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 O_2, <1 ppm H_2O). Hexane, toluene, and tetrahydrofuran were purified by using *Grubbs* columns (MBraun SPS, solvent purification system) and stored in a glovebox. Benzene-d_6 and toluene-d_8 were obtained from *Aldrich*, degassed, dried over Na for 24 h, and filtered. Tetrahydrofuran-d_8 was obtained from *Aldrich*, degassed, dried over CaH_2 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 $Ln(AlMe_4)_3$ (**1**) (Ln = Y, Ho) and $(LnMe_3)_n$ (**3**) (Ln = Y and Lu) were prepared according to literature methods.[13,15] $HNSiMe_3Ar^{iPr}$ and $KNSiMe_3Ar^{iPr}$ 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; ^{13}C: 125.77 MHz), a *Bruker*-AVANCE-DMX400 (5 mm BB, ^{1}H: 400.13 MHz; ^{13}C: 100.62 MHz), a *Bruker*-Avance II 400 (^{1}H: 400.13 MHz; ^{13}C: 100.61 MHz) and a Bruker Avance II 500 (^{1}H: 500.13 MHz; ^{13}C: 125.76 MHz). ^{1}H and ^{13}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*.

$Y(AlMe_4)_2(NSiMe_3Ar^{iPr})$ (2)

In a glovebox a solution of $Y(AlMe_4)_3$ (**1a**) (123.6 mg, 0.35 mmol) in hexane (3 ml) was added to a vigorously stirred suspension of $KNSiMe_3Ar^{iPr}$ (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 $C_{23}H_{50}NAl_2SiY$: C, 54.00; H, 9.85; N 2.74 %); $\tilde{\nu}$ (nujol)/cm^{-1} = 1309m, 1248s, 1227m, 1187s, 1107w, 1037w, 908s, 875m, 836s, 782m, 569m, 555m; δ_H (400.13 MHz, benzene-d_6) 7.01 (3H, m, H_{aryl}), 3.33 (2H, sept, $^3J_{HH}$ = 6.8 Hz, C*H*Me_2), 1.16 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 1.01 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 0.24 (9H, s, Si*Me$_3$*), –0.24 (24H, d, $^2J_{YH}$ = 2.5 Hz, Al*Me$_4$*); δ_C (100.61 MHz, benzene-d_6) 148.6 (C_{ipso}, C_6H_3*i*Pr_2), 138.7 (C_o, C_6H_3*i*Pr_2), 126.2 (C_p, C_6H_3*i*Pr_2), 126.0 (C_m, C_6H_3*i*Pr_2), 28.3 (*C*HMe_2), 26.5, 23.5 (CH*Me$_2$*), 3.7 (Si*Me$_3$*), 1.4 (Al*Me$_4$*).

$(HoMe_3)_n$ (3b)

In a glovebox, $Ho(AlMe_4)_3$ (**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 $(HoMe_3)_n$ (**3b**) as light pink powdery solid (68.6 mg, 0.33 mmol, 99%) (Found: C, 17.51; H, 4.49. Calc. for C_3H_9Ho: C, 17.16; H, 4.32 %); $\tilde{\nu}$ (nujol)/cm^{-1} = 1302m, 1192s, 1100w, 1023m, 885w, 689s, 537s, 435m, 422m.

Due to significant paramagnetic shifts and broadening effects, the ^1H and ^{13}C NMR spectra of **3b** are not informative.

(NSiMe$_3$Ar^{iPr})$_3$Y$_3$(μ_2-Me)$_3$(μ_3-Me)(μ_3-CH$_2$)(thf)$_3$ (4a)

Route 1: To a solution of Y(AlMe$_4$)$_2$(NSiMe$_3$Ar^{iPr}) (**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 $C_{62}H_{116}N_3O_3Si_3Y_3$: C, 57.17; H, 8.98; N 3.23 %).

Route 2: In a glovebox, a solution of HNSiMe$_3$Ar^{iPr} (149.7 mg, 0.60 mmol) in hexane (1 ml) was added to a suspension of (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 *in vacuo* to yield **4a** as off-white powder, which was washed three times with small amounts of hexane and dried *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 $C_{62}H_{116}N_3O_3Si_3Y_3$: C, 57.17; H, 8.98; N 3.23 %); $\tilde{\nu}$ (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; δ_H (500.13 MHz, benzene-d_6) 7.12-6.93 (9H, m, H_{aryl}), 4.02 (6H, sept, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 3.32 (s, thf), 2.32 (2H, ddd, $^2J_{YH}$ = 4.0 Hz, μ_3-CH_2), 1.39 (18H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.34 (18H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.19 (s, thf), 0.69 (3H, m, μ_3-*Me*), 0.54 (27H, s, SiMe_3), 0.12 (9H, s, μ_2-*Me*); δ_H (500.13 MHz, toluene-d_8) 7.10-6.93 (9H, m, H_{aryl}), 3.99 (6H, sept, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 3.26 (s, 12H, thf), 2.31 (2H, ddd, $^2J_{YH}$ = 4.1 Hz, CH_2), 1.39 (18H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.33 (18H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.24 (s, 12H, thf), 0.53 (27H, s, SiMe_3), 0.66 (3, μ_3-*Me*), 0.08 (9H, s br, μ_2-*Me*);

δ_H (500.13 MHz, thf-d_8) 6.94 (6H, d, $^3J_{HH}$ = 8.0 Hz, H_{aryl-m}), 6.72 (3H, t, $^3J_{HH}$ = 8.0 Hz, H_{aryl-p}), 3.90 (6H, sept, $^3J_{HH}$ = 6.8 Hz, CHMe$_2$), 3.58 (s, thf), 2.32 (2H, ddd, $^2J_{YH}$ = 4.0 Hz, μ_3-CH_2), 1.73 (s, thf), 1.23 (18H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.13 (18H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 0.30 (3H, s, μ_3-Me), 0.23 (27H, s, SiMe_3), –0.06 (9H, dd, $^2J_{YH}$ = 2.5 Hz, μ_2-Me); δ_C (125.76 MHz, benzene-d_6) 149.7 (C$_{ipso}$, C_6H_3iPr$_2$), 145.4 (C$_o$, C_6H_3iPr$_2$), 124.0 (C$_m$, C_6H_3iPr$_2$), 121.1 (C$_p$, C_6H_3iPr$_2$), 100.2 (μ_3-CH$_2$), 69.9 (thf), 31.9, 27.6, 26.3, 25.5, 23.8 (CHMe$_2$, CHMe_2), 23.0 (thf), 14.3 (Y-Me), 4.8 (SiMe_3); δ_C (125.76 MHz, thf-d_8) 151.7 (C$_{ipso}$, C_6H_3iPr$_2$), 146.0 (C$_o$, C_6H_3iPr$_2$), 124.2 (C$_m$, C_6H_3iPr$_2$), 121.1 (C$_p$, C_6H_3iPr$_2$), 103.0 (μ_3-CH$_2$), 32.7, 30.8, 28.0, 26.7, 23.7 (CHMe$_2$, CHMe_2), 14.6 (Y-Me), 5.4 (SiMe_3); δ_Y (24.5 MHz, toluene-d_8) 498.0.

(NSiMe$_3$Ar^{iPr})$_3$Ho$_3$(μ_2-Me)$_3$(μ_3-Me)(μ_3-CH$_2$)(thf)$_3$ (4b)

In a glovebox, a solution of HNSiMe$_3$Ar^{iPr} (44.9 mg, 0.18 mmol) in hexane (2 ml) was added to a suspension of (HoMe$_3$)$_n$ (**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 %); $\tilde{\nu}$ (nujol)/cm^{-1} =1309m, 1241m, 1182m, 1105w, 1042w, 1016w, 901m, 880w, 838s, 775m, 665w.

$(NSiMe_3Ar^{iPr})_3Lu_3(\mu_2\text{-}Me)_3(\mu_3\text{-}Me)(\mu_3\text{-}CH_2)(thf)_3$ (4c)

In a glovebox, a solution of $HNSiMe_3Ar^{iPr}$ (79.8 mg, 0.32 mmol) in hexane (1 ml) was added to a suspension of $(LuMe_3)_n$ (**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 $C_{62}H_{116}N_3O_3Si_3Lu_3$: C, 47.71; H, 7.49; N 2.69 %); $\tilde{\nu}$ (nujol)/cm^{-1} = 1590m, 1460s, 1378s, 1316s, 1248s, 1181m, 1114m, 1047m, 1016m, 922s, 907s, 886m, 840s, 788m, 747m, 726m, 669w, 628w, 576w, 519w, 436w; δ_H (400.13 MHz, benzene-d_6) 7.30-6.89 (9H, m, H_{aryl}), 4.01 (2H, sept, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 4.00 (2H, sept, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 3.85 (2H, sept, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 3.40 (s, thf), 2.33 (2H, s, μ_3-CH_2), 1.40 (6H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.34 (6H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.30 (6H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.25 (6H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.22 (s, thf), 1.20 (6H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.13 (6H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 0.80 (3H, m, μ_3-*Me*), 0.51 (9H, s, SiMe_3), 0.47 (18H, s, SiMe_3), 0.10 (6H, s br, μ_2-*Me*), −0.05 (3H, s br, μ_2-*Me*); δ_C (100.61 MHz, benzene-d_6) 150.9, 146.7, 146.4, 146.3, 144.6, 124.5, 123.7, 123.3, 122.4 (C_6H_3iPr$_2$), 100.2 (μ_3-CH$_2$), 71.2 (thf), 30.2, 28.4, 27.7, 27.3, 26.2, 26.0, 25.7, 25.6, 25.5, 24.8 (*C*HMe$_2$, CHMe_2), 23.8 (thf), 12.4 (Lu-*Me*), 4.3 (SiMe_3).

Reactivity toward 9-fluorenone, benzophenone and cyclohexanone:

In a glovebox, compounds **4** dissolved in benzene-d_6 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 ^{1}H 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 carbonylic reagent, the *J. Young* valve NMR tube was transferred into the glovebox and the same procedure as described for the first equivalent was followed.

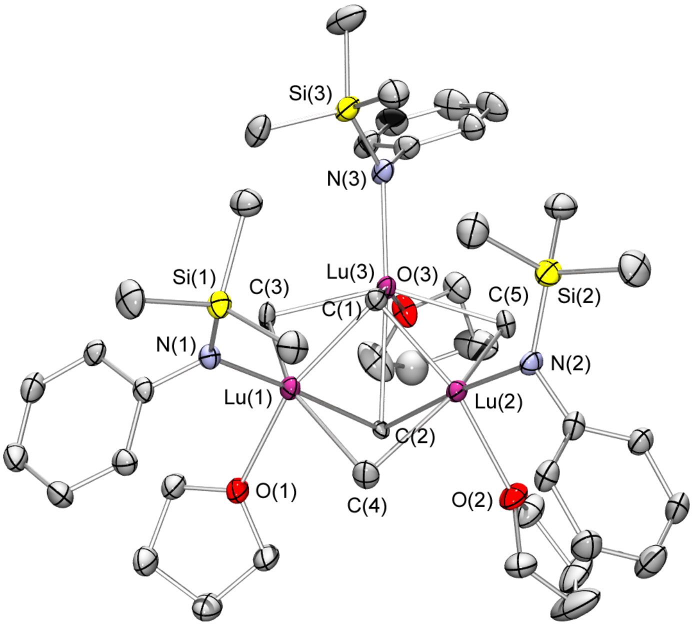

Fig. S1: Molecular structure of **4c** (atomic displacement parameters are set at the 30% level. Isopropyl groups in the 2 and 6 positions of the aryl rings and hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Lu(1)−C(1) 2.383(5), Lu(2)−C(1) 2.310(5), Lu(3)−C(1) 2.310(5), 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).

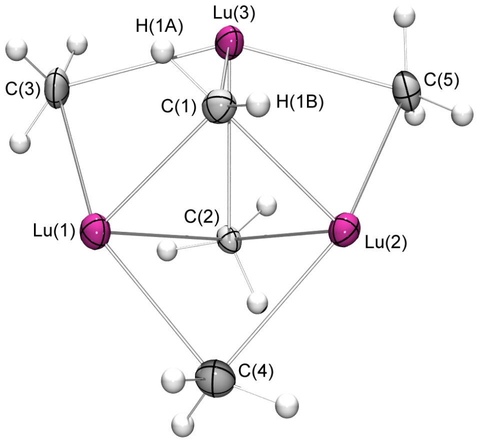

Fig. S2: Core structure of trinuclear cluster **4c** (atomic displacement parameters are set at the 50% level).

20 (a) Y.-W. Chao, P. A. Wexter and D. E. Wigley, *Inorg. Chem.*, 1989, **28**, 9; (b) C. Schädle, C. Meermann, K. W. Törnroos and R. Anwander, *Eur. J. Inorg. Chem.*, 2010, DOI: 10.1002/ejic.201000220.