

“Decarbonization” of an imino N-heterocyclic carbene ligand via triple benzyl migration from hafnium

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SUPPLEMENTARY INFORMATION

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EXPERIMENTAL SECTION

General experimental details. All manipulations were performed under rigorous exclusion of air and moisture using a nitrogen-filled glove box or a vacuum line and swivel frit apparatus. Hydrocarbon solvents were dried over and distilled from sodium benzophenone ketyl and stored over and vacuum-distilled from same immediately prior to use. Dichloromethane (Pharmco) was washed with concentrated H₂SO₄, water, aqueous NaHCO₃, and again water, and then distilled from P₂O₅; it was then stored over P₂O₅ and vacuum-distilled before use. NMR solvents were obtained from Cambridge Isotope Laboratories and were dried similarly to nondeuterated solvents. NMR spectra were recorded on a Varian unity Inova 400 MHz spectrometer, with chemical shifts referenced to residual solvent protons. Iminocarbene precursor **1**,¹ tetrabenzylhafnium,² and HfCl₄(THF)₂³ were synthesized according to literature procedures. HfCl₄ (99.9+%) used to prepare HfCl₄(THF)₂ was purchased from Strem. All other materials were purchased from Aldrich or Acros in the highest available purity and used as received. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, New Jersey, USA.

NMR tube formation of free iminocarbene (2). Iminoimidazolium chloride **1** (20 mg, 0.052 mmol) and potassium hexamethyldisilazide (11 mg, 0.055 mmol) were placed in a flame dried J Young NMR tube, and the tube was sealed with a PTFE stopcock. C₆D₆ (0.6 mL) was added via vacuum transfer, and the tube was shaken for 1 min. A ¹H NMR spectrum acquired after 15 min showed somewhat broadened resonances, with no imidazolium C2 proton present (bottom, Figure S1). ¹H NMR (400 MHz, C₆D₆): δ 8.16 (br s, 1 H), 7.44 (br s, 2 H), 7.02 (br s, 3 H), 6.92 (br s, 3 H), 6.27 (br s, 1 H), 3.24 (br s, 3 H, NCH₃), 3.16 (br s, 2 H, CHMe₂), 1.21 (br s, 6 H, CH₃), 1.00 (br s, 6 H, CH₃). Attempts to isolate the free iminocarbene from larger scale reactions resulted in material that contained significant impurities and decomposed faster in solution than the in situ-prepared iminocarbene. Therefore, the latter was used in preparative reactions.

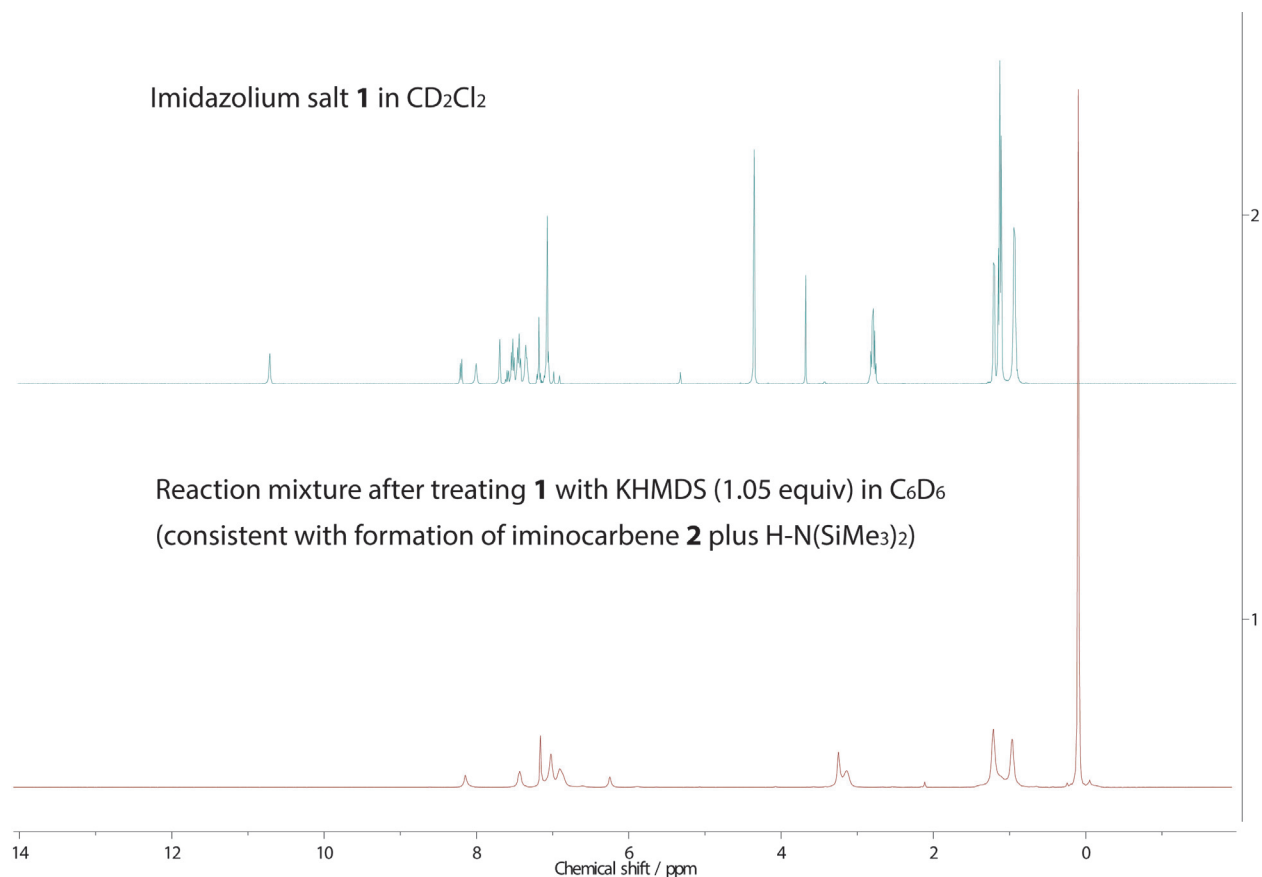


Figure S1. ^1H NMR spectra of imino-imidazolium salt precursor **1** (top) and in situ formation of iminocarbene **2** (bottom).

Synthesis of hafnium eneamido-amidinate complex 3. $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (0.132 g, 0.66 mmol) and **1** (0.24 g, 0.63 mmol) were stirred in 20 mL benzene for 30 min under N_2 . $\text{Hf}(\text{CH}_2\text{Ph})_4$ (0.34 g, 0.63 mmol) was added in one portion, and the mixture was stirred for 24 h at 25 °C. All traces of benzene were removed in vacuo, and the residue was extracted with pentane and filtered through a glass frit. The solution was concentrated to obtain a red solid, which was collected by filtration. Yield 0.15 g (27%). ^1H NMR (400 MHz, C_6D_6): δ 6.45 - 7.51 (m, 30 H), 3.97 (septet, $J=6.6$ Hz, 1 H, CH), 3.40 (d, $J=14.4$ Hz, 3 H, CH_2Ph), 3.27 (s, 3 H, CH_3 -imidazole), 3.01 (d, $J=14.4$ Hz, 3 H, CH_2Ph), 2.76 (septet, $J=6.6$ Hz, 1 H, CH), 2.56 (d, $J=12.1$ Hz, 1 H, CH_2Ph), 2.30 (d, $J=12.1$ Hz, 1 H, CH_2Ph), 1.43 (d, $J=6.6$ Hz, 3 H, CH_3), 1.18 (d, $J=6.6$ Hz, 3 H, CH_3), 0.85 (d, $J=6.6$ Hz, 3 H, CH_3), 0.20 (d, $J=6.6$ Hz, 3 H, CH_3). ^{13}C NMR (101 MHz, C_6D_6): δ 164.1, 147.6, 144.0, 143.4, 142.5, 140.3, 140.1, 130.8, 130.2, 129.7, 128.5, 128.4, 127.3, 126.4, 126.1,

125.1, 124.9, 122.1, 106.9, 82.9, 76.4, 40.7, 37.9, 28.3, 28.0, 25.3, 25.1, 24.9, 24.3. Anal. Calcd for $C_{51}H_{55}HfN_3$: C, 68.94; H, 6.24; N, 4.73 %. Found C, 68.86; H, 6.14; N, 4.77 %.

Low Temperature NMR study of 3. A sample of **3** (13 mg, 0.015 mmol) was placed in a flame-dried NMR tube, which was then sealed with a PTFE stopcock. Toluene- d_8 was added to the sample via vacuum distillation. The NMR tube was placed in the probe of the 500 MHz NMR spectrometer in a stream of dry nitrogen. The sample was cooled from 20 °C to -80 °C in 10 °C increments. NMR shims were adjusted every 10 °C, and spectra were collected every 20 °C. Relevant portions of the NMR spectra are shown in Figure S2.

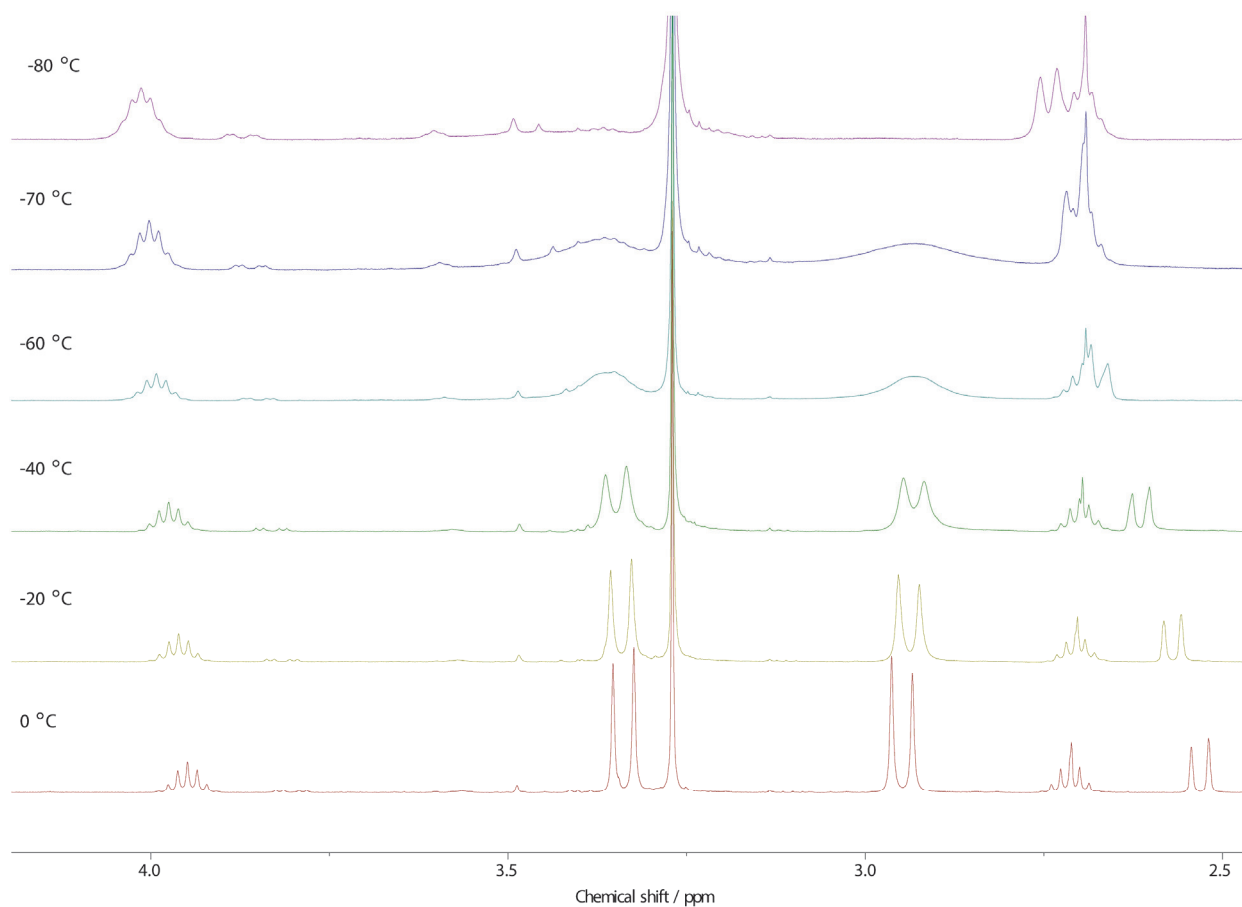


Figure S2. Variable temperature 1H NMR study of complex **3** in toluene- d_8 , showing broadening of the $-CH_2$ resonances of the tribenzylmethyl ligand at low temperature.

Synthesis of HfCl₄(iminocarbene) complex 4. Iminoimidazolium chloride **1** (0.20 g, 0.52 mmol) and lithium hexamethyldisilazide (0.096 g, 0.57 mmol) were stirred in 20 mL of benzene for 30 min. HfCl₄(THF)₂ (0.24 g, 0.52 mmol) was then added in one portion, and the mixture was stirred for 2 h at 25 °C. The solid precipitate was filtered off and washed twice with 5 mL of benzene. The solid was then triturated twice with CH₂Cl₂, followed by drying in vacuo to remove all traces of benzene. The solid was stirred with 10 mL of CH₂Cl₂, and the resulting mixture was filtered twice through Celite to remove residual salts. The solution was filtered once more through a sintered glass frit and then concentrated. Layering of cold pentane over the CH₂Cl₂ solution resulted in precipitation of a white solid, which was collected by filtration and dried in vacuo. To obtain analytically pure material, the compound was redissolved in CH₂Cl₂, filtered again through Celite, and recrystallized by layering pentane over the solution. White precipitate, yield 0.16 g, (47%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.51 (t, *J*=7.8 Hz, 1 H, CH), 7.40 (t, *J*=7.8 Hz, 2 H, CH), 7.28 (d, *J*=8.2 Hz, 2 H, CH), 7.16 - 7.25 (m, 1 H), 7.05 - 7.13 (m, 3 H), 6.95 (d, *J*=2.0 Hz, 1 H, CH), 4.17 (s, 3 H, CH₃), 3.31 (septet, *J*=6.6 Hz, 2 H, CH), 1.28 (d, *J*=6.6 Hz, 6 H, CHMe₂), 0.83 (d, *J*=6.6 Hz, 6 H, CHMe₂). ¹³C NMR (101 MHz, CD₂Cl₂): δ 199.9 (carbene), 163.3 (imine), 141.8, 141.4, 133.0, 129.8, 129.1, 128.1, 127.2, 125.0, 124.0, 121.2, 39.2 (imidazole CH₃), 28.5 (CHMe₂), 26.6 (CHMe₂), 24.1 (CHMe₂). Anal. Calcd for C₂₃H₂₇N₃Cl₄Hf: C 41.49, H 4.09, N 6.31. Found C 41.46, H 3.97, N 6.49.

Alkene polymerization procedure. Triisobutylaluminium (0.50 mmol, as a 1.0 M solution in hexanes), sulfated alumina activator-support (100 mg), co-monomer (if used), and catalyst (2.0 mg) were added in sequence through the charge port of a 3.8 L stainless steel reactor while venting isobutane vapor. The charge port was closed, and isobutane (2 L) was added to the reactor. The reactor contents were stirred and heated to 80 °C before being placed under ethylene pressure. The ethylene pressure was maintained at 31 bar (450 psig) for the 30 min duration of the run. The reactor was then vented and opened, and the polymer product was collected and dried under vacuum at 50 °C for 2 h.

The sulfated alumina activator-support was prepared by a disclosed procedure⁴ using synthetic Boehmite (“Alumina A”) from W. R. Grace Co., which had a surface area of approximately 300 m² g⁻¹, a pore volume of 1.3 mL g⁻¹, and an average particle size of 100 μm. The alumina was impregnated to incipient wetness with an aqueous solution (15 wt%) of

ammonium sulfate. The material was placed in a pan and dried in vacuo at approximately 110 °C for 16 h. The powdered material was fluidized in a stream of dry air at 550 °C for 6 h for calcination. The resulting sulfated alumina was collected and stored under dry nitrogen and used without further exposure to air.

X-RAY CRYSTALLOGRAPHIC DATA AND PROCEDURES

General Considerations. X-ray diffraction data were collected on a Bruker SMART APEX II single crystal diffractometer using graphite-monochromated Mo $k\alpha$ radiation ($\lambda=0.71073$ Å, sealed tube) and a combination of ϕ and ω scans. The crystal-to-detector distance was 6.0 cm. Unit cell determination and data collection utilized the Bruker SMART⁵ and APEX2⁶ software packages. Data integration employed SAINT.⁷ Multiscan absorption corrections were implemented using SADABS.⁸ Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software suite.⁹ Non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atoms (except as noted) were included in calculated positions (riding model) with isotropic U fixed at 1.5 times the U_{eq} of the attached atom for -CH₃ groups and 1.2 times the U_{eq} of the attached atom for other hydrogen atoms.

X-ray Crystallographic Analysis of 3. Red blocks were obtained by cooling a concentrated pentane solution of **3** at -35 °C in a glovebox freezer for several days. A sample measuring 0.32 x 0.25 x 0.14 mm was cut from a larger crystal and placed on the diffractometer goniometer, and reflection data were collected using 10 s scans. The sample was cooled to 115(1) K during data collection using a Bruker Kryoflex liquid nitrogen cooling device. During refinement, the CH₂ hydrogen atoms of the two benzyl groups involved in preagostic interactions were located in the difference Fourier map. For these atoms (H7A, H7B, H8A, H8B), a minimum C-H distance restraint of 0.99(1) Å was applied, with all other positional parameters allowed to refine freely. C₅₁H₅₅HfN₃, $M_r = 888.47$ g mol⁻¹, monoclinic, space group $P2_1/n$, $a = 10.2687(2)$, $b = 20.6876(4)$, $c = 20.1804(3)$ Å, $\beta = 101.885(1)^\circ$, $V = 4195.1(1)$ Å³, $Z = 4$, $Z' = 1$, $\rho_{\text{calcd}} = 1.407$ g cm⁻³, $\mu = 2.525$ mm⁻¹, $T = 115(2)$ K, $2\theta_{\text{max}} = 57.22^\circ$, 47669 total reflections, 10689 independent ($R_{\text{int}} = 0.040$),

8812 observed [$I > 2\sigma(I)$]. Final $R1$ [$I > 2\sigma(I)$] = 0.0260, $wR2$ (all data) = 0.0574, largest difference peak (hole) 1.382 (−0.840) e Å^{−3}. CCDC 1033344.

X-ray Crystallographic Analysis of 4. Yellow needles were obtained by slow diffusion of pentane into a CH₂Cl₂ solution of **4**. A sample measuring 0.40 x 0.06 x 0.04 mm was placed on the diffractometer goniometer, and reflection data were collected using 30 s scans. The sample was cooled to 115(1) K during data collection using a Bruker Kryoflex liquid nitrogen cooling device. C₂₃H₂₇Cl₄HfN₃, M_r = 665.77 g mol^{−1}, monoclinic, space group $P2_1/n$, a = 10.9712(1), b = 17.1071(2), c = 14.0693(2) Å, β = 105.427(1)°, V = 2545.46(5) Å³, Z = 4, Z' = 1, ρ_{calcd} = 1.737 g cm^{−3}, μ = 4.534 mm^{−1}, T = 115(2) K, $2\theta_{\text{max}}$ = 53.34°, 22478 total reflections, 5366 independent (R_{int} = 0.044), 4364 observed [$I > 2\sigma(I)$]. Final $R1$ [$I > 2\sigma(I)$] = 0.0266, $wR2$ (all data) = 0.0601, largest difference peak (hole) 0.957 (−0.658) e Å^{−3}. CCDC 1033345.

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