



Supporting Information

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Trimethylttrium and Trimethyllutetium

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Experimental Details

General Procedures. All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MBraun MB150B-G-II; <1 ppm O₂, <1 ppm H₂O). Hexane, THF, and diethylether were purified by using Grubbs columns (MBraun SPS, solvent purification system). C₆D₆ was obtained from Deutero GmbH, degassed, dried over Na/K alloy for 24 h, and filtered. Hexamethyldisilazane, TMEDA, and 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn) were purchased from Aldrich. Pentamethylcyclopentadiene (HCp*) and Di-*tert*butylmethanol were synthesized according to the literature (ref. A, 28). Trimethylaluminum (Strem), AlMe₂Cl (Aldrich), AlEt₃ (Aldrich), AlEt₂Cl (Aldrich), and AlMe₃ (Strem), were used as received. MeLi (Acros) was received as 1.6 M solution in diethylether, dried *in vacuo*, and stored in a glovebox. Homoleptic Ln(AlMe₄) (Ln = Lu, Y) were synthesized according to the literature (ref. 14). ¹H and ¹³C NMR data were obtained in C₆D₆ solution at 25 °C from a *FT-JEOL-JNM-GX-400* (¹H: 399.80 MHz; ¹³C: 100.51 MHz) and a *FT-JEOL-JNM-GX-270* (¹H: 270 MHz; ¹³C: 67.5 MHz) spectrometer. ¹H and ¹³C shifts are referenced to internal solvent resonances and reported relative to TMS. ¹H and ¹³C MAS NMR spectra were obtained at ambient temperature on a Bruker AV300 instrument in a magnetic field of 7.04 T (the resonance frequencies were 300.13 and 75.46 MHz), using 4 mm standard MAS probes. ¹³C NMR spectra were recorded using cross polarization and proton decoupling. ¹H and ¹³C NMR spectra were referenced to adamantane (¹H: 2.00 ppm; ¹³C: 29.46 ppm to adamantane). The following conditions were used in the measurements: ¹H, pulse repetition 2.0 s, spinning speed 8 kHz; ¹³C, pulse repetition 5.0 s, spinning speed 8 kHz. IR spectra were recorded on a Perkin Elmer FTIR spectrometer 1760X or a Jasco FT/IR – 460 Plus spectrometer using Nujol mulls sandwiched between CsI plates. Elemental analyses were performed in the microanalytical laboratory of the institute.

Tris(tetramethylaluminate)lutetium (1b). In a glovebox, $\text{Lu}(\text{NMe}_2)_3(\text{LiCl})_3$ (3.21 g, 9.21 mmol) was suspended in hexane. 6 Eq of AlMe_3 (3.98 g, 55.25 mmol) were dissolved in hexane and added under vigorous stirring. After stirring the reaction mixture for 24 h, LiCl was separated by centrifugation and the solvent removed *in vacuo*. Further purification was achieved by crystallization from hexane at $-35\text{ }^\circ\text{C}$ and subsequent sublimation at $90\text{ }^\circ\text{C}$ and 3.5×10^{-3} mbar, yielding 602 mg (15%) of the white crystalline product. IR (Nujol): $\nu = 1304$ w, 1222 vs, 1200 vs, 1103 w, 1034 m, 890 m, 696 vs, 572 vs, 549 vs, 453 s cm^{-1} . ^1H NMR (400 MHz, C_6D_6 , $25\text{ }^\circ\text{C}$): $\delta = -0.08$ ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , $25\text{ }^\circ\text{C}$): $\delta = 3.72$ (vbr) ppm. Elemental analysis calcd. for $\text{C}_{12}\text{H}_{36}\text{Al}_3\text{Lu}$ (436.333 g/mol): C 33.03, H 8.32; found: C 32.85, H 8.11, N < 0.1.

Trimethylttrium(III) (2a). In a glovebox, 3eq of cold diethylether (222 mg, 3.00 mmol) were diluted with 5 ml of cold hexane ($-35\text{ }^\circ\text{C}$) and added under vigorous stirring to $\text{Y}(\text{AlMe}_4)_3$ (**1**) (350 mg, 1.00 mmol) dissolved in 10 ml of cold hexane. Instant formation of a white precipitate was observed. After stirring the reaction mixture for 10 min, the product was separated by centrifugation and washed three times with hexane for complete removal of any soluble by-products. After drying for 6 h in high vacuum, the $[\text{YMe}_3]_n$ (**2a**) was obtained as a white powder in quantitative yield (133 mg) which is also insoluble in benzene and toluene. IR (Nujol): $\nu = 1191$ vs, 522 s, 431 s, 361 s, 320 w cm^{-1} . Far IR (polyethylene): 186 w cm^{-1} . ^1H MAS NMR (300.13 MHz, $25\text{ }^\circ\text{C}$): $\delta = 1.0, 0.1, -0.3$ ppm. ^{13}C MAS NMR (75.46 MHz, $25\text{ }^\circ\text{C}$): $\delta = 28.3$ ppm. Elemental analysis calcd. for $\text{C}_3\text{H}_9\text{Y}$ (134.010 g/mol): C 26.89, H 6.77; found: C 26.88, H 6.51. Following the procedure described above, a sample of $\text{Y}(\text{AlMe}_4)_3$ (350 mg, 1.00 mmol), which was not recrystallized twice and not put under high vacuum for several hours, and THF (216 mg, 3.00 mmol) also

quantitatively yielded **2a** (133 mg, 99 %) as a white powder. Elemental analysis calcd. C_3H_9Y (134.010 g/mol): C 26.89, H 6.77; found: C 28.37, H 7.30, N 0.1.

Trimethyllutetium(III) (2b). In a glovebox, $Lu(AlMe_4)_3$ (300 mg, 0.69 mmol) was dissolved in 10 mL of cold hexane (-35 °C). Diethylether (153 mg, 2.07 mmol) was dissolved in 5 mL of cold hexane (-35 °C) and added to the aluminate solution under vigorous stirring. The mixture immediately formed a white precipitate. Centrifugation and several washings of the precipitate with hexane yielded 150 mg (99%) of $[LuMe_3]_n$ (**2b**) as a white powder. IR (Nujol): 1304 w, 1202 vs, 1103 w, 1035 m, 889 m, 693 vs, 541 s, 440 s, 425 s cm^{-1} . 1H MAS NMR (300.13 MHz, 25 °C): $\delta = 1.0, 0.2$ ppm. ^{13}C MAS NMR (75.46 MHz, 25 °C): $\delta = 31.4$ ppm. Elemental analysis calcd. for C_3H_9Lu (220.071 g/mol): C 16.37, H 4.12; found: C 16.19, H 3.94.

Reaction of 2a with trimethylaluminum: formation of $Y(AlMe_4)_3$ (1a). In a glovebox, to a suspension of $[YMe_3]_n$ (50 mg, 0.37 mmol) in 5 mL of cold (-35 °C) hexane were added under vigorous stirring 3 eq of trimethylaluminum (81 mg, 1.12 mmol) dissolved in 5 mL of cold (-35 °C) hexane. After less than 1 min the reaction mixture cleared up and after 10 min stirring at ambient temperature a clear solution was obtained. Evaporation of the solvent in *vacuo* yielded $Y(AlMe_4)_3$ (**1a**, 131 mg) as colorless crystals in quantitative yield. Compound **1a** was identified by 1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Reaction of 2 with Cn: formation of $CnYMe_3$ (3). In a glovebox, to a suspension of $[YMe_3]_n$ (50 mg, 0.37 mmol) in 5 mL of cold (-35 °C) hexane was added under vigorous stirring 1 eq of Cn (63 mg, 0.37mmol) dissolved in 5 mL of cold (-35 °C) hexane. After warming up to ambient temperature and stirring for 30 min the reaction mixture did not clear up, however, the suspension became cloudier. The solvent was removed in *vacuo*

which quantitatively gave C_nYMe_3 (113 mg) as a white solid. IR (Nujol): 1300 s, 1209 w, 1153 m, 1080 s, 1066 s, 1009 vs, 985 m, 890 w, 771 m, 742 m cm^{-1} . 1H NMR (400 MHz, C_6D_6 , 25 °C): δ = 2.38 (s, 9H, NCH_3), 2.26 (m, 6H, NCH_2), 1.72 (m, 6H, NCH_2), -0.22 (d, 9H, YCH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6 , 25 °C): δ = 54.2 (NCH_2), 46.9 (NCH_3), 21.2 (YCH_3) ppm. ^{13}C MAS NMR (75.46 MHz, 25 °C): δ = 55.2 (NCH_2), 48.7 (NCH_3), 20.9 ppm (YCH_3). Elemental analysis calcd. for $C_{12}H_{30}N_3Y$ (305.295 g/mol): C 47.21, H 9.90, N 13.76; found: C 48.59, H 9.87, N 13.34.

Reaction of 2a with MeLi: formation of tris[*N,N,N',N'*-tetramethylethylenediamine]lithium]-hexamethylttrate [$Li(TMEDA)_2$] $[YMe_6]$ (4). In a glovebox, $[YMe_3]_n$ (50 mg, 0.37 mmol) and 3 eq MeLi (24.4 mg, 1.11 mmol) were cooled to -35 °C and suspended in cold (-35 °C) TMEDA (4 mL). After stirring for 2 h, the reaction mixture cleared up. After stirring for additional 2 h, the reaction mixture was filtered. Evaporation of the solvent *in vacuo* yielded 133 mg of **4** (0.24 mmol, 66 %) as a white crystalline product. IR (Nujol): 1292 s, 1254 w, 1179 w, 1158 m, 1129 m, 1118 m, 1065 m, 1038 m, 1020 m, 948 s, 790 m, 771 w, 585 s, 550-380 br,s cm^{-1} . 1H NMR (270 MHz, C_6D_6 , 25 °C): δ = 2.16 (s, 36H, NCH_3), 1.99 (m, 12H, NCH_2), -0.56 (d, 18H, YCH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6 , 25 °C): δ = 57.4 (NCH_2), 46.2 (NCH_3), 6.5 br (YCH_3) ppm. Elemental analysis calcd. for $C_{24}H_{66}Li_3N_6Y$ (548.556 g/mol): C 52.55, H 12.03, N 15.32; found: C 52.13, H 12.28, N 15.07.

Reaction of 2 with triethylaluminum: $Y(AlMeEt_3)_3$ (5). In a glovebox, $[YMe_3]_n$ (50 mg, 0.37 mmol) was suspended in 5 mL of hexane. 3 Eq of triethylaluminum (128 mg, 1.12 mmol) were dissolved in 5 mL of hexane. After cooling both educts to -35 °C, the triethylaluminum solution was added under vigorous stirring to the $[YMe_3]_n$ suspension. After several min the reaction mixture cleared up and after 30 min stirring at ambient

temperature, a clear solution formed. Evaporation of the solvent in *vacuo* yielded $\text{Y}(\text{AlMeEt}_3)_3$ (**5**, 172 mg, 97 %) as a light yellow oil. Note that the triethylaluminum employed has a purity of ca. 93% only. IR (Nujol): 1408 vs, 1303 w, 1220 vs, 1194 s, 1067 w, 985 vs, 955 vs, 918 m, 870 w, 686 vs (br), 548 vs, 468 cm^{-1} vs. ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 1.26$ (t, 9H, CH_2CH_3), 0.13 (m br, 6H, CH_2CH_3), -0.02 (d br, 3H, YCH_3 , AlCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 11.8, 11.2, 10.3, 10.0, 8.9$ ppm.

Tris(tetramethylgallate)yttrium(III) (6). In a glovebox, $[\text{YMe}_3]_n$ (50 mg, 0.37 mmol) was suspended in 5 mL of hexane and cooled to -35 °C. 3 Eq of GaMe_3 (128 mg, 1.12 mmol) were dissolved in 5 mL of hexane, cooled to -35 °C, and added under rigorous stirring. After stirring for 15 min, the reaction mixture cleared up. After stirring for another 15 min, the mixture was filtered. Evaporation of the solvent in *vacuo* yielded 169 mg of compound **6** (0.37 mmol, 95%) as a white crystalline product. IR (Nujol): 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): $\delta = 4.0$ (vbr) ppm. Elemental analysis calcd. for $\text{C}_{12}\text{H}_{36}\text{Ga}_3\text{Y}$ (478.492 g/mol): C 30.12, H 7.58; found: C 31.30, H 7.34, N < 0.2.

Reaction of 2 with hexamethyldisilazane: formation of $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (7). In a glovebox, to a suspension of $[\text{YMe}_3]_n$ (50 mg, 0.37 mmol) in cold (-35 °C) hexane were added 3 eq of hexamethyldisilazane (181 mg, 1.12 mmol) dissolved in cold (-35 °C) hexane. Instant gas formation occurred. After stirring for 15 min at ambient temperature the solvent was removed in *vacuo* which gave $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (211 mg, >99%) as a white solid. The product and its purity were identified by NMR spectroscopy. ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 0.29$ (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 4.3$ ppm.

Reaction of 2 with di(*tert*-butyl)methanol: formation of $[Y(OCHtBu)_3]_2$ (8**).** In a glovebox, to a suspension of $[YMe_3]_n$ (50 mg, 0.37 mmol) was suspended in cold (-35 °C) hexane were added 3 eq of bis(*tert*-butyl)methanol (161 mg, 1.12 mmol) dissolved in cold (-35 °C) hexane. Instant gas formation was observed and the reaction mixture cleared up within less than 5 min. The solvent was removed in *vacuo* yielded $[Y(OC_9H_{19})_3]_2$ (**8**, 190 mg, >99%) as a white crystalline solid. Upon crystallization from hexane colorless crystals were obtained. 1H NMR (400 MHz, C_6D_6 , 25 °C): δ = 3.40 (s, 3H, OCH), 1.21 (s, 54H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6 , 25 °C): δ = 91.6 (OC), 38.1 (CC_4), 30.2 (CH_3) ppm. IR (Nujol): 1101 s, 1080 s, 1046 w, 1015 w, 982 w, 953 w, 766 w, 659 vs, 612 w, 555 w, 519 w cm^{-1} . Elemental analysis calcd. $C_{27}H_{57}O_3Y$ (518.653 g/mol): C 62.53, H 11.08; found: C 61.78, H 11.47.

Mono(1,2,3,4,5-pentamethylcyclopentadienyl)bis(methyl)yttrium(III) (9**).** In a glovebox, $Cp^*Y(AlMe_4)_2$ (199 mg, 0.50 mmol) was dissolved in hexane. Tetrahydrofuran (72 mg, 1.00 mmol) was dissolved in hexane and added under rigorous stirring to the aluminate solution. Instantly, the formation of a white precipitate was observed. After stirring the reaction mixture for 5 min, the product had completely precipitated and was separated by centrifugation and washed 3 times with hexane. Drying *in vacuo* produced analytically pure complexes **9** as white powder in almost quantitative yield. 1H NMR (400 MHz, C_6D_6 , 25 °C): δ = 2.00 (s, 15H, Cp-Me); -0.41 (q, 6H, YMe) ppm. Elemental Analysis: cal. $C_{12}H_{21}Y$ (484.440 g/mol): C 56.70, H 8.33; found: C 57.03, H 8.45.

Reaction of 2 with dimethylaluminumchloride: formation of $AlMe_3$. In a glovebox, to a suspension of $[YMe_3]_n$ (25 mg, 0.19 mmol) in cold (-35 °C) C_6D_6 were added under vigorous stirring 3 eq of dimethylaluminumchloride (52 mg, 0.56 mmol) dissolved in cold (-35 °C) C_6D_6 . Instant color change of the insoluble parts from light yellow to white was

observed. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured without further purification and showed AlMe_3 as the only product. Attention: AlMe_2Cl contained small amounts of hexane. YCl_3 was not investigated by elemental analysis.

Reaction of 2 with diethylaluminumchloride: formation of AlEt_2Me (10). In a glovebox, to a suspension of $[\text{YMe}_3]_n$ (25 mg, 0.19 mmol) in 5 mL of cold ($-35\text{ }^\circ\text{C}$) hexane were added under vigorous stirring 3 eq of diethylaluminumchloride (67 mg, 0.56 mmol) dissolved in 5 mL of cold ($-35\text{ }^\circ\text{C}$) hexane. Instant color change of the insoluble parts from light yellow to white was observed. After 5 min YCl_3 (attention: not investigated by elemental analysis) was separated by filtration. The filtrate was evaporated in *vacuo* which gave AlMeEt_2 (10) as a light yellow oil (54 mg, 96%). ^1H NMR (400 MHz, C_6D_6 , $25\text{ }^\circ\text{C}$): $\delta = 1.09$ (t, 6H, CCH_3), 0.16 (q, 4H, AlCH_2), -0.11 (s, 3H, AlCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , $25\text{ }^\circ\text{C}$): $\delta = 8.5$ (CCH_3), 0.9 (AlCH_2), -9.5 (AlCH_3) ppm.

Additional references.

[A] HCp*: Fendrick, Carol M.; Schertz, Larry D.; Mintz, Eric A.; Marks, Tobin J.; Bitterwolf, T. E.; Horine, P. A.; Hubler, T. L.; Sheldon, J. A.; Belin, D. D., *Inorg. Synth.* **1992**, 29, 193.