β-Diketiminato Scandium Chemistry: Synthesis, Characterization, and Thermal Behavior of Primary Amido Alkyl Derivatives

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Treatment of the β-diketiminato-supported scandium dichlorides {[ArNC(R)CHC(R)NAr]-$ScCl_2$}$_n$ (Ar = 2,6-^{i}Pr$_2$-C_6H_3; R = CH_3, **1a**, *n* = 2; R = ^{t}Bu, **1b**, *n* = 1) with 1 equiv of a lithium amide reagent LiN(H)R′ (R′ = ^{t}Bu, 2,6-^{i}Pr$_2$-C_6H_3) gave scandium amido derivatives. For **1a**, use of LiN(H)^{t}Bu leads to the bis-amido derivative (**6a**) regardless of the equivalency of amide reagent employed, suggesting that facile ligand redistribution processes are operative when the ligand is the less bulky methyl-substituted example. For **1b**, mono-amido chlorides **2b** (R′ = ^{t}Bu) and **3b** (R′ = 2,6-^{i}Pr$_2$-C_6H_3) are obtained in good yields, and these compounds can be alkylated with MeLi to provide mono-amido methyl compounds **4b** (R′ = ^{t}Bu) and **5b** (R′ = 2,6-^{i}Pr$_2$-C_6H_3). All four of these compounds were characterized crystallographically. The amido ligand occupies the *exo* coordination site exclusively, and there is no evidence in solution for a diastereomer with the amido group in the *endo* site. DFT calculations suggest that there is a strong steric preference and a slight electronic bias for the amido ligand to assume the *exo* position. Thermolysis of the amido methyl complex **4b** leads to loss of CH_4 and production of a scandacylic product, **7**, formed via metalation with one of the *N*-aryl isopropyl methyl groups. This compound was characterized crystallographically. Deuterium labeling experiments suggest that **7** is produced via direct metalation and does not form via a scandium imido intermediate.

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Introduction

Imido ligands =NR play an important role in early transition metal organometallic chemistry as both spectator ligands and reactive intermediates.[3] For example, bulky imido donors have been used in an ancillary role as a Cp equivalent in group 5 and 6 metal-based olefin polymerization catalysts,[4] providing molecular fragments that are isolobal with group 4 metallocenes. Furthermore, highly reactive group 4 imido complexes, L_nM=NR, have been shown to be capable of activating C−H bonds by 1,2 addition across the M=N linkage in a remarkable reaction that both activates and functionalizes the alkane in one step.[5] Such intermediates are also implicated in catalytic cycles for the hydroamination of both allenes and alkynes by titanium- and zirconium-based catalyst precursors.[6] Extensive kinetic and experimental evidence suggests that generation of the L_nM=NR species is a critical first step in the cycle involving L_nMR_2 precursors; the imido intermediate is rapidly captured by substrate via a 2+2 cycloaddition, which is the key C−N bond forming step in the process.

Given the rich mosaic of group 4, 5, and 6 imido chemistry, it is surprising that group 3 imido chemistry is to date extremely limited. To our knowledge, no examples of discrete, monomeric compounds L_nM=NR for a group 3 metal have been prepared.[7] Recently, Hessen et al. have reported a dimeric scandium imido that implicates the intermediacy of a monomeric imido species,[8] but clearly the tendency to dimerize[9] in these very Lewis acidic complexes is a challenge to address in their preparation and in their potential competence as intermediates in catalytic cycles.

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(3) (a) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216−217*, 65. (b) Duncan, A. P.; Bergmann, R. G. *Chem. Rec.* **2002**, *2*, 431.

(4) (a) Chan, M. C. W.; Cole, J. M.; Gibson, V. C.; Howard, J. A. K.; Lehmann, C.; Poole, A.; Siemeling, U. *J. Chem. Soc., Dalton Trans.* **1998**, 103. (b) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J.; Siemeling, U.; Türk, T. *J. Chem. Soc., Dalton Trans.* **1996**, 4513. (c) Gibson, V. C. *Mod. Coord. Chem.* **2002**, 140.

(5) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705. (c) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (d) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591. (e) Wolczanski, P. T.; Bennett, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2179.

(6) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935.

(7) Emslie, D. J. H.; Piers, W. E. *Coord. Chem. Rev.* **2002**, *233−34*, 129.

(8) Beetstra, D. J.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2003**, *22*, 4372.

(9) Other related examples: (a) Gordon, J. C.; Giesbrecht, G. R.; Clark, D. L.; Hay, J.; Keogh, D. W.; Poli, R.; Scott, B. L.; Watkin, J. G.; *Organometallics* **2002**, *21*, 4726. (b) Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652.

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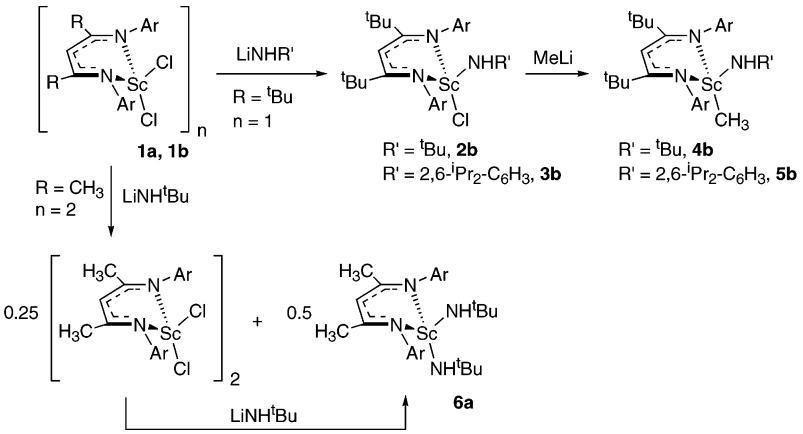
Scheme 1



Recently, we have reported a family of β-diketiminato ("nacnac")-supported organoscandium compounds [ArNC(R)CHC(R)NAr]ScR′$_2$ (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$; R = CH$_3$, series **a**, R = ^{t}Bu, series **b**; R′ = Me, Et, Bn, CH$_2$SiMe$_3$, CH$_2$CMe$_3$).[10] The bulky character of these particular nacnac ancillaries[11] allows for access to base-free scandium dichloride starting materials and bis-alkyl derivatives. We have recently observed that some of the bis-alkyl compounds are viable catalyst precursors for the intramolecular hydroamination of alkynes and alkynes.[12] While organo group 3 and lanthanide-based catalysts for this reaction have been explored in detail by Marks and co-workers, most are based on mono-alkyl or amido precursors[13] and utilize a mechanism whose foundation is the σ bond metathesis reaction.[14] Given that the bis-alkyl functionality of our catalyst precursors offers the opportunity for an imido-based mechanism similar to that seen in group 4 catalysts, we were interested in exploring the (nacnac)Sc fragment as a platform for imido chemistry.[15] Herein we report our initial investigations with this goal in mind, using a strategy pioneered by Bergman[5a,b] and Wolczanski[5c−e] in their seminal group 4 studies involving the thermolysis of primary amido methyl complexes of general formula (nacnac)Sc(CH$_3$)(NHR).

Results and Discussion

Synthetic Chemistry. The nacnac ligands employed in this study differ only in the substituent on the backbone of the ligand, one incorporating methyl groups (**a** series), the other the more bulky ^{t}Bu group (**b** series). Although the structural change is somewhat remote from the locus of coordination, ^{t}Bu-substituted ligand **b** is significantly more sterically imposing than ligand **a** since the larger ^{t}Bu groups push the *N*-aryl groups forward by 5−7° and hold them more perpendicular to the N$_2$C$_3$ ligand plane.[11] Thus, the scandium dichloride starting materials **1a** and **1b**, whose syntheses have been described previously,[10] differ in that **1a** exists as a mono-THF adduct upon initial preparation, while the more sterically congested **1b** is monomeric and THF-free. The THF can be removed from **1a**·THF under high vacuum, yielding a dimeric dichloride that is used to preclude inclusion of THF into subsequent products.[16]

Amido derivatives can be prepared from dichlorides **1** and LiNHR (R = ^{t}Bu, 2,6-^{i}Pr$_2$-C$_6$H$_3$). The steric differences between the ligands are apparent in their reactivity toward LiNH^{t}Bu (Scheme 1). **1b** reacts cleanly with 1 equiv of either lithium *tert*-butyl amide or the bulky lithium anilide LiNH-2,6-^{i}Pr$_2$C$_6$H$_3$ to give the amido-chlorides **2b** and **3b**; these can be subsequently alkylated with MeLi to give the methyl amido complexes **4b** and **5b**. While Mindiola et al. have shown that reaction between **1a**·THF and 1 equiv of LiNH-2,6-^{i}Pr$_2$C$_6$H$_3$ gives the amido chloride **3b**·THF,[17] reaction between base-free **1a** and LiNH^{t}Bu affords mixtures of the starting dichloride and the bis-amido complex **6a**. Compound **6a** can be separately prepared by using 2 equiv of LiNH^{t}Bu. Although we have not studied this reaction in detail, it appears that putative amido chloride **2a** is not stable toward ligand redistribution to **1a** and **6a**, probably due to the fact that the less sterically demanding methyl-substituted ligand **a** allows for formation of the dimeric transition states necessary for ligand exchange.

This tendency to redistribute ligands in the **a** series of compounds can be used to advantage for the preparation of the *tert*-butylamido methyl complex **4a** (Scheme 2). Equimolar mixtures of **1a** and the dimeric dimethyl complex shown[16] slowly redistribute the methyl and chloro ligands at room temperature to give pure samples of the methyl chloride complex. The process cannot be encouraged using heat, since this leads to metallative decomposition of the dimethyl complex, as reported earlier.[10] Treatment of the methyl chloride species with LiNH^{t}Bu gives the desired amido methyl derivative **4a**. Unfortunately, the thermolysis of this compound is also dominated by ligand redistribution processes; heating

(10) Hayes, P. G.; Lee, L. W. M.; Knight, L. K.; Piers, W. E.; Parvez, M.; Elsegood, M. R. J.; Clegg, W.; MacDonald, R. *Organometallics* **2001**, *20*, 2533.

(11) Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485.

(12) Lauterwasser, F.; Hayes, P. G.; Piers, W. E.; Brase, S.; Schafer, L. L. *Organometallics* **2004**, *23*, in press.

(13) Ryu, J.-S.; Li, G. Y.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12584.

(14) For a recent paper on mono-ligand bis-amido and alkyl precursors, see: Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768.

(15) These bulky β-diketiminato ligands have been used to generate monomeric group 13 imido complexes: (a) Cui, C. M.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4531. (b) Hardman, N. J.; Cui, C. M.; Roesky, H. W.; Fink, W. F.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2172.

(16) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622.

(17) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2003**, *22*, 4705.

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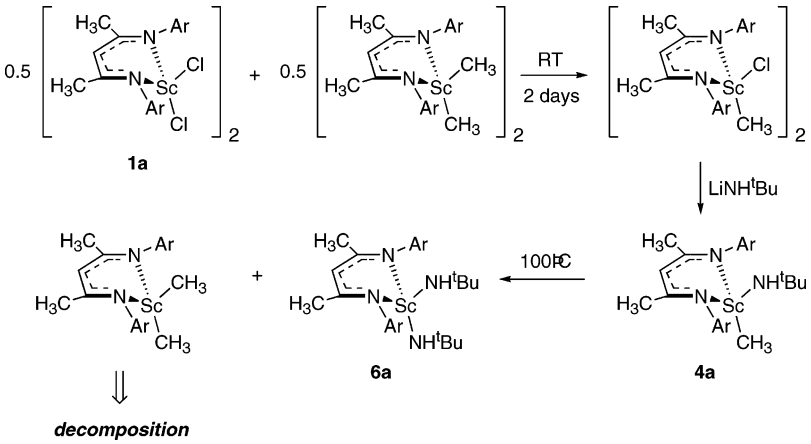
Scheme 2



to 100 °C yields samples of the bis-amido complex **6a** and the thermal decomposition products of the dimethyl species. Given the propensity of the amido complexes supported by the less sterically demanding **a** ligand to undergo ligand redistribution, we subsequently focused on the full characterization and thermolysis of the compounds **2**−**5b**, supported by the ^{t}Bu-substituted ligand system.

Solid State and Solution Characterization of 2−**5b.** All four of the amido compounds of ligand **b** reported here have been characterized crystallographically; the molecular structures of the *tert*-butyl amido complexes **2b** and **4b** are given in Figure 1, while those of the *N*-aryl amido compounds **3b** and **5b** are given in Figure 2. Selected metrical parameters for the four compounds are collected in Table 1, and crystal data and refinement details can be found in Table 3; full experimental details for all structure determinations are included as Supporting Information. Data associated with the ligand are similar to those found in a range of (nacnac)ScR_2 compounds;[10] in particular, the bite angle of the ligand defined by N(1)−Sc−N(2) is within the expected range for this ligand, and the Sc−N_{ligand} bond lengths of ∼2.1 Å are as anticipated. The Sc−N(3) distance to the amido nitrogen, however, is significantly shorter in all cases, and the distance of 1.986(2) Å for **2b** is to our knowledge the shortest Sc−N bond to date. While this might be attributable in part to the low coordination number of the compound, there is also likely a strong π-donation component to the bonding with the N(3) nitrogen in these compounds.

As for most four-coordinate complexes of scandium and other metals supported by the bulky nacnac ligand **b**, the metal dips out of the plane defined by the N_2C_3 atoms of the ligand backbone. This is primarily to allow the two other substituents on the metal to minimize interactions with the *N*-aryl isopropyl groups. For the *tert*-butyl amido compounds **2b** and **4b** the deviation of Sc from this plane (∼1.2 Å, Table 1) is more severe than that found for the *N*-aryl amido compounds (∼0.9 Å). This arrangement creates chemically distinct environments for the two coordination sites at the metal not occupied by the ligand. The *endo* position lies underneath the N_2C_3 ligand plane, while the *exo* site points away from this plane. As can be seen from Figures 1 and 2, in all four compounds **2**−**5b**, the amido ligand occupies the *exo* position, while the chloride or methyl groups are found in the *endo* coordination site.

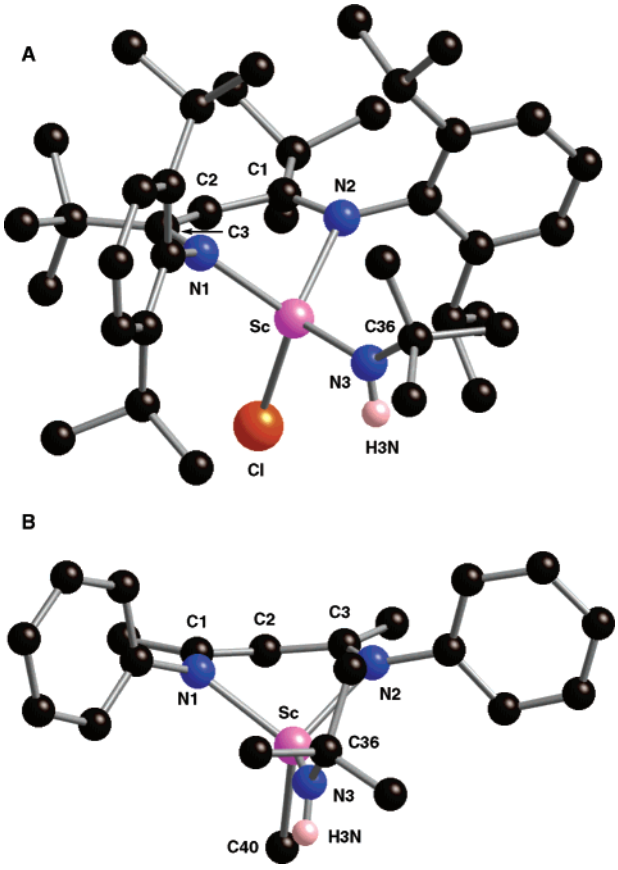


Figure 1. Crystalmaker diagrams of the *tert*-butyl amido complexes **2b** (A, above) and **4b** (B, below). In B, the *N*-aryl isopropyl groups and the methyl groups of the *tert*-butyl groups of the ligand backbone have been removed for clarity.

We have shown that the *endo* and *exo* positions are in fast exchange in solution for compounds (nacnac)-ScR_2 and that this exchange can be frozen out at low temperature on the NMR time scale.[10] Likely, this exchange takes place via a transition state of C_{2v} symmetry where the Sc atom lies in the N_2C_3 ligand plane; we thus term this exchange process the "ligand flip" mechanism. For compounds where the two ligands on Sc are different, this ligand flip process exchanges two diastereomers in which the two groups occupy different sites in each isomer. We have observed this behavior in the ion pairs formed from (Lig**b**)ScMe_2 and

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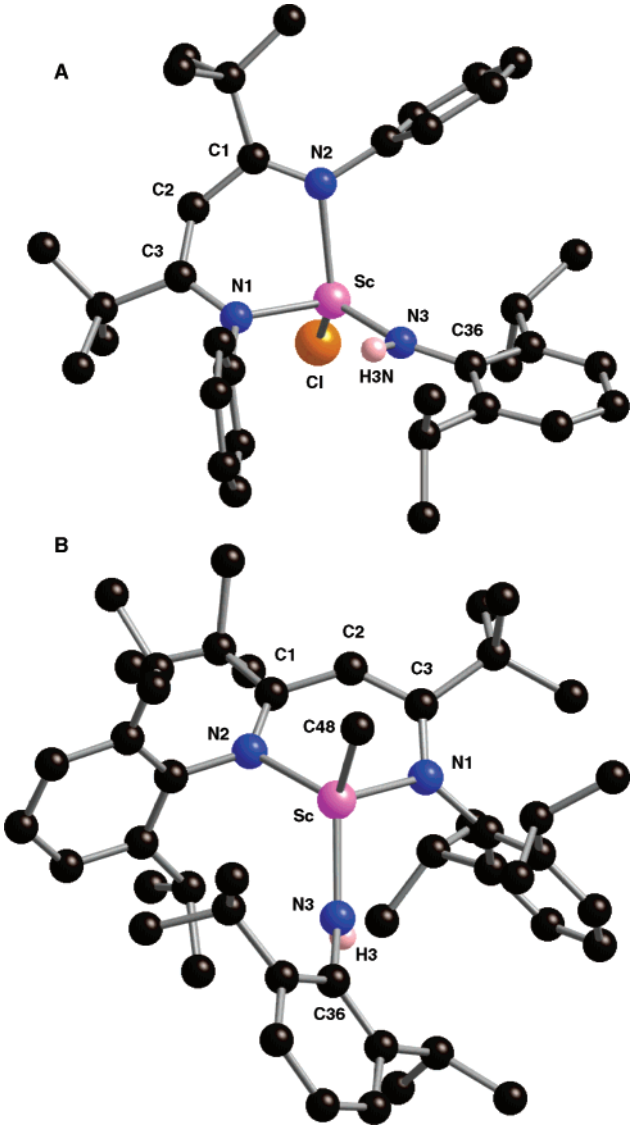


Figure 2. Crystalmaker diagrams of the 2,6-$^{i}Pr_2$-C_6H_3 anilido complexes **3b** (A, above) and **5b** (B, below). In A, the *N*-aryl isopropyl groups of the ligand have been removed for clarity.

Table 1. Selected Metrical Parameters for Scandium Mixed-Amido Compounds 2−5b

parameter	2b	4b	3b	5b
Selected Bond Distances (Å)				
Sc−N(1)	2.125(2)	2.131(2)	2.062(1)	2.097(1)
Sc−N(2)	2.115(2)	2.148(1)	2.165(1)	2.173(1)
Sc−N(3)	1.986(2)	2.000(2)	2.013(1)	2.040(1)
Sc−E[a]	2.125(2)	2.229(2)	2.3692(5)	2.212(2)
N_2C_3 plane−Sc	1.265(3)	1.207(2)	0.923(2)	0.920(2)
Selected Bond Angles (deg)				
N(1)−Sc−N(2)	92.82(8)	93.40(6)	91.90(5)	91.55(5)
C(1)−N(2)−C(24)	126.3(2)	126.2(2)	126.6(1)	126.0(1)
C(3)−N(1)−C(12)	127.6(2)	126.0(1)	124.8(1)	124.4(1)
Sc−N(3)−C(36)	140.3(2)	139.4(2)	149.5(1)	144.8(1)
E−Sc−N(3)	105.60(8)	108.72(9)	125.63(4)	119.68(8)
Selected Torsion Angle (deg)				
E[a]−Sc−N(3)−C(36)	179.3(3)	175.1(2)	49.8(2)	16.8(2)

[a] E = Cl for **2b** and **3b**, C(40) for **4b**, and C(48) for **5b**.

$B(C_6F_5)_3$, where two isomers are observed in an approximately 2:1 ratio at low temperature,[18] as well as some telluride and tellurolate derivatives.[19]

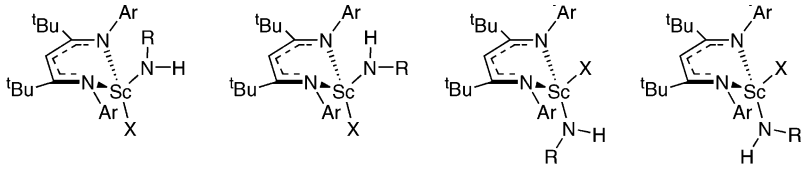
For compounds **2**−**5b**, which should also exhibit this sort of behavior, only one set of signals is observed in the ^{1}H NMR spectrum down to 185 K and up to 363 K, suggesting that the *exo*-amido isomer found in the solid state is significantly more stable than the *endo* isomer or that the barrier to exchange of the two diastereomers is high enough to make exchange on the NMR time scale slow. The latter explanation is unlikely, given that a ligand flip exchange of the two *tert*-butyl amido groups in **6a** is quite readily frozen out at 195 K ($\Delta G^{\ddagger} = 13.6$ kcal mol^{-1}), indicating that the presence of π donor amido ligands does not increase the barrier to ligand flipping significantly.[20] However, the fact that the mixed alkyl species [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]ScCH$_2$SiMe$_3$-(CH$_3$), which is sterically similar to **4b**, exhibits exchanging diastereomers, present in a 2:1 ratio at 185 K,[21] suggests that the π donating amido ligand may be playing a role in stabilizing the *exo*-amido isomer over the isomer with the amido group in the *endo* position. To probe this question further, a DFT computational study was conducted.

Using coordinates obtained from the X-ray structure of **2b**, the relative energies and Sc−N bond orders were calculated for the *exo* and *endo* isomers of (Lig**b**)ScCl-(NHR) (Table 2). To minimize steric factors, calculations for R = H were performed in addition to the genuine molecule where R = ^{t}Bu. In addition, for the calculations on the isomers of **2b**, the orientation of the *tert*-butyl group relative to Sc−Cl was varied. In the crystal structure, the *tert*-butyl group is located *trans* to the Sc−Cl vector (Cl−Sc−N(3)−C(36) = 179.3(3)°), comprising the *exo-trans* isomer. The other permutations are depicted in the heading of Table 2. Note that as the amido substitutent gets larger, deviations from pure *trans* and *cis* orientations are quite severe, as demonstrated by the E−Sc−N(3)−C(36) torsion angles of 49.8-(2)° and 16.8(2)° for **3b** and **5b**, respectively. Therefore, calculations were not performed on models of these compounds.

As can be seen in Table 2, in the sterically unencumbered NH_2 compounds, the *exo* isomer is calculated to be more stable than the *endo* isomer by 3.0 kcal mol^{-1}. This appears to be primarily due to an increased bond order between Sc and N in comparison to the *endo* structure. In general, the bond order between Sc and the amido nitrogen is indicative of some multiple bond character, while the bonds to the nacnac nitrogens more closely approximate Sc−N single bonds. This is in keeping with the observed differences in bond lengths to the two types of nitrogens. A similar but less pronounced trend of higher bond orders for the *exo* isomers is observed in the calculated structures for the *tert*-butyl amido compounds. In both the *trans* and *cis* oriented *exo* isomers, the bond order to the amido nitrogen is slightly higher than that observed in the corresponding *endo* isomers. However, in these compounds, steric factors play a much larger role in determining the relative energies of the isomers. The *exo-trans* species, corresponding to the solid state struc-

(18) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132.
(19) Knight, L. K.; Piers, W. E.; McDonald, R. *Chem. Eur. J.* **2000**, *6*, 4322.
(20) The barrier to ligand flip in (Lig**a**)Sc(CH$_2$CMe$_3$)$_2$ is 11.4 kcal mol^{-1}; see ref 10.
(21) Hayes, P. G.; Piers, W. E., unpublished results.

Table 2. Calculated Bond Orders and Relative Energies of Various Amide Chloride Compounds of Ligand b



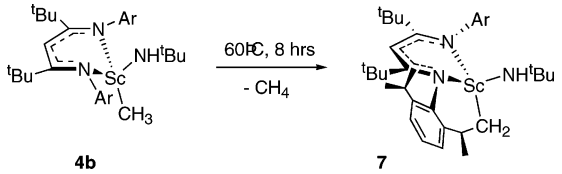
exo-trans ***exo-cis*** ***endo-trans*** ***endo-cis***

compound	Sc−N(1)	Sc−N(2)	Sc−N(3)	$\Delta E°_{rel}$ (kcal/mol)
L^{b}Sc(NHH)Cl-*exo*	0.84	0.82	1.35	0.0
L^{b}Sc(NHH)Cl-*endo*	0.83	0.81	1.30	3.0
L^{b}Sc(NH^{t}Bu)Cl-*exo-trans*	0.81	0.83	1.27	0.0
L^{b}Sc(NH^{t}Bu)Cl-*exo-cis*	0.82	0.83	1.29	25.9
L^{b}Sc(NH^{t}Bu)Cl-*endo-trans*	0.81	0.83	1.24	72.4
L^{b}Sc(NH^{t}Bu)Cl-*endo-cis*	0.81	0.83	1.24	11.1

Table 3. Summary of Data Collection and Structure Refinement Details for Complexes

	2b	**3b**	**4b**	**5b**	**7**
formula	$C_{39}H_{63}N_3ScCl$	$C_{50}H_{78}N_3ScCl$	$C_{40}H_{66}N_3Sc$	$C_{48}H_{74}N_3Sc$	$C_{39}H_{62}N_3Sc$
fw	654.33	801.56	633.92	738.06	617.88
cryst syst	monoclinic	triclinic	triclinic	orthorhombic	monoclinic
a, Å	18.3145(15)	10.9568(5)	11.2559(8)	13.5396(2)	12.147(3)
b, Å	17.6376(15)	12.9352(6)	12.4490(9)	18.1218(2)	17.490(5)
c, Å	12.6483(11)	19.6028(9)	15.4106(11)	18.5560(2)	18.028(6)
α, deg		77.8167(9)	88.2825(14)		
β, deg	105.0938(19)	73.7643(9)	89.3523(15)		96.116(12)
γ, deg		65.6747(9)	65.4512(15)		
V, Å^3	3944.7(6)	2416.02(19)	1963.3(2)	4552.94(10)	3808.3(19)
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$
Z	4	2	2	4	4
d_{calc}, mg m^{-3}	1.102	1.102	1.072	1.077	1.078
μ, mm^{-1}	0.282	0.242	0.216	0.195	0.221
R1	0.0553	0.0396	0.0481	0.045	0.0459
wR2	0.1662	0.1098	0.1352	0.105	0.1098
gof	1.171	1.020	1.024	1.02	1.033

Scheme 3



4b **7**

ture, was found to be the lowest in energy, with the other orientations of the *tert*-butyl amido ligand significantly destabilized relative to this isomer. Thus, for the substituted *tert*-butyl amido derivative, there is both an electronic and a steric preference for the amido ligand to occupy the *exo* coordination site, and equilibration to the *endo-trans* isomer via a ligand flip mechanism is not thermodynamically favored.

Thermolysis of Methyl Amido Compound 4b. The *exo-trans* geometry of **4b** seems poised to eliminate methane in chemistry analogous to that reported by Bergman[5a,b] and Wolczanski,[5c−e] and generation of a scandium imido complex. Heating NMR scale samples of **4b** in C_6D_6 or C_7D_8 to 60 °C indeed led to loss of CH_4 over the course of several hours, cleanly producing compound, **7**, whose ^{1}H NMR spectrum was consistent with metalation of one of the ^{i}Pr methyl groups of the *N*-aryl nacnac substitutents (Scheme 3). This process is the primary thermal decomposition pathway for the neutral dialkyl compounds $LScR_2$;[10] formation of **7** is qualitatively much slower than the metalation processes in $LScR_2$. However, a characteristic pattern of four methine multiplets and seven methyl doublets for the ^{i}Pr groups is clearly indicative of the outcome of this reaction. Furthermore, two doublets of doublets at 0.95 and 0.44 ppm ($^2J_{HH}$ = 12.4 Hz; $^3J_{HH}$ = 5.4 Hz) for the diastereotopic protons of the metalated methyl group are a hallmark of these metalated compounds. The structure of **7** was also confirmed by X-ray crystallography, and two views of the molecule are given in Figure 3, along with selected metrical data. While some disorder was present in the molecular core, it was successfully modeled (see Supporting Information) and the metalated nature of the compound is clearly exposed. From the front view of the molecule shown in Figure 3A, it is clear that a consequence of the metalation is a more "upright" set of *N*-aryl rings, which allows the Sc atom to slip back into the ligand's coordination plane (deviation of the Sc atom from the N_2C_3 plane is only 0.438(8) Å). Notably, the amido group again occupies the *exo* coordination site, and the Sc−C(35) distance of 2.251(4) Å is only slightly longer than the analogous bonds in **4b** and **5b**.

Two potential mechanisms for the formation of **7** are depicted in Scheme 4. One involves direct metalation via σ bond metathesis between the C−H bond of the ^{i}Pr group and the Sc−CH_3 bond,[22] while the other invokes the intermediacy of a reactive scandium imido species. Mindiola has reasonably speculated on the involvement of such an imido species to rationalize some deuterium scrambling processes in the related compound (Lig**a**)-

(22) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804.

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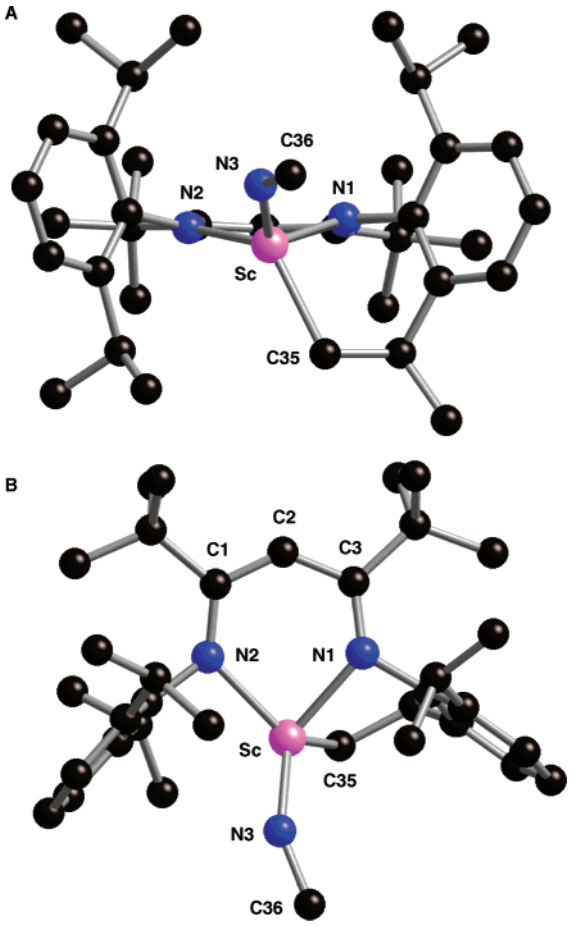


Figure 3. Crystalmaker diagrams of two views of the metalated amido complex **7**. Selected bond lengths (Å): Sc−N(1), 2.149(3); Sc−N(2), 2.140(3); Sc−N(3), 2.016(2); Sc−C(35), 2.251(4); N_2C_3 plane−Sc, 0.438(8). Selected bond angles (deg): N(1)−Sc−N(2), 83.6(1); C(1)−N(2)−C(24), 130.6(3); C(3)−N(1)−C(12), 127.8(2); Sc−N(3)−C(36), 143.5-(2); C(35)−Sc−N(3), 116.0(1). Selected torsion angles (deg): C(3)−N(1)−C(12)−C(13), 91.0(6); C(1)−N(2)−C(24)−C(25), 116.0(4); C(3)−N(1)−C(12)−C(17), −96.8(6); C(1)−N(2)−C(24)−C(29), −75.6(5).

$Sc(NHAr)HBEt_3$,[15] but no definitive evidence for its competence as an intermediate was put forward. We probed this question by monitoring the loss of CH_4/CH_3D from d_1-**4b**, selectively labeled in the ND position. As shown in Scheme 4, direct metalation should produce CH_4, while loss of CH_3D would indicate that formation of **7** involves the imide intermediate trapped by addition of an ^{i}Pr C−H bond across the reactive Sc=NR fragment. Heating samples of d_1-**4b** lead exclusively to production of CH_4, and both ^{1}H and ^{2}H NMR spectroscopy indicated that the deuterium label remains on the amido nitrogen, with no significant scrambling of the deuterium into other positions of the molecule. This observation argues against the intermediacy of a scandium imido species in this chemistry.

Summary and Conclusions

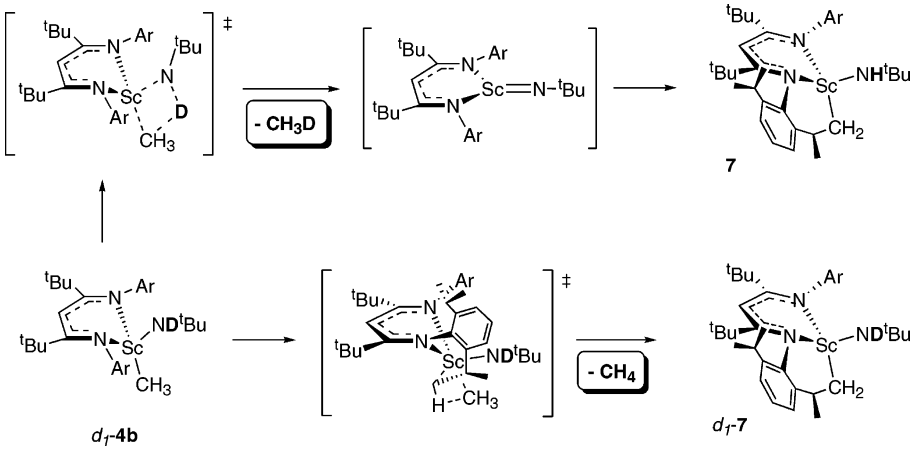
While the (nacnac)Sc fragment supports primary amido alkyl complexes, these compounds do not serve as precursors to scandium imido derivatives in the same way that amido alkyls of the group 4 metals do. Rather, metalation of the nacnac ligand is the low-energy pathway for CH_4 loss. Use of more metalation-resistant nacnac ligands or other approaches based on deprotonation strategies are currently being explored in attempts to realize well-defined scandium imido complexes. Our results do, however, suggest that scandium imido compounds are relatively high energy species and raise questions as to the viability of such intermediates in hydroamination cycles catalyzed by L_nMR_2 compounds,[12,14] where M is a group 3 or lanthanide metal.

Experimental Section

General Procedures. An MBraun or Vacuum Atmospheres argon-filled glovebox was employed for manipulation and storage of oxygen- and moisture-sensitive complexes. Reactions were performed utilizing a double-manifold argon/vacuum line and modified Schlenk line techniques. Matheson Oxisorb-W gas purification cartridges were used to remove residual moisture and oxygen in the argon stream. Hexane, toluene, and THF were dried and deoxygenated as they passed through a Grubbs/Dow purification system[23] and were stored in evacuated bombs over titanocene[24] (hexane and toluene) or sodium/benzophenone ketyl (THF).

NMR spectra were obtained on Bruker AC-200 MHz (^{1}H and ^{13}C{^{1}H}), AMX-300 MHz (^{1}H, ^{2}H, ^{1}H−^{1}H EXSY, and ^{1}H−^{1}H ROESY), and DRX-400 MHz (^{1}H, ^{13}C{^{1}H}, ^{1}H−^{13}C HMQC, ^{1}H−^{1}H EXSY, and ^{1}H−^{1}H COSY) instruments. All NMR spectral data are reported in ppm, and NMR spectra of ^{1}H, ^{2}H, and ^{13}C were internally referenced to the residual solvent peak. Temperature calibration for the NMR spectra was achieved by monitoring the ^{1}H NMR spectrum of methanol or ethylene glycol.[25] Elemental analyses were performed by Dorothy Fox or Roxanna Smith using a Control Equipment Corporation

Scheme 4



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(CEC) 440 elemental analyzer. The electrospray ionization mass spectrometry was undertaken by Qiao Wu with a Bruker Esquire 3000, and the high-resolution mass spectrometry was performed by Dorothy Fox with a Kratos MS80RFA.

All materials were obtained from Sigma-Aldrich and purified according to standard procedures. $ScCl_3{\cdot}THF_3$ was produced by refluxing Sc_2O_3 (purchased from Boulder Scientific) in concentrated HCl, and after the removal of the excess HCl, the reaction mixture was dried with thionyl chloride, $SOCl_2$, in refluxing THF.[26] The ligands **a** and **b** were synthesized and lithiated according to literature procedures. All amines/anilines were dried over CaH_2 and freshly distilled to another flask before lithiation with 1 equiv of ^{n}BuLi to produce the LiNRR′ salts. For the deuterium labeling studies, H_2N^tBu was mixed with 20 equiv of D_2O and stirred overnight to produce D_2N^tBu and dried as above.

Computational Procedures. All computational analyses were performed on the MACI cluster (Multimedia Advanced Computational Infrastructure) at the University of Calgary. All of the calculations have been carried out using the Amsterdam Density Function program package developed by Barends et al.[27] and vectorized by Ravenek.[28,29] The Becke−Perdew exchange correlation function[30] has been used throughout. The numerical integration scheme applied was developed by te Velde et al.[31] Auxialiary[32] s, p, d, f, and g STO functions centered on all nuclei were used to fit the Coulomb and exchange potentials during the SCF process. For the scandium atom, a standard triple-ζ STO basis set from the ADF database TZP was employed with 1s−3p electrons treated as frozen core. For the nonmetal elements, a standard double-ζ basis set with one set of polarization functions (ADF database DZP) was used, with 1s electron treated as frozen core for non-hydrogen atoms. The geometries were taken directly from the X-ray structures and were not further optimized. The geometries of the *endo* isomers were derived from those of the *exo* isomers by exchanging the amido ligand with the Cl or Me ligands. The geometries of the *cis* and *trans* isomers were derived by rotating the amido ligand around the Sc−N bond by 180° with no further adjustment. The bond orders were calculated following the scheme developed by R. F. Nalewajski and coworkers.[33]

Synthesis of 2b. Toluene (25 mL) was condensed into an evacuated flask containing **1b** (0.291 g, 0.472 mmol) and $LiNH^tBu$ (0.049 g, 0.619 mmol). The yellow reaction mixture was warmed to room temperature with a hot water bath and stirred for 1 h before the removal of the solvent under reduced pressure. Hexane (25 mL) was added to the flask, and the mixture was heated to approximately 40 °C to increase the solubility of the compound in hexane. The LiCl was removed by filtration, and the solid was washed with hexane (3 × 10 mL). Removal of hexane in vacuo gave crude product, and after recrystallization from the same solvent at −36 °C, pure **2b** was obtained. Yield: 0.222 g, 72%. ^{1}H NMR: 7.08−6.97 (m, 6H, C_6H_3), 5.82 (s, 1H, C*H*), 4.32 (br s, 1H, N*H*), 3.62, 3.03 (m, 2 × 2H, C*H*$(CH_3)_2$), 1.67, 1.38, 1.29, 1.23 (d, 4 × 6H, CH$(CH_3)_2$, J_{H-H} = 6.6 or 6.8 Hz), 1.15 (s, 18H, NCC$(CH_3)_3$), 0.81 (br s, 9H, NHC$(CH_3)_3$. ^{13}C{^{1}H} NMR: 175.2 (N*C*C$(CH_3)_3$), 144.8, 142.7, 140.8, 126.5, 124.8, 124.3 (C_6H_3), 93.1 (*C*H), 54.5 (NH*C*$(CH_3)_3$), 45.3 (NC*C*$(CH_3)_3$), 34.4 (NHC$(CH_3)_3$), 32.7 (NCC$(CH_3)_3$), 29.6 and 29.1 (*C*H$(CH_3)_2$), 27.5, 26.1, 25.2, and 25.0 ((CH$(CH_3)_2$). Anal. Calcd for $C_{39}H_{63}ClN_3Sc$: C, 71.77; H, 9.71; N, 6.43. Found: C, 71.92; H, 9.54; N, 6.42.

Synthesis of *d*$_1$-2b. This compound was prepared in a manner identical to the one previously described for **2b**, with the exception that $LiND^tBu$ was used in place of $LiNH^tBu$. The ^{1}H NMR spectrum of ***d*$_1$-2b** matched the spectrum of **2b**, except that no resonance was observed for the proton attached to the nitrogen of the amido group.

Synthesis of 3b. The method to prepare **3b** using **1b** (0.607 g, 0.984 mmol) and LiNH-2,6-^{i}Pr$_2$-C_6H_3 (0.215 g, 1.17 mmol) is similar to the procedure for **2b** above except that the reaction mixture was sonicated for approximately 5 min prior to stirring to increase the solubility of the reagents. On account of the reduced solubility of **3b** in comparison to **2b**, the precipitate was washed five times with hexane to extract any residual product. **3b** was recrystallized from hexane at −36 °C. Yield: 0.356 g, 48%. ^{1}H NMR: 7.02−6.90 and 6.75 (m, 9H, 3 × C_6H_3), 6.24 (br s, 1H, N*H*), 6.09 (s, 1H, C*H*), 3.75 and 3.09 (m, 2 × 2H, C*H*$(CH_3)_2$), 1.98 (m, 2H, NH-2,6-C*H*$(CH_3)_2C_6H_3$), 1.50, 1.29, 1.15, and 1.07 (d, 4 × 6H, CH$(CH_3)_2$, J_{H-H} = 6.7 or 6.8 Hz), 1.11 (s, 18H, NCC$(CH_3)_3$), 1.04 (d, 12H, NH-2,6-CH$(CH_3)_2C_6H_3$), J_{H-H} = 6.6 Hz). ^{13}C{^{1}H} NMR: 177.3 (N*C*C$(CH_3)_3$), 149.1, 143.7, 143.2, 142.0, 134.6, 127.4, 125.8, 124.8, 124.6, 124.2, 123.5, and 118.8 (3 × C_6H_3), 96.8 (*C*H), 45.0 (NC*C*$(CH_3)_3$), 32.5 (NCC$(CH_3)_3$), 32.2 (NH-2,6-*C*H$(CH_3)_2C_6H_3$), 31.0, 27.3, 25.6 and 25.5 (CH$(CH_3)_2$), 29.2 and 29.1 (*C*H$(CH_3)_2$), 25.1 (NH-2,6-CH$(CH_3)_2C_6H_3$). Anal. Calcd for $C_{47}H_{71}N_3ScCl$: C, 74.42; H, 9.44; N, 5.54. Found: C, 74.58; H, 9.12; N, 5.30.

Synthesis of 4b. Toluene (10 mL) was added to a flask charged with **2b** (0.796 g, 1.22 mmol) and MeLi (0.034 g, 1.55 mmol) and stirred overnight at 35 °C. The toluene was removed in vacuo and replaced with hexane (10 mL). Prior to filtration, the deep yellow reaction mixture was warmed to approximately 40 °C; after filtration, the residual product was extracted from the LiCl precipitate with hexane (3 × 5 mL). Upon removal of the solvent, a yellow powder was obtained. Crude **4b** was recrystallized from hexane at −36 °C, generating yellow crystals. Yield: 0.394 g, 51%. ^{1}H NMR: 7.10−6.99 (m, 6H, C_6H_3), 5.72 (s, 1H, C*H*), 3.68 and 3.09 (m, 2 × 2H, C*H*$(CH_3)_2$), 3.54 (br s, 1H, N*H*), 1.67, 1.40, 1.28 and 1.26 (d, 4 × 6H, CH$(CH_3)_2$, J_{H-H} = 6.7 Hz), 1.16 (s, 18H, NCC$(CH_3)_3$), 0.80 (s, 9H, NHC$(CH_3)_3$), −0.07 (s, 3H, ScCH_3). ^{13}C{^{1}H} NMR: 174.6 (N*C*C$(CH_3)_3$), 145.1, 142.5, 141.0, 126.1, 124.7, and 124.3 (C_6H_3), 93.2 (*C*H), 53.7 (NH*C*$(CH_3)_3$), 45.3 (NC*C*$(CH_3)_3$), 34.9 (NHC$(CH_3)_3$), 32.9 (NCC$(CH_3)_3$), 30.6 (Sc*C*H$_3$) 29.5 and 29.0 (*C*H$(CH_3)_2$), 27.3, 26.2, 25.2, and 25.0 (CH$(CH_3)_2$). 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.

Synthesis of *d*$_1$-4b. This compound was prepared in a manner identical to the one previously described for **4b**, with the exception that ***d*$_1$-2b** was used. The ^{1}H NMR spectrum of ***d*$_1$-4b** matched the analogous spectrum of **4b**, except that no resonance was observed for the proton attached to the nitrogen of the amido group. The synthesis of ***d*$_1$-4b** was also confirmed with ^{2}H NMR: 3.54 (N*D*).

Synthesis of 5b. This synthesis was similar to that described for **4b**, except that the reaction mixture of **3b** (0.728 g, 0.961 mmol) and MeLi (0.024 g, 1.09 mmol) was heated for a full 24 h at 35 °C. Yield: 0.330 g, 47%. ^{1}H NMR: 7.02−6.89 and 6.74 (m, 9H, 3 × C_6H_3), 5.99 (s, 1H, C*H*), 5.44 (br s, 1H, N*H*), 3.68 and 3.02 (m, 2 × 2H, C*H*$(CH_3)_2$), 2.18 (m, 2H, NH-

(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(24) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.
(25) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.
(26) Manzer, L. *Inorg. Synth.* **1982**, *21*, 135.
(27) (a) Baerends, E. J. Ph.D. Thesis, Free University, Amsterdam, The Netherlands, 1973. (b) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
(28) Ravenek, W. In *Algorithms and Applications on Vector and Parallel Computers*; te Riele, H. J. J., Dekker, T. J., van de Horst, H. A., Eds.; Elsevier: Amsterdam, The Netherlands, 1987.
(29) Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87.
(30) (a) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406. (c) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(31) te Velde, G.; Baerends, E. J. *Comput. Chem.* **1992**, *99*, 84.
(32) Krijn, J.; Baerends, E. J.; Vernoijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483.
(33) (a) Nalewajski, R. F.; Mrozek, J. *Int. J. Quantum Chem.* **1994**, *51*, 187. (b) Nalewajski, R. F.; Mrozek, J.; Mazur, G. *Can. J. Chem.* **1996**, *74*, 1121. (c) Mrozek, J.; Nalewajski, R. F.; Michalak, A. *Polish J. Chem.* **1998**, *72*, 1779.

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2,6-C*H*$(CH_3)_2C_6H_3$), 1.45, 1.30, 1.16, and 1.05 (d, 4 × 6H, CH-(CH_3)$_2$, J_{H-H} = 6.6 Hz or 6.8 Hz), 1.12 (s, 18H, NCC(CH_3)$_3$), 1.03 (d, 12H, NH-2,6-CH(CH_3)$_2C_6H_3$), J_{H-H} = 6.8 Hz), 0.13 (s, 3H, ScCH_3). $^{13}C\{^1H\}$ NMR: 177.1 (N*C*C(CH_3)$_3$), 149.8, 143.6, 143.4, 142.1, 134.2, 127.0, 125.5, 124.8, 123.4, and 117.7 (10 of 12 signals were observed for 3 × C_6H_3), 96.1 (*C*H), 45.0 (NC*C*(CH_3)$_3$), 32.7 (NCC(*C*H_3)$_3$), 30.7 (NH-2,6-[*C*H(CH_3)$_2$]-C_6H_3), 29.2 and 29.0 (*C*H(CH_3)$_2$), 27.1, 25.7, 25.3, and 25.0 (CH-(*C*H_3)$_2$), 24.8 (NH-2,6-CH(*C*H_3)$_2C_6H_3$), 23.4 (Sc*C*H_3). Anal. Calcd for $C_{48}H_{74}N_3Sc$: C, 78.11; H, 10.11; N, 5.69. Found: C, 77.88; H, 9.94; N, 5.66.

Synthesis of 7. Toluene (20 mL) was transferred into a round-bottom flask of a frit assembly containing **4b** (0.437 g, 0.690 mmol); the reaction mixture was heated overnight at 90 °C. After heating, the mixture became an opaque orange solution. The solvent was removed under reduced pressure, yielding an orange foam. Hexane (12 mL) was added to the flask, and the mixture was stirred at room temperature for 30 min. The hexane was removed in vacuo, affording an orange powder. The powder was suspended in hexamethyldisiloxane (7 mL) and isolated by filtration. Yield: 0.158 g, 37%. ^{1}H NMR: 7.31−6.95 (m, 6H, C_6H_3), 5.55 (s, 1H, C*H*), 3.48 and 2.99 (m, 1H, C*H*(CH_3)$_2$, J_{H-H} = 6.9 Hz), 3.22 (m, 2H, C*H*(CH_3)$_2$ and $CH_2CH(CH_3)$), 1.96 (br s, 1H, N*H*), 1.56, 1.50, 1.35, 1.34, 1.26 and 1.20 (d, 6 × 3H, CH(C*H*$_3$)$_2$, J_{H-H} = 6.8 or 6.4 Hz), 1.18 (br s, 12H, CH(C*H*$_3$)$_2$ and NCC(C*H*$_3$)$_3$), 1.17 (br s, 9H, NCC(C*H*$_3$)$_3$), 0.97, 0.91 (dd, 1H, C*H*$_2$CH(CH$_3$), $^2J_{H-H}$ = 12.2 Hz, $^3J_{H-H}$ = 5.4 Hz), 0.78 (s, 9H, NHC(C*H*$_3$)$_3$), 0.44 (br t, 1H, C*H*$_2$CH(CH$_3$)). $^{13}C\{^1H\}$ NMR: 174.2 and 173.9 (2 × N*C*C-(CH_3)$_3$), 147.9, 144.5, 143.8,142.4, 139.9, 139.4, 127.2, 126.9, 125.3, 125.1,124.3, and 123.2 (2 × *C*$_6$H$_3$), 98.1 (*C*H), 54.2 (Sc*C*H$_2$) 52.9 (NH*C*(CH_3)$_3$), 43.55 and 43.51 (2 × NC*C*(CH_3)$_3$), 35.0 (NHC(*C*H$_3$)$_3$), 33.1 and 32.3 (2 × NCC(*C*H$_3$)$_3$), 39.5, 28.9, 28.7, and 28.5 (3 × *C*H(CH$_3$)$_2$ and CH$_2$*C*H(CH$_3$)), 26.7, 26.6, 26.33, 26.29, 25.2, 24.0, and 23.2 (7 × CH(*C*H$_3$)$_2$); mass spectrum, *m*/*z* (relative intensity, %) 617 (M^+, 1), 544 (M^+ − H_2N^tBu, 3), 502 (M^+ − (H_2N^tBu + C_3H_6), 3), 9 (100); exact mass calcd for $C_{39}H_{62}N_3Sc$ 617.4503, found 617.4495.

Synthesis of *d*$_1$-7. In a sealed NMR tube, the deuterated scandium amido methyl complex ***d*$_1$-4b** was heated overnight at 60 °C in C_6D_6. ^{1}H NMR spectroscopy was employed to determine the products, and ***d*$_1$-7** was assigned on the basis of the noticeable *absence* of a peak at 1.98 ppm for the amido proton of the metalate complex, although all of the other peaks were present in the spectrum. In addition, only CH_4 at 0.14 ppm was observed in the reaction mixture; a resonance for CH_3D was not present in the NMR tube.

Synthesis of [ArNC(Me)CHC(Me)NAr]Sc(Cl)Me. Equimolar ratios of [ArNC(Me)CHC(Me)NAr]ScMe_2 (0.308 g, 0.625 mmol) and **1a** (0.335 g, 0.628 mmol) were combined in toluene (70 mL), and the reaction was stirred for 3 days. The reaction mixture was filtered and washed once with toluene (10 mL), and the filtrate was dried under reduced pressure, yielding a pale, yellow powder. Yield: 0.199 g, 62%. ^{1}H NMR: 7.13−7.00 (m, 6H, C_6H_3), 5.09 (s, 1H, C*H*), 3.42 and 2.73 (m, 2 × 2H, C*H*(CH_3)$_2$, J_{H-H} = 6.6 Hz), 1.63 (s, 6H, NCC*H*$_3$), 1.24, 1.22, 1.17, and 0.89 (d, 4 × 6H, CH(C*H*$_3$)$_2$, J_{H-H} = 6.6 Hz), 0.29 (s, 3H, Sc*CH*$_3$). $^{13}C\{^1H\}$ NMR (C_7D_8): 168.3 (NC*C*H$_3$), 145.6, 143.0, 141.1, 126.2, 124.7, and 123.6 (*C*$_6$H$_3$), 98.1 (*C*H), 39.6 (Sc*C*H$_3$), 29.1 and 28.0 (*C*H(CH$_3$)$_2$), 26.3, 25.0, 24.9, 24.7, and 24.3 (CH(*C*H$_3$)$_2$ and NC*C*H$_3$).

Synthesis of 4a. The scandium complex **L^{a}Sc(Me)Cl** (0.199 g, 0.388 mmol) was weighed into a two-neck round-bottom flask and dissolved in toluene (20 mL). A separate round-bottom flask was charged with LiNH^tBu (0.031 g, 0.392 mmol), and it was also dissolved in toluene (5 mL). The toluene solution of LiNH^tBu was added slowly via syringe to the scandium solution. The reaction mixture was stirred at ambient temperature for 30 min, resulting in a yellow solution with a white precipitate. The toluene was removed in vacuo, and hexane (25 mL) was transferred into the flask. The reaction mixture was warmed to room temperature, and the white solid was removed by filtration. The product was extracted from the precipitate with hexane (3 × 10 mL); the hexane was removed under reduced pressure from the filtrate, and the remaining yellow solid was recrystallized from dilute hexane at −36 °C. Yield: 0.072 g, 34%. ^{1}H NMR: 7.18−7.09 (m, 6H, C_6H_3), 5.03 (s, 1H, C*H*), 3.93 (br s, 1H, N*H*), 3.59 and 3.08 (m, 2 × 2H, C*H*(CH_3)$_2$, J_{H-H} = 6.6 Hz), 1.62 (s, 6H, NCC*H*$_3$), 1.56, 1.29, 1.25, and 1.06 (d, 4 × 6H, CH(C*H*$_3$)$_2$, J_{H-H} = 6.6 Hz), 0.87 (s, 9H, NHC(C*H*$_3$)$_3$), and 0.03 (s, 3H, Sc*CH*$_3$). $^{13}C\{^1H\}$ NMR: 167.8 (N*C*CH$_3$), 143.50, 143.45, 142.1, 126.9, 124.8, and 124.5 (*C*$_6$H$_3$), 95.5 (*C*H), 53.2 (NH*C*(CH_3)$_3$, 35.0 (NHC(*C*H$_3$)$_3$), 29.3 and 29.0 (*C*H(CH$_3$)$_2$), 26.5, 25.0, 24.8, and 24.7 (CH(*C*H$_3$)$_2$), 24.4 (NC*C*H$_3$), and 21.4 (Sc*C*H$_3$). Anal. Calcd for $C_{34}H_{54}N_3Sc$: C, 74.28; H, 9.90; N, 7.64. Found: C, 74.20; H, 9.42; N, 7.29.

Thermolysis of 4a. The thermolysis was performed only on an NMR tube scale, and the reaction was monitored by ^{1}H NMR spectroscopy. Upon heating of the scandium complex **4a** at 100 °C in toluene-d_8, the compound redistributed to **6a**, which was stable at 100 °C, and **L^{a}ScMe$_2$**, which decomposed as a mixture of species at this temperature.

Synthesis of 6a. A round-bottom flask was charged with **1a** (0.440 g, 0.825 mmol) and 2 equiv of LiNH^tBu (0.135 g, 1.71 mmol); after the combination of the two solids, toluene (20 mL) was transferred into the flask. The yellow, opaque, reaction mixture was heated overnight at 50 °C. Upon cooling to room temperature, the solution was filtered and the precipitate was washed with toluene (2 × 15 mL). The toluene was removed in vacuo from the filtrate, and hexane (15 mL) was added to the flask; the solution was warmed to ambient temperature and stirred for 20 min. A yellow powder resulted from the removal of hexane under reduced pressure, and it was used without further purification. Yield: 0.492 g, 98%. ^{1}H NMR (T = 298 K): 7.14−7.10 (m, 6H, C_6H_3), 5.02 (s, 1H, C*H*), 3.50 (br s, 2H, N*H*C(CH_3)$_3$), 3.44 (m, 4H, C*H*(CH_3)$_2$, J_{H-H} = 6.8 Hz), 1.63 (s, 6H, NCC*H*$_3$), 1.38, and 1.18 (d, 2 × 12H, CH(C*H*$_3$)$_2$, J_{H-H} = 6.8 Hz), and 1.03 (s, 18H, NHC(C*H*$_3$)$_3$); ^{1}H NMR (T = 195 K, toluene-d_8): 7.14−7.03 (m, 6H, C_6H_3), 4.84 (s, 1H, C*H*), 3.98 and 3.24 (br s, 2 × 1H, N*H*C(CH_3)$_3$), 3.98 and 3.04 (br m, 2 × 2H, C*H*(CH_3)$_2$), 1.65, 1.31, 1.11, and 0.98 (br d, 2 × 12H, CH(C*H*$_3$)$_2$), 1.52 (s, 6H, NCC*H*$_3$), 1.44 and 0.82 (br s, 2 × 9H, NHC(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR: 166.7 (N*C*(CH_3)$_3$), 144.0, 142.0, 125.9, and 124.1 (*C*$_6$H$_3$), 94.9 (*C*H), 52.5 (NH-*C*(CH_3)$_3$, 34.8 (NHC(*C*H$_3$)$_3$, 28.1 (*C*H(CH$_3$)$_2$), 25.1, and 24.6 (CH(*C*H$_3$)$_2$), and 24.0 (NC*C*H$_3$); high-resolution mass spectrum, *m*/*z* (relative intensity, %): 534 (M^+ − NH^tBu, 7), 460 (M^+ - $2H_2N^tBu$, 9), 418 (M^+ − ($2H_2N^tBu$ + C_3H_6), 24), 58 (100); exact mass calcd for $C_{33}H_{51}N_3Sc$ (M^+ − NH^tBu) 534.3642, found 534.3618. Electrospray ionization mass spectrum, *m*/*z*: 629 (M + Na^+) and 557 (M + Na^+ − H_2N^tBu).

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, and complete bond distances, angles, and torsion angles for **2b**, **3b**, **4b**, **5b**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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