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Intramolecular C–H Bond Activation by Lanthanoid Complexes Bearing a Bulky Aminopyridinato Ligand

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The present work is aimed towards the synthesis of C–H activation products of various group 3 and lanthanoid metals bearing a bulky aminopyridinato ligand, (2,6-diisopropylphenyl)[6-(2,6-dimethylphenyl)pyridin-2-yl]amine (**1**, Ap′H). Deprotonation of **1** using KH leads to polymeric $[Ap'K]_n$ (**2**), which undergoes clean salt metathesis reaction with MX_3 [M = Sc, Nd and Sm, and X = Cl or M = La and X = Br] forming mono thf adducts $[Ap'_2ScCl(thf)]$ (**3**), $[Ap'_2LaBr(thf)]$ (**4**), $[Ap'_2NdCl(thf)]$ (**5**), and $[Ap'_2SmCl(thf)]$ (**6**). However, reacting **2** with $LuCl_3$ leads to mono- as well as bis(aminopyridinato)lutetium complexes $[Ap'LuCl_2(thf)_2]$ (**7**) and $[Ap'_2LuCl(thf)]$ (**8**), respectively, while the analogous reaction with $LaCl_3$ at 50 °C produces the tris(aminopyridinato)lanthanum complex $[Ap'_3La]$ (**9**). For the selective synthesis of **8** in good yield amine elimination route was adopted. X-ray diffraction studies revealed a distorted octahedral coordination for the bis(aminopyridinato) complexes **3**, **4** and **6**, despite the differences in their ionic radii. Alkylation of the bis(aminopyridinato) monohalide complexes with equimolar amounts of $LiCH_2SiMe_3$ in hexane allowed the isolation of the corresponding alkyl derivatives. For the smaller metals like Sc and Lu affording $[Ap'_2ScCH_2SiMe_3(thf)]$ (**10**) and $[Ap'_2LuCH_2SiMe_3(thf)]$ (**11**), respectively. However, lanthanoids with large ionic radii such as La and Nd resulted in the formation of methyl group C–H bond activation products $[Ap'(Ap'_{-H})La(thf)_2]$ (**12**) and $[Ap'(Ap'_{-H})Nd(thf)]$ (**13**), respectively. Most likely an alkyl species was formed which then undergoes intramolecular C–H activation and C–H activation runs fast with regard to the rate of alkyl complex formation. The alkylation of **6** (Sm) with $LiCH_2SiMe_3$ did not give a clear product. The reaction of **11** with $PhSiH_3$ (Ph = phenyl) led via intramolecular C–H bond activation to $[Ap'(Ap'_{-H})Lu(thf)]$ (**14**). In this case most likely a hydride species was formed which then undergoes rapid C–H activation. The alkyl complex **10** (Sc) did not react with $PhSiH_3$. The molecular structures of **11**, **12** and **13** have been confirmed by X-ray crystal structure analysis.

Introduction

The activation of C–H bonds and in particular the activation of the C–H bonds of inert alkyls by transition metal and lanthanoid complexes is a reaction of general interest due to its relevance for the functionalization of organic molecules.[1] The chemistry of lanthanoid metals is characterized by their high electrophilicity, their tendency to high coordination numbers and their unique feature of varying the sizes of the rare earth atom[2] with a nearly identical coordination chemical behavior. Complexes of these metals are strong Lewis acids which may attack the electron density of C–H bonds, thus forming agostic[3] interactions and activate C–H bonds. Watson has even shown that methane, itself, could be activated by lanthanocene complexes such as $(Cp^*)_2LuCH_3$ (Cp^* = pentamethylcyclopentadienyl).[4] Consequently, intermolecular alkyl group C–H activation of spectator ligands of lanthanoid complexes has been observed for a variety of ligands, for instance, for methyl groups of the Cp* ligand.[5] Similar alkyl group C–H activation reactions have been described for non-metallocene lanthanoid complexes.[6]

Aminopyridinato ligands[7] have been used successfully for the stabilization of early transition metals and lanthanoids and we started recently a research program to investigate the reactivity of metal complexes coordinated by very bulky aminopyridinates.[8] In the course of these studies we observed that alkyl and hydrido yttrium complexes supported by the aminopyridinato ligand Ap′ {Ap′H = (2,6-diisopropylphenyl)[6-(2,6-dimethylphenyl)pyridin-2-yl]-amine, Figure 1} undergo methyl group C–H activation of one of the methyl groups of the 2,6-dimethylphenly moiety of the Ap′ ligand.[8i]

The alkyl complex $[Ap'_2YCH_2SiMe_3]$ undergoes this C–H activation rather slowly and the corresponding hydride does it more than 500 times faster.

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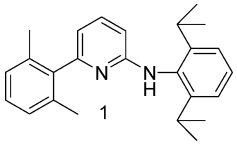
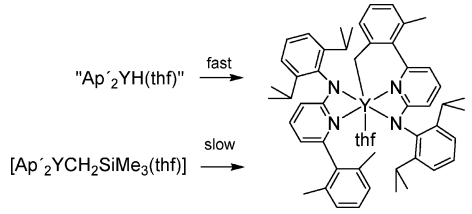


Figure 1. Used aminopyridine.

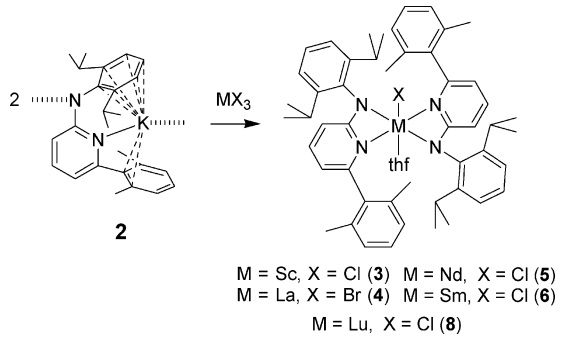
Since yttrium mimics the size of the late lanthanoids quite well we became interested in how this ligand metallation proceeds for early lanthanoids as well as for Lu and Sc. Herein we report on synthesis and characterization of lanthanoid monohalide complexes stabilized by bulky Ap′ ligands, their alkylation with $LiCH_2SiMe_3$ which leads – depending on the size of the lanthanoid ion – to C–H activation products or to (rather) stable alkyl complexes (Scheme 1).



Scheme 1. Ligand metallation (methyl group C–H activation) reaction of Ap′$_2$Y-alkyl and -hydride complexes.

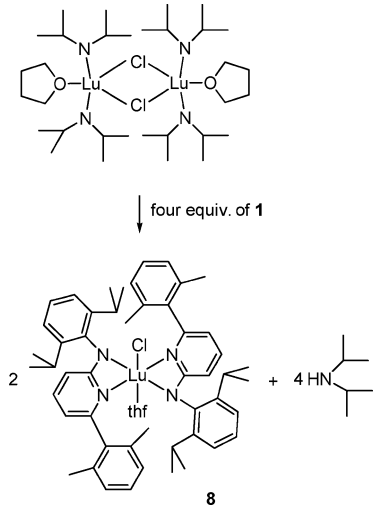
Results and Discussion

Polymeric **2** was prepared according to the literature reported procedure.[8a] Two equivalents of **2** were treated with MX_3 [M = Sc, Nd, and Sm, and X = Cl or M = La and X = Br] in a salt metathesis reaction to afford the corresponding bis(aminopyridinato) complexes [Ap′$_2$ScCl(thf)] (**3**), [Ap′$_2$LaBr(thf)] (**4**), [Ap′$_2$NdCl(thf)][8b] (**5**), and [Ap′$_2$SmCl(thf)] (**6**) in good yields (Scheme 2).



Scheme 2. Synthesis of bis(aminopyridinato) halide complexes.

However, in case of Lu both mono- as well as bis(aminopyridinato)lutetium complexes [Ap′$LuCl_2(thf)_2$] (**7**) and [Ap′$_2$LuCl(thf)] (**8**) were observed, respectively. Due to the poor solubility of **8** in hexane **7** can be separated easily in 24% yield if extracted with hexane. Residue **8** was extracted with toluene in a yield of 20%. Due to the poor yield of **8** we became interested in using an amine elimination route. Compound **8** was synthesized in (90%) yield by reacting four equivalents of **1** with $[(R_2N)_2LuCl(thf)]_2$ where R = diisopropyl (Scheme 3).



Scheme 3. Amine elimination synthesis of **8**.

The thf ligand is labile and a thf-free derivative of compound **3** was isolated after work up in toluene. However, crystals suitable for X-ray analysis were grown from concentrated toluene solution after adding a few drops of thf which coordinates to the vacant site of the metal centre. Compound **4** is isolated as yellow crystalline material from hexane in moderate yield. Compound **6** and **8** were isolated as yellow crystals by slow diffusion of hexane or toluene into a saturated thf solution of these complexes. This series of compounds is a rare example of lanthanoid complexes with the same ligand environment for which the same coordination number is observed despite their different ionic radii. The coordination of the bis(aminopyridinato)-lanthanoid halide complexes is best described as a distorted octahedron arising from the two bidentate aminopyridinates, the chloro/bromo as well the thf ligand, as shown in Figures 2, 3, 4, and 5. Crystallographic details of all structures are listed in Tables 1 and 2. It has been observed that in all cases the aminopyridinato ligands induce distortion from the ideal octahedral symmetry. $N_{pyridine}$–M–N_{amido} angles of 60.21, 52.98, 55.16 and 57.7° in **3**, **4**, **6** and **8**, respectively, were observed and are comparable to previously published **5** [54.5°].[8b] The longer M–$N_{pyridine}$ bond lengths compared to M–N_{amido} bond length is indicative of the localization of the anionic function of the ligand at the amido N-atoms.[9]

The compound **7** is dimeric in solid state and the coordination around each Lu can be best described as distorted pentagonal bipyramid (Figure 6). The two chloro ligands, the pair of nitrogen atoms and one thf ligand form the pentagonal (equatorial) plane and the remaining chloro and thf ligands occupy the axial positions of the polyhedron. The distortion is caused by the small N–Lu–N angle of 56.5(2)° due to the strained binding mode of the ligand. It leads to a situation in which all other angles in the pentagonal plane are over 72°. The N1–Lu–Cl2 and O2–Lu–Cl2 cis angles

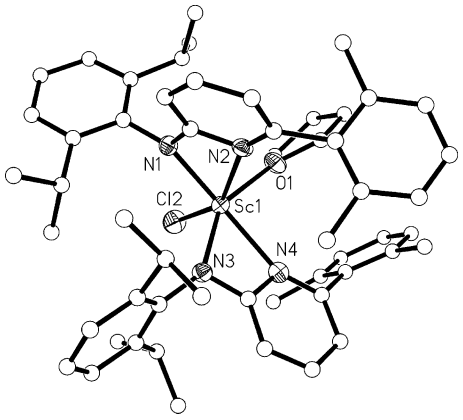


Figure 2. Molecular structure of **3**; selected bond lengths [Å] and angles [°]: N1–Sc1 2.109(5), N2–Sc1 2.403(6), N3–Sc1 2.151(6), N4–Sc1 2.314(5), O1–Sc1 2.190(5) Cl2–Sc1 2.365(2); N1–Sc1–N3 105.9(2), N1–Sc1–O1 101.61(19), N3–Sc1–O1 149.00(18), N1–Sc1–N4 160.4(2), N3–Sc1–N4 60.57(19), O1–Sc1–N4 89.09(19), N1–Sc1–Cl2 92.25(16), N3–Sc1–Cl2 101.97(16), O1–Sc1–Cl2 90.88(15), N4–Sc1–Cl2 104.05(16), N1–Sc1–N2 59.85(19), N3–Sc1–N2 94.0(2), O1–Sc1–N2 87.57(19), N4–Sc1–N2 104.89(19), Cl2–Sc1–N2 150.99(14).

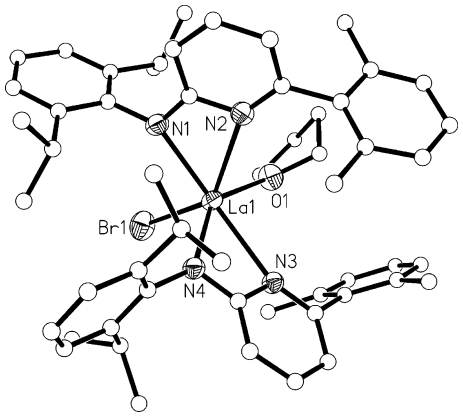


Figure 3. Molecular structure of **4**; selected bond lengths [Å] and angles [°]: N1–La1 2.418(3), N2–La1 2.650(4), N3–La1 2.639(3), N4–La1 2.433(3), O1–La1 2.525(3), Br1–La1 2.8625(6); N1–La1–N4 104.46(11), N1–La1–O1 110.29(11), N4–La1–O1 144.13(11), N1–La1–N3 151.20(11), N4–La1–N3 53.04(11), O1–La1–N3 91.22(10), N1–La1–N2 52.92(12), N4–La1–N2 102.77(11), O1–La1–N2 91.42(10), N3–La1–N2 109.73(11), N1–La1–Br1 89.59(9), N4–La1–Br1 103.33(8), O1–La1–Br1 85.80(7), N3–La1–Br1 111.59(8), N2–La1–Br1 138.63(8).

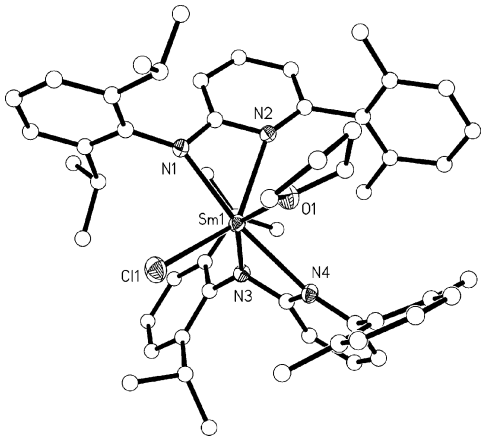


Figure 4. Molecular structure of **6**; selected bond lengths [Å] and angles [°]: N1–Sm1 2.334(2), N2–Sm1 2.572(2), N3–Sm1 2.352(2), N4–Sm1 2.519(2), O1–Sm1 2.4064(18), Cl1–Sm1 2.5681(6); N1–Sm1–N4 156.85(7), N1–Sm1–O1 103.58(7), N4–Sm1–O1 89.57(7), N1–Sm1–N3 107.83(7), N4–Sm1–N3 55.63(7), O1–Sm1–N3 144.80(7), N1–Sm1–N2 54.69(6), N4–Sm1–N2 107.57(6), O1–Sm1–N2 88.88(6), N3–Sm1–N2 96.43(7), N1–Sm1–Cl1 89.50(5), N4–Sm1–Cl1 109.53(5), O1–Sm1–Cl1 90.98(5), N3–Sm1–Cl1 104.61(5), N2–Sm1–Cl1 142.90(5).

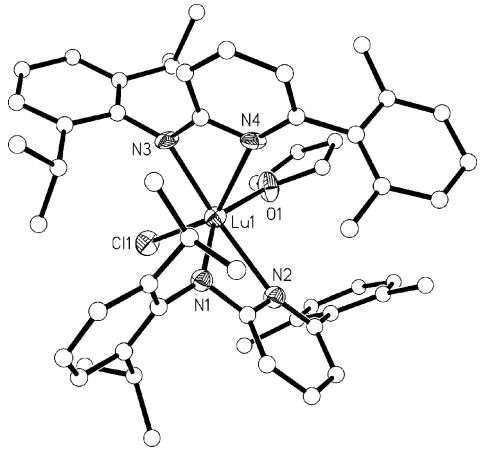


Figure 5. Molecular structure of **8**; selected bond lengths [Å] and angles [°]: [A°] and angles [°]: N1–Lu1 2.248(7), N2–Lu1–2.422(8), N3–Lu1 2.246(8), N4–Lu1 2.462(10), O1–Lu1 2.297(6), Cl1–Lu1 2.479(3); N1–Lu1–N4 95.0(3), N1–Lu1–O1 147.8(3), N4–Lu1–O1 88.5(4), N1–Lu1–N3 105.8(3), N4–Lu1–N3 56.7(3), O1–Lu1–N3 102.8(3), N1–Lu1–N2 58.7(2), N4–Lu1–N2 107.1(3), O1–Lu1–N2 89.7(3), N3–Lu1–N2 158.6(3), N1–Lu1–Cl1 102.8(3), N4–Lu1–Cl1 146.8(19), O1–Lu1–Cl1 90.9(2), N3–Lu1–Cl1 91.3(2), N2–Lu1–Cl1 106.1(2).

are 77.13(18) and 72.66(15)°. The N2–Lu–O2 angle is the widest [81.5(2)°] of all. The $O1_{ax}$–Lu–$O2_{eq}$ and Cl_{ax}–Lu–$O2_{eq}$ angles are 80.63(18) and 90.05(14)°, respectively.

Although structurally very similar, complexes **3** and **4** demonstrated different dynamic behaviour in solution. We essentially attribute this to the different radii of the lanthanoid ions. In **3** the signals of the two methyl groups are well separated as two sharp peaks at room temperature. At 330 K a very slow exchange between two methyl groups is observed. The exchange becomes faster at 350 K but the signals still remain inequivalent. The ^{1}H NMR spectrum of compound **4** at room temperature consists of one broad signal corresponding to methyl group. The cooling of the [D_8]toluene solution to 273 K afforded the splitting of the above signal into two broad resonances. Further cooling resulted first in sharpening of these signals (253 K) and then again into the broadening and splitting of each of them to a new pair of signals (233 K). Most likely, two dynamic processes are present, first the exchange of the positions of the two Ap ligand and secondly the freezing out of the rotation of the 2,6-dimethylphenyl substituent Figure 7.

Reacting two equivalents of **2** with $LaCl_3$ in thf at 65 °C without stirring it at room temperature leads to a homoleptic complex, [Ap′$_3$La] (**9**) in overall yield of 37%

Table 1. Details of the X-ray crystal structure analyses.

	3	$4 \cdot 1/2(C_6H_{14})$	**6**
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	12.6930(11)	12.2880(7)	12.8440(7)
b [Å]	14.030(12)	12.3570(7)	13.9910(8)
c [Å]	14.1790(12)	19.3060(11)	14.2110(8)
α [°]	73.880(10)	99.975(5)	104.986(4)
β [°]	79.920(10)	90.309(5)	99.473(4)
γ [°]	88.820(5)	113.791	90.957(4)
V [Å^3]	2391.2(4)	2632.8(3)	2428.5(2)
Crystal size [mm]	$0.22 \times 0.17 \times 0.15$	$0.21 \times 0.20 \times 0.19$	$0.49 \times 0.36 \times 0.22$
ρ_{calcd} [gcm^{-3}]	1.205	1.322	1.330
μ [mm^{-1}] (Mo-K_α)	0.252	1.611	1.305
T [K]	191(2)	191(2)	133(2)
θ range [°]	1.55 to 25.69	1.82 to 24.69	1.51 to 25.75
Number of reflections unique	3681	6434	8251
Number of reflections obsd. [$I > 2\sigma(I)$]	22008	28979	31719
Number of parameters	550	562	562
wR_2 (all data)	0.222	0.080	0.071
R value [$I > 2\sigma(I)$]	0.087	0.042	0.027

Table 2. Details of the X-ray crystal structure analyses.

	7	**8**	**9**
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [Å]	10.222(5)	12.7414(9)	13.7710(4)
b [Å]	18.663(5)	13.9751(13)	22.5550(8)
c [Å]	17.437(5)	14.1997(10)	20.1650(7)
α [°]		105.467(7)	
β [°]	93.047(5)	99.750(7)	91.11(3)
γ [°]		90.090(7)	
V [Å^3]	3322(2)	2898.8(3)	6262.2(4)
Crystal size [mm]	$0.17 \times 0.08 \times 0.07$	$0.23 \times 0.20 \times 0.18$	$0.59 \times 0.50 \times 0.35$
ρ_{calcd} [gcm^{-3}]	1.495	1.381	1.285
μ [mm^{-1}] (Mo-K_α)	0.71	2.155	0.73
T [K]	193(2)	133(2)	191(2)
θ range [°]	1.60 to 26.15	1.51 to 25.70	1. 35 to 25.7
Number of reflections obsd. [$I > 2\sigma(I)$]	2790	4437	10335
Number of reflections	6538	6249	81811
Number of parameters	361	544	881
wR_2 (all data)	0.064	0.139	0.076
R value [$I > 2\sigma(I)$]	0.033	0.057	0.030

(Scheme 4). Crystals of **9** suitable for X-ray analysis (crystallographic details are listed in Table 2) were grown by slow condensation of hexane into a saturated thf solution of **9**. The coordination around La can best be described as distorted trigonal prism as shown in Figure 8. The slightly elongated La–$N_{pyridine}$ bond length in **9** (2.745 Å, averaged value) indicates some steric overcrowding. The averaged La–pyridine distance is 2.703 (47 values taken from the CSD version 5.30).

As we have previously shown for yttrium[8i] that such bis(aminopyridinato)lanthanoid halide complexes can be successfully alkylated using $LiCH_2SiMe_3$. The reaction of these alkyls with $PhSiH_3$ to form the intramolecular C–H bond activation products is fast compared to the slow decomposition of the parent alkyls (Scheme 1). In order to investigate the role of the size of the used metal to form such intramolecular C–H bond activation products we extended our studies to various other lanthanoids. We observed that **3** and **8** comprised of smaller lanthanoids like Sc and Lu can be alkylated successfully by reacting them with one equivalent of $LiCH_2SiMe_3$ in hexane to give the corresponding alkyl complexes [Ap′$_2$ScCH$_2$SiMe$_3$] (**10**) and [Ap′$_2$LuCH$_2$SiMe$_3$(thf)] (**11**) in good yields of 62% and 86%, respectively (Scheme 5).

In the ^{1}H NMR spectrum of complex **10** we observed a singlet at δ = 0.13 ppm for the protons of the –$SiMe_3$ group and a broad singlet at δ = 0.22 ppm for the methylene protons. In the ^{13}C NMR we observed a sharp signal for the –$SiMe_3$ group at δ = 3.62 ppm, however a signal for methylene carbon could not be observed since the carbon signals of scandium alkyls are usually broad due to the 7/2 spin of Sc. Complex **10** is quite stable in solution and doesn′t show any detectable decomposition when its C_6D_6 solution was monitored for several weeks. Compound **11** (Figure 9) was

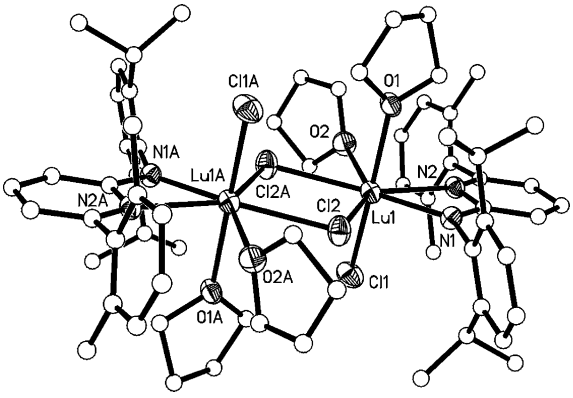


Figure 6. Molecular structure of **7**; selected bond lengths [Å] and angles [°]: Lu1–N1 2.283(5), Lu1–O1 2.341(5), Lu1–O2 2.375(5), Lu1–N2 2.474(6), Lu1–Cl1 2.516(2), Lu1–Cl2 2.675(2), Lu1–Cl2 2.718(2), 3.556; N1–Lu1–O1 86.21(17), O1–Lu1–O2 80.63(18), N1–Lu1–N2 56.5(2), O1–Lu1–N2 85.93(17), O2–Lu1–N2 81.5(2), N1–Lu1–Cl1 98.79(12), O1–Lu1–Cl1 170.23(13), O2–Lu1–Cl1 90.05(14), N2–Lu1–Cl1 89.83(14), N1–Lu1–Cl2 77.13(18), O1–Lu1–Cl2 94.14(12), O2–Lu1–Cl2 144.41(14), Cl1–Lu1–Cl2 95.16(7), O1–Lu1–Cl2 85.57(12), O2–Lu1–Cl2 72.66(15), N2–Lu1–Cl2 153.81(14), Cl1–Lu1–Cl2 94.48(7), Cl2–Lu1–Cl2 71.85(7).

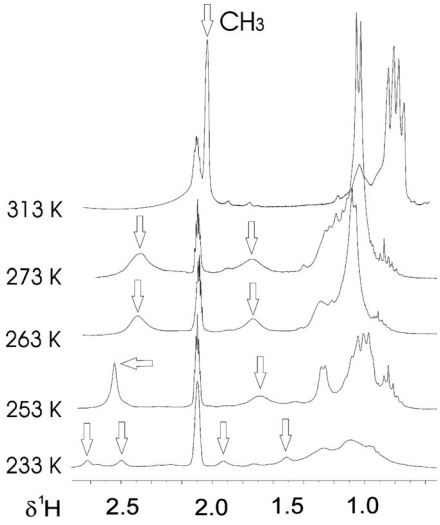
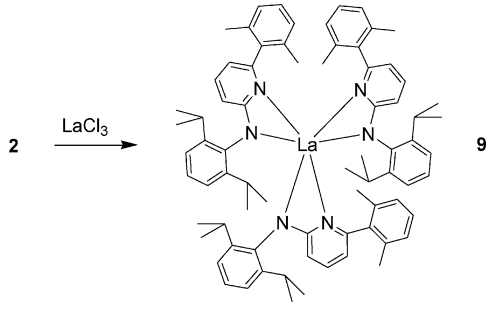


Figure 7. Variable-temperature ^{1}H NMR of **4** in C_7D_8.



Scheme 4. Synthesis of tris(aminopyridinato)lanthanum complex **9**.

crystallized by slow cooling of its concentrated hexane solution when layered with thf to –20 °C. X-ray analysis show one thf molecule per molecule of [Ap′$_2$LuCH$_2$SiMe$_3$(thf)]

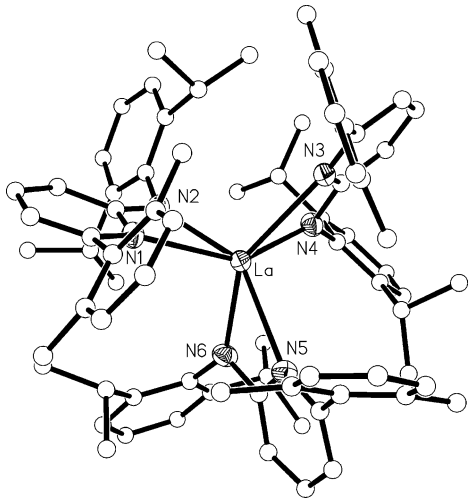
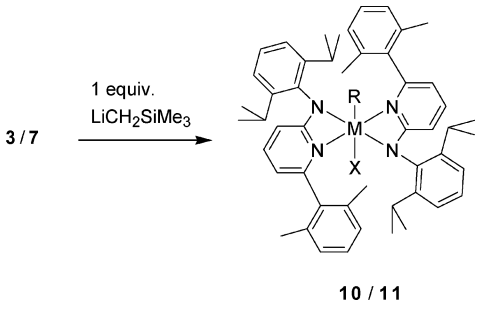


Figure 8. Molecular structure of **9**; selected bond lengths [Å] and angles [°]: N1–La 2.7249(17), N2–La 2.4446(18), N3–La 2.7302(17), N4–La 2.4478(19), N5–La 2.7815(17), N6–La 2.4365(18), N4–La–N2 96.75(6), N4–La–N6 98.69(6), N2–La–N6 100.64(6), N4–La–N1 144.11(6), N2–La–N1 52.31(6), N6–La–N1 104.22(6) N4–La–N3 52.24(5), N2–La–N3 103.74(6), N6–La–N3 143.72(6), N1–La–N3 111.92(5), N4–La–N5 105.61(6), N2–La–N5 146.32(6), N6–La–N5 51.84(6), N1–La–N5 110.25(5), N3–La–N5 109.84(5).



Scheme 5. Synthesis of **10** and **11** [**10**: M = (Sc, X = no thf); **11**: M = (Lu, X = thf), (R = CH_2SiMe_3)].

in the crystal. The structure refinement data are listed in Table 3. The coordination sphere of the lutetium atom is set up by four nitrogen atoms of two aminopyridinato ligands, one carbon atom of the alkyl group and one oxygen atom of the thf molecule resulting in the coordination number of six. The Lu–C bond length of 2.323(14) Å is slightly shorter than the values reported for related anilido phosphinimino (2.370 Å), 4,4,4′′-tri-*tert*-butyl-2,2′:6′,2′′-terpyridine (2.378 Å) and β-ketoiminato (2.402 Å) ligand complexes.[10]

In the ^{1}H NMR spectrum of complex **11** the hydrogen atoms of the methylene group attached to the lutetium atom appear as a broad singlet at δ = –0.65 ppm whereas in the ^{13}C NMR the appropriate carbon appears at δ = 47.8 ppm. Similarly in the ^{1}H NMR spectrum the nine protons of the $SiMe_3$ group appear as a singlet at δ = 0.15 ppm. It is noteworthy that the signal sets corresponding to the aminopyridinate fragments in the ^{1}H NMR spectrum of **11** is quite different from its parent chloro complex **7**. In the latter pro-

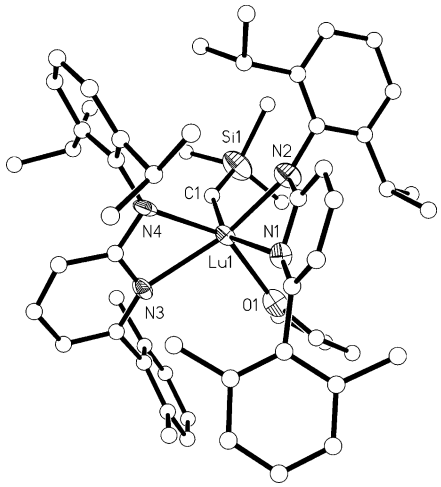
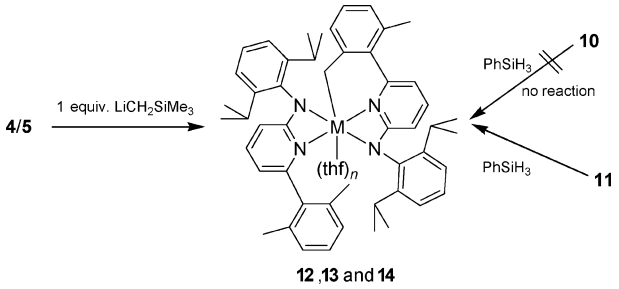


Figure 9. Molecular structure of **11**; selected bond lengths [Å] and angles [°]: N1–Lu1 2.536(9), N2–Lu1 2.242(9), N3–Lu1 2.426(9), N4–Lu1 2.310(10), O1–Lu1 2.294(9), C1–Lu1 2.323(14); N1–Lu1–N4 94.1(3), N1–Lu1–O1 84.3(3), N4–Lu1–O1 148.2(3), N1–Lu1–N3 108.3(3), N4–Lu1–N3 56.8(3), O1–Lu1–N3 93.5(3), N1–Lu1–N2 58.2(3), N4–Lu1–N2 101.3(3), O1–Lu1–N2 104.6(3), N3–Lu1–N2 155.3(3), N1–Lu1–C1 154.2(4), N4–Lu1–C1 100.1(4), Si1–Lu1–C1 149.8(7), O1–Lu1–C1 94.4(4), N3–Lu1–C1 97.5(4), N2–Lu1–C1 97.7(4).

tons of the methyl substituents appear as a singlet at δ = 2.90 ppm whereas the same group of protons in **11** gives two individual singlets at δ = 1.46 and 2.46 ppm. This different behavior can be explained in terms of the steric bulk of the alkyl group introduced that slows down the ligand exchange process due to increased hindrance to rotation. Complex **11** does not coordinate thf during the course of the reaction and results in the thf adduct if a few drops of thf are added during crystallization process. Compound **11** can be stored in solid state without decomposition at –20 °C while in solution it decomposes quite slowly at room temperature compared to its yttrium analogue eliminating $SiMe_4$.[8i]

In contrast to Sc and Lu the alkylation of the chloro complexes **4** and **5** comprised of the larger lanthanoids La and Nd with one equivalent of $LiCH_2SiMe_3$ did not yield the desired alkyl complexes and led directly to the intramolecular C–H bond activated products [Ap′(Ap$_{-H}$′)La(thf)] (**12**) and [Ap′(Ap$_{-H}$′)Nd(thf)] (**13**), in good yields of 61% and 63%, respectively (Scheme 6).



Scheme 6. Synthesis of C–H activation products [**12**: M = La, n = 2; **13**: M = Nd, n = 1; **14**: M = Lu, n = 1].

Orange crystals of **12** were grown by slow cooling of a concentrated thf/hexane (1:2) solution to –20 °C whereas brown crystals of **13** suitable for X-ray analysis were grown from a mixture of thf/pentane (1:10) at low temperature. The molecular structures of **12** and **13** are depicted in Figures 10 and 11, respectively. In **12** one extra thf coordinates to the La compared to the parent **4** increasing the coordination number to seven. Complex **13** shows strongly distorted octahedral coordination. The bond lengths of 2.601(4) and 2.519 (10) Å in **12** and **13**, respectively, between the corresponding metal (lanthanum/neodymium) and the "benzylic" carbon are elongated as expected compared to previously reported Y–C bond [2.420(11) Å].[8i] In comparison to the averaged bond length of La–C bonds which is 2.797 Å (averaged from 48 La···methyl distances, CSD version 5.30) and the corresponding Nd distance 2.649 Å (average of 55 distances, CSD version 5.30) the Ln–C bond lengths in **12** and **13** are a little shorter. Unlike the

Table 3. Details of the X-ray crystal structure analyses.

	11 · C_4H_8O	**12**	**13**
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2(1)$
a [Å]	12.5940(10)	12.2350(5)	9.7600(6)
b [Å]	12.6940(13)	23.4280(11)	20.8890(12)
c [Å]	18.972(2)	18.6550(8)	12.2070(7)
α [°]	75.789(8)		
β [°]	89.453(5)	103.847(3)	107.083(4)
γ [°]	83.858(7)		
V [Å^3]	2922.9(5)	5191.9(4)	2378.9(2)
Crystal size [mm]	0.14 × 0.11 × 0.06	0.28 × 0.25 × 0.23	0.15 × 0.15 × 0.11
ρ_{calcd} [g cm^{-3}]	1.274	1.276	1.299
μ [mm^{-1}] (Mo-K_α)	1.753	0.87	1.13
T [K]	133(2)	133(2)	173(2)
θ range [°]	1.63 to 25.7	1.42 to 25.6	1.75 to 25.7
Number of reflections obsd. [$I > 2\sigma(I)$]	5084	6999	6044
Number of reflections	9976	61178	25156
Number of parameters	638	588	522
wR_2 (all data)	0.154	0.087	0.110
R value [$I > 2\sigma(I)$]	0.071	0.038	0.062

chloro compounds **4** and **5**, in complexes **12** and **13** one aminopyridinato ligand is bidentate, while the second one becomes tridentate due to metallation of the methyl group of one of the $Me_2C_6H_3$ fragments and formation of the new M–C σ-bond. The interesting features of **12** and **13** are the different ways of coordination of the aminopyridinato ligands. We have observed in the chloro complexes that both of the ligands have amidopyridine binding modes. The type of coordination of the bidentate Ap′ ligand is similar to that observed in chloro complexes: one short M–N bond with amido nitrogen atom [La1–N1 2.489(3) and Nd1–N4 2.416(6)] Å and one long with the nitrogen atom of pyridine fragment [La1–N2 2.700(7) and Nd1–N3 2.556(8) Å]. In the tridentate Ap_{-H}' ligand formation of the M–C bond influences dramatically the bonding situation: the covalent bond between metal and amido nitrogen atom [La1–N4 2.565(3) and Nd1–N1 2.499(7) Å] becomes longer than the coordination bond between metal and pyridine nitrogen atom [La1–N3 2.528(3) and Nd1–N2 2.448(7) Å] which means a switch from the amidopyridine to the aminopyridinato form is observed.[9]

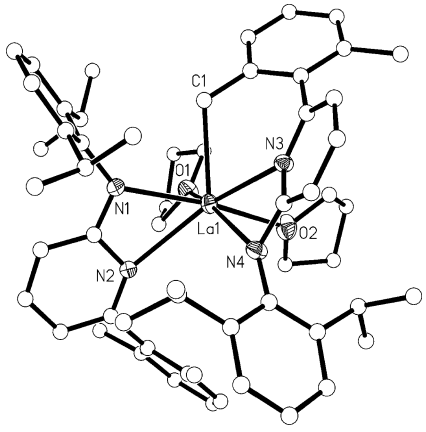


Figure 10. Molecular structure of **12**; selected bond lengths [Å] and angles [°]: N1–La1 2.489(3), N2–La1 2.700(3), N3–La1 2.528(3), N4–La1 2.565(3), O1–La1 2.554(2), O2–La1 2.609(2), C1–La1 2.601(4); La–C1–C2 117.4(2), N1–La1–N4 107.81(9), N1–La1–O1 90.44(9), N4–La1–O1 155.45(9), N1–La1–N3 119.46(9), N4–La1–N3 52.97(8), O1–La1–N3 131.32(8), N1–La1–N2 51.83(9), N4–La1–N2 99.29(8), O1–La1–N2 78.87(8), N3–La1–N2 149.74(8), N1–La1–C1 70.5(3), N4–La1–C1 112.37(10), O1–La1–C1 87.36(10), N3–La1–C1 66.43(10), N2–La1–C1 125.78(10), N1–La1–O2 159.17(9), N4–La1–O2 88.91(9), O2–La1–N3 80.39(11), O2–La1–N2 114.44(8), O1–La1–C1 117.7(3), O1–La1–O2 70.21(8), C1–La1–O2 109.18(10).

We observe a broad singlet at δ = 1.35 ppm for the La–CH_2 protons in the ^{1}H NMR spectrum that coincides with the signal of coordinated thf. However the respective signals were observed as a singlet at δ = 68.9 ppm in the ^{13}C NMR spectrum. In case of **13** the paramagnetic nature of the complex excludes the observations of this resonance.

We know from our previous studies that such C–H activated products are accessible if the parent alkyl is reacted with equimolar amount of $PhSiH_3$ therefore for smaller scandium and lutetium the σ-bond metathesis reactions of alkyl complexes **10** and **11** with phenylsilane were employed

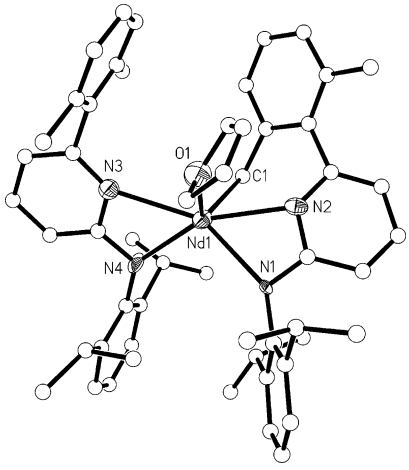


Figure 11. Molecular structure of **13**; selected bond lengths [Å] and angles [°]: N1–Nd1 2.499(7), N2–Nd1 2.448(7), N3–Nd1 2.556(8), N4–Nd1 2.416(6), O1–Nd1 2.462(6), C1–Nd1 2.519(10); N1–Nd1–N4 107.8(2), N1–Nd1–O1 91.3(2), N4–Nd1–O1 127.8(2), N1–Nd1–N3 147.6(2), N4–Nd1–N3 54.4(2), O1–Nd1–N3 83.7(2), N1–Nd1–N2 53.8(2), N4–Nd1–N2 148.9(2), O1–Nd1–N2 81.0(2), N3–Nd1–N2 154.1(2), N1–Nd1–C1 107.9(3), N4–Nd1–C1 99.8(3), O1–Nd1–C1 120.2(3), N3–Nd1–C1 102.3(3), N2–Nd1–C1 68.6(3).

as a synthetic approach to bis(aminopyridinato)lanthanoid hydrides or intramolecular C–H bond activation products. We observed that **10** was quite inert towards phenylsilane and did not undergo any observable change when the reaction was monitored by ^{1}H NMR spectroscopy. However stirring of **11** in toluene with phenylsilane for three days at room temperature and then cooling to –20 °C allowed the isolation of complex [Ap′(Ap_{-H}')Lu(thf)] (**14**) in 60% yield (Scheme 6).

In order to understand the role of the size of the used lanthanoid we studied the formation of complex **14** on NMR scale in [D_6]benzene at 296 K in the presence of phenylsilane. We observed that for lutetium the rate of formation of the C–H activation product is about twenty times slower than for the comparatively larger yttrium based on half-times.[8i] The ^{1}H NMR spectrum did not indicate the presence of a hydride specie in the reaction mixture.

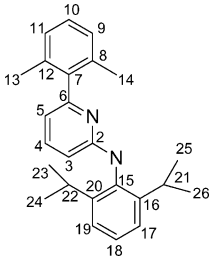
Conclusions

Several conclusions can be made from this study. The bulky aminopyridinato ligand Ap′ affords isostructural bis-aminopyridinate monohalide complexes from La to Sc despite of the large difference in the ionic radii of the metals. The corresponding alkyl complexes, synthesized via salt metathesis starting from the monohalides, can be unstable and can undergo intramolecular methyl group C–H activation depending on the size of the lanthanoids used. For larger lanthanoids the rate of decomposition of the parent alkyl at room temperature is fast and precludes the isolation of these alkyls. Gradual decrease of the metal size enables the isolation of stable alkyl complexes which may undergo intramolecular C–H activation via a transient hydride species

at reasonable rates at room temperature. C–H activation of 2,6-dimethylphenyl moieties can be avoided by using 2,6-dichlorophenyl instead.[11]

Experimental Section

General Procedures: All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and glovebox techniques. Non halogenated solvents were distilled from sodium benzophenone ketyl and halogenated solvents from P_2O_5. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. All chemicals were purchased from commercial vendors and used without further purification. Compound [Ap′$_2$NdCl(thf)] (**5**) was prepared according to previously published procedure.[8b] NMR spectra were obtained using either a Bruker ARX 250 or Varian Inova Unity 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent; an atom numbering scheme for signal assignments is given in Scheme 7. X-ray crystal structure analyses were performed by using a STOE-IPDS I or II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[12] SHELXL-9[13] and WinGX.[14] Crystallographic details are summarized in Tables 1, 2 and 3. Elemental analyses were carried out by means of a Vario elementar EL III or Leco CHN-932 elemental analyser.



Scheme 7. Numbering scheme for NMR labelling.

Synthesis of Lanthanoid Complexes

Synthesis of 3: thf (40 mL) was added to $ScCl_3$ (0.302 g, 2.00 mmol) and **2** (1.586 g, 4.00 mmol) in a Schlenk flask. The resulting bright yellow coloured reaction mixture was stirred overnight. The solvent was evaporated under vacuum and the product was extracted with toluene (30 mL). Toluene was fully evaporated and the resulting product was washed with hexane; yield (0.9 g, 52%). Crystals suitable for X-ray analysis were grown by adding a few drops of thf to a concentrated toluene solution. $C_{54}H_{66}ClN_4OSc$ (867.5): calcd. for thf coordinated crystals C 74.76, H 7.67, N 6.46; found. C 74.26, H 8.01, N 6.46. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.81–1.26 [m, 24 H, H^{23,24,25,26}], 1.47 [s, 6 H, H^{13,14}], 2.34 [s, 6 H, H^{13,14}], 3.28 [sept, 4 H, H^{21,22}], 5.60 [d, J = 8.4 Hz, 2 H, H^3], 5.68 [d, J = 7.2 Hz, 2 H, H^5], 6.67 [dd, 2 H, H^4], 7.02–7.18 [m, 12 H, H^{9,10,11,17,18,19}] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.2 [C^{13,14}], 24.7 [C^{23,24,25,26}], 29.9 [C^{13,14}], 104.8 [C$^{3/5}$], 110.6 [C$^{3/5}$], 124.1 [C^{17,19}], 124.4 [C^{9,11}], 129.2 [C^{10,18}], 135.7 [C^{8,12}], 137.3 [C^7], 141.6 [C^{16,20}], 144.0 [C^4], 144.5 [C^{15}], 156.1 [C^6], 168.7 [C^2] ppm.

Synthesis of 4: thf (40 mL) was added to $LaBr_3$ (0.757 g, 2.00 mmol) and **2** (1.58 g, 4.00 mmol) in a Schlenk flask. The resulting bright yellow colour reaction mixture was stirred overnight. The solvent was removed under vacuum and the product was extracted with hexane (30 mL). The filtrate was concentrated to afford bright yellow crystals suitable for X-ray analysis after 48 h at room temperature; yield (1.066 g, 53%). $C_{54}H_{66}BrLaN_4O$ (1005.94): calcd. C 64.47, H 6.61, N 5.57; found C 64.60, H 7.07, N 5.10. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.96–1.39 [m, 28 H, (4 H, β-CH$_2$, thf), 24 H, H^{23,24,25,26}], 2.12 [br., s, 12 H, H^{13,14}], 3.32 [br., s, 4 H, α-CH$_2$, thf], 3.45 [sept, 4 H, H^{21,22}], 5.57 [d, 2 H, J = 8.5 Hz, H^3], 5.75 [d, 2 H, J = 7.0 Hz, H^5], 6.70 [dd, 2 H, H^4], 6.88–7.21 [m,12 H, H^{9,10,11,17,18,19}] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 20.6 [C^{13,14}], 25.0 [C^{23,24,25,26}], 25.3 [β-CH$_2$, thf], 28.7 [C^{21,22}], 70.1 [α-CH$_2$, thf], 107.7 [C$^{3/5}$], 109.8 [C$^{3/5}$], 124.2 [C^{17,19}], 124.9 [C^{9,11}], 127.8 [C^{10,18}], 136.3 [C^{8,12}], 139.5 [C^7], 140.3 [C^4], 144.0 [C^{16,20}], 144.8 [C^{15}], 155.8 [C^6], 170.4 [C^2] ppm.

Synthesis of 6: A solution of **2** (0.34 g, 0.86 mmol) in thf (30 mL) was added to a suspension of $SmCl_3$ (0.11 g, 0.43 mmol) in thf (5 mL) and the reaction mixture was stirred for 7 h at 50 °C. After cooling to the room temperature thf was evaporated in vacuo and the remaining residue was extracted with toluene (30 mL). The extracts were filtered and the solvent was removed under vacuum and the resulting yellow solid was redissolved in thf. Slow condensation of hexane into concentrated thf solution afforded complex **6** as yellow crystals. The crystals were washed with cold hexane and dried in vacuo at room temperature; yield (0.33 g, 81%). $C_{54}H_{66}ClN_4OSm$ (972.94): calcd. C 66.66, H 6.84, N 5.76; found C 66.11, H 6.88, N 5.64.

Synthesis of 7 and 8: thf (40 mL) was added to $LuCl_3$ (0.562 g, 2.00 mmol) and **2**, (1.58 g, 4.00 mmol) in a Schlenk flask. The resulting yellow colour reaction mixture was stirred overnight. The solvent was removed under vacuum and hexane (30 mL) was added. The yellow reaction mixture was filtered and on standing at room temperature for 48 h, yellow crystals (suitable for X-ray analysis) of the title compound **7** were formed; yield (0.37 g, 24%). $C_{66}H_{90}Cl_4Lu_2N_4O_4$ (1495.19): calcd. C 53.02, H 6.07, N 3.75; found C 52.85, H 5.96, N 3.74. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.50–1.09 [br. m, 24 H, 24 H, H^{23,24,25,26}], 1.22 [br. s, 16 H, (4 H, β-CH$_2$, thf) H^{13,14}], 2.40 [br. s, 12 H, H^{13,14}], 3.76 [br. s, 16 H, α-CH$_2$, thf], 4.09 [sept, 4 H, H^{21,22}], 5.82 [br. d, 4 H, H$^{3/5}$], 6.87–7.25 [m,14 H, H^{4,9,10,11,17,18,19}] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 23.83 [C^{13,14}], 24.88 [C^{23,24,25,26}], 25.2 and 25.4 [β-CH$_2$, thf], 28.7 [C^{21,22}], 71.9 [α-CH$_2$, thf], 106.7 [C$^{3/5}$], 107.5 [C$^{3/5}$], 124.1 [C^{17,19}], 125.2 [C^{9,11}], 127.4 [C^{10,18}], 128.2 [C^{8,12}], 139.9 [C^7], 140.8 [C^4], 143.1 [C^{16,20}], 145.8 [C^{15}], 155.1[C^6], 168.1 [C^2] ppm.

Toluene (30 mL) was added to the residue of the reaction. The mixture was filtered and the filtrate was concentrated. A few drops of thf were added to afford bright yellow crystals of **8** suitable for X-ray analysis after 24 h at room temperature; yield (0.200 g, 20%). $C_{54}H_{66}ClLuN_4O$ (997.55): calcd. C 65.02, H 6.67, N 5.62; found C 64.15, H 6.80, N 5.33. ^{1}H NMR (400 MHz, C_7D_8, 298 K): δ = 0.88–1.11 [m, 28 H, (4 H, β-CH$_2$, thf), 24 H, H^{23,24,25,26}], 2.92 [s, 12 H, H^{13,14}], 3.28–3.59 [br., sept, 8 H, (4 H, α-CH$_2$, thf, 4 H, H^{21,22})], 5.79 [br. d, 4 H, H$^{3/5}$], 6.74–7.19 [m,14 H, H^{4,9,10,11,17,18,19}] ppm. ^{13}C NMR (C_7D_8, 298 K): δ = 20.4 [C^{13,14}], 21.3 [C^{23,24,25,26}], 23.8 and 24.9 [β-CH$_2$, thf], 28.1 [C^{21,22}], 72.7 [α-CH$_2$, thf], 104.2 [C$^{3/5}$], 109.9 [C$^{3/5}$], 124.2 [C^{17,19}], 125.2 [C^{9,11}], 129.2 [C^{10,18}], 135.9 [C^{8,12}], 139.5 [C^7], 141.3 [C^4], 144.3 [C^{16,20}], 148.0 [C^{15}], 156.4 [C^6], 157.4 [C^2] ppm.

Selective Synthesis of 8: {[(R$_2$N)$_2$LuCl (thf)]$_2$} (R = diisopropyl; 0.539 g, 1.11 mmol) and **1** (0.800 g, 2.23 mmol) were loaded together into a Schlenk flask in glove box. Toluene (40 mL) was added to the yellow reaction mixture. The mixture was stirred overnight. Toluene was fully removed in vacuo to yield **8**. The product was washed with hexane; yield (1.00 g, 90%).

Synthesis of 9: A solution of **2** (0.49 g, 1.24 mmol) in thf (30 mL) of was added to a suspension of $LaCl_3$ (0.152 g, 0.61 mmol) in thf (5 mL) and the reaction mixture was stirred for 20 h at 65 °C. After cooling to the room temperature thf was evaporated in vacuo and the remaining residue was extracted with toluene (30 mL). The solvent was removed under vacuum and the resulting solid residue was redissolved in thf. Slow condensation of hexane into concentrated thf solution afforded complex **9** as brown crystals. The crystals were washed with cold hexane and dried in vacuo at room temperature; yield (0.12 g, 32%). $C_{75}H_{87}LaN_6$ (1211.44): calcd. C 74.36, H 7.24, N 6.94; found C 73.81, H 7.42, N 7.10. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.57–1.16 [br. m, 36 H, $H^{23,24,25,26}$], 1.59 [br. s, 6 H, $H^{13,14}$], 2.24 [br. s, 6 H, $H^{13,14}$], 2.34 [br. s, 6 H, $H^{13,14}$], 2.83 [sept, J = 6.7 Hz, 2 H, $H^{21,22}$], 3.33 [sept, J = 6.7 Hz, 4 H, $H^{21,22}$], 5.57 [d, J = 8.7 Hz, 3 H, H^3], 5.78 [d, J = 7.0 Hz, 3 H, H^5], 6.61 [dd, J = 8.7, J = 7.1 Hz, 3 H, H^4], 6.82–7.23 [m,18 H, $H^{9,10,11,17,18,19}$] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 20.5 [$C^{13,14}$]; 24.7, 26.5, 26.7 [$C^{23,24,25,26}$]; 28.8, 29.1 [$C^{21,22}$], 109.0 [$C^{3/5}$], 112.0 [$C^{3/5}$], 124.5 [$C^{17,19}$], 125.0 [$C^{9,11}$], 125.3 [$C^{10,18}$], 138.1 [$C^{8,12}$], 140.9 [C^7], 144.0 [C^4], 145.7 [$C^{16,20}$], 145.9 [C^{15}], 156.0 [C^6], 171.0 [C^2] ppm.

Synthesis of 10: $LiCH_2SiMe_3$ (0.105 g, 1.11 mmol) in hexane (30 mL) was added to a stirred suspension of **3** (0.886 g, 1.11 mmol) in hexane and the reaction mixture was stirred for 24 h. The mixture was filtered and volume of the filtrate was reduced under vacuum. A light yellow crystalline material deposited at –25 °C after standing overnight; yield (0.572 g, 62%). $C_{54}H_{69}N_4ScSi$ (847.19): calcd. C 76.56, H 8.21, N 6.61; found C 77.25, H 7.82, N 6.72. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.13 [s, 9 H, $CH_2Si(CH_3)_3$], 0.22 [s, 2 H, $CH_2Si(CH_3)_3$], 0.81–1.27 [m, 24 H, $H^{23,24,25,26}$], 1.45 [s, 6 H, $H^{13,14}$], 2.18 [s, 6 H, $H^{13,14}$], 3.18–3.44 [sept, 4 H, $H^{21,22}$], 5.62 [br., dd, 4 H, $H^{3/5}$], 6.65 [br., dd, 2 H, H^4], 7.01–7.37 [m, 12 H, $H^{9,10,11,17,18,19}$] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 3.62 [$Si(CH_3)_3$], 21.26 [$C^{13,14}$], 23.66 [$C^{13,14}$], 24.7 and 24.8 [$C^{23,24,25,26}$], 25.1 and 25.4 [$C^{21,22}$], 29.2 [$C^{21,22}$], 105.5 [$C^{3/5}$], 110.4 [$C^{3/5}$], 124.4 [$C^{17,19}$], 125.9 [$C^{9,11}$], 128.4 [$C^{10,18}$], 136.3 [$C^{8,12}$],139.4 [C^7], 142.8 [$C^{16,20}$], 144.1 [C^4], 144.1 [C^{15}], 144.5 [C^6], 169.2 [C^2] ppm. (CH_2 signal could not be observed).

Synthesis of 11: $LiCH_2SiMe_3$ (0.094 g, 1.00 mmol) in hexane (30 mL) was added to a stirred suspension of **8** (1.0 g, 1.00 mmol) in hexane and the reaction mixture was stirred for 24 h. The mixture was filtered and yellow crystals of **11** suitable for X-ray analysis were obtained by slow cooling of the concentrated mixture thf/hexane (1:5). The crystals were dried under vacuum for two hours for elemental analysis; yield (0.900 g, 86%). $C_{58}H_{77}LuN_4OSi$ (1049.31): calcd. C 66.39, H 7.40, N 5.34; found C 66.73, H 7.29, N 5.71. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = –0.65 [s, 2 H, $CH_2Si(CH_3)_3$], 0.15 [s, 9 H, $CH_2Si(CH_3)_3$], 0.92–1.22 [m, 24 H, $H^{23,24,25,26}$], 1.40 [br. s, 4 H, -CH_2, thf], 1.46 [s, 6 H, $H^{13,14}$], 2.16 [s, 6 H, $H^{13,14}$], 3.29 [sept, J = 6.8 Hz, 4 H, $H^{21,22}$], 3.59 [thf, 4 H, β-CH_2], 5.62 [d, J = 8.4 Hz, 2 H, $H^{3/5}$], 5.67 [d, J = 6.9 Hz, 2 H, $H^{3/5}$], 6.70 [br., H^4, J = 7.9 Hz, 2 H, dd], 6.96–7.22 [m, 12 H, $H^{9,10,11,17,18,19}$] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 4.34 [$Si(CH_3)_3$], 19.5 [$C^{13,14}$], 21.1 [$C^{13,14}$], 24.1[$C^{23,24,25,26}$], 24.7[$C^{23,24,25,26}$] 25.0[$C^{23,24,25,26}$] 25.7 [β-CH_2, thf], 28.0 [$C^{21,22}$], 29.3 [$C^{21,22}$], 47.8[CH_2], 68.4 [β-CH_2, thf], 106.3 [$C^{3/5}$], 109.8 [$C^{3/5}$], 124.1 [$C^{17,19}$], 124.4 [$C^{17,19}$], 125.4 [$C^{9,11}$], 127.8 [$C^{9,11}$],128.5 [$C^{10,18}$], 135.7 [$C^{8,12}$], 136.2 [$C^{8,12}$], 139.4 [C^7], 140.8 [C^4], 144.1 [C^{15}], 144.2 [$C^{16,20}$], 156.0 [C^6], 168.0 [C^2] ppm.

Synthesis of 12: A toluene solution of $LiCH_2SiMe_3$ (0.043 g, 0.46 mmol) in (30 mL) was added to a suspension of **4** (0.46 g, 0.46 mmol) in toluene (5 mL) and then reaction mixture was stirred for 30 min at room temperature and for 1 h at 50 °C. After cooling to room temperature the mixture was filtered and toluene was removed in vacuo. The solid residue was dissolved in thf/hexane mixture (≈ 1:2). Slow cooling of the concentrated solution of complex **12** to –20 °C afforded brown crystals of **12**. The crystals were separated from the mother liquor by decantation, washed with cold hexane and dried in vacuo at room temperature (30 min); yield (0.28 g, 61%). $C_{58}H_{73}LaN_4O_2$ (997.1): calcd. C 69.86, H 7.38, N 5.62; found C 69.73, H 7.81, N 5.66. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.03, 1.21, 1.27 [d, J = 6.8 Hz, 24 H, $H^{23,24,25,26}$], 1.35 [br. s together, 10 H, β-CH_2, thf, CH_2La], 2.27, 2.42 [s, 9 H, $H^{13,14}$], 3.33 [br. s, 2 H, $H^{21,22}$], 3.48 [m, 2 H, $H^{21,22}$], 3.51 [br. s, 8 H, α-CH_2, thf], 5.79, 5.81 [d, J = 8.4 Hz, 2 H, H^3], 5.94, 6.46 [d, J = 7.2 Hz, 2 H, H^5,], 6.56–7.35 [m, 14 H, $H^{4,9,10,11,17,18,19}$] ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 20.4, 22.4 [$C^{13,14}$], 24.1, 25.1 [$C^{23,24,25,26}$], 25.2 [β-*C*H_2, thf], 28.4, 28.5 [$C^{21,22}$], 68.8[α-*C*H_2, thf], 68.9 [s, *C*H_2], 106.4, 108.4 [C^3], 108.0, 109.0 [C^5], 118.2, 122.8, 123.6, 123.8, 124.0, 127.4, 127.5, 127.6, 128.1 [$C^{9,10,11,17,18,19}$], 138.4, 139.3 [C^4], 134.3, 136.0, 141.7, 143.2, 143.6, 146.4, 147.1, 153.1 [$C^{7,8,12,15,16,20}$], 153.7, 155.8 [C^6], 166.7, 170.4 [C^2] ppm.

Synthesis of 13: A solution of $LiCH_2SiMe_3$ (0.045 g, 0.48 mmol) in (30 mL) hexane was added to a suspension of **5** (0.464 g, 0.48 mmol) in hexane (20 mL) and the reaction mixture was stirred for 1 h. The mixture was filtered and hexane was removed in vacuo. The solid residue was dissolved in a thf/pentane mixture (≈ 1:10). Slow cooling of the concentrated solution of complex **13** to –20 °C afforded brown crystals of **13**. The crystals were separated from the mother liquor by decantation, washed with cold hexane and dried in vacuo at room temperature; yield (0.29 g, 63%). $C_{54}H_{65}N_4NdO$ (930.36): calcd. C 69.71, H 7.04, N 6.02; found C 69.05, H 7.44, N 6.04.

Synthesis of 14: A solution of $PhSiH_3$ (0.061 g, 0.57 mmol) in toluene solution (3 mL) was added to a solution of **11** (0.600 g, 0.57 mmol) in toluene (30 mL) at room temperature and the reaction mixture was stirred for 72 h. The solution was concentrated to small volume and cooled to –25 °C affording yellow crystalline material; yield (0.319 g, 60%). $C_{54}H_{65}LuN_4O$ (961.09): calcd. C 67.48, H 6.82, N 5.83; found C 67.28, H 7.20, N 5.99. ^{1}H NMR (400 MHz, C_7D_8, 298 K): δ = 0.80–1.58 [m, together 32 H, $H^{23,24,25,26}$, β-CH_2, thf, CH_2Lu],1.78–2.33 [m,together 9 H, $H^{13,14}$], 3.19–3.45 [br., sept, 8 H, (4 H, α-CH_2, thf) (4 H, $H^{21,22}$)], 5.64 [m, 4 H, $H^{3/5}$], 6.63–7.27 [m,14 H, $H^{4,9,10,11,17,18,19}$] ppm. ^{13}C NMR (C_7D_8, 298 K): δ = 20.3, 20.5 [$C^{13,14}$], 23.0, 25.0 [$C^{23,24,25,26}$], 25.2 [β-CH_2, thf], 28.1,28.6 [$C^{21,22}$], 68.6 [α-CH_2, thf], 72.1 [s,*C*H_2], 103.7, 108.8 [$C^{3/5}$], 110.1, 114.5 [$C^{3/5}$], 124.2, 124.3, 124.8, 125.0, 127.5, 127.7, 128.5, 129.7 [$C^{9,10,11,17,18,19}$], 134.7, 135.2 [C^4], 135.9, 136.0, 138.9, 139.5, 140.8, 141.8, 144.4 [$C^{7,8,12,15,16,20}$], 148.0, 156.3 [C^6], 159.3, 159.9 [C^2] ppm.

CCDC-740977 (for **7**), -740978 (for **4**), -740979 (for **13**), -740980 (for **11**), -740981 (for **3**), -740982 (for **9**), -740983 (for **6**), -740984 (for **12**) and -741180 (for **8**) contain the supplementary Crystallographic details for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data centre via: www.ccdc.cam.ac.uk/conts/retrieving.html.

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