Carbon-Oxygen Bond Formation between a Terminal Alkoxo Ligand and a Coordinated Olefin. Evidence for Olefin Insertion into a Rhodium-Alkoxide

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Supporting Information

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General. Unless noted otherwise, all manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven-dried for approximately 1 h prior to use. THF, Et_2O, toluene, benzene and pentane were collected from a solvent purification system containing a 1 m column of activated alumina. C_6D_6, C_6D_{12} and THF-d_8 were dried over sodium benzophenone ketyl and vacuum transferred prior to use. ^{1}H NMR spectra were obtained on a 400- or 500-MHz spectrometer, and chemical shifts were recorded relative to residual protiated solvent. ^{13}C NMR spectra were obtained at 100.6 or 125.8 MHz on a 400- or 500-MHz instrument, and chemical shifts were recorded relative to the solvent resonance. Both ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{31}P NMR spectra were obtained at 161.9 MHz, and chemical shifts are reported in parts per million downfield of 85% H_3PO_4.

PEt_3, tetramethylsilane, methylmagnesium bromide, phenylmagnesium bromide, 2-methyl-4-penten-2-ol (**1e**), 2-phenyl-4-penten-2-ol (**1f**), 5-hexen-2-one, ethyl 4-pentenoate, ethyl 2-methyl-4-pentenoate, *N*-bromosuccinimide, KO^{t}Bu, CaH_2, 9-BBN, ethyl 4-pentynoate and deuterated acetic acid (AcOD) were commercially available and used as received. $\{[(COE)_2Rh(\mu\text{-}Cl)]_2\}$,[1] $[(PEt_3)_2RhN(SiMe_3)_2]$,[2] $[(PEt_3)_2Rh(\eta^3\text{-allyl})]$[2] and $[(PEt_3)_4RhH]$[3] were prepared according to literature procedures. 2-Methyl-5-hexen-2-ol (**1a**),[4] 2-phenyl-5-hexen-2-ol (**1b**)[4], 1,1-diphenyl-4-penten-1-ol (**1c**)[5] and 2,2-dimethyl-5-bromomethyltetrahydrofuran[6] were prepared using general procedures reported for the preparation of similar compounds. Kinetic studies of samples heated in an oil bath were conducted with a thermostated bath in which the temperature fluctuation was ±0.1 °C. The temperature of the samples of reactions monitored by NMR spectroscopy was measured with a thermocouple inserted through the instrument into a toluene solution in an NMR sample tube.

Preparation of 1,1-diphenyl-2-methyl-4-penten-1-ol (1c).[4] Into a 25 mL round bottom flask equipped with a magnetic stir bar was added PhMgBr (3.0 M in Et_2O; 3.7 mL, 11 mmol) and 5 mL of dry Et_2O. The mixture was stirred at 0 °C for 10 min. At 0 °C with vigorous stirring and N_2 flow, ethyl 2-methyl-4-pentenoate (710 mg, 5.00 mmol) was added dropwise as an Et_2O solution (3 mL). The resulting mixture was stirred at 0 °C for 30 minstir and then 8 h at room temperature, at which time the starting materials were fully consumed, as determined by GC. The reaction mixture was cooled to 0 °C and quenched by slow addition of a saturated aqueous solution of NH_4Cl (20 mL) at 0 °C. The resulting mixture was stirred at room temperature for 30 min and was then extracted with Et_2O (30 mL x 3). The organic layers were combined, washed with saturated aqueous $NaHCO_3$ (20 mL x 2) and brine (20 mL x 2), dried over Na_2SO_4, and concentrated *in vacuo*. Further purification by flash column chromatography (15% EtOAc/Hexanes) afforded **1c** as a pale-yellow oil (795 mg, 63%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.84 (d, *J*=6.7 Hz, 3H), 1.71-1.79 (m, 1H), 1.83 (s, 1H), 2.19-2.23 (m, 1H), 2.54-2.61 (m, 1H), 4.90-4.97 (m, 2H), 5.70-5.80 (m, 1H), 6.96-7.01 (m, 2H), 7.11 (brd t, *J*=7.7 Hz, 4H), 7.44-7.50 (m, 4H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 13.8, 36.2, 40.4, 80.8, 115.9, 125.91, 125.98, 126.36, 126.48, 128.14, 128.24, 137.8, 146.93, 146.95. Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.45; H, 7.72.

General Procedure for the Independent Preparation of 2,2-Disubstituted-5-Methylenetetrahydrofurans (3a-d). (a) Intramolecular bromoetherifications of γ,ω-olefinic alcohols (1a-d).[3] Into a 50 mL round bottom flask equipped with a magnetic stir bar was placed the corresponding γ,ω-olefinic alcohol (10.0 mmol), *N*-bromosuccinimide (1.10 equiv, 1.96 g) and CCl_4 (20 mL). The suspension was then stirred at room temperature for 3-10 h, and conversions were checked by TLC or GC. The mixture was then combined with pentane (30 mL)

and filtered. NaOAc (20 mg) was added to the filtrate before it was concentrated *in vacuo* to afford the 2,2-disubstituted-5-bromomethyltetrahydrofuran derivatives that were used without further purification.

Preparation of 2-Methyl-2-Phenyl-5-Bromomethyltetrahydrofuran. The general procedure for intramolecular bromoetherification of γ,ω-olefinic alcohol **1b** afforded 2-methyl-2-phenyl-5-bromomethyltetrahydrofuran as a mixture of 3.5:1 diastereomers (sticky yellow oil; 2.22 g, 87%). ^{1}H NMR (400 MHz, C_6D_6), major isomer: δ 1.31 (s, 3H), 1.32-1.40 (m, 1H), 1.60-1.75 (m, 2H), 1.83-1.88 (m, 1H), 2.89-2.93 (m, 1H), 3.13-3.18 (m, 1H), 4.11 (quintet, *J*=6.3 Hz, 1H), 7.08 (t, *J*=7.6 Hz, 1H), 7.19 (t, *J*=7.7 Hz, 2H), 7.39 (d, *J*=7.8 Hz, 2H). Minor isomer: δ 1.51 (s, 3H), 1.48-1.55 (m, 1H), 3.02-3.08 (m, 1H), 3.96 (quintet, *J*=5.5 Hz, 1H), 7.30 (d, *J*=7.7 Hz, 2H). Other proton signals for the minor isomer were not observed or partially obstructed by signals of the major isomer. ^{13}C NMR (125.8 MHz, C_6D_6), major isomer: δ 29.7, 30.40, 35.7, 39.0, 78.4, 85.4, 124.7, 126.6, 128.2, 148.7. Minor isomer: 30.0, 30.50, 36.2, 38.7, 77.7, 85.7, 124.5, 128.3, 148.0. The signal for one of the aromatic carbons for the minor isomer was not observed.

Preparation of 2,2-Diphenyl-5-Bromomethyltetrahydrofuran. The general procedure for intramolecular bromoetherification of γ,ω-olefinic alcohol **1c** afforded 2,2-diphenyl-5-bromomethyltetrahydrofuran as a sticky yellow gel (2.79 g, 88%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.46-1.53 (m, 1H), 1.59-1.68 (m, 1H), 2.15-2.31 (m, 2H), 2.95-2.30 (m, 1H), 3.11-3.15 (m, 1H), 4.05 (quintet, *J*=6.2 Hz, 1H), 6.97-7.05 (m, 2H), 7.08-7.15 (m, 4H), 7.39 (d, *J*=7.9 Hz, 2H), 7.45 (d, *J*=7.8 Hz, 2H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 30.1, 35.9, 38.2, 77.8, 89.1, 125.9 (two overlapping resonances), 126.8 (two overlapping resonances), 128.1, 128.3, 146.1, 146.8.

Preparation of 2,2-Diphenyl-3-Methyl-5-Bromomethyltetrahydrofuran. The general procedure for intramolecular bromoetherification of γ,ω-olefinic alcohol **1d** afforded 2,2-diphenyl-3-methyl-5-bromomethyltetrahydrofuran as a mixture of 1.4:1 diastereomers (sticky brown gel; 2.72 g, 82%). ^{1}H NMR (400 MHz, C_6D_6), major isomer: δ 0.64 (d, J=7.4 Hz, 3H), 1.21-1.28 (m, 1H), 1.80-1.84 (m, 1H), 2.71-2.77 (m, 1H), 3.13-3.17 (m, 1H), 3.26-3.30 (m, 1H), 3.81 (quintet, *J*=6.3 Hz, 1H), 6.98 (t, *J*=6.8 Hz, 2H), 7.07-7.14 (m, 4H), 7.40 (d, *J*=7.8 Hz, 2H), 7.45 (d, *J*=7.9 Hz, 2H). Minor isomer: δ 0.63 (d, J=7.4 Hz, 3H), 1.58-1.65 (m, 2H), 2.77-2.81 (m, 2H), 3.12-3.16 (m, 1H), 4.40 (quintet, *J*=6.8 Hz, 1H), 7.29 (d, *J*=7.8 Hz, 2H). Other aromatic proton signals for the minor isomer were partially obstructed by signals of the major isomer. ^{13}C NMR (125.8 MHz, C_6D_6), alphatic region of the major isomer: δ 20.0, 35.4, 38.58, 40.5, 75.6, 90.96. Aliphatic region of the minor isomer: 16.9, 36.1, 38.53, 40.1, 77.9, 91.19. The signals for the aromatic carbons of the two isomers could not be resolved due to partial overlapping and similar ratios of the major and minor diastereomers.

General Procedure for the Independent Preparation of 2,2-Disubstituted-5-Methylenetetrahydrofurans (3a-d). (b) Dehydrobromination of the 2,2-Disubstituted-5-Bromomethyltetrahydrofurans.[3] Into a 25 mL round bottom flask equipped with a magnetic stir bar was placed the corresponding 2,2-disubstituted-5-bromomethyltetrahydrofuran (1.0 mmol), KO^{t}Bu (1.0 equiv, 112 mg) and dry THF (10 mL). The mixture was then stirred at 60 °C for 3-6 h, and conversions were checked by TLC or GC. The mixture was then cooled to room temperature and all volatile materials were evaporated *in vacuo*. The residue was mixed with pentane (20 mL) and filtered. The filtrate was concentrated *in vacuo* to afford the crude 2,2-disubstituted-5-methylenetetrahydrofuran derivatives **3a-d**. Further purifications were achieved by flash column chromatography or recrystallization.

2,2-Dimethyl-5-methylenetetrahydrofuran (3a) via Dehydrobromination of 2,2-Dimethyl-5-Bromomethyltetrahydrofuran. Into a 50 mL round bottom flask equipped with a magnetic stir bar was placed 2,2-dimethyl-5-bromomethyltetrahydrofuran (193 mg, 1.00 mmol), KO^{t}Bu (2.00 equiv, 224 mg), CaH_2 (2.2 equiv, 92 mg) and dry Et_2O (20 mL). The mixture was then stirred at room temperature for 20 h, at which point the substrate was fully consumed, as determined by GC. All volatile materials were then transferred to a flask in a –95 °C bath by vacuum transfer without heating. The mixture was then carefully concentrated *in vacuo* (300 mbar, no heating) to remove most of the Et_2O. This procedure afforded crude **3a** as a colorless oil (55 mg, still containing small amount of Et_2O). This compound is highly volatile and decomposes above 60 °C, presumably by isomerization to form the more stable 2,2-dimethyl-5-methyl-2,3-dihydrofuran. This compound was, therefore, characterized by NMR spectroscopy without further purification. ^{1}H NMR (500 MHz, C_6D_6): δ 1.09 (s, 6H, partially obstructed by the proton signals of the Et_2O), 1.36 (*t*, *J*=7.7 Hz, 2H), 2.34 (t, *J*=7.7 Hz, 2H), 3.87 (s, 1H), 4.47 (s, 1H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 27.3, 29.6, 37.1, 79.0, 84.0, 162.7.

2-Methyl-2-Phenyl-5-Methylenetetrahydrofuran (3b) via Dehydrobromination of 2-Methyl-2-Phenyl-5-Bromomethyltetrahydrofuran. The general procedure for dehydrobromination with 2-methyl-2-phenyl-5-bromomethyltetrahydrofuran, followed by purification by flash column chromatography (5% EtOAc/Hexanes), afforded 2-methyl-2-phenyl-5-methylenetetrahydrofuran (**3b**) as light-yellow oil (138 mg, 78%). ^{1}H NMR (500 MHz, C_6D_6): δ 1.42 (s, 3H), 1.64-1.70 (m, 1H), 1.81-1.86 (m, 1H), 2.15-2.29 (m, 2H), 3.95 (s, 1H), 4.65 (s, 1H), 7.05 (t, *J*=7.7 Hz, 1H), 7.15 (t, *J*=7.0 Hz, 2H), 7.33 (d, *J*=8.1 Hz, 2H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 28.9, 29.1, 79.8, 87.5, 124.9, 127.1, 128.5, 147.0, 162.7. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.78; H, 8.32.

2,2-Diphenyl-5-Methylenetetrahydrofuran (3c) via Dehydrobromination of 2,2-Diphenyl-5-Bromomethyltetrahydrofuran. The general procedure for dehydrobromination with 2,2-diphenyl-5-bromomethyltetrahydrofuran, followed by purification by recrystallization in cold pentane, afforded 2,2-diphenyl-5-methylenetetrahydrofuran (**3c**) as light-brown crystals (145 mg, 61%). Although the analytical data for most of the new compounds in this work was acceptable and the spectral data of **3c** indicated similar purity, suitable analytical data were not obtained on this complex. NMR spectra are provided below to demonstrate purity (Figures S2-S3). ^{1}H NMR (500 MHz, C_6D_6): δ 2.24 (brd s, 4H), 3.99 (s, 1H), 4.73 (s, 1H), 7.00 (t, *J*=7.3 Hz, 2H), 7.09 (t, *J*=7.7 Hz, 4H), 7.42 (t, *J*=7.5 Hz, 4H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 28.8, 37.7, 80.2, 90.6, 125.9, 127.0, 128.2, 145.2, 162.0.

2,2-Diphenyl-3-Methyl-5-Methylenetetrahydrofuran (3d) via Dehydrobromination of 2,2-Diphenyl-3-Methyl-5-Bromomethyltetrahydrofuran. The general procedure for dehydrobromination with 2,2-diphenyl-3-methyl-5-bromomethyltetrahydrofuran, followed by purification by recrystallization in cold pentane, afforded 2,2-diphenyl-3-methyl-5-methylenetetrahydrofuran (**3d**) as white crystals (133 mg, 53%). ^{1}H NMR (500 MHz, C_6D_6): δ 0.70 (d, *J*=6.9 Hz, 3H), 2.06 (dd, *J*=15.5 Hz, 5.0 Hz, 1H), 2.43 (dd, *J*=15.0 Hz, 6.5 Hz, 1H), 2.79 (hexet, *J*=6.4 Hz, 1H), 4.00 (s, 1H), 4.74 (s, 1H), 6.97 (t, *J*=7.8 Hz, 1H), 7.02 (t, *J*=7.8 Hz, 1H), 7.07 (t, *J*=7.9 Hz, 2H), 7.11 (t, *J*=7.9 Hz, 2H), 7.38 (d, *J*=7.7 Hz, 2H), 7.48 (d, *J*=7.7 Hz, 2H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 16.8, 37.7, 40.0, 81.0, 92.9, 126.55, 126.63, 127.0, 127.5, 128.1, 128.6, 143.3, 145.7, 161.2. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.46; H, 7.11.

General Procedure for the Generation and *in situ* NMR Characterization of Bis(triethylphosphine) Rh(I) γ,ω-Olefinic Alkoxides (2a-d). Into a small vial equipped with a

magnetic stir bar was placed $(PEt_3)_2RhN(SiMe_3)_2$ (50 mg, 0.10 mmol) and toluene-d_8 (0.50 mL). The resulting solution was stirred briefly at room temperature before being transferred to a thick-walled NMR tube equipped with a screw cap and a Teflon seal, and was cooled to –78 °C. The γ, ω-olefinic alcohol (0.10 mmol, 1.0 equiv) was dissolved in toluene-d_8 (0.30 mL) and syringed into the NMR tube at –78 °C under a nitrogen flow. The mixture was allowed to sit at –78 °C for 10 min before being mixed by shaking several times for less than 10 s. An color change from deep purple to orange was observed, indicating full conversion of the starting silylamido precursor. The NMR tube was then immediately placed in the cold NMR probe (<-40 °C), and the subsequent NMR characterization was carried out at low temperatures to avoid decomposition.

Generation and *in situ* NMR Characerization of $[(PEt_3)_2RhOC(Me)_2CH_2CH_2CH{=}CH_2]$ (2a). The general procedure for generation of bis(triethylphosphine) Rh(I) γ,ω-olefinic alkoxides with 2-methyl-5-hexen-2-ol (**1a**) gave an orange solution of **2a** in quantitative yield. ^{1}H NMR (400 MHz, toluene-d_8, -40 °C): δ 0.75-1.05 (m, 24H, CH_3 signals for both PEt_3 ligands and CH_2 signals for one PEt_3 ligand), 1.53 (s, 3H, α-CH_3), 1.56 (s, 3H, α-CH_3), 1.50-1.76 (m, 6H, CH_2 signals for a PEt_3 ligand), 1.82 (d, J=10.8 Hz, 1H, CH_2CH=CH_2), 2.22 (t, J=12.4 Hz, 2H, CMe_2CH_2), 2.78 (t, J=15.1, 1H, CH_2CH=CH_2), 3.68 (brd s, 1H, CH=CH_2), 3.83 (brd s, 1H, CH=CH_2), 4.58 (d, J=13.6 Hz, 1H, CH=CH_2). ^{13}C NMR (125.8 MHz, toluene-d_8, -40 °C): δ 8.56, 8.95, 14.4 (d, J=19.8 Hz), 16.3 (d, J=23.4 Hz), 27.9, 34.2, 37.1 (d, J=7.1 Hz), 39.9, 59.4 (t, J=14.8 Hz), 71.1 (dd, J=15.6, 9.9 Hz), 71.3. ^{31}P NMR (161.9 MHz, toluene-d_8, -40 °C): δ 15.3 (dd, J_{PRh}=153.1 Hz, J_{PP}=42.1 Hz), 32.4 (dd, J_{PRh}=147.5 Hz, J_{PP}=42.4 Hz).

Generation and *in situ* NMR Characterization of $[(PEt_3)_2RhOC(Me)(Ph)CH_2CH_2CH{=}CH_2]$ (2b). The general procedure for generation of bis(triethylphosphine) Rh(I) γ,ω-olefinic alkoxides with 2-phenyl-5-hexen-2-ol (**1b**) gave an orange solution of **2b** as 1.0:0.7 mixture of diastereomers in quantitative overall yield. ^{1}H NMR (400 MHz, toluene-d_8, -40 °C), major isomer: δ 0.75-1.05 (m, 24H, CH_3 signals for both PEt_3 ligands and CH_2 signals for one PEt_3 ligand), 1.50-1.72 (m, 6H, CH_2 signals for a PEt_3 ligand), 1.78 (s, 3H, α-CH_3), 2.05-1.18 (m, 2H, CH_2CH=CH_2 and C(Me)(Ph)CH_2), 2.28 (t, *J*=11.5 Hz, 1H, C(Me)(Ph)CH_2), 2.70 (t, *J*=12.8 Hz, 1H, CH_2CH=CH_2), 3.69 (brd s, 1H, CH=CH_2), 3.81 (brd s, 1H, CH=CH_2), 4.40 (d, *J*=13.4 Hz, 1H, CH=CH_2), 7.13 (t, *J*=7.2 Hz, 1H, *para* aromatic), 7.38 (t, *J*=7.7 Hz, 2H, *meta* aromatic), 7.89 (d, *J*=7.5 Hz, 2H, *ortho* aromatic). Minor isomer: 1.82 (s, 3H, α-CH_3), 2.31 (t, *J*=12.4 Hz, 1H, C(Me)(Ph)CH_2), 3.02 (brd s, 1H, CH=CH_2), 3.94 (brd s, 1H, CH=CH_2), 4.49 (d, *J*=13.4 Hz, 1H, CH=CH_2), 7.18 (t, *J*=7.1 Hz, 1H, *para* aromatic), 7.35 (t, *J*=7.7 Hz, 2H, *meta* aromatic), 7.98 (d, *J*=7.5 Hz, 2H, *ortho* aromatic). Other aliphatic proton signals for the minor isomer were partially obstructed by signals of the major isomer. ^{13}C NMR (100.6 MHz, toluene-d_8, -40 °C), major isomer: δ 7.13, 7.15, 13.1 (d, *J*=19.4 Hz), 14.8 (d, *J*=25.2 Hz), 26.7, 33.2, 41.5, 59.5 (t, *J*=9.8 Hz), 70.8 (dd, *J*=16.2 Hz, 10.0 Hz), 74.3, 123.56, 125.1, 126.23, 157.5 (d, *J*=5.4 Hz). Minor isomer: δ 7.07 (d, *J*=3.9 Hz), 7.52 (d, *J*=8.8 Hz), 13.4 (d, *J*=18.4 Hz), 15.2 (d, *J*=25.4 Hz), 25.2, 34.6, 38.4, 53.6 (d, *J*=11.6 Hz), 61.3 (dd, *J*=17.8 Hz, 9.2 Hz), 74.9, 123.72, 125.9, 126.34, 153.8. ^{31}P NMR (161.9 MHz, toluene-d_8, -40 °C), major isomer: δ 15.0 (dd, J_{PRh}=156.6 Hz, J_{PP}=43.7 Hz), 33.4 (dd, J_{PRh}=140.2 Hz, J_{PP}=43.9 Hz). Minor isomer: δ 12.1 (dd, J_{PRh}=155.3 Hz, J_{PP}=44.8 Hz), 34.4 (dd, J_{PRh}=128.9 Hz, J_{PP}=44.4 Hz).

Generation and *in situ* NMR Characterization of $[(PEt_3)_2RhOC(Ph)_2CH_2CH_2CH{=}CH_2]$ (2c). The general procedure for generation of

bis(triethylphosphine) Rh(I) γ,ω-olefinic alkoxides with 1,1-diphenyl-4-penten-1-ol (**1c**) gave an orange solution of **2c** in quantitative yield. ^{1}H NMR (400 MHz, toluene-d_8, -40 °C): δ 0.75-1.02 (m, 24H, CH_3 signals for both PEt_3 ligands and CH_2 signals for one PEt_3 ligand), 1.30-1.65 (m, 6H, CH_2 signals for a PEt_3 ligand), 1.94 (brd s, 1H, C*H*$_2$CH=CH$_2$), 2.20 (brd s, 1H, C*H*$_2$CH=CH$_2$), 2.58-2.74 (m, 2H, CPh$_2$C*H*$_2$), 3.35 (brd s, 1H, CH=C*H*$_2$), 3.94 (brd s, 1H, CH=C*H*$_2$), 4.36 (d, *J*=13.3 Hz, 1H, C*H*=CH$_2$), 7.06 (t, *J*=7.1 Hz, 1H, *para* aromatic), 7.11 (t, *J*=7.3 Hz, 1H, *para* aromatic), 7.20 (t, *J*=7.5 Hz, 2H, *meta* aromatic), 7.28 (t, *J*=7.5 Hz, 2H, *meta* aromatic), 7.71 (d, *J*=7.7 Hz, 2H, *ortho* aromatic), 7.76 (d, *J*=7.6 Hz, 2H, *ortho* aromatic). ^{13}C NMR (100.6 MHz, toluene-d_8, -40 °C): δ 7.06, 7.23, 13.4 (d, *J*=18.8 Hz), 14.9 (d, *J*=23.9 Hz), 25.4, 37.2, 57.8 (d, *J*=11.8 Hz), 66.4 (dd, *J*=17.8 Hz, 8.7 Hz), 79.6, 123.65, 123.80, 125.8, 126.2, 126.7, 127.2, 153.6, 155.0 (d, *J*=4.9 Hz). ^{31}P NMR (161.9 MHz, toluene-d_8, -40 °C): δ 14.1 (dd, J_{PRh}=154.6 Hz, J_{PP}=45.3 Hz), 35.2 (dd, J_{PRh}=148.1 Hz, J_{PP}=45.0 Hz).

Generation and *in situ* NMR Characterization of [(PEt$_3$)$_2$RhOC(Ph)$_2$CH(Me)CH$_2$CH=CH$_2$] (2d). The general procedure for generation of bis(triethylphosphine) Rh(I) γ,ω-olefinic alkoxides with 1,1-diphenyl-2-methyl-4-penten-1-ol (**1d**) gave an orange solution of **2d** as 5:1 mixture of diastereomers in quantitative overall yield. ^{1}H NMR (400 MHz, toluene-d_8, -40 °C), major isomer: δ 0.65-0.95 (m, 24H, CH_3 signals for both PEt_3 ligands and CH_2 signals for one PEt_3 ligand), 1.42-1.60 (m, 6H, CH_2 signals for a PEt_3 ligand), 1.65-1.88 (m, 4H, β-CH_3 and C*H*$_2$CH=CH$_2$), 1.96 (brd s, 1H, CPh$_2$C*H*Me), 3.22 (brd s, 1H, C*H*$_2$CH=CH$_2$), 3.44 (brd s, 1H, CH=C*H*$_2$), 3.95 (brd s, 1H, CH=C*H*$_2$), 4.06 (d, *J*=17.2 Hz, 1H, C*H*=CH$_2$), 7.01 (t, *J*=7.1 Hz, 2H, *para* aromatic), 7.22 (t, *J*=7.5 Hz, 4H, *meta* aromatic), 7.76 (d, *J*=7.6 Hz, 4H, *ortho* aromatic). Minor isomer: 3.34 (brd s, 1H, CH=C*H*$_2$), 7.15 (t, *J*=7.9 Hz, 2H, *para* aromatic), 7.31 (t, *J*=6.1 Hz, 4H, *meta* aromatic), 7.55 (d, *J*=7.5 Hz, 4H, *ortho*

aromatic). Other proton signals for the minor isomer were not observed or partially obstructed by signals of the major isomer. ^{13}C NMR (125.8 MHz, THF-d_8, -40 °C), major isomer: δ 8.00, 8.28, 15.2 (d, *J*=19.4 Hz), 15.8 (d, *J*=25.6 Hz), 17.4, 31.9, 42.3, 63.1 (brd s), 70.8 (dd, *J*=17.7 Hz, 9.2 Hz), 82.6, 124.03, 124.19, 126.78, 126.99, 127.7 (brd s, two overlapping resonances), 154.5, 156.5. Minor isomer: δ 8.39, 8.72, 14.3 (d, *J*=19.0 Hz), 16.4 (d, *J*=25.0 Hz), 20.7, 34.8, 44.1, 62.1 (d, *J*=15.7 Hz), 65.3 (dd, J_1=18.2 Hz, J_2=8.8 Hz), 84.0, 124.62, 124.76, 127.21, 127.37, 127.6 (brd s, two overlapping resonances), 151.4, 155.3. ^{31}P NMR (161.9 MHz, toluene-d_8, -40 °C), major isomer: δ 17.1 (dd, J_{PRh}=154.6 Hz, J_{PP}=47.4 Hz), 35.2 (dd, J_{PRh}=148.5 Hz, J_{PP}=47.4 Hz). Minor isomer: δ 14.6 (dd, J_{PRh}=153.8 Hz, J_{PP}=47.6 Hz), 36.6 (dd, J_{PRh}=148.5 Hz, J_{PP}=47.4 Hz).

General Procedure for the Preparation of Bis(triethylphosphine) Rh(I) β,ω-Olefinic Alkoxides (2e, 2f). Into a 20 mL scintillation vial equipped with a magnetic stir bar was placed $(PEt_3)_2RhN(SiMe_3)_2$ (200 mg, 0.40 mmol) and Et_2O (5 mL). The corresponding β, ω-olefinic alcohol (0.40 mmol, 1.0 equiv) was dissolved in Et_2O (2 mL) and added dropwise under stirring. An instant color change from dark purple to red-orange was observed. The solution was stirred at room temperature for 5-10 min until the rhodium silylamide was fully converted, as determined by ^{31}P NMR spectroscopy. The volatile materials were evaporated under reduced pressure, affording the crude rhodium alkoxide product as a precipitate. Further purification was achieved by crystallization from Et_2O or pentane at –35 °C.

Preparation of $[(PEt_3)_2RhOC(Me)_2CH_2CH=CH_2]$ (2e). The general procedure for the preparation of bis(triethylphosphine)-ligated rhodium β,ω-olefinic alkoxide complexes, followed by crystallization from pentane at -35 °C, gave red-orange crystals of **2e** (134 mg, 77% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 0.83-0.92 (m, 9H, CH_3 signals for PEt_3 ligands), 0.98-1.15 (m, 15

H, CH_2 and CH_3 signals for PEt_3 ligands), 1.63 (s, 3H, OC(CH_3)$_2$), 1.65-1.90 (m, 7H, CH_2 signals for PEt_3 ligands and CH_2CH=CH_2), 1.96 (s, 3H, OC(CH_3)$_2$), 2.55 (dd, J_1=11.8 Hz, J_2=6.3 Hz, 1H, CH_2CH=CH_2), 4.06 (hexet, J=6.5 Hz, 1H, CH_2CH=CH_2), 4.15 (dd, J=13.4 Hz, 2.6 Hz, 1H, CH_2CH=CH_2), 4.23 (dt, J=7.2 Hz, 3.1 Hz, 1H, $CH_2$$CH$=$CH_2$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 8.53, 8.68, 16.4 (d, J=20.4 Hz), 17.9 (d, J=23.1 Hz), 33.8 (d, J=5.3 Hz), 39.7, 48.5, 66.7 (d, J=13.1 Hz), 78.8 (dd, J=17.0 Hz, 7.0 Hz), 85.0 (d, J=6.5 Hz). ^{31}P NMR (161.9 MHz, C_6D_6): δ 22.5 (dd, J_{PRh}=168.5 Hz, J_{PP}=46.3 Hz), 33.9 (dd, J_{PRh}=137.6 Hz, J_{PP}=46.6 Hz). Anal. Calcd for $C_{18}H_{41}OP_2Rh$: C, 49.32; H, 9.43. Found: C, 49.60; H, 9.19.

Preparation of [(PEt_3)$_2$RhOC(Me)(Ph)CH_2CH=CH_2] (2f). The general procedure for the preparation of bis(triethylphosphine)-ligated rhodium β,ω-olefinic alkoxide complexes, followed by crystallization from Et_2O at -35 °C, gave orange crystals of **2f** (131 mg, 66% overall yield) as a 6:1 mixture of diastereomers. ^{1}H NMR (400 MHz, toluene-d_8), major isomer: δ 0.95-1.18 (m, 24H, CH_3 signals for both PEt_3 ligands and CH_2 signals for one PEt_3 ligand), 1.51 (s, 3H, α-CH_3), 1.72-1.95 (m, 7H, CH_2 signals for another PEt_3 ligand and CH_2CH=CH_2), 2.53 (dd, J=13.8 Hz, 5.6 Hz, 1H, CH_2CH=CH_2), 3.52 (m, 1H, CH_2CH=CH_2), 3.75-3.88 (m, 2H, CH_2CH=CH_2 and $CH_2$$CH$=$CH_2$), 6.86 (t, J=7.2 Hz, 1H, *para* aromatic), 7.01 (t, J=7.6 Hz, 2H, *meta* aromatic), 7.40 (d, J=7.7 Hz, 2H, *ortho* aromatic). Minor isomer: 6.92 (t, J=7.2 Hz, 1H, *para* aromatic), 7.08 (t, J=7.7 Hz, 2H, *meta* aromatic), 7.76 (d, J=7.6 Hz, 2H, *ortho* aromatic). Other proton signals for the minor isomer were not observed or partially obstructed by signals of the major isomer. ^{13}C NMR (100.6 MHz, THF-d_8), major isomer: δ 8.16, 8.38, 16.2 (d, J=20.5 Hz), 17.4 (d, J=24.3 Hz), 39.1, 48.7, 65.3 (ddd, J_1=13.0 Hz, J_2=5.8 Hz, J_3=2.5 Hz), 78.7 (dd, J_1=16.2 Hz, J_2=7.9 Hz), 84.4 (d, J_1=6.4 Hz), 124.1, 125.5, 126.9, 156.7. Minor isomer: 7.95, 16.8 (d, J=20.0 Hz), 18.3 (d, J=24.7 Hz), 50.4, 124.4, 125.5, 126.8. Other carbon signals of the

minor isomer were not observed or partially obstructed by signals of the major isomer. ^{31}P NMR (161.9 MHz, C_6D_6), major isomer: δ 21.4 (dd, J_{PRh}=168.4 Hz, J_{PP}=46.5 Hz), 34.4 (dd, J_{PRh}=157.5 Hz, J_{PP}=46.0 Hz). Minor isomer: δ 19.1 (dd, J_{PRh}=169.7 Hz, J_{PP}=50.2 Hz), 35.0 (dd, J_{PRh}=132.6 Hz, J_{PP}=49.9 Hz). Anal. Calcd for $C_{23}H_{43}OP_2Rh$: C, 55.20; H, 8.66. Found: C, 54.89; H, 8.37.

General Procedure for the Cyclizations of *in situ* Generated Rh(I) γ,ω-Olefinic Alkoxide Complexes 2a-d. Into a small vial was placed 1.0 mg of 1,3,5-trimethoxybenzene (internal standard), C_6D_6 (0.50 mL) and the corresponding γ,ω-olefinic alcohol (0.020 mmol). The mixture was stirred at room temperature until it was homogeneous before being transferred to an NMR tube equipped with a screw cap and a Teflon seal. An initial ^{1}H NMR spectrum was acquired. $(PEt_3)_2RhN(SiMe_3)_2$ (10.0 mg, 1.0 equiv) and PEt_3 (23.6 mg, 10.0 equiv) were quickly added as a C_6D_6 solution (0.20 mL) by syringe, and the mixture was briefly shaken (in less than 30 sec) to allow good mixing and quantitative generation of the rhodium alkoxide complex **2a-d**. The solution was then heated in a thermostated oil bath at 25-35 °C for 10 - 90 min until the starting rhodium complex was fully consumed, as determined by ^{1}H or ^{31}P NMR spectroscopy. A second ^{1}H NMR spectrum was acquired, and the yields of the cyclization products **3a-d** were calculated.

Cyclization of *in situ* Generated Alkoxide 2a. The reaction of *in situ* generated **2a** (with 2.3 mg of **1a**, 0.020 mmol) with added PEt_3 (23.6 mg, 10.0 equiv) and 1,3,5-trimethoxybenzene as internal standard in C_6D_6 (0.7 mL) at 35 °C for 5 min gave 70% yield of **3a**, as determined by ^{1}H NMR spectroscopy. The same reaction was carried out at 25 °C for 15 min and gave 68% of **3a**, as determined by ^{1}H NMR spectroscopy.

Cyclization of *in situ* Generated Alkoxide 2b. The reaction of *in situ* generated **2b** (with 3.5 mg of **1b**, 0.020 mmol) with added PEt_3 (23.6 mg, 10.0 equiv) and 1,3,5-

trimethoxybenzene as internal standard in C_6D_6 (0.7 mL) at 35 °C for 10 min gave 80% yield of **3b**, as determined by ^{1}H NMR spectroscopy. The same reaction was carried out at 25 °C for 30 min and gave 87% of **3b**, as determined by ^{1}H NMR spectroscopy.

Cyclization of *in situ* Generated Alkoxide 2c. The reaction of *in situ* generated **2c** (with 4.8 mg of **1c**, 0.020 mmol) with added PEt_3 (23.6 mg, 10.0 equiv) and 1,3,5-trimethoxybenzene as internal standard in C_6D_6 (0.7 mL) at 35 °C for 1.5 h gave 92% yield of **3c**, as determined by ^{1}H NMR spectroscopy.

Cyclization of *in situ* Generated Alkoxide 2d. The reaction of *in situ* generated **2d** (with 5.0 mg of **1d**, 0.020 mmol) with added PEt_3 (23.6 mg, 10.0 equiv) and 1,3,5-trimethoxybenzene as internal standard in C_6D_6 (0.7 mL) at 35 °C for 1 h gave 74% yield of **3c**, as determined by ^{1}H NMR spectroscopy.

General Procedure for the β-Allyl Eliminations of Rh(I) β,ω-Olefinic Alkoxide Complexes 2e and 2f. Into a small vial was placed the rhodium alkoxide complex (0.010 mmol) and 1.0 mg of 1,3,5-trimethoxybenzene as internal standard. C_6D_6 (0.5 mL) was added, and the solution was stirred until it was homogeneous before being transferred to a thick-walled NMR tube equipped with a screw cap and a Teflon seal. An initial ^{1}H NMR spectrum was acquired. The solution was then heated in a thermostated oil bath at 90 °C for 1-2 h until the starting rhodium complex was fully consumed, as determined by ^{1}H or ^{31}P NMR spectroscopy. A second ^{1}H NMR spectrum was acquired, and the yield of the ketone and the rhodium phenyl product $(PEt_3)_3RhPh$ (**4**) were calculated.

β-Allyl Elimination of $[(PEt_3)_2RhOCMe_2CH_2CH{=}CH_2]$ (2e). The reaction of **2e** (4.4 mg, 0.010 mmol) and 1,3,5-trimethoxybenzene as internal standard in C_6D_6 (0.5 mL) at 90 °C for 2 h gave 85% yield of $(PEt_3)_2Rh(\eta^3$-allyl) and 74% yield of acetone, as determined by ^{1}H NMR

spectroscopy. When the same reaction was carried out with added PEt_3 (9.5 mg, 8.0 equiv), similar yields (88% of $(PEt_3)_2Rh(\eta^3$-allyl) and 71% of acetone) and reaction rate were measured (half-life ~ 20 min for both reactions).

β-Allyl Elimination of $[(PEt_3)_2RhOC(Me)(Ph)CH_2CH=CH_2]$ (2f). The reaction of **2f** (5.0 mg, 0.010 mmol) and 1,3,5-trimethoxybenzene as internal standard in C_6D_6 (0.5 mL) at 90 °C for 1 h gave 81% yield of $(PEt_3)_2Rh(\eta^3$-allyl) and 67% yield of acetophenone, as determined by ^{1}H NMR spectroscopy. When the same reaction was carried out with added PEt_3 (9.5 mg, 8.0 equiv), similar yields (84% of $(PEt_3)_2Rh(\eta^3$-allyl) and 70% of acetophenone) and reaction rate were measured (half-life ~ 10 min for both reactions).

Representative Procedure for the Kinetic Experiments Conducted on Cyclizations of *in situ* Generated $[(PEt_3)_2RhOCPh_2CH_2CH_2CH=CH_2]$ (2c) in the Presence of Added PEt_3. Into a small vial was placed $(PEt_3)_2RhN(SiMe_3)_2$ (10.0 mg, 0.020 mmol) and 1.0 mg of 1,3,5-trimethoxybenzene (internal standard). C_6D_6 (0.30 mL) and PEt_3 (7.1 mg, 3.0 equiv) were added by syringe. The mixture was stirred at room temperature until it was homogeneous. The solution was transferred to an NMR tube equipped with a screw cap and a Teflon seal. 1,1-Diphenyl-4-penten-1-ol (**1c**, 4.8 mg, 1.0 equiv) was quickly added as a C_6D_6 solution (0.20 mL) by syringe, and the mixture was briefly shaken (in less than 30 sec) to allow good mixing. The sample was immediately placed into the heated NMR probe (35.0 °C) ,and a ^{1}H NMR spectrum was obtained at fixed intervals. This procedure was repeated using different initial concentrations of PEt_3 or in different deuterated solvents.

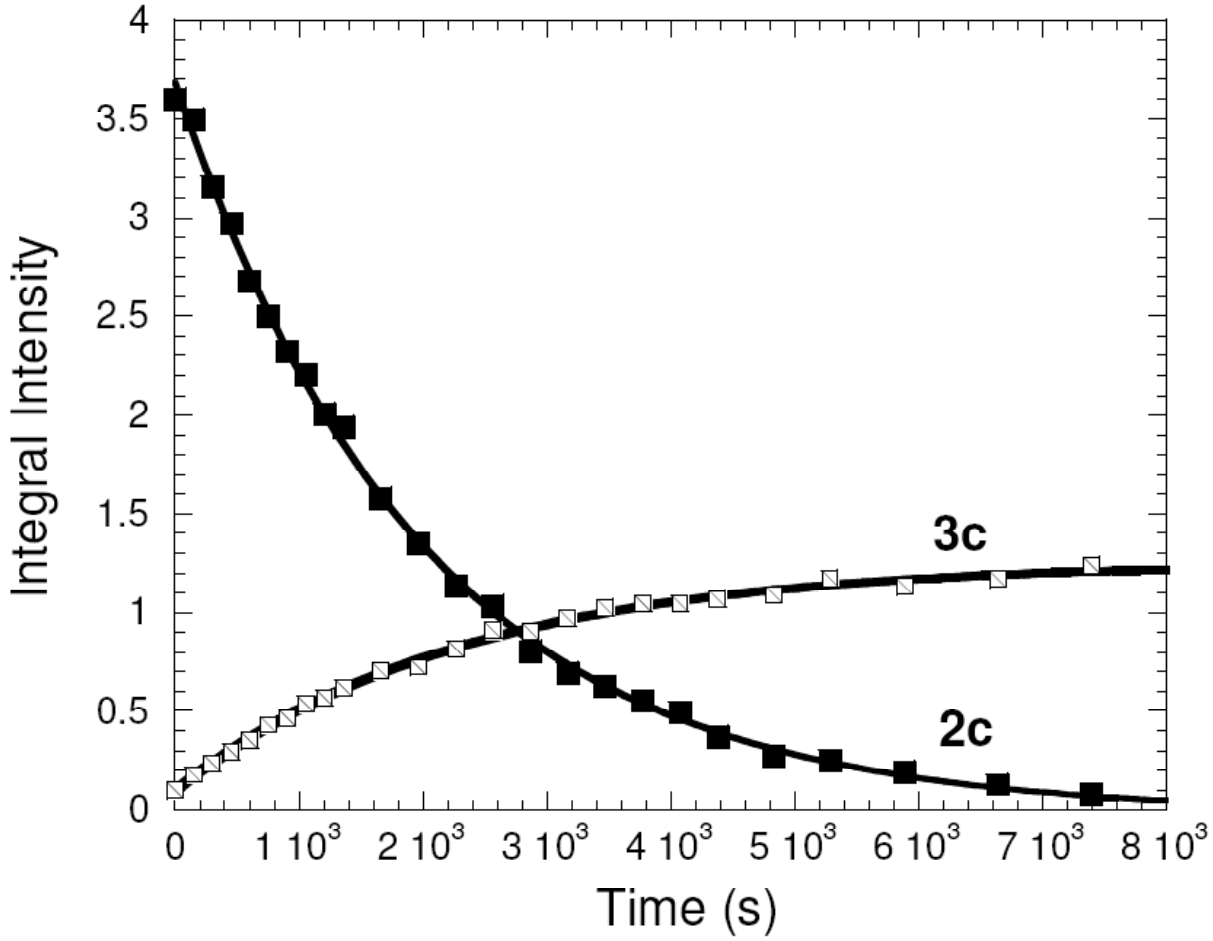

Figure S1. Representative kinetic plot for the cyclization of *in situ* generated $[(PEt_3)_2RhOCPh_2CH_2CH_2CH{=}CH_2]$ (**2c**, 0.040 M) in the presence of added PEt_3 (0.40 M) in THF-d_8 at 35 °C. The curve for the consumption of **2c** depicts the results of an unweighted least-square fit to y = a*exp(-b*x) + c (a = 3.71 ± 0.03, b = 0.00050 ± 0.00001, c = -0.02 ± 0.03). The curve for the accumulation of 2,2-diphenyl-5-methylenetetrahydrofuran (**3c)** depicts the results of an unweighted least-square fit to y = -a*exp(-b*x) + c (a = 1.15 ± 0.02, b = 0.00044 ± 0.00002, c = 1.25 ± 0.02). The differences between the integration values are due to various proton signal intensities used for integration: 4H for **2c** and 2H for **3c**.

Table S1. Effect of [PEt_3] on the rate constants and yield for the cyclization of in *situ* generated **2c** (0.040 M in C_6D_6, 35 °C).

[PEt_3] (M)	0.12	0.40	1.20
k_{obsd} (s^{-1})	0.00074	0.00079	0.00084
Yield of **3c**	49%	74%	82%

Preparation of Stereochemically Defined, ^{2}H-Labeled Alcohol *trans*-5-*d*-1a. (a) *trans*-5-*d*-Ethyl 4-Pentenoate. At 0 °C and under a nitrogen flow, 9-BBN (0.5 M in THF, 5.0 mL, 2.5 mmol) was slowly added to a stirred solution of ethyl 4-pentynoate (630 mg, 5.0 mmol, 2.0 equiv) in THF (20 mL) by syringe. The mixture was stirred at 0 °C for 30 min and then stirred at room temperature for 2 h to allow full consumption of 9-BBN. The mixture was stirred at 0 °C and deuterated acetic acid (AcOD, 150 μL, 1.1 equiv) was slowly added as a THF solution (2 mL). The mixture was stirred at room temperature for another 1 h and concentrated *in vacuo* to give a crude oil. The desired product, *trans*-5-*d*-ethyl 4-pentenoate was separated as colorless oil (132 mg, 41%) by preparative TLC (10% Et_2O/pentane) and was pure enough for subsequent transformations. **(b) *trans*-5-*d*-2-Methyl-5-hexen-2-ol (*trans*-5-*d*-1a).** At 0 °C and under a nitrogen flow, *trans*-5-*d*-ethyl 4-pentenoate (65 mg, 0.50 mmol) was slowly added to a stirred solution of MeMgBr (2.0 M in Et_2O, 0.55 mL, 2.2 equiv) in Et_2O (5 mL) as a Et_2O solution (2 mL). The solution was stirred at 0 °C for 30 min and then stirred at room temperature for 3 h. The reaction mixture was then carefully quenched with saturated aqueous NH_4Cl (10 mL) at 0 °C and extracted with Et_2O (20 mL x 3). The organic layers were combined and subsequently washed with saturated aqueous $NaHCO_3$ (15 mL x 2) and brine (15 mL x 2), dried over Na_2SO_4, and concentrated *in vacuo*. Further purification by flash column chromatography (10% EtOAc/Hexanes) afforded ***trans*-5-*d*-1a** as a colorless oil (32 mg, 55%). ^{1}H and ^{2}H NMR spectra indicated exclusive deuterium labeling at the *trans*-5 position (45% deuterium incorporation).

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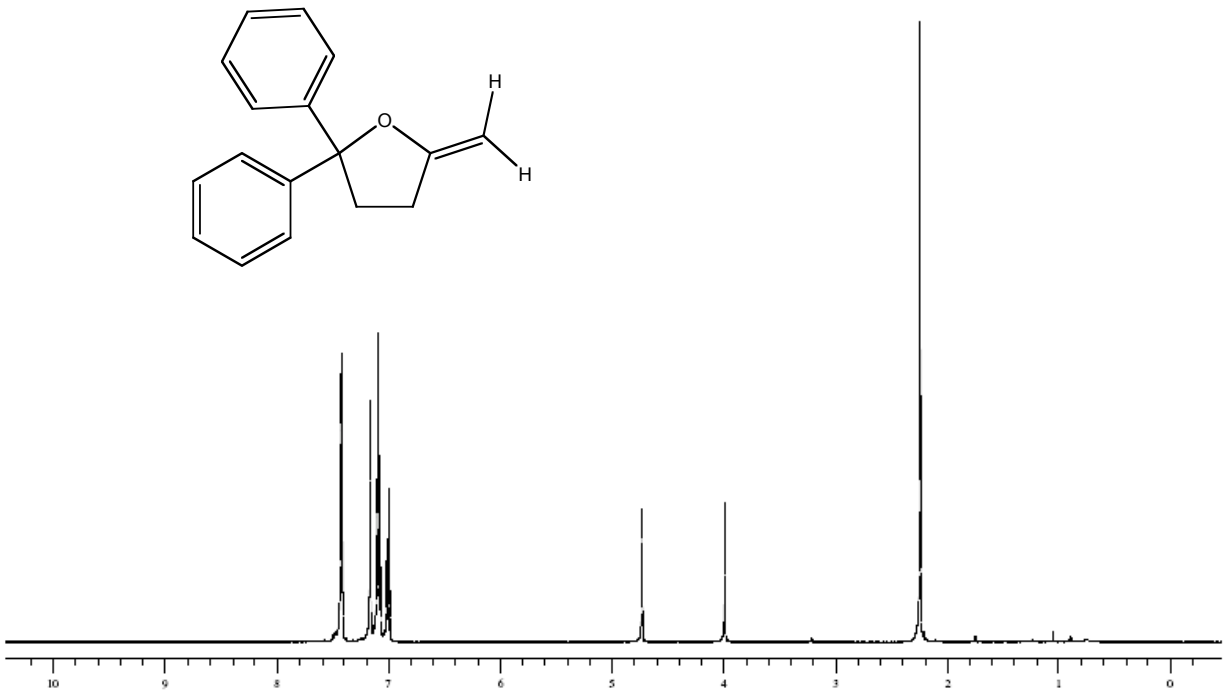

Figure S2. ^{1}H NMR spectrum (500 MHz, C_6D_6) of 2,2-diphenyl-5-methylenetetrahydrofuran (**3c**).

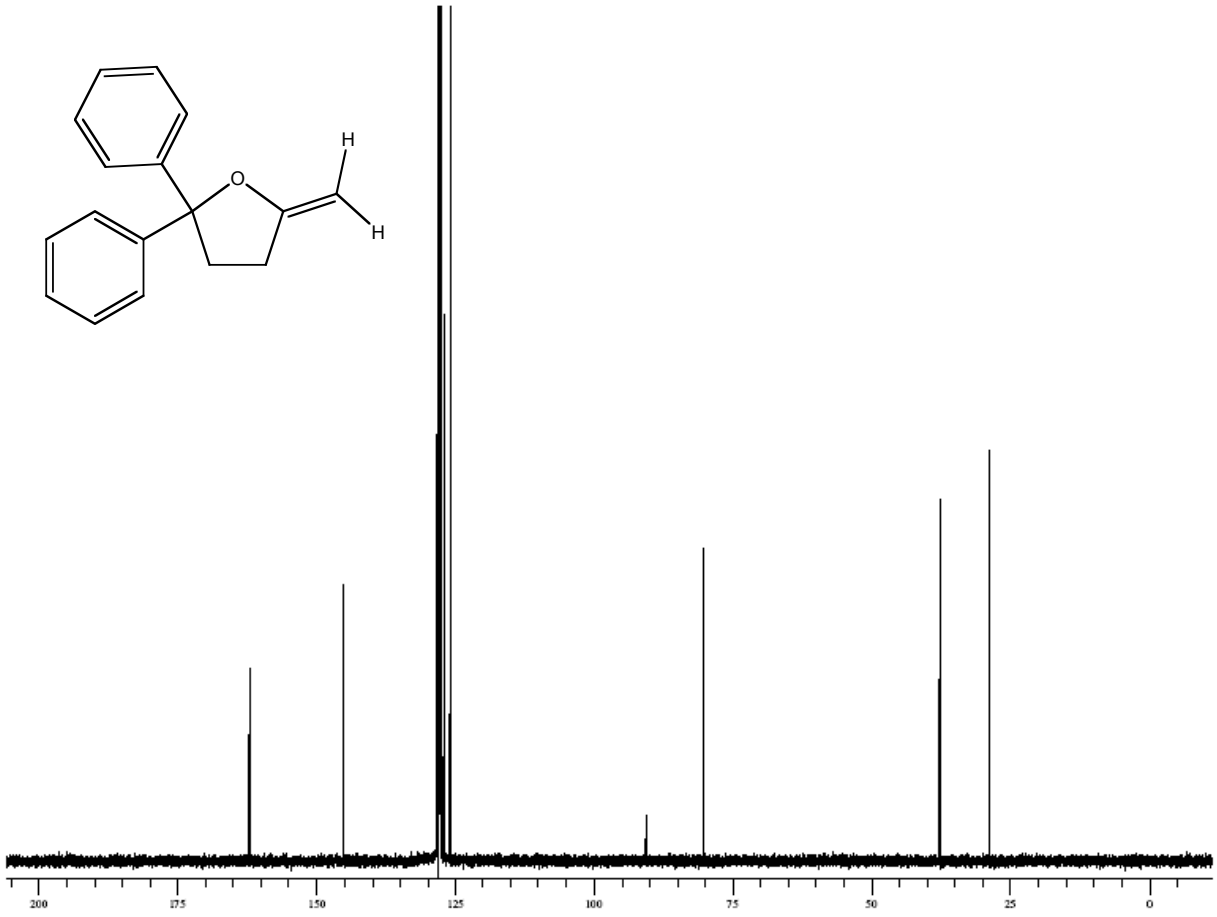

Figure S3. ^{13}C NMR spectrum (125.8 MHz, C_6D_6) of 2,2-diphenyl-5-methylenetetrahydrofuran (**3c**).

Experimental Procedure for the X-ray Diffraction of $[(PEt_3)_2RhOCMe_2CH_2CH{=}CH_2]$ (**2e**)

Data Collection

An orange block crystal of $C_{18}H_{41}OP_2Rh$ having approximate dimensions of 0.20 x 0.20 x 0.15 mm^3 was mounted with epoxy cement on the tip of a fine glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 9.2811(19) Å	α = 90 º
b = 15.630(3) Å	β = 98.85(3) º
c = 15.370(3) Å	γ = 90 º
V = 2203.1(8) $Å^3$	

For Z = 4 and F.W. = 438.36, the calculated density is 1.322 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (#14).

The data were collected at a temperature of 173(2) K to a maximum 2θ value of 56.56 °. Five omega scans consisting of 37, 29, 34, 29, and 17 data frames, respectively, were collected with a frame width of 2.0 ° and a detector-to-crystal distance, Dx, of 35.0 mm. Each frame was exposed twice (for the purpose of de-zingering) for a total of 50 s. The data frames were processed and scaled using the DENZO software package.[1]

Data Reduction

A total of 9806 reflections were collected of which 5438 were unique and observed (R_{int} = 0.0312). The linear absorption coefficient, μ, for Mo-Kα radiation is 9.21 cm^{-1}, and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. The final cycle of full-matrix least-squares refinement[3] on F was based on 5438 observed reflections ($I > 2.00\sigma(I)$) and 199 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0324$$

$$R_W = \{\Sigma[w \; (F_o^2 - F_c^2)^2] \; / \; \Sigma[w(F_o^2)^2]\}^{1/2} = 0.0802$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 0.541 and –0.791 $e^-/Å^3$ respectively.

References for the X-ray diffraction studies:

(1) Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press.

(2) *Acta Cryst*. **A46** (1990) 467-473

(3) Least Squares function minimized:
$$\Sigma w(F_o^2 - F_c^2)^2$$

Table S2. Crystal data and structure refinement for **2e**.

Empirical formula	$C_{18}H_{41}OP_2Rh$	
Formula weight	438.36	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.2811(19) Å	α= 90°.
	b = 15.630(3) Å	β= 98.85(3)°.
	c = 15.370(3) Å	γ = 90°.
Volume	2203.1(8) $Å^3$	
Z	4	
Density (calculated)	1.322 g/cm^3	
Absorption coefficient	9.21 cm^{-1}	
F(000)	928	
Crystal size	0.20 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.58 to 28.28°.	
Index ranges	-12<=h<=12, -18<=k<=20, -20<=l<=20	
Reflections collected	9806	
Independent reflections	5438 [R(int) = 0.0312]	
Completeness to theta = 28.28°	99.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8742 and 0.8372	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5438 / 0 / 199	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0324, wR2 = 0.0802	
R indices (all data)	R1 = 0.0457, wR2 = 0.0852	
Largest diff. peak and hole	0.541 and -0.791 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **2e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	3413(1)	1444(1)	3191(1)	21(1)
P(1)	2289(1)	1475(1)	1756(1)	25(1)
P(2)	5603(1)	999(1)	2957(1)	25(1)
O(1)	1553(2)	2060(1)	3417(1)	29(1)
C(1)	2950(2)	879(2)	861(1)	30(1)
C(2)	2014(3)	891(2)	-41(2)	54(1)
C(3)	1868(3)	2542(2)	1303(2)	44(1)
C(4)	3161(3)	3118(2)	1289(2)	52(1)
C(5)	449(2)	1056(2)	1750(2)	36(1)
C(6)	411(3)	116(2)	1986(2)	45(1)
C(7)	5850(2)	-31(2)	2424(2)	33(1)
C(8)	5204(3)	-780(2)	2858(2)	41(1)
C(9)	6516(3)	1722(2)	2273(2)	38(1)
C(10)	6777(3)	2620(2)	2664(2)	55(1)
C(11)	6937(2)	931(2)	3975(2)	32(1)
C(12)	8482(2)	622(2)	3914(2)	41(1)
C(13)	3402(2)	577(1)	4263(1)	29(1)
C(14)	3718(3)	1379(1)	4638(2)	27(1)
C(15)	2540(2)	1917(2)	4938(2)	34(1)
C(16)	1850(2)	2529(1)	4206(2)	30(1)
C(17)	2898(3)	3263(2)	4098(2)	41(1)
C(18)	427(3)	2898(2)	4429(2)	41(1)

Table S4. Bond lengths [Å] and angles [°] for **2e**.

Rh(1)-O(1)	2.0521(14)	P(2)-Rh(1)-P(1)	98.19(3)
Rh(1)-C(13)	2.135(2)	C(3)-P(1)-C(5)	100.40(12)
Rh(1)-C(14)	2.201(2)	C(3)-P(1)-C(1)	104.66(12)
Rh(1)-P(2)	2.2297(7)	C(5)-P(1)-C(1)	103.50(11)
Rh(1)-P(1)	2.2910(9)	C(3)-P(1)-Rh(1)	115.14(9)
P(1)-C(3)	1.827(2)	C(5)-P(1)-Rh(1)	106.53(9)
P(1)-C(5)	1.827(2)	C(1)-P(1)-Rh(1)	123.62(8)
P(1)-C(1)	1.843(2)	C(7)-P(2)-C(9)	100.58(12)
P(2)-C(7)	1.836(2)	C(7)-P(2)-C(11)	102.38(11)
P(2)-C(9)	1.837(2)	C(9)-P(2)-C(11)	102.28(11)
P(2)-C(11)	1.843(2)	C(7)-P(2)-Rh(1)	121.66(8)
O(1)-C(16)	1.407(3)	C(9)-P(2)-Rh(1)	114.39(9)
C(1)-C(2)	1.518(3)	C(11)-P(2)-Rh(1)	113.02(8)
C(3)-C(4)	1.503(4)	C(16)-O(1)-Rh(1)	109.40(12)
C(5)-C(6)	1.515(4)	C(2)-C(1)-P(1)	117.74(17)
C(7)-C(8)	1.517(4)	C(4)-C(3)-P(1)	115.35(18)
C(9)-C(10)	1.531(4)	C(6)-C(5)-P(1)	113.72(16)
C(11)-C(12)	1.530(3)	C(8)-C(7)-P(2)	113.34(17)
C(13)-C(14)	1.392(3)	C(10)-C(9)-P(2)	113.44(19)
C(14)-C(15)	1.506(3)	C(12)-C(11)-P(2)	118.71(17)
C(15)-C(16)	1.539(3)	C(14)-C(13)-Rh(1)	73.87(13)
C(16)-C(18)	1.528(3)	C(13)-C(14)-C(15)	120.8(2)
C(16)-C(17)	1.529(3)	C(13)-C(14)-Rh(1)	68.73(13)
O(1)-Rh(1)-C(13)	93.61(8)	C(15)-C(14)-Rh(1)	107.24(14)
O(1)-Rh(1)-C(14)	80.29(8)	C(14)-C(15)-C(16)	111.35(18)
C(13)-Rh(1)-C(14)	37.41(8)	O(1)-C(16)-C(18)	109.22(19)
O(1)-Rh(1)-P(2)	170.15(5)	O(1)-C(16)-C(17)	109.94(19)
C(13)-Rh(1)-P(2)	92.26(7)	C(18)-C(16)-C(17)	109.1(2)
C(14)-Rh(1)-P(2)	99.79(7)	O(1)-C(16)-C(15)	108.04(18)
O(1)-Rh(1)-P(1)	83.28(5)	C(18)-C(16)-C(15)	110.34(19)
C(13)-Rh(1)-P(1)	134.49(6)	C(17)-C(16)-C(15)	110.2(2)
C(14)-Rh(1)-P(1)	160.51(7)		

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	21(1)	26(1)	16(1)	1(1)	1(1)	0(1)
P(1)	24(1)	32(1)	18(1)	1(1)	0(1)	5(1)
P(2)	21(1)	34(1)	20(1)	4(1)	2(1)	0(1)
O(1)	27(1)	37(1)	23(1)	-7(1)	4(1)	5(1)
C(1)	26(1)	43(1)	20(1)	-4(1)	3(1)	-1(1)
C(2)	44(2)	90(2)	26(2)	-12(2)	-1(1)	2(2)
C(3)	55(2)	39(1)	35(2)	7(1)	-3(1)	13(1)
C(4)	77(2)	34(2)	45(2)	11(1)	11(2)	7(1)
C(5)	23(1)	58(2)	27(1)	-7(1)	-1(1)	2(1)
C(6)	33(1)	59(2)	45(2)	-11(1)	8(1)	-14(1)
C(7)	27(1)	45(1)	26(1)	-2(1)	4(1)	8(1)
C(8)	45(2)	36(1)	41(2)	-5(1)	8(1)	6(1)
C(9)	27(1)	55(2)	31(1)	14(1)	7(1)	-3(1)
C(10)	54(2)	59(2)	49(2)	15(2)	-5(1)	-26(1)
C(11)	25(1)	44(1)	26(1)	5(1)	0(1)	0(1)
C(12)	28(1)	60(2)	35(2)	6(1)	0(1)	5(1)
C(13)	32(1)	35(1)	22(1)	8(1)	6(1)	1(1)
C(14)	28(1)	37(1)	15(1)	3(1)	-1(1)	1(1)
C(15)	37(1)	43(1)	22(1)	-2(1)	5(1)	3(1)
C(16)	32(1)	34(1)	22(1)	-4(1)	5(1)	1(1)
C(17)	43(1)	37(1)	42(2)	-2(1)	6(1)	-2(1)
C(18)	40(1)	53(2)	30(1)	-5(1)	10(1)	13(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2e**.

	x	y	z	U(eq)
H(1A)	3923	1108	796	35
H(1B)	3087	275	1048	35
H(2A)	2482	548	-452	81
H(2B)	1903	1481	-254	81
H(2C)	1052	651	3	81
H(3A)	1350	2481	693	53
H(3B)	1191	2824	1652	53
H(4A)	2830	3671	1032	78
H(4B)	3832	2854	934	78
H(4C)	3663	3204	1891	78
H(5A)	-31	1388	2173	44
H(5B)	-120	1141	1157	44
H(6A)	-603	-67	1970	68
H(6B)	951	26	2579	68
H(6C)	861	-221	1561	68
H(7A)	5390	1	1800	39
H(7B)	6906	-133	2436	39
H(8A)	5369	-1309	2545	61
H(8B)	4154	-691	2836	61
H(8C)	5671	-825	3473	61
H(9A)	7465	1469	2193	45
H(9B)	5914	1769	1684	45
H(10A)	7261	2973	2268	83
H(10B)	7397	2581	3239	83
H(10C)	5841	2879	2734	83
H(11A)	7017	1507	4247	38
H(11B)	6527	547	4386	38
H(12A)	9067	625	4502	62
H(12B)	8929	1002	3525	62
H(12C)	8441	39	3677	62

H(13A)	2443	332	4333	35
H(13B)	4202	152	4353	35
H(14A)	4732	1468	4953	32
H(15A)	2961	2253	5461	41
H(15B)	1776	1539	5110	41
H(17A)	2446	3650	3633	61
H(17B)	3803	3031	3939	61
H(17C)	3116	3579	4654	61
H(18A)	2	3288	3960	61
H(18B)	625	3211	4988	61
H(18C)	-259	2431	4484	61

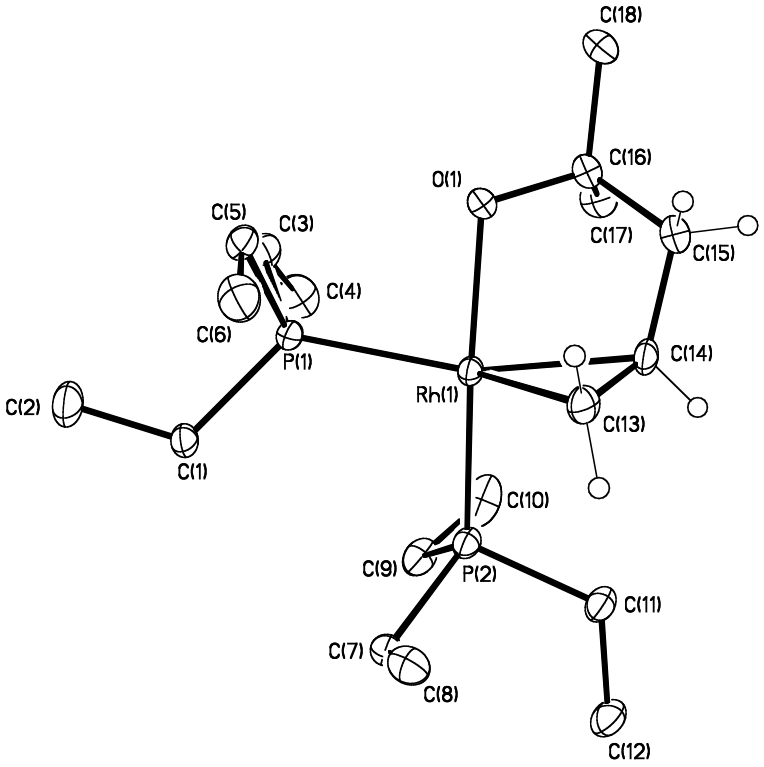

Figure S4. ORTEP diagram of $[(PEt_3)_2RhOCMe_2CH_2CH{=}CH_2]$ (**2e**).