Supplementary Information for

R-Group Reversal of Isomer Stability for $RuH(X)L_2(CCHR)$ *vs* $Ru(X)L_2(CCH_2R)$: Access to Four-Coordinate Ruthenium Carbenes and Carbynes

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Supplementary Information:

General Considerations. All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox unless otherwise noted. Solvents were distilled from Mg, Na, Na/benzophenone, P_2O_5, or CaH_2, degassed prior to use, and stored over 4Å molecular sieves in air-tight vessels. Anhydrous NMe_4F, NaO^tBu, and NaOPh were used as received from commercial vendors. NaOAd·0.5 THF was prepared from HOAd and NaH (THF content determined by ^1H NMR). $RuHClL_2(=C=CH_2)$ and $RuHClL_2(=C=CHPh)$; (L = P^iPr_3,[1] PCy_3[2]), $RuCl_2(P^iPr_3)_2(=CHMe)$[3], and $RuCl_2L_2(=CHPh)$; (L = P^iPr_3, PCy_3)[4,5] were prepared using published procedures. $RuCl_2L_2(=CH(CH_2Ph))$[3] was prepared by metathesis of $RuCl_2L_2(=CHPh)$; (L = P^iPr_3) with excess allylbenzene in CH_2Cl_2 followed by crystallization from CH_2Cl_2/acetone.[6] ^1H NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. ^{31}P and ^{19}F NMR spectra are referenced to external standards of 85% H_3PO_4 (0 ppm) or neat CF_3CO_2H (-78.5 ppm), respectively. NMR spectra were recorded with either a Varian Gemini 2000 (300 MHz ^1H; 121 MHz ^{31}P; 75 MHz ^{13}C, 282 MHz ^{19}F), a Varian Unity INOVA instrument (400 MHz ^1H; 162 MHz ^{31}P; 101 MHz ^{13}C, 376 MHz ^{19}F), or a Varian Unity INOVA instrument (500 MHz ^1H, 126 MHz ^{13}C). The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, q = quartet, vt = virtual triplet, dvt = doublet of virtual triplets, m = multiplet, br = broad, ap = apparent.

$RuH(OPh)(P^iPr_3)_2(=C=CH_2)$.

Method 1: Under argon, 15.0 mg (0.031 mmol) $RuHCl(P^iPr_3)_2(=C=CH_2)$ and 3.6 mg (0.031 mmol) NaOPh were combined in 0.5 mL THF-d_8 and added to an NMR tube equipped with a Teflon seal. NMR spectra taken after 1 hr of agitation showed >95 % conversion to the title compound. *Method 2:* Under argon, 15.0 mg (0.029 mmol) $RuCl_2(P^iPr_3)_2(=CHMe)$ and 6.7 mg (0.058 mmol) NaOPh were combined in 0.5 mL THF-d_8 and added to an NMR tube equipped with a Teflon seal. NMR spectra taken after 1 hr of agitation showed full conversion to the title compound and equimolar free phenol. ^1H NMR (300 MHz, THF-d_8, 20 °C): δ -15.71 (t, $^3J_{P-H}$ = 19 Hz, 1H, Ru*H*), δ 1.25 (dvt, J_{P-H} = $^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 1.29 (dvt, J_{P-H} = $^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 2.42 (m, 6H, P(C*H*Me$_2$)$_3$), δ 2.54 (br t, 2H, RuCC*H*$_2$), δ 6.36 (m, 3H, *o,p*-C_6H_5), δ 6.92 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-C_6H_5). $^{31}P\{^1H\}$ NMR (121 MHz, THF-d_8, 20 °C): δ 50.6 (s).

$RuH(OPh)(P^iPr_3)_2(=C=CHPh)$.

Method 1: Under argon, 15.0 mg (0.027 mmol) $RuHCl(P^iPr_3)_2(=C=CHPh)$ and 3.1 mg (0.027 mmol) NaOPh were combined in 0.5 mL C_6D_6 and added to an NMR tube equipped with a Teflon seal. NMR spectra taken after 1 hr of agitation showed quantitative conversion to the title compound. *Method 2:* Under argon, 15.0 mg (0.025 mmol) $RuCl_2(P^iPr_3)_2(=CH(CH_2Ph))$ and 5.8 mg (0.050 mmol) NaOPh were combined in 0.5 mL C_6D_6 and added to an NMR tube equipped with a Teflon seal. NMR spectra taken after 12 hrs of agitation showed >90 % conversion to the title compound and equimolar free phenol. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ -13.59 (t, $^3J_{P-H}$ = 20 Hz, 1H, Ru*H*), δ 1.13 (dvt, J_{P-H} = $^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 1.15 (dvt, J_{P-H} = $^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 2.15 (m, 6H, P(C*H*Me$_2$)$_3$), δ 4.38 (t, $^4J_{P-H}$ = 3 Hz,

1H, RuCC*H*Ph), δ 6.75 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, C_6H_5), δ 6.88 (t, $^3J_{H-H}$ = 7 Hz, 1H, C_6H_5), δ 7.20 (m, 7H, C_6H_5). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 51.0 (s).

[RuCl(H)(F)(P^iPr_3)$_2$(=C=CHPh)]NMe_4.

Under argon, 15.0 mg (0.027 mmol) RuHCl(P^iPr_3)$_2$(=C=CHPh) and 15.0 mg (0.16 mmol) anhydrous NMe_4F were stirred in 0.5 mL C_6D_6 for 30 minutes and then quickly filtered through Celite into an NMR tube equipped with a Teflon seal. NMR spectra taken immediately showed 40% of the title compound and the balance of material as final product, RuH(F)(P^iPr_3)$_2$(=C=CHPh). ^1H NMR (400 MHz, C_6D_6, 20 °C): δ -10.12 (dt, $^2J_{F-H}$ = 80 Hz, $^3J_{P-H}$ = 23 Hz, 1H, Ru*H*), δ 1.43 (br dvt, J_{P-H} = $^3J_{H-H}$ = 8 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 1.52 (br dvt, J_{P-H} = $^3J_{H-H}$ = 8 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 2.71 (br s, 6H, P(C*H*Me$_2$)$_3$), δ 2.80 (s, 12H, N*Me*$_4$), δ 4.17 (br s, 1H, RuCC*H*Ph), δ 6.91 (t, $^3J_{H-H}$ = 8 Hz, 1H, *p*-C_6H_5), δ 7.17 (ap t, $^3J_{H-H}$ = 8 Hz, 2H, *m*-C_6H_5), δ 7.44 (d, $^3J_{H-H}$ = 8 Hz, 2H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 49.7 (br s; $^2J_{P-F}$ unresolved). ^{19}F NMR (376 MHz, C_6D_6, 20 °C): δ -252.2 (br d, J_{F-H} = 80 Hz).

RuH(F)(P^iPr_3)$_2$(=C=CHPh).

After the NMR tube for the observation of [RuCl(H)(F)(P^iPr_3)$_2$(=C=CHPh)]NMe_4 above was allowed to stand for 12 hours, a minute amount of precipitate formed and NMR taken at this time showed only the title compound. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ -14.49 (ap q, $^3J_{P-H} \cong {}^2J_{F-H}$ = 18 Hz, 1H, Ru*H*), δ 1.21 (dvt, J_{P-H} = $^3J_{H-H}$ = 8 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 1.23 (dvt, J_{P-H} = $^3J_{H-H}$ = 8 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 2.32 (m, 6H, P(C*H*Me$_2$)$_3$), δ 4.32 (br s, 1H, RuCC*H*Ph), δ 6.87 (t, $^3J_{H-H}$ = 8 Hz, 1H, C_6H_5), δ 7.21 (m, 4H, C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 52.0 (d, $^2J_{F-P}$ = 18 Hz). ^{19}F NMR (376 MHz, C_6D_6, 20 °C): δ -154.9 (br s).

RuH(OPh)(PCy_3)$_2$(=C=CH_2).

Under argon, 15.0 mg (0.021 mmol) RuHCl(PCy_3)$_2$(=C=CH_2) and 2.4 mg (0.021 mmol) NaOPh were combined in 0.5 mL THF-d_8 and added to an NMR tube equipped with a Teflon seal. NMR spectra taken after 1 hr of agitation showed >95 % conversion to the title compound. ^1H NMR (400 MHz, THF-d_8, 20°C): δ -16.96 (t, $^3J_{P-H}$ = 18 Hz, 1H, Ru*H*), δ 1.21, 1.55, 1.65, 1.74, 1.96, 2.22 (m, 66H, P(C_6H_{11})$_3$), δ 2.41 (t, $^4J_{P-H}$ = 4 Hz, 2H, RuCCH_2), δ 6.38 (m, 3H, *o*,*p*-C_6H_5), δ 6.95 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20°C): δ 42.3 (s).

RuH(OPh)(PCy_3)$_2$(=C=CHPh).

Under argon, 75.0 mg (0.094 mmol) RuHCl(PCy_3)$_2$(=C=CHPh) and 10.9 mg (0.094 mmol) NaOPh were stirred overnight in 10 mL toluene and the solution was filtered through Celite. After removal of the volatiles to a liquid N_2 trap, the green solid was washed with pentane (1x10 mL) and dried *in vacuo*. Isolated yield 55 mg (68 %). ^1H NMR (400 MHz, C_6D_6, 20 °C): δ -13.76 (t, $^3J_{P-H}$ = 18 Hz, 1H, Ru*H*), δ 1.16, 1.60, 1.70, 2.05, 2.17 (m, 66H, P(C_6H_{11})$_3$), δ 4.47 (t, $^4J_{P-H}$ = 2 Hz, 1H, RuCC*H*Ph), δ 6.78 (ap t, $^3J_{H-H}$ = 8 Hz, 2H, C_6H_5), δ 6.90 (t, $^3J_{H-H}$ = 8 Hz, 1H, C_6H_5), δ 7.24 (m, 5H, C_6H_5), δ 7.36 (ap t, $^3J_{H-H}$ = 8 Hz, 2H, C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 42.6 (s).

$Ru(OPh)(P^iPr_3)_2(CCH_3)$.

Method 1: Under argon, 15.0 mg (0.031 mmol) $RuHCl(P^iPr_3)_2(=C=CH_2)$ and 3.6 mg (0.031 mmol) NaOPh were combined in 0.5 mL C_6D_6 and added to an NMR tube equipped with a Teflon seal. NMR spectra taken after 1 hour of agitation showed >90% conversion to the title compound. *Method 2:* Under argon, 15.0 mg (0.029 mmol) $RuCl_2(P^iPr_3)_2(=CHMe)$ and 6.7 mg (0.058 mmol) NaOPh were combined in 0.5 mL C_6D_6 and added to an NMR tube equipped with a Teflon seal. NMR spectra taken after 12 hrs of agitation showed >90 % conversion to the title compound and equimolar free phenol. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ -0.26 (t, $^4J_{P-H}$ = 3 Hz, 3H, RuCC*H*$_3$), δ 1.34 (dvt, J_{P-H} = $^3J_{H-H}$ = 8 Hz, 36H, P(CH*Me*$_2$)$_3$), δ 2.09 (m, 6H, P(C*H*Me$_2$)$_3$), δ 6.49 (d, $^3J_{H-H}$ = 8 Hz, 2H, *o*-C_6H_5), δ 6.62 (t, $^3J_{H-H}$ = 6 Hz, 1H, *p*-C_6H_5), δ 7.20 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 56.0 (s).

$Ru(OPh)(PCy_3)_2(CCH_3)$.

Under argon, 250 mg (0.345 mmol) $RuHCl(PCy_3)_2(=C=CH_2)$ and 40.1 mg (0.345 mmol) NaOPh were stirred in 30 mL toluene for 4 hours at room temperature. The solution was filtered and reduced to dryness *in vacuo*. The solid was then washed with *cold* pentane (2 x 10 mL) and dried *in vacuo* to yield a brown powder. Isolated yield: 195 mg (72 %). ^1H NMR (400 MHz, C_6D_6, 20°C): δ -0.04 (t, $^4J_{P-H}$ = 4 Hz, 3H, RuCC*H*$_3$), δ 1.20, 1.64, 1.81, 2.06, 2.36 (m, 66H, P(C$_6$*H*$_{11}$)$_3$), δ 6.55 (d, $^3J_{H-H}$ = 8 Hz, 2H, *o*-C_6H_5), δ 6.65 (t, $^3J_{H-H}$ = 6 Hz, 1H, *p*-C_6H_5), δ 7.24 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 45.0 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 20 °C): δ 27.2 (s, P(*C*$_6$H$_{11}$)$_3$), δ 28.1 (s, RuC*C*H$_3$), δ 28.3 (vt, J_{P-C} = 5 Hz, P(*C*$_6$H$_{11}$)$_3$), δ 31.1 (s, P(*C*$_6$H$_{11}$)$_3$), δ 35.3 (vt, J_{P-C} = 8 Hz, P(*C*$_6$H$_{11}$)$_3$), δ 113.3 (s, *C*$_6$H$_5$), δ 120.9 (s, *C*$_6$H$_5$), δ 129.6 (s, *C*$_6$H$_5$), δ 167.3 (s, *C*$_6$H$_5$), δ 260.5 (t, J_{P-C} = 21 Hz, Ru*C*CH$_3$).

$Ru(OPh)(P^iPr_3)_2(CPh)$.

Under argon, 250 mg (0.429 mmol) $RuCl_2(P^iPr_3)_2(=CHPh)$ and 99.6 mg (0.858 mmol) NaOPh were stirred in 25 mL THF for 4 hours at room temperature. The volatiles were removed to a liquid N_2 trap and the green residue was dried overnight *in vacuo* to remove HOPh. After extracting with pentane (2 x 20 mL) filtering, and concentrating the combined extracts to ~5-10 mL, a green solid precipitated upon cooling to –40 °C for two days. The solid was collected, washed with cold pentane (10 mL) and dried *in vacuo*. Isolated yield: 150 mg (53 %). ^1H NMR (300 MHz, C_6D_6, 20°C): δ 1.35 (dvt, J_{P-H} = $^3J_{H-H}$ = 7 Hz, 36H, P(CH*Me*$_2$)$_3$), δ 2.10 (m, 6H, P(C*H*Me$_2$)$_3$), δ 6.52 (d, $^3J_{H-H}$ = 6 Hz, 2H, *o*-C_6H_5), δ 6.65 (t, $^3J_{H-H}$ = 6 Hz, 1H, *p*-C_6H_5), δ 6.73 (ap t, $^3J_{H-H}$ = 6 Hz, 2H, *m*-C_6H_5), δ 6.92 (t, $^3J_{H-H}$ = 6 Hz, 1H, *p*-C_6H_5), δ 7.23 (ap t, $^3J_{H-H}$ = 6 Hz, 2H, *m*-C_6H_5), δ 7.61 (d, $^3J_{H-H}$ = 6 Hz, 2H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20°C): δ 54.8 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 20°C): δ 20.8 (s, P(CH*Me*$_2$)$_3$), δ 25.8 (vt, J_{P-C} = 8 Hz, P(*C*HMe$_2$)$_3$), δ 113.9 (s, *C*$_6$H$_5$), δ 115.9 (s, *C*$_6$H$_5$), δ 120.4 (s, *C*$_6$H$_5$), δ 127.2 (s, *C*$_6$H$_5$), δ 129.1 (s, *C*$_6$H$_5$), δ 129.7 (s, *C*$_6$H$_5$), δ 143.3 (s, *C*$_6$H$_5$), δ 167.0 (s, *C*$_6$H$_5$), δ 247.9 (t, J_{P-C} = 20 Hz, Ru*C*Ph).

$Ru(OPh)(PCy_3)_2(CPh)$.

Under argon, 200 mg (0.243 mmol) $RuCl_2(PCy_3)_2(=CHPh)$ and 56.4 mg (0.486 mmol) NaOPh were stirred in 20 mL THF for 12 hours at room temperature. The volatiles were removed to a liquid N_2 trap and the residue was dried overnight *in vacuo* to remove HOPh. The green solid was extracted with 15 mL toluene, filtered, and the resulting solution was reduced to near dryness. Pentane (20 mL) was then added to precipitate a light green solid that was separated via cannula, washed with pentane, and dried *in vacuo*. Isolated yield: 125 mg (61 %). ^1H NMR (400 MHz, C_6D_6, 20 °C): δ 1.03, 1.25, 1.62, 1.75, 1.96, 2.07, 2.28 (m, 66H, $P(C_6H_{11})_3$), δ 6.58 (d, $^3J_{H-H}$ = 7 Hz, 2H, *o*-C_6H_5), δ 6.67 (t, $^3J_{H-H}$ = 7 Hz, 1H, *p*-C_6H_5), δ 6.80 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-C_6H_5), δ 7.00 (t, $^3J_{H-H}$ = 7 Hz, 1H, *p*-C_6H_5), δ 7.26 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-C_6H_5), δ 7.72 (d, $^3J_{H-H}$ = 7 Hz, 2H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 43.8 (s).

$RuCl(OPh)(PCy_3)_2(=CHPh)$ and $Ru(OPh)_2(PCy_3)_2(=CHPh)$.

Under argon, 15.0 mg (0.018 mmol) $RuCl_2(PCy_3)_2(=CHPh)$ and 4.2 mg (0.036 mmol) NaOPh were combined in 0.5 mL THF-d_8 and added to an NMR tube equipped with a Teflon seal. NMR spectra were taken starting immediately, in 10-15 minute intervals for 60 minutes. During the course of the reaction to produce $Ru(OPh)(PCy_3)_2(CPh)$ and HOPh, two intermediates were seen in low population (~10-15 %). The first to appear (10 min) we attribute to $RuCl(OPh)(PCy_3)_2(=CHPh)$ and last to disappear (30 min) we assign as $Ru(OPh)_2(PCy_3)_2(=CHPh)$ from their similar Ru=C*H*Ph and Ru*P* signals relative to $RuCl_2(PCy_3)_2(=CHPh)$ and the fact that *no* free PCy_3 is observed. Selected NMR data follows. $RuCl(OPh)(PCy_3)_2(=CHPh)$: ^1H NMR (400 MHz, THF-d_8, 20 °C): δ 19.30 (br s, 1H, Ru=C*H*Ph). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 48.9 (s). $Ru(OPh)_2(PCy_3)_2(=CHPh)$: ^1H NMR (400 MHz, THF-d_8, 20 °C): δ 18.29 (br s, 1H, Ru=C*H*Ph). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 42.6 (s).

$Ru(O^tBu)_2(P^iPr_3)(=CHPh)$.

250 mg (0.429 mmol) $RuCl_2(P^iPr_3)_2(=CHPh)$ and 82.5 mg (0.858 mmol) NaO^tBu were stirred in 20 mL THF for 3 hours at room temperature and the solvent was removed *in vacuo*. The dark red-brown residue was extracted into 20 mL pentane, filtered, and the volatiles were removed to a liquid N_2 trap. The red-brown oil solidified to a pasty solid after drying *in vacuo* for 5 days to remove the liberated P^iPr_3. Isolated yield: 175 mg (87 %). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 1.22 (dd, $^3J_{P-H}$ = 14 Hz, $^3J_{H-H}$ = 7 Hz, 18H, $P(CHMe_2)_3$), δ 1.28 (s, 18H, $OCMe_3$), δ 2.31 (m, 3H, $P(CHMe_2)_3$), δ 7.16 (t, $^3J_{H-H}$ = 8 Hz, 1H, *p*-C_6H_5), δ 7.27 (apparent t, $^3J_{H-H}$ = 8 Hz, 2H, *m*-C_6H_5), δ 7.86 (d, $^3J_{H-H}$ = 8 Hz, 2H, *o*-C_6H_5), δ 15.36 (d, $^3J_{P-H}$ = 5 Hz, 1H, Ru=C*H*Ph). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 93.2 (s). The far downfield δ (^{31}P) value for this and related compounds is consistent with P *trans* to an empty coordination site. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C): δ 19.3 (s, $P(CHMe_2)_3$), δ 23.6 (d, J_{P-C} = 17 Hz, $P(CHMe_2)_3$), δ 34.2 (s, $OCMe_3$), δ 74.1 (s, $OCMe_3$), δ 124.2 (s, *m*-C_6H_5), δ 124.9 (s, *p*-C_6H_5), δ 129.5 (s, *p*-C_6H_5), δ 151.7 (s, *ipso*-C_6H_5), δ 230.1 (d, J_{P-C} = 16 Hz, Ru=*C*HPh).

$Ru(OAd)_2(P^iPr_3)(=CHPh)$.

Under argon, 30.0 mg (0.052 mmol) $RuCl_2(P^iPr_3)_2(=CHPh)$ and 21.8 mg (0.104 mmol) NaOAd·0.5 THF were combined in 0.5 mL THF-d_8 and added to an NMR tube equipped with a Teflon seal. ^1H and $^{31}P\{^1H\}$ NMR spectra taken after 12 hours show quantitative conversion to the title compound and equimolar free P^iPr_3. ^1H NMR (400 MHz, THF-d_8, 20 °C): δ 1.36 (dd, $^3J_{P-H}$ = 14 Hz, $^3J_{H-H}$ = 7 Hz, 18H, $P(CH\mathit{Me}_2)_3$), δ 1.37 (AB pattern, $^2J_{H-H}$ = 10 Hz, 12H, $OC_{10}\mathit{H}_{15}$), δ 1.51 (AB pattern, $^2J_{H-H}$ = 12 Hz, 12H, $OC_{10}\mathit{H}_{15}$), δ 1.94 (br s, 6H, $OC_{10}\mathit{H}_{15}$), δ 2.59 (m, 3H, $P(C\mathit{H}Me_2)$, δ 7.20 (t, $^3J_{H-H}$ = 7 Hz, 1H, *p*-$C_6\mathit{H}_5$), δ 7.26 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-$C_6\mathit{H}_5$), δ 7.70 (d, $^3J_{H-H}$ = 7 Hz, 2H, *o*-$C_6\mathit{H}_5$), δ 15.22 (d, $^3J_{P-H}$ = 4 Hz, 1H, Ru=C*H*Ph). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 93.4 (s). $^{13}C\{^1H\}$ NMR (75 MHz, THF-d_8, 20 °C): δ 19.4 (d, $^2J_{P-C}$ = 2 Hz, $P(CH\mathit{Me}_2)_3$), δ 22.6 (d, J_{P-C} = 18 Hz, $P(\mathit{C}HMe_2)_3$), δ 32.4 (s, $O\mathit{C}_{10}H_{15}$), δ 37.6 (s, $O\mathit{C}_{10}H_{15}$), δ 49.1 (s, $O\mathit{C}_{10}H_{15}$), δ 73.4 (s, $O\mathit{C}_{10}H_{15}$), δ 124.6 (s, *m*-C_6H_5), δ 125.0 (s, *p*-C_6H_5), δ 129.5 (s, *p*-C_6H_5), δ 152.2 (s, *ipso*-C_6H_5), δ 229.8 (d, J_{P-C} = 16 Hz, Ru=*C*HPh).

$Ru(O^tBu)_2(PCy_3)(=CHPh)$.

Under argon, 15.0 mg (0.018 mmol) $RuCl_2(PCy_3)_2(=CHPh)$ and 3.5 mg (0.036 mmol) NaO^tBu were combined in 0.5 mL THF-d_8 and added to an NMR tube equipped with a Teflon seal. ^1H and $^{31}P\{^1H\}$ NMR spectra taken after 3 hours show quantitative conversion to the title compound and equimolar free PCy_3. ^1H NMR (400 MHz, THF-d_8, 20 °C): δ 1.04 (s, 18H, $OC\mathit{Me}_3$), δ 1.26, 1.79 (br m, 30H, $P(C_6\mathit{H}_{11})_3$), δ 2.37 (m, 3H, $P(C_6\mathit{H}_{11})_3$), δ 7.20 (t, $^3J_{H-H}$ = 7 Hz, 1H, *p*-$C_6\mathit{H}_5$), δ 7.25 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-$C_6\mathit{H}_5$), δ 7.61 (d, $^3J_{H-H}$ = 7 Hz, 2H, *o*-$C_6\mathit{H}_5$), δ 15.31 (d, $^3J_{P-H}$ = 5 Hz, 1H, Ru=C*H*Ph). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 83.9 (s).

$Ru(OAd)_2(PCy_3)(=CHPh)$.

Under argon, 15.0 mg (0.018 mmol) $RuCl_2(P^iPr_3)_2(=CHPh)$ and 7.6 mg (0.036 mmol) NaOAd·0.5 THF were combined in 0.5 mL THF-d_8 and added to an NMR tube equipped with a Teflon seal. ^1H and $^{31}P\{^1H\}$ NMR spectra taken after 12 hours show quantitative conversion to the title compound and equimolar free PCy_3. ^1H NMR (400 MHz, THF-d_8, 20 °C): δ 1.26, 1.79 (br m, 30H, $P(C_6\mathit{H}_{11})_3$), δ 1.51 (m, 12H, $OC_{10}\mathit{H}_{15}$), δ 1.63 (m, 12H, $OC_{10}\mathit{H}_{15}$), δ 1.94 (br s, 6H, $OC_{10}\mathit{H}_{15}$), δ 2.37 (m, 3H, $P(C_6\mathit{H}_{11})_3$), δ 7.19 (t, $^3J_{H-H}$ = 7 Hz, 1H, *p*-$C_6\mathit{H}_5$), δ 7.26 (ap t, $^3J_{H-H}$ = 7 Hz, 2H, *m*-$C_6\mathit{H}_5$), δ 7.68 (d, $^3J_{H-H}$ = 7 Hz, 2H, *o*-$C_6\mathit{H}_5$), δ 15.22 (d, $^3J_{P-H}$ = 4 Hz, 1H, Ru=C*H*Ph). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 83.4 (s).

Computational Details.

The calculations were carried out using the Gaussian 98[7] set of programs within the framework of DFT at the B3PW91 level.[8,9] LANL2DZ effective core potential (quasi-relativistic for Ru) were used to replace the 28 innermost electrons of Ru,[10] as well as the 10 core electrons of P.[11] The associated double basis set was used[10,11] and was augmented by a d polarization function for P.[12] The other atoms were represented by a 6-31 (d,p) basis set (5d).[13] Full geometry optimization was performed with no symmetry restriction. The stationary point was characterized by analytical calculation of vibrational frequencies.

References

1. Wolf, J.; Stüer, W.; Gruenwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem*. **1998**, 11, 1827-34.
2. Wolf, J.; Stüer, W.; Grünwald, C.; Werner, H.; Schwab, P.; Schultz, M. *Angew. Chem. Intl. Ed.* **1998**, 37, 1124-1126.
3. Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, 1960-1962.
4. van der Schaaf, P. A.; Kolly, R.; Hafner, A. *Chem. Commun*. **2000**, 1045-1046.
5. Schwab, P. Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc*. **1996**, 118, 100-110.
6. Schwab, P.; France, M. B.; Willer, J. W.; Grubbs, R. H. *Angew. Chem. Intl. Ed. Engl.* **1995**, 34, 2039-2041.
7. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A7*, Gaussian, Inc., Pittsburgh, Pennsylvania, 1998.
8. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
9. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
10. Hay, P. G.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
11. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
12. Höllwarth, A. H.; Böhme, M. B.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237.
13. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.