

Supporting Information

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Kinetic Control and Multiple Mechanisms for C-H Bond Activation by a Zr=N Complex

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General Procedures. All air- and moisture-sensitive compounds were manipulated using standard Schlenk techniques, or in a glovebox under an inert atmosphere (N₂). Glassware was dried overnight at 180 $^{\circ}$ C or flame dried under vacuum immediately prior to use. Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock via a Cajon Ultra-Torr reducing union and then flame-sealing on a vacuum line at -196 $^{\circ}$ C. Glass reaction vessels fitted with ground glass joints and Teflon stopcocks are referred to as bombs.

All NMR spectra were obtained at ambient temperature using Bruker AVB-400, AVQ-400, DRX-500, or AV-500 spectrometers. Unless otherwise stated, all NMR data are reported in [D₆]benzene solvent. The ¹H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual protiated solvent. In cases where assignment of ¹H resonances was ambiguous, 2D NMR experiments (¹H-¹H NOESY or ¹H-¹H COSY) were performed. The ¹³C{¹H} NMR chemical shifts (δ) are reported in ppm relative to the carbon resonance of the deuterated solvent. Where assignment of ¹³C resonances was ambiguous, assignments were made by analysis of spectra from standard DEPT 135 pulse sequences and additional 2D NMR experiments (¹H-¹³C HSQC, ¹H-¹³C HMBC, etc) as necessary. The ¹⁹F NMR spectra

were recorded at 377 MHz, and chemical shifts (δ) are reported relative to external CFCl₃ (0 ppm). The ²H NMR spectra were recorded at 61 MHz and chemical shifts (δ) are reported relative to 5% v/v deuterated solvent (added for locking and calibration purposes). Elemental analyses were performed at the University of California, Berkeley Microanalytical facility.

Purification and full characterization of some of these complexes has been difficult due to extreme solubility in pentane and other solvents. In these cases, ¹H NMR spectra are provided in lieu of elemental analyses. Since deuterated analogs of protiated complexes were prepared in a manner similar to that of their protiated counterparts, only spectral data are given for the deuterated complexes.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Silica gel (Merck 60, 230-400) was dried under vacuum (~50 mTorr) at 250 °C for 48 h. Pentane, benzene, and THF (Fisher) were passed through a column of activated Alumina (type A2, size 12 x 32, UOP LLC) under nitrogen pressure and sparged with N₂ prior to use. Unless otherwise noted, all other reagents and deuterated solvents (Cambridge Isotope Laboratories) were vacuum transferred (or distilled) from calcium hydride into a glass bomb, were degassed by three freeze-pump-thaw cycles, or were sparged with N₂ gas for 10 min. prior to use. All hydrocarbons and deuterated solvents were stored over 3Å molecular sieves in a glovebox at -30 °C. Hydrocarbon reagents and deuterated solvents were additionally filtered through a plug of activated silica gel immediately prior to use. Complex Cp*CpZr=NCMe₃(THF) (1) was prepared, as reported, by thermolysis of the zirconium methyl amide complex Cp*CpZr(Me)(NHCMe₃) (4) in THF.^[1]

Cp*CpZr(NHCMe₃)(3,3-dimethyl-1-butyne) (3a). To a solution of complex 1 (0.028 g, 0.065 mmol) in pentane (5.0 mL) was added 20 equiv of 3,3-dimethyl-1-butyne (0.103 g, 1.25 mmol). An immediate change in color to dark purple was observed on mixing, which quickly lessened in intensity to ultimately give a solution of a faint purple color within 5 s. The volatile materials were removed under reduced pressure to yield analytically pure **3a** as a light purple oil (0.025 g, 86%). ¹H NMR (500 MHz, *c*-C₆D₁₂) δ 5.90 (s, 5H, *Cp*), 5.08 (s, 1H, N*H*), 1.95 (s, 15H, *Cp**), 1.17 (s, 9H, CC*Me*₃), 1.13 (s, 9H, NC*Me*₃) ppm. ¹³C{¹H} NMR (125 MHz, *c*-C₆D₁₂) δ 127.02 (Zr*C*), 122.96 (ZrC*C*), 117.79 (Cp*_q), 110.16 (*Cp*), 57.41 (N*C*Me₃), 34.59 (NC*Me*₃), 32.47 (CC*Me*₃), 29.10 (C*C*Me₃), 12.54 (Cp*_{*Me*}) ppm. Anal. Calcd for C₂₅H₃₉NZr: C, 67.50; H, 8.84; N, 3.15. Found: C, 67.11; H, 8.90; N, 3.00.

Cp*CpZr(NDCMe₃)(3,3-dimethyl-1-butyne) (3a- d_1). Substrate DC=CCMe₃ was prepared as previously described.^[2] ¹H NMR (500 MHz, c-C₆D₁₂) δ 5.90 (s, 5H, *Cp*), 1.95 (s, 15H, *Cp**), 1.17 (s, 9H, CC*Me*₃), 1.13 (s, 9H, NC*Me*₃) ppm. ²H NMR (61 MHz, 5% v/v c-C₆D₁₂/c-C₆H₁₂) δ 5.16 (ND) ppm. ¹³C{¹H} NMR (125 MHz, c-C₆D₁₂) δ 127.00 (ZrCC), 122.93 (ZrC), 117.74 (Cp*_q), 110.13 (*Cp*), 57.27 (NCMe₃), 34.52 (NC*Me*₃), 32.43 (CC*Me*₃), 29.07 (CCMe₃), 12.49 (Cp*_{*Me*}) ppm.

Cp*CpZr(NHCMe₃)(cyclopentenyl) (3b). A solution of complex 4 (0.068 g, 0.18 mmol) in cyclopentene (3.29 g, 48.4 mmol) was heated and stirred in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for 4 h at 105 °C. The volatile materials were removed under vacuum to yield **3b** as a yellow oil (0.074 g, 95%), which was then crystallized at -30 °C from pentane to yield analytically pure **3b** (0.032 g, 41%). ¹H NMR (500 MHz) δ 5.89 (s, 5H, *Cp*), 5.64 (t, *J* = 1.8 Hz, 1H, ZrC=CH), 5.13

(s, 1H, N*H*), 2.6-2.5 (m, 3H, C*H*₂), 2.4-2.3 (m, 1H, C*H*₂), 2.0-1.9 (m, 1H, C*H*₂), 1.8-1.7 (m, 1H, C*H*₂), 1.74 (s, 15H, *Cp**), 1.17 (s, 9H, C*Me*₃) ppm. ¹³C{¹H} NMR (125 MHz) δ 188.56 (Zr*C*=), 137.27 (ZrC=*C*), 116.67 (Cp*_{*q*}), 109.34 (*Cp*), 56.70 (*C*Me₃), 46.12 (*C*H₂), 35.50 (*C*H₂), 34.37 (*CMe*₃), 25.90 (*C*H₂), 11.86 (Cp*_{*Me*}) ppm. Anal. Calcd for C₂₄H₃₇NZr: C, 66.91; H, 8.66; N, 3.25. Found: C, 67.21; H, 8.59; N, 3.64.

Cp*CpZr(NHCMe₃)(*trans-2,3-dimethylcyclopropyl*) (3c). A solution of complex 4 (0.091 g, 0.24 mmol) in cis-1,2-dimethylcyclopropane (0.498 g, 7.11 mmol) was heated in a sealed NMR tube for 4 h at 105 °C. The volatile materials were removed under vacuum to yield a yellow powder (90%), and subsequent crystallization from a saturated solution of *n*-pentane at -30 °C gave analytically pure crystals of 3c (0.047 g, 45%). One diastereomer was observed in solution by ¹H NMR spectroscopy. The *trans* orientation of the Zr fragment relative to the two diastereotopic methyl substituents (Me_A and Me_B) on the cyclopropyl moiety was confirmed by 2D COSY and NOESY NMR spectroscopy. The COSY experiment afforded the correlation of the diastereotopic cyclopropyl proton signals β to the Zr center (H_A and H_B) to their corresponding methyl groups (Me_A and Me_B) β to the Zr center. The NOESY spectrum showed a strong correlation between the proton α to the Zr center and both diastereotopic methyl groups (a *cis* orientation), whereas neither H_A nor H_B (diastereotopic protons β to the Zr center) exhibited a correlation to its *trans* methyl group (no NOE observed between H_A and Me_B or H_B and Me_A). ¹H NMR (500 MHz) δ 5.90 (s, 5H, *Cp*), 4.55 (s, 1H, N*H*), 1.78 (s, 15H, Cp^*), 1.38 (d, J = 6.5 Hz, 3H, ZrCHCH_A Me_A), 1.36 (d, J = 6.3 Hz, 3H, ZrCHCH_B Me_B), 1.11 (s, 9H, CMe₃), 1.0-0.9 (m, 1H, ZrCHCH_AMe_A), 0.9-0.8 (m, 1H, ZrCHCH_BMe_B), -1.52 (t, J = 7.4 Hz, 1H, ZrCH) ppm. ¹³C{¹H} NMR (125 MHz) δ 116.33 (Cp*_a), 109.35

(*Cp*), 57.35 (*C*Me₃), 45.92 (*ZrC*), 34.72 (*CMe*₃), 25.46 (*ZrCHC*_AMe_A), 21.56 (*ZrCHC*_BMe_B), 18.39 (*ZrCHC*_AMe_A), 17.13(*ZrCHC*_BMe_B), 12.04 (*Cp**_{*Me*}) ppm. Anal. Calcd for C₂₄H₃₉NZr: C, 66.60; H, 9.08; N, 3.24. Found: C, 66.38; H, 9.16; N, 3.59.

Cp*CpZr(NHCMe₃)(neohexenyl) (**3d**). A solution of complex **4** (0.098 g, 0.26 mmol) in 3,3-dimethylbutene (2.574 g, 30.6 mmol) was heated and stirred in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for 4 h at 105 °C. The volatile materials were removed under vacuum to give a yellow oil. Complex **3d** was obtained as an analytically pure white crystalline solid upon crystallization from pentane at -30 °C (0.062 g, 53%). ¹H NMR (500 MHz) δ 6.33 (d, J = 18.5 Hz, 1H, ZrC*H*=), 5.85 (s, 5H, Cp), 5.83 (d, J = 18.5 Hz, 1H, ZrC*H*=C*H*), 4.94 (s, 1H, N*H*), 1.74 (s, 15H, Cp*), 1.18 (s, 18H, 2 x C*Me*₃) ppm. ¹³C{¹H} NMR (125 MHz) δ 166.61 (Zr*C*), 153.01 (ZrCH=*C*), 116.24 (Cp*_q), 109.80 (Cp), 56.76 (N*C*Me₃), 35.76 (C*C*Me₃), 34.48 (NC*Me*₃), 30.28 (CC*Me*₃), 12.00 (Cp*_{*Me*}) ppm. Anal. Calcd for C₂₅H₄₁NZr: C, 67.20; H, 9.25; N, 3.13. Found: C, 67.04; H, 9.43; N, 3.04.

Cp*CpZr(NDCMe₃)(neohexenyl) (3d-d₁). Deuterated neohexene (*trans*-1deutero-3,3-dimethyl-1-butene) was prepared as previously reported.^[3] ¹H NMR (500 MHz) δ 6.35 (d, J = 18.5 Hz, 1H, ZrCH=), 5.86 (s, 5H, Cp), 5.84 (d, J = 18.5 Hz, 1H, ZrCH=CH), 1.74 (s, 15H, Cp*), 1.20 (s, 9H, C Me_3) 1.19 (s, 9H, C Me_3) ppm. ¹³C{¹H} NMR (125 MHz) δ 166.59 (ZrC), 153.07 (ZrCH=C), 116.25 (Cp*_q), 109.82 (Cp), 56.66 (NCMe₃), 35.75 (CCMe₃), 34.43 (NC Me_3), 30.26 (CC Me_3), 11.97 (Cp*_{Me}) ppm. ²H NMR (77 MHz, 5% v/v C₆D₆/C₆H₆) δ 4.99 (br, ND) ppm.

Cp*CpZr(NHCMe₃)(3,5-bis(trifluoromethyl)phenyl) (3e). A solution of 4 (0.082 g, 0.21 mmol) in 1,3-bis(trifluoromethyl)benzene (6.12 g, 28.6 mmol) was heated

and stirred in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for 5 h at 105 °C. The volatile materials were removed under vacuum to yield **3e** as a yellow/orange solid (0.105 g, 83%). Analytically pure, colorless crystals of complex **3e** were obtained after crystallization from a concentrated *n*-pentane solution at -30 °C (0.059 g, 47%). Although all ¹³C resonances are reported here (assigned by a 2D ¹⁹F-¹³C HSMBC experiment), not all ¹³C resonances were evidenced in the ¹³C {¹H} NMR spectrum due to ¹³C-¹⁹F coupling (and overlapping solvent signals) under standard pulse sequences. ¹H NMR (500 MHz) δ 8.06 (s, 2H, Ar_o), 7.72 (s, 1H, Ar_p), 5.71 (s, 5H, *Cp*), 5.68 (s, 1H, N*H*), 1.45 (s, 5H, *Cp**), 1.13 (s, 9H, *CMe*₃) ppm. ¹³C {¹H} NMR (125 MHz) δ 187.78 (s, Zr*C*), 141.33 (s, Ar_o), 127.8 (q, ²J_{F-C} = 31 Hz, Ar_q-CF₃), 125.6 (q, ¹J_{F-C} = 273 Hz, *C*F₃) 117.88 (s, Cp*_q), 117.9-117.7 (m, Ar_p), 110.51 (s, *Cp*), 57.73 (s, *C*Me₃), 34.16 (s, *CMe*₃), 11.78 (s, Cp*_{Me}) ppm. ¹⁹F NMR (377 MHz, C₆D₆) δ ^{-61.13} (s) ppm. Anal. Calcd for C₂₇H₃₃F₆NZr: C, 56.22; H, 5.77; N, 2.43. Found: C, 56.33; H, 6.01; N, 2.50.

Cp*CpZr(NHCMe₃)(phenyl) (3f). A solution of complex 4 (0.077 g, 0.21 mmol) in benzene (3.67 g, 47.0 mmol) was heated and stirred in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for 4 h at 105 °C. The volatile materials were removed under vacuum to yield 3f as an analytically pure, colorless powder (0.088 g, 99%). ¹H NMR (500 MHz, c-C₆D₁₂) δ 7.27 (d, J = 7.2 Hz, 2H, Ar_o), 6.91 (t, J = 7.2, 2H, Ar_m), 6.81 (t, J = 7.2 Hz, 1H, Ar_p), 5.94 (s, 5H, *Cp*), 5.44 (s, 1H, N*H*), 1.74 (s, 15H, *Cp**), 1.21 (s, 9H, *CMe*₃) ppm. ¹³C{¹H} NMR (125 MHz, c-C₆D₁₂) δ 184.96 (Zr*C*), 141.73 (Ph_o), 126.74 (Ph_m), 124.35 (Ph_p), 117.79 (Cp*_q), 110.63 (*Cp*),

51.71 (*C*Me₃), 34.75 (*CMe*₃), 12.17 (*Cp*_{Me}*) ppm. Anal. Calcd for C₂₅H₃₅NZr: C, 68.12;
H, 8.00; N, 3.18. Found: C, 67.91; H, 7.92; N, 3.38.

Cp*CpZr(NDCMe₃)(C₆D₅) (3f-d₆). ¹H NMR (500 MHz, c-C₆D₁₂) δ 5.94 (s, 5H, *Cp*), 1.74 (s, 15H, *Cp**), 1.21 (s, 9H, *CMe*₃) ppm. ¹³C{¹H} NMR (125 MHz, c-C₆D₁₂) δ 184.63 (Zr*C*), 141.6-140.7 (m, *Ph*_D), 126.19 (t, *J* = 23.5 Hz, *Ph*_D), 124.2-123.3 (m, *Ph*_D), 117.76 (Cp*_{*q*}), 110.61 (*Cp*), 57.59 (*C*Me₃), 34.72 (*CMe*₃), 12.16 (Cp*_{*Me*}) ppm. ²H NMR (61 MHz, 5% v/v c-C₆D₁₂/c-C₆H₁₂) δ 7.3 (br, *Ph*_D), 7.1-6.5 (br, *Ph*_D), 5.5 (br, *ND*) ppm.

Cp*CpZr(NHCMe₃)(3,5-diisopropylphenyl) (**3g**). A solution of complex **4** (0.021 g, 0.056 mmol) in 1,3-diisopropylbenzene (0.75 g, 4.6 mmol) was heated in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for 4 h at 105 °C. The volatile materials were removed under vacuum. Analytically pure complex **3g** was obtained as a yellow solid after redissolution in benzene and subsequent removal of the volatile materials under vacuum (0.047 g, 84%). ¹H NMR (500 MHz) δ 7.28 (br s, 2H, Ar_o), 6.85 (s, 1H, Ar_p), 5.97 (s, 5H, *Cp*), 5.44 (s, 1H, N*H*), 2.91 (sept, *J* = 6.94 Hz, 1H, *CHM*e₂), 1.65 (s, 15H, *Cp**), 1.41 (d, *J* = 6.94 Hz, 12H, CH*M*e₂), 1.27 (s, 9H, *CM*e₃) ppm. ¹³C {¹H} NMR (125 MHz) δ 185.52 (Zr*C*), 145.71 (Ar_m), 137.2-136.7 (br, Ar_o), 25.06 (CH*M*e_AMe_B), 24.86 (CH*M*e_AMe_B), 11.93 (Cp*_{*Me*}) ppm. Anal. Calcd for C₃₁H₄₇NZr: C, 70.93; H, 9.02; N, 2.67. Found: C, 70.55; H, 9.07; N, 2.66.

Cp*CpZr(NHCMe₃)(mesityl) (3h). A solution of complex 4 (0.065 g, 0.17 mmol) in 1,3,5-trimethylbenzene (mesitylene) (3.69 g, 30.7 mmol) was heated in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for 4 h at 105 °C. The volatile materials were removed under vacuum to yield **3h** as a light yellow

crystalline solid (0.081 g, 99%). Analytically pure colorless material was obtained on crystallization from pentane at -30 °C (0.049 g, 60%). ¹H NMR (400 MHz) δ 6.80 (s, 2H, Ar_o), 6.57 (s, 1H, Ar_p), 5.69 (s, 5H, *Cp*), 4.98 (s, 1H, N*H*), 2.34 (s, 6H, Ar_{Me}), 2.30 (d, *J* = 10.1 Hz, 1H, ZrC*H*_AAr), 1.69 (s, 15H, *Cp**), 1.13 (s, 9H, *CMe*₃), 1.01 (d, *J* = 10.1 Hz, 1H, ZrC*H*_BAr) ppm. ¹³C{¹H} NMR (125 MHz) δ 154.79 (ZrCH₂Ar_q), 136.13 (Ar_q-Me), 125.75 (Ar_o), 122.02 (Ar_p), 116.13 (Cp*_q), 110.37 (*Cp*), 57.97 (*C*Me₃), 47.89 (ZrCH₂), 34.10 (*CMe*₃), 21.79 (Ar*Me*), 11.78 (Cp*_{*Me*}) ppm. Anal. Calcd for C₂₈H₄₁NZr: C, 69.65; H, 8.56; N, 2.90. Found: C, 69.50; H, 8.63; N, 2.99.

Cp*CpZr(NDCMe₃)(mesityl- d_{11}) (3h- d_{12}). ¹H NMR (500 MHz) δ 5.69 (s, 5H, Cp), 1.69 (s, 15H, Cp*), 1.13 (s, 9H, CMe₃) ppm. ²H NMR (61 MHz, C₆H₆) δ 6.79 (Ar_o), 6.59 (Ar_p), 5.00 (ND), 2.26 (br, Ar_{Me}, ZrCD_AAr), 0.95 (ZrCD_BAr) ppm. ¹³C{¹H} NMR (125 MHz; under these standard pulse sequences, carbon signals labeled with deuterium were not observed) δ 154.58 (ZrCD₂Ar_q), 135.86 (Ar_q-CD₃), 116.10 (Cp*_q), 110.36 (Cp), 57.85 (CMe₃), 34.06 (CMe₃), 11.76 (Cp*_{Me}) ppm.

Cp*CpZr(NHCMe₃)(CH₂SiMe₃) (3i). A solution of complex **4** (0.075 g, 0.20 mmol) in tetramethylsilane (1.841 g, 20.9 mmol) was heated and stirred in a glass vessel equipped with a vacuum stopcock for 4 h at 105 °C. The volatile materials were removed under vacuum to yield **3i** as a white film (0.084 g, 94%). Analytically pure white crystals of **3i** were obtained on crystallization from *n*-pentane at -30 °C (0.013 g, 15%). ¹H NMR (500 MHz) δ 5.92 (s, 5H, *Cp*), 4.49 (s, 1H, NH), 1.72 (s, 15H, *Cp**), 1.15 (s, 9H, *CMe*₃), 0.33 (s, 9H, Si*Me*₃), -0.34 (d, *J* = 12.1 Hz, 1H, ZrC*H*_ASi), -0.43 (d, *J* = 12.1 Hz, 1H, ZrC*H*_BSi) ppm. ¹³C{¹H} NMR (125 MHz) δ 116.47 (Cp*_{*q*}), 109.23 (*Cp*), 57.00 (*C*Me₃),

34.45 (*CMe*₃), 25.39 (*ZrC*), 12.07 (*Cp**_{*Me*}), 4.35 (Si*Me*₃) ppm. Anal. Calcd for C₂₃H₄₁NSiZr: C, 61.27; H, 9.17; N, 3.11. Found: C, 60.88; H, 9.20; N, 3.14.

Cp*CpZr(NHCMe₃)(*n*-pentyl) (**3j**). A solution of complex **4** (0.102 g, 0.270 mmol) in *n*-pentane (4.195 g, 48.6 mmol) was heated and stirred in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for 4.5 h at 105 °C. The volatile materials were removed under vacuum to a yellow oil (0.109 g, 92%), which was then crystallized at -30 °C from *n*-pentane to yield **3j** (0.039 g, 33%). ¹H NMR (400 MHz) δ 5.84 (s, 1H, *Cp*), 4.65 (s, 1H, *NH*), 1.73 (s, 15H, *Cp**), 1.7-1.6 (m, 2H, *CH*₂), 1.6-1.4 (m, 6H, *CH*₂), 1.15 (s, 9H, *CMe*₃), 1.06 (t (br), *J* = 6.5 Hz, 3H, *CH*₃), 0.50 (td, *J* = 11.9 Hz, *J* = 5.3 Hz, 1H, ZrCH_A), 0.13 (td, *J* = 11.9 Hz, *J* = 5.3 Hz, 1H, ZrCH_B) ppm. ¹³C{¹H} NMR (100 MHz) δ 115.77 (Cp*_q), 109.24 (*Cp*), 56.90 (*C*Me₃), 41.16 (ZrCH₂), 40.81 (*C*H₂), 34.76 (*C*H₂), 34.63 (*CMe*₃), 28.03 (*C*H₂), 14.78 (*C*H₃), 11.76 (Cp*_{*Me*}) ppm. Anal. Calcd for C₂₄H₄₁NZr: C, 66.29; H, 9.50; N, 3.22. Found: C, 65.98; H, 9.67; N, 3.22.

Cp*CpZr(NDCMe₃)(*n*-pentyl-*d*₁₁) (**3**j-*d*₁₂). ¹H NMR (500 MHz) δ 5.85 (s, 5H, *Cp*), 1.73 (s, 15H, *Cp**), 1.16 (s, 9H, *CMe*₃) ppm. ²H NMR (61 MHz, C₆D₆) δ 4.70 (s, ND), 1.7-1.0 (br, *CD*₂), 0.95 (br, *CD*₃), 0.50 (s, *ZrCD*_A), 0.03 (s, *ZrCD*_B) ppm. ¹³C{¹H} NMR (125 MHz; under these standard pulse sequences, carbon signals labeled with deuterium were not observed) δ 115.74 (Cp*_{*q*}), 109.22 (*Cp*), 56.78 (*CMe*₃), 34.57 (*CMe*₃), 11.72 (Cp*_{*Me*}) ppm.

 $Cp*CpZr(NHCMe_3)(2,3-dimethyl-2-butenyl)$ (3k). A solution of complex 4 (0.084 g, 0.22 mmol) in 2,3-dimethyl-2-butene (2.60 g, 30.9 mmol) was heated and stirred in a glass vessel equipped with a vacuum stopcock under an atmosphere of N₂ for

4 h at 105 °C. The volatile materials were removed under vacuum to yield **3k** as an orange oil (0.102 g, 100%). Analytically pure yellow crystals could be obtained from a pentane solution at -30 °C (0.026 g, 26%). ¹H NMR (500 MHz) δ 5.86 (s, 5H, *Cp*), 4.76 (s, 1H, N*H*), 2.00 (s, 3H, *Me*), 1.93 (s, 3H, *Me*), 1.89 (s, 3H, *Me*), 1.68 (s, 15H, *Cp**), 1.19 (s (br), 10H, ZrC*H*_A, NC*Me*₃), 1.04 (d, *J* = 10.4 Hz, 1H, ZrC*H*_B) ppm. ¹³C{¹H} NMR (125 MHz) δ 139.25 (*C*_q), 116.05 (Cp*_q), 110.21 (*Cp*), 109.74 (*C*_q), 57.82 (*C*Me₃), 47.68 (ZrCH₂), 34.59 (NC*Me*₃), 22.52 (*Me*), 21.88 (*Me*), 20.84 (*Me*), 11.73 (Cp*_{*Me*}) ppm. Anal. Calcd for C₂₅H₄₁NZr: C, 67.20; H, 9.25; N, 3.13. Found: C, 67.03; H, 9.03; N, 3.39.

Cp*CpZr-[N(CMe₃)-C(*p***-tol)]=C(***p***-tol)]- (5). In the glovebox, a solution of 1** (0.057 g, 0.13 mmol) in pentane (10.0 mL) was added to 1,2-di-*p*-tolylacetylene^[4] (0.027 g, 0.13 mmol). Upon mixing, the solution turned a dark green in color. The mixture became homogenous after stirring at room temperature for one hour, and the volatile materials were then removed under vacuum. The resulting green crystalline solid was washed three times with 1.0 mL portions of *n*-pentane to yield analytically pure complex **5** (0.046 g, 62%). ¹H NMR (500 MHz, *c*-C₆D₁₂) δ 7.31 (d, *J* = 7.93 Hz, 1H, Ar*H*), 7.02 (d, *J* = 7.78 Hz, 1H, Ar*H*), 6.82 (d, *J* = 7.93 Hz, 1H, Ar*H*), 6.67 (d, *J* = 7.78 Hz, 1H, Ar*H*), 6.56 (d, *J* = 7.93 Hz, 2H, Ar*H*), 6.24 (d, *J* = 7.78 Hz, 2H, Ar*H*), 6.17 (s, 5H, *Cp*), 2.28 (s, 3H, Ar*Me*), 2.08 (s, 3H, Ar*Me*), 1.87 (s, 15H, *Cp**), 1.09 (s, 9H, C*Me*₃) ppm. ¹³C{¹H} NMR (125 MHz, *c*-C₆D₁₂) δ 167.86 (*C*_q), 143.07 (*C*_q), 135.87 (*C*_q), 134.72 (*C*_q), 133.05 (Ar_t), 132.35 (Ar_t), 130.25 (*C*_q), 129.74 (*C*_q), 129.39 (Ar_t), 128.25 (Ar_t), 128.16 (Ar_t), 127.83 (Ar_t), 119.80 (Cp*_q), 110.64 (*Cp*), 56.94 (*C*Me₃), 35.20 (C*Me*₃), 21.45

(Ar*Me*), 21.05 (Ar*Me*), 12.37 (Cp*_{*Me*}) ppm. Anal. Calcd for C₃₅H₄₃NZr: C, 73.89; H, 7.62; N, 2.46. Found: C, 74.25; H, 7.99; N, 2.41.

(Cp)Me₄Cp-CH₂-Zr-C(*p*-tol)=C(*p*-tol)-NHCMe₃ (6). A solution of complex 5 in cyclohexane- d_{12} (500 µL) was heated in a sealed NMR tube at 135 °C for 18 h to give complex 6 in 95% yield (> 90% pure) by ¹H NMR spectroscopy (Figure S-1). Complex 6 was assigned as this regioisomer predominantly by the N*H*-to-NCMe₃ and N*H*-to-NCMe₃ correlations observed by 2D HMBC NMR spectroscopy. ¹H NMR (500 MHz, *c*-C₆D₁₂) δ 6.8-6.7 (m, 6H, Ar*H*), 6.53 (d, *J* = 7.5 Hz, 2H, Ar*H*), 5.59 (s, 5H, *Cp*), 5.46 (s, 1H, N*H*), 3.71 (d, *J* = 17.6 Hz, 1H, ZrCH_A), 3.38 (d, *J* = 17.6 Hz, 1H, ZrCH_B), 2.22 (s, 3H, CpMe), 2.14 (s, 3H, ArMe), 2.12 (s, 3H, ArMe), 2.10 (s, 3H, CpMe), 2.02 (s, 3H, CpMe), 1.96 (s, 3H, CpMe), 1.21 (s, 9H, CMe₃) ppm. ¹³C{¹H} NMR (125 MHz, *c*-C₆D₁₂) δ 186.46 (*C*_q), 161.44 (*C*_q), 150.26 (*C*_q), 141.09 (*C*_q), 134.13 (*C*_q), 133.03 (*C*_q), 130.94 (*C*_q), 128.95 (Ar_i), 128.13 (Ar_i), 127.77 (Ar_i), 119.27 (Cp_qMe), 117.81 (Cp_qMe), 115.96 (Cp_qMe), 111.99 (Cp_qMe), 110.59 (*Cp*), 58.40 (*C*Me₃), 37.90 (ZrCH₂), 34.77 (*CMe*₃), 21.26 (Ar*Me*), 21.23 (Ar*Me*), 12.63 (Cp*Me*), 12.48 (Cp*Me*), 12.25 (Cp*Me*), 11.56 (Cp*Me*) ppm.



Figure S-1. ¹H NMR spectrum of complex 6 in c-C₆D₁₂.

Kinetic Intermolecular Competition Experiments. To obtain a quantitative comparison of relative rates of RH activation, competition studies were carried out with pairs of the hydrocarbon substrates listed below (R_aH_a vs. R_bH_b , Table S-1). Typically, 10 mg of Cp*CpZr=NCMe₃(THF) complex **1** was dissolved in a 600 µL solution comprised of the appropriate molar ratio of hydrocarbons (y/x, Table S-1); concentrations were varied based on the reactivity of the reagent in order to observe both reaction products. In each case, a minimum of 10 molar equivalents (with respect to complex **1**) of each hydrocarbon was utilized to ensure that the concentration of the substrates remained effectively constant during the reactions. The solution was transferred to a J-

Young NMR tube. A sealed capillary tube containing a solution of $SiMe_4$ in CD_2Cl_2 was also added to the NMR tube to serve as an external standard. The sealed J-Young tube was then placed in a 45 °C oil bath and monitored by ¹H NMR spectroscopy.

Table S-1. Kinetic selectivity data for 1 with various hydrocarbon pairs.



R_aH_a	R_bH_b	y/x	$\#{ m H_{b}}/\#{ m H_{a}}^{[a]}$	a/b	$k_{\rm a}/k_{\rm b}$
HC≡CCMe ₃	cyclopentene	45/1	2/1	>20/1	>1800
cyclopentene	benzene	7/1	6/2	2/1	42
cis-1,2-dimethylcyclopropane	mesitylene	1/1.4	9/1	3/1	19
3,3-dimethyl-1-butene	benzene	4.3/1	6/1	1/2	13
1,3-bis(trifluoromethyl)benzene	mesitylene	1/1.8	9/1	1/2.1	2.4
benzene	mesitylene	6/1	9/6	1/8.5	1.1
1,3-diisopropylbenzene	mesitylene	1/7.7	9/1	1/1.1	1.04
mesitylene	SiMe ₄	70/1	12/9	1/10	9.3
mesitylene	<i>n</i> -pentane	8.3/1	6/9	1.8/1	10
benzene	2,3-dimethyl-2-butene	7.5/1	12/6	1.1/1	17
benzene	benzene-d ₆	3.3/1	6/6	2.2/1	7.4
mesitylene	mesitylene- d_{12}	2.1/1	9/9	4.2/1	8.8
<i>n</i> -pentane	<i>n</i> -pentane- d_{12}	1.6/1	6/6	5.6/1	8.9
HC≡CCMe ₃	DC≡CCMe ₃	1/1.9	1/1	1.5/1	$0.8^{[b]}$
3,3-dimethyl-1-butene- d_0	3,3-dimethyl-1-butene- d_1	2.3/1	1/1	3/1	6.9 ^[b]
mesitylene	benzene-d ₆	6/1	6/9	2.5/1	10

[a] Statistical factor to correct for the number of reactive C-H bonds in each substrate. [b] Measured at room temperature.

These competition studies were carried out at 45 °C such that the ratio of the two C-H activation products (a/b, Table S-1) was determined under kinetic conditions. The ratio of products was measured by integration of the Cp or Cp* resonance against the external standard (usually SiMe₄) a minimum of three times during the first three half-

lives to ensure that the ratio of products was invariant within experimental error. The product ratio (**a**/**b**) listed in Table S-1 is based on an average of these one-pulse ¹H NMR integration ratios. With the exception of reactions involving *n*-pentane, no change in the ratio of products was observed at 45 °C, even after prolonged heating (e.g., Figure S-2). For reactions involving *n*-pentane, no change in the product ratio was observed up to 50% conversion. Table S-1 lists the kinetic selectivity (k_a/k_b) of **1** for the hydrocarbon pair, statistically corrected for the number of reactive C-H bonds in each substrate ($\#H_b/\#H_a$).



Figure S-2. Monitoring the kinetic competition reaction of 1 with 1,3bis(trifluoromethyl)benzene versus mesitylene shows no significant change in the product ratio by 1 H NMR spectroscopy, even after 10 days of heating.

Determination of Kinetic Isotope Effects (KIE). The data for the KIE (k_a/k_b) competition studies are presented in Table S-1. The product ratio (**a**/**b**) was determined by comparing an average of the one-pulse ¹H NMR integration values of Cp, Cp*, and *t*-Bu resonances against an average of the (partially deuterated) hydrocarbyl ligand and amide resonances in benzene- d_6 . By monitoring these reactions by ¹H NMR spectroscopy, it was determined that the product ratios remained constant over the course of the reaction, with the exception of *n*-pentane (see below). The majority of the KIE experiments were conducted in a fashion analogous to that for *n*-pentane- d_0 vs. *n*-pentane- d_{12} (described below), with the exception that they were measured after the complete disappearance of starting complex **1**.

KIE for *n*-pentane-*d*₀ vs. *n*-pentane-*d*₁₂. A solution of complex 1 (0.010 g, 0.022 mmol), *n*-pentane-*d*₀ (0.187 g, 2.17 mmol), and *n*-pentane-*d*₁₂ (0.335 g, 3.42 mmol) was transferred to an NMR tube that was subsequently flame-sealed at -196 °C. The tube was placed in a 45 °C oil bath for 32 h (~20% conversion), and the volatile materials were removed under reduced pressure to yield a mixture of $3j/3j-d_{12}$ in a 5.6/1 ratio by ¹H NMR spectroscopy. Note: It was found that the ratio decreased with longer reaction times (e.g., apparent KIE = 5.4 at 50% conversion), presumably due to competitive extrusion of *n*-pentane-*d*₁₂ from products $3j/3j-d_{12}$ at 45 °C over increased reaction times.

KIE for HC=CCMe₃ vs. DC=CCMe₃. To a solution of complex 1 (0.011 g, 0.025 mmol) in *n*-pentane (10 mL) was added a pre-mixed solution of *t*-butylacetylene- d_0 (0.100 g, 1.22 mmol) and *E*-*t*-butylacetylene- d_1 (0.054 g, 0.65 mmol). Upon mixing, the solution became dark purple in color, and then quickly faded to light purple (lilac). The

solution was allowed to stir for 5 min. at room temperature, and the volatile materials were removed under reduced pressure to yield a mixture of $3a/3a-d_1$ in a 1.5/1 ratio by ¹H NMR spectroscopy. Note: no remaining complex 1 was observed by ¹H NMR spectroscopy.

Thermodynamic Intermolecular Competition Experiments. To obtain a quantitative comparison of the relative thermodynamic stability of the products of RH activation, competition experiments were carried out with pairs of the hydrocarbon substrates listed below (R_aH_a vs. R_bH_b, Table S-2). As these competition studies were conducted under reversible conditions (150 °C), Table S-2 lists the thermodynamic selectivity (K_{a/b}) of 1 for each hydrocarbon pair, statistically corrected for the number of reactive C-H bonds in each substrate $(\#H_b/\#H_a)$. Typically, 10 mg of $Cp*CpZr=NCMe_3(THF)$ 1 was dissolved in a 600 µL solution comprised of the appropriate molar ratio of hydrocarbons (y/x, Table S-2). In each case, a minimum of 10 molar equivalents (with respect to 1) of each hydrocarbon was utilized to ensure that the concentration of the substrates remained effectively constant during the reactions. The solution was transferred to an NMR tube and was flame-sealed at -196 °C under vacuum. Typically, the tube was then placed in a 150 °C oil bath for a time period long enough to ensure the reversible extrusion of R_aH_a and R_bH_b from products **a** and **b**, while generating minimal decomposition byproducts. The volatile materials were removed from these solutions under reduced pressure, and the ratio of the products (a/b, Table S-2) was determined by integration of the Cp or Cp* resonances of one-pulse ¹H NMR spectra recorded in benzene- d_6 .

The equilibrium isotope effect (EIE) competition study was conducted in a similar fashion (Table S-2). In this case, the product ratio is determined by comparing the integration values of Cp, Cp*, and *t*-Bu resonances against the (partially deuterated) ligand and amide resonances in benzene- d_6 . It was determined that a temperature of 150 °C was required to extrude benzene- d_6 from product **3f**- d_6 .

Table S-2. Thermodynamic selectivity data for 1 with various hydrocarbon pairs.



$\mathbf{R}_{\mathbf{a}}\mathbf{H}_{\mathbf{a}}$	R_bH_b	y/x	# H _b /	a/b	K _{a/b}	<i>T</i> (°C)	<i>t</i> (h)
			$#\mathbf{H}_{\mathbf{a}}^{[a]}$				
1,3-bis(trifluoromethyl)benzene	mesitylene	35/1	9/1	2.7/1	850	150	192
3,3-dimethyl-1-butene	mesitylene	3.5/1	9/1	1/1.3	24	150	16
cyclopentene	mesitylene	2.8/1	9/2	1/1	13	150	5
benzene	mesitylene	5.4/1	9/6	1/1.5	5.4	150	16
1,3-diisopropylbenzene	mesitylene	1/1.5	9/1	1/1.2	5.2	150	4
cis-1,2-dimethylcyclopropane	mesitylene	1/6	9/1	1/1.2	1.3	150	5
mesitylene	SiMe ₄	37/1	12/9	1/1.6	31	150	5
SiMe ₄	2,3-dimethyl-2-butene	1.2/1	12/12	1.4/1	1.7	105	10
benzene	benzene- d_6	1.2/1	6/6	1/1.2	1.02	150	9

[a] Statistical factor to correct for the number of reactive C-H bonds in each substrate.

General Procedures for measuring the Extrusion of RH from Products 10-R.

The di-*p*-tolylacetylene trapping reagent was used to measure the extrusion of hydrocarbons RH from the Cp*CpZr(R)(NHCMe₃) products **3-R** (Table S-3). Generally, a solution of 10 mg of the product **3-R** and 10 molar equivalents of di-*p*-tolylacetylene in

toluene- d_8 (500 µL) was monitored by ¹H NMR spectroscopy in a flame-sealed NMR tube. The temperatures reported for the extrusion of RH from **3-R** are those for which the disappearance of **3-R** occurred with an approximate half-life of 3 h or more (see Table S-3).



Table S-3. Temperature (T_e) required to extrude RH from products **3-R**.

[a] Product **3-R** formed from reaction of **2** with the explicitly drawn C-H bond in the corresponding substrate RH. [b] Temperature required for extrusion of RH ($t_{1/2} \ge 3$ h).

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