Electronic Supplementary Information for Dalton Transactions

Supplementary Information for

β-Diketiminate C-H Activation With Heavier Group 2 Alkyls

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Experimental Details

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox, NMR spectra were recorded either on a Bruker AV-400 spectrometer at 100.6 MHz (^{13}C), Bruker AV-300 at 75.5 MHz (^{13}C), spectrometer or a Bruker AV-250 spectrometer at 62.9 MHz (^{13}C). The spectra were referenced relative to residual solvent resonances. Data quoted was recorded at 298 K. Elemental analyses were performed by Stephen Boyer at SACS, London Metropolitan University. Solvents (benzene, THF, hexane) were dried by passage though a commercial solvent purification system, under nitrogen and stored in ampoules over molecular sieves. C_6D_6 and d_8-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. The β-diketiminate ligand precursor [ArNC(Me)CHC(Me)NHAr], the heavier group 2 dialkyl complexes and [{η^2-CH_2(2-(Me_2N)(C_6H_4)}K] were synthesised according to the literature procedures.[1-3]

Synthesis of 8

Compound **6** (400 mg, 0.79 mmol) and [ArNC(Me)CHC(Me)NHAr] (330 mg, 0.79 mmol) were weighed into a Schlenk tube. Hexane (30 mL) was added and the reaction mixture heated to 60 ^{o}C for 12 days. Following cooling to room temperature, the mixture was filtered to separate a small amount of insoluble material and the solvent volume reduced to ca. 10 mL to induce crystallisation of the product. Storage of this concentrated solution at 5 ^{o}C yielded a crop of colourless crystals of compound

8 (200 mg, 38 %). M.p 138-140 ^{o}C. Calc. for $C_{40}H_{68}CaN_2OSi_2$: C 69.71; H 9.94; N 4.06. Found: C 69.77; H 9.70; N 4.14. ^{1}H NMR (C_6D_6, 300 MHz, 298 K) -1.89 (s, 1H, C*H*), 0.09 (s, 18 H, Si), 1.20 (m, 4H), 1.22 (d, 12H, J = 6.8 Hz), 1.33 (d, 12H, J = 6.3 Hz), 1.66 (s, 6H), 3.00-3.30 (broad m, 4H), 3.50-3.70 (broad m , 4H), 4.78 (m, 1H), 7.14-7.18 (m, 6H); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 298 K) 6.0, 24.6, 25.0, 25.1, 25.4, 28.6, 69.5, 93.5, 124.3, 125.0, 141.4, 146.6, 166.5; ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 25°C): –7.4.

Synthesis of 9

Compound **6** (0.59 g, 1.07 mmol) and [ArNC(Me)CHC(Me)NHAr] (450 mg, 1.07 mmol) were weighed into a Schlenk-tube and hexane (30 mL) was added and the reaction mixture heated to 60 ^{o}C. The Schlenk-tube was sealed and the reaction left to stir at this temperature for 72 hours. Following cooling to room temperature, the solvent volume was reduced to ca. 10 mL to induce crystallisation. Storage at room temperature provided crystals of compound **9** suitable for an X-ray diffraction analysis. (200 mg, 32 %). M.p 179 ^{o}C (dec). Calc. for $C_{66}H_{96}N_4O_2Sr_2$: C 68.77; H 8.41; N 4.86. Found: C 68.59; H 8.39; N 4.79. ^{1}H NMR (D_8-THF, 300 MHz, 298 K) 1.03 – 1.31 (broad and unresolved coincident doublet resonances ^{i}Pr-CH_3), 1.50 (s, 3H, CH_3-dimer), 1.56 (s, 3H, CH_3-dimer), 1.78 (m, THF), 1.97 (dd, 1H, CH_2), 3.10 (m, 1H, ^{i}Pr-C*H*), 3.15 (coincident m, 2H, ^{i}Pr-C*H*), 3.38 (m, 1H, ^{i}Pr-C*H*), 3.68 (m, THF), 3.78 (d, 1H, $^{2}J_{HH}$ = 4.5 Hz, CH_2), 4.05 (d, 1H, $^{4}J_{HH}$ = 2.1 Hz, C*H*-C^{3} dimer), 4.55 (s, 1H, C*H*-C^{3} monomer), 6.78 – 7.10 (m, aryl-*H*). ^{13}C{^{1}H} NMR (D_8-THF, 75 MHz, 298 K) 12.9, 23.6, 23.8, 24.1, 24.4, 24.9, 26.7, 26.9, 27.6, 28.3, 31.1, 46.4, 85.5, 119.4, 121.7, 122.1, 139.7, 140.8, 141.2, 143.1, 149.7, 151.1, 163.1, 173.8.

Synthesis of 10

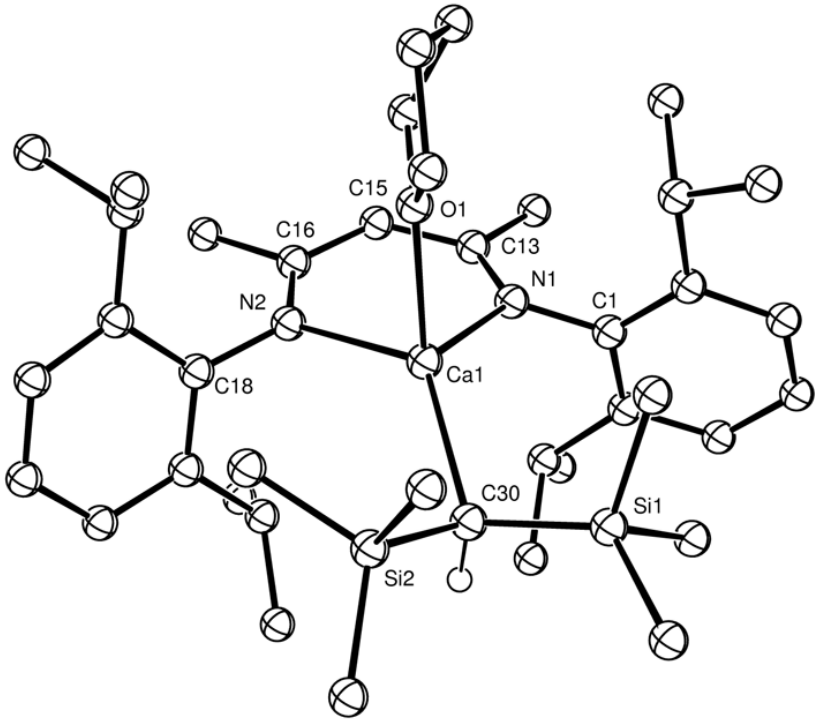
Compound **7** (400 mg, 0.60 mmol) and [ArNC(Me)CHC(Me)NHAr] (250 mg, 0.60 mmol) were weighed into a Schlenk-tube and benzene (20 mL) was added and the reaction mixture allowed to stand undisturbed for 72 hours at room temperature. During this time compound **10** crystallised as large colourless blocks suitable for an X-ray diffraction analysis. (220 mg, 59 %). M.p 190 ^{o}C (dec). Calc. for $C_{66}H_{96}Ba_2N_4O_2$: C 63.31; H 7.74; N 4.48. Found: C 63.38; H 7.68; N 4.51. ^{1}H NMR (D_6-DMSO, 300 MHz, 298 K) 1.01 – 1.24 (br d, 24H, ^{i}Pr-CH_3), 1.79 (m, 4H, THF), 2.42 (br. s, 3H, CH_3), 3.10 (br. m, 4H, ^{i}Pr-CH), 3.52 (br. m, 2H, CH_2), 3.65 (m, 4H, THF), 6.65 (br. m, 2H, *p*-C$_6H_3$), 6.83 (br. m, 4H, *m*-C$_6H_3$). ^{13}C{^{1}H} NMR (D_6-DMSO, 75 MHz, 298 K) 24.3, 23.9, 24.4, 25.5, 27.3, 67.37, 117.9, 118.7, 138.4, 139.3, 152.6.

Synthesis of 11

THF (30 mL) was added at -78 ^{o}C to a mixture of [ArNC(Me)CHC(Me)NHAr] (1.20 g, 2.87 mmol), CaI_2 (0.85 g, 2.87 mmol) and [{η^2-CH_2(2-(Me_2N)(C_6H_4)}K] (1.00 g, 5.74 mmol). The reaction mixture was stirred for 30 minutes, allowed to warm to room temperature and stirred for a further 2 h. The volatiles were removed *in vacuo*, the crude product extracted into hexane (40 mL) and the reaction mixture filtered. Concentrating this solution to *ca*. 15 mL followed by storage at 5 ^{o}C yielded a crop of yellow crystals contaminated by a colourless by-product. Manual separation of the crystals allowed the identification of compound **11** by X-ray diffraction and NMR spectroscopic analysis. (214 mg, 2:1 mixture of products). ^{1}H NMR (C_6D_6, 298 K, 300 MHz) 1.24 (d, 24 H, *J* = 6.5 Hz), 1.01 (m, 4H, THF), 1.55 (s, 2H), 1.72 (s, 6H), 1.95 (s, 6H), 2.94 (m, 4H, THF), 3.21 (hept, 4H, *J* = 6.5 Hz), 4.79 (s, 1H), 6.11 (ddd,

1H, J = 7.9, 6.8, 1.6), 6.52 (d, 1H, *J* = 7.9 Hz), 6.67 (dd, 1H, J = 8.1, 1.6 Hz), 6.75 (dd, 1H, *J* = 8.1, 6.8 Hz) 7.10-7.21 (m, 6H); ^{13}C NMR (C_6D_6, 298 K, 75.5 MHz) 23.1, 24.7, 24.8, 24.9, 28.6, 43.3, 68.4, 94.0, 108.8, 119.1, 123.0, 123.6, 124.4, 126.5, 132.9, 141.6, 147.3, 148.2, 165.4, $ArCH_2M$ not observed.

Figure S1: Ball and stick figure showing connectivity of Compound **8**



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