Supplementary Material

$Ln^{II}Al^{III}_2(alkyl)_8$: donor addition instead of donor-induced cleavage†

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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 (MB Braun MB200B; <0.1 ppm O_2, <0.1 ppm H_2O). Hexane, THF, and toluene were purified by using Grubbs columns (MBraun SPS, solvent purification system). C_6D_6 was obtained from Deutero GmbH, degassed, dried over Na/K alloy for 24 h, and filtered. $AlMe_3$ (*ABCR,* 98% purity), $AlEt_3$ (*Aldrich*, 94% purity), and 1,10-phenanthroline (*Aldrich*) were used as received. $Sm[N(SiMe_3)_2]_2(THF)_2$ (**1a**) was prepared according to published literature procedures by reacting $SmI_2(THF)_2$ with 1.9 eq. $KN(SiMe_3)_2$ in THF and crystallised from hexane [9]. $YbAl_2Et_8$ (**3b**) was synthesized according to [8]. ^1H and ^{13}C NMR data were obtained in C_6D_6 solution at 25 °C from a *BRUKER-AVANCE-DMX400* (^1H: 400.13 MHz; ^{13}C: 100. 62 MHz). ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported in *parts per million* relative to TMS. IR spectra were recorded on a *NICOLET-Impact 410 FTIR* spectrometer as Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an *Elementar Vario EL III.*

Procedure for synthesizing $SmAl_2Me_8$ (2a). In a glovebox, 0.50 mmol (308 mg) of $Sm[N(SiMe_3)_2]_2(THF)_2$ (**1a**) were dissolved in 10 ml of hexane. Upon addition of excess trimethylaluminum (288 mg, 3.99 mmol) diluted with 10 mL of hexane, **2a** precipitated quantitatively from the solution. The reaction mixture was stirred for 2 h at ambient temperature and then centrifuged, leaving a light purple precipitate and a clear colorless solution. The precipitate was washed several times with 3 mL of hexane to yield **2a** as a light purple powder in almost quantitative yield (154 mg, >95%). Compound **2a** is insoluble in aliphatic and aromatic hydrocarbons.

$SmAl_2Me_8$ (2). IR (Nujol, cm^{-1}): 1195 w, 1171 w, 1039 m, 795 w, 778 w, 705 m, 627 w, 602 w, 573 m, 554 m, 512 w, 476 w, 459 w, 424 w. Elemental analysis: calculated C (29.60), H (7.45); found C (30.53), H (7.54).

Procedure for synthesizing $SmAl_2Et_8$ (3a). In a glovebox, 1.00 mmol (615 mg) of $Sm[N(SiMe_3)_2]_2(THF)_2$ (**1a**) were dissolved in 5 ml of hexane. Upon addition of excess triethylaluminum (915 mg, 8.01 mmol) diluted with 5 mL of hexane, no visible reaction occured. The reaction mixture was stirred overnight at ambient temperature and then centrifuged (no precipitate), filtered and crystallized at -35 °C to form black crystals of **3a** in 80% yield (347 mg).

$SmAl_2Et_8$ (3a). ^1H NMR (C_6D_6, 25 °C): δ = -1.4 (s br, 24H, CH_3), - 38.3 (s br, 16H, CH_2). ^{13}C NMR (C_6D_6, 25 °C): -15.1 (CH_3). IR (Nujol, cm^{-1}): 1176 w, 1093 m, 973 m, 944 m, 649 m, 588 m, 498 w, 468 w. Elemental analysis: calculated C (43.99), H (9.23); found C (42.27), H (8.43).

General procedure for synthesizing donor adduct complexes $LnAl_2Et_8(THF)_2$. To a stirred solution of $LnAl_2Et_8$ in 8 ml of hexane were added 2 eq. of THF diluted with 8 mL of hexane (no visible reaction). After 2 hours stirring, half of the solvent was evaporated. The remaining solution was filtered and the product isolated by crystallisation from hexane at -35 °C.

$SmAl_2Et_8(THF)_2$ (4a). According to above procedure **3a** (130 mg, 0.30 mmol) and THF (44 mg, 0.6 mmol) gave black **4a** (131 mg, 0.23 mmol), 75% crystallized yield. ^1H NMR (C_6D_6, 25 °C): δ = 2.75 (s br, 8H, THF-II), 1.9 (s br, 24H, CH_3), -1.38 (s br, 8H, THF-I), -28.0 (s br, 16H, Al-CH_2). ^{13}C NMR (C_6D_6, 25 °C): 20.4 (THF), -5.2 (-$\mathit{C}H_3$). IR (Nujol, cm^{-1}): 1174 w, 1030 m, 980 m, 943 m, 885 w, 868 w, 771 w, 644 m. Elemental analysis: calculated C (49.61), H (9.71); found C (49.23), H (9.51).

$YbAl_2Et_8(THF)_2$ (4b). According to above procedure **3b** (138 mg, 0.30 mmol) and THF (46 mg, 0.64 mmol) gave light yellow **4b** (148 mg, 0.25 mmol), 82% crystallized yield. ^1H NMR (C_6D_6, 25 °C): δ = 3.33 (m, 8H, THF-I), 1.54 (t, $^3J_{H,H}$ = 7.8 Hz, 24H, CH_3), 1.17 (m, 8H, THF-II), 0.20 (q, $^3J_{H,H}$ = 7.8 Hz, 16H, Al-CH_2). ^{13}C NMR (C_6D_6, 25 °C): 70.3 (-$\mathit{C}H_2CH_2O$-), 25.2 (-$\mathit{C}H_2O$-), 12.0 (-$\mathit{C}H_3$), 7.0 (Al-$\mathit{C}H_2$-). IR (Nujol, cm^{-1}): 1154 w, 1020 m, 975 m, 925 w, 863 m, 634 m, 527 w. Elemental analysis: calculated C (47.75), H (9.35); found C (47.43), H (9.24).

General procedure for synthesizing donor adduct complexes $LnAl_2Et_8(Py)_2$. To a stirred solution of $LnAl_2Et_8$ in 8 ml of hexane were added 2 eq. of pyridine (Py) diluted with 8 mL of hexane. For Ln = Yb a colour change from yellow to red was observed. After 2 hours stirring, half of the solvent was evaporated. The remaining solution was filtered and cooled to -35 °C overnight yielding **5a** as oily product and **5b** as red crystals, respectively.

$SmAl_2Et_8(Py)_2$ (5a). According to above procedure **3a** (135 mg, 0.31 mmol) and pyridine (49 mg, 0.62 mmol) gave **5a** (111 mg, 0.19 mmol), black oil, yield 60%. ^1H NMR (C_6D_6, 25 °C): δ = 8.08 (br s, 4H, Py), 6.70 (br, 2H, Py), 6.35 (br, 4H, Py), 1.42 (t, $^3J_{H,H}$ = 7.9, 16H, Al-CH_2), 0.38 (q, $^3J_{H,H}$ = 7.9, Al-CH$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): 147.0, 139.6, 125.0, 10.4 (-*C*H$_3$), 0.5 (Al-*C*H$_2$-).-). IR (Nujol, cm^{-1}): 1610 m, 1215 w, 1185 w, 1156 w, 1073 m, 1054 m, 983 m, 946 m, 759 w, 698 m, 646 m, 629 m. Due to the oily composition of **5a** sufficient microanalytical data could not be obtained.

YbAl$_2$Et$_8$(Py)$_2$ (5b). According to above procedure **3b** (120 mg, 0.26 mmol) and pyridine (42 mg, 0.53 mmol) gave red **5b** (135 mg, 0.22 mmol), 84% crystallized yield. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 8.16 (br s, 4H, Py), 6.77 (br t, 2H, Py), 6.45 (br t, 4H, Py), 1.55 (t, $^3J_{H,H}$ = 7.8 Hz, 24 H, C*H$_2$*CH$_3$), 0.43 (q, $^3J_{H,H}$ = 7.8 Hz, 16H, C*H$_2$*CH$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): 149.0 (Py), 139.2 (Py), 121.9 (Py), 12.2 (-*C*H$_3$), 7.8 (Al-*C*H$_2$-). IR (Nujol, cm^{-1}): 1598 w, 1216 w, 1186 w, 1157 w, 1070 w, 1037 w, 981 m, 952m, 753 m, 698 m, 645 m, 630 m. Elemental analysis: calculated C (50.56), H (8.16); found C (49.65), H (7.90).

General procedure for synthesizing donor adduct complexes LnAl$_2$Et$_8$(phen). To a stirred solution of LnAl$_2$Et$_8$ in 8 ml of hexane was added 1 eq. of phenanthroline (phen) dissolved in 10 mL of toluene. For Ln = Yb a colour change from yellow to dark green was observed. After 2 hours stirring, half of the solvent was evaporated. The remaining solution was filtered and cooled to -35 °C overnight yielding **6a** as oily product and **6b** as dark green crystals, respectively.

SmAl$_2$Et$_8$(phen) (6a). According to above procedure **3a** (130 mg, 0.30 mmol) and phenanthroline (59 mg, 0.30 mmol) gave **6a** (124 mg, 0.20 mmol), dark red oil, yield 67%. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 16.09 (br s, 2H, phen), 5.66 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, phen), 3.41 (br s, 2H, phen), 2.66 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, phen), 1.05 (br s, 24 H, CH$_2$C*H$_3$*), -31.61 (br s, 16 H, C*H$_2$*CH$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): 173.9 (phen), 161.5 (phen), 120.2 (phen), 103.9 (phen), 87.9 (phen), -2.1 (-CH$_3$). IR (Nujol, cm^{-1}): 1520 w, 1155 w, 1082 w, 980 m, 946 m, 842 m, 773 w, 647 m. Elemental analysis: calculated C (54.50), H (7.84), N(4.54); found C (56.94), H (7.67), N (4.46).

YbAl$_2$Et$_8$(phen) (6b). According to above procedure **3b** (138 mg, 0.30 mmol) and phenanthroline (59 mg, 0.30 mmol) gave dark green **6b** (171 mg, 0.27 mmol), 89% crystallized yield. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 8.72 (d, $^3J_{H,H}$ = 4.3 Hz, 2H, phen), 7.24 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, phen), 6.80 (s, $^3J_{H,H}$ = 4.3 Hz, 2H, phen), 6.73 (dd, $^3J_{H,H}$ = 4,3 Hz, $^3J_{H,H}$ = 8.1 Hz, 2H, phen), 1.52 (t, $^3J_{H,H}$ = 7.6 Hz, 24H, CH$_2$CH$_3$),0.46 (q, $^3J_{H,H}$ = 7.6 Hz, 16H, CH$_2$CH$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): 150.1 (phen), 144.1 (phen), 138.9 (phen), 129.7 (phen), 127.1 (phen), 124.5 (phen), 12.0 (CH$_2$*C*H$_3$), 7.2 (*C*H$_2$CH$_3$). IR (Nujol, cm^{-1}): 1517 w, 1146 w, 1098 w, 980 m, 944 m, 841 m, 766 w, 649 m. Elemental analysis: calculated C (52.57), H (7.56), N (4.38); found C (53.17), H (7.52), N (4.45).