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Rare-Earth-Metal Hydrides

Methylaluminum-Supported Rare-Earth-Metal Dihydrides**

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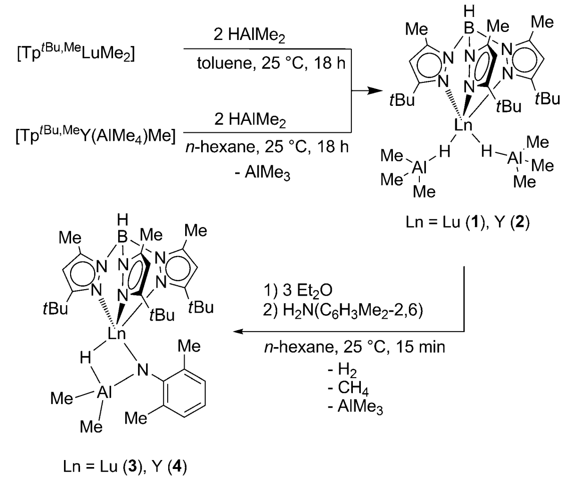
Compounds combining the large rare-earth-metal (Ln) centers with the smallest anionic ligand, H^- (hydrido), continue to pose challenging questions both in fundamental and applied chemistry.[1] The inherent bonding properties in solid-state binary LnH_x phases (e.g., causing metallic behavior) as well as in ligand-supported molecular counterparts (revealing unique cluster chemistry, see Supporting Information) have been the focus of extensive research. Moreover, heterobimetallic solid-state materials, such as Ni_5LaH_x, feature approved rechargeable battery components or, such as $LnAlH_6$ (obtained from $LnCl_3$ and $NaAlH_4$ by the release of hydrogen), are discussed as intermediate-temperature hydrogen-storage materials.[2] On the other hand, the quest for soluble molecular hydrides has triggered immense research efforts. In the meantime, mono and dihydrido derivatives "L_2LnH" and "$LLnH_2$" (L = monoanionic ligand), respectively, are assigned a crucial role in a variety of stoichiometric and catalytic transformations,[3] whereas complexes of type $[LnH_3(Do)_x]$ (Do = neutral donor ligand) are still elusive. While mono hydride complexes can exist as monomers, e.g., $[(C_5H_2tBu_3)_2CeH]$,[4] dihydrido species "$LLnH_2$", carrying only one ancillary ligand per lanthanide center, tend to form polynuclear complexes (see Supporting Information) containing as few as two[5] and up to six lanthanide metal centers.[6] Several types of ancillary ligands have been employed in an effort to stabilize complexes of low nuclearity, including sterically demanding cyclopentadienyl derivatives such as $C_5Me_4SiMe_3$[6] tris(pyrazolyl)borato scorpionates,[7] tetraazacycloamido,[8] bis(phosphinophenyl)amido pincer,[5] and pyridylamido[9] ligands as well as chelating diamido ligands (see Supporting Information).[10] However, the synthesis of a monomeric rare-earth-metal dihydride was not successful to date.

The group of Takats used the sterically demanding hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borato ligand ($Tp^{tBu,Me}$) to stabilize Ln^{2+} centers in species such as alkyls,[11] carbenes,[12] amides,[11b] halides,[11,13] or hydrides[14] and was also able to obtain lanthanide dihydride complexes using the less-bulky dimethyl, diisopropyl, or unsubstituted derivative of the Tp ligand, but reported the formation of a mixture of products for the more bulky $Tp^{tBu,Me}$ ligand because of possible side reactions involving the ligand *tert*-butyl group.[7,15] Since tetrameric $[(Tp^{R}LnH_2)_4]$ as well as the other dihydride clusters reported were all synthesized from alkyl precursors by the addition of H_2 or silanes, we tried to adopt a different route using $HAlMe_2$ as hydride source. For example, this reaction pathway could yield the desired $[Tp^{tBu,Me}LnH_2]$ complex as a mononuclear species owing to the steric bulk of the ligand by a direct alkyl hydrido exchange generating trialkyl aluminum as byproduct or result in the formation of a bimetallic adduct complex.

As use of the super-bulky tris(pyrazolyl)borato ligand $Tp^{tBu,Me}$ had enabled the isolation of soluble monomeric rare-earth-metal dimethyl complexes[16] we treated complex $[Tp^{tBu,Me}LuMe_2]$ with two equivalents of $HAlMe_2$ in toluene at ambient temperature (Scheme 1). Formation of a precipitate was not observed and upon partial evaporation of the solvent and storage at −35 °C crystals suitable for X-ray diffraction could be obtained.[17] The isolated compound was identified as a monomeric lutetium aluminum hydride adduct $[Tp^{tBu,Me}Lu\{(\mu\text{-}H)AlMe_3\}_2]$ (**1**), the first hydrido-bridged rare-earth-metal trialkylaluminum adduct.[18–21]



Scheme 1. Synthesis pathways toward dihydride $[Tp^{tBu,Me}Ln(HAlMe_3)_2]$ and imide $[Tp^{tBu,Me}Ln(NC_6H_3Me_2\text{-}2,6)(HAlMe_2)]$ (Ln = Y, Lu).

There are, however, a few other examples of structurally characterized, hydrido-bridged lanthanide aluminum bimetallic complexes, those reported by Bulychev and Soloveichik, $[\{(C_5H_5)_2LnAlH_4{\cdot}Do\}_2]$ (Ln = Lu, Do = NEt_3,[22] thf;[22] Ln = Y, Do = NEt_3,[23] OEt_2,[23] thf;[24] Ln = Yb, Do = NEt_3[25]) and a more recent scandium complex $[(LScCl)(AlH_4{\cdot}thf_2)]$ (L = (Ar)NC(*t*Bu)CHC(*t*Bu)N(Ar); Ar = 2,6-$C_6H_3iPr_2$-2,6) described by Piers et al.[26]

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The ^{1}H and ^{13}C NMR spectra of **1** showed only one set of signals for the $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand backbone, indicative of three equivalent pyrazolyl rings, as was also reported for the starting material $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{LuMe_2}]$.[16] Broad singlet signals for the bridging hydrido at $\delta = 7.82$ ppm and for the aluminate methyl groups ($\delta = -0.35$ ppm) observed in the ^{1}H NMR spectrum point toward some fluxionality in these moieties. The complex hardly dissolves in aliphatic solvents but is very soluble in aromatic solvents. However, decomposition of the complex in solution is observed within a day at ambient temperature.

Similarly, $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Y(Me)(AlMe_4)}]$[27] was treated with $\mathrm{HAlMe_2}$ employing a slightly modified synthesis approach. Since we expected to obtain a product similar to **1** the reaction was carried out in *n*-hexane (Scheme 1) to avoid decomposition and facilitating the removal of co-product trimethylaluminum. Owing to the low solubility of the Tp complexes in *n*-hexane, simply washing with *n*-hexane allowed the isolation of pure product which was identified as $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Y\{(\mu\text{-}H)AlMe_3\}_2}]$ (**2**), the yttrium analogue of **1**. The NMR spectra for **2** gave more insight into the bonding situation through the emergence of distinct coupling patterns caused by the presence of the ^{89}Y nucleus. As for **1** only one set of signals was obtained for the $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand in the ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum also showed a doublet at $\delta = 5.05$ ppm with a coupling constant $^{1}J(\mathrm{Y,H}) = 30.8$ Hz for the bridging hydrido ligand, a value which is remarkably larger than the Y–H coupling constants reported for $[(\mathrm{Tp}^{\mathrm{Me2}}\mathrm{YH_2})_4]$ ($^{1}J(\mathrm{Y,H}) = 12.1$ Hz)[15] and $[(\mathrm{Tp}^{i\mathrm{Pr2}}\mathrm{YH_2})_3]$ ($^{1}J(\mathrm{Y,H}) = 15.6$ Hz)[28] but lies well within the range for the coupling constants reported by Hou et al. for complexes $[\{(\mathrm{C_5Me_4R})\mathrm{YH_2}\}_n(\mathrm{thf})_x]$ ($\mathrm{R} = \mathrm{SiMe_3}$, $n = 5$, $x = 0$, $^{1}J(\mathrm{Y,H}) = 35.8$ Hz; $\mathrm{R} = \mathrm{Me}$, $n = 5$, $x = 2$, $^{1}J(\mathrm{Y,H}) = 32.8$ Hz)[6] employing low-temperature NMR spectroscopy. Interestingly, no coupling between the aluminate methyl groups and the yttrium metal center was observed suggesting that bonding occurs solely through the hydrido ligand. The ^{89}Y NMR spectrum of **2** obtained by an ^{89}Y DEPT45 experiment showed one sharp signal at $\delta = 404.27$ ppm which compares well with $[(\mathrm{Tp}^{\mathrm{Me2}}\mathrm{YH_2})_4]$ ($\delta = 453.76$ ppm)[15] given the chemical shift range for ^{89}Y of approximately $\delta = 1300$ ppm. The rather downfield resonance for **2** might indicate only little shielding of the ^{89}Y nucleus.[29]

The solid-state structures for **1** and **2** could unequivocally be determined by X-ray crystallography revealing isomorphous structures for the two complexes of which the representative yttrium structure is shown in Figure 1. In both complexes the coordination geometry around the lanthanide metal center is best described as distorted trigonal bipyramidal with N1 and H2 occupying the apical positions (N1-Ln-H2: Ln = Lu 156.1(7)°, Ln = Y 154.2(5)°) and N3, N5, H1 in the equatorial plane. The $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand adopts the commonly observed κ^3 coordination mode with two shorter and one longer Ln–N bonds.

Overall the Ln–N bond lengths in **1** (2.261(2)–2.251(2) Å) and **2** (2.312(2)–2.389(2) Å) are somewhat shorter than in the respective starting materials $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{LuMe_2}]$ (2.339(2)–2.383(2) Å)[16] and $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Y(Me)(AlMe_4)}]$ (2.357(2)–2.318(2) Å).[27a] Comparing the Ln–H distances (**1**: 2.04(3)/2.09(2) Å; **2**: 2.06(2)/2.11(2) Å) to those found in other $[\mathrm{TpLnH_2}]$-type complexes shows that they lie well within the observed range for $[(\mathrm{Tp}^{\mathrm{Me2}}\mathrm{LuH_2})_4]$ (1.87(6)–1.91(4) Å),[15] $[(\mathrm{Tp}^{i\mathrm{Pr2}}\mathrm{LuH_2})_3]$ (2.00(3)–2.05(3) Å),[28] $[(\mathrm{Tp}^{\mathrm{Me2}}\mathrm{YH_2})_4]$ (1.94(4)–1.97(4) Å),[15] and $[(\mathrm{Tp}^{i\mathrm{Pr2}}\mathrm{YH_2})_3]$ (2.01(2)–2.08(2) Å).[28] The Ln⋯Al separations, finally, are much shorter in both complexes than in $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Y(Me)(AlMe_4)}]$ (4.7086(7) Å) which does not come as a surprise since the bridging occurs through a hydrido rather than a methyl group.

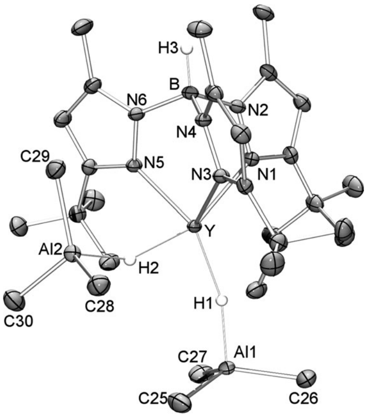

Figure 1. Solid-state structure of **2**, thermal ellipsoids set at 50% probability. Hydrogen atoms except for B–H and bridging hydrido ligands are omitted for clarity. Selected bond lengths [Å] and angles [°] for **2**: Y-N1 2.389(2), Y-N3 2.314(2), Y-N5 2.312(2), Y-H1 2.05(2), Y-H2 2.11(2), Al-H1 1.72(2), Al-H2 1.70(2), Y⋯Al1 3.7471(7), Y⋯Al2 3.712(2); H1-Y-H2 92.7(7), Y-H1-Al1 165(2), Y-H2-Al2 153(2), N1-Y-H2 154.2(5), N5-Y-H1 134.1(5), N3-Y-H1 131.0(5); and **1**: Lu-N1 2.351(2), Lu-N3 2.264(2), Lu-N5 2.261(2), Lu-H1 2.04(3), Lu-H2 2.09(2), Al-H1 1.71(3), Al-H2 1.68(2), Lu⋯Al1 3.7090(8), Lu⋯Al2 3.6667(9); H1-Lu-H2 94.6(10), Lu-H1-Al1 162(2), Lu-H2-Al2 153(2), N1-Lu-H2 156.1(7), N5-Lu-H1 134.6(8), N3-Lu-H1 128.8(8).

Attempts to eliminate the terminal trimethylaluminum moieties and obtain the dihydride complexes $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{LnH_2}]$ by application of high vacuum or donor-induced aluminate cleavage employing diethyl ether led only to mixtures of products and degradation as indicated by the formation of methane. Probing whether the bimetallic complexes exhibit a hydride-like reactivity, compounds **1** and **2** were treated with dimethylaniline; a small amount of diethyl ether was employed to prevent adduct formation between trimethylaluminum and the aniline (Scheme 1). In case of double deprotonation of dimethylaniline this would ultimately lead to imide complexes.[30] Much to our delight upon workup bimetallic imide complexes $[\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Ln\{\mu\text{-}N(C_6H_3Me_2\text{-}2,6)\}(\mu\text{-}H)AlMe_2}]$ (Ln = Lu (**3**), Y (**4**)) could be isolated and characterized. Complexes **3** and **4** are hardly soluble in aliphatic solvents but dissolve in aromatic solvents, where however, as observed for **1** and **2,** degradation takes place.

The ^{1}H and ^{13}C NMR spectra for **3** and **4** contain only one set of signals for the $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand which are slightly shifted compared to the dihydride precursors. Also for the imide-dimethylphenyl group only one set of signals is present in the ^{1}H and ^{13}C NMR spectra. For complex **4**, a broad doublet is observed at $\delta = 6.57$ ppm and assigned to the hydrido ligand bridging between the yttrium and aluminum metal center with a coupling constant of $^1J(Y,H) = 36.2$ Hz which is larger than the coupling observed in **2** but still within the range of yttrium hydrido coupling constants reported by Hou et al.[6] In the ^{89}Y NMR spectrum one sharp peak at $\delta = 467.81$ ppm is observed which is shifted downfield compared to **2**.

As for the dihydride complexes **1** and **2**, the coordination geometry around the yttrium center in imide complex **4** is best described as distorted trigonal bipyramidal with N1 and H2 in the apical positions (N1-Y-H2 173(2)°) and N3, N5, and N7 in the equatorial plane (Figure 2).[17] The $Tp^{tBu,Me}$ ligand adopts the usual κ^3 coordination mode, but interestingly all Y–N bond lengths are almost equal in **4** as opposed to the routinely observed two shorter and one longer Ln–N bonds. The Y–H distance in **4** is a bit longer than in **2** (2.18(5) Å vs. 2.05(2)/ 2.11(2) Å) while the Al–H distance is shorter. Comparing the Y–N(imide) bond length in **4** (Y–N7 2.133(2) Å) to other yttrium imide complexes such as tetrameric $[\{(C_5Me_4SiMe_3)Y(\mu_3\text{-}N)CH_2CH_3)\}_4]$ (2.193(3)–2.342(3) Å)[30] and dimeric $[(AlMe_4)Y(\mu_2\text{-}NMes^*)]_2$ (2.1089(9)/ 2.2909(9) Å)[31] ($Mes^* = C_6H_2tBu_3$-2,4,6) shows that it is well within the expected range. The yttrium–aluminum separation is much shorter than in starting material **2**, which is due to the formation of a 4-membered metallacycle. It is noteworthy that mono-rare-earth-metal imide complexes are still elusive and have been structurally authenticated only in case of the smallest Sc^{III} center (see Supporting Information).[26,32–34]

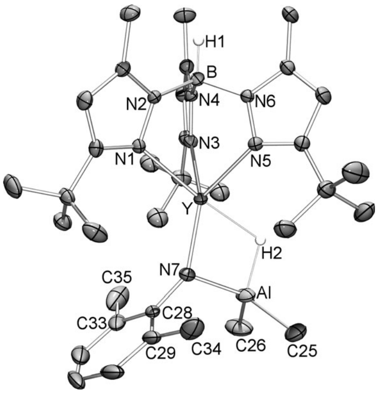

Figure 2. Solid-state structure of **4**, thermal ellipsoids set at 50% probability. Shown is the structural model[17] with a hydrido ligand bridging between yttrium and aluminum. The disorder in one *tert*-butyl group, toluene solvent, and hydrogen atoms except for B–H and bridging hydrido ligands are omitted for clarity. Selected bond lengths [Å] and angles [°] for **4**: Y-N1 2.428(2), Y-N3 2.433(2), Y-N5 2.430(2), Y-N7 2.133(2), Y-H2 2.18(5), Al-H2 1.61(4), Al-N7 1.891(2), Y···Al 3.0534(7); N1-Y-H2 173(2), N5-Y-N7 132.56(7), N1-Y-N7 115.79(7), N7-Y-H2 68(2), N7-Al-H2 87(2), Y-N7-C28 145.1(2), Y-H2-Al 107(2).

In this study we were able to synthesize the first hydrido-bridged lanthanide-hydride-trimethylaluminum complexes of yttrium and lutetium from methyl precursors employing the bulky tris(pyrazolyl) ligand $Tp^{tBu,Me}$. ^{89}Y DEPT45 NMR spectroscopy as well as single-crystal diffraction revealed the formation of discrete mono-rare-earth-metal complexes $[Tp^{tBu,Me}Ln(HAlMe_3)_2]$. Treatment with equimolar amounts of dimethylaniline provides access to scarce mono-rare-earth-metal imide complexes of type $[Tp^{tBu,Me}Ln(NC_6H_3Me_2\text{-}2,6)(HAlMe_2)]$. Hence, heterobimetallic complexes $[Tp^{tBu,Me}Ln(HAlMe_3)_2]$ display hydride-like reactivity, allowing their denotation as “masked hydride complexes” similar to the tetramethylaluminate complexes which are also referred to as “alkyls in disguise”.[35]

Experimental Section

2: A solution of $HAlMe_2$ (9 mg, 0.16 mmol) in *n*-hexane (1 mL) was added to a suspension of $[Tp^{tBu,Me}Y(Me)(AlMe_4)]$[27] (50 mg, 0.08 mmol) in *n*-hexane (2 mL) and the reaction mixture stirred at ambient temperature for 18 h. Afterwards the *n*-hexane soluble material was removed, the remaining white solid was washed with 2 × 2 mL *n*-hexane and carefully dried under vacuum (30 mg, 0.05 mmol, 62%). Recrystallization from a toluene/*n*-hexane mixture (3:1) afforded crystals suitable for crystallographic analysis. ^{1}H NMR ([D$_8$]toluene, 500 MHz, −35°C): $\delta = 5.34$ (s, 3H, 4-pz-*H*), 5.05 (d, 2H, $^1J(Y;H) = 30.8$ Hz, Y-*H*-Al), 4.41 (vb s, 1H, B-*H*), 1.87 (s, 9H, pz-C*H$_3$*), 1.30 (s, 27H, pz-C(C*H$_3$*)), −0.41 ppm (s, 18H, Al(C*H$_3$*)). ^{13}C {^{1}H} NMR ([D$_8$]toluene, 126 MHz, −35°C): $\delta = 165.0$ (5-pz-*C*), 148.2 (3-pz-*C*), 103.4 (4-pz-*C*), 33.1 (pz-*C*(CH$_3$)$_3$), 31.6 (pz-C(*C*H$_3$)$_3$), 12.9 (pz-*C*H$_3$), −6.7 ppm (Al(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR ([D$_8$]toluene, 160 MHz, 25°C): $\delta = -8.13$ ppm. ^{89}Y DEPT45 NMR ([D$_8$]toluene, 25 MHz, −35°C): $\delta = 404.27$ ppm. IR (KBr): $\tilde{\nu} = 3129$ w, 2965 s, 2934 s, 2880 s, 2815 s, 2569 m, 1692 vbr s, 1534 m, 1475 w, 1437 m, 1381 w, 1341 m, 1325 w, 1243 w, 1166 s, 1126 m, 1065 m, 1030 m, 987 w, 838 w, 805 m, 770 s, 688 s, 599 m, 519 m cm^{-1}. Elemental analysis Calcd (%) for $C_{30}H_{60}Al_2BN_6Y$ (658.53 g mol^{-1}): C 54.71, H 9.18, N 12.76. Found: C 55.14, H 8.21, N 12.78.

4: Three equivalents of diethyl ether (31 μL, 0.3 mmol) and a solution of $H_2N(C_6H_3Me\text{-}2,6)$ (12 mg, 0.1 mmol) in *n*-hexane (1.5 mL) were added dropwise to a suspension of **2** (66 mg, 0.1 mmol) in *n*-hexane (1 mL). While stirring the reaction mixture for 15 min at ambient temperature, gas evolution was observed and the suspension turned slightly yellow. Afterwards the white precipitate was isolated by centrifugation, washed with 2 × 1.5 mL *n*-hexane and dried under vacuum to obtain **4** in 77% yield (53 mg, 0.077 mmol). Crystals suitable for crystallographic analysis were obtained by recrystallization from toluene. ^{1}H NMR ([D$_6$]benzene, 500 MHz, 25°C): $\delta = 7.11$ (d, 2H, $^3J(H,H) = 7.2$ Hz, Ar-*H*$_{meta}$), 6.68 (t, 1H, $^3J(H,H) = 7.4$ Hz, Ar-*H*$_{para}$), 6.57 (d, 1H, $^1J(Y,H) = 36.2$ Hz, Y-*H*-Al), 5.57 (s, 3H, 4-pz-*H*), 4.16 (br s, 1H, B-*H*), 2.34 (s, 6H, Ar-C*H$_3$*), 1.97 (s, 9H, pz-C*H$_3$*), 1.35 (s, 27H, pz-C(C*H$_3$*)$_3$), 0.09 ppm (s, 6H, Al-C*H$_3$*). ^{13}C {^{1}H} NMR ([D$_6$]benzene, 126 MHz, 25°C): $\delta = 166.5$ (5-pz-*C*), 160.5 (Ar-C$_{ipso}$), 147.3 (3-pz-*C*), 127.9 (Ar-*C*$_{meta}$), 126.4 (Ar-*C*$_{ortho}$), 115.0 (Ar-*C*$_{para}$), 104.4 (4-pz-*C*), 32.0 (pz-*C*(CH$_3$)$_3$), 30.8 (pz-C(*C*H$_3$)$_3$), 22.9 (Ar-*C*H$_3$), 12.9 (pz-*C*H$_3$), −4.3 ppm (Al(*C*H$_3$)$_2$). ^{11}B{^{1}H} NMR ([D$_6$]benzene, 160 MHz, 25°C): $\delta = -7.93$ ppm. ^{89}Y DEPT45 NMR ([D$_6$]benzene, 25 MHz, 25°C): $\delta = 467.81$ ppm. IR (KBr): $\tilde{\nu} = 3056$ w, 3022 w, 2964 s, 2930 s, 2881 m, 2817 w, 2578 w, 1586 w, 1541 s, 1506 w, 1489 m, 1471 s, 1460 s, 1419 s, 1380 m, 1374 m, 1363 s, 1343 s, 1322 s, 1244, 1205 s, 1194 s, 1175 s, 1126 m, 1097 m, 1067 s, 1026 m, 1015 m, 985 m, 942 w, 911 w, 873 s, 845 w, 831 w, 803 m, 795 s, 786 m, 770 s, 759 s, 732 s, 720 s, 705 s, 697 s, 679 s, 648 s, 617 w, 606 m, 569 w, 533 w, 518 m, 499 m, 466 w, 442 w cm^{-1}. Elemental analysis Calcd (%) for $C_{34}H_{56}AlBN_7Y$ (689.55 g mol^{-1}): C 59.22, H 8.19, N 14.22. Found: C 59.00, H 7.39, N 13.67.

Full experimental and analytical details are available in the Supporting Information.

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[17] **1:** ($C_{30}H_{60}Al_2BN_6Lu$, $M_r = 744.58\,\mathrm{g\,mol^{-1}}$) crystallizes from toluene in the monoclinic spacegroup $P2_1/c$ with $a = 11.1043(15)$, $b = 31.265(4)$, $c = 12.1721(17)$ Å, $\beta = 114.812(2)°$, $V = 3835.8(9)$ Å^3, and $\rho_{\mathrm{calcd}} = 1.289\,\mathrm{g\,cm^{-3}}$ for $Z = 4$. Data were collected at 173(2) K on a Bruker SMART APEX II system. The structure was solved by direct methods, and least-square refinement of the model based on 7027 (all data) and 6814 reflections ($I > 2.0\sigma(I)$) converged to a final $R1 = 0.0178$ and $wR2 = 0.0388$ respectively. **2**: ($C_{30}H_{60}Al_2BN_6Y$, $M_r = 658.52\,\mathrm{g\,mol^{-1}}$) crystallizes from a toluene/*n*-hexane mixture in the monoclinic spacegroup $P2_1/c$ with $a = 11.0804(3)$, $b = 31.3878(9)$, $c = 12.2230(4)$ Å, $\beta = 114.4610(10)°$, $V = 3869.5(2)$ Å^3, and $\rho_{\mathrm{calcd}} = 1.130\,\mathrm{g\,cm^{-3}}$ for $Z = 4$. Data were collected at 100(2) K on a Bruker APEX DUO system. The structure was solved by direct methods, and least-square refinement of the model based on 11916 (all data) and 10301 reflections ($I > 2.0\sigma(I)$) converged to a final $R1 = 0.0300$ and $wR2 = 0.0717$ respectively. **4**: ($C_{34}H_{56}AlBN_7Y$, $M_r = 689.55\,\mathrm{g\,mol^{-1}}$) crystallizes from toluene in the monoclinic spacegroup $P2_1/n$ with $a = 20.3531(4)$, $b = 9.5377(2)$, $c = 22.3930(4)$, $\beta = 112.7592(10)°$, $V = 4008.51(14)$ Å^3 and $\rho_{\mathrm{calcd}} = 1.224\,\mathrm{g\,cm^{-3}}$ for $Z = 2$. Data were collected at 100(2) K on a Bruker APEX DUO system. The structure was solved by direct methods, and least-square refinement of the model based on 9938 (all data) and 7959 reflections ($I > 2.0\sigma(I)$) converged to a final $R1 = 0.0410$ and $wR2 = 0.0843$ respectively. The solid-state structure of **4** showed a substitutional disorder on the position of the hydrido ligand bridging between the yttrium and aluminum metal centers involving the hydrido and a methyl group. Modeling this substitutional disorder revealed that the structure with the hydrido ligand bridging between metal centers contributes with 67% to the final model and the methyl bridged structure (see Supporting Information) with 33%. Unfortunately a second substitutional disorder revealing the position of a terminal hydrido ligand in the case of a bridging methyl group could not be modeled. CCDC 942759 (**1**), 942760 (**2**) and 953181 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] Formation of such adducts, however, is well established for transition-metal complexes where several compounds, such as $[Cp_3Zr(\mu\text{-}H)AlEt_3]$ (Ref. [19]), $[Cp^*{}_2Zr][(\mu\text{-}\eta^1{:}\eta^2\text{-}Me_3SiCCH)(\mu\text{-}H)(i\mathrm{Bu}_2Al)]$ (Ref. [20]), and $[(Me_2Si)_2(C_5H_3)_2Zr(\mu\text{-}H)_3(Al\,i\mathrm{Bu}_2)_2][B(C_6F_5)_4]$ (Ref. [21]), have been structurally characterized.

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