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Supporting Information

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Carbon-Carbon Bond Formation at a Neutral Terminal Carbido Ligand: Generation of Cyclopropenylidene and Vinylidene Complexes

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Experimental

General Procedures. All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled MBRAUN Labmaster 130 glove box, unless otherwise specified. ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian Inova 300 MHz, 400 MHz, or 500 MHz NMR spectrometer. ^{1}H and ^{13}C spectra were referenced to solvent signals.[1] ^{11}B NMR spectra were referenced to external BF_3-etherate (d=0); ^{19}F NMR spectra were referenced to external $CFCl_3$ in $CDCl_3$ (d=0); ^{31}P NMR spectra were referenced to external 85% H_3PO_4 (d=0).

Materials. Vinyl-$^{13}C_2$ acetate, phenol, and dimethyl 1,3-cyclohexadiene-1,4-dicarboxylate were purchased from Aldrich. Dimethyl acetylenedicarboxylate (DMAD), 3,5-dimethylaniline, pyridine-*N*-oxide, iodomethane, acetyl chloride, acetylenedicarboxamide, vinyl acetate, phenylacetylene, and norbornene were purchased from Acros. Pinacolborane, benzyl bromide, 2-octynoic acid methyl ester, ethyl vinyl ether, diethyl diallylmalonate, and methyl propriolate were purchased from Alfa Aesar.

4-fluorostyrene was purchased from Matrix Scientific. Ethylene was purchased from Matheson Gas. All bulk solvents were obtained from VWR Scientific and dried by passage through solvent purification columns according to the method of Grubbs.[2] Deuterated solvents were purchased from CIL and dried over 4 Å molecular sieves. All liquid reagents were degassed and then dried over sieves or passed through activated alumina. Solid reagents were used as received. The starting compounds, [Ru(CH-*p*-C_6H_4Me)$(PCy_3)_2Cl_2$],[3] [Ru(CH-*p*-C_6H_4Me)$(PPh_3)_2Cl_2$],[3] [Ru(C)$(PCy_3)_2Cl_2$],[4] [Ru(C)$(H_2IMes)(PCy_3)Cl_2$],[5] and *trans*-2,3-dicarbomethoxymethylenecyclopropane (Feist's ester)[6] were synthesized according to published procedures. Cyclooctyne was obtained by generous donation from Prof. Aaron L. Odom (Michigan State Univ.).

Synthetic Procedures.

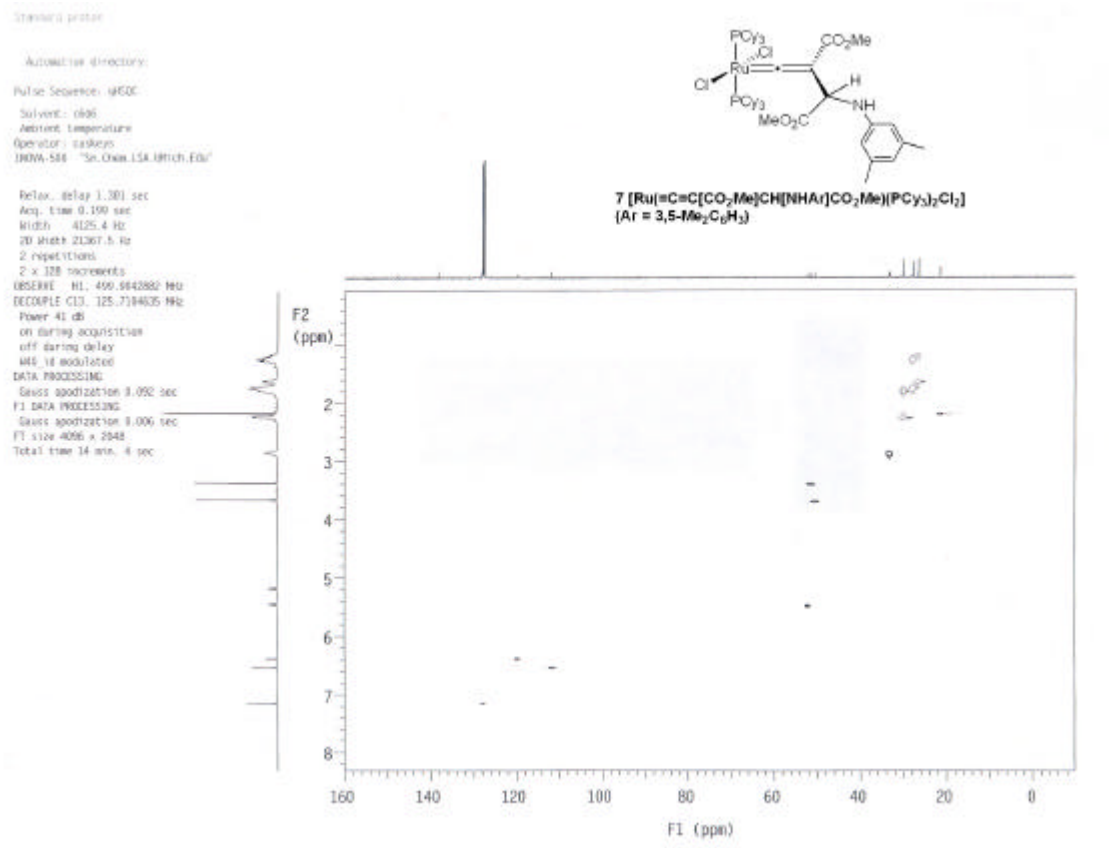
2-^{13}C [Ru(^{13}C)$(PCy_3)_2Cl_2$]: To a stirred purple solution of [Ru(CH-*p*-C_6H_4Me)$(PCy_3)_2Cl_2$] (0.2013 g, 0.2405 mmol) in CH_2Cl_2 (15 mL) was added vinyl-$^{13}C_2$ acetate (22.7 µL, 0.2399 mmol, 0.9975 equiv). The reaction mixture was stirred overnight over which time the solution turned pale yellow. The solution was then concentrated to dryness under vacuum. The yellow material was slurried with cold pentane (5 mL) for 30 minutes. The mixture was filtered, washed with cold pentane (2 x 3 mL), and dried in vacuo 5 hours. Yellow powder **2-^{13}C** (0.1428 g, 0.1915 mmol) was recovered in 79.6% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): d 2.59 (br s, 6 H, P*CH*), 2.17-2.14, 1.83-1.59, 1.28-1.24 (all m, 60H, PCy_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 80 scans): d 472.85 (br s, Ru*^{13}C*), 32.19 (t, J_{PC} = 9.9 Hz, *a*-C of $P(C_6H_{11})_3$), 30.38 (s, ?-C of

$P(C_6H_{11})_3$), 28.53 (t, J_{PC} = 5.3 Hz, ß-C of $P(C_6H_{11})_3$), 27.23 (s, *d*-C of $P(C_6H_{11})_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): d 38.7 (d, $^2J_{PC}$ = 3.1 Hz).

3 [Ru(=CC$_2$[CO$_2$Me]$_2$)(PCy$_3$)$_2$Cl$_2$]: To a stirred pale yellow solution of [Ru(C)(PCy$_3$)$_2$Cl$_2$] (**2**) (0.4018 g, 0.5401 mmol) in benzene (30 mL) was added dimethylacetylene dicarboxylate (DMAD) (82.2 µL, 0.644 mmol, 1.19 equiv). The reaction mixture was stirred for 2 hours over which time the solution turned blue. The solution was then concentrated to dryness under vacuum. The blue material was washed with cold pentane (10 mL) and slurried for 10 minutes. The mixture was filtered. The solid was washed with cold acetonitrile (2 x 4 mL) and cold pentane (3 x 5 mL) and dried in vacuo 5 hours. Blue powder **3** (0.3774 g, 0.4255 mmol) was recovered purely in 78.8% yield. ^1H NMR (400 MHz, C_6D_6): d 3.35 (s, 6H, -CO_2*CH$_3$*), 2.96 (br s, 6 H, P*CH*), 2.07-2.04, 1.78-1.61, 1.33-1.24 (all m, 60H, PCy$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): d 195.67 (t, J_{PC} = 10.7 Hz, Ru=*C*), 180.46 (s, *ipso*-C of -*C*$O_2$$CH_3$), 162.22 (s, -*C*=*C*-), 53.51 (s, -CO_2*C*H$_3$), 33.37 (t, J_{PC} = 9.2 Hz, *a*-C of $P(C_6H_{11})_3$), 30.60 (s, ?-C of $P(C_6H_{11})_3$), 28.50 (t, J_{PC} = 5.0 Hz, ß-C of $P(C_6H_{11})_3$), 27.25 (s, *d*-C of $P(C_6H_{11})_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): d 35.3 (s). Anal. Calcd. for $C_{43}H_{72}Cl_2O_4P_2Ru$: C, 58.23; H, 8.18. Found C, 58.36; H, 8.27.

7 [Ru(=C=C[CO$_2$Me]CH[NHAr]CO$_2$Me)(PCy$_3$)$_2$Cl$_2$] (Ar = 3,5-Me$_2$C$_6$H$_3$): To a stirred blue solution of [Ru(=CC$_2$[CO$_2$Me]$_2$)(PCy$_3$)$_2$Cl$_2$] (**3**) (0.1013 g, 0.1142 mmol) in benzene (10 mL) was added by syringe 3,5-dimethylaniline (14.2 µL, 0.114 mmol, 0.995 equiv). The reaction mixture was stirred overnight over which time the solution turned

dark orange. The solution was then filtered and washed through with benzene (2 x 4 mL). The filtrate was frozen and the benzene removed *in vacuo* as it thawed. The remaining residue was extracted into cold pentane (6 mL) and stirred for 10 minutes. The mixture was filtered and washed through with pentane (3 x 3 mL) leaving a tan insoluble impurity. The orange filtrate was concentrated to dryness under vacuum. The residue was dissolved in acetonitrile (ca. 2 mL), filtered through a pipette filter, and washed through with acetonitrile (1 mL). The orange filtrate was placed in the freezer at -35 ^{o}C. Orange powder **7** (0.0957 g, 0.0949 mmol) was recovered purely in 83.1% yield by decanting the mother liquor and drying *in vacuo* 4 hours. ^{1}H NMR (400 MHz, C_6D_6): d 6.53 (s, 2H, *o*-H of NAr), 6.34 (s, 1H, *p*-H of NAr), 5.46 (d, $^{3}J_{HH}$ = 9.9 Hz, 1H, C*H*[NHAr]), 5.19 (d, $^{3}J_{HH}$ = 10.1 Hz, 1H, CH[N*H*Ar]), 3.68 (s, 3H, -CO_2CH_3), 3.38 (s, 3H, -CO_2CH_3), 2.85 (br s, 6 H, P*CH*), 2.17 (s, 6H, 3,5-$Me_2C_6H_3$), 2.24-2.22, 1.79-1.60, 1.30-1.15 (all m, 60H, PCy_3). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): d 328.08 (t, J_{PC} = 12.6 Hz, Ru=*C*=), 173.25 and 168.57 (both s, -CO_2CH_3), 148.37 and 138.97 (both s, *ipso*-C and *m*-C of NAr) 120.65 (s, *p*-C of NAr), 113.38 (t, J_{PC} = 3.8 Hz, Ru=C=*C*), 112.57 (s, *o*-C of NAr), 52.90 (s, -*C*H[NHAr]), 52.29 and 51.32 (both s, -CO_2CH_3), 33.99 (t, J_{PC} = 9.2 Hz, *a*-C of $P(C_6H_{11})_3$), 30.73 (s, ?-C of $P(C_6H_{11})_3$), 28.51 (t, J_{PC} = 4.6 Hz, ß-C of $P(C_6H_{11})_3$), 27.21 (s, *d*-C of $P(C_6H_{11})_3$), 22.11 (s, 3,5-$Me_2C_6H_3$). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): d 25.1 (br s). Anal. Calcd. for $C_{51}H_{83}Cl_2NO_4P_2Ru$: C, 60.76; H, 8.30; N, 1.39. Found C, 60.49; H, 8.07; N, 1.56. HSQC is attached below.



8 [Ru(=C=C[CO_2Me]CH[Bpin]CO_2Me)(PCy_3)$_2$$Cl_2$]: To a stirred blue solution of [Ru(=CC_2[CO_2Me]$_2$)(PCy_3)$_2$$Cl_2$] (**3**) (0.1519 g, 0.1713 mmol) in benzene (10 mL) was added by syringe pinacolborane (0.250 mL, 1.72 mmol, 10.1 equiv). The reaction mixture was stirred for 1.5 hours over which time the solution turned dark orange. The solution was frozen and the benzene removed *in vacuo* as it thawed. The remaining residue was slurried in cold acetonitrile (4 mL) for 10 minutes. The mixture was filtered, washed with acetonitrile (3 x 5 mL), and the solid dried *in vacuo* 5 hours. The orange powder product (0.1377 g, 0.1357 mmol) was recovered purely in 79.2% yield. ^{1}H NMR (400 MHz, C_6D_6): d 3.68 (s, 3H, -CO_2*CH_3*), 3.50 (s, 3H, -CO_2*CH_3*), 3.48 (s, 1H, *CH*[Bpin]), 2.81 (br s, 6 H, P*CH*), 2.24-2.21, 1.80-1.64, 1.29-1.17 (all m, 60H, PCy_3),

1.22 (s, 12H, *Me*$_4$Bpin). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): d 330.41 (t, J_{PC} = 12.8 Hz, Ru=*C*=), 172.84 and 169.64 (both s, -*C*O_2CH_3), 109.88 (t, J_{PC} = 4.1 Hz, Ru=C=*C*), 83.8 (s, $BO_2C_2Me_4$ of Bpin), 67.78 (s, -*C*H[Bpin]), 51.30 and 51.14 (both s, -CO_2*C*H_3), 33.43 (br s, *a*-C of P(C_6H_{11})$_3$), 30.38 (br s, ?-C of P(C_6H_{11})$_3$), 28.19 (br s, ß-C of P(C_6H_{11})$_3$), 26.93 (s, *d*-C of P(C_6H_{11})$_3$), 25.39 and 24.95 (both s, *Me*$_4$Bpin). ^{11}B NMR (160.4 MHz, C_6D_6): d 21.0, 20.0 (br s, rotamers). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): d 25.5 (br s). Anal. Calcd. for $C_{49}H_{85}Cl_2BO_6P_2Ru$: C, 57.99; H, 8.44. Found C, 57.76; H, 8.43.

9 [Ru(=C=C[CO_2Me]CH[OH]CO_2Me)(PCy$_3$)$_2$Cl$_2$]: To a 20-mL scint vial was added a blue solution of [Ru(=CC_2[CO_2Me]$_2$)(PCy$_3$)$_2$Cl$_2$] (**3**) (0.1530 g, 0.1725 mmol) in benzene (10 mL) and a stirbar. The vial was sealed with a septum and secured with copper wire. The sealed solution was removed from the glove box. To the stirred solution was added by syringe water (31.1 µL, 1.722 mmol, 9.98 equiv). The vial was returned to the glove box. The reaction mixture was stirred for 5 hours over which time the solution turned dark orange. The solution was frozen and the benzene removed *in vacuo* as it thawed. The remaining residue was slurried in cold acetonitrile (6 mL) for 10 minutes. The mixture was filtered, washed with acetonitrile (3 x 5 mL), and the solid dried *in vacuo* 5 hours. The orange powder product (0.0973 g, 0.108 mmol) was recovered purely in 62.3% yield. ^1H NMR (400 MHz, C_6D_6): d 5.25 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*[OH]), 3.94 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH[O*H*]), 3.61 (s, 3H, -CO_2*CH*$_3$), 3.43 (s, 3H, -CO_2*CH*$_3$), 2.85 (br s, 6 H, P*CH*), 2.25-2.22, 1.84-1.62, 1.31-1.21 (all m, 60H, PCy$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): d 327.06 (t, J_{PC} = 12.4 Hz, Ru=*C*=), 173.53 and 167.76 (both s, -*C*O_2CH_3), 113.52 (t, J_{PC} = 3.7 Hz, Ru=C=*C*), 65.29 (s, -*C*H[OH]), 52.21 and 50.89 (both s, -

CO_2CH_3), 33.53 (t, J_{PC} = 9.2 Hz, *a*-C of $P(C_6H_{11})_3$), 30.35 (br s, ?-C of $P(C_6H_{11})_3$), 28.10 (t, J_{PC} = 5.0 Hz, ß-C of $P(C_6H_{11})_3$), 26.83 (s, *d*-C of $P(C_6H_{11})_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): d 25.6 (s). Anal. Calcd. for $C_{43}H_{74}Cl_2O_5P_2Ru$: C, 57.07; H, 8.24. Found C, 56.80; H, 8.23.

10 [Ru(=C=C[CO$_2$Me]CH[OPh]CO$_2$Me)(PCy$_3$)$_2$Cl$_2$]: To a stirred blue solution of $[Ru(=CC_2[CO_2Me]_2)(PCy_3)_2Cl_2]$ (**3**) (0.1025 g, 0.1156 mmol) in benzene (8 mL) was added a solution of phenol (0.0116 g, 0.123 mmol, 1.07 equiv) in benzene (2 mL). The phenol was washed in with benzene (2 mL). The reaction mixture was stirred overnight over which time the solution turned dark orange. The solution was concentrated to dryness. The remaining residue was slurried in cold pentane (4 mL) for 10 minutes. The mixture was filtered, washed with pentane (3 x 5 mL), and the solid dried *in vacuo* 5 hours. The orange powder product (0.0887 g, 0.0904 mmol) was recovered purely in 78.2% yield. ^1H NMR (500 MHz, C_6D_6): d 7.11 (m, 4H, *o*- and *m-H* of OPh), 6.76 (t, $^3J_{HH}$ = 6.7 Hz, 1H, *p*-H of OPh), 5.94 (s, 1H, C*H*[OPh]), 3.68 (s, 3H, -CO_2CH_3), 3.44 (s, 3H, -CO_2CH_3), 2.87 (br s, 6 H, P*CH*), 2.23, 1.81-1.60, 1.26-1.15 (all m, 60H, PCy_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): d 326.95 (t, J_{PC} = 11.9 Hz, Ru=*C*=), 170.78 and 167.00 (both s, -*C*O_2CH_3), 159.68, 130.03, 121.48 and 115.79 (all s, *OPh*), 112.61 (t, J_{PC} = 4.0 Hz, Ru=C=*C*), 70.57 (s, -*C*H[OPh]), 52.43 and 51.23 (both s, -CO_2CH_3), 34.09 (br s, *a*-C of $P(C_6H_{11})_3$), 30.70 (br s, ?-C of $P(C_6H_{11})_3$), 28.48 (br s, ß-C of $P(C_6H_{11})_3$), 27.21 (s, *d*-C of $P(C_6H_{11})_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): d 25.8 (s). Anal. Calcd. for $C_{49}H_{78}Cl_2O_5P_2Ru$: C, 59.99; H, 8.01. Found C, 60.01; H, 8.50.

11 [Ru(=C=C[CO_2Me]C[O]CO_2Me)(PCy_3)$_2$$Cl_2$]: To a stirred blue solution of [Ru(=CC_2[CO_2Me]$_2$)(PCy_3)$_2$$Cl_2$] (**3**) (0.1499 g, 0.1690 mmol) in CH_2Cl_2 (8 mL) was added a solution of pyridine-*N*-oxide (0.0173 g, 0.182 mmol, 1.08 equiv) in CH_2Cl_2 (2 mL). The pyridine-N-oxide was washed in with CH_2Cl_2 (2 mL). The reaction mixture was stirred for 1 hour over which time the solution turned red. The solution was concentrated to dryness. The remaining residue was slurried in cold acetonitrile (4 mL) for 10 minutes. The mixture was filtered through a pipette filter and washed with acetonitrile (3 x 2 mL). The yellow solid was washed through with benzene (4 mL), frozen, and the benzene was removed *in vacuo* as it thawed overnight. The yellow powder product (0.0401 g, 0.0444 mmol) was recovered purely in 26.3% yield. ^{1}H NMR (400 MHz, C_6D_6): d 3.62 (s, 3H, -CO_2*CH_3*), 3.52 (s, 3H, -CO_2*CH_3*), 2.80 (br s, 6 H, P*CH*), 2.21-2.17, 1.73-1.61, 1.24-1.11 (all m, 60H, PCy_3). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): d 321.80 (t, J_{PC} = 11.0 Hz, Ru=*C*=), 183.91 (s, -*C*[O]), 165.52 and 165.13 (both s, -*C*$O_2$$CH_3$), 116.73 (s, Ru=C=*C*), 51.70 and 50.88 (both s, -CO_2*C*H_3), 33.93 (t, J_{PC} = 9.2 Hz, *a*-C of P(C_6H_{11})$_3$), 30.33 (br s, *?*-C of P(C_6H_{11})$_3$), 28.17 (t, J_{PC} = 5.0 Hz, *ß*-C of P(C_6H_{11})$_3$), 26.68 (s, *d*-C of P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): d 32.6 (s). Anal. Calcd. for $C_{43}H_{72}Cl_2O_5P_2Ru$: C, 57.08; H, 8.04. Found C, 57.08; H, 8.06.

Reaction of 2 with MeI. [Ru(C)(PCy_3)$_2$$Cl_2$] (**2**) (0.0123 g, 0.0165 mmol) was dissolved in CD_2Cl_2 (0.8 mL) and cooled to -35 ^{o}C. Iodomethane (1.0 µL, 0.016 mmol, 0.97 equiv) was added by syringe to the stirred solution of compound **2**. The reaction was monitored by ^{31}P and ^{1}H NMR spectroscopy. After 24 h, the ^{31}P NMR spectrum showed: ^{31}P{^{1}H}

(121.5 MHz, CD_2Cl_2): d 38.6 (**2**, 98.2%) and 34.1 ([$MePCy_3$][I], 1.8%). The ^1H NMR spectrum showed starting material.

Reaction of 2 with MeC(O)Cl. To an NMR solution of [Ru(C)(PCy_3)$_2Cl_2$] (**2**) (0.0113 g, 0.0152 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe acetyl chloride (10.8 µL, 0.152 mmol, 10.0 equiv). The solution remained pale yellow. The reaction progress was monitored by ^1H and ^{31}P NMR. After 1 hour and after 20 hours, the ^{31}P NMR spectra showed only the presence of **2**.

Reaction of 2 with $PhCH_2Br$. To an NMR solution of [Ru(C)(PCy_3)$_2Cl_2$] (**2**) (0.0110 g, 0.0148 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe benzyl bromide (17.6 µL, 0.148 mmol, 10.0 equiv). The solution remained pale yellow. The reaction progress was monitored by ^1H and ^{31}P NMR. After 1 hour and after 20 hours, the ^{31}P NMR spectra showed only the presence of **2**.

Reaction of 2 with dimethyl 1,3-cyclohexadiene-1,4-dicarboxylate. To solid dimethyl 1,3-cyclohexadiene-1,4-dicarboxylate (90%) (0.0062 g, 0.028 mmol, 1.0 equiv) was added a solution of [Ru(C)(PCy_3)$_2Cl_2$] (**2**) (0.0206 g, 0.0277 mmol) in C_6D_6 (ca. 0.75 mL). The reaction mixture was transferred to a J. Young NMR tube and sealed. The sample was removed from the glove box, placed on a Schlenk line under N_2, and heated in an oil bath at 70 ºC. The solution remained pale yellow. The reaction progress was monitored by ^1H and ^{31}P NMR. After 1 hour and after 20 hours, the ^{31}P NMR spectra showed only the presence of **2**.

Reaction of 2 with cyclooctyne. To an NMR solution of [Ru(C)(PCy_3)$_2$$Cl_2$] (**2**) (0.0107 g, 0.0144 mmol) in CD_2Cl_2 (ca. 0.75 mL) was added by syringe cyclooctyne (2.0 µL, 0.016 mmol, 1.1 equiv). The solution remained pale yellow. The reaction progress was monitored by ^{1}H and ^{31}P NMR. After 15 minutes and after 20 hours, the ^{31}P NMR spectra showed only the presence of **2**.

Reaction of 2 with acetylenedicarboxamide. To solid acetylenedicarboxamide (95%) (0.0021 g, 0.019 mmol, 1.2 equiv) was added a solution of [Ru(C)(PCy_3)$_2$$Cl_2$] (**2**) (0.0115 g, 0.0154 mmol) in CD_2Cl_2 (ca. 0.75 mL). The solution was heterogeneous and remained pale yellow. The reaction progress was monitored by ^{1}H and ^{31}P NMR. After 24 hours and after 72 hours, the ^{31}P NMR spectra showed only the presence of **2**.

Reaction of 2 with 2-octynoic acid methyl ester. To solution of [Ru(C)(PCy_3)$_2$$Cl_2$] (**2**) (0.0116 g, 0.0156 mmol) in CD_2Cl_2 (ca. 0.75 mL) was added by syringe 2-octynoic acid methyl ester (13.0 µL, 0.0776 mmol, 4.97 equiv). The solution remained pale yellow. The reaction progress was monitored by ^{1}H and ^{31}P NMR. After 45 minutes and after 24 hours, the ^{31}P NMR spectra showed only the presence of **2**.

Reaction of Ru(C)(H_2IMes)(PCy_3)Cl_2 (4) with dimethylacetylene dicarboxylate (DMAD). To a yellow solution of [Ru(C)(H_2IMes)(PCy_3)Cl_2] (**4**) (0.0094 g, 0.012 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe DMAD (1.5 µL, 0.012 mmol, 1.0 equiv). The solution turned brown then orange over 1 hour. The reaction progress was

monitored by ^{1}H and ^{31}P NMR. After 15 minutes, the ^{1}H and ^{31}P NMR spectrum showed: $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): d 34.6 (**4**, 26.3%), 28.7 ([Ru(=CC_2[CO_2Me]$_2$)(H_2IMes)(PCy_3)Cl_2], 63.2%) and 23.3 (10.5%). ^{1}H NMR of [Ru(=CC_2[CO_2Me]$_2$)(H_2IMes)(PCy_3)Cl_2] (121.5 MHz, C_6D_6): 6.84 (s, 2H, Mes), 6.63 (s, 2H, Mes), 3.44 (s, 6H, -CO_2*CH_3*), 2.79 and 2.70 (s, 6H each, 2,6-*Me*-Mes), 2.15 and 2.12 (s, 3H each, 4-*Me*-Mes), 1.73-1.08 (m, 33 H, PCy_3). After 1.5 h, the ^{31}P NMR spectrum showed: $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2): d 31.2 (10.6%), 28.7 ([Ru(=CC_2[CO_2Me]$_2$)(H_2IMes)(PCy_3)Cl_2], 21.2%), 23.8 (4.2%), and 23.3 (63.8%). $^{13}C\{^{1}H\}$ NMR: δ 197.5 (d, $^{2}J_{PC}$ = 11 Hz, Ru=*C*)

Reaction of Ru(C)(H_2IMes)(PCy_3)Cl_2 (4) with methyl propiolate. To a yellow solution of [Ru(C)(H_2IMes)(PCy_3)Cl_2] (**4**) (0.0099 g, 0.013 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe excess methyl propiolate (10.7 µL, 0.128 mmol, 10.0 equiv). The solution turned dark red-brown over 1 hour. The reaction progress was monitored by ^{1}H and ^{31}P NMR. After 40 min, the ^{31}P NMR spectrum showed: $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): d 34.6 (**4**, 83.3%), 27.8 ([Ru(=C(CH)C[CO_2Me])(H_2IMes)(PCy_3)Cl_2], 16.7%). After 2 h, the ^{31}P NMR spectrum showed: $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): d 34.6 (**4**, 52.6%), 27.8 ([Ru(=C(CH)C[CO_2Me])(H_2IMes)(PCy_3)Cl_2], 47.4%). After 16 h, the ^{31}P NMR spectrum showed: $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): d 34.6 (**4**, 11.5%), 29.4 (5.1%), 28.8 (5.2%), 28.5 (11.5%) 27.8 ([Ru(=C(CH)C[CO_2Me])(H_2IMes)(PCy_3)Cl_2], 66.7%). ^{1}H NMR of [Ru(=C(CH)C[CO_2Me])(H_2IMes)(PCy_3)Cl_2] (121.5 MHz, C_6D_6): 9.62 (s, 1H, -C*H*=CO_2Me), 6.85 (s, 2H, Mes), 6.48 (s, 2H, Mes), 3.49 (s, 3H, -CO_2*CH_3*),

2.80 and 2.61 (s, 6H each, 2,6-*Me*-Mes), 2.14 and 2.06 (s, 3H each, 4-*Me*-Mes), 1.73-1.11 (m, 33 H, PCy_3). $^{13}C\{^1H\}$ NMR: δ 200.5 (d, $^2J_{PC}$ = 12 Hz, Ru=*C*)

Reaction of 3 with ethylene. To a J. Young NMR tube was added a solution of $[Ru(=CC_2[CO_2Me]_2)(PCy_3)_2Cl_2]$ (**3**) (0.0116 g, 0.0131 mmol) in C_6D_6 (ca. 0.75 mL). The solution was frozen, the overlying atmosphere was evacuated, and the solution was allowed to thaw. The J. Young tube was backfilled with ethylene (ca. 1 atm, 2.35 mL overhead volume, ca. 0.096 mmol, ca. 7.3 equiv) and sealed. The solution remained blue initially then turned light brown over 24 hours. The reaction progress was monitored by ^1H and ^{31}P NMR. After 24 hours, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 14.1%), 35.2 (**3**, 81.8%), 32.5 (1.2%), 29.7 (1.0%) and 24.0 (1.9%). The potential metathesis product, known $[Ru(=CH_2)(PCy_3)_2Cl_2]$,[3] was not observed.

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Reaction of 3 with 4-fluorostyrene. To an NMR solution of $[Ru(=CC_2[CO_2Me]_2)(PCy_3)_2Cl_2]$ (**3**) (0.0118 g, 0.0133 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe 4-fluorostyrene (15.9 μL, 0.133 mmol, 1.00 equiv). The solution remained blue initially, then turned brown over 20 hours. The reaction progress was monitored by ^1H and ^{31}P NMR. After 1 hour, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 3.0%) and 35.2 (**3**, 97.0%). After 20 hours, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 12.3%), 35.2 (**3**, 86.1%), 33.7 (1.4%) and 32.5 (0.2%). The potential metathesis products, known $[Ru(=CH_2)(PCy_3)_2Cl_2]$[3] and $[Ru(=CH\text{-}p\text{-}C_6H_4F)(PCy_3)_2Cl_2]$,[3] were not observed.

Reaction of 3 with vinyl acetate. To an NMR solution of [Ru(=$CC_2[CO_2Me]_2$)(PCy_3)$_2Cl_2$] (**3**) (12.2 g, 0.0138 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe vinyl acetate (12.7 µL, 0.137 mmol, 9.98 equiv). The solution remained blue. The reaction progress was monitored by ^1H and ^{31}P NMR. After 1 hour, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 3.1%) and 35.2 (**3**, 96.9%). After 20 hours, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 12.4%), 35.2 (**3**, 84.1%), 33.7 (2.7%) and 32.5 (0.9%). The potential metathesis products, known [Ru(=CH_2)(PCy_3)$_2Cl_2$][3] and Ru(=CHOAc)(PCy_3)$_2Cl_2$,[4] were not observed.

Reaction of 3 with ethyl vinyl ether. To an NMR solution of [Ru(=$CC_2[CO_2Me]_2$)(PCy_3)$_2Cl_2$] (**3**) (0.0118 g, 0.0133 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe ethyl vinyl ether (12.8 µL, 0.134 mmol, 10.1 equiv). The solution remained blue initially, then turned gray over 24 hours. The reaction progress was monitored by ^1H and ^{31}P NMR. After 30 minutes, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 1.1%), 35.2 (**3**, 98.3%) and 32.5 (0.6%). After 24 hours, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 13.4%), 35.2 (**3**, 69.9%), 33.7 (3.4%), 26.4 (5.9%), 22.4 (5.6%), and 19.7 (1.7%). The potential metathesis products, known [Ru(=CH_2)(PCy_3)$_2Cl_2$][3] and [Ru(=CHOEt)(PCy_3)$_2Cl_2$],[3] were not observed.

Reaction of 3 with diethyl diallylmalonate. To an NMR solution of [Ru(=$CC_2[CO_2Me]_2$)(PCy_3)$_2Cl_2$] (**3**) (0.0123 g, 0.0139 mmol) in C_6D_6 (ca. 0.75 mL) was

added by syringe diethyl diallylmalonate (67.0 μL, 0.277 mmol, 20.0 equiv). The solution remained blue initially, then turned red-brown over 20 hours. The reaction progress was monitored by ^{1}H and ^{31}P NMR. After 20 hours, no ring closing metathesis product, cyclopent-3-ene 1,1-dicarboxylic acid ethyl ester,[7] was observed.

Reaction of 3 with phenylacetylene. To an NMR solution of $[Ru(=CC_2[CO_2Me]_2)(PCy_3)_2Cl_2]$ (**3**) (0.0108 g, 0.0122 mmol) in C_6D_6 (ca. 0.75 mL) was added by syringe phenylacetylene (13.4 μL, 0.122 mmol, 10.0 equiv). The solution remained blue initially, then turned brown over 20 hours. The reaction progress was monitored by ^{1}H and ^{31}P NMR. After 1 hour, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 2.6%) and 35.2 (**3**, 97.4%). After 20 hours, the ^{31}P NMR spectrum showed: ^{31}P NMR (161.9 MHz, C_6D_6): d 39.0 (**2**, 9.6%), 35.2 (**3**, 69.3%), 33.7 (2.7%), 32.5 (0.9%), 31.3 (2.3%), 26.4 (4.4%), 22.0 (2.7%), 10.4 (PCy_3, 3.8%). No carbene peaks were observed in the carbene region the ^{1}H NMR spectra.

General method for attempted ring-closing metathesis (RCM) reactions with vinylidenes 7-11. To a 0.01 M solution of vinylidene complex in C_6D_6 was added by syringe diethyl diallylmalonate. The ^{1}H and ^{31}P NMR spectra were checked after 15 minutes and 16 hours and showed only the starting vinylidene complexes and unreacted diethyl diallylmalonate. The solution was then transferred to J. Young NMR tube, frozen and the overlying atmosphere was evacuated. The sample was thawed and the tube placed in an oil bath at 75 °C. The ^{1}H and ^{31}P NMR spectra were checked after 2 hours

and 72 hours of heating and showed only the starting vinylidene complexes and unreacted diethyl diallylmalonate.

General method for ring-opening metathesis polymerization (ROMP) of norbornene with vinylidenes 7-11. To a solution of norbornene (20 equiv) in minimal C_6D_6 was added a 0.01 M solution of vinylidene in C_6D_6. The solution was rapidly transferred to an NMR tube. The solutions each rapidly became viscous gels. The reactions each remained the color of the vinylidene solutions indicating propagation is more rapid than initiation. All free norbornene was consumed by ^{1}H NMR within 20 minutes. The vinylidene complexes appeared unchanged by ^{1}H and ^{31}P NMR overnight.

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