Supplementary information for:

Heavier Group 2 Element-Catalyzed Hydroamination of Isocyanates

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General Experimental

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either dinitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. NMR spectra were collected on either a Bruker AV-500 spectrometer (^{13}C NMR 125 MHz), a Bruker AV-400 spectrometer at (^{13}C NMR 100 Hz) or a Bruker AV-300 spectrometer (^{13}C NMR 75 MHz). Solvents (toluene, benzene, THF, hexane) were dried by distillation from standard drying reagents 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 distillation under nitrogen and storage over molecular sieves. Compound **1**, the heavier group 2 amides

[M{N(SiMe$_3$)$_2$}$_2$] (M = Ca, **2a**; Sr, **2b**; Ba, **2c**), and compound **3** were prepared by literature procedures.[1-3] Ar = 2,6-di-iso-propylphenyl and Ad = 1-adamantyl.

Crystallographic data for **3** and **5** were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with a low temperature device, using graphite monochromated MoKα radiation (λ= 0.71073 Å). Data were processed using the Nonius Software.[4] Structure solution, followed by full-matrix least squares refinement was performed using the WinGX-1.70 suite of programs throughout.[5]

*Synthesis of [{ArNC(Me)CHC(Me)NAr}Ca{OC(NAd)NPh$_2$}(THF)] (**4**):* To a solution of **3** (0.85 g, 1.22 mmol) in hexane (15 mL), under N_2, was added a solution of 1-adamantylisocyanate (0.22 g, 1.24 mmol) in the same solvent (10 mL). The reaction mixture was stirred for 4 h at room temperature and the solvent volume reduced to *ca* 15 mL. The product may be isolated by hot recrystallisation of this concentrated solution, filtration gave colourless crystals of **4** (0.38 g, 0.43 mmol, 36%). ^{1}H NMR (C_6D_6, 400 MHz, 298K) 1.16-1.20 (m, 6H), 1.19 (d, 12H, *J* = 6.8 Hz), 1.23 (m, 4H, *THF*), 1.34 (d, 12H, *J* = 6.4 Hz), 1.40-1.49 (m, 6H), 1.69-1.72 (m, 3H), 1.72 (s, 6H), 3.25 (broad heptet, 4H, *J* = 6.4 Hz), 3.72 (m, 4H, *THF*), 4.79 (s, 1H), 6.84 (t, 2H, *J* = 7.2 Hz), 6.93 (d, 4H, *J* = 8.0 Hz), 7.06-7.09 (m, 4H), 7.13-7.16 (m, 6H); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 24.5, 24.8, 25.0, 25.3, 28.3, 30.4, 36.8, 44.1, 51.7, 70.4, 93.5, 122.0, 122.5, 124.2, 124.4, 129.4, 141.5, 146.6, 146.8, 165.3, 165.5. Elemental analysis calc. for $C_{56}H_{74}CaN_4O_2$: C, 76.77; H, 8.45; N, 6.40. Found C, 76.77; H, 8.43; N, 6.31. X-ray diffraction data for **4**. $C_{56}H_{74}CaN_4O_2$, M = 875.27, monoclinic, $P2_1/n$, a = 12.3837(2) Å, b = 19.3136(3) Å, c = 21.3459(4) Å, β = 93.5240(10)^o, V = 5095.73(15) Å^3, Z = 4, ρ = 1.141 g cm^{-3}, Temperature 150(2) K, R_1 [I > 2σ(I)] =

0.0532, wR_2 [$I > 2\sigma(I)$] = 0.1118, R_1 [all data] = 0.0935, wR_2 [all data] = 0.1313, measured reflections = 51119, unique reflections = 11481, R_{int} = 0.0843.

*Synthesis of [AdNHC(O)NPh$_2$] (**5**)*: Under an atmosphere of dinitrogen, toluene (10 mL) was added to a solid mixture of adamantylisocyanate (0.53 g, 2.96 mmol), diphenylamine (0.5 g, 2.96 mmol) and [Ca{N(SiMe$_3$)$_2$}$_2$] (53 mg, 0.15 mmol, 5 mol %). The reaction mixture was stirred overnight, the toluene removed *in vacuo* and the crude dissolved in dichloromethane (100 mL). Washing the organic solution with water (3 x 10 mL), drying over magnesium sulfate and removing the solvent under reduced pressure gave a crude colourless product. Recrystallisation from a 1:1 mixture of hexane and diethylether gave **5** as a colourless crystalline solid (0.72 g, 2.07 mmol, 70 %). M.p (hexane:Et$_2$O) 159-160 ^{o}C. ^{1}H NMR (C_6D_6, 400 MHz, 298 K) 1.46-1.54 (m, 6H), 1.88 (m, 3H), 1.96-1.97 (m, 6H), 4.27 (broad s, 1H), 6.86-6.90 (m, 2H), 7.02-7.06 (m, 4H), 7.21-7.23 (m, 4H); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 29.9, 36.6, 42.3, 51.5, 125.5, 127.6, 129.3, 144.3, 154.3; Infrared (DCM film, cm^{-1}) 3335, 3050, 2906, 2984, 1682, 1591, 1506; Elemental analysis calc. for $C_{23}H_{26}N_2O$: C, 79.66; H, 7.50; N, 8.08. Found C, 79.69; H, 7.57; N, 8.03. HRMS calc. for $C_{23}H_{26}N_2NaO$ 369.1937 found 369.1901. X-ray diffraction data for **5**. $C_{23}H_{26}N_2O$, M = 346.46, orthorhombic, P b c a, a = 11.50010(10) Å, b = 16.1708(2) Å, c = 19.6834(2) Å, V = 3660.44(7) Å^3, Z = 8, ρ = 1.257 g cm^{-3}, Temperature 150(2) K, R_1 [$I > 2\sigma(I)$] = 0.0531, wR_2 [$I > 2\sigma(I)$] = 0.1285, R_1 [all data] = 0.0786, wR_2 [all data] = 0.1466, measured reflections = 65006, unique reflections = 5343, R_{int} = 0.0571.

*Synthesis of [ArNHC(O)NPh$_2$] **6***: Under an atmosphere of dinitrogen, toluene (10 mL) was added to a solid mixture of 2,6-di-iso-propylphenylisocyanate (0.15 g, 0.73

mmol), diphenylamine (0.137 g, 0.81 mmol) and [Sr{N(SiMe$_3$)$_2$}$_2$] (16 mg, 0.04 mmol, 5 mol %). The reaction mixture was stirred at 60^{o}C overnight, following cooling to room temperature the toluene was removed *in vacuo* and the crude dissolved in dichloromethane (100 mL). Washing the organic solution with water (3 x 10 mL), drying over magnesium sulfate and removing the solvent under reduced pressure gave a crude colourless product. Purification by flash column chromatography upon silica gel using a 75:25 petroluem spirit 40-60^{o}C: ethylacetate eluent system gave **6** as a colourless crystalline solid (0.130 g, 0.35 mmol, 48 % yield). M.p (hexane) 108-111 ^{o}C. ^{1}H NMR (C_6D_6, 300 MHz, 298 K) 1.12 (d, 12H, *J* = 6.6 Hz), 3.20 (hept, 2H, *J* = 6.6 Hz), 5.57 (broad s, 1H, *NH*), 6.80 (t, 1H, *J* = 7.4 Hz), 6.91-7.08 (m, 10H), 7.25 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 23.8, 29.3, 122.6, 123.6, 126.1, 127.4, 128.1, 129.6, 143.6, 146.8, 154.6; Infrared (DCM film, cm^{-1}) 3328, 3065, 2961, 2947, 2868, 1698, 1646, 1590, 1487, 1295, 1260; Elemental analysis calc. for $C_{25}H_{28}N_2O$: C, 80.61; H, 7.58; N, 7.52. Found C, 80.67; H, 7.55; N, 7.49.

Figure S1. ORTEP representation of **5**. Thermal ellipsoids at 50 % probability. H-atoms with the exception of the urea proton omitted for clarity. Selected bond lengths (Å) and angles (°) N(1)-C(1) 1.3540(17), N(2)-C(1) 1.4063(15), C(1)-O 1.2151(15), N(1)-C(1)-N(2) 113.98(11), N(1)-C(1)-O 124.14(12), N(2)-C(1)-O 121.86(11).

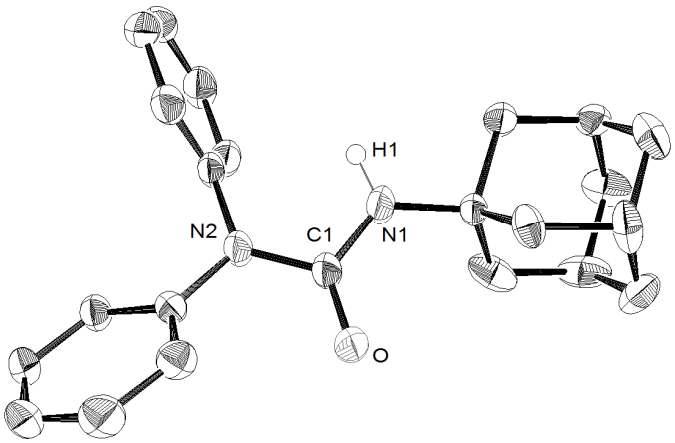
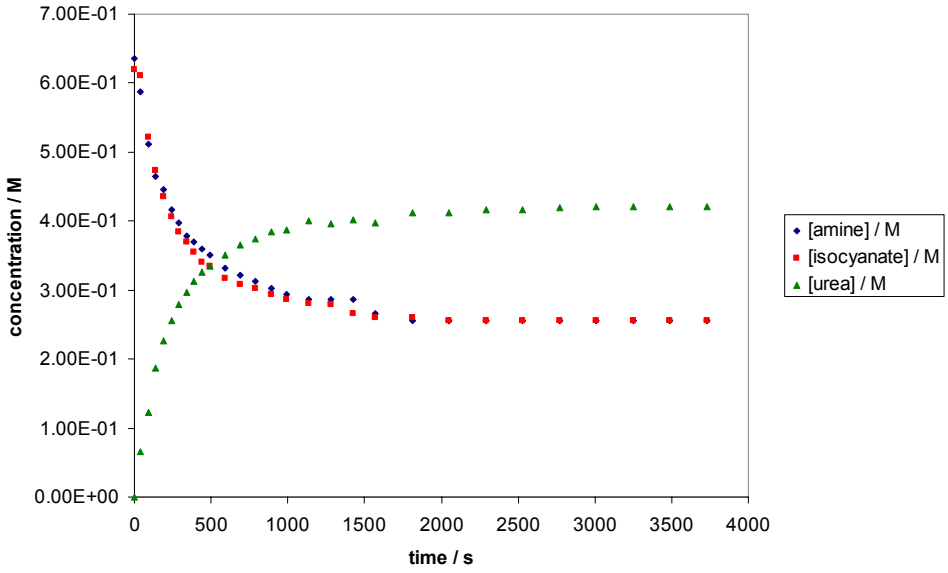


Figure S2. Plot of [substrate] and [product] *versus* time for the reaction of 2,6-di-iso-propylphenylisocyanate with diphenylamine with 6 mol % [Sr{N(SiMe$_3$)$_2$] at 60°C.



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