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Reactivity of Yttrium Methyl Complexes: Hydrido Transfer Capability of Selected Alkylalanes

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Supporting Information

ABSTRACT: The reactivity of alkylaluminum hydrides HAlMe₂, HAl(CH₂SiMe₃)₂, and H₂AlMes^{*} (Mes^{*} = C₆H₂tBu₃-2,4,6) toward yttrium methyl complexes was assessed. From the reaction with [Cp₂YMe]₂ the corresponding methylated alkylaluminum compounds could be isolated and characterized along with [Cp₂Y(thf)(μ -H)]₂, obtained upon workup in thf (Cp = C₅H₅ =



 $HAIR_2 = HAIMe_2$, $HAI(CH_2SiMe_3)_2$, $H_2AIC_6H_2tBu_3-2,4,6$

cyclopentadienyl). Structurally characterized complexes $Cp_{14}Y_6H_3Cl$ and $Cp_{15}Y_6H_3$ represent side-products of the transformation. The reactions of $[YMe_3]_n$ and $[(C_5Me_5)YMe_2]_3$ indicated occurrence of hydrido transfer for H_2AlMes^* and led to product mixtures for $HAl(CH_2SiMe_3)_2$. Following the reaction of $HAlMe_2$ with these compounds as well as the half-sandwich derivatives $(C_5Me_4R)Y(AlMe_4)_2$ (R = Me, SiMe_3) indicated reversible hydrido binding, leading ultimately to the formation of insoluble hydride clusters. The organoaluminum compounds $[HAl(CH_2SiMe_3)_2]_3$, $[(\mu-H)(Me)AlMes^*]_2$, and Me_2AlMes^* were analyzed by X-ray crystallography.

■ INTRODUCTION

Alkylalanes, especially diisobutylaluminum hydride (DIBAH), are routinely employed as cocatalysts in rare-earth-metalcatalyzed transformations, such as the polymerization of butadiene and isoprene,¹ ethylene,² and thf³ and in the copolymerization of butadiene/styrene,⁴ isoprene/styrene,⁴ or isoprene/ ε -caprolactone.⁵ However, the structure and composition of complexes forming in these reaction systems as well as the role of the aluminum hydride are still not well understood. Empirical studies on polymerization have shown that DIBAH is an efficient chain transfer agent and involved in the formation of the catalytically active species,^{6,7} while Bercaw and Brintzinger were able to identify cationic, bimetallic hydride complexes $[(rac-Me_2Si(1-Ind)_2)Zr(\mu-H)_3(AlR_2)_2]^+$ (Ind = indenyl; R = iBu, Me) as key components in zirconium-based catalyst mixtures.⁸ We have previously shown that lanthanide hydride complexes are accessible from the reaction of DIBAH with lanthanide silylamides rac-[Me₂Si(2-Me-C₉H₅)₂]Ln[N- $(SiHMe_2)_2$ (Ln = Y, Ho) by two possible pathways: one involving direct hydrido transfer from aluminum and one involving a β -hydride elimination route.⁹ Different from our findings Kempe et al. observed transfer of the ancillary ligand from the lanthanide to the aluminum metal center when aminopyridinato-stabilized lanthanide amide complexes were reacted with DIBAH.¹⁰

Due to various possible reaction pathways, we decided to further investigate the reactivity of alkylaluminum hydrides toward organolanthanide complexes. Looking for aluminum hydrides not prone to side reactions such as β -hydride elimination and carrying alkyl moieties of different steric bulk, we envisaged HAlMe₂, ^{8b} HAl(CH₂SiMe₃)₂, ¹¹ and H₂AlMes* (Mes* = 2,4,6-tBu₃C₆H₂) as suitable reagents.¹² Previous

reactions of HAlMe₂ with organolanthanide complexes afforded unprecedented alkyl-hydrido heteroaluminates Tp^{fBu,Me}Ln[(μ -H)AlMe₃]₂ (**A**; Ln = Y, Lu; Tp^{fBu,Me} = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate; Chart 1)¹³ and [Cp*₂Y(μ -H)AlMe₂(μ -

Chart 1. Structurally Characterized Rare-Earth-Metal Alkyl-Hydrido Heteroaluminate Complexes



H)AlMe₂(μ -CH₃)]₂ (**B**; Cp^{*} = C₅Me₅).¹⁴ While monomeric **A** could be obtained from alkyl complexes Tp^{fBu,Me}LuMe₂ and Tp^{fBu,Me}Y(Me)(AlMe₄), dimeric **B**, featuring a 12-membered ring structure, resulted from benzoate Cp^{*}Y(OOCC₆H₂Me₃-2,4,6). Herein, we present a full account on the reactivity of alkylaluminum hydrides HAlMe₂, HAl(CH₂SiMe₃)₂, and H₂AlMes^{*} toward yttrium methyl complexes.¹⁵ The yttrium alkyl complexes [Cp₂YMe]₂,¹⁶ [YMe₃]_n,¹⁷ [Cp^{*}YMe₂]₃,¹⁸ and (C₅Me₄R)Y(AlMe₄)₂ (Cp = C₅H₅, R = Me,¹⁹ SiMe₃²⁰) were chosen due to well-established, high-yield synthesis routes²¹

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and the intrinsic properties of the $^{89}{\rm Y}$ nucleus for NMR spectroscopy (100% abundance, spin 1/2) facilitating the identification of possible reaction products via distinct coupling patterns.

RESULTS AND DISCUSSION

All aluminum hydride precursors employed in this study are literature-known compounds with established synthesis protocols; however, the solid-state structure for $[HAl(CH_2SiMe_3)_2]_3$ (1) has not been reported to date. In the original paper by Beachley and Tessier-Youngs¹¹ describing the synthesis of 1, a trimeric structure was proposed based on cryoscopic molecular weight data and infrared spectroscopy. Repeating the synthesis, we were able to obtain crystals of 1 suitable for crystallographic analysis from an *n*-hexane solution at -35 °C (Figure 1).



Figure 1. Solid-state structure of 1 with thermal ellipsoids set at the 50% level. Methyl groups of the SiMe₃ moieties and hydrogen atoms except for those bridging aluminum metal centers are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1–H1 1.67(7), Al1–H3 1.73(7), Al2–H2 1.71(7), Al2–H1 1.70(6), Al3–H3 1.63(7), Al3–H2 1.72(7), H1–Al1–H3 94(3), H1–Al2–H2 94(3), H2–Al3–H3 92(3), Al1–H1–Al2 144(4), Al2–H2–Al3 137(4), Al3–H3–Al1 143(4).

The originally proposed connectivity displaying "a sixmembered ring composed of alternating dialkylaluminum groups and hydrogen atoms"¹¹ could be confirmed, revealing a close similarity to isostructural di(*tert*-butyl)alane, which is also trimeric, forming a six-membered Al–H ring.²² Both structures reveal similar Al–H distances (1.72 Å vs average 1.70 Å in 1), while the H–Al–H (89° vs average 93° in 1) and Al– H–Al (151° vs average 141° in 1) angles are markedly different.

We began our study using the least sterically demanding alkylaluminum hydride $HAIMe_2$, which was reacted with $[Cp_2YMe]_2$ in toluene (Scheme 1, a). After separating a white solid from the toluene solution we were able to obtain a colorless oil upon vacuum concentrating, which was identified

as hydrido transfer product AlMe₃ by ¹H NMR spectroscopy. The remaining white solid turned out to be soluble in hot thf. Upon cooling of the clear solution, a crystalline material could be obtained and identified as $[Cp_2Y(thf)(\mu-H)]_2$ by ¹H NMR spectroscopy (SI Figure S1). The ¹H NMR spectrum displays a triplet at 1.98 ppm with a coupling constant of 27 Hz, a feature that is characteristic for a hydrido ligand bridging between two yttrium metal centers, as reported in the seminal paper by Evans et al.²³

Neosilylaluminum hydride HAl(CH₂SiMe₃)₂ showed similar reactivity to HAlMe₂ (Scheme 1, a), also forming a white precipitate in the course of the reaction. After separation of the white solid and drying of the supernatant solution under vacuum a colorless oil was obtained and identified as MeAl(CH₂SiMe₃)₂ by ¹H NMR spectroscopy.²⁴ Again, the white solid was soluble in hot thf and identified as the yttrium hydride complex $[Cp_2Y(thf)(\mu-H)]_2$. On one occasion we were able to collect a few crystals from the toluene solution for crystallographic analysis. The obtained crystal structure revealed two overlapping molecules of general formulas $[Cp_{14}Y_6H_3Cl]$ (2a) and $[Cp_{15}Y_6H_3]$ (2b)²⁵ (Figure 2), with 2b exhibiting a metallacycle consisting of six yttrium atoms bridged by three hydrido and three cyclopentadienyl ligands. Complex 2a differs only in a chlorido ligand instead of a Cp ligand bridging between yttrium metal centers; the chlorido ligand stems from the precursor for [Cp₂YMe]₂, namely, [Cp₂YCl]₂.

There are only a few reports on yttrium hydride clusters containing as much as six yttrium nuclei, one example being a complex synthesized by Hou et al. consisting of six $[(C_5Me_4SiMe_3)YH_2]$ units.²⁶ In the same paper the corresponding penta- and tetranuclear complexes are also described. Such half-sandwich complexes adopt more tightly packed geometries of distorted octahedral, square pyramidal, and tetrahedral metal core structures.²⁷ A cyclic yttrium hydride complex was reported by Evans et al. consisting of three $[(C_5H_3Me_2)YH]$ units.²⁸ In complexes 2 yttrium–hydrido bond lengths vary between 2.03(7) and 2.20(6) Å, covering about the same range as in dimeric complexes $[(C_5H_4Me)_2Y-(thf)(\mu-H)]_2$ (2.17(8)/2.19(8) Å)²³ and $[(C_5H_3Me_2)_2Y(thf)-(\mu-H)]_2$ (2.03(7)/2.27(6) Å).²⁸ The yttrium Cp(terminal, centroid) distances found in 2 range from 2.275 to 2.431 Å and are markedly shorter than those found in $[(C_5H_3Me_2)YH]_3$, $[(C_5H_3Me_2)_2Y(thf)(\mu-H)]_2$, and $[(C_5H_4Me)_2Y(thf)(\mu-H)]_2$ (2.62/2.69/2.69 Å) but compare better to those found in the homoleptic yttrocene YCp₃ (2.393-2.503 Å).²⁹ Different from the terminal Cp ligands the distances of the yttrium metal centers to the bridging Cp ligands (centroids) fall among the longer bond lengths (2.547-2.576 Å) in comparison with the above-mentioned complexes. It is also noteworthy that the

Scheme 1. Reactivity of Alkylaluminum Hydrides toward [Cp₂YMe]₂



 $R = CH_3, CH_2SiMe_3^a; Mes^* = C_6H_2tBu_3-2,4,6$



Figure 2. Solid-state structure of 2 with ellipsoids of Y, Cl, and bridging Ct's set at the 50% level. Terminal Ct's were drawn as balland-stick models, and nonbridging hydrogen atoms were omitted for clarity. Shown in (a) is the structural model with a chlorido bridging Y1 and Y6 (2a) and in (b) the structural model with a Ct ring on the same position (2b). Selected bond lengths [Å] and angles [deg] for 2a: Y1-H1 2.08(7), Y1-Cl 2.679(3), Y2-H1 2.09(7), Y2-Ct1 2.547, Y3-Ct1 2.555, Y3-H2 2.20, Y4-H2 2.06, Y4-Ct2 2.576, Y5-Ct2 2.564, Y5-H3 2.14(7), Y6-H3 2.03(7), Y6-Cl 2.666(3), Y1-H1-Y2 171(4), Y2-Ct1-Y3 174, Y3-H2-Y4 173(3), Y4-Ct2-Y5 178, Y5-H3-Y6 176(4), Y1-Cl-Y6 130.6(2); for 2b Y1-Ct3 2.33, Y6-Ct3 2.55, Y1-Ct3-Y6 168; all other values are the same as for 2a. (Ct = cyclopentadienyl centroid.)

structural motif of η^5 -bridging Cp ligands is well known for other lanthanide complexes of, for example, lanthanum,³⁰ samarium,³¹ and ytterbium.³² The yttrium chlorido distances in **2a** (2.666(3)/2.679(3) Å) are well within the range of those found in [Cp₂YCl]₂ (2.674(4)/2.689(4) Å).³³

Inspired by the work of Power and Wehmschulte on the reaction system $Cp_2ZrMe_2/H_2AlMes^{*34}$ we examined the reactivity of the bulky aluminum dihydride H_2AlMes^* toward $[Cp_2YMe]_2$ (Scheme 1, b and c). As for the dialkylaluminum hydrides an insoluble white solid could be isolated and identified as $[Cp_2Y(thf)(\mu-H)]_2$ upon addition of thf. Furthermore, depending on the employed Y:Al ratio, two different alkylaluminum species were identified and fully characterized. Using a Y:Al ratio of 1:1 led to the formation of mixed alkylaluminum hydride $[(\mu-H)(Me)AlMes^*]_2$ (3) (Scheme 1, b), while using a Y:Al ratio of 2:1 the dimethylaluminum compound Me_2AlMes^* (4) was obtained (Scheme 1, c). In accordance with these findings the reaction of Cp_2ZrMe_2 with H_2AlMes^* resulted in the formation of Cp_2ZrH_2 and Me_2AlMes^* , showing the same methyl-hydrido

exchange.³⁴ While a possible intermediate $Cp_2(H)Zr(\mu-H)_2Al-(Me)Mes^*$ could be isolated from the reaction mixture and structurally characterized, further analytical data of Me₂AlMes^{*} remained elusive.³⁴

The ¹H NMR spectrum of $[(\mu-H)(Me)AlMes^*]_2$ (3) compares well to the starting material H₂AlMes^{*}. It shows sharp singlets for the aryl protons at 7.47 ppm and for the *tert*-butyl groups in *ortho-* and *para*-position (1.49 and 1.37 ppm) as well as broad signals for the hydrido ligand (4.72 ppm) and the Al-Me group (-0.34 ppm). A very similar NMR spectrum was also obtained for Me₂AlMes^{*} (4) with resonances for the aryl protons and *tert*-butyl groups at 7.44, 1.42, and 1.36 ppm, respectively, as well as a sharp singlet for the two methyl groups at -0.08 ppm.

The solid-state structures of both aluminum compounds could be determined by X-ray crystallography. Similar to the dihydride starting material H₂AlMes^{*},¹² the isolated $[(\mu-H)(Me)AlMes^*]_2$ (3) also forms a dimer with bridging hydrido ligands in the solid state (Figure 3) resembling the aluminum



Figure 3. Solid-state structure of 3 with ellipsoids set at the 50% level. Hydrogen atoms except for the bridging hydrido ligands were omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al–C1 1.968(3), Al–C19 1.946(4), Al–H1 1.69(5), Al–H1' 1.73(5), Al···Al' 2.647(2), C1–Al–C19 138.5(2), C1–Al–H1 105(2), C1–Al–Al' 108.4(2), C2–C1–Al–C19 101.1(3).

hydride dialkyl moiety found coordinated to Cp₂ZrH₂ in the previously mentioned $Cp_2(H)Zr(\mu-H)_2Al(Me)\tilde{Mes}^{*.34}$ Dimerization via bridging hydrido ligands is also observed in other aluminum complexes such as $[2,6\text{-Trip}_{2}C_{6}H_{3}AlH_{2}]_{2}^{35}$ (Trip = $C_{6}H_{2}iPr_{3}$ -2,4,6), $[2,6\text{-Mes}_{2}C_{6}H_{3}AlH_{2}]_{2}^{35}$ (Mes = $C_{6}H_{2}Me_{3}$ -2,4,6), $Ar^{iPr4}AlH_{2}]_{2}$ (Ar^{iPr4} = $C_{6}H_{3}$ -2,6-($C_{6}H_{3}iPr_{2}$ -2,6),³⁶ and $[Ar^{iPr8}AlH_{2}]_{2}$ (Ar^{iPr8} = $C_{6}H$ -2,6-($C_{6}H_{2}iPr_{3}$ -2,4,6)-3,5-*i*Pr₂);³⁶ however, 3 appears to be the first example of a defined arylmethyl-aluminum hydride. When comparing these structures it needs to be mentioned that the crystal structures of [2,6- $Trip_2C_6H_3AlH_2]_2$ and $[2,6-Mes_2C_6H_3AlH_2]_2$ are contaminated by the presence of -OH impurities on hydrido positions (14% and 28%, respectively).³⁵ Overall these four complexes show very similar structural features around the aluminum metal centers. The Al-H distances in 3 (1.69(5)/1.73(5) Å)compare well with those found for the bridging hydrido ligands in \hat{H}_2 AlMes* (1.69(4)/1.70(4) Å)¹² and lie well within the range of those found in [2,6-Trip₂C₆H₃AlH₂]₂ (1.65(5) Å)³⁵ and $[2,6-Mes_2C_6H_3AlH_2]_2$ $(1.74(5)^{35}$. Also the Al-C1 distance observed in 3 (1.968(3) Å) and the other compared complexes $(H_2AlMes^* 1.966(3) \text{ Å}, [2,6-Trip_2C_6H_3AlH_2]_2$ 1.963(4) Å, $[2,6-\text{Mes}_2C_6H_3\text{AlH}_2]_2$ 1.956(3) Å) match very closely. Only the Al…Al separations differ slightly with 3 (2.647(2) Å), being intermediate between H₂AlMes* (2.652(2) Å) and $[2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{AlH}_2]_2$ (2.630(2) Å).

Different from dimeric $[(\mu-H)(Me)AlMes^*]_2$ the second hydrido transfer product, Me₂AlMes^{*} (4, Figure 4), is a



Figure 4. Solid-state structure of 4 with ellipsoids set at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al-C1 1.993(2), Al-C19 1.965(2), Al-C20 1.964(3), C1-Al-C19 121.2(2), C1-Al-C20 123.2(2), C19-Al-C20 115.6(2), C2-C1-Al-C19 96.5(2).

monomer in the solid state similar to the halide analogues X_2 AlMes* (X = Br,³⁷ Cl³⁸). It is also one of the few examples of a mixed aryl-alkyl-aluminum compound featuring a threecoordinate aluminum center as for example in Dipp*AlEt $_2^{39}$ or $DcpAlEt_2^{39}$ (Dipp* = 2,6-(C₆H₃iPr₂-2,6)₂C₆H₃, Dcp = 2,6- $(C_6H_3Cl_2-2,6)_2C_6H_3$). The crystal structure of 4 features an aluminum metal center in a trigonal planar coordination environment with angles close to 120°, the largest deviation being the C19-Al-C20 angle $(115.6(2)^{\circ})$. It also shows the typical rotation of the C19-Al-C20 plane relative to the Mes* plane, both being almost orthogonal to each other (torsion angle C6-C1-Al-C20 = 96.3(2)°). The Al-C1 distance in 4 (1.993(2) Å) is longer compared to related complexes (3) 1.946(4), Dipp*AlEt₂ 1.968(2), DcpAlEt₂ 1.985(6) Å), while the Al–C19 and Al–C20 bond lengths (1.965(2)/1.964(3) Å) lie between those found for 3 (1.946(4) Å) and Dipp*AlEt₂ (1.969(2)/1.978(2) Å). For both Mes*AlCl₂ and Mes*AlBr₂ short contacts between two hydrogen atoms of the ortho-tertbutyl groups and the aluminum (2.1 Å) were reported, implying an agostic interaction between the two. This effect does not seem to be as pronounced in 4 since only one close contact of 2.15 Å is found, while the others range from 2.21 to 2.56 Å.

Intrigued by the ability of the alkylalanes to generate yttrium hydride complexes, we investigated their reactivity toward polymeric $[YMe_3]_n^{17}$ aiming at the hitherto elusive molecular trihydride $[LnH_3](M)_x$ (M = stabilizing, solubilizing molecules).⁴⁰ Reasoning that the bulky Mes* backbone would be beneficial for stabilizing a possible adduct complex, we reacted H₂AlMes* with $[YMe_3]_n$ in toluene (Scheme 2, a). Upon addition of the reactants, a clear solution was obtained, from which a white solid precipitated in the course of the reaction. From the toluene solution another white solid was isolated and identified as 4, while attempts to further characterize the white precipitate gave inconclusive results, although stoichiometry suggests the formation of " $[YH_3]_n$ ".

Visual inspection of the reaction between $HAl(CH_2SiMe_3)_2$ and $[YMe_3]_n$ (Scheme 2, b) suggested a similar methyl-hydrido exchange, as evidenced by formation of a clear solution, from which a white solid precipitated upon workup. However, the colorless oil isolated from the toluene solution was a mixture of products, as evidenced by ¹H NMR spectroscopy.





^aNuclearity not accounted for.

Following the reaction in situ by ¹H NMR spectroscopy did not allow for the identification of a major reaction product either.

Finally, we treated $[YMe_3]_n$ suspended in toluene with $HAIMe_2$ in a Y:Al ratio of 1:3 (Scheme 2, c). The occurrence of a reaction was again visually indicated by the formation of a clear solution after 2 min, which started to produce an intractable white precipitate after 15 min. Analysis of the soluble part via ¹H NMR spectroscopy allowed for the identification of trimethylaluminum as reaction product, indicating the occurrence of hydrido transfer. For further investigation, the reaction was monitored in situ via ¹H NMR spectroscopy, and the obtained spectrum revealed a doublet at 4.68 ppm with a coupling constant ${}^{1}J_{Y-H} = 20.5$ Hz, clearly indicating yttrium—hydrido bonding (SI, Figure S9). In addition to this tentative heteroaluminate species "Y-(AlHMe_3)₃" we could unambiguously identify Y(AlMe_4)₃ and Al₂Me₆ from the reaction mixture.⁴¹

On the basis of the independent work of Okuda⁴² and Hou^{26,43} on half-sandwich dihydride complexes we next assessed the reactivity of the aluminum hydrides toward yttrium dimethyl complex $[Cp*YMe_2]_3$. The reaction with H₂AlMes* in toluene proceeded in a manner similar to the previous reactions; upon addition of the aluminum hydride to the yttrium alkyl, a clear solution was obtained, from which an insoluble white precipitate formed (Scheme 3, a). From the

Scheme 3. Reactivity of Alkylalanes toward $[Cp*YMe_2]_3^a$



^{*a*}Nuclearity not accounted for.

toluene solution hydrido transfer product 3 could be isolated as expected. Interestingly, the same reaction performed in *n*-hexane allowed the isolation of hydrido transfer product 4, which can be rationalized by the lower solubility of the dihydride, allowing a double methyl-hydrido exchange to occur more easily (Scheme 3, b). Although one possible yttrium hydride complex, $(Cp*YH_2)_6$, was isolated and structurally characterized earlier by Hou et al.,²⁶ the nature of the yttrium species in this case remained elusive.

Moving on to the neosilylaluminum hydride, progression of the reaction was evidenced by formation of a clear solution, from which a white intractable solid precipitated. From the toluene solution a product mixture in the form of a colorless oil was obtained, which did not allow further purification (Scheme 3, c).

In anticipation of a dihydride complex of low nuclearity we next followed the reaction of $[Cp*YMe_2]_3$ with HAlMe₂ (Y:Al 1:2) by ¹H NMR spectroscopy (Scheme 3, d). Unfortunately, the formation of a mixture of products was observed, as evidenced by a vast number of signals in the *CpMe* region. Reasoning that the reaction might be forced toward a hydride complex using an excess of the aluminum hydride, reactions with Y:Al ratios of 1:4 and 1:10 were performed. From the clear solutions in the beginning a white precipitate started to form, and the ¹H NMR spectra of the remaining soluble parts showed again a mixture of products along with the signals for the excess aluminum hydride.

A more conclusive ¹H NMR spectrum was obtained when $HAlMe_2$ was used for the reaction in an Y:Al ratio of 1:1. Next to a number of signals in the Cp region that could not be assigned, signal sets from $Cp*Y(AlMe_4)_2$ and free $AlMe_3$ were observed as well as a further set of signals that would belong to a species formally denoted as $Cp*Y(H)(AlMe_4)$ (Figure 5). A



Figure 5. ¹H NMR spectrum (benzene- d_6 , 400 MHz, 25 °C) of the reaction Cp*YMe₂ + HAlMe₂ (nuclearity not accounted for). Signal assignment: Cp*Y(AlMe₄)H δ = 3.88 (Y–H), 1.82 (C₅(CH₃)₅), -0.29 (Al(CH₃)₄) ppm. Cp*Y(AlMe₄)₂ δ = 1.74 (C₅(CH₃)₅), -0.33 (Al(CH₃)₄) ppm. AlMe₃ δ = -0.41 (Al(CH₃)₃) ppm.

striking feature of the spectrum is the observed doublet at 3.88 ppm, which implies that the hydrido ligand is bonded to only one yttrium metal center. Otherwise a triplet or quartet would be observed when two or three yttrium centers, respectively, are involved in bonding. Taking this and the availability of trimethylaluminum into account a better proposal for the observed species would be $Cp^*Y(HAIMe_3)(AIMe_4)$.

Since $Cp^*Y(AlMe_4)_2$ readily formed in the reaction mixture, as evidenced by ¹H NMR spectroscopy, and due to its better solubility in organic solvents compared to $[Cp^*YMe_2]_3$, we reacted this complex with one equivalent of HAlMe₂, also trying to reduce the number of species present in solution (Scheme 4). The ¹H NMR spectrum obtained from the reaction mixture looked very similar to the one found before showing sets of signals for precursor $Cp^*Y(AlMe_4)_2$, free AlMe₃, a species $Cp^*Y(HAlMe_3)(AlMe_4)$ with a doublet signal

Scheme 4. Reactivity of (CpMe₄R)Y(AlMe₄)₂ toward HAlMe₂

 $(C_5Me_4R)Y(AIMe_4)_2$ + HAIMe₂ benzene- d_6 , 25 °C

 $R = Me_{SiMe_{3}} (C_{5}Me_{4}R)Y(HAIMe_{3})(AIMe_{4}) + Y(AIMe_{4})_{3} + AIMe_{3}$

103

at 3.87 ppm (${}^{1}J_{Y-H}$ = 25.5 Hz), and additionally one doublet signal for homoleptic Y(AlMe₄)₃. The observed coupling constant is much smaller than those reported for terminal yttrium hydride complexes $Ind_{2}^{*}YH(thf)$ (${}^{1}J_{Y-H} = 82.0 Hz$, Ind* = heptamethylindenyl)⁴⁴ and ($C_{3}H_{4}SiMe_{3}$)₂YH(thf) $({}^{1}J_{Y-H} = 74.8 \text{ Hz})^{45}$ and lies more in the range of halfsandwich yttrium hydrides $[(C_5Me_4R)YH_2]_n(thf)_x$ (R = SiMe₃, $n = 5, x = 0, {}^{1}J_{Y-H} = 35.8 \text{ Hz}; R = Me, n = 5, x = 2, {}^{1}J_{Y-H} = 32.8 \text{ Hz}; obtained from low-temperature NMR data)^{26} and the$ earlier mentioned $[Cp_2YH(\hat{thf})]_2$ (27.0 Hz)²³ and Tp^{tBu,Me}Y- $[(\mu-H)AlMe_3]_2$ (A_Y) (doublet at 5.05 ppm with a coupling constant ${}^{1}J_{Y-H} = 30.8$ Hz).¹³ Attempts to crystallize an yttrium hydride species from the reaction mixture were not successful because at -35 °C only crystals of precursor Cp*Y(AlMe₄)₂ could be harvested in almost quantitative yield. Attempts to grow crystals at ambient temperature led to the formation of a completely insoluble white precipitate of unknown composition. Formation of hydride clusters, which are soluble at first, causing the observed Cp signals in the ¹H NMR spectrum, and becoming insoluble upon agglomeration to complexes of higher nuclearity, might be one explanation.

We then decided to use additional NMR spectroscopic methods to shed further light on the reaction. First, we wanted to verify that the observed doublet at 3.87 ppm really stems from an yttrium coupling and did so by taking an ⁸⁹Y decoupled ¹H NMR spectrum. In this spectrum the doublet collapsed to a broad singlet, as did the other doublet signals observed for the methyl groups of $Cp*Y(AlMe_4)_2$ and $Y(AlMe_4)_3$. We then went on and performed an ⁸⁹Y DEPT45 NMR experiment, which yielded a spectrum containing three sharp signals for Cp*Y(AlMe₄)₂ (223 ppm), Y(AlMe₄) (394 ppm), and one at 175 ppm, which we assigned to the previously proposed species Cp*Y(HAlMe₃)(AlMe₄). Finally, we also conducted a variabletemperature ¹H NMR experiment in the temperature range from -90 to 25 °C (Figure 6), which gave us some insight into the dynamics. The most interesting information from this experiment was that the hydride formation seems to be



Figure 6. ¹H VT-NMR spectrum of the reaction mixture Cp*Y- $(AlMe_4)_2$ + HAlMe₂. The small inset shows the region of the anticipated yttrium-hydride signal.

reversible.⁴⁶ At lower temperature the main component in the solution is starting material Cp*Y(AlMe₄)₂, and at increasing temperatures the concentration of Cp*Y(HAlMe₃)(AlMe₄) increases until it seems to be the main, but not the only, component in solution at ambient temperature. This finding is also in accordance with the previous observation that we could only crystallize Cp*Y(AlMe₄)₂ from chilled solutions (-35 °C). In the aluminate region of the ¹H NMR spectrum we also observed the characteristic splitting of the peak for free trimethylaluminum into two singlets, with a 3:6 ratio of the integrals, belonging to the bridging and terminal methyl groups of the Al₂Me₆ dimer.

Our final approach trying to eventually isolate a halfsandwich yttrium hydride species was to switch to the ligand Cp^{SiMe3} (= $C_5H_4SiMe_3$).²⁶ As before, we started from the readily available $Cp^{SiMe3}Y(AlMe_4)_{22}$ reacted it with one equivalent of HAlMe₂ (Scheme 4), and monitored the reaction by ¹H NMR spectroscopy. Similar to the previous reaction we found sets of signals in the NMR spectrum belonging to starting material $Cp^{SiMe3}Y(AIMe_4)_2$, homoleptic $Y(AIMe_4)_3$, and one set that could be accounted for by a formal species Cp^{SiMe3}Y(HAlMe₃)(AlMe₄) with a characteristic doublet at 3.93 ppm (${}^{1}J_{Y-H}$ = 24.5 Hz). Additionally, two minor peaks observed in the ¹H NMR spectrum at 2.16 and 2.07 ppm match closely to those reported for the Cp-methyl groups in $[Cp^{SiMe3}YH_2]_4(thf)^{43b}$ (2.16 and 2.06 ppm), although no thf is present in the reaction mixture. The corresponding peaks for the thf-free $[Cp^{SiMe3}YH_2]_n$ complexes $(n = 4, 2.37/2.20 \text{ ppm};^{47} n = 5 2.53/2.28 \text{ ppm}^{26})$, however, are shifted a bit further downfield, but nonetheless formation of a polynuclear yttrium hydride cluster can be anticipated, taking also the formation of free trimethylaluminum into account.

Unfortunately, we were again not able to crystallize an yttrium hydride complex and turned to NMR spectroscopic investigations. As for the Cp* derivative, we collected a ⁸⁹Y decoupled ¹H NMR spectrum in which the prominent doublet at 3.93 ppm collapsed into a broad singlet together with the signals for the aluminates in $Cp^{SiMe3}Y(AlMe_4)_2$ and $Y(AlMe_4)_3$, confirming the ⁸⁹Y coupling. An ⁸⁹Y DEPT45 NMR experiment yielded a spectrum with three sharp signals, which we assigned to $Y(AIMe_4)_3$ (395 ppm), $Cp^{SiMe3}Y(AIMe_4)_2$ (216 ppm), and the formal species $Cp^{SiMe3}Y(HAIMe_3)(AIMe_4)$ (173 ppm). Interestingly, the chemical shifts for the Cp^{SiMe3} species match closely to those found for the Cp* species, suggesting the presence of structurally similar complexes. A variable lowtemperature ¹H NMR experiment in the range from -90 to -50 °C finally showed a behavior different from that observed using Cp* as ancillary ligand. The signals for the Cp SiMe3 ligand did not change over the measured temperature range and stayed also the same in a final spectrum taken at room temperature, indicating the presence of Cp^{SiMe3}Y(HAlMe₃)-(AlMe₄) even at low temperatures. This was also evidenced by the observation of the corresponding doublet signal at 3.93 ppm. Distinct splitting patterns were, however, observed for the aluminate signals.

CONCLUSION

Reacting $[Cp_2YMe]_2$ with alkylaluminum hydrides of different steric demand led to a direct methyl-hydrido exchange, as evidenced by the isolation of well-known yttrium hydride complex $[Cp_2Y(thf)(\mu-H)]_2$ after workup with the as well as the corresponding methyl aluminum complexes. Interestingly, varying the steric demand of the alkylaluminum hydrides did not have an influence on the reaction pathway in that no adduct formation occurred, which might have been expected for the less sterically demanding aluminum hydrides. The structurally characterized cyclic yttrium complexes $Cp_{14}Y_6H_3Cl$ and $Cp_{15}Y_6H_3$ allowed some insight into the possible structure of a donor-free CpYH species. Furthermore, the hydrido transfer products $[(\mu-H)(Me)AlMes^*]_2$ and Me_2AlMes^* were isolated and completely characterized, one forming a dimer in the solid state similar to the starting material H_2AlMes^* , while the other is monomeric, similar to the corresponding halide compounds, adding to the library of fully characterized three-coordinated aryl-alkyl aluminum compounds.

Probing the reactivity of the selected alkylalanes toward $[YMe_3]_n$ and $[Cp*YMe_2]_3$, only mixtures of products were obtained for bis-neosilylaluminum hydride, while for supermesityl- and dimethylaluminum hydride isolation of the corresponding methylated aluminum compounds suggests occurrence of hydrido transfer. However, isolation of an yttrium hydride species was not successful. The similar reaction of half-sandwich yttrium tetramethylaluminate complexes $Cp*Y(AlMe_4)_2$ and $(C_5Me_4SiMe_3)Y(AlMe_4)_2$ with dimethylaluminum hydride also did not produce any isolable yttrium hydride complex, but NMR spectroscopic methods propose the following scenario: Upon mixing together the two reagents, trimethylaluminum is released and a transient species, Cp^RY-(HAlMe₃)(AlMe₄), forms. This transient species then reacts further to ultimately form vttrium hydride clusters while releasing more trimethylaluminum, which then drives the formation of homoleptic yttrium aluminates. Overall this shows that the reaction yields a variety of products by forming adducts and higher nuclearity complexes and by ligand scrambling. These findings may also have implications for polymerization catalyst mixtures where a defined precursor or a preformed alkyl complex is treated with an alkylaluminum hydride as a cocatalyst.

EXPERIMENTAL SECTION

General Considerations. All operations were performed with rigorous exclusion of air and water, using standard Schlenk and glovebox techniques (MBraun 200B; <1 ppm of O₂, <1 ppm of H₂O). Solvents were purified using Grubbs columns (MBraun SPS, solvent purification system) and stored in a glovebox. Benzene- d_6 and thf- d_8 were purchased from Eurisotop, degassed, dried over sodium for a minimum of 48 h, and purified by vacuum transfer. $[Cp_2YMe]_{2^{1}}^{16}$ $[YMe_3]_{n^{17}}^{17} [Cp^*YMe_2]_{3^{18}}^{18} Cp^*Y(AlMe_4)_{2^{19}} Cp^{SiMe3}Y(AlMe_4)_{2^{20}}^{20} (Cp = C_5H_5, Cp = C_5Me_5, Cp^{SiMe3} = C_5Me_4SiMe_3), HAl(CH_2SiMe_3)_{2^{11}}^{11}$ HAlMe₂,⁸⁵ and H₂AlMes^{*12} (Mes* = C₆H₂tBu₃-2,4,6) were synthesized according to literature procedures. NMR spectra of airand moisture-sensitive compounds were recorded using J.-Young valve NMR tubes on a Bruker AVII+400 spectrometer (¹H, 400.13 MHz; $^{13}\text{C}\text{, }$ 100.61 MHz) and a Bruker AVII+500 spectrometer (1H, 500.13 MHz; ¹³C, 125.76 MHz; ⁸⁹Y, 24.50 MHz). ¹H and ¹³C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. DRIFT spectra were obtained on a Nicolet 6700 FT-IR spectrometer using dried KBr powder and KBr windows. Elemental analyses were performed on an EL Vario MICRO Cube.

Reaction of [Cp₂YMe]₂ with HAIMe₂. A solution of HAIMe₂ (9 mg, 0.15 mmol) in 2 mL of toluene was added to a suspension of $[Cp_2YMe]_2$ (37 mg, 0.15 mmol) in 3 mL of toluene and stirred at ambient temperature for 18 h. After removal of the white residue the remaining solution was dried under vacuum to obtain a colorless oil containing AlMe₃. The white residue was dried under vacuum, redissolved in 2 mL of hot thf (55 °C), and stored at -35 °C to obtain two batches of crystalline material, which was identified as Cp₂YH-(thf)²³ (39 mg, 0.13 mmol, 88%) by ¹H NMR spectroscopy.

Reaction of [Cp₂YMe]₂ with HAI(CH₂SiMe₃)₂. A solution of HAI(CH₂SiMe₃)₂ (61 mg, 0.3 mmol) in 5 mL of toluene was slowly added to a suspension of $[Cp_2YMe]_2$ (73 mg, 0.3 mmol) in 5 mL of toluene and stirred at ambient temperature for 18 h. Then the white residue was filtered off, and from the remaining toluene solution a colorless oil was obtained by removing the volatiles in vacuo and identified as MeAI(CH₂SiMe₃)₂²⁴ (49 mg, 0.23 mmol, 77%) by ¹H NMR spectroscopy. The toluene solution afforded a few single crystals, which were identified as complex **2**. Parts of the white residue were dissolved in thf-*d*₈ and could be identified as Cp₂YH(thf)²³ by ¹H NMR spectroscopy.

Reaction of [Cp₂YMe]₂ with H₂AlMes*. (a) A solution of H₂AlMes* (0.3 mmol, 82 mg) in 5 mL of toluene was added to a suspension of [Cp₂YMe]₂ (73 mg, 0.3 mmol) in 5 mL of toluene and stirred for 18 h at ambient temperature. Subsequently the white precipitate was separated, and the remaining toluene solution was stored at -35 °C to obtain clear, colorless crystals of $[(\mu$ -H)(Me)AlMes*]₂ (3, 63 mg, 0.22 mmol, 73%). ¹H NMR (benzene d_{6} , 500 MHz, 25 °C): $\delta = 7.47$ (s, 2 H, Phen-H), 4.72 (br s, 1 H, AlH), 1.49 (s, 18 H, o-C(CH₃)₃), 1.37 (s, 9 H, p-C(CH₃)₃), -0.34 (br s, 3 H, AlCH₃) ppm. ¹³C{¹H} NMR (benzene- d_6 , 126 MHz, 25 °C): δ = 158.7 (o-C(2)), 150.2 (p-C(4)), 136.4 (i-C(1), taken from HMBC measurement), 120.6 (m-C(3)), 38.3 (o-C(CH₃)₃), 34.7 (p-C(CH₃)₃), 32.8 (o-C(CH₃)₃), 31.3 (p-C(CH₃)₃), -3.9 (AlCH₃) ppm. IR (KBr, cm⁻¹): 3065 vw, 3049 vw, 2962 vs, 2950 vs, 2903 s, 2859 s, 2730 vw, 2705 vw, 1866 w, 1592 m, 1524 m, 1507 s, 1454 s, 1391 s, 1362 s, 1245 m, 1210 m, 1194 m, 1126 w, 1037 w, 936 m, 880 m, 831 s, 662 m, 570 w, 477 w. Anal. Calcd for C₁₉H₃₃Al (288.45 g·mol⁻¹): C, 79.11; H, 11.53. Found: C, 79.10; H, 10.62. The white residue was dissolved in thf and could be identified as $Cp_2YH(thf)^{23}$ by ¹H NMR spectroscopy.

(b) A solution of H₂AlMes* (0.2 mmol, 55 mg) in 5 mL of toluene was added to a suspension of [Cp₂YMe]₂ (97 mg, 0.4 mmol) in 5 mL of toluene and stirred for 18 h at ambient temperature. Subsequently, the white precipitate was separated, and the remaining toluene solution was stored at -35 °C to obtain clear, colorless crystals of Me₂AlMes* (4, 46 mg, 0.15 mmol, 76%). ¹H NMR (benzene-d₆, 400 MHz, 25 °C): δ = 7.44 (s, 2 H, Phen-H), 1.42 (s, 18 H, o-C(CH₃)₃), 1.36 (s, 9 H, p-C(CH₃)₃), -0.08 (s, 6 H, Al(CH₃)₂) ppm. ¹³C{¹H} NMR (benzene- d_{6} 100 MHz, 25 °C): δ = 157.9 (o-C(2)), 149.7 (p-C(4)), 136.1 (i-C(1)), 120.5 (m-C(3)), 38.2 (o-C(CH₃)₃), 34.5 (p- $C(CH_3)_3)$, 32.9 (o- $C(CH_3)_3$), 31.6 (p- $C(CH_3)_3$), -4.0 (AlCH₃) ppm. IR (KBr, cm⁻¹): 3063 vw, 2953 vs, 2859 s, 2838 m, 1597 m, 1527 m, 1475 m, 1456 m, 1388 m, 1663 m, 1344 m, 1255 m, 1246 m, 1196 s, 1187 s, 1170 m, 1128 w, 1041 w, 1007 vw, 934 w, 904 m, 875 m, 777 m, 716 s, 672 vs, 606 m, 573 w, 552 w. Anal. Calcd for C₂₀H₃₅Al (302.48 g·mol⁻¹): C, 79.42; H, 11.66. Found: C, 79.36; H, 10.72. The white residue was dissolved in thf and could be identified as Cp₂YH(thf)²³ by ¹H NMR spectroscopy.

Reaction of [YMe₃]_n with H₂AlMes*. To a suspension of [YMe₃]_n (20 mg, 0.15 mmol) in toluene (3 mL) was slowly added a solution of H₂AlMes* (61 mg, 0.23 mmol) in toluene (3 mL). Upon addition, a clear solution was obtained, from which a white solid precipitated after several minutes and the reaction was further stirred for 18 h at ambient temperature. After separation from the white precipitate the remaining solution was dried under vacuum to obtain a white powder, which was identified as Me₂AlMes* (4, 48 mg, 0.16 mmol, 69%) by NMR spectroscopy. Further analysis of the precipitate via NMR spectroscopy was hampered because of a lack of solubility, and the results from IR spectroscopy and elemental analysis were inconclusive.

Reaction of [YMe₃]_n with HAl(CH₂SiMe₃)₂. To a suspension of [YMe₃]_n (42 mg, 0.31 mmol) in 4 mL of toluene was added a solution of HAl(CH₂SiMe₃)₂ (189 mg, 0.93 mmol) in toluene (4 mL), and the reaction mixture stirred at ambient temperature for 18 h. A clear solution was obtained upon addition of the aluminum hydride, and a white precipitate started to form several minutes later. After separation from the white solid the remaining solution was dried under vacuum to obtain a colorless, oily product. NMR spectroscopic investigations

showed a mixture of compounds including also starting material HAl(CH₂SiMe₃)₂.

Reaction of [YMe₃]_n with HAIMe₂. To a suspension of $[YMe_3]_n$ (42 mg, 0.31 mmol) in toluene (3 mL) was slowly added a solution of HAIMe₂ (54.6 mg, 0.94 mmol) in toluene (3 mL). Upon addition, a clear solution was obtained within 2 min, and after another 15 min formation of a white precipitate was observed. Further analysis of the precipitate via NMR spectroscopy was hampered because of a lack of solubility, and the results from IR spectroscopy and elemental analysis were inconclusive. ¹H NMR spectroscopic analysis of the solubles however showed formation of AlMe₃ (36 mg, 0.5 mmol, 53%).

[YMe₃]_n/**HAIMe₂** (NMR-Scale). In a 1 mL vial [YMe₃]_n (20 mg, 0.14 mmol) was suspended in 0.3 mL of benzene- d_6 , and a solution of HAIMe₂ (26 mg, 0.44 mmol) in 0.3 mL of benzene- d_6 added. The forming clear solution was transferred into a J.-Young valve NMR tube, and the reaction was monitored by ¹H NMR spectroscopy. ¹H NMR (benzene- d_6 , 400 MHz, 25 °C): "Y(HAIMe₃)₃" δ = 4.68 (d, ¹J_{Y-H} = 20.5 Hz, 3 H, Y-H-Al), -0.17 (s, 27 H, Al(CH₃)₃) ppm. Y(AIMe₃)₄ δ = -0.24 (d, ²J_{Y-H} = 2.3 Hz, 36 H, Al(CH₃)₄) ppm. AlMe₃ δ = -0.35 (s, 9 H, Al(CH₃)₃) ppm.

Reaction of [Cp*YMe₂]₃ with H₂AlMes*. (a) A solution of H₂AlMes* (55 mg, 0.2 mmol) in 5 mL of *n*-hexane was added to a suspension of [Cp*YMe₂]₃ (25 mg, 0.1 mmol) in 5 mL of *n*-hexane and stirred at ambient temperature for 18 h. The suspension cleared up within a few minutes before a white precipitate started to form again. After separation of the precipitate a white solid could be obtained upon removal of the volatiles under vacuum and indentified as $[(\mu-H)(Me)AlMes^*]_2$ (3, 46 mg, 0.16 mmol, 79%) by NMR spectroscopy.

(b) A solution of H_2AlMes^* (143 mg, 0.52 mmol) in 5 mL of toluene was slowly added to a suspension of $[Cp^*YMe_2]_3$ (66 mg, 0.26 mmol) in toluene (5 mL), and the resulting clear solution stirred at ambient temperature for 18 h. After ca. 20 min a white precipitate started to form, which was separated from the toluene solution upon completion of the reaction. From the remaining solution a white solid was obtained and identified as Me_2AlMes^* (4, 67 mg, 0.22 mmol, 43%) by NMR spectroscopy.

In both cases the insolubility of the remaining solid hampered further analysis.

Reaction of [Cp*YMe₂]₃ with HAI(CH₂SiMe₃)₂. To a suspension of [Cp*YMe₂]₃ (102 mg, 0.4 mmol) in 5 mL of toluene was added a solution of HAI(CH₂SiMe₃)₂ (162 mg, 0.8 mmol) in 5 mL of toluene, and the reaction mixture stirred at ambient temperature for 18 h. After a few minutes a clear solution was obtained, from which a white solid started to precipitate within 30 min. Upon removal of the precipitate, the remaining solution was dried under vacuum to obtain a white solid, which was identified as a mixture of compounds by NMR spectroscopy. Unfortunately attempts to separate the components by crystallization were not successful.

General Procedure of NMR-Scale Reactions. Each yttrium complex was weighed in a glovebox into a 1 mL vial and dissolved/ suspended in 0.3 mL of benzene- d_6 or toluene- d_8 . Aluminum hydride HAlMe₂ was weighed into a second 1 mL vial and also dissolved in benzene- d_6 or toluene- d_8 , respectively. The aluminum hydride solution was transferred to the yttrium complex solution, and the resulting reaction mixture was stirred for a given amount of time. Then the solution was transferred into a J.-Young valve NMR tube for analysis.

[*Cp***YMe*₂]₃/*HAlMe*₂ (*Y*:*Al* = 1:1). [*Cp***YMe*₂]₃ (10 mg, 0.039 mmol), HAlMe₂ (2.3 mg, 0.039 mmol), benzene-*d*₆, 20 min. After about 2 min a clear solution was obtained. ¹H NMR (benzene-*d*₆, 400 MHz, 25 °C): Cp*Y(AlMe₄)H δ = 3.88 (d, ¹*J*_{Y-H} = 25.3 Hz, 1 H, Y-H), 1.82 (s, 15 H, C₅(CH₃)₅), -0.29 (d, ²*J*_{Y-H} = 2.5 Hz, 12 H, Al(CH₃)₄) ppm. Cp*Y(AlMe₄)₂ δ = 1.74 (s, 15 H, C₅(CH₃)₅), -0.33 (d, ²*J*_{Y-H} = 2.2 Hz, 24 H, Al(CH₃)₄) ppm. AlMe₃ δ = -0.41 (s, 9 H, Al(CH₃)₃) ppm.

 $[Cp*YMe_2]_3$ /HAIMe₂ (Y:AI = 1:2). $[Cp*YMe_2]_3$ (10 mg, 0.039 mmol), HAIMe₂ (4.5 mg, 0.078 mmol), benzene- d_6 , 20 min and 18 h. After about 1 min a clear solution was obtained. Both ¹H NMR spectra indicate the formation of a mixture of products.

 $[Cp*YMe_2]_3/HAIMe_2$ (Y:AI = 1:4). $[Cp*YMe_2]_3$ (4 mg, 0.016 mmol), HAIMe_2 (4.5 mg, 0.063 mmol), benzene- d_6 , 20 min and 18 h. Upon addition of HAIMe_2 a clear solution formed, and after several hours precipitation of a white solid was observed. The ¹H NMR spectrum showed signals for HAIMe_2 and a mixture of other products.

 $[Cp*YMe_2]_3/HAIMe_2$ (Y:Al = 1:10). $[Cp*YMe_2]_3$ (18 mg, 0.07 mmol), HAIMe_2 (40 mg, 0.7 mmol), benzene- d_6 , 20 min and 18 h. Upon addition of HAIMe_2 a clear solution formed, and after several hours precipitation of a white solid was observed. The ¹H NMR spectrum after 20 min showed a mixture of products, while the ¹H NMR spectrum after 18 h showed only signals for HAIMe_2.

 $\begin{array}{l} Cp^*Y(AlMe_4)_2/HAlMe_2 \ (Y:Al = 1:1). \ Cp^*Y(AlMe_4)_2 \ (14 \ mg, \ 0.04 \ mmol), \ HAlMe_2 \ (2.4 \ mg, \ 0.04 \ mmol), \ benzene-d_6, \ 20 \ min. \ ^1H \ NMR \ (benzene-d_6, \ 400 \ MHz, \ 25 \ ^{\circ}C): \ Cp^*Y(AlMe_4)H \ \delta = 3.87 \ (d, \ ^1J_{Y-H} = 25.5 \ Hz, \ 1 \ H, \ Y-H), \ 1.82 \ (s, \ 15 \ H, \ C_5(CH_3)_5), \ -0.30 \ (d, \ ^2J_{Y-H} = 2.5 \ Hz, \ 12 \ H, \ Al(CH_3)_4) \ ppm. \ Cp^*Y(AlMe_4)_2 \ \delta = 1.74 \ (s, \ 15 \ H, \ C_5(CH_3)_5), \ -0.33 \ (d, \ ^2J_{Y-H} = 2.2 \ Hz, \ 24 \ H, \ Al(CH_3)_4) \ ppm. \ Y(AlMe_4)_3 \ \delta = -0.25 \ (d, \ ^2J_{Y-H} = 2.4 \ Hz, \ 36 \ H, \ Al(CH_3)_4) \ ppm. \ AlMe_3 \ \delta = -0.36 \ (s, \ 9 \ H, \ Al(CH_3)_3) \ ppm. \ ^{89}Y \ DEPT45 \ NMR \ (benzene-d_6, \ 25 \ MHz, \ 25 \ ^{\circ}C): \ \delta = 394 \ (s, \ Y(AlMe_4)_3), \ 223 \ (s, \ Cp^*Y(AlMe_4)_2), \ 175 \ (s, \ Cp^*Y(AlMe_4)H) \ ppm. \ VT-NMR: \ Cp^*Y- \ (AlMe_4)_2 \ (20 \ mg, \ 0.05 \ mmol), \ HAlMe_2 \ (2.9 \ mg, \ 0.05 \ mmol), \ toluene-d_8. \ ^{1}H \ NMR \ spectra \ were \ recorded \ on \ the \ Bruker \ AVII+500 \ spectrometer \ in \ the \ temperature \ range \ from \ -90 \ to \ 25 \ ^{\circ}C. \ Cp^{SIMe3}Y(AlMe_4)_2 \ (20 \ mg, \ 0.5 \ MIMe_4)_2 \ (20 \ mg, \$

Cp^{SIMES}Y(*AlMe*₄)₂/*HAlMe*₂ (*Y*:*Al* = 1:1). Cp^{SIMES}Y(*AlMe*₄)₂ (20 mg, 0.044 mmol), HAlMe₂ (2.5 mg, 0.044 mmol), benzene-*d*₆, 20 min. ¹H NMR (benzene-*d*₆, 400 MHz, 25 °C): Cp^{SIME3}Y(*AlMe*₄)H δ = 3.93 (d, ¹*J*_{Y-H} = 24.5 Hz, 1 H, Y-H), 2.08 (s, 6 H, C₅(CH₃)₄), 1.78 (s, 6 H, C₅(CH₃)₄), 0.26 (s, 9 H, C₅Me₄Si(CH₃)₃), -0.27 (d, ²*J*_{Y-H} = 2.5 Hz, 12 H, Al(CH₃)₄) ppm. Cp^{SIME3}Y(*AlMe*₄)₂ δ = 1.99 (s, 6 H, C₅(CH₃)₄), 1.74 (s, 6 H, C₅(CH₃)₄), 0.23 (s, 9 H, C₅Me₄Si(CH₃)₃), -0.29 (d, ²*J*_{Y-H} = 2.2 Hz, 24 H, Al(CH₃)₄) ppm. Y(*AlMe*₄)₃ δ = -0.37 (s, 9 H, Al(CH₃)₃) ppm. ⁸⁹Y DEPT45 NMR (benzene-*d*₆, 25 MHz, 25 °C): δ = 395 (s, Y(*AlMe*₄)₃), 216 (s, Cp^{SIME3}Y(*AlMe*₄)₂), 173 (s, Cp^{SIMe3}Y(*AlMe*₄)H) ppm. VT-NMR: Cp^{SIMe3}Y(*AlMe*₄)₂ (20 mg, 0.044 mmol), HAlMe₂ (2.5 mg, 0.044 mmol), toluene-*d*₈. ¹H NMR spectra were recorded on the Bruker AVII+500 spectrometer in the temperature range from -90 to 25 °C.

Crystallography. Crystals suitable for X-ray crystallography were grown by standard techniques from toluene solutions at -35 °C. Suitable single crystals were selected in a glovebox, coated with Parabar 10312 (Hampton Research, formerly known as Paratone-N) and fixed on a glass fiber (1, 3) or a nylon loop (2, 4). Data of 1 and 3 were collected on a Stoe IPDS 2T instrument using Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. Raw data were processed using Stoe's X-Area software suite;⁴⁸ structure solution and final model refinement was done using the WinGX⁴⁹ suite of programs including SHELXS,⁵⁰ SHELXL,⁵⁰ and PLATON.⁵¹ Corrections for absorption effects were applied using MulAbs as implemented in PLATON. Data of 2 were collected on a Bruker AXS II instrument, and data of 4 were collected on a Bruker APEX DUO instrument using Mo K α radiation (λ = 0.710 73 Å). The raw data were processed using APEX2⁵² and SAINT;⁵³ structure solution and final model refinement were done with SHELXTL.⁵⁴ Corrections for absorption effects were applied using SADABS.⁵⁵ All graphics were produced employing ORTEP-3⁵⁶ and POV-Ray.⁵⁷ Further details of the crystallographic analysis can be found in the Supporting Information. CCDC-968685 (1), 968686 (2), 968687 (3), and 968688 (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.

ASSOCIATED CONTENT

S Supporting Information

NMR spectroscopic data and crystallographic details. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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DEDICATION

This article is dedicated to the memory of Professor Michael F. Lappert.

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