ELECTRONIC SUPPORTING INFORMATION

for

C-H Activation (γ-deprotonation) of a Sm(III) bis(trimethylsilyl)amide complex *via* macrocyclic stabilisation of the sodium counter ion

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Synthesis of **3**. Potassium metal (0.19 g, 4.8 mmol) was added to **1**, (1.09 g, 2.00 mmol) in thf (80 mL) and refluxed for 3 hrs. The solution was filtered to remove excess potassium metal and other insoluble impurities. SmI_2 (0.1 M in thf, 20 mL) was added dropwise to the stirred filtrate over 20 mins and stirred for a further 3 hrs. The green solution was filtered and the filtrate concentrated *in vacuo* to *ca.* 40 mL giving a brown solid (1.42 g). To a thf solution (80 mL) of this brown solid (1.00 g), a solution of iodine (0.13 g, 0.50 mmol) in thf (20 mL) was added dropwise with stirring giving a yellow solution. Sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.0 mL) was added to the stirred solution and stirring continued overnight. The solvent was removed *in vacuo* and toluene (60 mL) was added, the solution filtered and concentrated to *ca.* 20 mL giving yellow crystals of **3** (0.64 g, 75%). Anal. Calcd for $C_{42}H_{66}N_3O_2Si_2Sm$: C, 59.24; H, 7.81; N, 4.93. Found: C, 59.30; H, 7.93; N, 5.01%. ^{1}H NMR (C_6D_6, 399.694 MHz, 298 K, ppm): -5.89 (m, 4H, CH_2), -3.14 (s, 18H, $SiCH_3$), -1.65 (t, ^3J = 6.0 Hz, 12H, CH_3), 1.10 (m, 4H, CH_2), 1.77 (m, 4H, CH_2), 2.24 (t, ^3J = 6.8 Hz, 12H, CH_3), 4.48 (s, 4H, =CH), 4.67 (m, 4H, CH_2), 15.14 (s, 4H, =CH). ^{13}C NMR (C_6D_6, 100.512 MHz, 298 K, ppm): 3.0 (Si*C*H$_3$), 5.2 (CH_3), 9.2 (CH_3), 21.3 (CH_2), 26.5 (CH_2), 47.0 (*C*Et$_2$), 102.8 (=CH), 126.8 (=CH), 152.0 (=CR), 152.2 (=CR).

Synthesis of **4**. To a solution of **3** (0.50 g, 0.59 mmol) in thf (30 mL), sodium bis(trimethylsilyl)amide (1.0 M solution in THF, 0.60 mL) was added and the mixture stirred for three hrs at 55 °C. The solvent was removed *in vacuo* and toluene (10 mL) was added. The mixture was heated for 5 minutes and let stand for one week, after which time the red crystalline product precipitated and was collected (0.12 g, 20%). Anal. Calcd for $C_{49}H_{71}N_3O_2NaSi_2Sm.1/2(C_7H_8)$: C, 62.33; H, 7.67; N, 4.15. Found: C, 62.12; H, 7.69; N, 4.17. ^{1}H NMR (thf-d^8, 399.694 MHz, 298 K, ppm): 0.10 (t, ^3J = 7.6 Hz, 6H, CH_3), 0.14 (t, ^3J = 7.6 Hz, 6H, CH_3), 0.20 (s, 9H, $SiMe_3$), 0.31 (t, ^3J = 7.6 Hz, 6H, CH_3), 0.44 (m, 2H, CH_2), 0.55 (t, ^3J = 7.2 Hz, 6H, CH_3), 0.63 (m, 2H, CH_2), 0.93 (m, 4H, CH_2), 1.81 (s, 6H, $Si(CH_3)_2$), 1.82 (m, 2H, CH_2), 1.96 (m, 2H, CH_2), 2.14 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 3.07 (s, 2H, =CH), 3.35 (s, 4H, =CH), 5.56 (s, 2H, $SiCH_2$), 6.69 (s, 2H, =CH), 7.24 (s, 4H, =CH) (toluene was removed *in vacuo* during sample preparation and was not detected by ^{1}H NMR spectroscopy). ^{13}C NMR assignment was not possible due to low solubility and complexity.