

**Carboamination: Additions of Imine C=N Bonds Across Alkynes
Catalyzed by Imidozirconium Complexes****

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Supporting Information

General Procedures. Unless otherwise noted, reactions and manipulations were performed at ambient temperature in an inert atmosphere (N₂) glovebox, or using standard Schlenk and high vacuum line techniques. Glassware was dried overnight at 150 °C or flame-dried under vacuum immediately prior to use. All NMR spectra were obtained at ambient temperature using Bruker AVB-400 or AVQ-400 spectrometers. ¹H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual protiated solvent. ¹³C NMR chemical shifts (δ) are reported in ppm relative to the carbon resonance of the deuterated solvent. Infrared (IR) spectra were recorded on a Thermo-Nicolet AVATAR 370 FT-IR. Elemental analyses were performed at the University of California, Berkeley Microanalytical facility on a Perkin Elmer 2400 Series II CHNO/S Analyzer.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification.

Tetrahydrofuran, pentane, hexanes and toluene (Fisher) were passed through a column of activated alumina (type A2, size 12 x 32, Purify Co.) under nitrogen pressure and sparged with N₂ prior to use. Benzene-*d*₆ was stored in the glove box over 3A MS. All imines are known compounds and were prepared by condensation of the requisite aniline and benzaldehyde derivatives. Bis(*p*-methoxyphenylacetylene)^[1] and methylzirconocene (*p*-tolyl)amide and azazirconacyclobutene **14a**^[2] were prepared by known literature methods.

Methylzirconocene (*p*-methoxyphenyl)amide 18. Recrystallized *p*-anisidine (237 mg, 1.92 mmol) was dissolved in THF (5 mL) in a scintillation vial. *n*-Butyllithium (1.6 M in hexanes, 1.20 mL, 1.92 mmol) was added by syringe, and the resulting mixture was stirred for 20 min at room temperature. Cp₂Zr(CH₃)Cl (476 mg, 1.75 mmol) in THF (2 mL) was added to the solution. The reaction mixture was stirred an additional 45 min, at which time the solvent was removed under vacuum. Toluene (5 mL) was added, and stirring was resumed for 45 min. The reaction mixture was filtered through a pipet with glass fiber filter paper. The filtrate was collected in a scintillation vial and solvent removed under vacuum. The solid was dissolved in toluene (1 mL), which was, in turn, layered with hexane (2 mL). The vial was placed in the -35 °C freezer overnight. Orange crystals were collected by filtration, and residual solvent was removed under

vacuum to afford 477 mg (76%) of **18**. ^1H NMR (C_6D_6 , 400 MHz) δ 6.80 (d, $J=8.8$ Hz, 2H), 6.66 (d, $J=8.4$ Hz, 2H), 6.53 (s, 1H), 5.63 (s, 10H) 3.41 (s, 3H), 0.27 (s, 3H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 153.9, 149.8, 121.4, 113.8, 109.4, 54.8, 19.6 ppm. Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NOZr}$: C, 60.29; H, 5.90; N, 3.91. Found: C, 60.12; H, 5.73 N, 3.55.

Azazirconacyclobutene 14b. Methylzirconium amide **18** (359 mg, 0.96 mmol) and diphenylacetylene (223 mg, 1.25 mmol) were dissolved in benzene (8 mL) and transferred to a reaction vessel with a Teflon stopper. The vessel was removed from the glovebox, de-gassed with three freeze-pump-thaw cycles and heated at 105 °C for 24 h. The reaction mixture was cooled to room temperature and returned to the glovebox. The solution was transferred to a scintillation vial, and benzene was removed under vacuum. The green solid was dissolved in toluene (2 mL), which was layered with hexane (5 mL), and the vial was placed in the -35 °C freezer overnight. The resulting green crystals were isolated and triturated with pentane, and residual solvent was removed under vacuum to afford 352 mg (68%) of **14b**. ^1H NMR spectroscopy revealed the product to be contaminated with a small amount of the relevant imidozirconocene dimer, leading to failure of elemental analysis. ^1H NMR (C_6D_6 , 400 MHz) δ 7.28 (d, $J=7.7$ Hz, 2H), 7.22 (t, $J=7.5$ Hz, 2H), 6.92-7.04 (m, 6H), 6.70

(d, $J=8.7$ Hz, 2H), 6.26 (d, $J=8.7$ Hz, 2H), 5.84 (s, 10H), 3.30 (s, 3H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 181.5, 153.0, 148.0, 146.8, 132.3, 129.0, 128.3, 128.1, 127.9, 126.6, 123.2, 122.6, 121.3, 114.1, 111.7, 54.7 ppm.

Azazirconacyclobutene 14c. Methylzirconocene (*p*-tolyl)amide (240 mg, 0.67 mmol) and bis(*p*-methoxyphenyl)acetylene (200 mg, 0.84 mmol) were dissolved in benzene (3.5 mL) and transferred to a reaction vessel with a Teflon stopper. The vessel was removed from the glovebox, de-gassed with three freeze-pump-thaw cycles and heated at 135 °C for 24 h. The reaction mixture was cooled to room temperature and returned to the glovebox. The solution was transferred to a scintillation vial, and benzene was removed under vacuum. The green solid was dissolved in toluene (2 mL), which was layered with hexane (4 mL), and the vial was placed in the -35 °C freezer overnight. The resulting green crystals were isolated and triturated with pentane, and residual solvent was removed under vacuum to afford 222 mg of **14c** as a 4:1 mixture of **14c**:alkyne by ^1H NMR spectroscopy. Peaks originating from the alkyne have been subtracted from the data reported here. ^1H NMR (C_6D_6 , 400 MHz) δ 7.26 (d, $J=8.8$ Hz, 2H), 6.85-6.96 (m, 6H), 6.65 (d, $J=8.8$ Hz, 2H), 6.39 (d, $J=8.3$ Hz, 2H), 3.40 (s, 3H), 3.18 (s, 3H), 2.18 (s, 3H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 181.3,

158.7, 156.6, 151.1, 140.4, 130.7, 129.1, 128.4, 126.7, 124.5, 121.3, 120.8, 113.8, 113.6, 111.6, 54.5, 54.2, 20.5 ppm.

Procedure for catalytic chemistry using azazirconacyclobutene 14

as catalyst. Please see Table 1 in the text for the correct reagents to employ. Azazirconacyclobutene **14** (0.025 mmol, 10 mol %) and imine **15** (0.25 mmol) were combined in C₆D₆ (400 μL) in a small vial in the glovebox. The solution was transferred to a medium-walled NMR tube charged with alkyne **16** (0.25 mmol).

Additional C₆D₆ (100 μL) was used to rinse the vial and was added to the reaction mixture in the NMR tube. The NMR tube was fitted with a Cajon adapter, removed from the glove box and flame-sealed under vacuum. The reaction mixture was heated at 145 °C with reaction progress monitored by ¹H NMR spectroscopy. When all imine **15** had been consumed, the NMR tube was cooled to room temperature and the product purified by silica gel chromatography to afford the yellow α,β-unsaturated imine product **17**. The products were pure by NMR spectroscopy after chromatography but were recrystallized as below to analytical purity.

α,β-Unsaturated imine 17a. The reaction was conducted at 145 °C for 96 h. Chromatography (50% CH₂Cl₂:hexane) afforded 69 mg (71%) **17a** as a yellow solid. The product was recrystallized from hexane to analytical purity. ¹H NMR (C₆D₆, 400 MHz) δ 8.36

(d, $J=7.3$ Hz, 2H), 7.36 (dd, $J=8.3, 9.0$ Hz, 4H), 7.03–7.15 (m, 3H), 6.91–7.03 (m, 4H), 6.89 (d, $J=8.0$ Hz, 2H), 6.74 (d, $J=6.8$ Hz, 4H), 1.94 (s, 3H), 1.93 (s, 3H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 167.2, 149.1, 139.8, 138.3, 137.8, 135.6, 133.6, 132.8, 130.8, 130.6, 129.5, 129.3, 129.1, 128.70, 128.68, 128.5, 127.1, 126.3, 119.4, 20.8, 20.5 ppm. FT-IR (ZnSe): 1610 (s), 1503 (s) cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{N}$: C, 89.88; H, 6.50; N, 3.61. Found: C, 89.88; H, 6.54; N, 3.90.

α,β -Unsaturated imine 17b. The reaction was conducted at 145 °C for 40 h. Chromatography (60% CH_2Cl_2 :hexane) afforded 72 mg (71%) **17b** as a yellow solid. The product was recrystallized from hexane/ CH_2Cl_2 to analytical purity. ^1H NMR (C_6D_6 , 400 MHz) δ 8.38 (d, $J=7.3$ Hz, 2H), 7.33–7.42 (m, 4H), 7.06–7.15 (m, 3H), 6.91–7.06 (m, 4H), 6.90 (d, $J=8.0$ Hz, 2H), 6.75 (d, $J=7.8$ Hz, 2H), 6.49 (d, $J=8.5$ Hz, 2H), 3.13 (s, 3H), 1.95 (s, 3H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 167.3, 159.6, 149.1, 139.8, 138.3, 132.8, 130.8, 130.6, 130.2, 129.0, 128.9, 128.74, 128.71, 128.6, 127.6, 127.4, 126.2, 119.4, 114.0, 54.4, 20.6 ppm. FT-IR (ZnSe): 1605 (s), 1504 (s) cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{NO}$: C, 86.32; H, 6.24; N, 3.47. Found: C, 86.07; H, 6.27; N, 3.46.

α,β -Unsaturated imine 17c. The reaction was conducted at 145 °C for 80 h. Chromatography (70% CH_2Cl_2 :hexane) afforded 85 mg (82%) **17c** as a yellow solid. The product was recrystallized

from hexane/CH₂Cl₂ to analytical purity. ¹H NMR (C₆D₆, 400 MHz) δ 8.47 (d, *J*=7.2 Hz, 2H), 7.49 (d, *J*=8.7 Hz, 2H), 7.40 (d, *J*=7.5 Hz, 2H) 6.90–7.15 (m, 9H), 6.76 (d, *J*=8.0 Hz, 2H), 6.25 (d, *J*=8.8 Hz, 2H), 2.32 (s, 6H), 1.94 (s, 3H) ppm. ¹³C {¹H} NMR (C₆D₆, 100 MHz) δ 168.1, 149.8, 149.4, 140.2, 138.5, 132.7, 131.6, 130.9, 130.7, 130.6, 128.9, 128.8, 128.7, 128.5, 126.8, 126.0, 124.6, 119.6, 112.0, 39.3, 20.6 ppm. FT-IR (ZnSe): 1598 (s), 1504 (s) cm⁻¹. Anal. Calcd for C₃₀H₂₈N₂: C, 86.50; H, 6.78; N, 6.73. Found: C, 86.30; H, 6.73; N, 6.67.

α,β-Unsaturated imine 17d. The reaction was conducted at 145 °C for 30 h. Chromatography (2:1 CH₂Cl₂:hexane) afforded 78 mg (80%) **17d** as a yellow solid. The product was recrystallized from hexane/CH₂Cl₂ to analytical purity. ¹H NMR (C₆D₆, 400 MHz) δ 8.33 (d, *J*=7.3 Hz, 2H), 7.41 (d, *J*=7.5 Hz, 2H), 7.38 (d, *J*=7.5 Hz, 2H), 7.03–7.15 (m, 4H), 6.84–7.02 (m, 8H), 6.49 (d, *J*=8.7 Hz, 2H), 3.15 (s, 3H) ppm. ¹³C {¹H} NMR (C₆D₆, 100 MHz) δ 166.3, 156.8, 144.4, 139.5, 138.5, 136.8, 136.4, 130.8, 130.6, 128.9, 128.7, 128.64, 128.57, 128.5, 127.9, 126.4, 121.2, 113.6, 54.4 ppm. FT-IR (ZnSe): 1606 (s), 1501 (s) cm⁻¹. Anal. Calcd for C₂₈H₂₃NO: C, 86.34; H, 5.95; N, 3.60. Found: C, 86.18; H, 5.93; N, 3.55.

α,β-Unsaturated imine 17e. The reaction was conducted at 145 °C for 52 h. Chromatography (60% CH₂Cl₂:hexane) afforded 81 mg

(80%) **17e** as a yellow solid. The product was recrystallized from hexane to analytical purity. ^1H NMR (C_6D_6 , 400 MHz) δ 8.37 (d, $J=7.1$ Hz, 2H), 7.35-7.42 (m, 4H), 7.05-7.15 (m, 4H), 6.89-7.04 (m, 5H), 6.74 (d, $J=7.9$ Hz, 2H), 6.51 (d, $J=8.8$ Hz, 2H), 3.14 (s, 3H), 1.92 (s, 3H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 166.7, 156.8, 144.5, 139.7, 138.5, 137.8, 135.8, 133.6, 130.8, 130.6, 129.3, 129.0, 128.7, 128.61, 128.59, 127.6, 126.3, 121.3, 113.6, 54.4, 20.8 ppm. FT-IR (ZnSe): 1610 (s), 1502 (s) cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{NO}$: C, 86.32; H, 6.24; N, 3.47. Found: C, 86.17; H, 6.09; N, 3.41.

α,β -Unsaturated imine 17f. The reaction was conducted at 145 $^\circ\text{C}$ for 30 h. Chromatography (2:1 CH_2Cl_2 :hexane) afforded 86 mg (85%) **17f** as a yellow solid. The product was recrystallized from hexane to analytical purity. ^1H NMR (C_6D_6 , 400 MHz) δ 8.34 (d, $J=7.0$ Hz, 3H), 7.36-7.41 (m, 3H), 7.04-7.15 (m, 4H), 6.91-7.03 (m, 5H), 6.87 (t, $J=7.7$ Hz, 1H), 6.73 (d, $J=7.5$ Hz, 1H), 6.51 (d, $J=8.8$ Hz, 2H), 3.15 (s, 3H), 1.98 (s, 3H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 166.4, 156.7, 144.4, 139.6, 138.6, 137.7, 136.6, 136.2, 131.0, 130.5, 130.1, 128.7, 128.6, 128.5, 128.4, 127.6, 126.3, 125.7, 121.2, 113.6, 54.4, 20.9 ppm. FT-IR (ZnSe): 1612 (s), 1501 (s) cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{N}$: C, 89.88; H, 6.50; N, 3.61. Found: C, 89.53; H, 6.52; N, 3.50.

α,β -Unsaturated imine 17g. The reaction was conducted at 160 °C for 96 h. Chromatography (2:1 CH₂Cl₂:hexane) afforded 65 mg (58%) **17g** as a very light yellow solid. The product was recrystallized from hexane:CH₂Cl₂ to analytical purity. ¹H NMR (C₆D₆, 400 MHz) δ 8.37 (d, *J*=8.7 Hz, 2H), 7.47 (d, *J*=8.1 Hz, 2H), 7.37 (d, *J*=8.8 Hz, 2H), 7.04 (s, 1H), 6.96 (d, *J*=8.2 Hz, 2H), 6.82 (d, *J*=8.2 Hz, 2H), 6.79 (d, *J*=8.2 Hz, 2H), 6.72 (d, *J*=9.0 Hz, 2H), 6.63 (d, *J*=8.9 Hz, 2H), 3.18 (s, 3H), 3.14 (s, 3H), 1.97 (s, 6H) ppm. ¹³C {¹H} NMR (C₆D₆, 100 MHz) δ 166.7, 162.0, 159.4, 149.4, 137.3, 135.5, 134.0, 132.5, 132.2, 131.1, 130.5, 129.3, 129.0, 128.9, 128.2, 119.6, 114.2, 114.0, 54.43, 54.37, 20.8, 20.6 ppm. FT-IR (ZnSe): 1600 (s), 1509 (s) cm⁻¹. Anal. Calcd for C₃₁H₂₉NO₂: C, 83.19; H, 6.53; N, 3.13. Found: C, 83.19; H, 6.68; N, 3.06.

References

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