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Trimethylyttrium and Trimethyltutetium***H. Martin Dietrich, Gabriele Raudaschl-Sieber, and
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Permethylated transition-metal complexes, as represented by neutral $M(\text{CH}_3)_x$ and anionic $[M(\text{CH}_3)_y]^{n-}$, have attracted considerable interest not only for displaying the simplest truly organometallic derivatives but also for their intrinsic bonding phenomena.^[1,2] While structural and theoretical investigations have led to enormous progress for thermally labile homoleptic Group 4, 5, 6, and 7 derivatives, monometallic Group 3 and lanthanide congeners have remained elusive.^[2,3] For example, the synthesis of rare-earth-metal-alkyl complexes such as LnEt_3 ($\text{Ln} = \text{Sc}, \text{Y}$) was claimed as early as 1938, however, striking evidence of their existence, be it spectroscopic data or clarifying follow-up chemistry, has never been reported.^[4] Moreover, the ease of β -hydride elimination in such early transition-metal-alkyl complexes led to controversial discussions.^[5,6] Nevertheless, a considerable number of silylalkyl complexes including homoleptic, donor-coordinated, donor-functionalized, and ate-type derivatives have been unambiguously identified.^[7–11] In the early 1980s, Schumann et al. reported the synthesis of thermally stable ate complexes of the type $[\text{Li}_3(\text{donor})_3][\text{Ln}(\text{CH}_3)_6]$ (donor = TMEDA (*N,N,N',N'*-tetramethylethylenediamine), DME (1,2-dimethoxyethane)), which featured an octahedral coordination geometry, for the entire series of rare-earth metals.^[12] Approximately ten years later, Evans et al. described permethylated derivatives $[\text{Nd}(\text{GaMe}_4)_3]$ and $[\text{Ln}(\text{AlMe}_4)_3]$ ($\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}$) which can be viewed as trimethylgallium and trimethylaluminum adduct complexes, respectively, of the elusive LnMe_3 .^[13,14] Meanwhile, heterobimetallic derivatives $[\text{Ln}\{(\mu\text{-Me})_2\text{AlMe}_2\}_3]$ are available for the entire Group 3 and 4f series except for scandium and promethium.^[15,16] Herein, another ten years later, we describe the synthesis and derivatization of homoleptic trimethylyttrium and trimethyltutetium.

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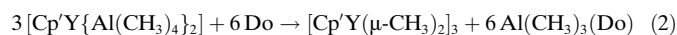
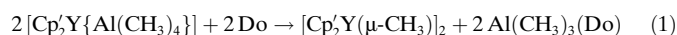
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Donor (Do)-induced cleavage of tetraalkylaluminates (Do = THF, diethyl ether, pyridine) has been previously applied to convert heteroleptic lanthanidocene and half-lanthanidocene complexes, $[\text{Cp}'_2\text{Ln}(\text{AlR}_4)]$ and $[\text{Cp}'\text{Ln}(\text{AlR}_4)_2]$ (Cp' = substituted cyclopentadienyl), into the corresponding σ -bonded alkyl derivatives [Eqs. (1) and (2)].^[17–20]



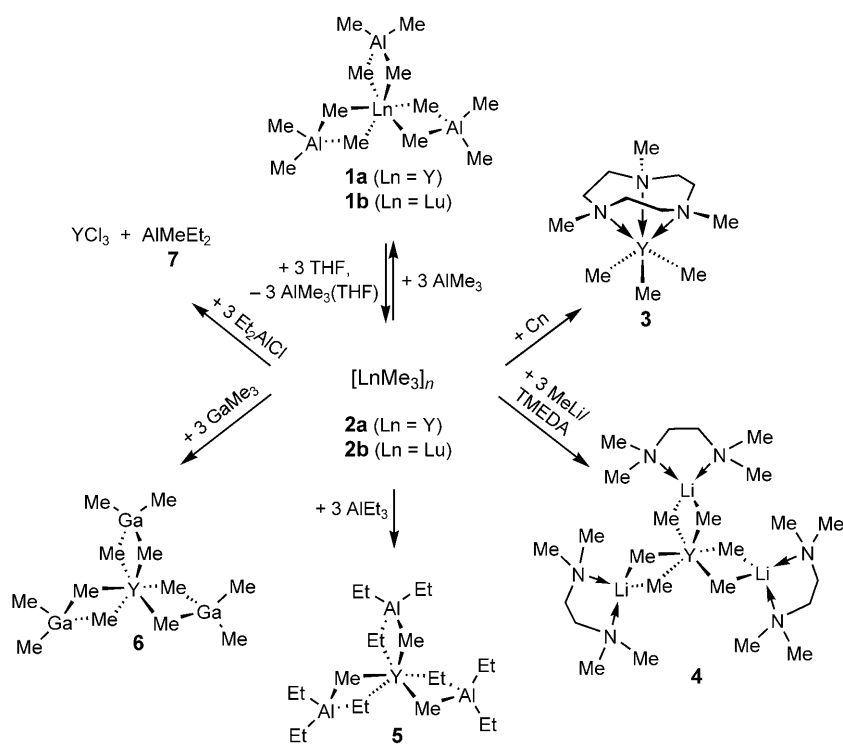
We found that homoleptic $[\text{Y}(\text{AlMe}_4)_3]$ (**1a**) and $[\text{Lu}(\text{AlMe}_4)_3]$ (**1b**) are also amenable to this donor-induced tetraalkylaluminate cleavage. Accordingly, addition of a stoichiometric amount of THF (3 equiv) to a solution of **1a** in hexane at ambient temperature produced a white precipitate, which was insoluble in aliphatic and aromatic solvents (Scheme 1). After several washings with hexane and drying

among the most volatile of rare-earth metal compounds.^[22]

Such optimized reaction conditions were crucial for the synthesis of pure $[\text{LuMe}_3]_n$ (**2b**). The precursor $[\text{Lu}(\text{AlMe}_4)_3]$ (**1b**) was most efficiently separated from the coproduct of the synthesis, $[\text{Me}_2\text{Al}(\mu\text{-NMe}_2)]$, by fractional sublimation (ca. 90 °C at 10^{-3} mbar; > 20 % yield).^[23] (Caution! Compound **2b** which is also obtained quantitatively as a white powder like the yttrium derivative **2a** detonates spontaneously when exposed to air; it also decomposes spontaneously at elevated temperature under high vacuum (ca. 80 °C at 10^{-4} mbar) to yield a black powder.) In addition to the C, H microanalytical data, unambiguous evidence for the formation of compounds **2a, b** stemmed from the complete reversibility of this donor-induced cleavage reaction (Scheme 1).^[18] That is, treatment of the precipitated compounds **2** (non-isolated, as formed from the initial reaction mixture) and likewise the isolated compounds **2**, which were resuspended in hexane, with 3 equivalents of AlMe_3 both led to quantitative re-formation of the homoleptic complexes **1**. Visually, this was indicated by the immediate formation of a clear solution.

A uniform coordination environment at the rare-earth-metal center in compounds **2** was confirmed by solid-state FTIR and MAS NMR spectroscopy. Nujol mulls of $[\text{LnMe}_3]_n$ gave IR spectra that displayed a characteristic vibration at $\tilde{\nu} = 1191$ and 1202 cm^{-1} for the yttrium and lutetium derivatives, respectively, and a broad, intense low-energy band featuring three maxima at $\tilde{\nu} = 522$, 431 , and 361 cm^{-1} (**2a**). The ^1H MAS NMR spectrum of **2a** showed a broad resonance centered at $\delta = -0.3\text{ ppm}$ that exhibited two well-resolved shoulders at around $\delta = 0.1$ and 1.0 ppm . The ^{13}C CPMAS NMR spectra of compounds **2** are shown in Figures 1 a and b. For each, one signal was detected for the methyl carbon atoms at $\delta = 28.3$ (**2a**) and 31.4 ppm (**2b**). For comparison, the yttrium precursor complex **1a** revealed two signals at $\delta \approx -10$ and 18.0 ppm which can be assigned to $\text{Y-CH}_3\text{-Al}$ bridging and Al-CH_3 terminal methyl ligands (Figure 1 c), whereas the half-yttrocene $[\text{Cp}^*\text{Y}(\mu\text{-Me})_2]_3$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$), which is discussed later, exhibits ^{13}C resonances at $\delta = 11.9$, 30.3 , and 118.7 ppm that are attributed to carbon atoms of $\text{CH}_3(\text{Cp}^*)$ substituents, $\text{Y-CH}_3\text{-Y}$ bridging methyl ligands, and the Cp^* ring, respectively (Figure 1 d).^[19] Similar solid-state NMR chemical shifts have been previously reported for the complex $[\text{Cp}_2^*\text{Th}(\text{CH}_3)_2]$ (Cp^* : $\delta = 123.1$ and 12.0 ppm ; $\text{Th-CH}_3(\text{terminal})$: $\delta = 68.4\text{ ppm}$).^[24] These findings clearly indicate the formation of homoleptic complexes **2** (ether donor ligands can be ruled out by the ^{13}C CPMAS NMR spectra) and to the absence of any methyl groups bonded to aluminum centers.^[25,26] Carbon resonances of “ Al-CH_3 ” moieties were previously shown to appear upfield,^[27] and this is also corroborated by the spectrum of precursor compound **1a** (Figure 1 c).

Preliminary investigations into the reaction behavior of $[\text{LnMe}_3]_n$ were performed using the yttrium derivative **2a**



Scheme 1. Synthesis and derivatization of $[\text{LnMe}_3]_n$ (**2**). Detailed reaction conditions are given in the Supporting Information (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane).

under high vacuum, the white powder was identified as polymeric $[\text{YMe}_3]_n$ (**2a**). Optimized conditions for this cleavage reaction comprised the use of freshly sublimed **1a** as well as the less Lewis basic donor diethyl ether as a cleavage reagent, and a low reaction temperature (-35°C).^[21] ^1H NMR experiments in C_6D_6 confirmed $\text{Al}(\text{CH}_3)_3(\text{OEt}_2)$ as the only soluble byproduct of the cleavage reaction ($\delta = -0.42$ (s, 9H, AlCH_3), 0.73 (t, 6H, CH_3), 3.25 ppm (q, 4H, OCH_2)). Note that owing to its relatively low sublimation point (80 °C at 10^{-3} mbar; > 90 % yield), compound **1a** is

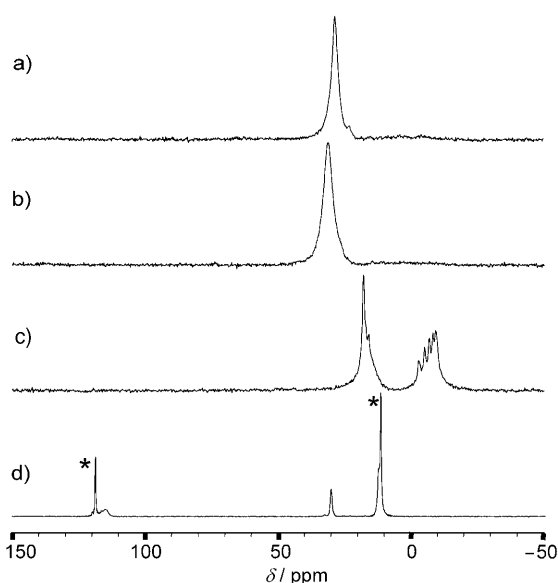


Figure 1. ^{13}C cross-polarization magic-angle-spinning (CPMAS) NMR spectra of a) neat $[\text{YMe}_3]_n$ (**2a**), b) neat $[\text{LuMe}_3]_n$ (**2b**), c) neat $[\text{Y}(\text{AlMe}_4)_3]$ (**1a**), and d) neat $[\text{Cp}^*\text{YMe}_2]_3$. Resonances due to C_5Me_5 (Cp^*) are indicated by asterisks (*).

(Scheme 1). Although the isolation of simple ether adduct complexes, such as $[\text{YMe}_3(\text{thf})_x]$, was not successful, addition of a stoichiometric amount of 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn) to a suspension of $[\text{YMe}_3]_n$ in hexane gave $[\text{CnYMe}_3]$ (**3**) in almost quantitative yield.^[28] The solid-state ^{13}C NMR spectrum of complex **3** (not shown) was similar to its spectrum in solution (C_6D_6) and gave signals at $\delta = 55.2$ (NCH_2), 48.7 (NCH_3), and 20.9 ppm (YCH_3). In the presence of TMEDA as an N-donor solvent, treatment of $[\text{YMe}_3]_n$ with 3 equivalents of MeLi gave Schumann's ate complex $[\text{Li}_3(\text{tmEDA})][\text{Y}(\text{CH}_3)_6]$ (**4**) in moderate yield.^[12] Given the "reversibility" of the formation of $[\text{LnMe}_3]_n$, we anticipated that other strong Lewis acids might redissolve $[\text{LnMe}_3]_n$ as well. Accordingly, AlEt_3 and GaMe_3 form heterobimetallic/heteroleptic $[\text{YAl}_3\text{Me}_3\text{Et}_3]$ (**5**) and heterobimetallic/homoleptic $[\text{YGa}_3\text{Me}_{12}]$ (**6**) in almost quantitative yields (Scheme 1).^[29] Whereas compound **5** was obtained as an oily residue, tetramethylgallate complex **6** yielded colorless crystals from solutions in hexane. Complex **6** shows a very broad ^1H NMR signal in C_6D_6 which is indicative of a decreased fluxional behavior of the bridging and terminal methyl ligands relative to tetramethylaluminate **2a**.

Instantaneous evolution of methane was observed when compound $[\text{YMe}_3]_n$ was treated with Brønsted acidic substrates such as $\text{HN}(\text{SiMe}_3)_2$, HOCHtBu_2 , and HC_5Me_5 (HCp^*) in hexane. The reactions of 3 equivalents of either the silylamine or the alcohol with **2a** gave the homoleptic complexes $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and $[\text{Y}(\text{OCHtBu}_2)_3]$, respectively, in high yields (see Supporting Information).^[30,31] Owing to ligand scrambling, half-yttrocene complex $[\text{Cp}^*\text{Y}(\mu\text{-Me})_2]_3$ did not form selectively upon addition of 1 equivalent of HCp^* to compound **2a**, however, its presence could be identified by means of ^1H NMR spectroscopy.^[19] A $\text{Me} \rightarrow \text{Cl}$ transformation with formation of YCl_3 occurred upon treat-

ment of compound **2** with AlMe_2Cl and documents the comparatively higher halophilicity of the rare-earth elements. Use of AlEt_2Cl as a halogenating reagent afforded the mixed alkylaluminum AlMeEt_2 (**7**) as a coproduct.

In conclusion, we have shown that homoleptic rare-earth-metal-methyl complexes can be obtained through donor-induced tetraalkylaluminate cleavage of $[\text{Ln}(\mu\text{-Me})_2\text{AlMe}_2]_3$ ($\text{Ln} = \text{Y}, \text{Lu}$). Compounds $[\text{LnMe}_3]_n$ are highly condensed materials. Notably, those derived from the smaller rare-earth-metal cations are stable at ambient temperature and accessible to a variety of ligand-exchange and addition reactions. Current investigations of $[\text{LnMe}_3]_n$ compounds are focused on 1) the accessibility of derivatives of the large rare-earth-metal cations, 2) the feasibility of controlled alkyl-elimination reactions, and 3) their potentials as catalysts.

Experimental Section

2a: In a glovebox, a solution of diethyl ether (3 equiv; 222 mg, 3.00 mmol) in hexane (5 mL) at -35°C was added under vigorous stirring to a solution of $\text{Y}(\text{AlMe}_4)_3$ (**1a**; 350 mg, 1.00 mmol) in cold (-35°C) hexane (10 mL). Instant formation of a white precipitate occurred. After stirring the reaction mixture for 10 min, the product was separated by centrifugation and washed three times with hexane to completely remove any soluble byproducts. After drying for 6 h under high vacuum, $[\text{YMe}_3]_n$ (**2a**) was obtained as a white powder in quantitative yield (133 mg). IR (Nujol): $\tilde{\nu} = 1191$ (vs), 522 (s), 431 (s), 361 (s), 320 cm^{-1} (w); far-IR (polyethylene): $\tilde{\nu} = 186$ cm^{-1} (w); ^1H MAS NMR (300.13 MHz, 25°C): $\delta = 1.0, 0.1, -0.3$ ppm; ^{13}C MAS NMR (75.46 MHz, 25°C): $\delta = 28.3$ ppm; elemental analysis (%): calcd for $\text{C}_3\text{H}_5\text{Y}$ (134.010 g mol^{-1}): C 26.89, H 6.77; found: C 26.88, H 6.51.

Typical procedure for addition reactions, as shown for the synthesis of **6**: In a glovebox, a solution of GaMe_3 (3 equiv; 128 mg, 1.12 mmol) in hexane (5 mL) cooled to -35°C was added under vigorous stirring to a suspension of $[\text{YMe}_3]_n$ (**2a**, 50 mg, 0.37 mmol) in hexane (5 mL) also cooled to -35°C . The reaction mixture became clear after 15 min stirring. After a further 15 min, the reaction mixture was filtered, and the filtrate was retained. Evaporation of the solvent in vacuo yielded compound **6** as a white crystalline product (169 mg, 95%). IR (Nujol): $\tilde{\nu} = 1302$ (w), 1202 (s), 967 (w), 571 (s), 530 (s), 416 cm^{-1} (m); ^1H NMR (400 MHz, C_6D_6 , 25°C): $\delta = -0.10$ ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25°C): $\delta = 4.0$ ppm (v br); elemental analysis (%): calcd for $\text{C}_{12}\text{H}_{36}\text{Ga}_3\text{Y}$ (478.492 g mol^{-1}): C 30.12, H 7.58; found: C 31.30, H 7.34, N < 0.2.

Full experimental and physicochemical details for complexes **1–7** are available in the Supporting Information.

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