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

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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)₂][NH(mes*)] (Ln = Y, La; mes* = C₆H₃(C₂H₅)₂-3,5). The treatment of Cp*Ln(AlMe₄)₂[NH(mes*)] with tetrahydrofuran led to intramolecular C–H bond activation of a tBu group with the formation of Cp*YMe[Li(t-Bu₂-2,4-(CMe₂CH₂)-6)](AlMe₃)(thf). A similar methyl-anilide species Cp*LaMe[Li(t-Bu₂-2,4-(CMe₂CH₂)-6)](AlMe₃) (Cp* = 2,3,4,5-tetramethyl-1-(8-quinolylicyclopentadienyl) was synthesized, revealing the formation of Cp*Lu[Li(t-Bu₂-2,4-(CMe₂CH₂)-6)](Al₂Me₃) as well as the side-product AlMe₃[NH(ad)]. The reactivity of Cp*²Y[AlMe₃] toward H₃NAd (Ad = adamantyl) ultimately led to the methyl-amide complex Cp*²YMe[NH(Ad)](AlMe₃), corroborating the presence of competing deprotonation and donor-induced methylaluminate cleavage reactions. The halfsandwich complexes Cp*²Lu[AlMe₃]₂, Cp*²Y[AlMe₃][NH(mes*)], Cp*²YMe[Li(t-Bu₂-2,4-(CMe₂CH₂)-6)](AlMe₃)(thf), Cp*²LuMe[Li(t-Bu₂-2,4-(CMe₂CH₂)-6)](AlMe₃) and Cp*²YMe[NH(Ad)](AlMe₃) as well as the side-product AlMe₃[NH(ad)] were fully characterized by NMR/FTIR spectroscopy, elemental analysis, and X-ray crystallography.

Introduction

Halfsandwich rare-earth metal bis(hydrocarbyl) complexes¹ have emerged as versatile synthesis precursors (e.g., for hydrido clusters)² and emminent (pre)catayst for polymerization reactions (e.g., fabrication of syndiotactic polystyrene).³ In 2003, we introduced halfsandwich rare-earth metal bis(methylaluminate) complexes as thermally quite stable variants of the afore-mentioned bis(alkyl) derivatives.⁴ Upon cationization with fluorinated phenylborane/borate reagents complexes Cp*²Ln[AlMe₄]₂ promote the living 1,4-trans-selective polymerization of isoprene (synthetic gutta-percha)⁵ and butadiene.⁶ Such catalyst activation proceeds via well-established protonolysis and alkyl abstraction pathways.⁷ The feasibility of protonolysis reactions was also demonstrated for the syntheses of metalloccenes⁸ as well as silica-grafted hybrid materials and respective alkoxide/siloxide model complexes.⁹ Furthermore, complexes of the type Cp*²Ln(AlMe₄)₂ were successfully applied in C–H bond activation protocols giving access to the first structurally characterized rare-earth metal methylidyne¹⁰ and methylene complexes.¹¹,¹² In the following, we adopted the concept of alkylaluminate-based organoaluminium-assisted deprotonation for the synthesis of rare-earth metal imide complexes.¹³ One major finding was that the superbulky monanionic Tp(Bu₃Me)₂Ln[N(C₆H₅)=CH₂]¹⁴ is able to monofunctionalize derivatives of the type [(Tp(Bu₃Me)₂Ln[N(C₆H₅)=CH₂]) Ar = C₆H₅Me₂-2,6]¹⁴ and [(Tp(Bu₃Me)₂Ln[N(C₆H₅)=CH₂])] Ar = Y, Ho; R = tBu, adamantyl,¹⁵ the isolation of rare-earth metal complexes [(Tp(Bu₃Me)₂Ln[N=C₆H₅-LiMe₂-C₆H₅)]) Ar = C₆H₅Me₂-2,6; Ln = Lu; Ar = C₆H₅Li₃(C₆H₅)=CH₂,3-5] with a terminally bonded imido ligand was achieved by an aluminium-free synthesis procedure.¹⁶ 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)¹⁷ is a viable strategy toward Ln imide complexes.¹⁸,¹⁹

Given the plethora of group 4 imide complexes,¹⁹ rare-earth metal imide chemistry is still in its infancy.²⁰ Mountford and coworkers examined the efficiency of deprotonation reactions utilizing, e.g. TICl₃ or Tl(NMe₄)₃ in amine elimination and transamination/transimination reactions, respectively.²¹ It is noteworthy that such synthesis protocols are not applicable for the rare-earth metals (vide infra).

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Based on the successful synthesis of rare-earth metal imide complexes exploiting the synergistic effect associated with organooaluminium moieties and the superbly 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[AlMe4]2 and CpQLn[AlMe4]2 toward potassium (2,4,6-tri-tert-butylphenyl)imide and 1-adamantylamine, respectively (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, 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 Scheme 1, various mixed amide–alkyl complexes (including cationic (II) and anionic rare-earth metal entities (VI)) have been accessed in the presence of a stabilizing N-donor (I, II, IV, V) and cyclopentadienyl ancillary ligands (III, VI).

Results and discussion
Reactivity of Cp*Ln[AlMe4]2 (1)

The salt-metathesis reaction of half-sandwich complexes Cp*Ln[AlMe4]2 (Ln = Y (1a), La (1b)) with 1 equivalent potassium (2,4,6-tri-tert-butylphenyl)imide, K[NH(mes*)], in n-hexane at ambient temperature yielded [Cp*Ln(AlMe4)[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)[AlMe4][NAr]]17 is the only other example featuring an NH(Ar) ligand adjacent to an organooaluminium moiety (V, Scheme 1). The latter complex V was obtained from Sm(NHAr)3 and AlMe3. For comparison, excess addition of trimethylaluminium to Nd(NHPh)3 (Ph = phenyl) led to a completely deprotonated imide complex [Nd(AlMe4)[NHPh][AlMe4]]2, and co-product [[NHPh][AlMe4]] formed by anilido-methyl exchange.18 Aryloxide derivatives [Cp*Ln[AlMe4][OArBu,R]] (Ln = Lu, Y; R = H, Me) reminiscent of complexes 2 were obtained by the treatment of [Cp*Ln(OArBu,R)]2 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 AlMe4 ligands. The five methyl groups of the Cp* ring appear as one singlet at +2.85 ppm (2a), +2.80 ppm (2b), respectively. The signals at 5.05 ppm (2a) and 5.83 ppm (2b) can be assigned to the NH functionalities. The metal-bonded methyl groups show one sharp signal at ambient temperature (2a, −0.33 ppm; 2b, −0.43 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–(AlMe4) moiety.

Single crystals of [Cp*Y[AlMe4][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[AlMe4]]2.25 (Ln = Y, La, Sm) with the yttrium metal centers being bridged by two μ2-η1:η1 coordinated AlMe4 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)/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*LnN[mes*] from 2a via Lewis base-induced methane elimination, as described earlier for other alkyl–amide complexes, were not successful.19 Upon addition of thf to 2a no visual changes were observed, meaning the mixture remained as a yellow solution. However, evacuation of the solvent, drying in vacuo, and recrystallization from the residue in n-hexane produced single crystals of complex 3, revealing AlMe4 cleavage and C–H bond activation of one of the tert-butyl groups (Scheme 2, Fig. 2). The generated monomeric complex is 7-coordinate by the C–H activated primary amido ligand, (μ2-Me)AlMe4[NH2C6H2Bu2(2,4-(CMe3CH2)2)-6], a η5-Cp* ligand, a thf molecule, and a terminal methyl group. The Y–N(amido) bond length of 2.489(2) Å is significantly elongated compared to 2a (Y–N(amido) = 2.186(4)/2.226(3) Å), which is due to the formation of a four-membered Y–C(aryl)–Al–N metalacycle. This four-membered metalacycle is fused via the Al–N bond to a six-membered metalacycle, which itself is annulated to the (anilido)phenyl ring. The Y–C bond lengths differ markedly with the terminal Y–C(CH3)2 distance being quite short (2.406(3) Å) similar to the diketiminate complex [L]YMe2 (L = MeC[Ni(C5H5)2]2,6; Y = CH2CH2N(Me)CH2CH2NMMe2) (av. 2.233 Å)20 and hydrotris(pyrrozolyl)borate compound [Tp(µ3-CH2)2AlMe4]2 YMe2 (Y = CH2)2 = 2.382(3) Å; Y–C[µ2-CH2] = 2.715(3) Å),20 while the Y–C[µ2-CH2] (2.827(3) Å) distance is relatively long in comparison to 2a (av. 2.697 Å) and [Cp*2Y(AlMe4)]25a (2.66 Å). Unfortunately, 1H and 13C NMR spectroscopic investigations were hampered by fast decomposition of the product.

Reactivity of CpQLn[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 CpQLn[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.30 CpQLu[AlMe4]2 was prepared by a slightly modified procedure than described earlier for the yttrium and lanthanum congeners.31

Accordingly, quinolyl-substituted half-sandwich complex CpQLu[AlMe4]2 (4) was obtained via protonolysis of homoleptic Lu[AlMe4]3 with HGCQ. Brown powdery 4 is readily soluble in toluene, but only sparingly soluble in n-hexane. The 1H NMR spectrum of 4 in C6D6 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 congeners13 the CpQ 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–C4–Al2–C23 = 5.16(8)°), accounting for an overall heptacoordinate Lu(n) 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 [TpBu₂Me]YMe(AlMe₄) (Y = 1, 2, 3). The AlMe₄ group is sterically demanding tridentate (NNN) ligands (n = 1, 2).

Interestingly, the salt metathesis reaction of Cp₂Lu(AlMe₄)₂ (4) and K[NH(mes*)] led to complex Cp₂LuMe[NH[C₆H₂Bu₂-2,4-(CMe₂CH₂)-6]](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 2JHH = 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 Cp₂ ligand via the n³-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 2.334(2) Å and 2.703(2) Å, respectively, and the Lu–N(amido) bond distances of 2.417(1) Å and 2.423(3) Å, respectively, whereas the bridging carbon bonds Lu–C(μ-CH₃) can differ markedly ranging from 2.385(9) Å to 2.737(3) Å. Considering the difference of the Ln(III) ionic radii. For comparison, complexes Cp₂LuMe₂Li(thf)₂ and [Cp₂LuMe₄]⁺ 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) Å to 2.737(3) Å. The bending of the nonlinear Lu₁–N₁–C₃₂(ipso) fragment of 129.0(1)° in 5 is much more pronounced than in the related complex [Cp₂LuMe₂[NHAr]][Li(12-crown-4)] (Ar = C₆H₄iPr₂-2,6) (Lu–N = 2.245(4) Å, Lu–N–C = 155(3)°).

Remarkably, the reaction of Cp₂Y(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 [TpBu₂Me]YMe(AlMe₄) (Y = Al, Ga) with primary amines/anilines, is also a viable strategy to access inside species (TpBu₂Me)YIn[In–NR] or (TpBu₂Me)YIn(NR)AlMe₃. For assessing the feasibility of the protonolysis protocol for Cp-based systems, we reacted Cp₂Y(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
6 with H₂NAd afforded amide complex Cp⁵YMe[NH(Ad)][AlMe₄] (7) together with adduct Me₃Al-NH₂(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(AlMe₄)₃ (Ln = Y, Lu) with 1-adamantylamine was previously shown to produce [LnMe₃] and Me₃Al-NH₂(Ad). Such distinct reactivity clearly shows that the type of ancillary ligand (Cp versus Tp = tris(pyrazolyl)borate) affects organoaluminium-assisted deprotonation¹⁰,¹³ and Lewis base-induced aluminate cleavage¹⁴ as competing reaction pathways and the action of primary amines as Brønsted acids or Lewis bases.

Anilide species 7 is sparingly soluble in aliphatic hydrocarbons but soluble in aromatic solvents. The ¹H NMR spectrum of 7 shows the expected set of signals for the coordinated Cp⁵ 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 methane 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 1.28 ppm (6H), respectively. Only one doublet at 0.06 ppm, 12H), which implies a high methyl group mobility.

Anilide species 7 is heptacoordinate by one terminal and one bridging methyl group, the amido nitrogen atom as well as the Cp⁵ ligand binding via the Cp ring (η⁵) and the nitrogen atom of the quinolyl moiety (see Fig. 5). The amido ligand and the (μ-Me)AlMe₂ 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).¹³ The mean metal–ring carbon distances Ln–C(CpQ) (av. 2.656(2) Å) and the Y–N(quinolyl) bond length (2.527(2) Å) are similar to those found in 6.¹³ The bond length of the terminal methyl group Y–C(CH₃) (2.392(2) Å) compares well to that found in 3 while the distance of the bridging Y–C(μ-CH₃) moiety (3.006(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(CH₃) (2.645(2) Å) in homoaluminate precursor 6.³³ The Y–N(amide) 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 Cp⁵Ln(AlMe₄)₃ and KNHR (Scheme 4a) and protonolysis involving Cp⁵Ln(AlMe₄)₃ and H₂NR (Scheme 4b) afford intermediate ², 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–CH₃ moiety (¹), which reacts instantly with another amine molecule via methane elimination to generate 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 AlMe₃(H₂NR) (8) in equimolar reactions of 6 and H₂NAd. Intermediate 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 tetramethylaluminato ligands. As a consequence the amido...
Experimental section

General considerations

All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MBraun 200B, <1 ppm O2, <1 ppm H2O). THF, toluene and n-hexane were purified by using Grubbs columns (MBraun SPS, solvent purification system) and stored inside a glovebox. C6D6 and toluene-d8 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 HCp3,37 heteroleptic complexes Cp*Ln(AlMe4)2 (Ln = Y, La) (1) and Cp*Y(AlMe4)2 (6), and potassium [2,4,6-tri-tert-butylyphenyl]-amide15 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 AVII+400 (1H: 400 MHz; 13C: 101 MHz) and a Bruker AVII+500 (1H: 500 MHz; 13C: 126 MHz).1H and 13C 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*Ln(AlMe4)[NH(mes*)]x\}2

A solution of (Cp*)Ln(AlMe4) in n-hexane (2 mL) was added to a stirred suspension of potassium [2,4,6-tri-tert-butylyphenyl]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[AlMe4] 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 °C.

\{Cp*Y(AlMe4)[NH(mes*)]x\}2 \(\text{(2a)}\). Following the procedure described above, (Cp*)Y(AlMe4)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).1H NMR (500 MHz, C6D6, 26 °C, TMS): \(\delta = 7.38 \text{ (s, 4H, } \text{Ar})\), 5.05 (s, 2H, NH), 1.89 (s, 30H, CH2, Cp*), 1.44 (s, 18H, (C(CH3)3)para), 1.41 (s, 36H, (C(CH3)3)meta), 4.35 (s, 24H, C2H2, Al(CH3)3), 1.85 (s, 30H, CH2, Cp*).13C NMR (126 MHz, C6D6, 26 °C) \(\delta = 151.3 \text{ (Ar, } C_{ipso})\),
C \text{analysis calcd (\%)} for C_{35}H_{61}AlNOY (627.75 \text{ g mol}^{-1}):
\begin{align*}
&\text{C 67.23, H 10.05, N 2.45; found: C 67.26, H 10.13, N 2.32.}
\end{align*}

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Elemental analysis calcd (\%)
\begin{align*}
\text{for C}_{32}H_{57}AlNY (571.69 \text{ g mol}^{-1}) &\quad \text{C 67.83, H 11.07, N 2.32; found: C 67.91, H 11.16, N 2.34.}
\end{align*}

2

Tetrahydrofuran (1 ml) was added to solid 2b (90 mg, 0.20 mmol) and K[\text{NH}[\text{mes}]] (60 mg, 0.20 mmol) yielded yellow powder (108 mg, 0.17 mmol, 87\%).

H NMR (500 MHz, C_{6}D_{6}, 26 °C, TMS): \( \delta = 7.38 \) (s, 2H, \text{Ar}), 5.83 (s, 1H, \text{NH}), 2.04 (s, 15H, \text{CH}_{3}), C_{\text{para}}. 1.42 (s, 9H, (\text{C(CH}_{3})_{3})_{\text{para}}), 1.33 (s, 18H, (\text{C(CH}_{3})_{3})_{\text{ortho}}), -0.43 (s, br, 12H, Al(CH}_{3})_{3}. 13C NMR (126 MHz, C_{6}D_{6}, 26 °C) \( \delta = 150.2 \) (Ar, \text{ortho}), 139.9 (Ar, \text{para}), 134.6 (Ar, \text{ortho}), 125.3 (Ar, \text{meta}), 123.4 (C(CH}_{3})_{3}), 36.5 ((\text{C(CH}_{3})_{3})_{\text{ortho}}), 35.0 ((\text{C(CH}_{3})_{3})_{\text{para}}), 32.3 ((\text{C(CH}_{3})_{3})_{\text{para}}), 31.4 ((\text{C(CH}_{3})_{3})_{\text{ortho}}), 11.8 (C(CH}_{3})_{3}). 2.6 (Al(CH}_{3})_{3}) ppm.

DRIFT (KBr): 3045vw, 3019vs, 2951vs, 2902s, 2865s, 2754w, 2625s, 1619w, 1535vs, 1511vs, 1467w, 1428w, 1408vs, 1387s, 1345w, 1304s, 1284s, 1264s, 1199w, 1179m, 1157w, 1120m, 1103w, 1014m, 921v, 878w, 863w, 830w, 814w, 778w, 752s, 736m, 695s, 627w, 559w, 520w, 473w cm\(^{-1}\). Elemental analysis calcd (\%) for C_{35}H_{61}AlNOY (627.75 g mol\(^{-1}\)): C 67.26, H 10.13, N 2.32.

Cp^{3}LuMe[\text{NH}[\text{C}_{2}H_{6}Bu_{2}-2,4-(\text{CMe}_{2}CH}_{2})_{6}][\text{AlMe}_{3}] (5)

To a stirred suspension of K[\text{NH}[\text{mes}]] in toluene (1 ml) a solution of 84 mg, 0.14 mmol in toluene (3 ml) was added. The brown suspension was stirred 3 h at ambient temperature and the product then separated by centrifugation, decanted, and filtered. The solid product and K[\text{AlMe}_{4}] was extracted with additional toluene (2 × 1 ml). The combined extracts were dried and washed with n-hexane (3 × 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 °C afforded yellow crystals of 5 suitable for X-ray diffraction analysis.

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H NMR (500 MHz, C_{6}D_{6}, 26 °C, TMS): \( \delta = 8.03 \) (d, 1H, \( ^{3}J_{HH} = 4.0 \text{ Hz, quin-H})), 7.67 (d, 1H, \( ^{3}J_{HH} = 2.3 \text{ Hz, quin-H})), 7.45–7.43 (m, 3H, quin-H), 7.30 (d, 1H, \( ^{3}J_{HH} = 8.5 \text{ 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 \text{ Hz and 3.2 Hz})), 4.76 (s, 1H, \text{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, C(CH}_{3})_{3}), 1.49 (s, 6H, C(CH}_{3})_{3}), 1.36 (s, 9H, C(CH}_{3})_{3}), 0.85 (d, 1H, \( ^{3}J_{HH} = 14.5 \text{ Hz, Al-CH}_{2}), 0.67 (d, 1H, \( ^{3}J_{HH} = 14.5 \text{ 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.

13C NMR from H^{13}C HSSQC and HMBC (126 MHz, C_{6}D_{6}, 26 °C) \( \delta = 152.3 \) (quin-C), 150.1 (quin-C), 145.1 (quin-C), 142.2 (Ar), 140.2 (Ar), 138.4 (Ar), 137.3 (Ar), 139.5 (quin-C), 128.6 (Ar, quin-C, overlapping with solvent signal), 126.4 (Ar, quin-C), 124.6 (Ar), 124.0 (quin-C), 122.5 (quin-C), 121.0 (quin-C), 119.2 (Cp), 117.4 (Cp), 38.8 (CCH}_{3}), 37.9 (C(CH}_{3})_{3}), 34.9 (C(CH}_{3})_{3}), 34.2 (C(CH}_{3})_{3}), 32.4 (C(CH}_{3})_{3}), 31.9 (C(CH}_{3})_{3}), 31.5 (C(CH}_{3})_{3}), 29.4 (CH}_{3}), 28.8 (Al-CH}_{2}), 0.9 (Lu-CH}_{3}), -9.2 (Al-CH}_{3}) ppm. DRIFT (KBr): 3394vw (NH), 3348vw, 3045vw, 2951vs, 2902s, 2865s, 2754w, 1630w, 1586w, 1506m, 1475w, 1467w, 1423s, 1396w, 1362w, 1334w, 1303w, 1281w, 1261w, 1237w, 1223m, 1183w, 1159w, 1191m, 841w, 829w, 821w, 806m, 788m, 776m, 757m, 738w, 699m, 687m, 656w, 648w, 626w cm\(^{-1}\). Elemental analysis calcd (\%) for C_{29}H_{35}AlLuN_{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.

Cp^{3}LuMe[\text{NH}[\text{C}_{2}H_{6}Bu_{2}-2,4-(\text{CMe}_{2}CH}_{2})_{6}][\text{AlMe}_{3}] (7)

A solution of 1-adamantylamine (30 mg, 0.20 mmol) in toluene (2 ml) was added to a solution of Cp^{3}Y[\text{AlMe}_{3}] (51 mg, 0.10 mmol) in toluene (1 ml). The resulting yellow-brown solution was stirred for 1 h at ambient temperature, then dried under reduced pressure, washed with n-hexane (2 × 2 ml), and dried in vacuo (57 mg, 0.10 mmol, quant.). Crystallization from a toluene–n-hexane solution at −35 °C afforded yellow crystals of 7 suitable for X-ray diffraction analysis.

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H NMR (400 MHz, C_{6}D_{6}, 26 °C, TMS): \( \delta = 8.88 \) (dd, 1H, \( ^{3}J_{HH} = 4.9 \text{ and 1.5 Hz, quin-H})), 7.36–7.33 (m, 1H, quin-H), 7.29 (dd, 1H, \( ^{3}J_{HH} = 6.0 \text{ and 2.7 Hz, quin-H})),
7.11–7.10 (m, 1H, quin-H), 6.96 (m, 1H, quin-H), 6.57 (dd, 1H, J = 8.3 and 5.0 Hz, quin-H), 2.28 (d, 6H, J = 2.2 Hz, CH2 Ad), 2.20 (s, 6H, CH3 Cp), 2.14 (m, 3H, CH Ad), 2.11 (s, 1H, NH), 1.79–1.61 (m, 6H, CH3 Ad), 1.78 (s, 6H, CH3 Cp), –0.06 (d, 12H, J = 1.5 Hz, Y–CH3). 13C{1H} NMR (126 MHz, CδD4, δ = 0.71073 Å). Data for compounds 2a and 5 were collected on a Bruker SMART APEX II instrument equipped with a fine focus sealed tube and a graphite monochromator using MoKα radiation (λ = 0.71073 Å). Data for compounds 2a and 5 were collected on a Bruker SMART APEX II instrument equipped with a fine focus sealed tube and a graphite monochromator using MoKα radiation (λ = 0.71073 Å). The Data collection strategy was determined using COSMO38 employing ω- and ϕ scans. Raw data were processed using APEX38 and SAINT38 corrections for absorption effects were applied using SADABS.38 The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F2 using SHELXTL38 and ShelXL.39 All Graphics were produced employing ORTEP-340 and POV-Ray.41 Further details of the refinement and crystallographic data are listed in Table S1 (ESI†) and in the CIF files. CCDC 1055068-1055073.

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Notes and references

12 In 1979, Schumann *et al.* reported on the synthesis of lutetium and erbium allyldienes, [Li][Lu(CH\(_2\)SiMe\(_3\))\(_2\)(CHSiMe\(_3\))] and [Er(CH\(_2\)SiMe\(_3\))(CHSiMe\(_3\))]: H. Schumann and J. Müller, *J. Organomet. Chem.*, 1979, 169, C1.


