Room Temperature *Z*-Selective Homocoupling of Olefins by Tungsten Catalysts

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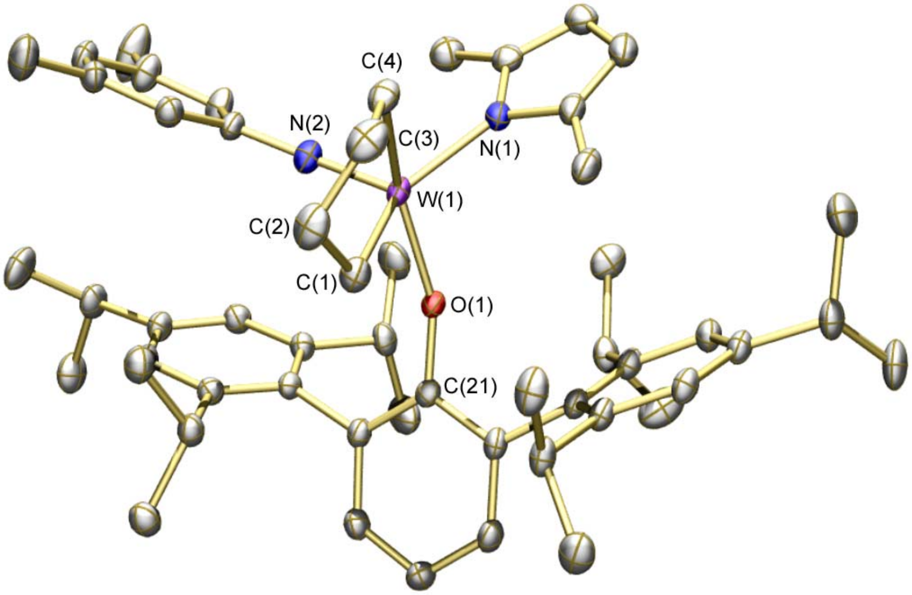

Figure S1. Thermal ellipsoid drawing of W(3,5-$Me_2C_6H_3N$)(2,5-Me_2pyr)(OHIPT)(C_4H_8) (**11**). Selected distances (Å) and angles (deg): W(1)-N(2) = 1.7571(19) Å, W(1)-N(1) = 2.0540(17) Å, W(1)-O(1) = 1.9796(14) Å, W(1)-C(1) = 2.048(2) Å, W(1)-C(2) = 2.359(3) Å, W(1)-C(3) = 2.076(2) Å, W(1)-N(2)-C(61) = 164.33(16)°, W(1)-O(1)-C(11) = 157.73(14)°, N(1)-W(1)-C(1) = 131.10(9)°, N(1)-W(1)-C(3) = 144.95(9)°, C(1)-W(1)-C(3) = 83.26(10)°.

Experimental Section

General. All manipulations of air and moisture sensitive materials were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or on a dual-manifold Schlenk line. Glassware, including NMR tubes, were oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns and stored over 4 Å Linde-type molecular sieves. Dimethoxyethane, cyclooctene, and cyclopentene were vacuum distilled from a dark purple solution of sodium benzophenone ketyl, and degassed three times by freeze-pump-thaw technique. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. Proton and carbon NMR spectra were acquired at room temperature (unless otherwise noted) using Varian spectrometers and referenced to the residual ^{1}H/^{13}C resonances of the deuterated solvent (^{1}H: $CDCl_3$, δ 7.26; C_6D_6, δ 7.16; CD_2Cl_2, δ 5.32; C_7D_8, δ 7.09, 7.00, 6.98, 2.09. ^{13}C: $CDCl_3$, δ 77.23; C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00; C_7D_8, δ 137.86, 129.24, 128.33, 125.49, 20.4) and are reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

W(3,5-$Me_2C_6H_3N)_2Cl_2$(dme) (4). 3,5-$Me_2C_6H_3NH_2$ (7.34 mL, 58.8 mmol) was added via syringe to a suspension of WO_2Cl_2 (8.430 g, 29.4 mmol) in dimethoxyethane (150 mL). Triethylamine (16.4 mL, 117.6 mmol, 4 equiv) and chlorotrimethylsilane (37.32 mL, 294 mmol) were added via syringe. The solution became deep red. The reaction mixture was stirred at room temperature overnight. Copius amounts of salts were formed. The deep red mixture was filtered through Celite and the salts were washed with toluene and dimethoxyethane. The solvents were removed from the filtrate under vacuum to leave a red oil, which was used in the next step without purification.

W(3,5-$Me_2C_6H_3N)_2(CH_2CMe_2Ph)_2$ (5). A 0.5 M diethyl ether solution of $ClMgCH_2CMe_2Ph$ (117.6 mL, 58.8 mmol) was added dropwise to a -35 °C solution of W(3,5-$Me_2C_6H_3N)_2Cl_2$(dme) (29.4 mmol) in diethyl ether (100 ml). The reaction mixture was stirred overnight at room temperature. The volatiles were removed from the dark yellow solution under vacuum. The dialkyl species was extracted with THF (100 mL), the THF was filtered through Celite, and the solvent was removed from the filtrate under vacuum. The compound was washed with minimalether to generate a yellow solid, which can be recrystallized further from THF to obtain 5.35 g of yellow crystals (yield over two steps = 27%): ^{1}H NMR (500 MHz, C_6D_6) δ 7.39 (d, 4H, *Ar*, *J* = 7.5 Hz), 7.24-7.05 (m, 10H, *Ar*), 6.51 (s, 2H, *Ar*), 2.08 (s, 12H, *Me*), 1.62 (s, 12H, *Me*), 1.37 (s, 4H, C*H*$_2$); ^{13}C NMR (125 MHz, C_6D_6) δ 153.6, 137.3, 128.8, 127.4, 126.6, 125.7, 96.7, 44.2, 35.3, 21.7. Anal. Calcd for $C_{36}H_{44}N_2W$: C, 62.79; H, 6.44; N, 4.07. Found: C, 62.40; H, 6.43; N, 4.08.

$W(3,5\text{-}Me_2C_6H_3N)(OTf)_2(CHCMe_2Ph)(dme)$ (6). Triflic acid (2.80 g, 18.7 mmol, 3 equiv) was added dropwise to a -35 °C solution of $W(3,5\text{-}Me_2C_6H_3N)_2(CH_2CMe_2Ph)_2$ (4.29 g, 6.2 mmol, 1 equiv) in diethyl ether (200 mL). The reaction mixture was stirred overnight at room temperature. The volatiles were removed from the orange solution under vacuum. The bistriflate species was extracted with benzene (100 mL), the mixture was filtered through Celite, and the solvents were removed from the filtrate *in vacuo*. Pentane (10 mL) was added and the yellow solid that formed was filtered off and washed with pentane; yield 3.44 g (67%) of pale yellow solid. The compound is obtained as a mixture of *cis* and *trans* isomers: ^{1}H NMR (500 MHz, C_6D_6) *cis*-**6** δ 11.91 (s, 1H, *syn*-W=C*H*, J_{CH} = 122.8 Hz), 7.42 (d, 2H, *Ar*, *J* = 7.5 Hz), 7.11 (t, 2H, *Ar*, *J* = 7.5 Hz), 7.05 (s, 2H, *Ar*), 6.95 (t, 1H, *Ar*, *J* = 7.5 Hz), 3.15 (s, 3H, O*Me*), 3.10 (s, 3H, O*Me*), 2.87-2.79 (m, 1H, OCH_2), 2.22-2.15 (m, 1H, OCH_2), 2.08 (s, 3H, *Me*), 2.03 (s, 6H, *Me*), 1.61 (s, 3H, *Me*); ^{1}H NMR (500 MHz, C_6D_6) *trans*-**6** δ 10.76 (s, 1H, *syn*-W=C*H*, J_{CH} = 116.8 Hz), 7.59 (s, 2H, *Ar*), 7.52 (d, 2H, *Ar*, *J* = 7.5 Hz), 7.26 (t, 2H, *Ar*, *J* = 7.5 Hz), 7.03 (t, 2H, *Ar*, *J* = 7.5 Hz), 6.53 (s, 1H, *Ar*), 3.09 (s, 3H, O*Me*), 3.04 (s, 3H, O*Me*), 3.05 (t, 2H, OCH_2, *J* = 5.0 Hz), 2.62 (t, 2H, OCH_2, *J* = 5.0 Hz), 2.01 (s, 6H, *Me*), 1.98 (s, 6H, *Me*); ^{13}C NMR (125 MHz, C_6D_6) δ 288.0, 154.7, 153.4, 139.1, 131.4, 129.0, 128.7, 126.9, 126.8, 124.1, 121.6, 119.0, 116.5, 74.4, 70.2, 64.8, 64.4, 63.3, 63.2, 55.0, 34.1, 33.7, 21.7, 21.3; ^{19}F (282 MHz, C_6D_6) *cis*-**6** δ -76.71; ^{19}F (282 MHz, C_6D_6) *trans*-**6** δ -76.21, -77.64. Anal. Calcd for $C_{24}H_{31}F_6NO_8S_2W$: C, 35.01; H, 3.79; N, 1.70. Found: C, 34.66; H, 3.69; N, 1.46.

$W(3,5\text{-}Me_2C_6H_3N)(CHCMe_2Ph)(NC_4H_4)_2(dme)$ (7a). Solid lithium pyrrolide (64.0 mg, 0.8 mmol, 2 equiv) was added portionwise to a -35 °C solution of $W(3,5\text{-}Me_2C_6H_3N)(OTf)_2(CHCMe_2Ph)(dme)$ (361 mg, 0.4 mmol, 1 equiv) in toluene (20 mL). The reaction mixture was stirred at room temperature for 3 hours. The solution became dark brown. The reaction mixture was filtered through Celite and the volatiles were removed from the filtrate *in vacuo*. Pentane was added to the brown residue and the yellow-brown solid was collected on a medium porosity frit and washed with pentane; yield 105 mg (36%): ^{1}H NMR (500 MHz, C_6D_6) δ 10.33 (s, 1H, *syn*-W=C*H*, J_{CH} = 114.0 Hz), 7.48 (d, 2H, *Ar*, *J* = 7.5 Hz), 7.23 (t, 2H, *Ar*,

J = 7.5 Hz), 7.10 (br, 4H, NC_4H_4), 7.05 (t, 1H, *Ar*, J = 7.5 Hz), 7.01 (br, 2H, *Ar*), 6.72 (br, 4H, NC_4H_4), 6.49 (s, 1H, *Ar*), 2.99 (s, 6H, *OMe*), 2.24 (s, 4H, OCH_2), 1.90 (s, 6H, *Me*), 1.84 (s, 6H, *Me*); ^{13}C NMR (125 MHz, C_6D_6) δ 325.8, 139.0, 133.5, 129.3, 128.7, 127.2, 126.3, 124.6, 109.0, 71.6, 62.1, 54.1, 21.5. Anal. Calcd for $C_{30}H_{39}N_3O_2W$: C, 54.80; H, 5.98; N, 6.39. Found: 54.64; H, 5.94; N, 6.10.

$W(3,5\text{-}Me_2C_6H_3N)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$ (7b). Solid $2,5\text{-}Me_2NC_4H_2Li$ (132.6 mg, 1.3 mmol, 2 equiv) was added portionwise to a -35 °C solution of $W(3,5\text{-}Me_2C_6H_3N)(OTf)_2(CHCMe_2Ph)(dme)$ (540.2 g, 0.7 mmol, 1 equiv) in toluene (20 mL). The reaction mixture was stirred overnight at room temperature. The solution became dark yellow. The reaction mixture was filtered through Celite. The volatiles were removed from the filtrate *in vacuo*. Pentane was added and the yellow solid obtained was collected on a medium porosity frit and washed with pentane (355.8 mg, yield = 87%): ^1H NMR (500 MHz, C_6D_6) δ 10.65 (s, 1H, *syn*-W=C*H*, J_{CH} = 125.7 Hz), 7.37 (d, 2H, *Ar*, J = 8.0 Hz), 7.12 (t, 2H, *Ar*, J = 8.0 Hz), 7.00 (t, 1H, *Ar*, J = 8.0 Hz), 6.66 (s, 2H, *Ar*), 6.55 (s, 1H, *Ar*), 5.95 (br, 4H, NC_4H_2), 2.19 (s, 12H, *Me*), 2.03 (s, 6H, *Me*), 1.68 (s, 6H, *Me*); ^{13}C NMR (125 MHz, C_6D_6) δ 278.4, 156.6, 152.4, 140.4 (br), 138.6, 128.7, 127.4, 126.0, 124.3, 107.1 (br), 55.4, 33.8, 21.6, 18.4. Anal. Calcd for $C_{30}H_{37}N_3W$: C, 57.79; H, 5.98; N, 6.74. Found: C, 57.48; H, 5.86; N, 6.61.

$W(3,5\text{-}Me_2C_6H_3N)(CHCMe_2Ph)(2\text{-}MesNC_4H_3)_2$ (7c). Solid $2\text{-}MesNC_4H_3Na$ (356.2 mg, 1.719 mmol, 2 equiv) was added portionwise to a -35 °C solution of $W(3,5\text{-}Me_2C_6H_3N)(OTf)_2(CHCMe_2Ph)(dme)$ (708 mg, 0.860 mmol, 1 equiv) in toluene (20 mL). The reaction mixture was stirred at room temperature for 3 hours. The reaction mixture was filtered through Celite. The volatiles were removed filtrate *in vacuo*. Diethyl ether was added and the yellow solid was collected on a medium porosity frit and washed with ether; yield 445 mg (65%): ^1H NMR (500 MHz, C_6D_6) δ 7.61 (s, 1H, *syn*-W=C*H*, J_{CH} = 111.7 Hz, J_{WH} = 15.4 Hz), 7.36 (d, 2H, *Ar*, J = 7.6 Hz), 7.12 (t, 2H, *Ar*, J = 7.6 Hz), 7.05 (d, 2H, *Ar*, J = 1.6 Hz), 7.00 (t, 1H, *Ar*, J = 7.6 Hz), 6.81 (s, 2H, *Ar*), 6.62 (s, 2H, *Ar*), 6.53 (s, 1H, *Ar*), 6.46 (t, 2H, *Ar*, J = 2.9 Hz), 6.43 (s, 2H, *Ar*), 6.16 (s, 2H, *Ar*, J = 1.6 Hz), 2.13 (s, 6H, *Me*), 2.01 (s, 6H, *Me*), 1.98 (s, 12H, *Me*), 1.47 (s, 6H, *Me*); ^{13}C NMR (125 MHz, C_6D_6) δ 262.4, 156.9, 151.1, 140.9, 140.4, 139.7, 138.3,137.6, 134.3, 133.5, 129.2, 129.0, 128.9, 128.8, 127.0, 126.5, 124.5, 113.5, 113.4, 111.7, 53.7, 33.5, 21.6, 21.3. Anal. Calcd for $C_{44}H_{49}N_3W$: C, 65.75; H, 6.15; N, 5.23. Found: C, 65.57; H, 5.93; N, 5.12.

W(3,5-Me$_2$C$_6$H$_3$N)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(OHIPT) (8a). A J-Young NMR tube was charged with a solution of W(3,5-Me$_2$C$_6$H$_3$N)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (127 mg, 0.203 mmol) and HIPTOH (101 mg, 0.203 mmol) in a total of 1.0 mL C_6D_6. The NMR tube was heated at 80 °C overnight for total consumption of starting material. Formation of W(3,5-Me$_2$C$_6$H$_3$N)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(OHIPT) was observed by ^{1}H NMR spectroscopy. The volatiles were removed *in vacuo* and the residue was recrystallized from pentane; yield 150 mg of yellow crystals (72%): ^{1}H NMR (500 MHz, C_6D_6) δ 9.53 (s, 1H, *syn*-W=C*H*, J_{CH} = 119.9 Hz, J_{WH} = 16.0 Hz), 7.25 (d, 2H, *Ar*, *J* = 7.6 Hz), 7.18 (s, 2H, *Ar*), 7.14 (s, 3H, *Ar*), 7.07 (t, 2H, *Ar*, *J* = 7.6 Hz), 6.99 (d, 2H, *Ar*, *J* = 7.6 Hz), 6.94 (t, 1H, *Ar*, *J* = 7.6 Hz), 6.57 (s, 2H, *Ar*), 6.47 (s, 1H, *Ar*), 5.97 (s, 2H, NC$_4$*H*$_2$), 3.05 (sept, 2H, MeC*H*Me, *J* = 6.8 Hz), 2.96 (sept, 2H, MeC*H*Me, *J* = 6.8 Hz), 2.84 (sept, 2H, MeC*H*Me, *J* = 6.8 Hz), 1.98 (s, 6H, *Me*), 1.91 (s, 6H, *Me*), 1.55 (s, 3H, *Me*), 1.34 (s, 3H, *Me*), 1.30 (d, 6H, *Me*CH*Me*, *J* = 6.8 Hz), 1.24 (t, 12H, *Me*CH*Me*, *J* = 6.8 Hz), 1.17 (d, 6H, *Me*CH*Me*, *J* = 6.8 Hz), 1.12 (d, 12H, *Me*CH*Me*, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 262.9, 159,1, 156.9, 152.3, 148.8, 147.4, 138.0, 137.2, 134.5, 132.5, 132.4, 127.2, 126.2, 125.1, 122.7, 122.1, 121.9, 110.4, 53.7, 35.1, 24.5 (br), 21.5 (br), 18.5 (br). Anal. Calcd for $C_{60}H_{78}N_2OW$: C, 70.16; H, 7.65; N, 2.73. Found: C, 70.26; H, 7.53; N, 2.72.

W(3,5-Me$_2$C$_6$H$_3$N)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(OTPP) (8b). A 20 mL vial equipped with a magnetic stir bar was charged with W(3,5-Me$_2$C$_6$H$_3$N)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (303 mg, 0.486 mmol) and tetraphenylphenol (194 mg, 0.486 mmol). Diethyl ether (5 mL) was added and the reaction mixture was stirred at room temperature for 3 h until the phenol was completely consumed. The volatiles were then removed *in vacuo*, and the yellow solid was washed with diethyl ether; yield 358 mg (79%): ^{1}H NMR (500 MHz, C_6D_6) δ 8.45 (s, 1H, *syn*-

W=C*H*, J_{CH} = 115.8 Hz, J_{WH} = 15.0 Hz), 7.35 (s, 1H, *Ar*), 7.32-6.81 (m, 25H, *Ar*), 6.49 (s, 1H, *Ar*), 6.42 (s, 2H, *Ar*), 6.10 (s, 2H, NC_4H_2), 2.15 (s, 6H, *Me*), 1.94 (s, 6H, *Me*), 1.67 (s, 3H, *Me*), 1.35 (s, 3H, *Me*); ^{13}C NMR (125 MHz, C_6D_6) δ 260.6, 159.4, 156.9, 152.1, 142.5, 142.2, 138.0, 137.3, 135.5, 131.9 (br), 131.1, 130.6, 128.8, 128.7, 128.6, 128.5, 128.3, 127.6, 127.1, 126.7, 126.3, 124.8, 110.7, 53.2, 34.5, 32.4, 21.5, 17.5. Anal. Calcd for $C_{54}H_{50}N_2OW$: C, 69.98; H, 5.44; N, 3.02. Found: C, 70.28; H, 5.53; N, 3.22.

W(3,5-$Me_2C_6H_3N$)(C_3H_6)(NC_4H_4)(OHIPT) (9a). A 25 mL Schlenk flask equipped with a magnetic stir bar and a side arm was charged with a mixture of a pentane and diethyl ether (1:1) solution of W(3,5-$Me_2C_6H_3N$)($CHCMe_2Ph$)(NC_4H_2)$_2$(dme) (256 mg, 0.390 mmol) and HIPTOH (199 mg, 0.389 mmol, 1 equiv). The reaction mixture was stirred at room temperature for 15 minutes. The mixture was degassed three times and then exposed to 1 atm of ethylene for 15 minutes. The volume of the reaction mixture was concentrated to half. After exposing the reaction mixture again to 1 atm of ethylene, yellow solids were generated. The solids were collected on a medium porosity frit and washed with pentane; yield 240 mg (68%). X-ray quality crystals were grown from a heptane solution at -35 °C: ^1H NMR (500 MHz, C_6D_6) δ 7.54 (br, 2H, *Ar*), 7.26 (d, 2H, *Ar*, *J* = 7.5 Hz), 7.24 (s, 4H, *Ar*), 6.90 (t, 1H, *Ar*, *J* = 7.5 Hz), 6.33 (s, 3H, *Ar*), 6.28 (s, 2H, *Ar*), 4.11 (br, 2H, WCH_α), 3.52 (br, 2H, WCH_α), 2.90 (sept, 2H, MeC*H*Me, *J* = 6.8 Hz), 3.40-2.40 (br, 4H, MeC*H*Me), 1.80 (s, 6H, *Me*), 1.32 (d, 12H, *Me*CH*Me*, *J* = 6.8 Hz), 1.30-1.10 (br, 24H, *Me*CH*Me*), -0.82 (br, 1H, WCH_β), -1.25 (br, 1H, WCH_β). The ^{13}C NMR could not be recorded due to the instability of the complex in solution. Anal. Calcd for $C_{51}H_{68}N_2OW$: C, 67.39; H, 7.54; N, 3.08. Found: C, 67.55; H, 7.53; N, 3.01.

W(3,5-$Me_2C_6H_3N$)(C_3H_6)(2-$MesNC_4H_3$)(OTPP) (9b). A 25 mL Schlenk flask was charged with a 10 mL toluene solution of W(3,5-$Me_2C_6H_3N$)($CHCMe_2Ph$)(2-$MesNC_4H_3$)$_2$ (178 mg, 0.222 mmol) and tetraphenylphenol (88.3 mg, 0.222 mmol, 1 equiv). The reaction mixture was heated at 60 °C for two days, until the starting material was totally consumed. Formation of W(3,5-$Me_2C_6H_3N$)($CHCMe_2Ph$)(2-$MesNC_4H_3$)(OTPP) was observed by ^1H NMR spectroscopy [δ 8.56 (s, 1H, *syn*-W=C*H*, J_{CH} = 113.6 Hz, J_{WH} = 14.3 Hz)]. A 25 mL Schlenk flask was charged with a 4 mL pentane solution of W(3,5-$Me_2C_6H_3N$)($CHCMe_2Ph$)(2-$MesNC_4H_3$)(OTPP) (226 mg, 0.222 mmol). Two mL of diethyl ether were added to the reaction mixture. The flask was degassed three times and then exposed to 1 atm of ethylene. A yellow precipitate formed immediately. The yellow solid was collected on a medium porosity frit and washed with pentane; yield 139 mg (68%): ^{1}H NMR (500 MHz, C_6D_6) δ 8.33 (s, 1H, *Ar*), 8.04 (br, 2H, *Ar*), 7.40-6.84 (m, 19H, *Ar*), 6.80 (t, 1H, *Ar*, *J* = 2.8 Hz), 6.40 (s, 1H, *Ar*), 6.36 (s, 2H, *Ar*), 6.22 (s, 1H, *Ar*), 5.81 (s, 2H, *Ar*), 3.72 (m, 2H, WCH_α), 3.16 (m, 2H, WCH_α), 2.22 (s, 6H, *Me*), 1.83 (s, 6H, *Me*), 1.82 (s, 3H, *Me*), -1.38 (br, 1H, WCH_β), -1.95 (br, 1H, WCH_β); ^{13}C NMR (125 MHz, C_6D_6) δ 157.5, 150.8, 143.2, 142.9, 142.8, 139.1, 139.0, 137.4, 136.6, 136.0, 133.5 (br), 132.7 (br), 132.0, 131.9, 131.8, 131.6, 130.7, 130.5, 129.1, 129.0, 128.9, 128.0, 127.0, 126.9, 125.5, 125.1, 111.9, 110.7, 98.3 (br), 66.3, 22.3, 22.2, 21.4, -4.8 (br). Anal. Calcd for $C_{54}H_{50}N_2OW$: C, 69.98; H, 5.44; N, 3.02. Found: C, 70.13; H, 5.40; N, 2.97.

W(3,5-$Me_2C_6H_3N$)(CH_2)(2,5-$Me_2NC_4H_2$)(OHIPT) (10). A J-Young NMR tube was charged with a solution of W(3,5-$Me_2C_6H_3N$)($CHCMe_2Ph$)(2,5-Me_2pyr)(OHIPT) (87 mg, 0.085 mmol) in 1.0 mL C_6D_6 (85 mM). The NMR tube was degassed three times and then filled with 1 atm of ethylene. The NMR tube was kept at 20 °C overnight. After the ethylene was consumed, the NMR tube was exposed again to 1 atm of C_2H_4, until the starting material was totally consumed. The color changed from yellow to red. Formation of W(3,5-$Me_2C_6H_3N$)(CH_2)(2,5-$Me_2NC_4H_2$)(OHIPT) was observed by ^{1}H NMR spectroscopy: ^{1}H NMR (500 MHz, C_6D_6) – selected peaks- δ 10.13 (d, 1H, W=CH_2, J_{CH} = 160.5 Hz, J_{WH} = 26.6 Hz, J_{HH} = 9.0 Hz), 8.71 (d, 1H, W=CH_2, J_{CH} = 133.5 Hz, J_{HH} = 9.0 Hz). The volatile materials were removed under vacuum, and 0.5 mL of pentane was added. That solution was allowed to stand at -35 °C for two months. Red crystals of the metallacyclopentane complex, W(3,5-$Me_2C_6H_3N$)(2,5-Me_2pyr)(OHIPT)(C_4H_8) (**11**), were formed. An X-ray structural study of one of these crystals is shown in Figure S1.

***E,Z,E*-$CH_3(CH_2)_4CH=CH(CH_2)_2CH=CH(CH_2)_2CH=CH(CH_2)_4CH_3$ (12).** Solid W(3,5-$Me_2C_6H_3N$)(C_3H_6)(NC_4H_4)(OHIPT) (5.0 mg, 0.0055 mmol, 2 mol%) was added to neat olefin E-CH_2=CH(CH_2)$_2$CH=CH(CH_2)$_4$$CH_3$ (42.0 mg, 0.275 mmol). The reaction mixture was stirred at room temperature. The conversion was monitored by ^{1}H NMR spectroscopy. After 8 h, 61% conversion of the starting material has been observed. No further change in conversion was determined. The volatile materials were removed under vacuum. The mixture was plugged through silica gel and the olefin was isolated (45.6 mg, yield = 60%). ^{1}H NMR (500 MHz, C_6D_6) δ 5.54-5.42 (m, 6H), 2.20-1.96 (m, 12H), 1.40-1.20 (m, 12H), 0.89 (t, 6H, *Me*, J = 6.5 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 131.5, 130.4, 130.2, 33.6, 33.4, 32.1, 30.1, 28.3, 23.3, 14.7.

X-Ray Structure Determination

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker D8 three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Cu K_α radiation (λ = 1.54178 Å). All structures were solved by direct methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[2] using established refinement techniques.[3] All non-hydrogen atoms were refined anisotropically. Unless otherwise noted below all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Compound **9a** crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit along with one molecule of heptane. The hydrogen atoms on C81, C82 and C83 were observed in the difference Fourier synthesis, however, they were included into the model at geometrically calculated positions and refined using a riding model.

Compound **9b** crystallizes in the monoclinic space group $C2/c$ with one molecule and half a molecule of diethylether in the asymmetric unit. The diethylether is located near a two-fold rotation axis, which leads to a non-integer number in the empirical formula for oxygen. The diethylether is disordered over four positions, two of which are pairwise related to the other two by the crystallographic twofold. This disorder was refined with the help of distance restraints on the 1,2-distances and similarity restraints on the 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Coordinates for the hydrogen atoms on C1, C2 and C3 were taken from the difference Fourier synthesis and refined semi-freely with the help of distance restraints and constraining the U_{iso} value of the hydrogen atom to 1.2 times the U_{eq} value of the carbon atom to which the hydrogen binds.

Compound **11** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit along with one molecule of pentane. The pentane is disordered over three positions and was refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Coordinates for the hydrogen atoms on C1, C2 and C3 were taken from the difference Fourier synthesis and refined semi-freely with the help of distance restraints and constraining the U_{iso} value of the hydrogen atom to 1.2 times the U_{eq} value of the carbon atom to which the hydrogen binds.

Table S1. Crystal data and structure refinement for W(3,5-$Me_2C_6H_3N$)(C_3H_6)(NC_4H_4)(OHIPT) (**9a**).

Identification code	d10041	
Empirical formula	C_{58} H_{84} N_2 O W	
Formula weight	1009.12	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.0469(2) Å	α = 82.7973(12)°
	b = 13.1911(3) Å	β = 86.6985(13)°
	c = 23.8059(5) Å	γ = 70.7499(13)°
Volume	2660.55(10) Å^3	
Z	2	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	4.301 mm^{-1}	
F(000)	1056	
Crystal size	0.20 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.87 to 66.59°	
Index ranges	-10<=h<=10, -15<=k<=15, 0<=l<=28	
Reflections collected	9198	
Independent reflections	9198 [R(int) = 0.0000]	
Completeness to theta = 66.59°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5647 and 0.4800	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9198 / 0 / 573	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0204, wR2 = 0.0508	
R indices (all data)	R1 = 0.0207, wR2 = 0.0509	

Largest diff. peak and hole	0.620 and -0.719 e.Å^{-3}

Table S2. Crystal data and structure refinement for W(3,5-$Me_2C_6H_3N$)(C_3H_6)(2-MesNC_4H_3)(OTPP) (**9b**).

Identification code	d10090	
Empirical formula	C_{56} H_{55} N_2 $O_{1.50}$ W	
Formula weight	963.87	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 44.1194(7) Å	α = 90°
	b = 9.5497(2) Å	β = 115.1040(10)°
	c = 23.8428(4) Å	γ = 90°
Volume	9096.7(3) $Å^3$	
Z	8	
Density (calculated)	1.408 Mg/m^3	
Absorption coefficient	5.028 mm^{-1}	
F(000)	3928	
Crystal size	0.40 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.21 to 69.31°	
Index ranges	-53<=h<=53, -11<=k<=9, -28<=l<=28	
Reflections collected	89456	
Independent reflections	8479 [R(int) = 0.0311]	
Completeness to theta = 69.31°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6333 and 0.2383	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8479 / 173 / 636	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0219, wR2 = 0.0544	
R indices (all data)	R1 = 0.0233, wR2 = 0.0553	

Largest diff. peak and hole	0.683 and -0.499 e.Å^{-3}

Table S3. Crystal data and structure refinement for W(3,5-$Me_2C_6H_3N$)(2,5-Me_2pyr)(OHIPT)(C_4H_8) (**11**).

Identification code	d10129	
Empirical formula	$C_{59} H_{86} N_2 O W$	
Formula weight	1023.15	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.0576(2) Å	α = 90°
	b = 12.8834(2) Å	β = 100.2540(10)°
	c = 33.4802(6) Å	γ = 90°
Volume	5542.29(16) $Å^3$	
Z	4	
Density (calculated)	1.226 Mg/m^3	
Absorption coefficient	4.136 mm^{-1}	
F(000)	2144	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.68 to 69.31°	
Index ranges	-15<=h<=15, -13<=k<=15, -40<=l<=40	
Reflections collected	110804	
Independent reflections	10376 [R(int) = 0.0325]	
Completeness to theta = 69.31°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6825 and 0.4917	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10376 / 258 / 698	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0288, wR2 = 0.0704	
R indices (all data)	R1 = 0.0314, wR2 = 0.0721	

Largest diff. peak and hole 2.585 and -0.986 e.Å^{-3}

References

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2. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
3. Müller, P. *Crystallography Reviews* **2009**, *15*, 57-83.