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, C₆D₆, THF, pentane, were dried over NaK/Ph₂CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. Compounds [(COD)RhCl]₂, 1a-c and 2a-c were prepared as described previously. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (¹H NMR, 399.755 MHz; ¹³C NMR, 100.518 MHz; ³¹P NMR, 161.822 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ¹H and ¹³C NMR spectra, the residual solvent peak was used as an internal reference. ³¹P NMR spectra were referenced externally using 85 % H₃PO₄ at 0 ppm. ¹⁹F NMR was referenced externally to 1.0 M CF₃COOH in CDCl₃ 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 BX2 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.

\((\text{TPNP})\text{RhH}_2\) (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 °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\(_6\)D\(_6\)): \(\delta\) 6.86 (d, 4H, \(J = 7\) Hz, Ar-\(H\)), 6.49 (t, 2H, \(J = 7\) Hz, Ar-\(H\)), 3.01 (s, 4H, -\(\text{CH}_2\text{CH}_2\)), 1.99 (m, 4H, \(\text{CHMe}_2\)), 1.15 (app. quartet (dvt), 12H, CH\(\text{Me}_2\)), 0.98 (app. quartet (dvt), 12H, CH\(\text{Me}_2\)), -15.3 (dt, 2H, \(J_{\text{Rh}-\text{H}} = 21\) Hz, \(J_{\text{P}-\text{H}} = 10\) Hz, Rh-H). \(^{13}\)C\(_{\{^1\text{H}\}}\) NMR (C\(_6\)D\(_6\)): \(\delta\) 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, CH\(_2\)CH\(_2\)), 25.0 (very broad, CH\(\text{Me}_2\)), 19.9 (br, CH\(\text{Me}_2\)), 18.4 (br, CH\(\text{Me}_2\)). \(^{31}\)P\(_{\{^1\text{H}\}}\) NMR (C\(_6\)D\(_6\)): \(\delta\) 67.8 (d, \(J_{\text{Rh}-\text{P}} = 124\) Hz). Elem. An. Found (Calculated) for C\(_{26}\)H\(_{40}\)RhNP\(_2\): 58.92 (58.76); 7.63 (7.59).
**(MePNP)RhH₂ (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. NaBH₄ (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 (MePNP)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 NaBH₄ (7.9 mmol) at room temperature. This mixture was heated at 60 °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 (C₆D₆): 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-CH₃), 1.98 (m, 4H, CHMe₂), 1.20 (app. quartet (dvt), 12H, CHMe₂), 1.03 (app. quartet (dvt), 12H, CHMe₂), -13.82 (dt, 2H, J_H-Rh = 20 Hz, J_H-P = 9 Hz, Rh-H). \(^{13}\)C\(^{\{1\}}\)NMR (C₆D₆): 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, CHMe₂), 20.5
(s, Ar-CH3), 19.9 (t, J = 4 Hz, CHMe2), 18.6 (br, CHMe2) \(^{31}\)P\(_{\{^1\text{H}\}}\) NMR (C\(_6\)D\(_6\)): 64.8 (d, \(J_{\text{P,Rh}} = 129\) Hz).

\((^8\text{FPNP})\text{RhH}_2\) (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 °C 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 °C. Yellow solids were obtained (30 mg, 48%). \(^1\)H NMR(C\(_6\)D\(_6\)): \(\delta\) 7.49 (m, 2H, Ar-H), 6.81 (m, 2H, Ar-H), 6.74 (m, 2H, Ar-H), 1.76 (m, 4H, CHMe2), 1.06 (appt quartet (dt), 12H, \(J = 7\) Hz, \(J = 17\) Hz, CHMe2), 0.86 (appt quartet (dt), 12H, \(J = 7\) Hz, \(J = 15\) Hz, CHMe2), -13.7 (dt, 2H, \(J = 9\) Hz, \(J = 20\) Hz, RhH\(_2\)). \(^{31}\)P\(_{\{^1\text{H}\}}\) NMR (C\(_6\)D\(_6\)): \(\delta\) 63.8 (d, \(J = 129.7\) Hz). \(^{13}\)C NMR (C\(_6\)D\(_6\)): \(\delta\) 161.3 (vt, \(J_{\text{P,C}} = 12\) Hz, aryl N-C), 154.8 (dvt, \(J_{\text{C,F}} = 235\) Hz, \(J_{\text{C,P}} = 4\) Hz,), 124.6 (vtd, \(J_{\text{C,F}} = 5\) Hz, \(J_{\text{C,P}} = 15\) Hz), 118.2 (d, \(J_{\text{C,F}} = 20\) Hz), 117.7 (d, \(J_{\text{C,F}} = 22\) Hz), 114.4 (m), 24.7 (vt, \(J_{\text{C,F}} = 12\) Hz, CHMe2), 19.6 (vt, \(J_{\text{C,F}} = 5\) Hz, CHMe2), 18.3 (s, CHMe2). \(^{19}\)F\(_{\{^1\text{H}\}}\) NMR (C\(_6\)D\(_6\)): \(\delta\) -132.4 (s).

\((^7\text{PNP})\text{Rh(CO)}\) (8a). Under 1 atm of CO, NaBEt\(_3\)H (91 \(\mu\)L, 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%). \(^1\)H NMR(C\(_6\)D\(_6\)): \(\delta\) 6.81 (br, 4H, Ar-H), 6.45 (t, \(J = 7\) Hz, 2H, Ar-H), 2.92 (s, 4H, CH\(_2\)CH\(_2\)), 2.14 (br, 4H, CHMe2), 1.25 (appt quartet (dt), 12H, \(J = 7\) Hz, \(J = 8\) Hz, CHMe2), 1.02 (m, 12H, CHMe2). \(^{31}\)P\(_{\{^1\text{H}\}}\) NMR (C\(_6\)D\(_6\)): \(\delta\) 64.1 (d, \(J = 125\) Hz). \(^{13}\)C NMR (C\(_6\)D\(_6\)): \(\delta\) 198.0 (dt, \(J_{\text{Rh,C}} = 65\) Hz, \(J_{\text{P,C}} = 14\) 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).
Hz), 114.9 (t, J = 4 Hz), 40.7 (s, CH₂CH₂), 25.8 (br, CHMe₂), 19.5 (s, CHMe₂), 18.3 (s, CHMe₂). IR: νCO (Toluene) = 1943 cm⁻¹. Anal. Calcd for C₂₇H₃₈NOP₂Rh: C, 58.23; H, 7.08. Found: C, 58.17; H, 6.87.

(MePNP)Rh(CO) (8b). Under 1 atm of CO, NaBEt₃H (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%). ¹H NMR (C₆D₆): 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, CHMe₂), 1.26 (appt quartet (dt), 12H, J = 7 Hz, J = 17 Hz, CHMe₂), 1.03 (appt quartet (dt), 12H, J = 7 Hz, J = 15 Hz, CHMe₂).

³¹P NMR (C₆D₆): δ 61.5 (d, J = 131.4 Hz). ¹³C{¹H} NMR (C₆D₆): 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: νCO (Toluene) = 1945 cm⁻¹.

(FPNP)Rh(CO) (8c). A solution of 3c (20 mg, 0.037 mmol) in C₆D₆ was stirred under 1 atm CO for 2 h. ¹H NMR and ³¹P NMR data indicate quantitative conversion to 8c. ¹H NMR (C₆D₆): δ 7.36 (m, 2H, Ar-H), 6.78 (m, 2H, Ar-H), 6.67 (m, 2H, Ar-H), 1.93 (br, 4H, CHMe₂), 1.15 (appt quartet (dt), 12H, J = 7 Hz, J = 16 Hz, CHMe₂), 0.91 (appt quartet (dt), 12H, J = 7 Hz, J = 15 Hz, CHMe₂). ³¹P{¹H} NMR (C₆D₆): δ 61.5 (d, J = 130.5 Hz). ¹³C{¹H} NMR (C₆D₆): δ 197.5 (dt, J_Rh-C = 64 Hz, J_P-C = 14 Hz, Rh-CO), 160.7 (vvt, J_P-C = 13 Hz, aryl N-C), 154.6 (dvt, J_C-F = 235 Hz, J_C-P = 5 Hz), 122.8 (vtdd, J_C-F = 5 Hz, J_C-P = 18 Hz), 118.0 (d, J_C-F = 22 Hz), 117.9 (d, J_C-P = 21 Hz), 115.1 (m), 25.5
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(vt, $J_{C\cdot P} = 12$ Hz, CHMe$_2$), 19.2 (vt, $J_{C\cdot P} = 3$ Hz, CHMe$_2$), 18.2 (s, CHMe$_2$). $^{19}$F$\{^1$H$\}$

NMR (C$_6$D$_6$): $\delta$ -132.0 (s). IR: $\nu$CO (Toluene) = 1950 cm$^{-1}$.

(^[1]PNP)Rh([^[2]Ph-C≡C-CHCHPh-trans] (7a-Ph). Phenylacetylene (34 $\mu$L, 0.30 mmol) was added to 3a (80 mg, 0.15 mmol) dissolved in C$_6$D$_6$ 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 °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$_6$D$_6$): $\delta$ 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$_2$CH$_2$), 2.95 (br, 2H, CH$_2$CH$_2$), 2.34 (br, 1H, CHMe$_2$), 1.95 (br, 3H, CHMe$_2$), 1.71 (br, 3H, CHMe$_2$), 1.58 (br, 3H, CHMe$_2$), 1.20 (br, 3H, CHMe$_2$), 0.99 (br, 3H, CHMe$_2$), 0.78 (br, 3H, CHMe$_2$), 0.69 (br, 9H, CHMe$_2$). $^{13}$C

$\{^1$H$\}$ NMR (C$_6$D$_6$): $\delta$ 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$_2$CH$_2$), 27.6 (br, 1C of $^3$Pr), 26.7 (br, 1C of $^3$Pr), 21.0 (br, 4C of $^3$Pr), 18.3 (br, 2C of $^3$Pr), 16.3 (br, 2C of $^3$Pr), 15.5 (br, 2C of $^3$Pr). $^{31}$P$\{^1$H$\}$ NMR (C$_6$D$_6$): $\delta$ 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$_6$D$_6$. Alkyne (3.29
mmol) was added to the solution, and the closed NMR tube was heated at 100 °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 ¹H NMR and GC/MS as well as by comparison to the literature data.⁴a-⁴f The product yield was determined from the ¹H NMR data (vs. the dioxane standard).

Selected NMR data for the enyne compounds follow:

**trans-PhC≡CCH=CHPh:** ¹H NMR (C₆D₆) 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- FC₆H₄C≡CCH=CHC₆H₄F:** ¹H NMR (C₆D₆): 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). ¹⁹F {¹H} NMR (C₆D₆): δ -113.5 (m), -115.2 (m). ¹³C{¹H} NMR (C₆D₆): δ 163.2 (d, J = 247 Hz), 162.8 (d, J = 248 Hz), 140.3 (s, -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=Ar), 91.2 (s, -C≡C), 89.0 (s, -C≡C). M⁺ = 240.

**trans-C₄H₉C≡CCH=CHC₄H₉:** ¹H NMR (C₆D₆) 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, C₆H₉). GC-MS: m/z = 164 (M⁺).

**trans-C₃H₇C≡CCH=CHC₃H₇:** ¹H NMR (C₆D₆) 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, C₃H₇). GC-MS: m/z = 136 (M⁺).

**trans-Me₂NH₂CC≡CCH=CHCH₂NMe₂:** ¹H NMR (C₆D₆) δ 6.12 (dt, 1H, J = 15.8, J = 6.2 Hz), 5.59 (d, 1H, J = 15.8 Hz), 3.19 (s, 2H, H₂CC≡), 2.65 (d, 2H, J = 6.2 Hz, =CHCH₂), 2.11 (s, 6H, NMe₂), 1.95 (s, 6H, NMe₂). GC-MS: m/z = 165 (M⁺-1, very
weak), 121 (M+ -45). Selected NMR data for the B type isomer: $^1$H NMR (CD$_6$D$_6$) $\delta$ 5.39 (s), 5.29 (s).

trans-Me$_3$SiC≡CCH=CHSiMe$_3$: $^1$H NMR (CD$_6$D$_6$) $\delta$ 6.44 (d, 1H, $J$ = 19.6 Hz), 5.92 (d, 1H, $J$ = 19.6 Hz), 0.16 (s, 9H, SiMe$_3$), -0.08 (s, 9H, SiMe$_3$). GC-MS: m/z = 196 (M$^+$).

Selected NMR data for the Trimer: $^1$H NMR (CD$_6$D$_6$) $\delta$ 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$_3$CC≡CCH=CHCMes: $^1$H NMR (CD$_6$D$_6$) $\delta$ 6.01 (d, 1H, $J$ = 16.0 Hz), 5.37 (d, 1H, $J$ = 16.0 Hz), 1.18 and 0.84 (s, CMe$_3$). GC-MS: m/z = 164 (M$^+$). Me$_3$CC≡CH Trimer: $^1$H NMR (CD$_6$D$_6$) $\delta$ 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$_3$CC≡CH Tetramer: GC-MS: m/z = 328 (M$^+$).

trans-Me$_3$SiOCH$_2$C≡CCH=CHCH$_2$OSiMe$_3$: $^1$H NMR (CD$_6$D$_6$) $\delta$ 6.12 (dt, 1H, $J$ = 15.6, $J$ = 4.4 Hz), 5.88 (d, 1H, $J$ = 15.6 Hz), 4.29 (s, 2H, H$_2$C≡C), 3.84 (m, 2H, =CHCH$_2$), 0.12 and 0.00 (s, OSiMe$_3$). $^{13}$C{1H} NMR (CD$_6$D$_6$): $\delta$ 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$_2$C≡CCH=CHCH$_2$OH: 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$_3$OD) $\delta$ 6.20 (dt, 1H, $J$ = 15.6, $J$ = 4.5 Hz), 5.76 (d, 1H, $J$ = 15.6 Hz), 4.28 (s, 2H, CH$_2$C≡), 4.11 (d, 2H, $J$ = 4.5 Hz, =CHCH$_2$). $^{13}$C{1H} NMR (CD$_3$OD): $\delta$ 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 (CD$_6$D$_6$) $\delta$ 5.49 (s, 1H), 5.38 (s, 1H).
**trans-CH₃C₆H₄C≡CCH=CHC₆H₄CH₃:** 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 CDCl₃ (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%). ¹H NMR (CDCl₃) 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, CH₃). GC-MS: m/z = 232 (M⁺).

**Experiment with HC≡CCO₂Et.** This reaction was carried out using the same method as for other alkynes. The results are as follows.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time</th>
<th>A: X₁:X₂</th>
<th>Total Conv.,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>24 h</td>
<td>18:36:64</td>
<td>33%</td>
</tr>
<tr>
<td>3b</td>
<td>120 h</td>
<td>3:35:65</td>
<td>60%</td>
</tr>
</tbody>
</table>

* A: trans-EtO₂CC≡CCH=CHCO₂Et; X₁: Triethyl-1,3,5-benzenetricarboxylate; X₂: Triethyl-1,2,4-benzenetricarboxylate.

Selected NMR and GC-MS data:

**trans-EtO₂CC≡CCH=CHCO₂Et:** ¹H NMR (C₆D₆) 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:** ¹H NMR (C₆D₆) δ 8.88 (s). GC/MS: m/z = 294 (M⁺).

**1,2,4-Triethyl 1,3,5-Benzenetricarboxylate:** ¹H NMR (C₆D₆) 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 C₆D₆, 37 µL PhC≡CH (0.34 mmol), and 3a (0.0017 mmol). Then the NMR tube was closed off, placed into a 100 °C 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 C₆D₆ was added under air. The NMR tube was exposed to air for 5 min, placed into a 100 °C 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 C₆D₆, 37 µL PhC≡CH (0.34 mmol), 25 µL catalyst stock solution of 3a (0.0017 mmol). 10 µL H₂O (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 °C 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 C₆D₆, 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 °C oil bath. The tube was removed from the oil bath and cooled for NMR analysis after 1 h and after 7 h.
Table: 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 C₆D₆. The NMR tube was placed into a 100 °C 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).

Table: 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 \( \mu \)L dioxane, 215 \( \mu \)L \( p\)-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 \( \mu \)L, 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 °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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[S2]/[3a]</th>
<th>catalyst</th>
<th>Time</th>
<th>A:B</th>
<th>Total Conv. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>3a</td>
<td>1 h</td>
<td>98:2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9 h</td>
<td>98:2</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>3a</td>
<td>1 h</td>
<td>98:2</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9 h</td>
<td>98:2</td>
<td>91</td>
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<tr>
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<td>10</td>
<td>3a</td>
<td>1 h</td>
<td>98:2</td>
<td>24</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>9 h</td>
<td>98:2</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>3a</td>
<td>1 h</td>
<td>98:2</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9 h</td>
<td>98:2</td>
<td>95</td>
</tr>
</tbody>
</table>
4. Cross dimerization of PhCCH(D) and n-PrCCH

\[
\begin{align*}
\text{Ph} & \equiv \text{X} \\
\text{H} & \equiv \text{nPr}
\end{align*}
\]

\[+ \quad 0.5\% \ 3a \quad \text{C}_6\text{D}_6 \]

\[
\begin{align*}
\text{S3} & \quad \text{S4}
\end{align*}
\]

\[X = \text{H, D.}\]

0.0035 mmol of 3a was added to a solution of 38 µL PhC≡CX (X = H, D) and 35 µL nPrC≡CH in 0.5 mL C6D6 separately. The two NMR tubes were placed into a 100 °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 (TPNP)RhH$_2$ (3a), (PNP)RhH$_2$ (3b), and (FPNP)RhH$_2$ (3c), the hydride resonances not shown.

Figure S2. $^1$H NMR spectra of ($^7$PNP)Rh(CO) (8a), (PNP)RhCO (8b), and ($^6$PNP)Rh(CO) (8c).
Figure S3. $^1$H NMR spectrum of 7a-Ph in C$_6$D$_6$. The singlet at $\delta$ 0.28 ppm corresponds to the trace impurity of poly(dimethylsiloxane) (silicon grease). The triplet at $\delta$ 0.86 ppm and a multiplet at ca. $\delta$ 1.2 ppm correspond to pentane of crystallization.

Figure S4. The portion of the $^1$H NMR spectrum of 7a-Ph in C$_6$D$_6$ corresponding to the aromatic and olefinic hydrogens.
SI References.


