[15] with $YI_3(THF)_{3.5}$ for 1.5 h at 90 °C in toluene gave **1b** in 87% yield. The ^{1}H and ^{13}C NMR spectra of **1a** reveal that one molecule of THF remains coordinated to yttrium, whereas the backbone ^{t}Bu groups in **1b** force greater steric bulk toward the metal center and consequently discourage THF retention in this compound.[16] Both **1a** and **1b** display an otherwise symmetrical pattern in the ^{1}H NMR spectrum, which suggests these complexes are fluxional at room temperature, similar to analogous β-diketiminato scandium dichloride complexes,[10a] although here the dynamic behavior was not probed further. The solid-state structure of **1b** (Figure S1) reveals the dimeric nature of this complex in the solid state.

Scheme 1



Contrary to what was reported by Liddle and Arnold, we found that these β-diketiminato yttrium diiodide complexes can conveniently be alkylated with organolithium or potassium reagents to give yttrium bis-alkyl complexes (Scheme 1). Key to their isolation is a timely workup prior to product losses through metalative loss of alkane.

When the backbone substituent is the less bulkyl methyl group, as in series "**a**", THF can remain coordinated at the metal center upon alkylation. For example, reaction of **1a** with 2 equiv of benzyl potassium in THF yields dibenzyl complex **2a**, in which 1 equiv of THF is retained. X-ray quality crystals of **2a** were grown from a cold toluene solution, and the structure is shown in Figure 1. Moderate steric crowding around the metal center causes the yttrium center to tilt 0.735(3) Å out of the ligand plane, resulting in a distorted trigonal bipyramidal geometry at yttrium. Furthermore, one benzyl ligand is coordinated in an η^2-binding fashion (*vida infra*), with a Y−C(1)−C(32) bond angle of 92.27(16)° and Y−C(1) and Y−C(32) bond lengths of 2.454(3) and 2.903(13) Å, respectively. The Y−O(1) bond length (2.3973(19) Å) is within the range of known THF adducts of similar yttrium bis-alkyl complexes,[11c,17] but it is toward the longer end of this group.

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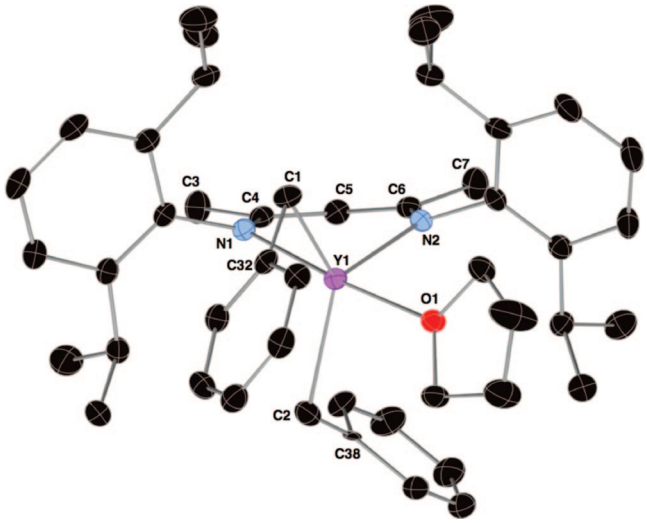

Figure 1. Solid-state structure of **2a** shown as 50% ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Y(1)−N(1), 2.408(2); Y(1)−N(2), 2.333(2); Y(1)−O(1), 2.3973(19); Y(1)−C(1), 2.454(3); Y(1)−C(2), 2.450(3); Y(1)−C(32), 2.903(3); Y(1)−N_2C_3 plane, 0.735(3). Selected bond angles (deg): C(1)−Y(1)−C(2), 128.94(10); N(1)−Y(1)−C(1), 93.14(9); N(1)−Y(1)−C(2), 96.12(9); N(2)−Y(1)−C(1), 115.00(8); N(2)−Y(1)−C(2), 116.05(9); N(1)−Y(1)−N(2), 80.65(7); N(1)−Y(1)−O(1), 175.71(6); Y(1)−C(1)−C(32), 92.27(16); Y(1)−C(2)−C(38), 107.43(17).

In contrast, dibenzyl complex **2b**, derived from reaction of **1b** and benzyl potassium, remains free of coordinating base, even when THF is the reaction solvent. The monomeric and base-free nature of **2b** attests to the more pronounced steric protection afforded by the *tert*-butyl ligand. Single-crystal X-ray diffraction of **2b** (Figure 2) indicates that the metal lies 1.309(4) Å outside the ligand plane, rendering the benzyl substituents diastereotopic. The *endo* benzyl group, which lies down and under the ligand plane,[11a] coordinates only through the benzylic carbon, whereas the *exo* benzyl group, directed up and out from the ligand, is coordinated through an η^2-binding interaction. The acute Y−C(1)−C(38) bond angle (91.4(2)°) and short Y−C(1) and Y−C(38) bond distances of 2.391(4) and 2.823(4) Å, respectively, are comparable to those found in known lanthanide complexes containing η^2-bound benzyl ligands,[18,19] while the long Y−C(39) *ortho* bond distance of 3.225(5) Å is outside the accepted range for η^3-bound benzyl ligands.[15,20] In previously reported scandium mixed bis-alkyl complexes, the larger substituent preferentially occupied the more open *exo* position,[10a] so the position of the η^2-bound benzyl ligand in **2b** is in agreement with this previous work. Interestingly, however, the scandium congener of **2b** does not display any mulit-hapto binding of either benzyl group; the larger yttrium ionic radius is believed to be responsible for the extra coordination in the present case.

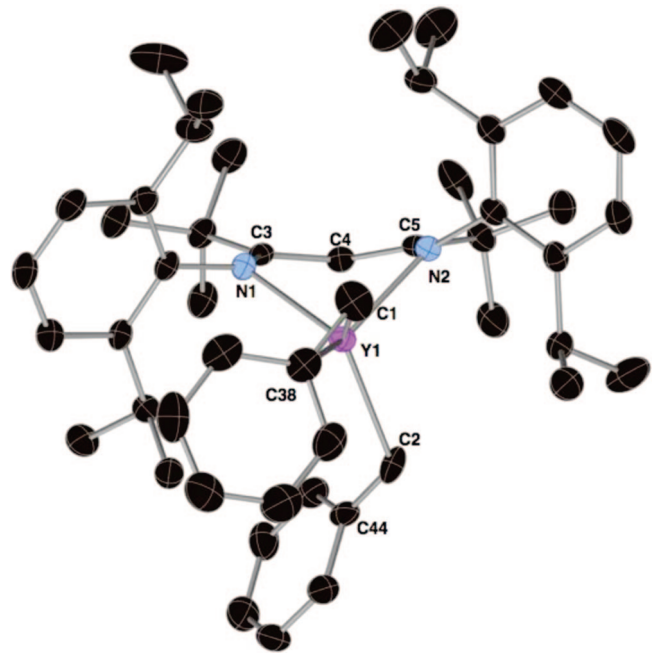

Figure 2. Solid-state structure of **2b** shown as 50% ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Y(1)−N(1), 2.273(3); Y(1)−N(2), 2.258(3); Y(1)−C(1), 2.392(4); C(1)−Y(1)−C(2), 124.29(15); N(1)−Y(1)−C(1), 107.51(14); N(1)−Y(1)−C(2), 124.82(1); N(2)−Y(1)−C(1), 95.21(13); N(2)−Y(1)−C(2), 103.63(11); N(1)−Y(1)−N(2), 88.03(10); Y(1)−C(1)−C(38), 91.4(2).

While the solid-state structure of **2b** demonstrates out-of-plane bonding of yttrium to the ligand, room-temperature solution NMR spectra are consistent with a symmetrical in-plane C_{2v} solution structure, indicative of the fluxional out-of-plane exchange elucidated for known β-diketiminato scandium alkyl complexes.[11a] At lower temperatures, this "ligand-flip" process can be slowed sufficiently so that the less symmetrical (C_s) species identified in the solid state can be observed on the NMR time scale, where the diastereotopic alkyl groups can be distinguished. The barrier for this exchange for **2b** at 243 K is 11.4(3) kcal mol^{-1}. The yttrium bis-alkyls reported here have barriers for "ligand-flip" that are slightly smaller than those previously determined for the scandium bis-alkyls.[11a] This observation is rationalized on the basis of the larger ionic radius for yttrium; as a consequence, the metal sits further from the ligand, facilitating exchange through a congested planar (C_{2v}) intermediate.

In **2b**, the benzyl methylene ^{13}C NMR resonance found at 56.4 ppm ($^1J_{CH}$ = 122 Hz) suggests that both benzyl ligands exhibit average η^1-binding in solution.[16] Variable-temperature experiments were conducted below the coalescence temperature of ligand-flip in order to evaluate the possibility of significant η^2-binding of a benzyl group at lower temperatures in solution. At 203 K in toluene-d_8, in the slow-exchange regime for ligand-flip, two distinct ^{13}C NMR resonances are found, at 57.6 ppm ($^1J_{CH}$= 125 Hz) and 52.3 ppm ($^1J_{CH}$ = 122 Hz), which indicates that even at reduced temperatures the dominant mode of benzyl coordination in solution is likely via η^1-interactions.

Diiodide **1a** can also be reacted with $LiCH_2SiMe_2Ph$ to form bis-alkyl **3a**, and here the sizable alkyl groups preclude THF coordination. The solid-state structure of **3a** is shown in Figure 3 and is a member of a rare class[2i] of four-coordinate yttrium bis-alkyl complexes unsupported by multihapto or agostic binding. The geometry at yttrium is only slightly distorted from

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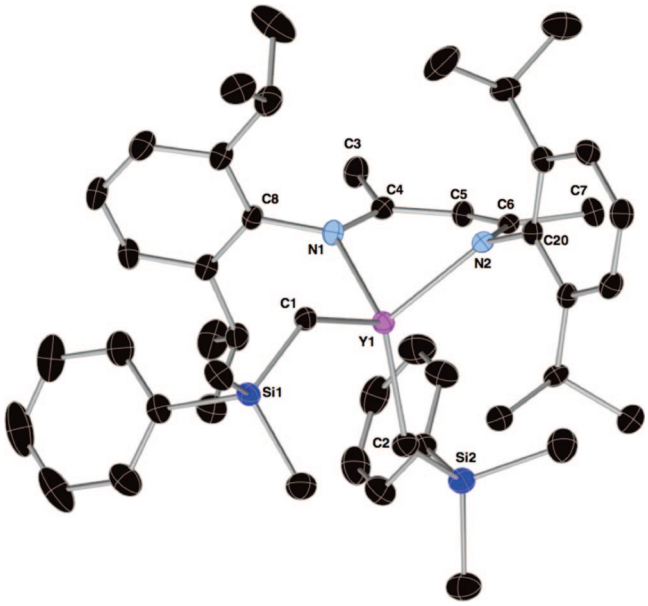

Figure 3. Solid-state structure of **3a** shown as 50% ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Y(1)−N(1), 2.272(2); Y(1)−N(2), 2.274(2); Y(1)−C(1), 2.365(3); Y(1)−C(2), 2.396(3); Y(1)−N_2C_3 plane, 1.240(4). Selected bond angles (deg): C(1)−Y(1)−C(2), 116.01(10); N(1)−Y(1)−C(1), 104.15(10); N(1)−Y(1)−C(2), 117.00(10); N(2)−Y(1)−C(1), 109.56(10); N(2)−Y(1)−C(2), 119.07(10); N(1)−Y(1)−N(2), 86.13(9); Y(1)−C(1)−Si(1), 129.46(16).

tetrahedral, and there is no evidence of any β-Si−C interaction, as indicated by the ^{29}Si NMR resonance at −7.2 ppm;[21] furthermore, the closest of the β-Si−C contacts, Y(1)−C(33), is 4.241(4) Å, and this is too long to be considered for any electronic stabilization.

Although the β-diketiminato ligand can potentially donate up to 10 electrons to the metal center, according to DFT investigations by Tolman and Solomon,[22] most of the bonding interactions take place through in-plane σ-bonding via the nitrogen lone pairs. Although examples of further donation from the ligand backbone in an κ^3-manner are known for Ti and Zr,[23] as well as Cr[24] complexes, these manifest in significant puckering of the backbone carbon (C5) toward the metal. While

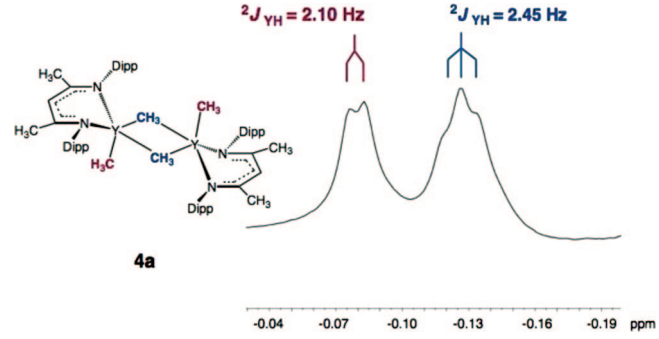

Figure 4. Partial ^{1}H NMR spectra of **4a** (300 MHz, 243 K) in d_8-toluene depicting the Y−CH_2 region.

in **3a** the yttrium atom sits 1.240(4) Å out of the ligand plane, the nearly planar configuration of the N−C−C−C-N ligand backbone and the lack of puckering of C(5) toward the metal suggests that σ-donation from N(1) and N(2) is the only significant electronic contribution from the ligand. This is in agreement with the analysis of known β-diketiminato scandium complexes,[11a] and thus in these yttrium complexes the positioning of the metal outside of the ligand plane is instead driven by steric interactions of the *N*-aryl groups with the alkyl substituents.

Although bis-alkyl **3b** was observed when **1b** was reacted with 2 equiv of $LiCH_2SiMe_2Ph$ on the NMR scale, it was not isolable upon scale-up due to its rapid decomposition via metalative decay (*vida infra*), which is driven by the increased steric congestion imposed by the ligand.[11a,25,26]

Diiodide complexes **1** have also been alkylated with methyl potassium in order to generate yttrium dimethyl complexes **4** (Scheme 1). Although solid-state structural analyses of **4** have yet to be obtained, the solution NMR studies (^{1}H and ^{13}C NMR) presented herein, along with elemental analysis, corroborate the proposed structures of both **4a** and **4b**.

Variable-temperature ^{1}H NMR experiments revealed that **4a** is dimeric, as the broad Y−CH_3 resonance at −0.12 ppm splits into one doublet ($^2J_{YH}$ = 2.10 Hz) and one triplet ($^2J_{YH}$ = 2.45 Hz) at 243 K, indicating that there are two terminal methyl groups and two bridging methyl groups within the dimer, respectively (see Figure 4). This dimeric structure again brings to light the ligand scaffold's steric influence on the molecular structure. Although THF coordination is precluded in **4a**, unlike in **2a**, the open coordination sphere around the metal center (along with the relatively smaller methyl functionality) facilitates dimerization. Interestingly, even at low temperatures, only one isomer of dimer **4a** is observed in solution, which contrasts the behavior observed in dimeric β-diketiminato scandium tellurolates, where *endo-endo*, *endo-exo*, and *exo-endo* dimeric isomers were characterized in solution.[27] While it appears that **4a** exists as only one isomer, it is also possible that ligand-flip to exchange isomers is still facile in the temperature regime monitored.

At room temperature, dimethyl complex **4b** exhibits a broad resonance at −0.37 ppm for the Y−CH_3 protons, and this signal does not sharpen even as the temperature is lowered to −30 °C, and the ^{13}C NMR spectrum at this temperature also reveals a broad peak for Y−*C*H_3. With this ambiguous NMR data and lack of X-ray analysis, the monomeric nature of **4b** cannot be confirmed; however, the high solubility of this complex at room

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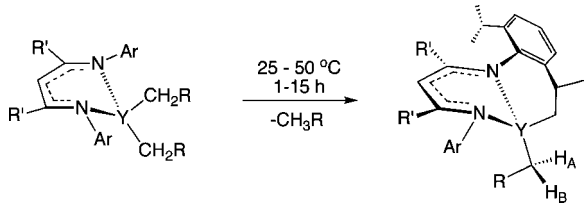
Scheme 2



temperature and its propensity to metalation support the assignment that the structure is indeed monomeric.

While this new family of yttrium bis-alkyl complexes exhibits moderate thermal stability in aromatic solvents, they are susceptible to intramolecular metalative alkane elimination whereby one alkyl moiety is lost via σ-bond metathesis with one of the C−H bonds of the *N*-aryl isopropyl methyl groups, producing a C_1 symmetric yttrium alkyl product with a tridentate ligand structure (Scheme 2). This mode of clean decomposition is a well-documented process for β-diketiminato scandium complexes,[10a] although the yttrium complexes decompose more readily.

For example, while **3a** remains largely unaffected (5% metalation) overnight at room temperature in solution, at elevated temperatures it cleanly eliminates Me_3SiPh to form **5a**. The dimeric structure of metalate **5a** (Figure 5) is unique among β-diketiminato cyclometalated species. Intramolecular C−H activation occurs at one of the ^{i}Pr-CH_3 *N*-aryl groups, and the resulting *exo* methylene group bridges two yttrium centers. The "intermolecular" Y(1)−C(28′) bond length (2.474(2) Å) is shorter than the intramolecular bond distance, where Y(1)−C(28) is 2.573(2) Å. While this is longer than the Y(1)−C(1) bond at 2.374(2) Å, they are still within the reasonable bonding range for this type of molecule. Within the Y(1)−C(28)−Y(1′)−C(28′) metallacyle, the C−Y−C bond angle is 91.86(7)°, while the Y−C−Y bond angle is 88.13(7)°. Looking at the asymmetric unit of the **5a** dimer, Figure 5, the large open face at the metal center reveals the propensity for this metalated product to dimerize.

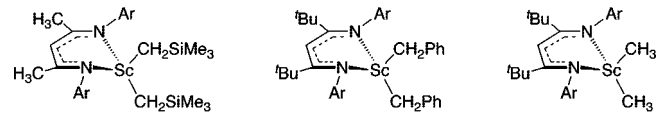
The ^{1}H NMR spectrum of **5a** in d_8-THF (where the dimeric structure has been disrupted) reveals the C_1 symmetry of this molecule (Figure S10); four distinct ^{i}Pr-methine septet signals are observed, along with seven ^{i}Pr-methyl doublet resonances. The now diastereotopic protons, H_A and H_B, on the remaining silylalkane moiety appear as two doublets of doublets ($^3J_{HH}$ = 11.3 Hz, $^2J_{YH}$ = 3.6 Hz), while the Y−CH_2CHCH_3 resonances appear as multiplets at 0.25 and −0.24 ppm. Further indication of the monomeric asymmetric structure is found in the ^{13}C NMR spectrum of **5a**, where the newly formed methylene carbon resonance is split into a doublet ($^1J_{YC}$ = 47 Hz) rather than a triplet.

Similar to known organoscandium β-diketiminato complexes, the yttrium compounds described here exhibit metalation rates that are dependent on both ligand bulk and alkyl group. Specifically, the **b** series, such as **2b** and **4b**, exhibit moderate metalation rates at room temperature, while **3a** is more robust under these conditions and requires heating to reach a similar rate of metalation (Table 1). Other complexes of the **a** series do not cleanly eliminate alkane to produce one metalate product, although they do decompose at elevated temperatures. It is also of note that the yttrium complexes described above undergo metalative alkane elimination more rapidly than known organoscandium β-diketiminate complexes, again owing to the larger metal ionic radius.

Despite the susceptibility of **2**−**4** to metalation or decomposition at elevated temperatures, these bis-alkyls are nevertheless isolable as solids that can be stored indefinitely at −35 °C. With these complexes in hand, our attention turned to investigating the activation of these bis-alkyl complexes in hopes of preparing well-characterized cationic yttrium alkyl complexes.

Table 1. Half-Lives and k_{obsd}(calculated) for Comparable Metalation Reactions

Ar = 2,6-^{i}PrC$_6$H$_3$



$L_{Me}Sc(CH_2SiMe_3)_2$ $L_{tBu}Sc(CH_2Ph)_2$ $L_{tBu}Sc(CH_3)_2$

complex	temperature (K)	$t_{1/2}$ (h)	k_{obsd} (s^{-1})
3a	320	7.33	$1.89(4) \times 10^{-3}$
2b	298	6.90	$1.98(4) \times 10^{-3}$
4b	298	0.28	$4.90(2) \times 10^{-2}$
$L_{Me}Sc(CH_2SiMe_3)_2$	377	5.46	$2.54(2) \times 10^{-3}$
$L_{tBu}Sc(CH_2Ph)_2$	333	11.7	1.65×10^{-5}
$L_{tBu}Sc(CH_3)_2$	333	0.53	3.59×10^{-4}

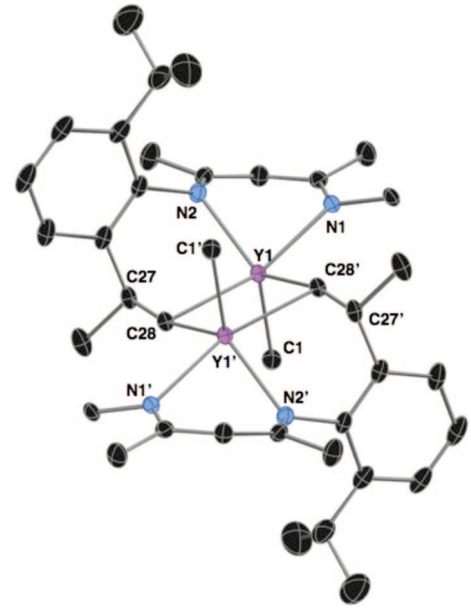


Figure 5. Solid-state structure of **5a** shown as 50% ellipsoids. Hydrogen atoms, noncyclometalated *N*-aryl groups, and −$SiMe_2$Ph fragments are removed for clarity. Selected bond lengths (Å): Y(1)−N(1), 2.3756(19); Y(1)−N(2), 2.2960(19); Y(1)−C(1), 2.374(2); Y(1)−C(28), 2.573(2); Y(1)−C(28′), 2.474(2). Selected bond angles (deg): N(1)−Y(1)−N(2), 80.46(7); N(1)−Y(1)−C(1), 106.13(8); N(2)−Y(1)−C(1), 127.90(8); N(1)−Y(1)−C(28), 163.34-(7); N(1)−Y(1)−C(28′), 87.66(7); N(2)−Y(1)−C(28), 86.14(7); N(2)−Y(1)−C(28), 124.54(8); Y(1)−C(1)−Si(1), 137.77(13).

Cationic Yttrium Alkyl Complexes. Reactions of neutral bis-alkyls **2**−**4** with typical protonolysis and alkide abstraction reagents were investigated in order to study the potential for isolating monomeric yttrium alkyl cations. Reaction of **3a** with 1 equiv of the Brønstead acid [$NHMe_2Ph$][$B(C_6F_5)_4$] in toluene results in the formation of an orange oil. However, when the reaction was performed in bromobenzene, the clean formation of ion pair **6a** was observed, along with free silane, CH_3SiPh (Scheme 3). Although there are a number of known cationic group 4 complexes that coordinate the NMe_2Ph base upon reaction with this activator (Table 4),[28] typical coordination is through a nitrogen-based dative interaction. In the case of **6a**, however, the significant upfield shift of the *ortho*- and *para*-phenyl resonances, as observed in the ^{1}H NMR spectrum (H_{para}

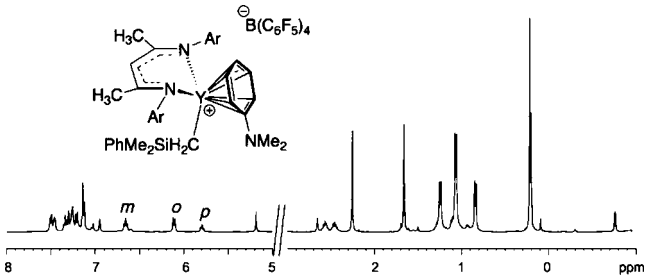
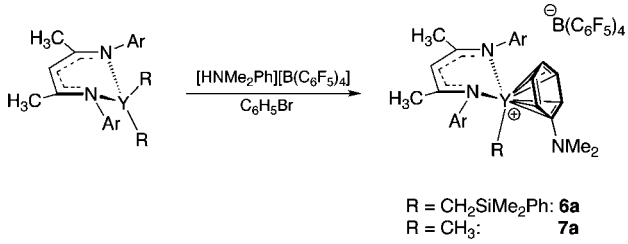


Figure 6. 400 MHz ^{1}H NMR spectrum of **6a** in d_5-bromobenzene at 298 K.

Scheme 3



= 5.79 ppm, H_{ortho} = 6.11 ppm), relative to free aniline (H_{para} = 6.74 ppm, H_{ortho} = 6.60 ppm), is instead suggestive of η^6-arene coordination of aniline (Figure 6). Similar reactivity was observed when **4a** was reacted with $[HNMe_2Ph][B(C_6F_5)_4]$, producing metal cation **7a**. To date there has only been one other report of a cationic metal complex with η^6-coordinated dimethylaniline.[29] However, recent reports of scandium methyl cations that coordinate aromatic solvent molecules with η^6-hapticity,[30] along with the identification of a dinuclear yttrium η^6-biphenyl complex,[31] make the postulated structure of **6a** plausible.[32]

Although crystals of **6a** and **7a** suitable for X-ray diffraction were not obtained, extensive spectroscopic characterization provides further evidence for arene binding. For example, a 2D ROESY NMR experiment was utilized to analyze any relevant NOE in **6a** and **7a** between the ligand and the NMe_2Ph moiety. The spectrum of **7a** reveals distinct cross-peaks between each of the *ortho*-, *meta*-, and *para*-hydrogens of the coordinated NMe_2Ph moiety and the ^{i}Pr-CH_3 groups from the ligand (Figure 7). These correlations indicate the close coordination of the arene, and assuming that the NMe_2Ph occupies the less congested *exo* position (in agreement with previous work investigating mixed bis-alkyl scandium complexes),[11a] the ROESY NMR spectrum suggests that the NMe_2 group is oriented downward and out away from the ligand, with the *para*-hydrogens pointed up, above the ligand plane.

As further proof of the η^6-arene coordination of NMe_2Ph in **6a**, bis-alkyl **3a** was treated with $[^{15}NHMe_2Ph][B(C_6F_5)_4]$. Literature precedent exists for the observation of one-bond coupling between ^{89}Y and ^{15}N (2−16 Hz),[33] but the reaction of **3a** with labeled activator exhibits a singlet in the ^{15}N NMR spectrum at 75.4 ppm (free aniline at 45.3 ppm) with $\nu_{1/2}$ = 3.2 Hz, which suggests that there is no direct one-bond dative interaction between the yttrium metal and the aniline nitrogen. Although the arene ^{13}C NMR chemical shifts of the NMe_2Ph moiety are not unusually upfield (C_{meta} = 131.8 ppm, C_{para} = 112.1 ppm, C_{ortho} = 110.6 ppm) and appear as singlets, literature examples of this η^6-arene binding in d^0 metal complexes do not exhibit any indicative changes in ^{13}C chemical shift.[29]

Previous reports of scandium alkyl cations describe exchange between various arene moieties, where more electron-rich arenes exhibit preferential binding.[28] While **6a** and **7a** did not exhibit exchange with other arenes, such as bromobenzene and toluene, there was observable exchange between free and coordinated aniline, as determined by 2D EXSY spectroscopy.

Although cations **6a** and **7a** exhibit remarkable thermal stability, with metalation rates that are slower that those of the parent neutral bis-alkyls, attempts to generate stable yttrium cations of the **b** series were largely unsuccessful. Treatment of dibenzyl **2b** with $B(C_6F_5)_3$ at −40 °C led to the formation of ion pair **8**, which undergoes rapid metalation at room temperature (Scheme 4). Furthermore, reaction of **2b** and **4b** with $[CPh_3][B(C_6F_5)_3]$ at low temperatures generates cationic products that rapidly decompose above 0 °C. Once again, the bulkier *tert*-butyl ligand appears to influence the overall stability of the yttrium alkyl products. In addition, the increased stability of **6a** and **7a** suggests that the coordinated arene impedes otherwise facile reactions from taking place at the metal center.

Summary and Conclusions. The β-diketiminato ligand has been employed to prepare a series of yttrium bis-alkyl complexes. Equipped with bulky 2,6-^{i}Pr$_2$C$_6$H$_3$ *N*-aryl groups, these ligands provide an ideal scaffold for supporting these low-coordinate and electronically unsaturated compounds, similar to that observed in previously reported organoscandium chemistry. Ligand backbone substitution influences both the coordination number and the overall stability of the bis-alkyls, as observed through structure determination of many of the complexes and solution ^{1}H NMR studies. These yttrium complexes are susceptible to thermal alkane elimination according to a well-established metalation process;[11a] it is a more rapid process here than for known scandium compounds. Stable yttrium alkyl cations supported by η^6-arene coordination of *N,N*-dimethylaniline have also been prepared, and this unique binding mode has been studied spectroscopically. The coordinatively unsaturated and highly electrophilic nature of these new organoyttrium complexes makes them interesting candidates for catalytic studies, and work investigating this potential is currently underway.

Experimental Section

General Procedures. All operations were performed under a purified argon atmosphere using glovebox or vacuum-line techniques. Toluene, hexanes, and THF solvents were dried and purified by passing through activated alumina and Q5 columns.[34] Pentane and bromobenzene were dried over Na, with a benzophenone indicator. Deuterated NMR solvents were dried according to their respective standard procedures. ^{1}H, ^{13}C{^{1}H}, HMQC, ^{15}N, and ^{29}Si−^{1}H HMBC NMR experiments were performed on a Bruker

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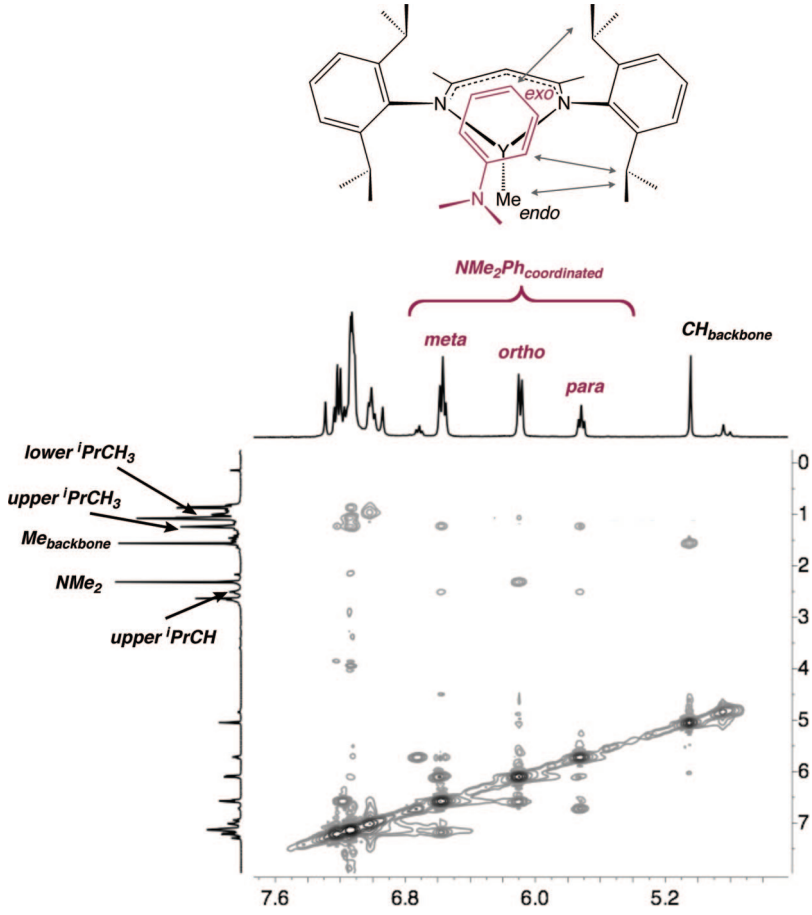
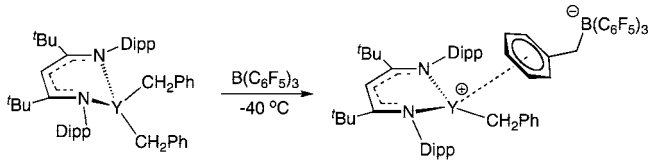


Figure 7. 2D ROESY NMR spectrum of **7a** at 298 K.

Scheme 4



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AMX-300 and WH-400, and data are given in ppm relative to solvent signals for ^{1}H and ^{13}C signals, NH_3 for ^{15}N, and $SiMe_4$ for ^{29}Si spectra. Elemental analyses were performed by Mrs. Dorothy Fox and Mr. Jianjun Li of this department. Yttrium-containing complexes were regularly found to be low in carbon, possibly as a result of metal-catalyzed silicon carbide formation, leading to incomplete combustion;[35] relevant ^{1}H and ^{13}C NMR spectra can be viewed in the Supporting Information. The ligands HL (L= ArNC(R)CHC(R)NAr, where Ar = 2,6-$^{i}Pr_2C_6H_3$ and R = CH_3, ^{t}Bu),[14] KCH_2Ph,[36] $LiCH_2SiMe_2Ph$,[15] and KCH_3[37] were prepared according to literature procedures. YI_3 was purchased from Alfa Aesar and converted to $YI_3(THF)_{3.5}$ by stirring in THF solvent at room temperature for 1 h. All other materials were obtained from Sigma-Aldrich and purified according to standard procedures.

Preparation of [ArNC(CH$_3$)CH(CH$_3$)NAr]YI$_2$(THF), 1a. A 100 mL round-bottom flask was charged with KL_{Me} (966 mg, 2.115 mmol) and $YI_3(THF)_{3.5}$ (1.527 g, 2.115 mmol), and THF (75 mL) was condensed into the flask. The solution was stirred at room temperature overnight, and then the solvent was removed *in vacuo*. The resultant yellow powder was slurried in toluene (40 mL) and filtered. The remaining KI was washed again with toluene (10 mL). Toluene was removed *in vacuo*, and the residue was triturated with pentane to give **1a** as a pale beige solid in 63% yield (1.054 mg, 1.323 mmol). ^{1}H NMR (C_7D_8): δ 7.13−6.96 (m, 6H; C_6H_3), 5.14 (s, 1H; CH), 3.51(sp, 4H; C*H*Me$_2$, $^{2}J_{H-H}$ = 6.9 Hz), 3.41 (br, 4H; OC*H*$_2$CH$_3$), 1.63 (s, 6H; NC*Me*), 1.45 (d, 12H; CH*Me*$_2$, $^{2}J_{H-H}$ = 6.9 Hz), 1.17 (ov m, 16 H; CH*Me*$_2$, OCH$_2$C*H*$_2$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 168.1 (N*C*Me), 143.6 (C_{ipso}) 143.5, 127.1, 124.7 (C_6H_3), 99.2 (d, $^{4}J_{Y-H}$ = 10.0 Hz; *C*H), 71.8 (O*C*H$_2$CH$_2$), 29.1 (*C*HMe$_2$), 25.0 (NC*Me*), 24.9 (CH*Me*$_2$), 24.8 (OCH$_2$*C*H$_2$). Anal. Calcd for $C_{33}H_{49}N_2O_2I_2Y$: C, 47.54; H, 5.92; N, 3.36. Found: C, 46.44; H, 6.27; C, 2.99.

Preparation of [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]YI$_2$, 1b. A 100 mL round-bottom flask was charged with KL_{tBu} (1.000 g, 1.848 mmol) and $YI_3(THF)_{3.5}$ (1.456 g, 2.001 mmmol), to which toluene (90 mL) was added. The reaction mixture was warmed to 90 °C and stirred for 75 min, after which it was filtered and washed with more toluene (2 × 10 mL), and the solvent was removed *in vacuo* to afford a sticky yellow solid. Hexanes (20 mL) was added, and the reaction mixture was sonicated for 5 min, filtered, and washed (3 × 10 mL). Removal of hexanes under reduced pressure gave **1b** as a bright yellow solid in 87% yield (1.345 g, 1.620 mmol). ^{1}H NMR (C_7D_8, 343 K): δ 6.99−6.69 (m, 6H; C_6H_3), 5.82 (s, 1H; C*H*), 3.05 (sp, 4H; C*H*Me$_2$, J_{HH} = 6.7 Hz), 1.44 (d, 12H, CH*Me*$_2$, J_{HH} = 6.7 Hz), 1.26 (d, 12H, CH*Me*$_2$, J_{H-H} = 6.Hz), 1.13 (s, 18H; NCC*Me*$_3$). $^{13}C\{^{1}H\}$ NMR (C_7D_8, 343K): δ 173.2 (N*C*CMe$_3$), 143.1 (C_{ipso}), 140.6, 126.9, 124.4 (C_6H_3) 88.0 (CH), 45.1 (NC*C*(CH$_3$)$_3$), 32.2 (NCC(*C*H$_3$)$_3$), 30.3 (*C*HMe$_2$), 24.0 (CH*Me*$_2$). Anal. Calcd for $C_{35}H_{53}N_2I_2Y$: C, 49.71; H, 6.32; N, 3.31. Found: C, 49.17; H, 6.44; N, 3.07.

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Preparation of [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]Y($CH_2C_6H_5$)$_2$·THF, 2a. Toluene (45 mL) was condensed into a flask charged with **1a** (240 mg, 0.301 mmol) and then warmed to room temperature. Solid $KCH_2C_6H_5$ (94 mg, 0.723 mmol) was added to the stirring solution over 30 min. The resulting solution was stirred for 1 h, during which time the color changed from orange to yellow. The solution was then filtered and toluene removed *in vacuo*. Hexanes (10 mL) was condensed into flask at −78 °C, which was then sonicated until an orange precipitate formed. The resulting orange powder was filtered and washed with another portion of hexanes (5 mL), yielding **2a** (36 mg, 0.047 mmol) in 16% yield. ^{1}H NMR (C_6D_6, 298 K): δ 7.24 (b, 6H, C_6H_3), 7.04 (t, 4H, *m*-C_6H_5, $^2J_{HH}$ = 7.5 Hz), 6.77 (d, 4H, *o*-C_6H_5, $^2J_{HH}$ = 7.5 Hz), 6.77 (t, 2H, *p*-C_6H_5, $^2J_{HH}$ = 7.5 Hz), 5.13 (s, 1H, NCC*H*), 3.19 (sp, 4H, ^{i}PrC*H*, $^2J_{HH}$ = 6.8 Hz), 3.09 (b, 4H, OCH_2), 1.96 (d, 4H, YCH_2, $^2J_{YH}$ = 2.8 Hz), 1.71 (s, 6H, NCCH_3), 1.36 (b, 4H, OCCH_2), 1.32, 1.20 (d, 24H, ^{i}PrCH_3, $^2J_{HH}$ = 6.8 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 167.6 (N*C*(CH_3)), 152.5 (BnC_{ipso}), 145.2 (NArC_{ipso}), 142.8 (NAr*C*), 130.4 (Bn*C*), 126.6 (Bn*C*), 124.7 (NAr*C*), 123.3 (NAr*C*), 118.7 (Bn*C*), 95.9 (NC*C*CN), 70.0 (OCH_2), 58.2 (d, Y*C*, $^1J_{YC}$ = 33.3 Hz), 36.0 (OC*C*H_2), 29.2 (NC(CH_3)), 25.5, 25.2 (^{i}Pr*C*).

Preparation of [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]Y($CH_2C_6H_5$)$_2$, 2b. Solid $KCH_2C_6H_5$ (56 mg, 0.430 mmol) was slowly added into a stirring solution of **1b** (174 mg, 0.210 mmol) in toluene (30 mL). The reaction mixture was stirred at room temperature for 5 h and then filtered. Solvent was removed *in vacuo*, yielding an orange-yellow solid. Pentane (15 mL) was added, and the mixture was sonicated before filtering and washing with pentane (2 × 5 mL), affording 101 mg of the desired product (0.129 mmol, 61%). ^{1}H NMR (C_7D_8, 298 K): δ 7.01−6.98 (m, 6H, −C_6H_3), 6.93, (m, 4H, *m*-C_6H_5) 6.50 (m, 6H, *o,p*-C_6H_5) 5.71 (s, 1H, NCC*H*), 2.97 (sp, 4H, C*H*Me$_2$, $^2J_{HH}$ = 6.7 Hz), 1.75 (d, 4H, YCH_2, $^2J_{YH}$ = 2.9 Hz), 1.21 (d, 12H, CH*Me*$_2$, $^2J_{HH}$ = 6.7 Hz), 1.15 (d, 12H, CH*Me*$_2$, $^2J_{HH}$ = 6.7 Hz), 1.09 (s, 18H, NCC*Me*$_3$). ^{13}C{^{1}H} NMR (C_7D_8, 298 K): 171.1 (N*C*(C(CH_3)$_3$)), 150.8 (BnC_{ipso}), 143.6 (NArC_{ipso}), 140.7 (NAr*C*), 130.5 (Bn*C*), 125.5 (NAr*C*), 123.9 (NAr*C*), 123.2 (Bn*C*), 118.5 (Bn*C*), 91.4 (NC*C*CN), 56.4 (d, Y*C*, $^1J_{YC}$ = 43.3 Hz), 44.6 (NC*C*(CH_3)$_3$), 31.9 (NCC(*C*H_3)$_3$), 28.7, 26.0, 23.9 (^{i}Pr*C*). Anal. Calcd for $C_{49}H_{63}N_2OY$: C, 76.14; H, 8.74; N, 3.62. Found: C, 75.82; H, 8.83; N, 3.53.

Preparation of [ArNC(CH_3)CHC(CH_3)NAr]Y(CH_2SiMe_2Ph)$_2$, 3a. A 100 mL round-bottom flask was charged with **1a** (700 mg, 0.879 mmol) and $LiCH_2SiMe_2Ph$ (275 mg, 1.76 mmol), and toluene (50 mL) was condensed into the flask at −78 °C. The flask was allowed to slowly warm to room temperature and stirred for 3 h. The toluene solution was filtered, and the remaining LiI was washed once with toluene (5 mL). The toluene was removed from the filtrant *in vacuo*, leaving a crude yellow solid. Hexanes (10 mL) was added, and the mixture was sonicated for 5 min, cooled to −78 °C, cold filtered, and washed with cold pentane (2 × 5 mL), yielding 253 mg of pale yellow powder (0.314 mmol, 36% yield). ^{1}H NMR (C_7D_8, 298 K): δ 7.52 (m, 4H, *m*-C_6H_5), 7.23 (m, 6H, *o,p*-C_6H_5) 7.00−6.98 (m, 6H, C_6H_3), 5.01 (s, 1H, C*H*), 3.08 (sp, 4H, C*H*Me$_2$, $^2J_{HH}$ = 6.7 Hz), 1.61 (s, 6H, NC*Me*), 1.28 (d, 12H, CH*Me*$_2$, $^2J_{HH}$ = 6.7 Hz), 1.09 (d, 12H, CH*Me*$_2$, $^2J_{HH}$ = 6.7 Hz), 0.19 (s, 12H, Si*Me*$_2$), −0.23 (d, 4H, YCH_2, $^2J_{YH}$ = 3.0 Hz). ^{13}C (C_7D_8, 298 K): δ 167.1 (N*C*CH_3), 146.7 (SiC_{ipso}), 144.8 (NArC_{ipso}), 142.7 (NAr*C*), 133.7 (SiPh*C*), 127.8 (SiPh*C*), 127.4 (SiPh*C*), 126.3, (NAr*C*), 124.5 (NAr*C*), 96.2 (NC*C*CN), 34.7 (d, YCH_2, $^1J_{YC}$ = 40.3 Hz), 28.7 (NCCH_3), 25.3 (^{i}Pr*C*H), 24.8 (^{i}Pr*C*H_3), 2.9 (Si*C*H_3). ^{29}Si NMR (C_7D_8, 298 K): δ −7.2 (^{1}H−^{29}Si HMBC). Anal. Calcd for $C_{47}H_{67}N_2Si_2Y$: C, 70.11; H, 8.39; N, 3.48. Found: C, 68.30; H, 8.52; N, 3.32.

Preparation of [ArNC(CH_3)CHC(CH_3)NAr]Y(CH_3)$_2$, 4a. THF (30 mL) was added to a 50 mL round-bottom flask containing **1a** (500 mg, 0.628 mmol) and KMe (100 mg, 1.88 mmol). The mixture was sonicated for 10 min and then stirred at room temperature for 3 h. THF was removed *in vacuo*, and the mixture was then filtered in 30 mL of toluene to remove KI. The volatiles were removed, and then the resultant off-white powder was washed with pentane (3 × 5 mL) and dried under vacuum for 1 h (0.317 mmol, 50.5% yield). ^{1}H NMR (C_6D_6, 298 K): δ 7.01−7.11 (m, 6H; C_6H_3), 5.03 (s, 1H; C*H*), 3.29 (sp, 4H; C*H*Me$_2$, $^2J_{H-H}$ = 6.8 Hz), 1.72 (s, 6H; NCCH_3), 1.36 (d, 12H; CH*Me*$_2$, $^2J_{H-H}$ = 6.8 Hz), 1.23 (d, 12H; CH*Me*$_2$, $^2J_{HH}$ = 6.8 Hz), −0.27 (br s, 6H; Y*Me*$_2$). ^{1}H NMR (C_7D_8, 240 K): δ 7.00−7.14 (m, 6H; C_6H_3), 4.85 (s, 1H; C*H*), 3.16 (sp, 4H; C*H*Me$_2$, $^2J_{H-H}$ = 6.7 Hz), 1.63 (s, 6H; NCCH_3), 1.28 (d, 12H; CH*Me*$_2$, $^2J_{H-H}$ = 6.7 Hz), 1.18 (d, 12H; CH*Me*$_2$, $^2J_{H-H}$ = 6.7 Hz), −0.09 (d, 3H; *terminal* Y−CH_3, $^2J_{Y-H}$ = 2.10 Hz), −0.13 (t, 3H; *bridging* Y−CH_3, $^2J_{Y-H}$ = 2.45 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 167.8 (N*C*(CH_3)), 147.2 (NArC_{ipso}), 142.8 (NAr*C*), 126.3 (NAr*C*), 124.8 (NAr*C*), 97.2 (*C*H), 35.3 (Y−*C*H_3, broad), 28.8 (NC(*C*H_3)), 26.0 (^{i}Pr*C*H), 25.6, 25.1 (^{i}Pr*C*H_3). Anal. Calcd for $C_{31}H_{47}N_2Y$: C, 69.38; H, 8.83; N, 5.22. Found: C, 67.00; H, 8.44; N, 5.25.

Preparation of [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]Y(CH_3)$_2$, 4b. THF (30 mL) was condensed into a 50 mL round-bottom flask charged with **1b** (300 mg, 0.360 mmol) and KMe (58 mg, 1.08 mmol). The reaction was stirred at room temperature for 1 h before the THF was removed *in vacuo*. Toluene (25 mL) was added to the flask, and the solution was filtered to remove KI before solvent was again removed *in vacuo*. Pentane (15 mL) was added to the flask, which was then sonicated for 10 min, over which time the product precipitated. The mixture was filtered, washed with pentane (5 mL), and then isolated as an orange powder in 79% yield (177 mg, 0.285 mmol), which was stored at −30 °C. ^{1}H NMR (C_7D_8, 243 K): δ 6.99 (b, 6H, C_6H_3), 5.79 (s, 1H, C*H*), 3.21(b, 4H, ^{i}PrC*H*), 1.30 (d, 24H, ^{i}PrCCH_3, $^2J_{HH}$ = 6.4 Hz), 1.12 (s, 18H, NCC(CH_3)$_3$), −0.27 (b, 6H, Y−CH_3). ^{13}C{^{1}H} NMR (C_7D_8, 243 K): δ 172.4 (N*C*C(CH_3)$_3$), 145.1 (NArC_{ipso}), 139.0 (NAr*C*), 124.0 (NAr*C*), 122.8 (NAr*C*), 94.2 (*C*H), 44.0 (NC*C*(CH_3)$_3$), 31.4 (NCC(*C*H_3)$_3$), 28.9 (^{i}Pr*C*H), 25.2 (Y*C*H_3), 24.0 (^{i}Pr*C*H_3). Anal. Calcd for $C_{31}H_{47}N_2Y$: C, 71.59; H, 9.58; N, 4.51. Found: C, 69.20; H, 9.31; N, 4.31.

Preparation of κ^3-[ArNC(CH_3)CHC(CH_3)N-^{i}Pr-C_6H_3]YCH_2-SiMe$_2$Ph, 5a. An NMR tube containing **3a** (27.5 mg, 0.042 mmol) and toluene (0.6 mL) was sealed and heated at 60 °C overnight, during which time crystals were observed to form. ^{1}H NMR (d_8-THF, 298 K): δ 7.31−7.05 (m, 11H, ArC*H*), 5.07 (s, 1H, C*H*), 3.23 (sp, 2H, C*H*Me$_2$, $^3J_{HH}$ = 7.2 Hz) 3.05 (sp, 1H, C*H*Me$_2$, $^3J_{HH}$ = 7.2 Hz), 2.94 (m, 1H, Y−CC*H*Me$_2$) 1.75 (s, 3H, NC*CH*), 1.71 (s, 3H, NC*Me*), 1.31 (d, 3H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.29 (d, 3H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.25 (d, 3H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.24 (d, 3H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.22 (d, 3H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.14 (d, 3H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.07 (d, 3H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 0.14 (dd, 1H, Y*C*H$_2$CHMe, $^2J_{HH}$ = 12.2 Hz, $^2J_{YH}$ = 2.8 Hz), −0.21 (dd, 1H, Y*C*H$_2$CHMe, $^2J_{HH}$ = 12.2 Hz, $^2J_{YH}$ = 2.5 Hz), −0.27 (s, 3H, SiCH_3), −0.32 (s, 3H, SiCH_3), −0.99 (ddd, 1H, Y−CH_2SiMe$_2$Ph, $^2J_{YH}$ = 3.6 Hz, $^2J_{HH}$ = 11.3 Hz), −1.092 (ddd, 1H, Y−CH_2SiMe$_2$Ph, $^2J_{YH}$ = 3.6 Hz, $^2J_{HH}$ = 11.3 Hz). ^{13}C{^{1}H} NMR (d_8-THF) δ 166.1, 165.8 (N*C*CH$_3$), 145.9, 145.3, 144.5, 144.0, 143.1, 141.5, 141.0 (ArC_{quat}), 134.3 (SiPhC_{ortho}), 129.7, 128.6, 127.9, 126.8, 126.0, 125.5, 125.1, 124.0, 123.6, 123.2, 122.8 (Ar*C*H), 98.0 (NC*C*CN), 58.6 (d, Y*C*H$_2$CHMe, $^1J_{YC}$ = 47.3 Hz), 38.6 (YCH$_2$*C*HMe), 29.8 (^{i}Pr*C*H), 29.7 (d, Y*C*H$_2$SiMe$_2$Ph, $^1J_{YC}$ = 42 Hz), 28.7 (^{i}Pr*C*H), 27.5, 26.1, 25.8, 25.2, 25.1, 24.8, 24.2 (^{i}Pr*C*H_3), 3.2, 2.3 (Si*C*H_3).

Preparation of {[ArNC(CH_3)CHC(CH_3)NAr]Y(CH_2SiMe_2Ph)-(NMe$_2$Ph)}{B(C_6F_5)$_4$}, 6a. An NMR tube was charged with **3a** (25 mg, 0.031 mmol) dissolved in toluene (0.4 mL). Solid [$HNMe_2Ph$]-[$B(C_6F_5)_4$] (24 mg, 0.030 mmol) was added to the solution, and the tube was shaken vigorously and then left to sit at room temperature for 10 min. The resultant orange oil was extracted from the toluene and dissolved in C_6D_5Br. ^{1}H NMR, ^{13}C NMR, and HMQC experiments were performed and confirm there is one

isomer of **6a** and that aniline remains coordinated. ^{1}H NMR (C_6D_5Br, 298 K): δ 7.26−7.14 (m, 6H; C_6H_3), 6.66 (t, 2H; *m*-$C_6H_5NMe_2$, $^3J_{HH}$ = 7.6 Hz), 6.11 (d, 2H; *o*-$C_6H_5NMe_2$, $^3J_{HH}$ = 7.6 Hz), 5.79 (t, 1H; *p*-$C_6H_5NMe_2$), 5.18 (s, 1H; C*H*), 2.57 (sp, 2H; ^{i}PrC*H*, $^3J_{HH}$ = 6.8 Hz), 2.46 (sp, 2H; ^{i}PrCH_3, $^3J_{HH}$ = 6.8 Hz), 2.26 (s, 6H; N(CH_3)$_2$), 1.66 (s, 6H; NC(CH_3)), 1.24 (d, 6H; ^{i}PrCH_3, $^3J_{HH}$ = 6.8 Hz), 1.06 (d, 12H; ^{i}PrCH_3, $^3J_{HH}$ = 6.8 Hz), 0.84 (d, 6H; ^{i}PrCH_3, $^3J_{HH}$ = 6.8 Hz), 0.20 (s, 6H; Si(CH_3)$_2$), −0.76 (d, 2H; YCH_2, $^2J_{YH}$ = 2.8 Hz). ^{13}C{^{1}H} NMR (C_6D_5Br, 298 K): δ 166.7 (N*C*CH$_3$), 150.5 (*ipso*-$C_6H_5NMe_2$), 140.4 (C_6H_3, C_{ipso}), 139.8, 139.2 (C_6H_3), 131.8 (*m*-$C_6H_5NMe_2$), 127.4, 126.5, 123.3 (C_6H_3), 112.1 (*p*-$C_6H_5NMe_2$), 110.6 (*o*-$C_6H_5NMe_2$), 91.9 (*C*H), 37.5 ($C_6H_5N(CH_3)_2$), 35.4 (d, Y−*C*H$_3$, $^1J_{YC}$ = 37.8 Hz), 27.2, 26.8 (^{i}Pr*C*H), 24.5, 23.5, 23.0, 21.7 (^{i}Pr*C*H$_3$), −2.5 (Si*Me*$_2$Ph). ^{19}F NMR (C_6D_5Br, 298 K): δ −131.9 (d, $^3J_{FF}$ = 19 Hz, F_{ortho}), −162.1 (t, $^3J_{FF}$ = 19 Hz, F_{meta}), −166.1 (t, $^3J_{FF}$ = 19 Hz, F_{para}). ^{11}B NMR (C_6D_5Br, 298 K): δ −16.5.

Preparation of {[ArNC(CH$_3$)CHC(CH$_3$)NAr]Y(CH$_3$)(NMe$_2$Ph)}{B(C$_6$F$_5$)$_4$}, 7a. An NMR tube was charged with **4a** (15 mg, 0.031 mmoles) and [HNMe$_2$Ph][B(C_6F_5)$_4$] (19 mg, 0.030 mmol), to which C_6D_5Br was added. The tube was sonicated for 10 min and then left to sit at room temperature for 10 min. ^{1}H NMR (C_6D_5Br, 298 K): δ 7.29−7.01 (m, 6H; NAr*C*), 6.56 (t, 2H; *m*-$C_6H_5NMe_2$, $^3J_{HH}$ = 7.2 Hz), 6.08 (d, 2H; *o*-$C_6H_5NMe_2$, $^3J_{HH}$ = 7.2 Hz), 5.71 (t, 1H; *p*-$C_6H_5NMe_2$, $^3J_{HH}$ = 7.2 Hz), 5.04 (s, 1H; C*H*), 2.67 (sp, 2H; C*H*CH$_3$, $^3J_{HH}$ = 7.2 Hz), 2.51 (sp, 2H; C*H*CH$_3$, $^3J_{HH}$ = 7.2 Hz), 2.31 (s, 6H; NCH_3), 1.56 (s, 6H; NCCH_3), 1.23 (d, 6H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.08 (d, 6H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), 1.07 (d, 6H; CHCH_3, $^3J_{HH}$ = 7.2 Hz), −0.63 (d, 3H; YCH_3 = $^2J_{YH}$ = 2.0 Hz). ^{13}C{^{1}H} NMR (C_6D_5Br, 298 K, C_6F_5 resonances not reported): δ 168.5 (N*C*CH$_3$), 151.6 (*ipso*-$C_6H_5NMe_2$), 143.5 (NArC_{ipso}), 141.5, 139.3 (NAr*C*), 133.1 (*m*-$C_6H_5NMe_2$), 128.1, 125.1, 124.6 (C_6H_3), 113.0 (*p*-$C_6H_5NMe_2$), 112.0 (*o*-$C_6H_5NMe_2$), 96.9 (NC*C*CN), 39.0 ((*C*H$_3$)$_2$NPh), 29.2 (NC*C*H$_3$), 28.4 (d, Y−*C*H$_3$, $^1J_{YC}$ = 33.6 Hz), 28.2, 26.2 (^{i}Pr*C*H), 24.3, 24.2, 24.08, 23.1 (^{i}Pr*C*H$_3$). ^{19}F NMR (C_6D_5Br, 298 K): δ −131.4 (d, $^3J_{FF}$ = 22.6 Hz, F_{ortho}), −161.9 (t, $^3J_{FF}$ = 22.6 Hz, F_{meta}), −165.7 (t, $^3J_{FF}$ = 22.6 Hz, F_{para}). ^{11}B NMR (C_6D_5Br, 298 K): δ −16.5.

Synthesis of {[ArNC(*t*Bu)CHC(*t*Bu)NAr]Y(CH$_2$Ph)}{PhCH$_2$B(C$_6$F$_5$)$_3$}, 8. A 1 dram vial was charged with **2b** (50 mg, 0.0647 mmol) and hexane (2.0 mL). In a second vial, B(C_6F_5)$_3$ (33 mg, 0.647 mmol) was suspended in hexane (2 mL), and both vials were cooled to −32 °C in the glovebox freezer. After 30 min, the B(C_6F_5)$_3$ mixture was added dropwise to the stirring solution of **2b**. The orange precipitate of **8** immediately precipitated, and the solution was stored overnight at −32 °C to allow the solid to settle. The supernatant was removed via syringe, and the solid was dried briefly under vacuum to afford an orange solid of **8** (52 mg, 0.0401 mmol, 62% yield). ^{1}H NMR (C_6D_5Br/C_7D_8, 223 K): δ 7.18−6.98 (m, 14H; C_6H_3, $C_6H_5CH_2$), 6.18 (b, 3H; *m,p*-$C_6H_5CH_2B$), 5.50 (s, 1H; C*H*), 3.38 (b, 2H; B−CH_2), 2.36 (sp, 2H; ^{i}PrC*H*), 2.20 (sp, 2H; ^{i}PrC*H*), 1.54 (b, 2H; Y−CH_2), 1.13 (d, 6H; ^{i}PrCH_3), 1.04 (d, 6H; ^{i}PrCH_3), 0.96 (d, 6H; ^{i}PrCH_3), 0.94 (d, 6H; ^{i}PrCH_3), 0.87 (s, 18H; NCC(CH_3)). ^{13}C{^{1}H} NMR (C_6D_5Br/C_7D_8, 223 K): δ 175.4 (N*C*(CH$_3$)), 149.3 (*ipso*-C_6H_3), 147.0 (*ipso*-$C_6H_5CH_2Y$), 143.4 (*ipso*-$C_6H_5CH_2B$), 139.8, 139.5, 139.0, 135.7, 133.6, 132.2, 130.3, 129.8, 125.8, 124.4 (C_6H_3, $C_6H_5CH_2$), 86.1 (NC*C*H), 57.2 (b, Y−*C*H$_2$), 35.2 (B−*C*H$_2$), 33.6, 31.8 (^{i}Pr*C*H), 32.4, 31.3, (^{i}Pr*C*H$_3$), 28.8 (NC(*C*H$_3$), 25.1, 24.5. ^{19}F NMR (C_6D_5Br, 273 K): δ −131.6 (*o*-F), −165.0 (*p*-F), −167.8 (*m*-F). ^{11}B NMR (C_6D_5Br, 223 K): δ −12.7.

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Supporting Information Available: Crystallographic data for compounds **1b**, **2a**, **2b**, **3a**, and **5a**, including ORTEP diagrams and crystallographic information (CIF). ^{1}H and ^{13}C NMR spectra of **2**−**4**. ^{1}H NMR spectra of **5a**. Table of known NMe$_2$Ph-bound metal cations. This material is available free of charge via the Internet at http://pubs.acs.org.

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