Supporting Information for

Catalytic Hydroacetylenation of Carbodiimides With Homoleptic Alkaline Earth Hexamethyldisilazides

Merle Arrowsmith, Mark R. Crimmin, Myra Sae Heng, Sarah L. Lomas, Michael S. Hill,* Peter B. Hitchcock, Gabriele Kociok-Köhn.

General Procedures
All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in an MBraun Labmaster Glovebox. NMR spectra were collected on either a Bruker AV-500 spectrometer \(^{13}\text{C}\{(1\text{H})\text{ NMR 126 MHz}\), or a Bruker AV-300 spectrometer \(^{13}\text{C}\{(1\text{H})\text{ NMR 75 MHz}\). Solvents (toluene, hexane) were dried by passage through the columns of a commercial solvent purification system. C\textsubscript{6}D\textsubscript{6} and d\textsubscript{8}-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distillation under argon and storage over molecular sieves. The heavier group 2 amides \([M\{\text{N(SiMe}_3\}_2\}_2(THF)_2]\) (M = Mg \textbf{1a}, Ca \textbf{1b}, Sr \textbf{1c}) were synthesised following literature procedures.\textsuperscript{1} \([\text{BaK}\{\text{N(SiMe}_3\}_2\}_3]\) was isolated following the same procedure as \textbf{1a–1c}. Carbodiimides and acetylenes were purchased from Sigma Aldrich, Alfa Aesar or TCI Europe. Liquid substrates were dried over molecular sieves and submitted to three freeze-pump-thaw cycles prior to transferal into the glovebox. Elemental analyses on compounds were performed by Stephen Boyer at London Metropolitan University. Mass Spectrometric data was acquired on a Bruker ESI MicroTOF at the University of Bath.

Synthesis of calcium bis(\textit{N},\textit{N}’-di-\textit{iso}propyl-2-phenylethynylamidinate) dimer, \textbf{2b}
Phenylacetylene (0.22 mL, 1.98 mmol) and \textit{di-iso}propylcarbodiimide (0.31 mL, 1.98 mmol) were dissolved in 2.0 mL of toluene and added to \textbf{1b} (0.5 g, 0.99 mmol) in toluene. The reaction mixture was stirred overnight at room temperature prior to concentration in \textit{vacuo} to incipient crystallisation. After 48 hours at 4°C, complex \textbf{2b} was obtained as a colourless crystalline solid and isolated by filtration (0.30 g, 0.3 mmol, 61%). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}): 7.39–7.47 (m, 16H, Ph-H), 6.93–6.96 (m, 24H, Ph-H), 4.34 + 4.33 + 4.27 (three sept, 2H:2H:4H, 0.30 g, 0.3 mmol, 61%).
1Pr-CH, $^3J = 6.3$ Hz), 1.56 (d, 12H, $^3$Pr-CH$_3$, $^3J = 6.3$ Hz), 1.44 (d, 12H, $^3$Pr-CH$_3$, $^3J = 6.3$ Hz), 1.32–1.58 (broad overlapping with d, 24H, $^3$Pr-CH$_3$). 13C(1H) NMR (C$_6$D$_6$): 160.4, 158.5, 129.8, 129.6, 129.1, 128.9, 123.7, 122.4, 98.2, 95.7, 81.2, 80.1, 50.9, 50.4, 27.6, 26.6. Elemental analysis for C$_6$H$_7$Ca$_2$N$_8$ ($M_w = 989.5$): C, 72.83; H, 7.74; N, 11.32. Found: C, 72.82; H, 7.66; N, 11.37.

**Synthesis of strontium bis(N,N'-di-isopropyl-2-phenylethynylamidinate) dimer, 2c**

Phenylacetylene (0.20 mL, 1.80 mmol) and di-isopropylcarbodiimide (0.28 mL, 1.80 mmol) were dissolved in 2.0 mL of toluene and added to 2b (0.5 g, 0.91 mmol) in toluene. The reaction mixture was stirred overnight at room temperature prior to concentration in vacuo to incipient crystallisation. After 48 hours at –30°C, complex 2b was obtained as a colourless crystalline solid and isolated by filtration (0.30 g, 0.28 mmol, 61%). 1H NMR (d$_8$-tol): 7.40–7.42 (m, 4H, Ph-H), 6.96–7.00 (m, 6H, Ph-H), 4.38 (broad sept, 2H, $^3$Pr-CH), 4.24 (broad sept, 2H, $^3$Pr-CH), 1.49 (broad d, 12H, $^3$Pr-CH$_3$), 1.42 (broad d, 12H, $^3$Pr-CH$_3$). 13C(1H) NMR (d$_8$-tol): 158.8, 158.6, 132.5, 129.8, 129.1, 128.9, 124.0, 122.5, 97.9, 97.8, 81.7, 80.0, 51.3, 50.5, 27.5, 26.7. Elemental analysis for C$_6$H$_7$Sr$_2$N$_8$ ($M_w = 1084.6$): C, 66.51; H, 6.98; N, 10.34. Found: C, 66.53; H, 6.96; N, 10.30.

**Synthesis of barium potassium tris(N,N'-di-isopropyl-2-phenylethynylamidinate), 3**

Phenylacetylene (13.1 μL, 0.12 mmol) and di-isopropylcarbodiimide (18.6 μL, 0.12 mmol) were added to a solution of [BaK{N(SiMe$_3$)$_2$}] (39.5 mg, 60 μmol) in 0.5 mL of C$_6$D$_6$. Complex 3 crystallised within 2 hours at room temperature as a colourless solid (45 mg, 52 μmol, 87%). Single crystals suitable for X-ray crystallographic analysis were obtained by slow recrystallisation from hot benzene. The compound is fluxional at room temperature in solution and displays only one broadened NMR amidinate environment. 1H NMR (d$_8$-tol): 7.46–7.48 (m, 2H, Ph-H), 6.96–6.99 (m, 3H, Ph-H), 4.28 (broad sept, 2H, $^3$Pr-CH), 1.41 (broad d, 12H, $^3$Pr-CH$_3$). 13C(1H) NMR (d$_8$-tol): 156.8, 132.5, 128.9, 128.8, 124.3, 94.4, 82.8, 51.0, 27.6. The product consistently yielded unsatisfactory elemental analysis due to the extreme air- and moisture-sensitivity of the isolated crystals. NMR spectra are provided as additional proof of formulation.

**Catalytic hydroacetylenation of carbodiimides**

To 0.5 mL of a solution of the relevant catalyst in a 9:1 C$_6$D$_6$/d$_8$-THF mixture were added 0.2 mmol of the carbodiimide derivative followed by 0.2 mmol of the acetylene derivative in the
glovebox. The reaction mixture was transferred into a sealed Youngs tap NMR tube. The reaction was heated at 60–100°C and regularly monitored by ¹H NMR spectroscopy to determine conversions.

**N,N'-di-isopropyl-2-phenylethynylamidine**

¹H NMR (CD₂D₂/THF 9:1): 7.36–7.40 (m, 2H, Ph-H), 7.01–7.04 (m, 3H, Ph-H), 4.41 (s, 1H, NH), 4.19 (sept, 2H, ²Pr-CH₃, ³J = 6.0 Hz), 1.18 (broad d, 12H, ²Pr-CH₃, ³J = 6.0 Hz). ¹³C{¹H} NMR (CD₂D₂/THF 9:1): 141.0, 132.5, 129.7, 129.1, 122.7, 90.5, 81.3, 49.3, 44.3, 25.1, 24.5. ESI-MS for [C₁₅H₂₀N₂+H⁺]: calc. 229.1705; exp. 229.1754.

**N,N'-dicyclohexyl-2-phenylpropargylamidine**

¹H NMR (CD₂D₂/THF 9:1): 7.40–7.44 (m, 2H, Ph-H), 6.99–7.02 (m, 3H, Ph-H), 4.31 (s, 1H, NH), 3.88–3.98 (m, 2H, Cy-CH), 1.99–2.06 (m, 4H, Cy-CH₂), 1.62–1.74 (m, 4H, Cy-CH₂), 1.06–1.54 (m, 12H, Cy-CH₂). ¹³C{¹H} NMR (CD₂D₂/THF 9:1): 141.0, 132.5, 129.6, 129.1, 122.7, 90.6, 81.6, 60.5, 48.6, 35.1 (broad), 26.8, 25.9. ESI-MS for [C₂₁H₂₈N₂+H⁺]: calc. 309.2331; exp. 309.2383.

**N,N'-di-tert-butyl-2-phenylethynylamidine**

¹H NMR (CD₂D₂/THF 9:1): 7.36–7.39 (m, 2H, Ph-H), 6.98–7.02 (m, 3H, Ph-H), 4.23 (s, 1H, NH), 1.52 (s, 9H, ³Bu-H), 1.35 (s, 9H, ³Bu-H). ¹³C{¹H} NMR (CD₂D₂/THF 9:1): 138.0, 132.0, 129.7, 129.2, 128.9, 120.7, 89.5, 84.5, 53.6, 52.1, 31.4, 29.3. ESI-MS for [C₁₇H₂₄N₂+H⁺]: calc. 257.2018; exp. 257.2094.

**N,N'-bis(2,6-di-isopropylphenyl)-2-phenylethynylamidine**

¹H NMR (CD₂D₂/THF 9:1): 11.73, 7.24–7.29 (m, 6H, Ar-H), 6.67–6.86 (m, 5H, Ar-H), 3.72 (m, 4H, ²Pr-CH), 1.43 (d, 12H, ³Pr-CH₃, ³J = 6.6 Hz), 1.20 (broad d, 12H, ³J = 6.8 Hz). ¹³C{¹H} NMR (CD₂D₂/THF 9:1): 149.3, 145.0, 140.8, 132.7, 132.6, 129.9, 128.8, 123.7, 121.4, 97.4, 81.0, 29.1, 25.2, 23.6 (broad). ESI-MS for [C₃₃H₄₁N₂+H⁺]: calc. 465.3270; exp. 465.3401.

**N,N'-di-isopropyl-2-n-butylethynylamidine**

¹H NMR (CD₂D₂/THF 9:1): 4.18 (sept overlapping with broad s, 3H, NH + ²Pr-CH, ³J = 6.0 Hz), 2.08 (t, 2H, C≡CCH₂, ³J = 6.7 Hz), 1.20–1.32 (m, 4H, CH₂), 1.18 (d, 6H, ³Pr-CH₃, ³J = 6.0 Hz), 1.16 (d, 6H, ³Pr-CH₃, ³J = 6.0 Hz), 0.76 (t, 3H, CH₃, ³J = 6.7 Hz). ¹³C{¹H} NMR

N,N'-di-isopropyl-2-cyclohexylethynlamidine

¹H NMR (C₆D₆/THF 9:1): 4.14 (sept, 2H, ¹Pr-CH, ³J = 6.6 Hz), 4.00 (s, 1H, NH), 2.34 (tt, 1H, Cy-CH, ³J = 8.7, 3.7 Hz), 1.63–1.69 (m, 2H, Cy-CH₂), 1.52–1.59 (m, 2H, Cy-CH₂), 1.38–1.50 (m, 4H, Cy-CH₂), 1.09–1.18 (m, 24H, ¹Pr-CH₃ + Cy-CH₂). ¹³C{¹H} NMR (C₆D₆/THF 9:1): 141.4, 73.3, 69.1, 49.3, 46.8, 33.0, 29.8, 26.4, 25.3, 24.4–24.8 (broad). ESI-MS for [C₁₃H₂₆N₂⁺H]⁺: calc. 235.2174; exp. 235.2250.

N,N'-di-isopropyl-2-tert-butylethynlamidine

¹H NMR (C₆D₆/THF 9:1): 4.10 (sept, 2H, ¹Pr-CH, ³J = 6.3 Hz), 3.96 (s, 1H, NH), 1.13 (d, 12H, ¹Pr-CH₃, ³J = 6.3 Hz), 1.12 (s, 9H, ¹Bu-CH₃). ¹³C{¹H} NMR (C₆D₆/THF 9:1): 140.7, 72.0, 67.7, 49.3, 49.2, 43.6, 31.0, 24.4–24.8 (broad). ESI-MS for [C₁₃H₂₅N₂⁺H]⁺: calc. 209.2018; exp. 209.2102.

N,N'-di-isopropyl-2-p-tolylethynlamidine

¹H NMR (C₆D₆/THF 9:1): 7.33 (d, 2H, tol-H, ³J = 8.2 Hz), 6.85 (d, 2H, tol-H, ³J = 8.2 Hz), 4.33 (s, 1H, NH), 4.21 (sept, 2H, ¹Pr-CH, ³J = 6.5 Hz), 2.01 (s, 3H, tol-CH₃), 1.19 (broad d, ¹Pr-CH₃, ³J = 6.5 Hz). ¹³C{¹H} NMR (C₆D₆/THF 9:1): 141.1, 139.9, 132.5, 129.9, 119.7, 80.8, 77.8, 49.3, 43.4, 24.6, 24.3, 21.7. ESI-MS for [C₁₃H₂₆N₂⁺H]⁺: calc. 243.1861; exp. 243.1945.

N,N'-di-isopropyl-2-methoxypropargylamidine

¹H NMR (C₆D₆): 4.14 (sept, 2H, ¹Pr-CH, ³J = 6.5 Hz), 3.85 (s, 2H, OCH₂), 3.62 (broad, 1H, NH), 3.09 (s, 3H, OCH₃), 1.10–1.20 (broad, 12H, ¹Pr-CH₃). ¹³C{¹H} NMR (C₆D₆): 139.8, 87.1, 78.2, 60.0, 57.8, 49.5 (broad), 24.3 (broad). ESI-MS for [C₁₁H₂₀N₂O⁺H]⁺: calc. 197.1654; exp. 197.1644.

N,N'-di-isopropyl-2-(N''-dimethylamino)propargylamidine

¹H NMR (C₆D₆): 4.18 + 4.16 (two overlapping sept, 1H:1H, ¹Pr-CH, ³J = 6.2 Hz), 3.78 (broad s, 1H, NH), 3.15 (s, 2H, NCH₂), 2.13 (s, 3H, NCH₃), 1.36 (d, 6H, ¹Pr-CH₃, ³J = 6.2 Hz), 1.97 (d, 6H, ¹Pr-CH₃, ³J = 6.2 Hz). ¹³C{¹H} NMR (C₆D₆): 140.4, 86.9, 77.4, 55.4, 48.4, 44.4, 42.9, 25.8, 23.1. ESI-MS for [C₁₂H₃₃N₃⁺H]⁺: calc. 210.1970; exp. 210.1945.
**Kinetic analyses**

Samples for kinetic analysis were prepared and sealed in Youngs tap NMR tubes in the glovebox, immediately frozen in liquid nitrogen and heated up to room temperature prior to inserting into the NMR spectrometer at 60°C. Conversions were calculated by integrating the \(^{1}\)Pr-methine protons of the substrate versus the hexamethyldisilazane standard of the precatalyst.

**Figure S1.** Kinetic analyses performed at five different concentrations of initial amidine in 0.5 mL of C\(_6\)D\(_6\)/d\(_8\)-THF 9:1 with 2.5 mol% of 1c at 60°C.

**Figure S2.** Kinetic analyses performed at four different catalyst loadings of 1c in an 0.04 M solution of phenylacetylene and N,N’-di-isopropylcarbodiimide in 0.5 mL of C\(_6\)D\(_6\)/d\(_8\)-THF 9:1 at 60°C.
$^1$H and PENDANT $^{13}$C NMR spectra for isolated compound 3 in $d_8$-toluene

$\text{d}_8$-toluene; $n$-hexane (from recrystallisation)
**Crystallographic details**

Data for compounds 2b and 2c were collected at 173 K on a KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at Imperial College, London. Data for compounds 3 and 4 were collected at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at the University of Bath. Data were processed using the Nonius Software. Structure solution, followed by full-matrix least-squares refinement was performed using the WINGX-1.70 suite of programmes throughout.

**Notes on refinement for compound 4:** the crystals showed non-merohedral twinning (41%) with 180.0° rotation about the (–3, 0, 2) direct lattice direction. The asymmetric unit contains one ligand molecule and one solvent molecule of benzene. The heteroatom hydrogen atoms show 50% occupancy and form hydrogen bonds with another compound molecule, thus forming dimers.
References