General Information. All reactions were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk line techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic alkyne substrates were received from commercial sources and used without further purification. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a GE GN-Omega 300 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP 5970 GC/MS spectrometer. High resolution FAB mass spectra were performed at the Center of Mass Spectrometry, Washington University, St. Louis, MO. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

Preparation of $[(PCy_3)_2(CO)(Cl)Ru{=}CHCH{=}C(CH_3)_2]^+BF_4^-$ (1). The ruthenium-alkylidene complex **1** was prepared by following the literature procedure.[12] To a Et_2O (30 mL) solution of **6b** (100 mg, 0.13 mmol), $HBF_4{\cdot}OEt_2$ (25 μL, 0.17 mmol, 54 wt. %) was added dropwise at room temperature. After stirring for 30 min at room temperature, the mixture was concentrated to about 10 mL, and the solution was triturated with 10 mL of hexanes. The resulting yellow precipitate was collected by a filtration, and washed several times with small amounts of Et_2O and hexanes to give **1** as a bright yellow solid (89 mg, 80% yield).

^1H NMR (CD_2Cl_2, 300 Mhz) δ 15.88 (d, J = 11.1 Hz, Ru=CH), 7.51 (d, J = 11.1 Hz, C*H*=C$(CH_3)_2$), 2.55 (br s, CH_3), 1.93-1.70, 1.50-1.19 (m, P$(C_6H_{11})_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz) δ 286.4 (br s, Ru=CH), 197.3 (br s, CO), 165.0 (Ru=C*H*CH=), 147.1 (=*C*$(CH_3)_2$), 35.8 (pseudo t, J_{PC} = 9.4 Hz, C_{ipso} of P$(C_6H_{11})_3$), 30.4 (d, J_{PC} = 54 Hz, C_{ortho} of P$(C_6H_{11})_3$), 28.1 (m, C_{meta} of P$(C_6H_{11})_3$), 26.5 (C_{para} of P$(C_6H_{11})_3$), 22.7 and 15.7 (=C(*C*$H_3)_2$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.6 MHz) δ 48.6 (s, PCy_3); FAB-MS: 793.4 (M^+-BF_4).

Preparation of $(PCy_3)_2(CO)(Cl)RuH$ (5). The ruthenium complex $[RuCl_2(COD)]_2$ (500 mg, 1.78 mmol) and PCy_3 (1.00 g, 3.56 mmol) were charged in a 50 mL Schlenk tube equipped with a Teflon valve in a glove box. A 20 mL of anhydrous ethanol was added to the reaction tube *via* a syringe.

The Teflon valve was closed, and the reaction tube was heated for 2 days in an oil bath at 90-95 °C. The yellowish microcrystalline solid was precipitated during the reaction. After cooling the reaction mixture to room temperature, the solid was filtered and washed with ethanol and Et_2O. Drying under vacuum led to analytically pure product **5** as a bright yellow microcrystalline solid in 85% yield (1.27 g).

^1H NMR (CD_2Cl_2, 300 MHz) δ 2.40-2.32, 2.04-1.71 and 1.54-1.23 (m, $P(C_6H_{11})_3$), -24.7 (t, J_{PH} = 18.0 Hz, Ru-H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz) δ 201.9 (t, J_{PC} = 13.6 Hz, CO), 34.9 (pseudo t, J = 9.6 Hz, C_{ipso} of $P(C_6H_{11})_3$), 30.43 (C_{meta} of $P(C_6H_{11})_3$), 28.33 (C_{ortho} of $P(C_6H_{11})_3$), 27.20 (C_{para} of $P(C_6H_{11})_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.6 MHz) δ 46.6 (s, PCy_3); Anal. Calcd for $C_{37}H_{67}OP_2ClRu$: C, 61.26; H, 9.31. Found: C, 61.26; H, 8.97.

Preparation of $(PCy_3)_2(CO)(Cl)RuCH=CHR$ (R = Ph (6a), $C(CH_3)=CH_2$(6b)). The ruthenium-vinyl complex **6** was prepared by following the literature procedure.[12] To a suspension of **5** (100 mg, 0.14 mmol) in 15 mL of benzene, was added desired alkyne RC≡CH (0.18-0.20 mmol) *via* a microsyringe. The mixture became clear red-purple solution upon stirring for a few minutes at room temperature. After stirring for 30 min, the solvent was removed under vacuum, and the residue was washed with dry acetone (5 mL, 3 times). Drying under a vacuum gave **6** as a red-purple solid in 90-95% yields.

For **6a**: ^1H NMR (C_6D_6, 300 MHz) δ 8.92 (d, J = 14.8 Hz, RuCH=), 7.34 (d, J = 7.8 Hz, Ph_{ortho}), 7.24 (t, J = 7.2 Hz, Ph_{meta}), 6.94 (t, J = 7.5 Hz, Ph_{para}), 6.20 (d, J = 14.8 Hz, =CHPh), 2.64-2.05, 1.69-1.53 and 1.28-1.11 (m, $P(C_6H_{11})_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 204.1 (t, J_{PC} = 13.0 Hz, CO), 151.5 (t, J_{PC} = 11.2 Hz, Ru-CH=), 140.0 (=CHPh), 134.8 (Ph_{ipso}), 129.3 (Ph_{ortho}), 128.9 (Ph_{para}) and 124.8 (Ph_{meta}), 35.4 (pseudo t, J = 9.6 Hz, C_{ipso} of $P(C_6H_{11})_3$), 30.8 (C_{meta} of $P(C_6H_{11})_3$), 28.4 (m, C_{ortho} of $P(C_6H_{11})_3$), 27.2 (C_{para} of $P(C_6H_{11})_3$); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.6 MHz) δ 29.0 (s, PCy_3); FAB-MS: 828.5 (M^+); Anal. Calcd for $C_{45}H_{73}OP_2ClRu$: C, 65.23; H, 8.88. Found: C, 66.05, H, 9.38

For **6b**: ^1H NMR (C_6D_6, 300 MHz) δ 8.47 (d, J = 13.2 Hz, Ru-CH=), 6.30 (dm, J = 13.2 Hz,

Ru-CH=C*H*), 4.70 and 4.53 (br s, =CH_2), 2.67-2.59, 2.22-2.05, 1.75-1.50 and 1.29-1.15 (m, P(C_6H_{11})$_3$), 2.08 (s, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 204.0 (t, J_{PC} = 13.5 Hz, CO), 150.9 (t, J_{PC} = 11.7 Hz, Ru-CH=), 142.3 (*C*(CH_3)=), 138.7 (=*C*H-C(CH_3)), 105.6 (=*C*H_2), 35.4 (pseudo t, J = 9.4 Hz, C_{ipso} of P(C_6H_{11})$_3$), 30.7 (d, J_{PC} = 26.1 Hz, C_{meta} of P(C_6H_{11})$_3$), 28.4 (m, C_{ortho} of P(C_6H_{11})$_3$), 27.3 (C_{para} of P(C_6H_{11})$_3$); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.6 MHz): 28.6 (s, PCy_3); FAB-MS: 792.4 (M^+); Anal Calcd for $C_{42}H_{73}OClP_2Ru$: C 63.65, H 9.28. Found: C, 63.73, H, 9.42.

General Procedure of the Catalytic Hydrovinylation and [2+2] Cycloaddition Reactions of Alkynes and Ethylene. In a 25 mL Schlenk tube equipped with a Teflon stopcock, complex **1** (4 mg, 3 mol %) was charged with R'C≡CR" (0.15 mmol) in 5 mL of CH_2Cl_2. Excess CH_2=CH_2 (3.2 mmol, ca. 2.5 atm) was transferred *via* a vacuum line, and the reaction mixture was heated at 75 °C under a closed system. The volatiles were evaporated under vacuum, and the residue was chromatographed on a silica gel column (Et_2O : hexanes = 1 : 3) in air. The product was isolated after evaporation of solvent by a rotary evaporator.

For **2a**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.47-6.96 (m, Ph), 6.78 (dd, J = 17.0, 11.0 Hz, CH_2=C*H*), 6.64 (s, =CHPh), 5.19 (br d, J = 11.0 Hz, C*H*H=), 4.87 (br d, J = 17.0 Hz, CH*H*=); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 141.9 (CH_2=*C*H), 138.0 (Ph*C*=CHPh), 136.8 (=CHPh), 131.7-127.1 (Ph carbons), 116.6 (=CH_2); GC-MS *m/z* = 206 (M^+).

For **2b**: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.62 (dd, J = 17.4, 10.5 Hz, CH_2=C*H*), 5.46 (t, J = 7.5 Hz, CH=C*H*CH_2), 5.08 (br d, J = 17.4 Hz, CH*H*=), 4.91 (br d, J = 10.5 Hz, C*H*H=), 2.20 (t, J = 7.5 Hz, =CC*H*$_2$$CH_2CH_3$), 2.09 (q, J = 7.5 Hz, =CHC*H*$_2$$CH_2CH_3$), 1.40 (m, CH_2C*H*$_2$$CH_3$, 4H), 0.92 (t, J = 7.5 Hz, CH_3, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 140.8 (CH_2=*C*H), 138.7 (CH=*C*CH_2), 133.7 (C=*C*HCH_2), 110.3 (*C*H_2=CH), 30.5 and 28.5 (=C*C*H_2), 23.1 and 22.4 (CH_2*C*$H_2$$CH_3$), 14.5 and 14.1 ($CH_2CH_2$*C*$H_3$); GC-MS *m/z* = 138 ($M^+$).

For **2c**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31 (dd, J = 8.1 Hz, Ar, 2H), 7.13 (d, J = 8.1 Hz, Ar, 2H), 6.77 (dd, J = 15.6, 10.5 Hz, C*H*=CHTol), 6.55 (d, J = 15.9 Hz, CH=C*H*Tol), 6.52 (ddd, J =

16.5, 10.5, 9.9 Hz, CH_2=C*H*), 5.33 (d, *J* = 16.5 Hz, C*H*H=), 5.16 (d, *J* = 9.9 Hz, CH*H*=), 2.34 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 137.6 (CH=*C*HTol), 137.5 (CH_2=*C*H), 134.5 (*C*H=CHTol), 132.9 (Tol_{ipso}), 129.5 (Tol_{ortho}), 128.8 (Tol_{meta}), 126.5 (Tol_{para}), 117.2 (*C*H_2=CH), 21.4 (CH_3); GC-MS *m/z* = 144 (M^+).

For **2d**: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.54 (dd, *J* = 18.0, 9.6 Hz, C*H*=CHSiEt_3), 6.36 (ddd, *J* = 16.8, 9.9, 9.6 Hz, CH_2=C*H*), 5.83 (d, *J* = 18.0 Hz, CH=C*H*SiEt_3), 5.21 (br d, *J* = 16.8 Hz, CH*H*=), 5.11 (br d, *J* = 9.9 Hz, C*H*H=), 0.94 (t, *J* = 7.8 Hz, Si(CH_2CH_3)$_3$), 0.58 (q, *J* = 7.8 Hz, Si(CH_2CH_3)$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 146.2 (CH_2=*C*H), 140.3 (*C*H=CHSiEt_3), 131.5 (CH=*C*HSiEt_3), 117.4 (*C*H_2=CH), 7.54 (Si(*C*H_2CH_3)$_3$), 3.66 (Si(CH_2CH_3)$_3$); GC-MS *m/z* = 168 (M^+).

For **2e**: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.31 (ddd, *J* = 16.8, 10.5, 10.2 Hz, CH_2=C*H*), 6.14 (dd, *J* = 15.6, 10.5 Hz, CH_2=CHC*H*), 5.67 (dt, *J* = 15.0, 7.2 Hz, =C*H*CH_2CH_2), 5.03 (br d, *J* =15.9 Hz, CH*H*=), 5.00 (d, *J* = 10.2 Hz, C*H*H=), 3.67 (t, *J* = 6.3 Hz, CH_2C*H*$_2$OH), 2.35 (dt, *J* = 9.6, 6.3 Hz, =CHC*H*$_2$$CH_2$), 1.90 (br s, *J* = 6.6 Hz, OH); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 137.8 (CH_2=*C*H), 134.0 (CH=*C*CH_2), 131.7 (*C*H=CHCH_2), 116.0 (*C*H_2=CH), 62.3 (CH_2*C*H_2OH), 36.7 (*C*$H_2$$CH_2$OH); GC-MS *m/z* = 98 ($M^+$).

For **2f**: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.40 (dd, *J* = 17.4, 10.5 Hz, CH_2=C*H*), 5.88 (s, =C*H*CO_2Me), 5.56 (d, *J* = 17.4 Hz, C*H*H=CH), 5.51 (d, *J* =10.5 Hz, CH*H*=CH), 3.90 and 3.73 (s, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 161.8 (*C*O_2Me), 142.7 (MeO_2*C*C=CHCO_2Me), 132.9 (MeO_2CC=*C*HCO_2Me), 124.2 (CH_2=*C*H), 119.9 (*C*H_2=CH), 52.8 and 52.1 (CH_3); GC-MS *m/z* = 170 (M^+).

For **3c**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.27 (d, *J* = 7.8 Hz, Ar_{ortho}, 2H), 7.12 (d, *J* = 7.8 Hz, Ar_{meta}, 2H), 6.37 (d, *J* = 16.2 Hz, =CHTol), 6.13 (dd, *J* = 16.2, 6.9 Hz, CHC*H*=CHTol), 5.89 (ddd, *J* = 16.8, 10.2, 6.6 Hz, CH_2=C*H*), 5.10-5.01 (m, *J* = 16.8 Hz, C*H*$_2$=CH, 2H), 3.03 (m, C*H*CH_3), 2.34 (s, C_6H_4C*H*$_3$), 1.21 (d, *J* = 6.9 Hz, CH*C*H$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 142.8 (CH_2=CH),

136.9 (CH=*C*HTol), 135.1 (*C*H=CHTol), 133.5 (Tol_{ipso}), 129.4 (Tol_{ortho}), 128.7 (Tol_{meta}), 126.2 (Tol_{para}), 113.4 (CH_2=CH), 40.8 ($CHCH_3$), 21.3 ($C_6H_4CH_3$), 20.1 ($CHCH_3$); GC-MS *m/z* = 172 (M^+).

For **3f**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.4-7.1 (m, Ph), 6.33 (d, *J* = 15.9 Hz, CH=C*H*Ph), 6.12 (dd, *J* = 15.9, 6.9 Hz, C*H*=CHPh), 5.82 (ddd, *J* = 16.5, 10.2, 6.6 Hz, CH_2=C*H*), 5.02 (d, *J* = 17.1 Hz, C*H*H=CH), 4.97 (d, *J* = 9.9 Hz, CH*H*=CH), 2.98 (m, C*H*CH_3), 1.15 (d, *J* = 6.9 Hz, CHC*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 142.6 (CH_2=*C*H), 137.2 (CH=*C*HPh), 129.8 (*C*H=CHPh), 128.8 (Ph_{ipso}), 128.6 (Ph_{ortho}), 127.2 (Ph_{para}), 126.2 (Ph_{meta}), 113.5 (CH_2=CH), 40.8 ($CHCH_3$), 19.6 ($CHCH_3$); GC-MS *m/z* = 158 (M^+).

For **4a**: ^1H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, CH_3, 6H), 2.66 (s, CH_2, 4H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 161.8 (CO_2Me), 142.7 (=CCO_2Me), 52.1 (CH_3), 27.3 (CH_2); GC-MS *m/z* = 170 (M^+).

For **4b**: ^1H NMR ($CDCl_3$, 300 MHz) δ 3.76 (s, CH_3, 6H), 2.66 (s, C*H*C(CO_2Me)=), 2.24 (br s, CH_2C*H*CH, 2H), 1.60 (m, C*H*HCHCH, 2H), 1.06 (m, CH*H*CHCH, 2H), 1.31 and 1.11 (m, CHCH_2CH, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 161.8 (CO_2Me), 142.4 (=CCO_2Me), 52.0 (CO_2CH_3), 47.5 (=C*C*H), 33.9 (CH_2*C*HCH), 30.5 (CH*C*H_2CH), 28.0 (CH_2CH(CH_2)CH); GC-MS *m/z* = 236 (M^+).

For **8**: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.96 (d, *J* = 18.6, 7.5 Hz, C*H*=CH$SiEt_3$), 5.78 (dq, *J* = 5.4, 1.8 Hz, CH_2CH=C*H*CH),), 5.62 (dq, *J* = 5.4, 2.1 Hz, CH_2C*H*=CHCH), 5.53 (d, *J* = 18.6, 1.2 Hz, CH=C*H*$SiEt_3$), 3.33 (m, =CHC*H*(CH=)CH_2), 2.25 (m, 2H, =CHC$H_2$$CH_2$), 1.81 (m, 2H, =CH$CH_2CH_2$CH), 0.92 (t, 9H, Si($CH_2CH_3$)$_3$), 0.54 (q, 6H, Si(C$H_2$$CH_3$)$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 151.9 (*C*H=CH$SiEt_3$), 134.0 (CH=*C*H$SiEt_3$), 131.6 (CH=*C*HCHCH_2), 123.9 (CH_2*C*H=CHCH), 52.7 (=CH*C*H(CH=)CH_2), 32.3 and 30.5 (CH_2), 7.5 ($SiCH_2CH_3$), 3.7 ($SiCH_2CH_3$); GC-MS *m/z* = 208 (M^+).