Cationic Group 3 Alkyl Complexes with Isopropyl-Substituted Triazacyclononane-amide Ligands: Synthesis, Structure, and Thermal Decomposition Processes

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Yttrium and lanthanum dialkyl complexes with the isopropyl-substituted triazacyclononane-amide monoanionic ligands [*i*Pr$_2$TACN-(B)-N*t*Bu] (B = $(CH_2)_2$, **L1**; $SiMe_2$, **L2**) are described. For Y, these were obtained by reaction of $Y(CH_2SiMe_3)_2(THF)_2$ with H**L**, whereas for La in situ peralkylation of $LaBr_3(THF)_4$ preceded reaction with H**L**. In C_6D_5Br solvent, reaction of **L**MR_2 with $[PhNMe_2H][B(C_6F_5)_4]$ results in rapid decomposition involving loss of propene from the ligand. This decomposition is prevented (Y) or retarded (La) in THF solvent. For yttrium, salts of the cations $[\mathbf{L}YR(THF)]^+$ were isolated and structurally characterized. ES-MS of these cations revealed facile desolvation. At increased nozzle voltages, fragmentation is observed with initial loss of $SiMe_4$, followed by loss of propene. Thus decomposition is likely to involve initial cyclometalation of a ligand *i*Pr group, followed by propene extrusion. Decomposition of $[\mathbf{L2}LaR(THF)_x]^+$ in THF solution yields the dinuclear dication $\{[t\text{BuN}(Me_2Si)N\text{-}(C_2H_4)_2N(C_2H_4)Ni\text{Pr}]_2La_2(THF)_2\}^{2+}$, which was structurally characterized. Kinetic data of the decomposition suggest that the process involves initial THF dissociation.

Introduction

Cationic electron-deficient transition-metal alkyl complexes have been extensively studied for their efficiency in catalytic olefin polymerization processes.[1] In contrast, cationic alkyl complexes of the group 3 metals and lanthanides, $[LLnR]^+$, have only relatively recently been explored as olefin polymerization catalysts. Although several families of compounds of this type have now been found to be active catalysts for olefin polymerization,[2−8] much of their properties still need to be explored. An important feature in determining potential usefulness in catalysis is catalyst stability. A potential source of catalyst deactivation is the degradation of the ancillary ligand system by intra- or intermolecular metalation reactions involving the reactive metal−alkyl bond of the catalyst species. In one of the families of catalysts developed in our group, bearing monoanionic tetradentate 1,4,7-triazacyclononane-amide[4a,9] and bis(2-dimethylamino)amine-amide[10] ancillary ligands, we have observed evidence for the occurrence of ligand metalation reactions. In particular, the cationic yttrium alkyl species $\{[i\text{Pr}_2\text{-}TACN(CH_2)_2N t\text{Bu}]YCH_2SiMe_3\}^+$ was found to decompose rapidly by loss of $SiMe_4$ and propene,[4a] a reaction proposed to be initiated by intramolecular metalation of one of the ligand

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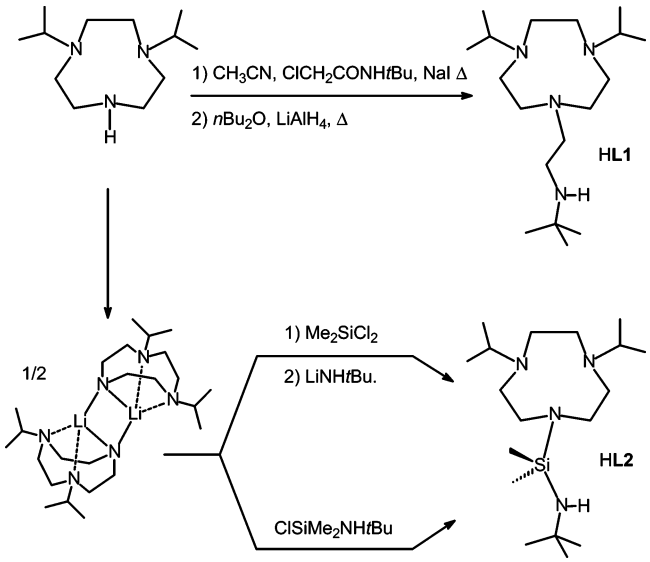
Scheme 1



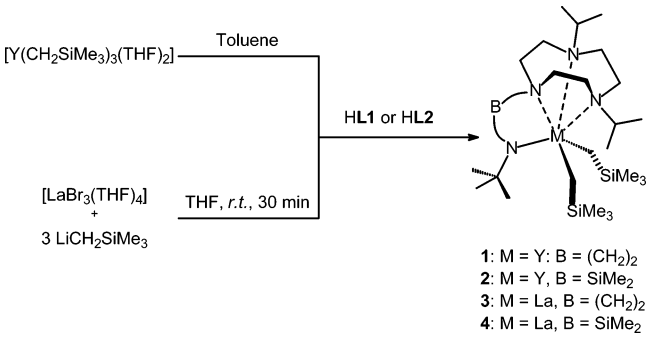
*i*Pr substituents. In this paper we describe the synthesis and characterization of neutral dialkyl and cationic monoalkyl species of yttrium and lanthanum with the [*i*Pr$_2$TACN(B)N*t*Bu]$^-$ (B = $(CH_2)_2$, $SiMe_2$) ligand and a study of their thermal decomposition.

Results and Discussion

Ligand Synthesis. The ligands employed in this study are *N*-*tert*-butyl-2-(4,7-diisopropyl-1,4,7-triazanon-1-yl)ethylamine (H**L1**) and *N*-*tert*-butyl(4,7-diisopropyl-1,4,7-triazanon-1-yl)-dimethylsilylamine (H**L2**). H**L1** is prepared by reaction of known 1,4-diisopropyl-1,4,7-triazacyclononane[11] with *N*-*tert*-butylchloroacetamide in refluxing actonitrile, with a catalytic amount of NaI, yielding the corresponding *N*-*tert*-butyl-(4,7-diisopropyl-1,4,7-triazacyclonon-1-yl)acetamide. This was then reduced at the carbonyl function with $LiAlH_4$ in refluxing dibutyl ether (nBu_2O) instead of diglyme as previously reported,[9] affording H**L1** in 89% yield after hydrolysis and acid−base extraction (Scheme 1). Ligand H**L2** can be prepared either by treating neat Me_2SiC1_2 first with Li[4,7-*i*Pr$_2$-TACN][12] and then with lithium *tert*-butylamide or by reacting [4,7-*i*Pr$_2$-TACN]Li with $ClSiMe_2NHtBu$ in hexanes (Scheme 1). The latter procedure affords H**L2** spectroscopically pure (by ^{1}H NMR) as a light yellow oil in 84% yield.

Synthesis and Characterization of TACN-amide Yttrium and Lanthanum Dialkyls. Yttrium dialkyl complexes [**L**]Y$(CH_2SiMe_3)_2$ were made via the well-established alkane elimination route,[13] by reaction of the yttrium tris(alkyl) Y$(CH_2SiMe_3)_3(THF)_2$[14] with the neutral ligand H**L1** or H**L2** in toluene at ambient temperature (Scheme 2). After evaporation of the volatiles under reduced pressure the residue was washed with cold (−20 °C) pentane, providing the complexes [**L1**]Y$(CH_2SiMe_3)_2$ (**1**) and [**L2**]Y$(CH_2SiMe_3)_2$ (**2**) as white microcrystalline solids in about 75% yield.

Scheme 2



Since a related lanthanum tris(alkyl) La$(CH_2SiMe_3)_3(THF)_x$ is not available, we followed the in situ approach we described before for TACN-amide and amidinate dialkyl complexes of the larger lanthanide metal ions.[7b,9] In a single-pot procedure, a suspension of $LaBr_3(THF)_4$ in THF was reacted with 3 equiv of $LiCH_2SiMe_3$ at ambient temperature for 30 min, after which H**L1** or H**L2** was added. After removal of the volatiles the residues were extracted with hexanes/toluene (1:1, at −0 °C) to afford the complexes [**L**]La$(CH_2SiMe_3)_2$ (**L** = **L1**, **3**; **L2**, **4**) in moderate yields of about 45%. It is noteworthy that the lanthanum dialkyl **4**, with the $SiMe_2$-bridged ligand, can be isolated under these conditions. Earlier we reported that the related complex with the 4,7-di*methyl*-substituted TACN-amide ligand undergoes rapid ligand NMe metalation at low temperature to produce the dinuclear species {[Me(μ-CH_2)TACN-$(SiMe_2)$N*t*Bu]La(CH_2SiMe_3)}$_2$.[9] Apparently, the *i*Pr substituents on the ligand sufficiently shield the metal−alkyl bonds to prevent intermolecular C−H activation. It will be seen later that the *i*Pr substituents do give rise to *intra*molecular C−H activation processes.

NMR Spectroscopic Data of [LM$(CH_2SiMe_3)_2$]. Compounds **1**−**4** were studied by NMR spectroscopy. At ambient temperature, yttrium compound **1** (with the C_2-bridged ligand) displays ^{1}H and ^{13}C NMR spectra consistent with an asymmetric structure, e.g., showing four doublets for the alkyl methylene protons and two resonances for the alkyl methylene carbons. The latter are found at δ 33.7 (J_{YC} = 37 Hz; J_{CH} = 95 Hz) and 31.0 ppm (J_{YC} = 39 Hz; J_{CH} = 95 Hz). In contrast, the other three complexes display room-temperature spectra suggesting (averaged) C_s symmetry. At lower temperatures, all compounds give spectra consistent with an asymmetric ground-state structure. Variable-temperature ^{1}H NMR spectra in THF-d_8 solvent allowed us to estimate the symmetrization barrier for all four compounds from the coalescence behavior of the alkyl $SiMe_3$ resonances.[15] Coalescence temperatures T_c and calculated free energies of activation $\Delta G^{\ddagger}_{Tc}$ (in kcal mol^{-1}) are as follows: **1** (44.6 °C, 17.0), **2** (−25.7 °C, 12.6), **3** (−12.2 °C, 13.4), **4** (−37.4 °C, 11.9). From these data it is clear that the highest activation barriers are found for the C_2-bridged ligand **L1**, due to the conformation of the backbone, and for the metal with the smaller ionic radius (Y^{3+}: 1.04 Å, La^{3+}: 1.17 Å), due to the increased steric congestion around the metal center. Also notable is that there are considerable differences in chemical shifts between the lanthanum complexes and their yttrium congeners in the ^{13}C NMR spectra. For complexes **3** and **4** the M−CH_2 carbon

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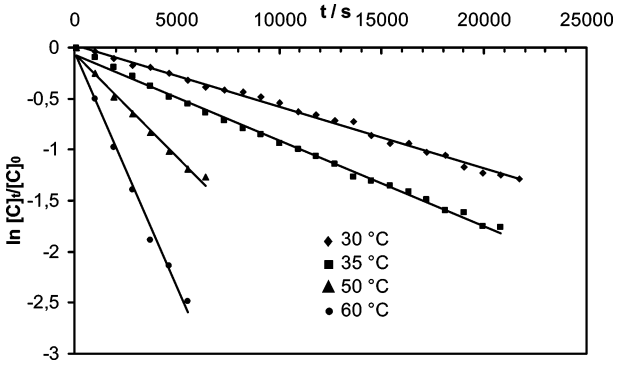


Figure 1. First-order plot for the thermal decomposition of **4** at different temperatures in C_6D_6.

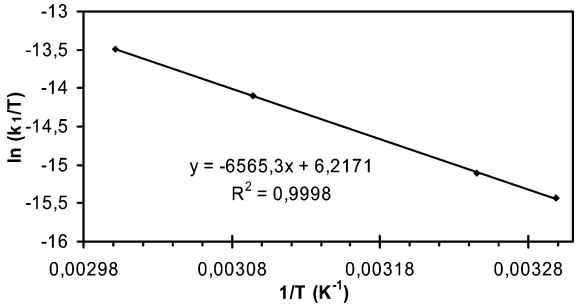


Figure 2. Eyring plot for the thermal decomposition of **4** in C_6D_6.

resonances are found approximately 15 ppm downfield relative to those in **1** and **2**.

Thermal Stability of the Dialkyl Complexes. Complexes **1**−**4** decompose gradually at ambient temperature in C_6D_6 solution. Compound **4** is the least stable of the series, with a half-life at 35 °C of 30 min. The La compounds **3** and **4** are also insufficiently stable in the solid state to be subjected to elemental analysis. The decomposition is accompanied by the release of equimolar amounts of $SiMe_4$ and propene. Nevertheless, a well-defined organometallic product could not be identified, and at higher temperatures the second alkyl group is also liberated as $SiMe_4$ in a subsequent process. The thermolysis of **4** in C_6D_6 solvent was followed at four different temperatures by NMR spectroscopy. The reaction was found to follow simple first-order kinetics, indicative of an *intra*molecular process (Figure 1). Activation parameters of $\Delta H^{\ddagger} = 54.6 \pm 0.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = 27 \pm 20$ J K^{-1} mol^{-1} were derived from the Eyring plot (Figure 2). Interestingly, **4** seems to be somewhat more stable in THF-d_8 solvent. A similar analysis of the decomposition on this solvent yields the (apparent) activation parameters $\Delta H^{\ddagger} = 69 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = 71 \pm 19$ J K^{-1} mol^{-1}. The significantly positive entropy of activation in THF solvent may indicate that, although isolated **4** is free from coordinated THF (even when obtained from THF-containing media), in neat THF some additional solvation takes place.

Crystal Structures of the Dialkyl Complexes. Crystallization of the dialkyl complexes from pentane or toluene/pentane mixtures provides large, clear crystals of the compounds. The structures of **1**, **2**, and **4** were determined by single-crystal X-ray diffraction (shown in Figures 3−5, respectively). All three compounds show a distorted octahedral geometry, with the three nitrogen atoms of the TACN moiety in facial arrangement. The sterically demanding ligand *i*Pr groups and the metal-bound alkyl groups are staggered, and the compounds are asymmetric due to the bridge between the TACN and amide ligand moieties. This asymmetry is reflected for example in the large difference

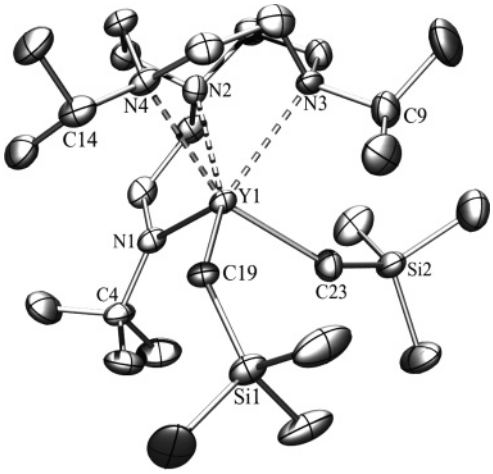


Figure 3. Molecular structure of [*i*Pr$_2$TACN(CH$_2$)$_2$N*t*Bu]Y(CH$_2$SiMe$_3$)$_2$ (**1**) (ellipsoid probability level at 50%).

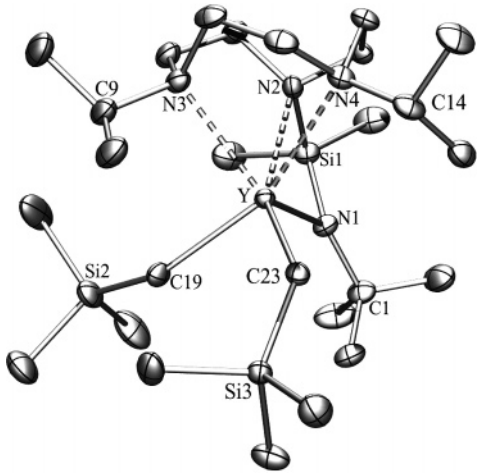


Figure 4. Molecular structure of [*i*Pr$_2$TACN(SiMe$_2$)N*t*Bu]Y(CH$_2$SiMe$_3$)$_2$ (**2**) (ellipsoid probability level at 50%).

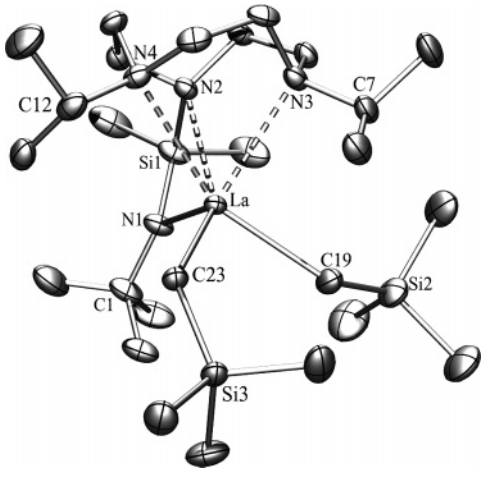
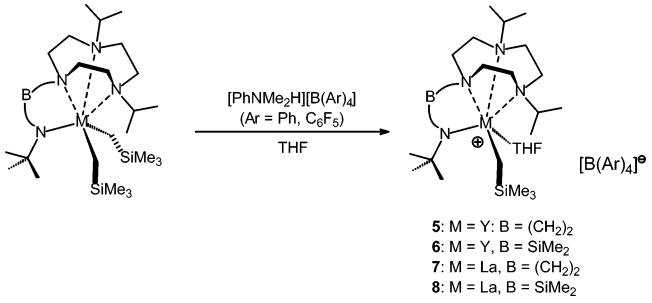


Figure 5. Molecular structure of [*i*Pr$_2$TACN(SiMe$_2$)N*t*Bu]La(CH$_2$SiMe$_3$)$_2$ (**4**) (ellipsoid probability level at 50%).

between the two $N_{amide}-M-CH_2$ angles within each complex, for instance, 98.22(13)° for C19 and 118.12(13)° for C23 in complex **2**.

As reported in the previous paragraph, the fluxional behavior of the complexes is strongly influenced by the nature of the bridge in the ligand and the size of the metal center. It is therefore useful to compare some of the metrical parameters for the complexes in the solid state. The effect of the bridging

Scheme 3



moiety of the TACN-amide ligand can be seen in comparing the structures of **1** and **2**. The $N_{amido}-Y-N_{bridgehead}$ ligand "bite" angle for the $(CH_2)_2$ bridge in **1** of 72.4(2)° is noticeably larger than for the $SiMe_2$ bridge in **2** (64.5(1)°), indicating the greater geometric constraint in the latter. Nevertheless, the effect of this constraint on the Y−N−C angle of the amido substituent is only modest, as this increases by only 1.3° upon changing from the $(CH_2)_2$ bridge to the $SiMe_2$ bridge. This effect is significantly smaller than that of 4.0° observed in the "constrained geometry" cyclopentadienyl-amide titanium complexes $[C_5H_4(bridge)NtBu]TiCl_2$.[16] A possible reason for this is that the TACN ligand moiety has many more degrees of freedom available to relax geometrical constraints than the planar conjugated cyclopentadienyl moiety. A comparison of the (isomorphous) structures of **2** and **4** shows the effects of the increase in metal ionic radius. In the La complex **4**, the increased metal−N distances not only lead to a smaller $N_{amido}-Y-N_{bridgehead}$ "bite" angle of 60.8(1)° but also to smaller $M-N-C_{iPr}$ angles, one of which is as small as 102.9(3)°. This orientation of the ligand *i*Pr substituent relative to the La−alkyl bond may facilitate C−H activation of the *i*Pr methyl groups as a thermal decomposition route of the complex.

A feature that is common to all three structures is that one of the nitrogen atoms of the TACN moiety shows a significantly longer M−N bond distance than the other two, by as much as 0.12 (**1**) to 0.17 Å (**4**). This nitrogen atom invariably is the one that is essentially *trans* to one of the metal-bound alkyl groups (N−M−C angles of 151−155°). Earlier we observed in an yttrium dialkyl complex with a noncyclic triamino-amide that, in the absence of the geometric constraint of the cyclic nature, this effect is even more pronounced, with a bond length difference of 0.28 Å.[17]

Generation and Characterization of the Ionic Species $[LMCH_2SiMe_3(THF)]^+[B(Ar)_4]^-$ (M = Y, La; Ar = Ph, C_6F_5). Upon reaction of the dialkyl complexes **1**−**4** with the Brønsted acid $[PhNMe_2H][B(C_6F_5)_4]$ in C_6D_5Br solvent, instantaneous liberation of 2 equiv of Me_4Si and 1 equiv of propene is observed by ^1H NMR spectroscopy. This is in contrast to earlier observations on related complexes with Me_2-TACN-amide ligands, where the formation of relatively stable cationic monoalkyl species $[(TACN\text{-}amide)M(CH_2SiMe_3)]^+$ was seen.[4] This decomposition of the cationic alkyl species can be prevented (Y) or substantially retarded (La) when the reaction is performed in THF-d_8 solvent (Scheme 3). For yttrium, cationic alkyl species $[\mathbf{L}YCH_2SiMe_3(THF\text{-}d_8)]^+$ (**L** = **L1**, **5**; **L2**, **6**) appear to be stable in THF-d_8 at ambient temperature for several days, whereas for lanthanum the cationic $[\mathbf{L}LaCH_2SiMe_3(THF\text{-}d_8)_x]^+$ (**L** = **L1**, **7**; **L2**, **8**) species can be readily observed by ^1H NMR, but gradually decompose with release of $SiMe_4$ and propene (vide infra).

The cationic yttrium alkyl species **5** and **6** were isolated as their BPh_4 salts, in single crystalline form in about 70% yield, from the reaction of dialkyls **1** and **2** with equimolar amounts of $[PhNMe_2H][B(C_6H_5)_4]$ in THF, followed by layering with hexanes at ambient temperature. Figures 6 and 7 show the molecular structures of **5** and **6**, respectively, and selected bond lengths and angles are compiled in Table 2. The geometry around the yttrium center in the cations is again distorted octahedral, as in the corresponding neutral dialkyls. The differences in Y−N and $Y-CH_2$ distances between the neutral and cationic species are relatively small, with one exception.

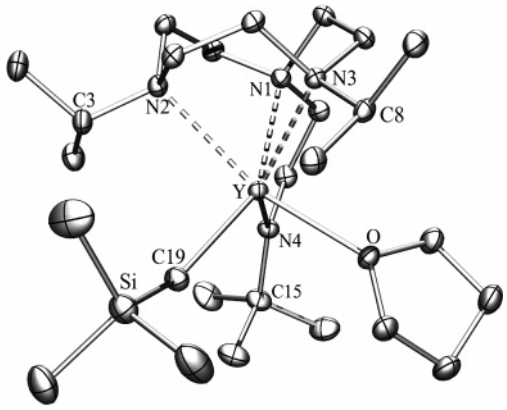


Figure 6. Molecular structure of **5** (ellipsoid probability level at 50%). Anion is omitted.

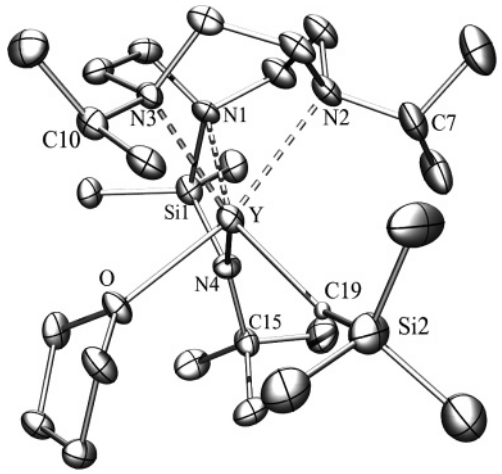


Figure 7. Molecular structure of **6** (ellipsoid probability level at 50%). Anion is omitted.

Table 1. Selected Bond Lengths and Angles for 1, 2, and 4

	1 (M = Y)	**2** (M = Y)	**4** (M = La)
	Bond Lengths (Å)		
M−C19	2.476(5)	2.420(4)	2.599(5)
M−C23	2.421(7)	2.465(4)	2.616(4)
M−N1	2.231(5)	2.271(3)	2.388(4)
M−N2	2.541(5)	2.574(4)	2.771(3)
M−N3	2.618(5)	2.595(4)	2.727(4)
M−N4	2.740(5)	2.747(3)	2.902(3)
	Bond Angles (deg)		
N1−M−N2	72.38(17)	64.47(12)	60.84(12)
N1−M−C19	113.8(2)	98.22(13)	100.24(16)
N1−M−C23	95.9(2)	118.12(13)	121.50(12)
$N4-M-C_{alkyl-trans}$	155.3(2)	152.87(12)	151.35(14)
$M-N1-C_{amido}$	129.8(4)	131.1(3)	125.7(3)
$M-N3-C_{iPr}$	110.8(4)	108.4(3)	102.9(3)
$M-N4-C_{iPr}$	112.1(4)	112.0(2)	108.8(2)

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Table 2. Selected Bond Lengths and Angles for 5 and 6

	5 (bridge = $(CH_2)_2$)	**6** (bridge = $SiMe_2$)
	Bond Lengths (Å)	
Y−C19	2.4466(18)	2.459(3)
Y−O	2.3721(11)	2.379(3)
Y−N1	2.5211(14)	2.530(4)
Y−N2	2.5999(14)	2.568(4)
Y−N3	2.5630(14)	2.502(4)
Y−N4	2.2333(14)	2.242(3)
	Bond Angles (deg)	
N4−Y−N1	73.56(5)	65.90(13)
N4−Y−C19	111.31(5)	110.71(12)
N4−Y−O	88.76(4)	89.83(12)
N2−Y−O	155.23(4)	155.34(11)

The position taken in the neutral dialkyl complexes by the alkyl group with the largest C−Y−N*i*Pr angle (around 150°) is occupied in **5** and **6** by the coordinated THF molecule. The Y−N distance *trans* to it is considerably shorter than in the neutral dialkyl complexes, so that the difference between the two Y−N*i*Pr distances in these complexes is only 0.036 (**5**) to 0.066 (**6**) Å instead of the 0.12−0.14 Å in the dialkyls **1** and **2**. This shows that the Y−N(amine) distance in these complexes is very sensitive to the nature of the group *trans* to it.

In the room-temperature ^{1}H NMR spectra (THF-d_8 solvent) of the yttrium cations **5** and **6** only a single M−CH_2 resonance is seen. Cooling the solutions induces decoalescence to reveal the separate resonances for the diastereotopic alkyl protons: for **5** (−10 °C) at δ −1.14 and −1.17 ppm (J_{YH} = 2.9 Hz, J_{HH} = 10.7 Hz), for **6** (−20 °C) at δ −0.90 and −0.95 ppm (J_{YH} = 2.7 Hz, J_{HH} = 11.0 Hz). In the ^{13}C NMR spectra the YCH_2 resonances for the cations are found approximately 4 ppm downfield from those in the neutral dialkyl precursors, while the J_{YC} coupling constant increases by about 5 Hz.

Reaction of the lanthanum dialkyls **3** and **4** with equimolar amounts of $[PhNMe_2H][B(C_6F_5)_4]$ in THF-d_8 solvent was monitored by ^{1}H NMR spectroscopy (20 °C). Formation of the cationic lanthanum monoalkyl complexes $[\mathbf{L}LaCH_2SiMe_3(THF\text{-}d_8)_x]^+$ (**L** = **L1**, **7**; **L2**, **8**), together with $SiMe_4$, is instantaneous. Interestingly, also a small amount of propene is detected, suggesting a ligand metalation process, as observed for the neutral precursors **3** and **4**. At low temperature (−50 °C) decomposition is slowed and the alkyl methylene group now shows resonances for the two diastereotopic protons: **7** (−0.93 and −1.10 ppm, J_{HH} = 9.4 Hz); **8** (−0.82 and −0.90 ppm, J_{HH} = 10.2 Hz). Unfortunately, at that temperature the ^{13}C NMR spectra of both complexes show severe broadening, precluding the extraction of chemical shifts and coupling constants for **7** and **8**.

Thermal Decomposition of [LMCH$_2$SiMe$_3$(THF)] Cations. As mentioned above, the thermal decomposition of the unsolvated cations $[\mathbf{L}MCH_2SiMe_3]^+$, generated in situ, is fast and releases equimolar amounts of $SiMe_4$ and propene. As attempts to observe well-defined products or intermediates of this process in solution by NMR spectroscopy were unsuccessful, the decomposition process was studied in the gas phase for M = Y. To this end, ES-MS (electrospray mass spectrometry)[18−20] was applied to freshly prepared 10^{-3} M solutions of $[\mathbf{L}YCH_2SiMe_3(THF)][B(C_6F_5)_4]$ in THF. Even at low nozzle voltages (40 V), only the unsolvated alkyl cations $[\mathbf{L}YR]^+$ (**5a**: *m*/*z* 487.2; **6a**: *m*/*z* 517.2) are observed (see Figure 8, top). In addition, a trace of the H_2O adduct is observed (**5a**·H_2O *m*/*z* 505.2; **6a**·H_2O *m*/*z* 535.2). This indicates that the THF molecule is only relatively loosely bound to the metal center in these species. Increasing the nozzle voltage to 160 V leads to collision-induced decay (CID) and gives spectra in which the $[\mathbf{L}YR-SiMe_4-C_3H_6]^+$ species (**5b**: *m*/*z* 356.9; **6b**: *m*/*z* 386.9) are now dominant. For the C_2-bridged ligand system **L1**, closer inspection reveals a small peak at *m*/*z* 399.2 for the $[\mathbf{L}YR-SiMe_4]^+$ (**A**) species (along with its water adduct, **A**·H_2O: $[\mathbf{L}YR\cdot H_2O-SiMe_4]^+$ = *m*/*z* 517.2) (Figure 8, bottom), suggesting that decomposition may involve initial C−H activation of one of the N*i*Pr methyl groups, followed by rapid propene elimination. For complex **6** (with **L2**), a corresponding peak was not observable under the same conditions, suggesting that the subsequent propene elimination is even faster in this system.

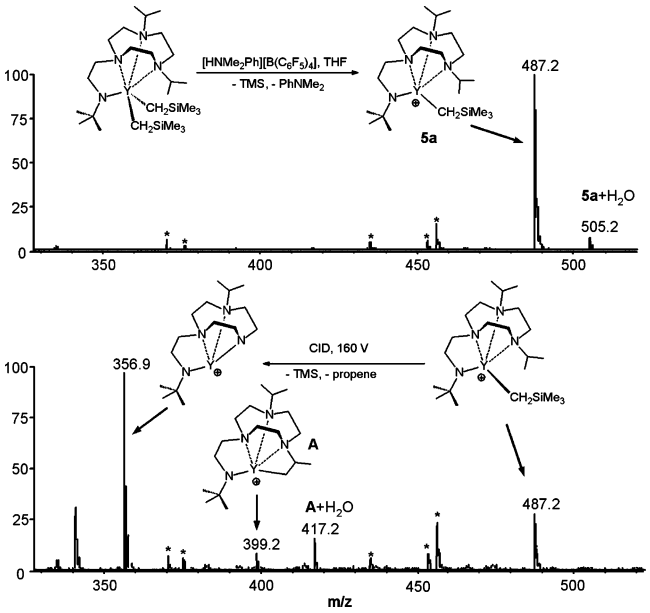

Figure 8. ES-MS of $\{[i\mathrm{Pr}_2\mathrm{TACN}(CH_2)_2\mathrm{N}t\mathrm{Bu}]Y(CH_2SiMe_3)(THF)\}^+$ (**5**) in THF as a function of the nozzle voltage (40 V, top; 160 V, bottom). *Background impurities.

Whereas the yttrium alkyl cations **5** and **6** are quite stable at ambient temperature in THF solution, the corresponding lanthanum derivatives decompose in this solvent at rates that allow a kinetic evaluation of the process. For complex **8**, with the $SiMe_2$-bridged ligand, the disappearance from a THF-d_8 solution was monitored by ^{1}H NMR spectroscopy at four different temperatures (see Supporting Information). This decomposition follows clean first-order kinetics, and from an Eyring plot the activation parameters $\Delta H^{\ddagger}$ = 94 ± 3 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 164 ± 7 J K^{-1} mol^{-1} were obtained. The large positive entropy of activation for this process suggests that dissociation of a THF molecule from the metal center is involved in the rate-determining step. As the activation parameters of the thermal decomposition of the neutral lanthanum dialkyl complex **4** in C_6D_6 and THF-d_8 solvent suggest that already in this case additional solvation by THF is possible, we do not wish to speculate on the number of THF molecules effectively coordinated to the cation **8** in neat THF solvent.

After full decomposition of **8** in THF-d_8, the ^{1}H NMR spectrum of the remaining inorganic species looks complex, but not ill-defined. In an attempt to obtain the decomposition product in crystalline form, a THF solution of **8** with the BPh_4 anion as

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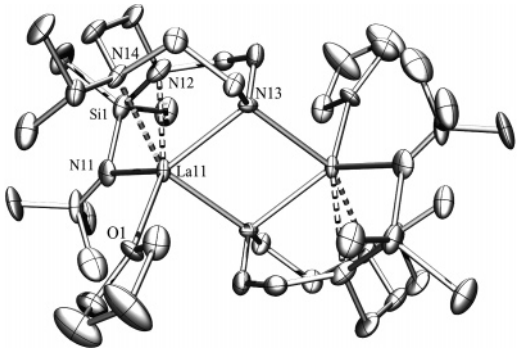
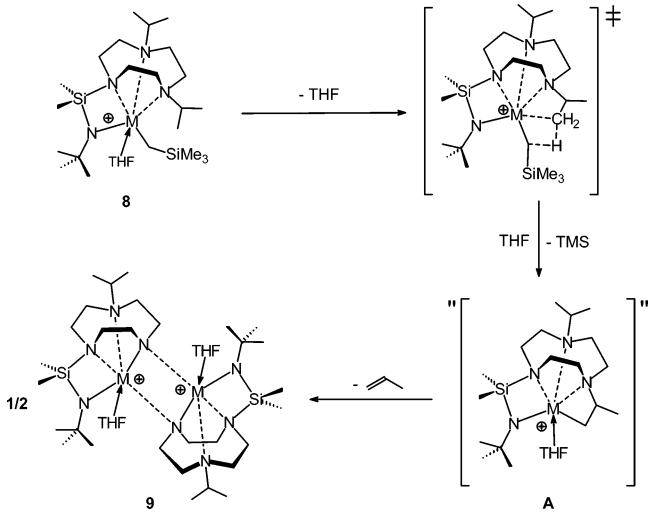


Figure 9. Molecular structure of **9** (ellipsoid probability level at 10%). Anions are omitted.

Scheme 4



counterion (to improve crystallization behavior) was generated by the reaction of dialkyl **4** with $[PhNMe_2H][BPh_4]$. Layering the solution with hexanes, and allowing it to stand overnight at ambient temperature, yielded crystals that appeared suitable for single-crystal X-ray diffraction. Despite considerable problems associated with the modest crystal quality and what appears to be a low-temperature phase transition, a structure determination at a temperature of 200 K allowed an unambiguous identification of the product as the tetraphenylborate salt of the dinuclear dicationic species $\{[i\text{PrTACN}(SiMe_2)N t\text{Bu}]La(THF)\}_2^{2+}$ (**9**, Figure 9). From each of the TACN-amide ligands in this complex, one of the *i*Pr groups has been lost from one of the TACN nitrogen atoms, resulting in a dianionic diamine-diamide ligand. The nitrogen that has lost its substituent is now bridging between the two metal centers in the dinuclear complex. The NMR spectra of the isolated product in THF are also in agreement with the stoichiometry and the symmetry of the compound in the crystal. The yttrium analogue of **9** could be obtained in a similar manner in 85% isolated yield, but now the reaction was performed in bromobenzene (to induce decomposition) to which some THF was added after 1 hr.

Thus it appears that the general reaction scheme for the thermolysis of the cationic monoalkyl complexes can be described as summarized in Scheme 4.

We conclude that the formation of **9** is the result of ligand metalation at one of the nitrogen isopropyl (methyl) substituents with concomitant protonolysis of the metal-bound alkyl (CH_2SiMe_3) that is eliminated as $SiMe_4$, generating a cationic cyclometalated species **A** (Scheme 4). This species **A**, also proposed in the decomposition of the yttrium analogues described above, is short-lived and undergoes a four-center electron rearrangement, liberating propene. Two cationic diamine-diamide lanthanum species then combine to form dimer **9**.

Conclusions

The isopropyl-substituted monoanionic $i\text{Pr}_2$TACN-amide ligands **L1** and **L2** can be used to obtain neutral TACN-amide dialkyl complexes of yttrium and of lanthanum, the largest rare earth metal. The isopropyl substituents improve the thermal stability of the neutral La dialkyl derivatives over those with the Me_2TACN-amide ligands: the latter suffers from rapid NMe metalation when the bridging moiety in the ligand is $SiMe_2$.[9] Nevertheless, the isopropyl substituents also open up another decomposition route: intramolecular cyclometalation of the isopropyl methyl group followed by propene loss. This makes the derived cationic $i\text{Pr}_2$TACN-amide monoalkyl species distinctly *less* stable than their analogues with Me_2TACN-amide ligands. This decomposition can be retarded by interaction of the metal center with Lewis bases (as shown for THF).

As the decomposition of the cationic monoalkyl complexes by *i*Pr metalation and propene extrusion eliminates the last metal−carbon bond in the complex, it is also a possible catalyst deactivation mechanism when these species are employed in catalytic ethene polymerization. Apparently, the balance between the tendency toward metalation and the stabilization of the cationic alkyl species by the Lewis basic alkene substrate is delicate: in ethene polymerization studies involving the four metal−ligand combinations described,[4b] only the yttrium catalyst with the least constraining ligand bridge, $[i\text{Pr}_2\text{TACN}(CH_2)_2N t\text{Bu}]Y(CH_2SiMe_3)^+$ (i.e., the cation derived from **1**), was found to be competent in catalytic ethene polymerization.

Experimental Section

General Considerations. All preparations were performed under an inert nitrogen atmosphere, using standard Schlenk or glovebox techniques, unless mentioned otherwise. Toluene, pentane, and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried over Al_2O_3 (Fluka). All solvents were degassed prior to use and stored under nitrogen. Deuterated solvents (C_6D_6, C_7D_8, C_4D_8O; Aldrich) were vacuum transferred from Na/K alloy, prior to use. Reagents Me_3SiCH_2Li,[21] $YCl_3(THF)_{3.5}$, $Y(CH_2SiMe_3)_3(THF)_2$,[22] $i\text{Pr}_2$-TACNH,[23] $i\text{Pr}_2$-TACNLi,[24] and $ClSiMe_2NH t\text{Bu}$,[25] were prepared according to published procedures. $[PhNMe_2H][B(C_6F_5)_4]$ (Strem) was used as received. NMR spectra were recorded on Varian Gemini VXR 300 or Varian Inova 500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ^1H NMR spectra were referenced to resonances of residual protons in deuterated solvents. The ^{13}C NMR spectra were referenced to carbon resonances of deuterated solvents and reported in ppm relative to TMS (δ 0 ppm).

The electrospray ionization mass spectrometry (ES-MS) experiments were conducted on a Nermag R3010 triple quadrupole MS system with a custom-built IonSpray (pneumatically assisted

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electrospray) source[26] equipped with a gas curtain, which are contained in a closed chamber that can be evacuated, flushed, and maintained under nitrogen. Typical sample preparation: in a glovebox, a sample of 10 μmol of the yttrium dialkyl and 10 μmol of $[Me_2NPhH][B(C_6F_5)_4]$ or alternatively 10 μmol of the isolated ion pairs $[\{(i\text{Pr})_2\text{-TACN-SiMe}_2\text{N}t\text{Bu}\}\text{Y}(CH_2SiMe_3)(THF)][BPh_4]\cdot(THF)$, $[\{(i\text{Pr})_2\text{-TACN-CH}_2\text{N}t\text{Bu}\}\text{Y}(CH_2SiMe_3)(THF)][BPh_4]\cdot(THF)$ were dissolved in 1 mL of solvent (THF or C_6H_5Br) and diluted 10-fold with THF, generating a 10^{-3} M solution. The samples were taken up into a 500 μL syringe (Model 1750 RNR, Hamilton) and electrosprayed via a syringe pump operating at 10 μL/min. The capillary voltage was 3.5 kV. Mass spectra were recorded from *m*/*z* 200 to 900 at 10 s per scan under control of the Sciex API 3 data system. The sampling orifice (nozzle) voltage was increased from +40 to +160 V to induce ion fragmentation. The skimmer located behind the sampling orifice was at +25 V in all experiments. Elemental analyses were performed at the Microanalytical Department of H. Kolbe (Mülheim an der Ruhr).

Synthesis of $(i\text{Pr})_2\text{TACN(CH}_2)_2\text{NH}t\text{Bu}$ (HL1). (a) *N-tert*-Butyl-(4,7-diisopropyl-1,4,7-triazanon-1-yl)acetamide. To a solution of 4,7-diisopropyl-1,4,7-triazacyclononane (1.30 g, 6.30 mmol) in acetonitrile (20 mL) were added *N-tert*-butylchloroacetamide (0.95 g, 6.30 mmol) and NaI (100 mg). After 6 h of reflux the brownish solution was diluted with water (100 mL) acidified with concentrated hydrochloric acid (pH $\approx$ 2) and washed with ether (3 $\times$ 100 mL), made basic with KOH (pH $\approx$ 9) and extracted with CH_2Cl_2 (3 $\times$ 100 mL). The combined extracts were dried over Na_2SO_4 and filtrated, and solvent was removed by a rotary evaporator, yielding the product as a dark yellow oil (1.65 g, 5.0 mmol, 80%). ^{1}H NMR ($CDCl_3$): δ 7.9 (br, NH), 3.04 (s, 2H, NCH_2CO), 2.83 (sept, 2H, J_{HH} = 6.6 Hz, *i*Pr CH), 2.64−2.58 (m, 8H, NCH_2), 2.56 (s, 4H, NCH_2), 1.30 (s, 9H, *t*Bu), 0.91 (d, J_{HH} = 6.6 Hz, 12H, *i*PrMe).

(b) *N-tert*-Butyl-2-(4,7-diisopropyl-1,4,7-triazanon-1-yl)ethylamine. Solid $LiAlH_4$ (2.5 g) was added to a solution of *N-tert*-butyl-(4,7-diisopropyl-1,4,7-triazanon-1-yl)acetamide (1.60 g, 5.0 mmol) in 30 mL of di-*n*-butyl ether ($n\text{Bu}_2\text{O}$). After refluxing for 5 h the mixture was cooled with an ice bath and diethyl ether (100 mL) was added to allow for a controlled hydrolysis of excess $LiAlH_4$ with water (which was added dropwise via a mounted cooler). The white solids were filtered off and washed with diethyl ether (2 $\times$ 100 mL). The combined ether fractions were dried over Na_2SO_4 and filtrated, and the solvent was removed by rotary evaporation, yielding the product as a yellow oil (1.40 g, 4.4 mmol, 89%). ^{1}H NMR (300 MHz, C_6D_6, δ): 2.82 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, *i*Pr CH), 2.76−2.73 (m, 4H, NCH_2), 2.62−2.54 (m, 8H, NCH_2), 2.51(s, 4H, NCH_2N), 1.06 (s, 9H, NH*t*Bu), 0.91 (d, $^3J_{HH}$ = 6.6 Hz, 6H, $NCHMe_2$). ^{13}C NMR (75.4 MHz, C_6D_6, δ): 58.7 (d, J_{CH} = 130.32 Hz, $NCHMe_2$), 56.1 (t, J_{CH} = 131.7, NCH_2), 54.6 (t, J_{CH} = 132.42 Hz, NCH_2), 52.8 (t, J_{CH} = 128.1 Hz, NCH_2), 52.6 (t, J_{CH} = 128.1 Hz, NCH_2), 49.9 ($NCMe_3$), 40.3 (t, J_{CH} = 133.0 Hz, NCH_2), 29.0 (q, J_{CH} = 124.4 Hz, $NCMe_3$), 18.3 (q, J_{CH} = 124.4 Hz, $NCHMe_2$).

Synthesis of $(i\text{Pr})_2\text{TACN(SiMe}_2)\text{NH}t\text{Bu}$ (HL2). Method a. To 30 mL of pure Me_2SiCl_2 was added $Li[TACN(i\text{Pr})_2]$ (0.92 g, 4.24 mmol in portions) at ambient temperature. The reaction mixture turned yellow and was stirred for 4 h. The excess Me_2SiCl_2 was removed under reduced pressure, and the remainder was dissolved in toluene (30 mL). Subsequently, $LiNH\text{tBu}$ (0.33 g, 4.24 mmol) was added to the solution at room temperature. After 18 h the toluene was removed under vacuum. The remaining sticky residue was extracted with pentane (2 $\times$ 100 mL). Evaporation of the pentane yielded 0.98 g (68%) of the title compound as a brownish oil (95% by ^{1}H NMR).

Method b. A solution of $ClSiMe_2NH\text{tBu}$ (0.98 g, 5.92 mmol) in hexanes (10 mL) was added dropwise at ambient temperature to a solution of $Li[TACN(i\text{Pr})_2]$ (1.30 g, 5.92 mmol) in hexanes (50 mL). The precipitated LiCl was filtered off, and the filtrate was evaporated to dryness, yielding the product, spectroscopically pure (NMR) as a light yellow oil (1.70 g, 4.95 mmol, 84%). ^{1}H NMR (300 MHz, 25 °C, C_6D_6): δ 3.01 (m, 4H, NCH_2), 2.74 (sept, $^3J_{HH}$ = 6.3 Hz, 2H, *i*Pr CH), 2.68 (m, 4H, NCH_2), 2.50 (s, 4H, NCH_2), 2.34 (s, 1H, NH) 1.18 (s, 9H, *t*Bu Me), 0.93 (d, $^3J_{HH}$ = 6.3 Hz, 12H, *i*Pr Me), 0.22 (s, 6H, Me_2Si). ^{13}C NMR (75.4 MHz, 25 °C, C_6D_6): δ 54.5 (t, J_{CH} = 127.3 Hz, NCH_2), 54.2 (d, J_{CH} = 141.2, *i*Pr CH), 53.5 (t, J_{CH} = 129.6 Hz, NCH_2), 51.5 (t, J_{CH} = 130.7 Hz, NCH_2), 46.3 (*t*Bu C), 33.8 (q, J_{CH} = 124.4, *t*Bu Me), 18.4 (q, J_{CH} = 124.3 Hz, *i*Pr Me), 1.6 (q, J_{CH} = 117.5 Hz, $SiMe_2$).

Synthesis of $[(i\text{Pr})_2\text{TACN(CH}_2)_2\text{N}t\text{Bu}]\text{Y(CH}_2\text{SiMe}_3)_2$ (1). At ambient temperature, a solution of H**L1** (0.32 g, 1.00 mmol) in toluene (2 mL) was added dropwise to a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.49 g, 1.00 mmol) in toluene (5 mL). The reaction mixture was stirred for 2 h, after which the volatiles were removed under reduced pressure. The residue was washed with cold pentane (−20 °C, 5 mL) and subsequently dried in a vacuum, yielding the title compound (0.45 g, 0.78 mmol, 78%). This material is pure by NMR spectroscopy, identical to the crystallized material communicated previously.[4a] Full NMR spectroscopic data can be found in the Supporting Information.

Synthesis of $[(i\text{Pr})_2\text{TACN(SiMe}_2)\text{N}t\text{Bu}]\text{Y(CH}_2\text{SiMe}_3)_2$ (2). At ambient temperature, a solution of H**L2** (0.34 g, 1.00 mmol) in pentane (10 mL) was added dropwise to a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.49 g, 1.00 mmol) in pentane (30 mL). The reaction mixture was stirred for 3 h (20 °C), after which the volatiles were removed in a vacuum. The residue was stripped of remaining THF by stirring with 5 mL of pentane, which was subsequently removed under reduced pressure. The resulting sticky solid was then extracted with pentane (20 mL). Cooling the extract to −30 °C produces analytically pure crystalline product in modest yield (0.21 g, 0.34 mmol, 34%) due to its high solubility. A higher yield (75%) of material, pure by NMR spectroscopy, can be obtained by simple evaporation of the solvent from the reaction mixture, followed by rinsing of the solid with cold pentane (−20 °C, 5 mL) and drying in vacuo. ^{1}H NMR (500 MHz, −50 °C, THF-d_8): δ 4.01 (sept, J_{HH} = 6.6 Hz, 1H, *i*Pr CH), 3.69 (sept, J_{HH} = 6.6 Hz, 1H, *i*Pr CH), 3.31 (m, 1H, NCH_2), 3.10 (m, 1H, NCH_2), 3.02 (m, 1H, NCH_2), 2.93 (m, 2H, NCH_2), 2.84 (m, 2H, NCH_2), 2.73 (m, 3H, NCH_2), 2.60 (m, 2H, NCH_2), 1.47 (d, J_{HH} = 6.6 Hz, 3H, *i*Pr Me), 1.36 (d, J_{HH} = 6.6 Hz, 3H, *i*Pr Me), 1.32 (s, 9H, N*t*Bu), 1.05 (d, J_{HH} = 6.6 Hz, 3H, *i*Pr Me), 1.01 (d, J_{HH} = 6.6 Hz, 3H, *i*Pr Me), 0.33 (s, 3H, Me_2Si), 0.16 (s, 3H, Me_2Si), 0.03 (s, 9H, Me_3SiCH_2), −0.06 (s, 9H, Me_3SiCH_2), −0.59 (dd, J_{HH} = 10.5 Hz, J_{YH} = 2.7 Hz, 1H, YCH_2), −0.79 (dd, J_{HH} = 10.5 Hz, J_{YH} = 2.0 Hz, 1H, YCH_2), −1.03 (dd, J_{HH} = 10.5 Hz, J_{YH} = 2.1 Hz, 1H, YCH_2), −0.12 (dd, J_{HH} = 10.4 Hz, J_{YH} = 2.2 Hz, 1H, YCH_2). ^{13}C NMR (125.7 MHz, −50 °C, THF-d_8): δ 58.1 (t, J_{CH} = 136.1 Hz, NCH_2), 57.1 (d, J_{CH} = 133.7, *i*Pr CH), 57.0 (t, J_{CH} = 138.2 Hz, NCH_2), 56.6 (t, J_{CH} = 138.8 Hz, NCH_2), 56.1 (t, J_{CH} = 136.0 Hz, NCH_2), 53.5 (N*t*Bu C), 44.9 (t, J_{CH} = 137.9 Hz, NCH_2), 43.8 (t, J_{CH} = 135.8 Hz, NCH_2), 37.7 (q, J_{CH} = 125.0, N*t*Bu Me), 33.1 (dt, J_{CH} = 95.4 Hz, J_{YH} = 34.8 Hz, YCH_2), 32.8 (dt, J_{CH} = 94.8 Hz, J_{YH} = 35.5 Hz, YCH_2), 25.7 (q, J_{CH} = 126.0 Hz, *i*Pr Me), 24.6 (q, J_{CH} = 126.0 Hz, *i*Pr Me), 14.0 (q, J_{CH} = 125.1 Hz, *i*Pr Me), 13.8 (q, J_{CH} = 125.5 Hz, *i*Pr Me), 6.0 (q, J_{CH} = 116.7 Hz, Me_3SiCH_2), 5.5 (q, J_{CH} = 117.1 Hz, Me_2Si), 3.9 (q, J_{CH} = 117.1 Hz, Me_2Si). Anal. Calcd for $C_{26}H_{61}N_4Si_3Y$ (604.34): C, 51.62; H, 10.50; N, 9.26; Y, 14.70. Found: C, 49.21; H, 10.15; N, 8.78; Y, 14.22. Elemental analysis values for **2** (several batches) show inconsistencies that appear not to be associated with carbide formation and that we have been unable to trace to soluble or insoluble impurities.

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Synthesis of [(*i*Pr)$_2$TACN(CH$_2$)$_2$N*t*Bu]La(CH$_2$SiMe$_3$)$_2$ (3). Solid $LaBr_3(THF)_4$ (0.66 g, 1.00 mmol) and $LiCH_2SiMe_3$ (0.28 g, 3.00 mmol) were dissolved in THF (30 mL). The solution was stirred for 30 min (RT), after which H**L1** (0.31 g, 1.00 mmol, dissolved in 5 mL of THF) was added. The yellowish reaction mixture was stirred for 1 h, after which the volatiles were removed under reduced pressure. The residue was stripped of remaining THF by stirring twice with 5 mL of pentane (0 °C), which was subsequently removed under reduced pressure. The solid was extracted with a hexane/toluene mixture (25 mL each, 0 °C). The filtrate was dried in a vacuum, affording 0.36 g of the crude product. This material was recrystallized from hexane/toluene (10:1, 5.0 mL, −30 °C), yielding colorless crystals of the title compound (0.27 g, 43%). ^{1}H NMR (500 MHz, −50 °C, THF-d_8): δ 3.91 (sept, J_{HH} = 6.3 Hz, 1H, *i*Pr CH), 3.51 (sept, J_{HH} = 5.9 Hz, 1H, *i*Pr CH), 3.40−3.30 (m, 3H, NCH_2), 3.16−3.04 (m, 2H, NCH_2), 2.99−2.89 (m, 4H, NCH_2), 2.83−2.74 (m, 3H, NCH_2), 2.68 (m, 2H, NCH_2), 2.49 (d, J_{HH} = 12.2, 1H, NCH_2), 2.13 (d, J_{HH} = 11.5, 1H, NCH_2), 2.51 (d, J_{HH} = 6.3 Hz, 3H, *i*Pr Me), 1.36 (d, J_{HH} = 6.3 Hz, 3H, *i*Pr Me), 1.33 (s, 9H, *t*Bu), 1.06 (d, J_{HH} = 5.9 Hz, 3H, *i*Pr Me), 0.99 (d, J_{HH} = 5.9 Hz, 3H, *i*Pr Me), −0.06 (s, 9H, *Me*$_3$SiCH$_2$), −0.09 (s, 9H, *Me*$_3$SiCH$_2$), −0.60 (d, J_{HH} = 10.5 Hz, 1H, $LaCH_2$), −1.09 (d, J_{HH} = 10.5 Hz, 1H, $LaCH_2$), −1.13 (d, J_{HH} = 10.0 Hz, 1H, $LaCH_2$), −1.32 (d, J_{HH} = 10.0 Hz, 1H, $LaCH_2$). ^{13}C NMR (125.7 MHz, −50 °C, THF-d_8): δ 59.3 (t, J_{CH} = 127.0 Hz, NCH_2), 58.2 (t, J_{CH} = 129.2 Hz, NCH_2), 56.1 (t, J_{CH} = 127.1 Hz, NCH_2), 55.9 (d, J_{CH} = 136.5 Hz, *i*Pr CH), 55.5 (d, J_{CH} = 136.4 Hz, *i*Pr CH), 55.4 (t, J_{CH} = 133.0 Hz, NCH_2), 53.1 (t, J_{CH} = 135.7 Hz, NCH_2), 52.9 (s, *t*Bu C), 52.8 (t, J_{CH} = 137.4 Hz, NCH_2), 48.3 (t, J_{CH} = 101.4 Hz, $LaCH_2$), 46.7 (t, J_{CH} = 129.4 Hz, NCH_2), 46.5 (t, J_{CH} = 100.3 Hz, $LaCH_2$), 43.1 (t, J_{CH} = 132.3 Hz, NCH_2), 42.9 (t, J_{CH} = 135.0 Hz, NCH_2), 31.8 (q, J_{CH} = 122.8, *t*Bu Me), 24.5 (q, J_{CH} = 126.3 Hz, *i*Pr Me), 24.2 (q, J_{CH} = 126.2 Hz, *i*Pr Me), 14.1 (q, J_{CH} = 125.0 Hz, *i*Pr Me), 13.8 (q, J_{CH} = 125.0 Hz, *i*Pr Me), 6.4 (q, J_{CH} = 117.0 Hz, *Me*$_3$SiCH$_2$La), 6.2 (q, J_{CH} = 117.0 Hz, *Me*$_3$SiCH$_2$La). The compound is thermally too unstable to be sent out for elemental analysis.

Synthesis of [(*i*Pr)$_2$TACN(SiMe$_2$)N*t*Bu]La(CH$_2$SiMe$_3$)$_2$ (4). Solid $LaBr_3(THF)_4$ (0.66 g, 1.00 mmol) and $LiCH_2SiMe_3$ (0.28 g, 3.00 mmol) were dissolved in THF (30 mL). The solution was stirred for 30 min (RT), after which **L2**H (0.34 g, 1.00 mmol, dissolved in 5 mL of THF) was added. The yellowish reaction mixture was stirred for 1 h, after which the volatiles were removed under reduced pressure. The residue was stripped of remaining THF by stirring twice with 5 mL of pentane (0 °C), which was subsequently removed under reduced pressure. The solid was extracted with a hexane/toluene mixture (25 mL each, 0 °C). The filtrate was dried in a vacuum, affording 0.40 g of the crude product. This material was recrystallized from hexane/toluene (10:1, 5 mL, −30 °C), yielding colorless crystals of the title compound (0.29 g, 44%). ^{1}H NMR (500 MHz, −60 °C, THF-d_8): δ 4.03 (sept, J_{HH} = 6.0 Hz, 1H, *i*Pr CH), 3.59 (sept, J_{HH} = 6.1 Hz, 1H, *i*Pr CH), 3.21 (m, 1H, NCH_2), 3.06−2.90 (m, 4H, NCH_2), 2.78−2.70 (m, 4H, NCH_2), 2.62−2.50 (m, 3H, NCH_2), 1.46 (d, J_{HH} = 6.0 Hz, 3H, *i*Pr Me), 1.33 (s, 9H, *t*Bu), 1.28 (d, J_{HH} = 6.0 Hz, 3H, *i*Pr Me), 1.03 (d, J_{HH} = 6.1 Hz, 3H, *i*Pr Me), 0.97 (d, J_{HH} = 6.1 Hz, 3H, *i*Pr Me), 0.28 (s, 3H, Me$_2$Si), 0.08 (s, 3H, Me$_2$Si), −0.10 (s, 9H, *Me*$_3$SiCH$_2$), −0.13 (s, 9H, *Me*$_3$SiCH$_2$), −0.67 (d, J_{HH} = 10.5 Hz, 1H, $LaCH_2$), −0.77 (d, J_{HH} = 10.5 Hz, 1H, $LaCH_2$), −1.04 (d, J_{HH} = 10.5 Hz, 1H, $LaCH_2$), −1.12 (d, J_{HH} = 10.5 Hz, 1H, $LaCH_2$). ^{13}C NMR (125.7 MHz, −60 °C, THF-d_8): δ 58.2 (t, J_{CH} = 133.0 Hz, NCH_2), 57.0 (t, J_{CH} = 134.2 Hz, NCH_2), 55.8 (d, J_{CH} = 136.4 Hz, *i*Pr CH), 55.6 (d, J_{CH} = 136.4 Hz, *i*Pr CH), 55.5 (t, J_{CH} = 133.6 Hz, NCH_2), 52.4 (s, *t*Bu C), 50.3 (t, J_{CH} = 97.6 Hz, $LaCH_2$), 48.0 (t, J_{CH} = 100.8 Hz, $LaCH_2$), 44.9 (t, J_{CH} = 131.0 Hz, NCH_2), 43.5 (t, J_{CH} = 131.5 Hz, NCH_2), 43.1 (t, J_{CH} = 134.2 Hz, NCH_2), 36.5 (q, J_{CH} = 123.3, *t*Bu Me), 24.1 (q, J_{CH} = 125.2 Hz, *i*Pr Me), 23.2 (q, J_{CH} =124.5 Hz, *i*Pr Me), 17.4 (q, J_{CH} =124.0 Hz, *i*Pr Me), 14.0 (q, J_{CH} =124.0 Hz, *i*Pr Me), 6.1 (q, J_{CH} = 118.2 Hz, *Me*$_3$-SiCH$_2$La), 5.4 (q, J_{CH} = 117.5 Hz, Me$_2$Si), 5.5 (q, J_{CH} = 117.5 Hz, Me$_2$Si). The compound is thermally too unstable to be sent out for elemental analysis.

Reaction of [(*i*Pr)$_2$TACN(CH$_2$)$_2$N*t*Bu]Y(CH$_2$SiMe$_3$)$_2$ with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. (a) In the Absence of THF. A solution of **1** (12 mg, 20.8 μmol) in C_6D_5Br (0.6 mL) was added to [HNMe$_2$-Ph][B(C$_6$F$_5$)$_4$] (17 mg, 20.8 μmol). The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed the evolution of 2 equiv of $SiMe_4$ and 1 equiv of propene. Resonances of the yttrium species are broad and could not be interpreted.

(b) In the Presence of THF. A solution of **1** (24 mg, 41.6 μmol) in C_6D_5Br (0.6 mL) with three drops of additional THF-d_8 was added to [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (34 mg, 41.6 μmol). The obtained solution was transferred into a NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic monoalkyl species [**L1**YCH$_2$SiMe$_3$(THF-d_8)][B(C$_6$F$_5$)$_4$], $SiMe_4$, and free PhNMe$_2$. ^{1}H NMR (500 MHz, −30 °C, C_6D_5Br): δ 7.23 (t, J_{HH} = 7.5 Hz, 2H, m-H PhNMe$_2$), 6.77 (t, J_{HH} = 7.5 Hz, 1H, p-H PhNMe$_2$), 6.58 (d, J_{HH} = 7.5 Hz, 2H, o-H PhNMe$_2$), 3.48 (sept, J_{HH} = 6.0 Hz, 1H, *i*Pr CH), 3.40 (t, J_{HH} = 13.0 Hz, 1H, NCH_2), 2.79−2.75 (m, 2H, NCH_2), 2.72 (s, 6H, PhNMe$_2$), 2.68−2.59 (m, 3H, NCH_2), 2.57 (br, 1H, *i*Pr CH), 2.55−2.48 (m, 2H, NCH_2), 2.42−2.29 (m, 3H, NCH_2), 2.25−2.17 (m, 3H, NCH_2), 1.18 (d, J_{HH} = 6.0 Hz, 6H, *i*Pr Me), 1.15 (s, 9H, *t*Bu), 0.84 (d, J_{HH} = 5.5 Hz, 3H, *i*Pr Me), 0.80 (d, J_{HH} = 5.5 Hz, 3H, *i*Pr Me), 0.09 (s, 9H, *Me*$_3$SiCH$_2$), 0.07 (s, 12H, Me$_4$Si), −1.29 (dd, J_{HH} = 11.0 Hz, J_{YH} = 3.0 Hz, 1H, YCH_2), −1.35 (dd, J_{HH} = 11.0 Hz, J_{YH} = 3.0 Hz, 1H, YCH_2).

Synthesis of [{(*i*Pr)$_2$TACN(CH$_2$)$_2$N*t*Bu}Y(CH$_2$SiMe$_3$)(THF)]-[BPh$_4$]·(THF) (5). THF (0.5 mL) was added to a mixture of 100 mg (173 μmol) of **1** and 76 mg (173 μmol) of [HNMe$_2$Ph][BPh_4]. The resulting yellowish solution was layered with 2 mL of hexanes. Upon standing overnight at ambient temperature, colorless crystals formed. The mother liquor was decanted, and the crystals were washed with hexanes. Drying in a vacuum yielded 141 mg of the title compound (148 μmol, 86%). ^{1}H NMR (500 MHz, −10 °C, THF-d_8): δ 7.25 (br, 8H, o-H BPh_4), 6.87 (t, J_{HH} = 6.9 Hz, 8H, m-H BPh_4), 6.74 (t, J_{HH} = 6.9 Hz, 4H, p-H BPh_4), 3.50 (sept, J_{HH} = 6.5 Hz, 1H, *i*Pr CH), 3.15 (t, J_{HH} = 11.5 Hz, 2H, NCH_2), 2.86−2.70 (m, 9H, NCH_2), 2.65 (sept, J_{HH} = 6.5 Hz, 1H, *i*Pr CH), 2.51 (d, J_{HH} = 11.8 Hz, 1H, NCH_2), 2.40 (t, J_{HH} = 11.5 Hz, 2H, NCH_2), 2.11 (t, J_{HH} = 12.3 Hz, 1H, NCH_2), 2.01 (t, J_{HH} = 11.6 Hz, 1H, NCH_2), 1.34 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 1.30 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 1.14 (s, 9H, *t*Bu Me), 0.93 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 0.91 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), −0.15 (s, 9H, Me_3SiCH_2), − 1.14 (dd, J_{YH} = 2.8 Hz, J_{HH} = 10.7 Hz, 1H, YCH_2), − 1.17 (dd, J_{YH} = 2.8 Hz, J_{HH} = 10.7 Hz, 1H, YCH_2). ^{13}C NMR (125.7 MHz, 25 °C, THF-d_8): δ 165.7 (q, 49.8 Hz, ipso-BPh_4), 138.0 (dt, J = 153.2 Hz, 6.96 Hz, o-BPh_4), 126.8 (d, J = 153.0 Hz, m-BPh_4), 123.0 (dt, J = 156.8 Hz, 7.55 Hz, p-BPh_4), 59.8 (t, J_{CH} = 140.2 Hz, NCH_2), 57.6 (d, J_{CH} = 138.4 Hz, *i*Pr CH), 57.3 (d, J_{CH} = 138.4 Hz, *i*Pr CH), 56.5 (t, J_{CH} = 137.0 Hz, NCH_2), 56.0 (t, J_{CH} = 137.2 Hz, NCH_2), 55.3 (s, *t*Bu C), 54.0 (t, J_{CH} = 136.0 Hz, NCH_2), 53.7 (t, J_{CH} = 139.6 Hz, NCH_2), 46.3 (t, J_{CH} = 133.5 Hz, NCH_2), 44.6 (t, J_{CH} = 138.3 Hz, NCH_2), 44.1 (t, J_{CH} = 137.8 Hz, NCH_2), 38.3 (dt, J_{YC} = 40.4 Hz, J_{CH} = 92.1 Hz, YCH_2), 32.4 (q, J_{CH} = 123.8, *t*Bu Me), 24.5 (q, J_{CH} =126.7 Hz, *i*Pr Me), 24.2 (q, J_{CH} =125.8 Hz, *i*Pr Me), 15.9 (q, J_{CH} =126.7 Hz, *i*Pr Me), 14.5 (q, J_{CH} =126.7 Hz, *i*Pr Me), 5.5 (q, J_{CH} = 117.0 Hz, *Me*$_3$SiCH$_2$Y). Anal. Calcd for [$C_{26}H_{58}N_4OSiY$]·[$C_{24}H_{20}B$] (879.00): C, 68.32; H, 8.94; N, 6.37. Found: C, 68.06; H, 8.98; N, 5.73.

Table 3. Crystal Data and Collection Parameters of Complexes 1, 2, and 4

	1	2	4
formula	$C_{26}H_{61}N_4Si_2Y$	$C_{26}H_{63}N_4Si_3Y$	$C_{26}H_{63}LaN_4Si_3$
fw	574.87	604.98	654.98
cryst color	colorless	colorless	colorless
cryst size (mm)	0.05 × 0.10 × 0.30	0.47 × 0.39 × 0.34	0.26 × 0.21 × 0.16
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	9.815(1)	9.9434(6)	10.0781(5)
b (Å)	9.859(1)	17.752(1)	17.8056(8)
c (Å)	17.291(3)	19.563(1)	19.7373(9)
α (deg)	95.60(1)	91.197(1)	90.996(1)
β (deg)	90.68(1)	94.254(1)	94.522(1)
γ (deg)	98.63(1)	91.353(1)	91.577(1)
V (Å^3)	1645.7(4)	3441.8(3)	3528.8(3)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	1.160	1.168	1.233
μ (cm^{-1})	18.6	18.18	13.32
F(000), electrons	624	1312	1384
θ range (deg)	1.64, 26.0	2.30, 26.73	2.20, 28.28
R1	0.0731	0.0637	0.0537
wR2(all data)	0.1800	0.1516	0.1307
index ranges (*h*, *k*, *l*)	0→12, ±12, ±21	±12, ±22, ±24	±13, ±23, ±24
T (K)	130	100	100
GOF	1.016	1.069	1.004

Table 4. Crystal Data and Collection Parameters of Complexes 5, 6, and 9

	5	6	9
formula	$[C_{26}H_{58}N_4OSiY]^+[C_{24}H_{20}B]^-$	$[C_{26}H_{60}N_4OSi_2Y]^+[C_{24}H_{20}B]^-\cdot C_4H_8O$	$0.5[C_{38}H_{84}La_2N_8O_2Si_2]^{2+}\cdot [C_{24}H_{20}B]^-\cdot 0.5(C_6H_{12})$
fw	879.00	981.21	807.87
cryst color	colorless	colorless	colorless
cryst size (mm)	0.45 × 0.39 × 0.17	0.42 × 0.21 × 0.03	0.31 × 0.12 × 0.09
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
a (Å)	12.1829(6)	17.775(2)	14.573(1)
b (Å)	13.6520(7)	20.181(2)	16.465(1)
c (Å)	14.8613(8)	30.309(3)	18.963(1)
α (deg)	86.335(1)	90.00(1)	
β (deg)	88.358(1)	90.00(1)	96.348(1)
γ (deg)	78.635(1)	90.00(1)	
V (Å^3)	2418.0(2)	10872(2)	4522.2(5)
Z	2	8	4
ρ_{calcd} (g cm^{-3})	1.207	1.199	1.279
μ (cm^{-1})	12.7	11.59	12.79
F(000), electrons	944	4224	1824
θ range (deg)	2.11, 28.28	2.42, 25.35	2.24, 25.68
R1	0.0335	0.0622	0.1099
wR2(all data)	0.0852	0.1637	0.2929
index ranges (*h*, *k*, *l*)	±16, ±16, ±19	±21, ±20, ±36	±17, ±19, ±23
T (K)	100	100	200
GOF	1.009	0.972	1.521

Reaction of [(*i*Pr)$_2$TACN(SiMe$_2$)N*t*Bu]Y(CH$_2$SiMe$_3$)$_2$ with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. (a) In the Absence of THF. A solution of **2** (12 mg, 19.9 μmol) in C_6D_5Br (0.6 mL) was reacted with $[HNMe_2Ph][B(C_6F_5)_4]$ (16 mg, 19.9 μmol). The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed the evolution of 2 equiv of $SiMe_4$ and 1 equiv of propene. Resonances of the yttrium species are broad and could not be interpreted.

(b) In the Presence of THF. A solution of **2** (24 mg, 39.8 μmol) in C_6D_5Br (0.6 mL) with a drop of added THF-d_8 was reacted with $[HNMe_2Ph][B(C_6F_5)_4]$ (32 mg, 39.8 μmol). The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic monoalkyl species $\{[\mathbf{L2}Y(CH_2SiMe_3)(THF\text{-}d_8)\}[B(C_6F_5)_4]$, $SiMe_4$, and free $PhNMe_2$. ^{1}H NMR (500 MHz, −30 °C, C_6D_5Br): δ 7.23 (t, J_{HH} = 7.5 Hz, 2H, m-H $PhNMe_2$), 6.77 (t, J_{HH} = 7.5 Hz, 1H, p-H $PhNMe_2$), 6.58 (d, J_{HH} = 7.5 Hz, 2H, o-H $PhNMe_2$), 3.30 (sept, J_{HH} = 6.0 Hz, 2H, *i*Pr CH), 2.76−2.69 (m, 4H, NCH_2), 2.63 (s, 6H, $PhNMe_2$), 2.56−2.24 (m, 8H, NCH_2), 1.12 (d, J_{HH} = 6.0 Hz, 6H, *i*Pr Me), 1.10 (s, 9H, *t*Bu), 0.72 (br, 6H, *i*Pr Me), 0.22 (s, 6H, $SiMe_2$), 0.01 (s, $SiMe_4$), − 0.02 (s, 9H, YCH_2SiMe_3), −0.84 (d, J_{HH} = 11.5 Hz, 1H, YCH_2), −0.91 (d, J_{HH} = 11.0 Hz, 1H, YCH_2).

Synthesis of [{(*i*Pr)$_2$TACN(SiMe$_2$)N*t*Bu}Y(CH$_2$SiMe$_3$)(THF)][BPh$_4$]·(THF) (6). THF (0.5 mL) was added to a mixture of 100 mg (165 μmol) of $[(iPr)_2TACNSiMe_2NtBu]Y(CH_2SiMe_3)_2$ and 73 mg (165 μmol) of $[HNMe_2Ph][BPh_4]$. The resulting yellowish solution was layered with 2 mL of hexanes. Upon standing overnight at ambient temperature, colorless crystals formed. The mother liquor was decanted and the crystals were washed with hexanes. Drying in a vacuum yielded 126 mg of the title compound (128 μmol, 78%). ^{1}H NMR (500 MHz, −50 °C, THF-d_8): δ 7.23 (br, 8H, o-H BPh_4), 6.86 (t, ^3J = 7.0 Hz, 8H, m-H BPh_4), 6.73 (t, ^3J = 7.0 Hz, 4H, p-H BPh_4), 3.00 (br, 1H, *i*Pr CH), 2.88 (sept, J_{HH} = 6.5 Hz, 1H, *i*Pr CH), 2.73−1.57 (m, 8H, NCH_2), 2.42 (m, 3H, NCH_2), 2.23 (m, 1H, NCH_2), 1.39 (br, 6H, *i*Pr Me), 1. 62 (s, 9H, N*t*Bu), 1.01 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 0.98 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 0.28 (s, 6H, Me_2Si), −0.04 (s, 9H, Me_3SiCH_2), −0.06 (s, 9H, Me_3SiCH_2), −0.86 (d, J_{YH} = 2.9 Hz, 2H, YCH_2). ^{13}C NMR (125.7 MHz, −50 °C, THF-d_8): δ 165.7 (q, 48.8 Hz, ipso-BPh_4), 137.9 (d, J = 154.0 Hz, o-BPh_4), 126.7 (d, J = 150.5

Hz, m-BPh_4), 123.0 (d, J = 154.1 Hz, p-BPh_4), 57.6 (d, J_{CH} = 135.1, *i*Pr CH), 57.4 (t, J_{CH} = 141.1 Hz, NCH_2), 56.9 (d, J_{CH} = 134.2, *i*Pr CH), 56.2 (t, J_{CH} = 133.0 Hz, NCH_2), 56.3 (N*t*Bu C), 45.0 (t, J_{CH} = 140.3 Hz, NCH_2), 44.3 (t, J_{CH} = 135.4 Hz, NCH_2), 42.9 (t, J_{CH} = 137.8 Hz, NCH_2), 37.2 (q, J_{CH} = 122.5, N*t*Bu Me), 37.3 (dt, J_{CH} = 94.1 Hz, J_{YH} = 41.0 Hz, YCH_2), 24.9 (q, J_{CH} = 124.7 Hz, *i*Pr Me), 24.3 (q, J_{CH} = 127.0 Hz, *i*Pr Me), 14.7 (q, J_{CH} = 124.8 Hz, *i*Pr Me), 14.0 (q, J_{CH} = 126.5 Hz, *i*Pr Me), 5.6 (q, J_{CH} = 117.3 Hz, Me_3SiCH_2), 4.5 (q, J_{CH} = 118.1 Hz, Me_2Si), 4.3 (q, J_{CH} = 117.9 Hz, Me_2Si). Anal. Calcd for $[C_{26}H_{60}N_4OSi_2Y]\cdot[C_{24}H_{20}B]\cdot(C_4H_8O)$ (981.21): C, 66.10; H, 9.04; N, 5.71. Found: C, 65.42; H, 9.25; N, 5.66.

Reaction of [(*i*Pr)$_2$TACN(CH$_2$)$_2$N*t*Bu]La(CH$_2$SiMe$_3$)$_2$ with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. A solution of **3** (25 mg, 40.0 μmol) in THF-d_8 (0.6 mL) was added to $[HNMe_2Ph][B(C_6F_5)_4]$ (32 mg, 40.0 μmol). The obtained solution was transferred into a NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic monoalkyl species {**L1**La(CH_2SiMe_3)(THF-d_8)}$[B(C_6F_5)_4]$ (**7**), $SiMe_4$, and free $PhNMe_2$. ^{1}H NMR (500 MHz, −50 °C, THF-d_8): δ 7.14 (t, J_{HH} = 6.7 Hz, 2 H, m-H $PhNMe_2$), 6.71 (t, J_{HH} = 7.6 Hz, 1 H, p-H $PhNMe_2$), 6.60 (d, J_{HH} = 6.7 Hz, 2H, o-H $PhNMe_2$), 4.01 (sept, J_{HH} = 6.4 Hz, 1H, *i*Pr CH), 3.83 (sept, J_{HH} = 6.4 Hz, 1H, *i*Pr CH), 3.62 (m, 2 H, NCH_2), 3.45−3.30 (m, 4H, NCH_2), 3.13 (m, 2H, NCH_2), 2.91 (s, 6H, $PhNMe_2$), 2.80−2.70 (m, 4H, NCH_2), 2.65−2.52 (m, 4H, NCH_2), 1.47 (d, J_{HH} = 6.4 Hz, 3H, *i*Pr Me), 1.44 (d, J_{HH} = 6.4 Hz, 3H, *i*Pr Me), 1.31 (s, 9H, *t*Bu), 1.10 (d, J_{HH} = 6.4 Hz, 3H, *i*Pr Me), 1.06 (d, J_{HH} = 6.4 Hz, 3H, *i*Pr Me), 0.00 (s, 12H, $SiMe_4$), −0.13 (s, 9H, Me_3SiCH_2), −0.93 (d, J_{HH} = 9.4 Hz, 1H, $LaCH_2$), −1.10 (d, J_{HH} = 9.4 Hz, 1H, $LaCH_2$).

Reaction of [(*i*Pr)$_2$TACN(SiMe$_2$)N*t*Bu]La(CH$_2$SiMe$_3$)$_2$ with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. A solution of **4** (26 mg, 40.0 μmol) in THF-d_8 (0.6 mL) was added to $[HNMe_2Ph][B(C_6F_5)_4]$ (32 mg, 40.0 μmol). The obtained solution was transferred into a NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic monoalkyl species {**L2**La(CH_2SiMe_3)(THF-d_8)}$[B(C_6F_5)_4]$ (**8**), $SiMe_4$, and free $PhNMe_2$. As propene is gradually released upon standing in solution (as detected by ^{1}H NMR), indicating thermolysis of the title compound, NMR spectroscopy was performed at low temperatures, at which the ^{13}C NMR spectra are uninterpretable due to severe broadening of the resonances. ^{1}H NMR (500 MHz, −50 °C, THF-d_8): δ 7.14 (t, J_{HH} = 6.7 Hz, 2H, m-H $PhNMe_2$), 6.71 (t, J_{HH} = 7.6 Hz, 1H, p-H $PhNMe_2$), 6.60 (d, J_{HH} = 6.7 Hz, 2H, o-H $PhNMe_2$), 3.76 (sept, J_{HH} = 6.5 Hz, 1H, *i*Pr CH), 3.29 (sept, J_{HH} = 6.3 Hz, 1H, *i*Pr CH), 3.19 (m, 2H, NCH_2), 3.10−3.00 (m, 4H, NCH_2), 2.96 (m, 2H, NCH_2), 2.91 (s, 6H, $PhNMe_2$), 2.86−2.75 (m, 3H, NCH_2), 2.46 (m, 1H, NCH_2), 1.49 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 1.45 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 1.34 (s, 9H, *t*Bu), 1.12 (d, J_{HH} = 6.3 Hz, 3H, *i*Pr Me), 1.08 (d, J_{HH} = 6.3 Hz, 3H, *i*Pr Me), 0.25 (s, 3H, $SiMe_2$), 0.20 (s, 3H, $SiMe_2$), 0.00 (s, 12H, $SiMe_4$), −0.12 (s, 9H, Me_3SiCH_2), −0.82 (d, J_{HH} = 10.2 Hz, 1H, $LaCH_2$), −0.90 (d, J_{HH} = 10.2 Hz, 1H, $LaCH_2$).

Synthesis of {[*i*PrTACN(SiMe$_2$)N*t*Bu]La(THF)}$_2$[BPh$_4$]$_2$ (C$_6$H$_{12}$) (9). A solution of **4** (61 mg, 100 μmol) in THF (1 mL) was reacted with $[HNMe_2Ph][BPh_4]$ (44 mg, 100 μmol). The obtained solution was layered with hexanes (2 mL). Upon standing overnight at ambient temperature, colorless crystals formed. The mother liquor was decanted, and the crystals were washed with hexanes. Drying in a vacuum yielded 118 mg of the title compound (68 μmol, 68%). ^{1}H NMR (500 MHz, 20 °C, THF-d_8): δ 7.25 (br, 8H, o-H BPh_4), 6.85 (t, ^3J = 7.0 Hz, 8H, m-H BPh_4), 6.71 (t, ^3J = 7.0 Hz, 4H, p-H BPh_4), 3.83 (m, 1H, NCH_2), 3.28 (m, 1H, NCH_2), 3.18 (m, 1H, NCH_2), 3.03−2.84 (m, 5H, NCH_2), 2.76 (sept, J_{HH} = 6.5 Hz, 1H, *i*Pr CH), 2.58 (m, 2H, NCH_2), 2.46 (m, 1H, NCH_2), 2.39 3.28 (m, 1H, NCH_2), 1.25 (s, 12H, C_6H_{12}), 1.19 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 1.16 (s, 9H, N*t*Bu), 0.97 (d, J_{HH} = 6.5 Hz, 3H, *i*Pr Me), 0.23 (s, 3H, Me_2Si), 0.17 (s, 3H, Me_2Si). ^{13}C NMR (125.7 MHz, 20 °C, THF-d_8): δ 165.9 (q, 49.0 Hz, ipso-BPh_4), 137.9 (d, J = 152.0 Hz, o-BPh_4), 126.7 (d, J = 150.9 Hz, m-BPh_4), 123.0 (d, J = 155.4 Hz, p-BPh_4), 57.0 (d, J_{CH} = 132.5, $NCHMe_2$), 56.8 (N*t*Bu C), 55.0 (t, J_{CH} = 138.9 Hz, NCH_2), 54.8 (t, J_{CH} = 135.0 Hz, NCH_2), 54.0 (t, J_{CH} = 136.3 Hz, NCH_2), 50.9 (t, J_{CH} = 138.4 Hz, NCH_2), 49.6 (t, J_{CH} = 134.6 Hz, NCH_2), 48.3 (t, J_{CH} = 136.8 Hz, NCH_2), 36.9 (q, J_{CH} = 123.4, N*t*Bu Me), 21.7 (q, J_{CH} = 126.7 Hz, *i*Pr Me), 18.7 (q, J_{CH} = 124.7 Hz, *i*Pr Me), 5.7 (q, J_{CH} = 117.5 Hz, Me_2Si), 4.6 (q, J_{CH} = 117.9 Hz, Me_2Si). Anal. Calcd for $[C_{38}H_{84}N_8O_2Si_2La]\cdot[C_{24}H_{20}B](C_6H_{12})$ (1741.75): C, 63.44; H, 7.87; N, 6.43. Found: C, 63.32; H, 7.97; N, 6.19.

Preparation of [{(*i*Pr)TACN(SiMe$_2$)N*t*Bu}Y(THF)][BPh$_4$]. A solution of **2** (60 mg, 100 μmol) in C_6H_5Br (2 mL) was reacted with $[HNMe_2Ph][BPh_4]$ (44 mg, 100 μmol). The solution was allowed to stand at ambient temperature for 1 h, after which THF (0.5 mL) was added. The solution was then layered with hexanes (2 mL). Upon standing overnight at ambient temperature, colorless crystals formed. The mother liquor was decanted, and the crystals were washed with hexanes. Drying in a vacuum yielded 66 mg of the title compound (85 μmol, 85%). Anal. Calcd for $[C_{19}H_{42}N_4OSiY][C_{24}H_{20}B]$ (778.79): C, 66.32; H, 8.02; N, 7.19. Found: C, 66.18; H, 8.11; N, 7.06. Resonances in the ^{1}H and ^{13}C NMR spectra (THF-d_8 solvent) are very broad and could not be interpreted.

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Supporting Information Available: Crystallographic data for **1**, **2**, **4**, **5**, **6**, and **9** including atomic coordinates, full bond distances, and bond angles as well as anisotropic thermal parameters (CIF), fits used for determination of rate constants and Eyring plot of thermal decomposition of **4** and **8** in THF, and text of full NMR data of various compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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