Supplementary Material

Amido-Stabilized Rare-Earth Metal Mixed Methyl Methylidene Complexes†

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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 MBLab; <1 ppm O₂, <1 ppm H₂O). Hexane, toluene, and tetrahydrofuran were purified by using Grubbs columns (MBraun SPS, solvent purification system) and stored in a glovebox. Benzene-\(\text{d}_6\) and toluene-\(\text{d}_8\) were obtained from Aldrich, degassed, dried over Na for 24 h, and filtered. Tetrahydrofuran-\(\text{d}_8\) was obtained from Aldrich, degassed, dried over CaH₂ for four days and vacuum transferred. 9-Fluorenone and benzophenone were obtained from Fluka and sublimed prior to use. Cyclohexanone was obtained from Acros and vacuum transferred prior to use.

Homoleptic Ln(AlMe₄)₃ (1) (Ln = Y, Ho) and (LnMe₃)₉ (3) (Ln = Y and Lu) were prepared according to literature methods.¹³,¹⁵ HNSiMe₃ArPr and KNSiMe₃ArPr were synthesized by a modification of the published procedure.²⁰ The NMR spectra of air and moisture sensitive compounds were recorded by using J. Young valve NMR tubes at 25 °C on a Bruker-BIOSPIN-AV500 (5 mm BBO, \(^1\)H: 500.13 Hz; \(^1\)C: 125.77 MHz), a Bruker-AVANCE-DMX400 (5 mm BB, \(^1\)H: 400.13 MHz; \(^1\)C: 100.62 MHz), a Bruker-Avance II 400 (\(^1\)H: 400.13 MHz; \(^1\)C: 100.61 MHz) and a Bruker Avance II 500 (\(^1\)H: 500.13 MHz; \(^1\)C: 125.76 MHz). \(^1\)H and \(^1\)C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. Coupling constants are given in Hertz. IR spectra were recorded on a NICOLET Impact 410 FTIR spectrometer and a NICOLET 6700 FTIR spectrometer as Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an Elementar Vario EL III and an Elementar Vario Micro Cube.
**Y(AlMe)₂(NSiMe₃Ar)Pr** (2)

In a glovebox a solution of Y(AlMe)₃ (1a) (123.6 mg, 0.35 mmol) in hexane (3 ml) was added to a vigorously stirred suspension of KNSiMe₃ArPr (100.6 mg, 0.35 mmol) in hexane (2 ml) at ambient temperature. The reaction mixture was stirred for 2 h at ambient temperature and the hexane solution then separated by centrifugation, decanted and filtrated. Compound 2 was obtained by crystallization from a concentrated hexane solution at −35 °C as colorless crystals (130.5 mg, 0.26 mmol, 74%) (Found: C, 54.02; H, 10.25; N, 2.67. Calc. for C₂₃H₅₀NAl₂SiY: C, 54.00; H, 9.85; N 2.74 %); ν (nujol)/cm⁻¹ = 1309m, 1248s, 1227m, 1187s, 1107w, 1037w, 908s, 875m, 836s, 782m, 569m, 555m; δ (400.13 MHz, benzene-δ) 7.01 (3H, m, Haryl), 3.33 (2H, sept, JHH = 6.8 Hz, CHMe₂), 1.16 (6H, d, JHH = 6.8 Hz, CHMe₂), 1.01 (6H, d, JHH = 6.8 Hz, CHMe₂), 0.24 (9H, s, SiMe₃), −0.24 (24H, d, JYH = 2.5 Hz, AlMe₄); δ (100.61 MHz, benzene-δ) 148.6 (Cipso, C₆H₃Pr₂), 138.7 (Co, C₆H₃Pr₂), 126.2 (Cp, C₆H₃Pr₂), 126.0 (Cm, C₆H₃Pr₂), 28.3 (CHMe₂), 26.5, 23.5 (CHMe₂), 3.7 (SiMe₃), 1.4 (AlMe₄).

**(HoMe₃)n** (3b)

In a glovebox, Ho(AlMe)₃ (1b) (142.0 mg, 0.33 mmol) was dissolved in 10 mL of hexane. Diethylether (2 mL) was added to the aluminate solution under vigorous stirring. The mixture immediately formed a light pink precipitate. Centrifugation and several washings of the precipitate with hexane yielded (HoMe₃)n (3b) as light pink powdery solid (68.6 mg, 0.33 mmol, 99%) (Found: C, 17.51; H, 4.49. Calc. for C₃H₉Ho: C, 17.16; H, 4.32 %); ν (nujol)/cm⁻¹ = 1302m, 1192s, 1100w, 1023m, 885w, 689s, 537s, 435m, 422m.

Due to significant paramagnetic shifts and broadening effects, the ¹H and ¹³C NMR spectra of 3b are not informative.
(\text{NSiMe}_3\text{Ar}^{\text{Pr}})_3\text{Y}_3(\mu_2-\text{Me})_3(\mu_3-\text{Me})(\mu_3-\text{CH}_2)(\text{thf})_3 (\text{4a})

Route 1: To a solution of \(\text{Y(AlMe}_4)_2(\text{NSiMe}_3\text{Ar}^{\text{Pr}})\) (\(2\)) (30.2 mg, 0.06 mmol) in hexane (2 ml) two drops of thf were added. The reaction mixture was shaken and left standing for 30 min at ambient temperature. The product can be crystallized at ambient temperature or precipitated as white solid material from the colorless mother liquor at \(-35\) °C (18.8 mg, 0.01 mmol, 72%) (Found: C, 57.03; H, 8.76; N, 3.25. Calc. for \(\text{C}_62\text{H}_{116}\text{N}_3\text{O}_3\text{Si}_3\text{Y}_3\): C, 57.17; H, 8.98; N 3.23 %).

Route 2: In a glovebox, a solution of \(\text{HNSiMe}_3\text{Ar}^{\text{Pr}}\) (149.7 mg, 0.60 mmol) in hexane (1 ml) was added to a suspension of \((\text{YMe}_3)_n\) (\(3a\)) (80.4 mg, 0.60 mmol) in hexane (2 ml) at ambient temperature under vigorous stirring. To the resulting orange suspension thf (1 ml) was added slowly. After 10 min the mixture cleared and the reaction mixture was stirred for an additional 1 h at ambient temperature. The orange solution was filtered and 4a crystallized from a thf/hexane mixture at \(-35\) °C. Alternatively, all volatiles can be removed \textit{in vacuo} to yield 4a as off-white powder, which was washed three times with small amounts of hexane and dried \textit{in vacuo} (powder yield: 211.0 mg, 0.16 mmol, 80%, crystalline yield: 75.2 mg, 0.06 mmol, 29%) (Found: C, 57.47; H, 9.01; N, 3.00. Calc. for \(\text{C}_62\text{H}_{116}\text{N}_3\text{O}_3\text{Si}_3\text{Y}_3\): C, 57.17; H, 8.98; N 3.23 %); \(\nu\) (nujol)/cm\(^{-1}\) = 1463s, 1379s, 1311m, 1263m, 1247m, 1237m, 1189w, 1153w, 1105w, 1042m, 1021m, 968m, 932m, 905s, 879w, 842s, 779m, 721s, 668w, 626w, 568w, 526w, 442w; \(\delta\) (500.13 MHz, benzene-\(d_6\)) 7.12-6.93 (9H, m, \(H_{aryl}\)), 4.02 (6H, sept, \(^3J_{HH} = 6.8\) Hz, CHMe2), 3.32 (s, thf), 2.32 (2H, ddd, \(^2J_{YH} = 4.0\) Hz, \(\mu_3\)-CH2), 1.39 (18H, d, \(^3J_{HH} = 6.8\) Hz, CHMe2), 1.34 (18H, d, \(^3J_{HH} = 6.8\) Hz, CHMe2), 1.19 (s, thf), 0.69 (3H, m, \(\mu_3\)-Me), 0.54 (27H, s, SiMe3), 0.12 (9H, s, \(\mu_2\)-Me); \(\delta\) (500.13 MHz, toluene-\(d_8\)) 7.10-6.93 (9H, m, \(H_{aryl}\)), 3.99 (6H, sept, \(^3J_{HH} = 6.8\) Hz, CHMe2), 3.26 (s, 12H, thf), 2.31 (2H, ddd, \(^2J_{YH} = 4.1\) Hz, CH2), 1.39 (18H, d, \(^3J_{HH} = 6.8\) Hz, CHMe2), 1.33 (18H, d, \(^3J_{HH} = 6.8\) Hz, CHMe2), 1.24 (s, 12H, thf), 0.53 (27H, s, SiMe3), 0.66 (3, \(\mu_3\)-Me), 0.08 (9H, s br, \(\mu_2\)-Me);
δ_H (500.13 MHz, thf-d8) 6.94 (6H, d, ^3J_HH = 8.0 Hz, H_aryl-p), 3.90 (6H, sept, ^3J_HH = 6.8 Hz, C_HMe2), 3.58 (s, thf), 2.32 (2H, ddd, ^2J_YH = 4.0 Hz, CHMe2), 1.73 (s, thf), 1.23 (18H, d, ^3J_HH = 6.8 Hz, CHMe2), 0.30 (3H, s, CHMe2), 0.23 (27H, s, SiMe3), –0.06 (9H, dd, ^2J_YH = 2.5 Hz, CHMe2); δ_C (125.76 MHz, benzene-d6) 149.7 (C_ipso, C6H3iPr2), 145.4 (C_o, C6H3iPr2), 124.0 (C_m, C6H3iPr2), 121.1 (C_p, C6H3iPr2), 100.2 (μ3-CH2), 69.9 (thf), 31.9, 27.6, 26.3, 25.5, 23.8 (CHMe2, CHMe2), 23.0 (thf), 14.3 (Y-Me), 4.8 (SiMe3); δ_Y (24.5 MHz, toluene-d8) 498.0.

(NSiMe3Ar^Pr)_3Ho_3(μ2-Me)_3(μ3-Me)(μ3-CH2)(thf)_3 (4b)

In a glovebox, a solution of HNSiMe3Ar^Pr (44.9 mg, 0.18 mmol) in hexane (2 ml) was added to a suspension of (HoMe3)_n (3b) (37.8 mg, 0.18 mmol) in hexane (2 ml) at ambient temperature under vigorous stirring. To the resulting orange-pink suspension thf (1 ml) was added slowly. After 10 min the mixture cleared and the reaction mixture was stirred for an additional 1 h at ambient temperature. The orange-pink solution was filtered and 4b crystallized from a thf/hexane mixture at –35 °C. Alternatively, all volatiles can be removed in vacuo to yield 4b as a yellowish/orange powder, which was washed three times with small amounts of hexane and dried in vacuo (powder yield: 72 mg, 0.05 mmol, 79%, crystalline yield: 15.1 mg, 0.01 mmol, 17 %) (Found: C, 46.41; H, 7.62; N, 2.58. Calc. for C_{62}H_{116}N_3O_3Si_3Ho_3: C, 46.65; H, 7.64; N 2.75 %); ν (nujol)/cm⁻¹ =1309m, 1241m, 1182m, 1105w, 1042w, 1016w, 901m, 880w, 838s, 775m, 665w.
In a glovebox, a solution of HNSiMe₃ArPr (79.8 mg, 0.32 mmol) in hexane (1 ml) was added to a suspension of (LuMe₃)₃ (3c) (70.4 mg, 0.32 mmol) in hexane (2 ml) at ambient temperature under vigorous stirring. To the resulting orange suspension thf (1 ml) was added slowly. After 10 min the mixture cleared and the reaction mixture was stirred for an additional 1 h at ambient temperature. The orange solution was filtered and 4c crystallized from a thf/hexane mixture at −35 °C. Alternatively, all volatiles can be removed in vacuo to yield 4c as off-white powder, which was washed three times with small amounts of hexane and dried in vacuo (powder yield: 159.9 mg, 0.10 mmol, 95%, crystalline yield: 111.8 mg, 0.07 mmol, 65%) (Found: C, 48.01; H, 7.89; N, 2.76. Calc. for C₆₂H₁₁₆N₃O₃Si₃Lu₃: C, 47.71; H, 7.49; N 2.69 %); ν (nujol)/cm⁻¹ = 1590m, 1460s, 1378s, 1316s, 1248s, 1181m, 1114m, 1047m, 1016m, 922s, 907s, 886m, 840s, 788m, 747m, 726m, 669w, 628w, 519w, 436w; δH (400.13 MHz, benzene-d₆) 7.30-6.89 (9H, m, Haryl), 4.01 (2H, sept, JHH = 6.8 Hz, CHMe₂), 4.00 (2H, sept, JHH = 6.8 Hz, CHMe₂), 3.85 (2H, sept, JHH = 6.8 Hz, CHMe₂), 3.40 (s, thf), 2.33 (2H, s, µ₃-CH₂), 1.40 (6H, d, JHH = 6.8 Hz, CHMe₂), 1.34 (6H, d, JHH = 6.8 Hz, CHMe₂), 1.30 (6H, d, JHH = 6.8 Hz, CHMe₂), 1.25 (6H, d, JHH = 6.8 Hz, CHMe₂), 1.22 (s, thf), 1.20 (6H, d, JHH = 6.8 Hz, CHMe₂), 1.13 (6H, d, JHH = 6.8 Hz, CHMe₂), 0.80 (3H, m, µ₃-Me), 0.51 (9H, s, SiMe₃), 0.47 (18H, s, SiMe₃), 0.10 (6H, s br, µ₂-Me), −0.05 (3H, s br, µ₂-Me); δC (100.61 MHz, benzene-d₆) 150.9, 146.7, 146.4, 146.3, 144.6, 124.5, 123.7, 123.3, 122.4 (C₆H₃Pr₂), 100.2 (µ₃-CH₂), 71.2 (thf), 30.2, 28.4, 27.7, 27.3, 26.2, 26.0, 25.7, 25.6, 25.5, 24.8 (CHMe₂, CHMe₂), 23.8 (thf), 12.4 (Lu-Me), 4.3 (SiMe₃).

Reactivity toward 9-fluorenone, benzophenone and cyclohexanone:

In a glovebox, compounds 4 dissolved in benzene-d₆ were placed in a J. Young valve NMR tube and 1 eq of the carbonylic reagent was added. The NMR tube was shaken several times and the ¹H NMR spectra were recorded after 10 min. The reaction mixtures turned slightly
yellow upon addition of the respective substrate and decolorized immediately. All substrates were converted quantitatively. For the addition of 2-5 equivalents of the carboxyllic reagent, the *J. Young* valve NMR tube was transferred into the glovebox and the same procedure as described for the first equivalent was followed.

**Fig. S1**: Molecular structure of 4c (atomic displacement parameters are set at the 30% level. Isopropyl groups in the 2 and 6 positions of the aryl rings and hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Lu(1)–C(1) 2.383(5), Lu(2)–C(1) 2.310(5), Lu(3)–C(1) 2.310(5), Lu(1)–C(2) 2.751(5), Lu(2)–C(1) 2.310(5), Lu(2)–C(2) 2.736(5), Lu(3)–C(2) 2.723(5), Lu(1)–C(3) 2.517(6), Lu(2)–C(4) 2.512(6), Lu(3)–C(5) 2.539(5), Lu(1)–N(1) 2.233(4), Lu(2)–N(2) 2.241(4), Lu(3)–N(3) 2.255(5), Lu(1)–O(1) 2.420(4), Lu(2)–O(2) 2.414(4), Lu(3)–O(3) 2.391(4); Lu(1)–C(1)–Lu(2) 88.6(2), Lu(1)–C(1)–Lu(3) 88.73(18), Lu(2)–C(1)–Lu(3) 87.8(2), Lu(1)–C(2)–Lu(2) 73.38(12), Lu(1)–C(2)–Lu(3) 73.68(12), Lu(2)–C(2)–Lu(3) 71.87(11), Lu(1)–C(4)–Lu(2) 82.2(2), Lu(2)–C(5)–Lu(3) 78.9(2), Lu(1)–C(3)–Lu(3) 81.7(2), N(1)–Lu(1)–O(1) 101.08(15), N(2)–Lu(2)–O(2) 98.41(16), N(3)–Lu(3)–O(3) 94.19(17).
Fig. S2: Core structure of trinuclear cluster 4c (atomic displacement parameters are set at the 50% level).