Supplementary Material (ESI) for Chemical Communications

Supporting information

Skeletal Change In The PNP Pincer Ligand Leads To A Highly Regioselective Alkyne Dimerization Catalyst

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Experimental

General considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, ethyl ether, C_6D_6, THF, pentane, were dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. Compounds $[(COD)RhCl]_2$[1], **1a-c** and **2a-c**[2,3] were prepared as described previously. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz.) spectrometer. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85 % H_3PO_4 at 0 ppm. ^{19}F NMR was referenced externally to 1.0 M CF_3COOH in $CDCl_3$ at -78.5 ppm. Gas chromatography/mass spectra (GC/MS) were recorded on a Hewlett Packard G1800C

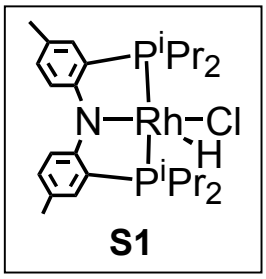
GCD System (GCD Plus Gas Chromatograph Electron Ionization Detector) employing HP-5MS from Agilent Technologies (30 m (column length) 0.25 mm (i.d.)). FT-IR spectra were recorded on Perkin Elmer spectrometer BX_2 by using v2.00 software.

NMR integration. Our empirical observations lead us to utilize a ±3% error for the product fractions calculated from NMR integrations. Thus, all values for percent fractions should be taken with a ±3% margin of error. This probably varies depending on what the ratios are exactly. A determination of a 98:2 ratio is more accurate in absolute terms than a 50:50 determination. Cases where the integration error is assumed to be larger are so noted.

(^{T}PNP)RhH$_2$ (3a). To 429 mg of **2a** (0.74 mmol) in 20 mL of 2-propanol was added 0.35 g of $NaBH_4$ (3.7 mmol) and the mixture was stirred at room temperature for 4 h. Then all volatiles were removed in vacuo. The residue was extracted with pentane several times and filtered through a pad of Celite. The filtrate was concentrated and cooled at -35 ^{o}C for 12 h. Compound **3a** (yellow solid) was collected by filtration and dried in vacuo. Yield: 0.26 g (64 %). ^{1}H NMR (C_6D_6): δ 6.86 (d, 4H, J = 7 Hz, Ar-*H*), 6.49 (t, 2H, J = 7 Hz, Ar-*H*), 3.01 (s, 4H, -C*H*$_2$C*H*$_2$-), 1.99 (m, 4H, C*H*Me$_2$), 1.15 (app. quartet (dvt), 12H, CH*Me*$_2$), 0.98 (app. quartet (dvt), 12H, CH*Me*$_2$), -15.3 (dt, 2H, J_{Rh-H} = 21 Hz, J_{P-H} = 10 Hz, Rh-H). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.7 (dt, J = 12 Hz, J = 2 Hz), 134.2 (t, J = 5 Hz), 133.6 (s), 130.7 (s), 124.6 (t, J = 15 Hz), 115.0 (d, J = 3 Hz), 40.7 (s, *C*H$_2$*C*H$_2$), 25.0 (very broad, *C*HMe$_2$), 19.9 (br, CH*Me*$_2$), 18.4 (br, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 67.8 (d, J_{Rh-P} = 124 Hz). Elem. An. Found (Calculated) for $C_{26}H_{40}RhNP_2$: 58.92 (58.76); 7.63 (7.59).

(^{Me}PNP)RhH$_2$ (3b). Method 1. In a Teflon gas tight round bottom flask was combined the following: **1b** (0.718 g, 1.61 mmol), [(COD)RhCl]$_2$ (0.400 g, 1.61 mmol Rh), and 20 mL of fluorobenzene. The solution was stirred for 10 minutes and then was evaporated to dryness in vacuo. The residue was placed into a 70°C oil bath for 4 h. The resulting green solid (0.793 g, 1.36 mmol) was dissolved in 20 mL of THF and 20 mL of 2-propanol. $NaBH_4$ (0.514 g, 13.6 mmol) was added and the mixture was stirred for 1.5 h, during which time the color of solution changed from deep green to orange-brown. The solution was evaporated to dryness under vacuum, extracted with ether and filtered through a pad of Celite and then through a plug of silica gel. The volatiles were removed from the filtrate in vacuo and the residue was recrystallized from diethyl ether to afford pure product. Yield after recrystallization: 0.38 g (45 %).

Method 2. **3b** can also be prepared from (^{Me}PNP)RhHCl (**S1**)[3] as follows. To 522 mg of **S1** (0.92 mmol) in 20 mL of 2-propanol was added 0.75 g of $NaBH_4$ (7.9 mmol) at room temperature. This mixture was heated at 60 ^{o}C for 4 h; the solvent was then removed in vacuo. The residue was extracted with toluene several times and filtered through a suction funnel. The filtrates were combined and the solvent was evaporated to dryness to afford product that was >95% pure by NMR. Yield: 0.350 g (71 %). ^{1}H NMR (C_6D_6): δ 7.84 (d, 2H, J = 8 Hz, Ar-*H*), 6.93 (s, 2H, Ar-*H*), 6.88 (d, J = 8 Hz, 2H, Ar-*H*), 2.21 (s, 6H, Ar-CH_3), 1.98 (m, 4H, C*H*Me$_2$), 1.20 (app. quartet (dvt), 12H, CH*Me*$_2$), 1.03 (app. quartet (dvt), 12H, CH*Me*$_2$)), -13.82 (dt, 2H, $J_{H\text{-}Rh}$ = 20 Hz, $J_{H\text{-}P}$ = 9 Hz, Rh-*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.2 (dt, J = 2 Hz, J = 12 Hz), 132.7 (s), 132.0 (s), 124.8 (t, J = 3 Hz), 123.4 (t, J = 16 Hz), 114.9 (t, J = 5 Hz), 24.9 (m, *C*HMe$_2$), 20.5



S1

(s, Ar-*C*H_3), 19.9 (t, J = 4 Hz, CH*Me*$_2$), 18.6 (br, CH*Me*$_2$) $^{31}P\{^1H\}$ NMR (C_6D_6): 64.8 (d, $J_{P\text{-}Rh}$ = 129 Hz).

(^{F}PNP)RhH$_2$ (3c). To 64 mg of **2c** (0.11 mmol) in 20 mL 2-propanol was added 90 mg of $NaBH_4$ (0.94 mmol) at room temperature. This mixture was heated to 60 ^oC for 4 h; the solvent was then removed in vacuo. The residue was extracted with pentane and passed through celite pad. The pentane solution was concentrated and kept in the freezer at -35 ^oC. Yellow solids were obtained (30 mg, 48%). ^1H NMR(C_6D_6): δ 7.49 (m, 2H, Ar-H), 6.81 (m, 2H, Ar-H), 6.74 (m, 2H, Ar-H), 1.76 (m, 4H, C*H*Me$_2$), 1.06 (appt quartet (dt), 12H, J = 7 Hz, J = 17 Hz, CH*Me*$_2$), 0.86 (appt quartet (dt), 12H, J = 7 Hz, J = 15 Hz, CH*Me*$_2$), -13.7 (dt, 2H, J = 9 Hz, J = 20 Hz, Rh*H*$_2$) . $^{31}P\{^1H\}$ NMR (C_6D_6): δ 63.8 (d, J = 129.7 Hz). ^{13}C NMR (C_6D_6): δ 161.3 (vt, $J_{P\text{-}C}$ = 12 Hz, aryl N-C), 154.8 (dvt, $J_{C\text{-}F}$ = 235 Hz, $J_{C\text{-}P}$ = 4 Hz), 124.6 (vtd, $J_{C\text{-}F}$ = 5 Hz, $J_{C\text{-}P}$ = 15 Hz), 118.2 (d, $J_{C\text{-}F}$ = 20 Hz), 117.7 (d, $J_{C\text{-}F}$ = 22 Hz), 114.4 (m), 24.7 (vt, $J_{C\text{-}P}$ = 12 Hz, *C*HMe$_2$), 19.6 (vt, $J_{C\text{-}P}$ = 5 Hz, CH*Me*$_2$), 18.3 (s, CH*Me*$_2$). $^{19}F\{^1H\}$ NMR (C_6D_6): δ -132.4 (s).

(^{T}PNP)Rh(CO) (8a). Under 1 atm of CO, $NaBEt_3H$ (91 μL, 0.091 mmol) was added portionwise to a solution of **2a** (53 mg, 0.091 mmol) in ether. The green solution became red-orange immediately. The product was isolated after filtration and removal of volatiles in vacuo to give a yellow-brown solid, which can be further purified by recrystallization in cold pentane. Yield: 26 mg (50%). ^1H NMR(C_6D_6): δ 6.81 (br, 4H, Ar-*H*), 6.45 (t, J = 7 Hz, 2H, Ar-*H*), 2.92 (s, 4H, CH_2CH_2), 2.14 (br, 4H, C*H*Me$_2$), 1.25 (appt quartet (dt), 12H, J = 7 Hz, J = 8 Hz, CH*Me*$_2$), 1.02 (m, 12H, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 64.1 (d, J = 125 Hz). ^{13}C NMR (C_6D_6): δ 198.0 (dt, $J_{Rh\text{-}C}$ = 65 Hz, $J_{P\text{-}C}$ = 14 Hz , Rh-CO), 162.8 (dt, J = 2 Hz, J = 11 Hz), 134.6 (t, J = 5 Hz), 133.6 (s), 130.1 (s), 122.8 (t, J = 17

Hz), 114.9 (t, J = 4 Hz), 40.7 (s, CH_2CH_2), 25.8 (br, $CHMe_2$), 19.5 (s, $CHMe_2$), 18.3 (s,$CHMe_2$). IR: ν_{CO} (Toluene) = 1943 cm^{-1}. Anal. Calcd for $C_{27}H_{38}NOP_2Rh$: C, 58.23; H, 7.08. Found: C, 58.17; H, 6.87.

(^{Me}PNP)Rh(CO) (8b). Under 1 atm of CO, $NaBEt_3H$ (91 μL, 0.091 mmol) was added portionwise to a solution of **2b** (53 mg, 0.091 mmol) in ether. The green solution became orange-yellowish instantly. The title compound can be isolated in pure form by using the similar method as in **8a.** Yield: 32 mg (52%). ^{1}H NMR (C_6D_6): δ 7.70 (dt, J_{HH} = 8 Hz, J_{HP} = 2 Hz, 2H, Ar-*H*), 6.90 (s, 2H, Ar-*H*), 6.81 (d, J_{HH} = 8 Hz, 2H, Ar-*H*), 2.18 (s, 6H, Ar-*Me*), 2.13 (m, overlap with Ar-Me signal, 4H, $CHMe_2$), 1.26 (appt quartet (dt), 12H, J = 7 Hz, J = 17 Hz, $CHMe_2$), 1.03 (appt quartet (dt), 12H, J = 7 Hz, J = 15 Hz, $CHMe_2$).

^{31}P NMR (C_6D_6): δ 61.5 (d, J = 131.4 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 198.2 (dt, J_{Rh-C} = 63 Hz, J_{P-C} = 14 Hz , Rh-CO), 162.5 (t, J = 14 Hz), 132.3 (s), 132.2 (s), 124.8 (t, J = 3 Hz), 121.4 (t, J = 18 Hz), 115.5 (t, J = 6 Hz), 25.6 (t, J = 13 Hz), 20.5 (s, Ar-*Me*), 19.4 (t, J = 3 Hz), 18.4 (s). IR: ν_{CO} (Toluene) = 1945 cm^{-1}.

(^{F}PNP)Rh(CO) (8c). A solution of **3c** (20 mg, 0.037 mmol) in C_6D_6 was stirred under 1 atm CO for 2 h. ^{1}H NMR and ^{31}P NMR data indicate quantitative conversion to **8c.** ^{1}H NMR (C_6D_6): δ 7.36 (m, 2H, Ar-*H*), 6.78 (m, 2H, Ar-*H*), 6.67 (m, 2H, Ar-*H*), 1.93 (br, 4H, $CHMe_2$), 1.15 (appt quartet (dt), 12H, J = 7 Hz, J = 16 Hz, $CHMe_2$), 0.91 (appt quartet (dt), 12H, J = 7 Hz, J = 15 Hz, $CHMe_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.5 (d, J = 130.5 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 197.5 (dt, J_{Rh-C} = 64 Hz, J_{P-C} = 14 Hz , Rh-CO), 160.7 (vt, J_{P-C} = 13 Hz, aryl N-*C*), 154.6 (dvt, J_{C-F} = 235 Hz, J_{C-P} = 5 Hz), 122.8 (vtd, J_{C-F} = 5 Hz, J_{C-P} = 18 Hz), 118.0 (d, J_{C-F} = 22 Hz), 117.9 (d, J_{C-F} = 21 Hz), 115.1 (m), 25.5

(vt, $J_{C\text{-}P}$ = 12 Hz, *C*HMe$_2$), 19.2 (vt, $J_{C\text{-}P}$ = 3 Hz, CH*Me*$_2$), 18.2 (s, CH*Me*$_2$). ^{19}F{^{1}H} NMR (C_6D_6): δ -132.0 (s). IR: ν_{CO} (Toluene) = 1950 cm^{-1}.

(^{T}PNP)Rh(η^2-Ph-*C*≡*C*-CHCHPh-*trans*) (7a-Ph). Phenylacetylene (34 μL, 0.30 mmol) was added to **3a** (80 mg, 0.15 mmol) dissolved in C_6D_6 in a J. Young NMR tube. The reaction was monitored by ^{31}P NMR until completion. The solution was transferred to a flask and the volatiles were removed under vacuum. The residue was dissolved in pentane and passed through a pad of Celite. The resulting filtrate was then concentrated and kept in a -35 ^{o}C freezer for 7 h. The solid orange **7a-Ph** was collected by filtration and was dried under vacuum. Yield: 80 mg (73%). ^{1}H NMR (C_6D_6): δ 8.04 (d, *J* = 7 Hz, 2H, Ar-*H*), 7.74 (d, 1H, *J* = 16 Hz, olefinic *H*), 7.42 (d, 2H, *J* = 7 Hz, Ar-*H*), 7.21 (t, 2H, *J* = 8 Hz, Ar-H), 7.13 (m, 2H, Ar-H, overlapped with solvent residue), 7.04 (m, 2H, Ar-H), 6.96 (d, 1H, *J* = 16 Hz, olefinic *H*), 6.83 (d, 2H, *J* = 7 Hz, Ar-H), 6.66 (br, 2H, Ar-H), 6.39 (m, 2H, Ar-*H*), 3.11 (br, 2H, CH_2CH_2), 2.95 (br, 2H, CH_2CH_2), 2.34 (br, 1H, C*H*Me$_2$), 1.95 (br, 3H, C*H*Me$_2$), 1.71 (br, 3H, CH*Me*$_2$), 1.58 (br, 3H, CH*Me*$_2$), 1.20 (br, 3H, CH*Me*$_2$), 0.99 (br, 3H, CH*Me*$_2$), 0.78 (br, 3H, CH*Me*$_2$), 0.69 (br, 9H, CHMe$_2$). ^{13}C {^{1}H} NMR (C_6D_6): δ 162.8 (t, *J* = 8 Hz), 138.3 (s), 137.9 (s), 134.1 (br), 133.4 (s), 131.3 (s), 129.8 (s), 129.6 (s), 129.1 (s), 128.3 (s), 127.7 (s), 127.0 (s), 126.6 (s), 124.0 (t, *J* = 16 Hz), 114.6 (s), 114.5 (s), 93.9 (dt, *J* = 7 Hz, *J* = 4 Hz, C≡C), 86.8 (d, *J* = 12 Hz, C≡C), 41.0 (s, CH_2CH_2), 27.6 (br, 1C of ^{i}Pr), 26.7 (br, 1C of ^{i}Pr), 21.0 (br, 4C of ^{i}Pr), 18.3 (br, 2C of ^{i}Pr), 16.3 (br, 2C of ^{i}Pr), 15.5 (br, 2C of ^{i}Pr). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.9 (d, *J* = 124 Hz).

Catalytic dimerization of alkynes. In a typical run, to a J. Young NMR tube was added **3a**, **3b or 3c** (8.8 mg, 0.0164 mmol) dissolved in 0.5 mL of C_6D_6. Alkyne (3.29

mmol) was added to the solution, and the closed NMR tube was heated at 100 ^{o}C. After the reaction was complete, the reaction mixture was cooled to room temperature, and 25 μL dioxane was added to the tube as a NMR internal standard. The product identity was confirmed by ^{1}H NMR and GC/MS as well as by comparison to the literature data.[4a-4f] The product yield was determined from the ^{1}H NMR data (vs. the dioxane standard).

Selected NMR data for the enyne compounds follow:

***trans*-PhC≡CCH=CHPh:** ^{1}H NMR (C_6D_6) δ 7.50-7.47, 7.12-6.99 (m, Ph), 6.95 (d, 1H, *J* = 16 Hz), 6.28 (d, 1H, *J* = 16 Hz). GC-MS: m/z = 204 (M^+).

***trans*- $FC_6H_4C≡CCH=CHC_6H_4F$:** ^{1}H NMR (C_6D_6): δ 7.24 (m, 2H, Ar-*H*), 6.81 (m, 3H, Ar-*H* overlapped with one vinyl proton), 6.63 (m, 4H, Ar-*H*), 6.09 (d, 1H, *J* = 16 Hz). ^{19}F {^{1}H} NMR (C_6D_6): δ -113.5 (m), -115.2 (m). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.2 (d, *J* = 247 Hz), 162.8 (d, *J* = 248 Hz), 140.3 (s, -*C*=C-Ar), 133.6 (d, *J* = 8 Hz), 132.6 (d, *J* = 3 Hz), 128.2 (overlapped with solvent residue resonance), 120.0 (d, *J* = 4 Hz), 115.9 (d, *J* = 22 Hz), 115.8 (d, *J* = 22 Hz), 108.1 (s, -*C*=C-Ar), 91.2 (s, -C≡C), 89.0 (s, -C≡C). M^+ = 240.

***trans*-$C_4H_9C≡CCH=CHC_4H_9$:** ^{1}H NMR (C_6D_6) δ 6.01 (dt, 1H, *J* = 15.6, *J* = 7.2 Hz), 5.47 (d, 1H, *J* = 15.6 Hz), 2.2-0.7 (m, C_4H_9). GC-MS: m/z = 164 (M^+).

***trans*-$C_3H_7C≡CCH=CHC_3H_7$:** ^{1}H NMR (C_6D_6) δ 6.01 (dt, 1H, *J* = 16.0, *J* = 6.8 Hz), 5.48 (d, 1H, *J* = 16.0 Hz), 2.4-0.7 (m, C_3H_7). GC-MS: m/z = 136 (M^+).

***trans*-$Me_2NH_2CC≡CCH=CHCH_2NMe_2$:** ^{1}H NMR ($C_6D_6$) δ 6.12 (dt, 1H, *J* = 15.8, *J* = 6.2 Hz), 5.59 (d, 1H, *J* = 15.8 Hz), 3.19 (s, 2H, H_2CC≡), 2.65 (d, 2H, *J* = 6.2 Hz, =CHCH_2), 2.11 (s, 6H, NMe_2), 1.95 (s, 6H, NMe_2). GC-MS: m/z = 165 (M^+-1, very

weak), 121 (M^+-45). Selected NMR data for the **B** type isomer: ^{1}H NMR (C_6D_6) δ 5.39 (s), 5.29 (s).

***trans*-$Me_3SiC{\equiv}CCH{=}CHSiMe_3$:** ^{1}H NMR ($C_6D_6$) δ 6.44 (d, 1H, *J* = 19.6 Hz), 5.92 (d, 1H, *J* = 19.6 Hz), 0.16 (s, 9H, Si*Me*$_3$), -0.08 (s, 9H, Si*Me*$_3$). GC-MS: m/z = 196 (M^+). Selected NMR data for the Trimer**:** ^{1}H NMR (C_6D_6) δ 6.87 (d, 1H, *J* = 18.4 Hz), 6.72 (d, 1H, *J* = 18.4 Hz), 6.36 (s, 1H). GC-MS: m/z = 294 (M^+).

***trans*-$Me_3CC{\equiv}CCH{=}CHCMe_3$:** ^{1}H NMR ($C_6D_6$) δ 6.01 (d, 1H, *J* = 16.0), 5.37 (d, 1H, *J* = 16.0 Hz), 1.18 and 0.84 (s, CMe_3). GC-MS: m/z = 164 (M^+). $Me_3CC{\equiv}CH$ Trimer**:** ^{1}H NMR (C_6D_6) δ 6.51 (d, 1H, *J* = 15.2 Hz), 6.29 (d, 1H, *J* = 15.2 Hz), 6.89 (s, 1H), 1.21, 1.08 and 1.01 (s, CMe_3). GC-MS: m/z = 246 (M^+). $Me_3CC{\equiv}CH$ Tetramer**:** GC-MS: m/z = 328 (M^+).

***trans*-$Me_3SiOCH_2C{\equiv}CCH{=}CHCH_2OSiMe_3$:** ^{1}H NMR ($C_6D_6$) δ 6.12 (dt, 1H, *J* = 15.6, *J* = 4.4 Hz), 5.88 (d, 1H, *J* = 15.6 Hz), 4.29 (s, 2H, $H_2C{\equiv}C$), 3.84 (m, 2H, $=CHCH_2$), 0.12 and 0.00 (s, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 142.6 (s), 109.0 (s), 88.8 (s), 83.6 (s), 62.3 (s), 51.7 (s), -0.164 (s), -0.55(s). GC-MS: m/z = 256 (M^+).

***trans*-$HOCH_2C{\equiv}CCH{=}CHCH_2OH$:** This compound has lower solubility in benzene. After heating the NMR tube in the 100 °C oil bath for 3 h, a lot of precipitate was formed. All volatiles were removed under vacuum to afford the title compound. Yield: 0.195 g (96%). ^{1}H NMR (CD_3OD) δ 6.20 (dt, 1H, *J* = 15.6, *J* = 4.5 Hz), 5.76 (d, 1H, *J* = 15.6 Hz), 4.28 (s, 2H, $CH_2C{\equiv}$), 4.11 (d, 2H, *J* = 4.5 Hz, $=CHCH_2$). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 143.7 (s), 110.1 (s), 89.0 (s), 83.6 (s), 62.7 (s), 51.1 (s). GC-MS: m/z = 112 (M^+). Selected NMR data for **B** type isomer: ^{1}H NMR (C_6D_6) δ 5.49 (s, 1H), 5.38 (s, 1H).

***trans*-$CH_3C_6H_4C{\equiv}CCH{=}CHC_6H_4CH_3$:** This compound has a lower solubility in benzene. When the reaction mixture cooled down to ambient temperature, it precipitated out in the NMR tube. The reaction mixture was evaporated to dryness and dissolved in $CDCl_3$ (NMR yield: 98%). Then the volatiles were removed under vacuum and the residue was washed with pentane. The resulting solid was dried under vacuum to afford the title compound as the off-white solid. Yield: 250 mg (67%). ^{1}H NMR ($CDCl_3$) δ 7.39-7.14 (m, 8H, Ph), 7.01 (d, 1H, *J* =16 Hz), 6.34 (d, 1H, *J* = 16 Hz), 2.36 (s, 6H, CH_3). GC-MS: m/z = 232 (M^+).

Experiment with $HC{\equiv}CCO_2Et$. This reaction was carried out using the same method as for other alkynes. The results are as follows.

Catalyst	Time	**A**:$\mathbf{X_1}$:$\mathbf{X_2}$	Total Conv.,%
3a	24 h	18:36:64	33%
3b	120 h	3:35:65	60%

A: *trans*-$EtO_2CC{\equiv}CCH{=}CHCO_2Et$; **X1**: Triethyl-1,3,5-benzenetricarboxylate; **X2:** Triethyl-1,2,4-benzenetricarboxylate.

Selected NMR and GC-MS data.[4g] ***trans*-$EtO_2CC{\equiv}CCH{=}CHCO_2Et$:** ^{1}H NMR ($C_6D_6$) δ 6.52 (d, *J* = 16 Hz), 6.12 (d, *J* = 16 Hz). GC/MS: m/z = 196 (M^+). **1,3,5-Triethyl 1,3,5-Benzenetricarboxylate**: ^{1}H NMR (C_6D_6) δ 8.88 (s). GC/MS: m/z = 294 (M^+). **1,2,4-Triethyl 1,3,5-Benzenetricarboxylate:** ^{1}H NMR (C_6D_6) δ 8.43 (d, J = 2 Hz), 7.97 (dd, *J* = 8 Hz, *J* = 2 Hz), 7.49 (d, *J* = 8 Hz). GC/MS: m/z = 294 (M^+).

Additional catalytic experiments.

1. Influence of water, air, and 7a-Ph as catalyst.

Entry 1: In a glovebox, a J. Young NMR tube was charged with 0.5 mL C_6D_6, 37 μL PhC≡CH (0.34 mmol), and **3a** (0.0017 mmol). Then the NMR tube was closed off, placed into a 100 ^oC oil bath. The tube was removed from the oil bath and cooled for NMR analysis after 1 h and after 7 h.

Entry 2: In a glovebox, a J. Young NMR tube was charged with 37 μL PhC≡CH (0.34 mmol) and 25 μL catalyst stock solution of **3a** (0.0017 mmol). Then 0.5 mL C_6D_6 was added under air. The NMR tube was exposed to air for 5 min, placed into a 100 ^oC oil bath. The tube was removed from the oil bath and cooled for NMR analysis after 1 h and after 7 h.

Entry 3: In a glovebox, a J. Young NMR tube was charged with 0.5 mL C_6D_6, 37 μL PhC≡CH (0.34 mmol), 25 μL catalyst stock solution of **3a** (0.0017 mmol). 10 μL H_2O (0.17 mmol) was then added to the tube quickly under air and the tube was closed off. This NMR tube was placed into a 100 ^oC oil bath. The tube was removed from the oil bath and cooled for NMR analysis after 1 h and after 7 h.

Entry 4: In a glovebox, a J. Young NMR tube was charged with 0.5 mL C_6D_6, 37 μL PhC≡CH (0.34 mmol), 25 μL catalyst stock solution of **7a-Ph** (0.0017 mmol). Then NMR tube was placed into a 100 ^oC oil bath. The tube was removed from the oil bath and cooled for NMR analysis after 1 h and after 7 h.

Entry	Catalyst	Time	**A**:**B**	Total Conv.,%
1	**3a**	1 h	98:2	42
		7 h	98:2	92
2	**3a**	1 h	98:2	20
		7 h	98:2	76
3	**3a**	1 h	98:2	35
		7 h	98:2	72
4	**7a-Ph**	1 h	98:2	32
		7 h	98:2	63

2. Catalyst re-use

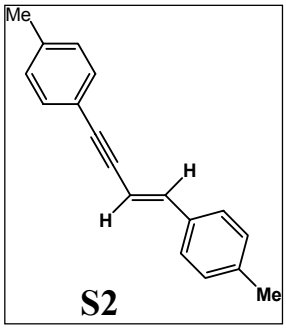
A J. Young NMR tube was charged with 1-pentyne (220 μL, 2.2 mmol), **3a** (6.0 mg, 0.011 mmol) and 0.5 mL C_6D_6. The NMR tube was placed into a 100 ^oC oil bath and the reaction was periodically monitored by ^1H NMR. When the reaction was completed, another 220 μL 1-pentyne was added to the same NMR tube. This was repeated for 4 cycles and the results are shown below (Time was recorded for individual repeated cycle; total conversion was based on the total amount of acetylene added).

Recycle	catalyst	Time	**A**:**B**	TON*	Total TON
1	**3a**	1 h	99:1	194	194
2	**3a**	8 h	98:2	174	368
3	**3a**	18 h	98:2	190	558
4	**3a**	72 h	98:2	66	624

* For each cycle only.

3. Dimerization of p-MeC$_6$H$_4$CCH in the presence of free enyne

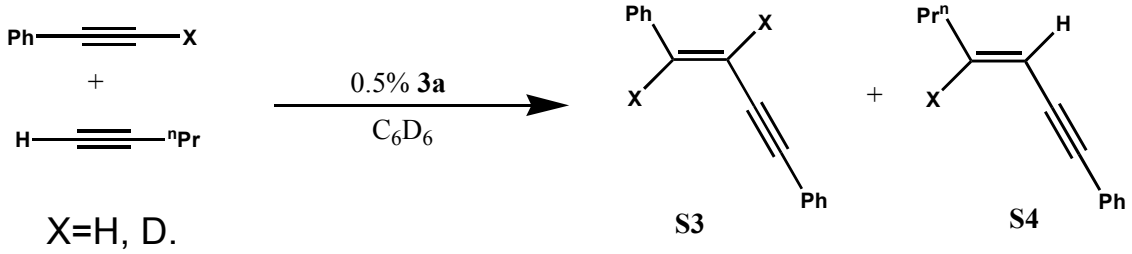
50 μL dioxane, 215 μL *p*-MeC$_6$H$_4$C≡CH (1.7 mmol) and 2.5 mL C$_6$D$_6$ were mixed in a vial. 0.500 mL of this mixture was added to each of 4 J. Young NMR tubes (containing ca. 0.31 mmol *p*-MeC$_6$H$_4$CCH). Stock C$_6$D$_6$ solution of **3a** (25 μL, 0.0017 mmol) was added to each NMR tube. **S2** was added to three of those 4 NMR tubes. Then all tubes were placed into a 100 ^{o}C oil bath. Those tubes were removed from the oil bath after 1 h and 9 h for NMR analysis. Yield and selectivity are shown in the following table.



S2

Entry	[**S2**]/[**3a**]	catalyst	Time	**A**:**B**	Total Conv. %
1	**0**	**3a**	1 h	98:2	27
			9 h	98:2	93
2	**5**	**3a**	1 h	98:2	23
			9 h	98:2	91
3	**10**	**3a**	1 h	98:2	24
			9 h	98:2	96
4	**25**	**3a**	1 h	98:2	24
			9 h	98:2	95

4. Cross dimerization of PhCCH(D) and n-PrCCH



X=H, D.

0.0035 mmol of **3a** was added to a solution of 38 μL PhC≡CX (X = H, D) and 35 μL ^{n}PrC≡CH in 0.5 mL C_6D_6 separately. The two NMR tubes were placed into a 100 ^{o}C oil bath. **S3** was the only cross-dimer isomer observed. The resonances of the vinyl protons of the cross-coupling products **S3** (X = H, D) and the m/z values of their parent MS peaks are as follows.

S4 (X = H): 5.66 (dt, J = 2 Hz, J = 16 Hz), 6.16 (dt, J = 7 Hz, J = 16 Hz); M^+ = 170.

S4 (X = D): 5.66 (t, J = 2 Hz); M^+ = 171.

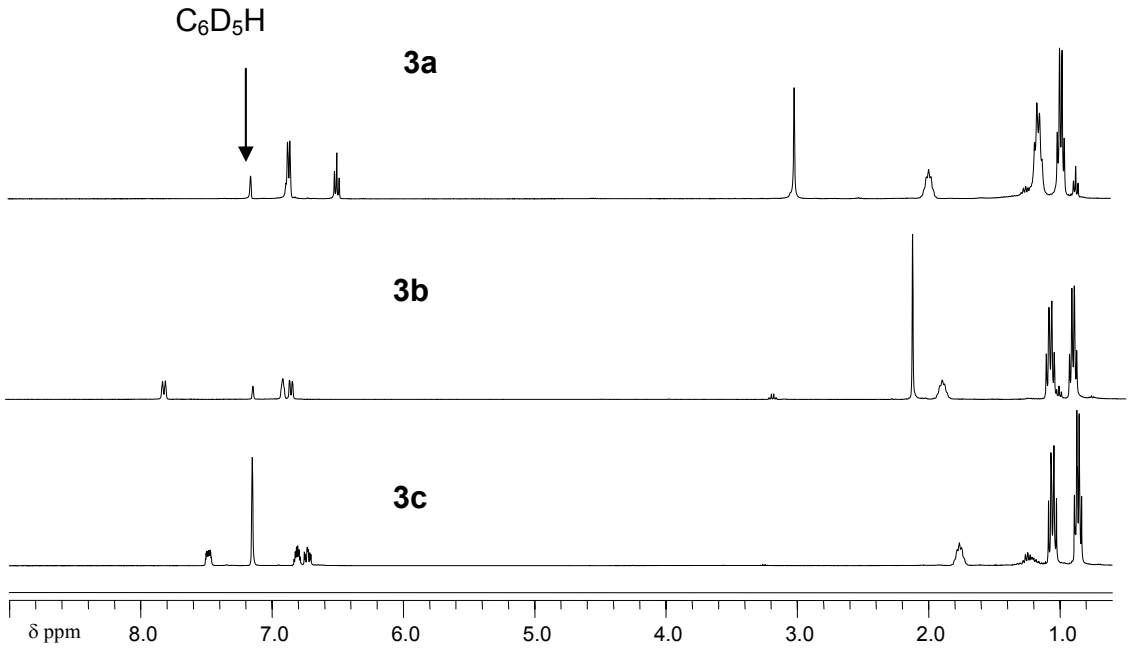


Figure S1. ^{1}H NMR spectra of (^{T}PNP)RhH$_2$ (**3a**), (PNP)RhH$_2$ (**3b**), and (^{F}PNP)RhH$_2$ (**3c**), the hydride resonances not shown.

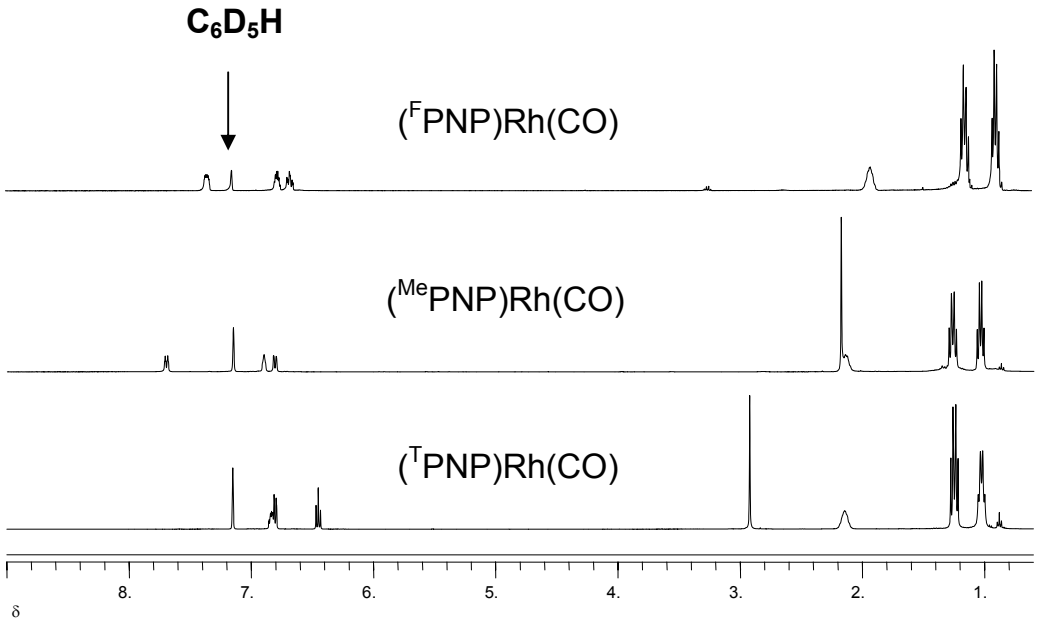


Figure S2. ^{1}H NMR spectra of (^{T}PNP)Rh(CO) (**8a**), (PNP)RhCO (**8b**), and (^{F}PNP)Rh(CO) (**8c**).

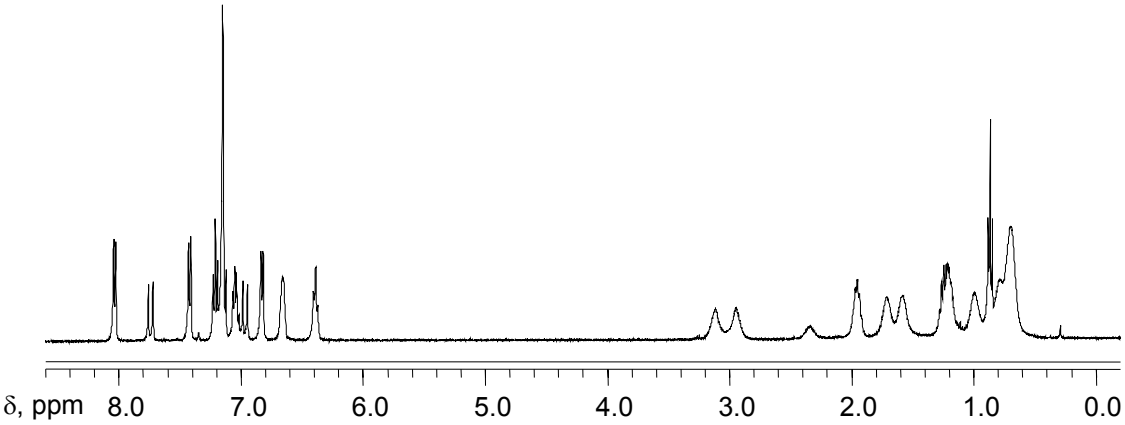


Figure S3. ^{1}H NMR spectrum of **7a-Ph** in C_6D_6. The singlet at δ 0.28 ppm corresponds to the trace impurity of poly(dimethylsiloxane) (silicon grease). The triplet at δ 0.86 ppm and a multiplet at ca. δ 1.2 ppm correspond to pentane of crystallization.

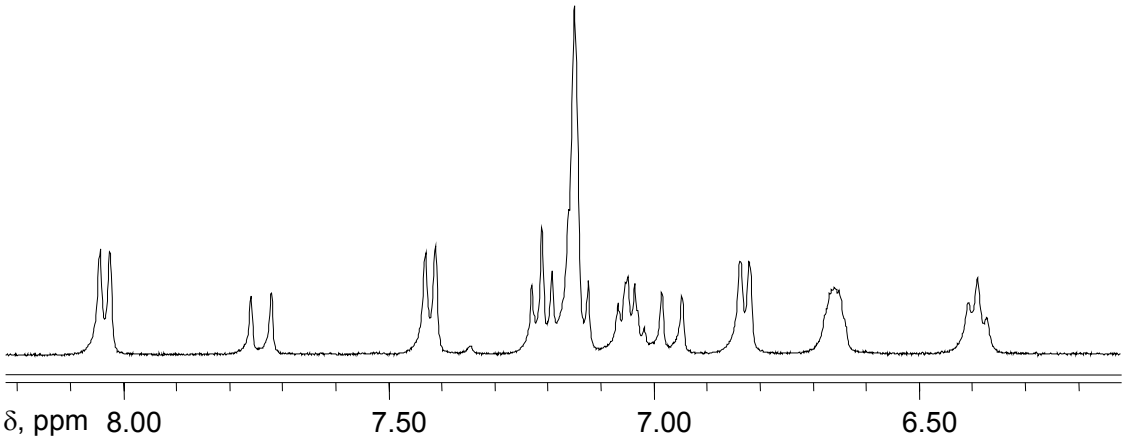


Figure S4. The portion of the ^{1}H NMR spectrum of **7a-Ph** in C_6D_6 corresponding to the aromatic and olefinic hydrogens.

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