Reactivity of halfsandwich rare-earth metal methyaluminates toward potassium (2,4,6-tri-tert-butylphenyl)amide and 1-adamantylamine†

Dorothea Schädle,a Markus Enders,b Christoph Schädle,a Cäcilia Maichle-Mössmer,a Karl W. Tönroos c and Reiner Anwander*a

The equimolar reaction of potassium (2,4,6-tri-tert-butylphenyl)amide with Cp*Ln(AlMe4)2 (Cp* = 1,2,3,4,5-pentamethyl cyclopentadienyl) yielded (Cp*Ln(AlMe4)[NH(mes*)]), (Ln = Y, La; mes* = C6H2(Bu3)-2,4,6). The treatment of Cp*Ln[AlMe4][NH(mes*)] with tetrahydrofuran led to intramolecular C–H bond activation of a tBu group with the formation of Cp*YMe[NH(C6H2(Bu3)-2,4,6-(CMe2CH2)]-6][AlMe4](thf). A similar methyl-anilide species Cp*5LuMe[NH(C6H2(Bu3)-2,4,6-(CMe2CH2)]-6][AlMe4]) (Cp* = 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl) with a C–H bond activated ligand backbone formed by the reaction of Cp*5Lu[AlMe4]2 and K[NH(mes*)]. The reactivity of Cp*5Y[AlMe4]2 toward H3NAd (Ad = adamantyl) ultimately led to the methyl-amine complex Cp*5YMe[NH(Ad)](AlMe4), corroborating the presence of competing deprotonation and donor-induced methyaluminate cleavage reactions. The halfsandwich complexes Cp*5Lu[AlMe4]2, Cp*Y[AlMe4][NH(mes*)], Cp*YMe[NH(C6H2(Bu3)-2,4,6-(CMe2CH2)]-6][AlMe4] and Cp*5YMe[NH(Ad)](AlMe4) as well as the side-product AlMe3(H3NAd) were fully characterized by NMR/FTIR spectroscopy, elemental analysis, and X-ray crystallography.

Introduction

Halfsandwich rare-earth metal bis(hydrocarbyl) complexes have emerged as versatile synthesis precursors (e.g., for hydrido clusters) and eminent (pre)catalysts for polymerization reactions (e.g., fabrication of syndiotactic polystyrene). In 2003, we introduced halfsandwich rare-earth metal bis(methylaluminate) complexes as thermally quite stable variants of the aforementioned bis(alkyl) derivatives. Upon cationization with fluorinated phenylborane/borate reagents complexes Cp*5Ln[AlMe4]2 promote the living 1,4-trans-selective polymerization of isoprene (synthetic gutta-percha) and butadiene. Such catalyst activation proceeds via well-established protonolysis and alkyl abstraction pathways. The feasibility of protonolysis reactions was also demonstrated for the syntheses of metalloccenes as well as silica-grafted hybrid materials and respective alkoxide/siloxide model complexes. Furthermore, complexes of the type Cp*5Ln(AlMe4)2 were successfully applied in C–H bond activation protocols giving access to the first structurally characterized rare-earth metal methylidyne and methylene complexes. In the following, we adopted the concept of alkylaluminate-based organoaluminium-assisted deprotonation for the synthesis of rare-earth metal imide complexes. One major finding was that the superbulky monanionic TpBu2Me (= hydrotris(3-tert-buty1-5-methyl-pyrazolyl)borate) ligand can afford monolanthanide derivatives of the type [(TpBu2Me)Ln[Nar][AlHMe3]] (Ar = C6H3Me2-2,6) and [(TpBu2Me)Ln[Nar][AlMe4]] (Ln = Y, Ho; R = tBu, adamantyl,15). The isolation of rare-earth metal complexes [(TpBu2Me)Ln=NR(dmap)][Ln = Y, Ar = C6H3Me2-2,6; Ln = Lu, Ar = C6H3(CF3)2-3,5] with a terminally bonded imido ligand was achieved by an aluminium-free synthesis procedure. Prior to our studies it has been shown that the deprotonation of rare-earth metal anilide complexes with organoaluminium or alkyl lithium reagents (e.g. Scheme 1, V) is a viable strategy toward Ln[Im] imide complexes. The plethora of group 4 imide complexes, rare-earth metal imide chemistry is still in its infancy. Mountford and coworkers examined the efficiency of deprotonation reactions utilizing, e.g. TiCl4 or Ti[NMe4]3 in amine elimination and transamination/transimination reactions, respectively. It is noteworthy that such synthesis protocols are not applicable for the rare-earth metals (vide infra).
Based on the successful synthesis of rare-earth metal imide complexes exploiting the synergistic effect associated with organoaluminium moieties and the superbulky monanionic TpBu,RMe, we have now set out to explore cyclopentadienyl-supported rare-earth metal bis(tetramethylaluminate)s as potential precursors for imide complexes. Herein, we describe the reactivity of Cp*Ln[AlMe 4] 2 and Cp*Ln[AlMe 4] 2 toward potassium (2,4,6-tri-tert-butylphenyl)amide and 1-adamantylamine, respectively (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, Cp Q = 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl). Overall, this study discloses a better understanding of why steric/electronic mismatches in isolable mixed amide–alkyl complexes hamper their conversion into the respective imide derivatives.22–24 As compiled in isolable mixed amide–alkyl complexes hamper their conversion into the respective imide derivatives.22–24 As compiled

Results and discussion

Reactivity of Cp*Ln[AlMe 4] 2 (1)
The salt-metathesis reaction of half-sandwich complexes Cp*Ln[AlMe 4] 2 (Ln = Y (1a), La (1b))9 with 1 equivalent potassium (2,4,6-tri-tert-butylphenyl)amide, K[NH(mes*)], in n-hexane at ambient temperature yielded [Cp*Ln[AlMe 4] 2 ]K[NH(mes*)] 2 (Ln = Y (2a), x = 2; Ln = La (2b)) in 83% and 87% yield, respectively (Scheme 2). Rather surprisingly, the reaction came to a halt at the heteroleptic amide–methylaluminate complex and the subsequent deprotonation of the NH anilido functionality did not occur. The mixed amide–imide complex [Sm(NHAr)[AlMe 4] 2 ]N(Ar) 2 17 is the only other example featuring an NH(Ar) ligand adjacent to an organoaluminium moiety (V, Scheme 1). The latter complex V was obtained from Sm(NHAr) 3 and AlMe 3 . For comparison, excess addition of trimethylaluminium to Nd[NHPh] 3 (Ph = phenyl) led to a completely deprotonated imide complex [Nd(AlMe 4) 2 ]NPh 1 and co-product [[NPhAlMe 4 ] 2 ], formed by anilido-methyl exchange.18b Aryl oxide derivatives [Cp*Ln[AlMe 4] 2 ][OAr(Ph,R)] (Ln = Lu, Y; R = H, Me) reminiscent of complexes 2 were obtained by the treatment of [Cp*Ln(OAr(Ph,R))] with an excess of trimethylaluminium.9b

Colourless crystals of 2 were sparingly soluble in aliphatic hydrocarbons but soluble in aromatic solvents. The 1H NMR spectra of complexes 2 show one set of signals for the Cp* NH(mes*), and AlMe 4 ligands. The five methyl groups of the Cp* ring appear as one sharp signal at ambient temperature (2a, −0.33 ppm), which implies a rapid exchange between bridging and terminal methyl groups. For yttrium complex 2a signal splitting of the bridging and terminal methyl groups into two broad singlets at −0.37 ppm and −0.11 ppm occurred at approximately −90 °C. Variable-temperature 1H NMR studies on lanthanum complex 2b did not reveal any signal splitting at temperatures from +25 to −90 °C indicative of a higher mobility of the La–(AlMe 4) moiety.

Single crystals of [Cp*Y[AlMe 4] 2 NH(mes*)] 2 (2a) were grown from saturated n-hexane solutions at −35 °C. The X-ray crystallographic analysis revealed a structural motif as found in the solid-state structure of [Cp*Y[AlMe 4] 2 ] 8,25 (Ln = Y, La, Sm) with the yttrium metal centers being bridged by two μ2-η1:η1 coordinated AlMe 4 ligands (Y1–C1–Al1 = 174.8(2); Y2–C3–Al1 = 169.3(2))
while the Cp* and amido ligands are coordinated terminally (Fig. 1). The NH(mes*) ligands exhibit two distinct coordination modes with the most striking difference being the Y–N(amido) – C(aryl) bond angles of Y1–N1–C5 = 150.7(4)° and Y1–N2–C05 = 93.1(3)°. The Y–N(amido) bond lengths of 2.186(4) Å and 2.226(3) Å are in the expected range. The bent amido ligand features additional Ln···arene interactions involving two short contacts to the ipso and ortho carbon atoms of the aryl ring. Both amido ligands show secondary interactions with the Y(III) center through one of the methyl groups of the tert-butyl substituents.

Attempts to synthesize putative Cp*LnNmes* from 2a via Lewis base-induced methane elimination, as described earlier for other alkyl–amide complexes, were not successful. Upon addition of toluene–hexane mixture at −35 °C and hydrogen atoms except for the NH protons are omitted for clarity. Selected bond distances [Å] and angles [°] (deg): Y1–C1 2.325, Y2–C2 2.328, Y1–C22 2.980(6), Y2–C012 2.819(4), Y2–C05 2.683(4), Y2–C010 2.805(4), Y1–N1–C5 150.7(4), Y2–N2–C05 93.1(3), Y1–C1–Al1 174.8(2), Y2–C3–Al1 169.3(2).

Fig. 1 Molecular structure of 2a. Atoms are represented by atomic displacement ellipsoids set at the 50% level. Solvent molecules (n-hexane) and hydrogen atoms except for the NH protons are omitted for clarity. Selected bond distances [Å] and angles (deg): Y1–C1 2.325, Y2–C2 2.328, Y1–C22 2.980(6), Y2–C012 2.819(4), Y2–C05 2.683(4), Y2–C010 2.805(4), Y1–N1–C5 150.7(4), Y2–N2–C05 93.1(3), Y1–C1–Al1 174.8(2), Y2–C3–Al1 169.3(2).

Reactivity of Cp2Lu(AlMe4)2 (4 and 6)

In order to enhance the steric pressure at the rare-earth metal center during the tetramethylaluminate displacement we decided to use the N-donor substituted bis(tetramethylaluminate) precursor Cp2Lu(AlMe4)2 (Ln = Y, Lu). The presence of the rigid quinolyl functionality was anticipated to minimize any undesired C–H bond activation at the N-donor substituent. Cp2Lu(AlMe4)2 was prepared by a slightly modified procedure than described earlier for the yttrium and lanthanum congeners.33

Accordingly, quinolyl-substituted half-sandwich complex Cp2Lu(AlMe4)2 (4) was obtained via protonolysis of homoleptic Lu(AlMe4)3 with HGP2. Brown powdery 4 is readily soluble in toluene, but only sparingly soluble in n-hexane. The 1H NMR spectrum of 4 in CD2Cl2 at ambient temperature shows one signal for the AlMe4 ligands at −0.13 ppm, two singlets for the cyclopentadienyl methyl groups at 1.78 and 2.02 ppm and one set of signals for the quinolyl moiety.

Single crystals of 4 suitable for X-ray structure analysis were grown from a toluene–n-hexane mixture at −35 °C. As for the yttrium and lanthanum congeners33 the Cp2 ligand binds to the metal center in an η5 fashion through all five carbon atoms and via the quinolyl nitrogen atom (Fig. 3). Not surprisingly, in the sterically more congested lutetium complex one of the AlMe4 ligands coordinates in an η4 fashion while the other exhibits the usually observed planar η2 coordination mode (Lu1–C24–Al12–C23 = 5.16(8)°), accounting for an overall hepta-coordinate Lu(η4) metal center. Such η4 coordination mode of
the AlMe₃ ligand with an almost linear Lu–C(μ-CH₃)–Al bond angle of 166.51(9)° has been observed before in [Tp₅Bu₂Me)YMe(AlMe₃)] (1–C(μ-CH₃)–Al = 161.0(1)°) and [(ArNMMe₂)₂NC₅H₃]La(AlMe₄)(thf) (Ar = C₆H₄iPr₂-2,6–CH₃)–Al = 165.0(4)°), supported by sterically demanding tridentate (NNN) ligands (n = 1, 2).

Interestingly, the salt metathesis reaction of CpQY(AlMe₄)₂ with H₂Nmes* or K[NH(mes*)] led to complex CpQLuMe{NH[C₆H₂(tBu₂-2,4-(CMe₂CH₂)-6]Al(AlMe₄) (5) (Scheme 3) revealing a structural motif reminiscent of that found in 3, with the hard quinolyl donor now occupying the position of the thf coordination site. In the ¹H NMR the proton of the NH functionality was clearly evidenced by a singlet at 4.76 ppm, while the presence of three singlets at 0.21, −0.25, and −0.35 ppm for the metal bonded methyl groups and two doublets at 0.85 and 0.67 ppm with a geminal coupling constant of 2J_HH = 14.5 Hz for the methylene group are consistent with the solid-state structure.

An X-ray diffraction study of 5 revealed that the lutetium metal center is coordinated by the Cp ligand via the π-C₆Me₄ moiety and the quinolyl nitrogen donor, one terminal and one bridging methyl group as well as the aluminium-linked amido ligand resulting in an overall coordination number of seven (see Fig. 4). The Lu–C(CH₃) and Lu–C(μ-CH₃) bond lengths of 2.334(2) Å and 2.703(2) Å, respectively, and the Lu–N(amido) distance of 2.479(2) Å compare well to those detected in complex 3 considering the difference of the Ln(III) ionic radii. For comparison, complexes Cp*₂LuMe₂Li(thf) ²²c and [Cp*₂LuMe₂] ²¹ show similar terminal Lu–C(CH₃) bond lengths of 2.361(9) Å and 2.423(3) Å, respectively, whereas the bridging carbon bonds Lu–C(μ-CH₃) can differ markedly ranging from 2.385(9) ²²c to 2.737(3) Å. The bending of the nonlinear Lu1–N1–C32(n) fragment of 129.0(1)° in 5 is much more pronounced than in the related complex [Cp*₂LuMe₂(NHAr)][Li(12-crown-4)] (Ar = C₆H₄iPr₂-2,6) (Lu–N = 2.245(4) Å, Lu–N–C = 155(3)) ²²c.

Remarkably, the reaction of CpQY(AlMe₄)₂ with H₂Nmes* or K[NH(mes*)] led to the formation of several metal-containing species. However, we have recently shown that protonolysis of complexes (Tp₅Bu₂Me)YMe(MMe₄) (M = Al, Ga) with primary amines/anilines, is also a viable strategy to access inside species (Tp₅Bu₂Me)La(NR)(AlMe₄) ¹⁵,¹⁶ and also a viable strategy to access inside species (Tp₅Bu₂Me)La(NR)(AlMe₄). ¹⁵,¹⁶ For assessing the feasibility of the protonolysis protocol for Cp-based systems, we reacted CpQY(AlMe₄)₂ with 1-adamantylamine (H₂NAd). Primary amine H₂NAd was selected in order to minimize any C–H bond activation at the ligand backbone. Accordingly, the reaction of

**Scheme 3** Synthesis of anilide complexes 5 and 7.
6 with H$_2$NAd afforded amide complex Cp$^6$YMe[NH(Ad)][AlMe$_3$] (7) together with adduct Me$_3$Al-NH$_2$[Ad] (8) (Scheme 3). As anticipated C-H bond activation of the amide ligand did not occur. The observed reactivity comes not as a total surprise since the reaction of Ln(AlMe$_4$)$_3$ (Ln = Y, Lu) with 1-adamantylamine was previously shown to produce [LnMe$_3$]$_2$ and Me$_3$Al-NH$_2$[Ad]. Such distinct reactivity clearly shows that the type of ancillary ligand (Cp versus Tp = tris(pyrazolyl)borate) affects organoaluminium-assisted deprotonation$^{16,13}$ and Lewis base-induced aluminane cleavage$^{34}$ as competing reaction pathways and the action of primary amines as Bronsted acids or Lewis bases.

Anilide species 7 is sparingly soluble in aliphatic hydrocarbons but soluble in aromatic solvents. The $^1$H NMR spectrum of 7 shows the expected set of signals for the coordinated Cp$^0$ ligand. The four methyl groups of the Cp ring appear as two singlets at 1.78 and 2.20 ppm and the signals of the quinolyl protons were found in the range from 6.57 to 8.88 ppm. All signals are shifted 0.1–0.3 ppm upfield compared to those of 6, indicating the coordination of the adamantylamide ligand to the rare-earth metal center. The resonances assignable to the adamantyl methylene and methine groups were detected as a doublet at 2.28 ppm (6H), a multiplet ranging from 1.79 to 1.61 ppm (6H) and methylene and methine groups were detected as a doublet at 2.14 ppm (3H), respectively. Only one doublet at 2.20 ppm (6H) and a broad singlet at 1.78 ppm (3H) were observed before in (Tp$^3$BuMe)$_2$YMe[NH(Ad)]. The open coordination sphere at the yttrium metal center seems to enable enhanced methyl group mobility.

Single crystals of 7 suitable for X-ray structure analysis were grown from toluene–n-hexane mixtures at −35 °C. In the solid state, complex 7 is heptacoordinate by one terminal and one bridging methyl group, the amido nitrogen atom as well as the Cp$^0$ ligand binding via the Cp ring ($\eta^5$) and the nitrogen atom of the quinolyl moiety (see Fig. 5). The amido ligand and the (μ-Me)AlMe$_2$ moiety form a heterobimetallic four-membered ring, which is considerably bent (torsion angle Y1–N2–Al3–C22 = 55.70(9)°), resulting in a smaller Y···Al separation of 3.0417(6) Å than in precursor 6 (av. 3.1784(7) Å)$^{33}$ The mean metal–ring–carbon distances Ln–C(Cp$^0$) (av. 2.656(2) Å) and the Y–N(quinolyl) bond length (2.527(2) Å) are similar to those found in 6.$^{33}$ The bond length of the terminal methyl group Y–C(CH$_3$) (2.392(2) Å) is significantly longer than the one found in 3 (Y1–C1 = 2.827(3) Å) and markedly longer than the average distances Y–C(CH$_3$) (2.645(2) Å) in homooluminate precursor 6.$^{33}$ The Y–N(amido) bond length of 2.428(2) Å is slightly shorter than in 3, reflecting a less sterically crowded coordination environment around the metal center.

In Scheme 4, we propose a plausible mechanistic scenario for the formation of half-sandwich amide complexes 3, 5, and 7: both salt metathesis involving Cp$^6$Ln(AlMe$_4$)$_3$ and KNHR (Scheme 4a) and protonolysis involving Cp$^6$Ln(AlMe$_4$)$_3$ and H$_2$NR (Scheme 4b) afford intermediate 8, which in the absence of donor functionalities can be isolated as shown for 2a and 2b. The protonolysis reaction is preceded by an amine-induced tetramethylaluminate cleavage and the formation of a transient terminal Ln–CH$_3$ moiety (I$^1$), which reacts instantly with another amine molecule via methane elimination to generate I$^2$. The occurrence of donor-induced tetramethylaluminate cleavage as the rate-determining step along reaction path b is supported by the formation of considerable amounts of 7 along with AlMe$_3$(H$_2$NR) (8) in equimolar reactions of 6 and H$_2$NAd. Intermediate I$^2$ is not stable in the presence of donor functionalities (quinolyl or thf), which can exert enhanced steric pressure on the amido as well as tetramethylaluminate ligands. As a consequence the amido

**Fig. 5** Molecular structure of 7. Atoms are represented by atomic displacement ellipsoids set at the 50% level. Selected bond distances [Å] and angles [deg]: Y1–C1 2.392(2), Y1–C2 3.006(2), Y1–N1 2.527(2), Y1–N2 2.428(2), Y1···Ct1 2.366, Y1···Al3 3.0417(6), Al3–C20 1.964(2), Al3–C21 2.007(2), Al3–C22 2.022(2), Al3–N2 1.920(2), Y1–N2–C23 126.91(8), Y1–N2–Al3 87.98(7), C19–Y1–C22 144.61(7), N1–Y1–N2 140.16(6), C19–Y1–N2 103.26(7), C19–Y1–N1 95.24(7), C22–Y1–N1 78.49(6), Y1–N2–Al3–C22 = 55.70(9).

**Scheme 4** Proposed reaction mechanism for the formation of 3, 5, and 7.
nitrogen can approach the aluminate ligand (blue arrow), which might experience a $\eta^1-\eta^5$ coordination switch, ultimately leading to an aluminate cleavage and concomitantly to the formation of a stable Al-N bond as well as a (second) Ln-CH$_3$ moiety (isolation of complex 7). In the case of proximal alkyl moieties, the organoaluminium fragment can trigger C-H bond activation (green arrows), as evidenced for the formation of complexes 3 and 5.

Synthesis and characterization of Me$_3$Al NH$_2$(Ad) (8)

Byproduct 8, which could be separated from 7 by extraction with n-hexane, was independently synthesized in quantitative yield via the addition of AlMe$_3$ to a toluene solution of 1-adamantylamine. Recrystallization from toluene-n-hexane at $-35\,\text{°C}$ gave colourless crystals. In the solid-state, the aluminium center adopts a distorted tetrahedral coordination geometry (Fig. 6). The average Al-C(CH$_3$) bond length of 1.983 Å and the Al-N(amino) distance of 2.032(1) Å are in accord with the corresponding structural parameters observed for the related complex Me$_3$Al NH$_2$(Bu)$_3$ (av. Al-C = 1.96 Å, Al-N = 2.027(3) Å) and 7 (av. Al-C = 1.998 Å), but are considerably elongated compared to the Al-N(amido) bond length in 7 (Al-N = 1.920(2) Å). As expected, the $^1$H NMR spectrum of aluminium complex 8 in CD$_3$OD shows one high-field signal for the methyl groups at $-0.36$ ppm (9H), a singlet for the NH$_2$ functionality at 1.59 ppm (2H), a broad singlet for the methine groups (3H), a doublet at 1.20 ppm and a multiplet at 1.27 ppm for the methylene groups integrating six protons each, respectively.

Conclusion

The reactions of monocyclopentadienyl rare-earth metal bis(tetramethylaluminate) complexes with 1-adamantylamine or potassium [2,4,6-tri-tert-butylenyl]amide yield half-sandwich mixed alkyl-amide complexes. The reactivity of the metal-bonded alkyl groups toward adjacent NH functionalities appears strongly reduced and further deprotonation was not observed. This is in sharp contrast to previously examined complexes (Tp$^{Bu,Me}$-YMe(AlMe$_4$)$_2$), which do react with primary amines/anilines to afford Lewis-acid stabilized imido derivatives (Tp$^{Bu,Me}$-Ln[NR]$\cdot$(AlMe$_4$)$_3$). Such changed reactivity of complexes Cp*Ln(AlMe$_4$)$_2$ and Cp$^\text{III}$Ln(AlMe$_4$)$_2$ might be caused by a steric misfit of the metal-alkyl and N-H groups, since the former still exhibit high reactivity as shown for the C-H activation of the NH(mes*) amido ligand backbone. Though substitution of mes* by adamantyl decreases the reactivity of the NH moiety ($p_K_a$ criterion), the occurrence of undesired side-reactions is impeded. Previous studies from the Hessen and Hou groups revealed that imides could only be obtained from reactive Cp ligated rare-earth metal hydride and diene complexes via the insertion of benzonitrile.$^{25,26}$ Overall, the present study reinforces that primary alkylamines not only act as protic substrates but also as Lewis bases and that the steric and electronic properties of the ancillary ligands are crucial factors directing the formation of either heteroleptic alkyl-amide complexes or imide species.$^{15}$

Experimental section

General considerations

All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MBräun 200B; <1 ppm O$_2$, <1 ppm H$_2$O). THF, toluene and n-hexane were purified by using Grubbs columns (MBräun SPS, solvent purification system) and stored inside a glovebox. Cp$_2$D$_2$ and toluene-$d_6$ were obtained from Aldrich, degassed, dried over Na for 24 h, and filtered. 1-Adamantylamine was received from abcr and used as received. Pro-ligand H Cp$^\text{III}$ (3) and heteroleptic complexes Cp*$^\text{III}$Ln(AlMe$_4$)$_2$ (Ln = Y, La) (6), and Cp$^\text{III}$Y(AlMe$_4$)$_2$ (6),$^{33}$ and potassium [2,4,6 tri-tert-butylenyl]amide$^{14}$ were synthesized according to literature procedures. The NMR spectra of air and moisture sensitive compounds were recorded by using J. Young valve NMR tubes at variable temperature on a Bruker AVIII+400 ($^1$H: 400 MHz; $^{13}$C: 101 MHz) and a Bruker AVIII+500 ($^1$H: 500 MHz; $^{13}$C: 126 MHz)$^{13}$H and $^{13}$C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. Coupling constants are given in Hertz. DRIFT spectra were recorded on a NICOLET 6700 FTIR spectrometer using dried KBr and KBr windows. Elemental analyses were performed on an Elementar Vario Micro Cube.

General procedures for the synthesis of \{Cp*$^\text{III}$Ln(AlMe$_4$)$_2$(NH(mes*))$_x$\}

A solution of (Cp$^*$)Ln(AlMe$_4$)$_2$ in n-hexane (2 mL) was added to a stirred suspension of potassium [2,4,6 tri-tert-butylenyl]amide K[NH(mes*)] in n-hexane (2 mL). The reaction mixture was stirred for 2 h at ambient temperature and the n-hexane solution then separated by centrifugation, decanted, and filtrated. The solid residue product and K(AlMe$_4$) were extracted with additional n-hexane (2 x 2 mL). Compounds 2 were obtained as powders or by crystallization from n-hexane solutions at $-35\,\text{°C}$.

\{Cp$^\text{III}$Y(AlMe$_4$)$_2$(NH(mes*))$_2$\}$_2$ (2a). Following the procedure described above, (Cp$^*$)Y(AlMe$_4$)$_2$ (80 mg, 0.20 mmol) and K[NH(mes*)] (60 mg, 0.20 mmol) yielded 2a as colourless crystals (121 mg, 0.20 mmol, quant., 83% crystalline yield). $^1$H NMR (500 MHz, CD$_3$D$_2$, 26 °C, TMS): $\delta = 7.38$ (s, 4H, Har$_2$), 5.05 (s, 2H, NH), 1.89 (s, 30H, CH$_3$), $^3$C (C(CH$_3$)$_3$)$_{ortho}$), 1.44 (s, 18H, $^3$C(CH$_3$)$_3$)$_{para}$), 1.41 (s, 36H, $^3$C(CH$_3$)$_3$)$_{meta}$), $-0.33$ (d, 24H, $^3$J$\text{HH} = 2.5$ Hz, Al(CH$_3$)$_3$)$_{ortho}$), $^{13}$C NMR (126 MHz, CD$_3$D$_2$, 26 °C) $\delta = 151.3$ (Ar, $C^\text{ortho}$),...
Elemental analysis calcd (%) for C$_{35}$H$_{61}$AlNOY (627.75 g mol$^{-1}$): C 61.82, H 9.24, N 2.25; found: C 61.58, H 9.60, N 1.98.

Tetrahydrofuran (1 ml) was added to solid 2a (57 mg, 0.10 mmol) at ambient temperature. The obtained yellow solution was dried in vacuo and recrystallized in n-hexane at $-35^\circ$C (estimated yield 29 mg, 46%). Single crystals of 3 were suitable for X-ray diffraction analysis. DRIFT (KBr): 3402 vw (NH), 2958 vs, 2927 s, 2907 s, 2887 s, 2741 w, 1457 m, 1423 s, 1394 w, 1361 w, 1335 m, 1286 w, 1228 s, 1189 w, 1120 m, 1100 m, 1041 m, 921 w, 878 w, 863 w, 830 w, 814 w, 778 w, 752 s, 736 m, 695 s, 627 w, 559 w, 520 w, 473 cm$^{-1}$. Elemental analysis calcd (%) for C$_{35}$H$_{61}$AlNOY (627.75 g mol$^{-1}$): C 66.97, H 9.79, N 2.23; found: C 66.37, H 10.24, N 2.01.

Cu$^2$Lu[AlMe$_4$]$_2$(4). A solution of Lu[AlMe$_4$]$_2$ (87 mg, 0.20 mmol) in n-hexane (3 ml) was added to a stirred suspension of HCP$^\text{Q}$ (50 mg, 0.20 mmol) in n-hexane (1 ml). Instant gas formation was observed and the solution turned yellow with a thick, brown slurry at the bottom. The reaction mixture was stirred another 3 h at ambient temperature and then dried under vacuum. To the residue toluene (2 ml) was added and the brown solution was stirred for another 3 h at ambient temperature. The product was dried in vacuo and washed with n-hexane (5 x 2 ml). The obtained brown solid was dried under reduced pressure (113 mg, 95%). Crystals of 4 were obtained from a saturated, yellow toluene–n-hexane solution at $-35^\circ$C. $^1$H NMR (500 MHz, C$_6$D$_6$, 26 $^\circ$C, TMS): $\delta$ = 8.31 (d, 1H, $^3$J$_{HH}$ = 4.0 Hz, quin-H), 7.32 (d, 1H, $^3$J$_{HH}$ = 8.0 Hz, quin-H), 7.29 (dd, 1H, $^3$J$_{HH}$ = 3.9 Hz and 2.3 Hz), 7.12–7.08 (m, 2H, quin-H), 6.53 (m, 1H, quin-H), 2.02 (s, 6H, Cp, CH$_3$), 1.78 (s, 6H, Cp, CH$_3$), 1.03 (s, 3H, Al–CH$_3$). Elemental analysis calcd (%) for C$_{35}$H$_{61}$AlNOY (627.75 g mol$^{-1}$): C 66.97, H 9.79, N 2.23; found: C 66.37, H 10.24, N 2.01.

Cu$^2$YMe[Al[NH(mes*)]](AlMe$_4$)$_2$(5). To a stirred suspension of K[Al(NH(mes*)] in toluene (1 ml) a solution of 4 (87 mg, 0.14 mmol) in toluene (3 ml) was added. The brown suspension was stirred at ambient temperature and the product then separated by centrifugation, decanted, and filtered. The solid residue product and K[AlMe$_4$] was extracted with additional toluene (2 x 1 ml). The combined extracts were dried and washed with n-hexane (3 x 2 ml), followed by drying under reduced pressure (96 mg, 0.12 mmol, 91%, 30% crystalline yield). Crystallization from a toluene–n-hexane solution at $-35^\circ$C afforded yellow crystals of 5 suitable for X-ray diffraction analysis.

$^1$H NMR (500 MHz, C$_6$D$_6$, 26 $^\circ$C, TMS): $\delta$ = 8.03 (d, 1H, $^3$J$_{HH}$ = 4.0 Hz, quin-H), 7.67 (d, 1H, $^3$J$_{HH}$ = 2.3 Hz, quin-H), 7.45–7.43 (m, 3H, quin-H), 7.30 (d, 1H, $^3$J$_{HH}$ = 8.5 Hz, quin-H), 7.20 (s, 1H, Ar), 7.13–7.00 (m, 2H, quin-H and Ar), 6.41 (dd, 1H, $^3$J$_{HH}$ = 8.1 Hz and 3.2 Hz), 4.76 (s, 1H, NH), 2.28 (s, 3H, Cp, CH$_3$), 2.06 (s, 3H, Cp, CH$_3$), 2.04 (s, 3H, Cp, CH$_3$), 1.84 (s, 3H, Cp, CH$_3$), 1.53 (s, 3H, Cp, CH$_3$), 1.49 (s, 6H, Cp, CH$_3$), 1.36 (s, 9H, Cp, CH$_3$), 0.85 (d, 1H, $^3$J$_{HH}$ = 14.5 Hz, Al–CH$_2$), 0.67 (d, 1H, $^3$J$_{HH}$ = 14.5 Hz, Al–CH$_2$), 0.21 (s, 3H, Lu–CH$_3$), 0.25 (s, 3H, Al–CH$_3$), $-$0.35 (s, 3H, Al–CH$_3$) ppm. DRIFT (KBr): 3416 vw (NH), 2959 vs, 2912 s, 2887 s, 2741 w, 1457 m, 1423 s, 1394 w, 1361 m, 1335 m, 1286 w, 1228 s, 1189 w, 1120 m, 1100 m, 1041 m, 921 w, 878 w, 863 w, 830 w, 814 w, 778 w, 752 s, 736 m, 695 s, 627 w, 559 w, 520 w, 473 cm$^{-1}$. Elemental analysis calcd (%) for C$_{35}$H$_{61}$AlN$_2$ (754.82 g mol$^{-1}$): C 62.06, H 7.48, N 3.71; found: C 60.53, H 5.92, N 3.72. Multiple attempts to obtain a better microanalysis failed.
7.11–7.10 (m, 1H, quin-H), 6.96 (m, 1H, quin-H), 6.57 (dd, 1H, \(J_{HH} = 8.3\) and 5.0 Hz, quin-H), 2.28 (d, 6H, \(J_{HH} = 2.2\) Hz, \(CH_2\) Ad), 2.60 (s, 3H, \(CH_3\) F), 2.14 (m, 3H, \(CH_2\) Ad), 2.11 (s, 1H, \(NH\)), 1.79–1.61 (m, 6H, \(CH_2\) Ad), 1.78 (s, 6H, \(CH_3\) Cp), –0.06 (d, 12H, \(J_{HH} = 1.5\) Hz, Y—CH\(_3\)). \(^{13}\)C NMR (126 MHz, \(CD_2CN\) 26 °C) \(\delta\) = 153.0 (quin-C), 150.1 (quin-C), 139.9 (quin-C), 135.5 (quin-C), 133.0 (quin-C), 129.4 (quin-C), 127.0 (C Cp), 121.9 (CCH\(_3\) Cp), 121.4 (CCH\(_3\) Cp), 121.3 (quin-C), 58.3 (NC(CH\(_2\))\(_3\)(CH)(CH\(_3\))\(_3\)), 49.5 (NC(CH\(_2\))\(_3\)(CH)(CH\(_3\))\(_2\)), 37.0 (NC(CH\(_2\))\(_3\)(CH\(_2\))\(_2\)), 31.8 (NC(CH\(_2\))\(_3\)(CH\(_2\))\(_2\)), 13.2 (CH\(_3\) Cp), 12.7 (CH\(_3\) Cp), 3.8 (CH\(_3\) Al), 2.20 (s, 6H, C\(_{ad}\)). Suitable crystals for X-ray structure determination of 2a, 3 and 4 were obtained by slow evaporation of a solution of 2a, 3 and 4 in toluene–hexane or –hexane–toluene. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2015

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