

## Supporting Information for

### Ruthenium Metallacycles Derived from 14-Electron Complexes—New Insights Into Olefin Metathesis Intermediates

Anna G. Wenzel and Robert H. Grubbs

#### I. Materials and Methods.

**I.A. Materials.** Unless otherwise indicated, all compounds were purchased from Aldrich and/or Fisher. NMR solvents were purchased from Cambridge Isotope Laboratories, Inc., and distilled from calcium hydride (CaH<sub>2</sub>) under an atmosphere of argon before use. Ethylene (99.999%) was purchased from Matheson Tri-Gas and dispensed utilizing a regulator equipped with a Matheson in-line gas purification system. 3-<sup>13</sup>C-labeled propene was purchased from Cambridge Isotope Laboratories, Inc. Gas samples for NMR reactions were measured utilizing the Schlenk technique specified in: Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032-5033, and references therein. Anhydrous dichloromethane, benzene, diethyl ether, and tetrahydrofuran were obtained via elution through a solvent column drying system<sup>1</sup> and degassed with argon prior to use. The flash chromatography of organometallic compounds was performed utilizing silica gel 60 (230-400 mesh) purchased from TSI; the flash chromatography of all other compounds was performed utilizing silica gel 60 (32-63 micron) purchased from Bodman Industries. Stainless steel syringes or cannulae were used to transfer air or moisture-sensitive liquids. Catalyst [(IMesH<sub>2</sub>)Cl<sub>2</sub>Ru=CH(PCy<sub>3</sub>)](BF<sub>4</sub>) was prepared according to literature procedures.<sup>2</sup>

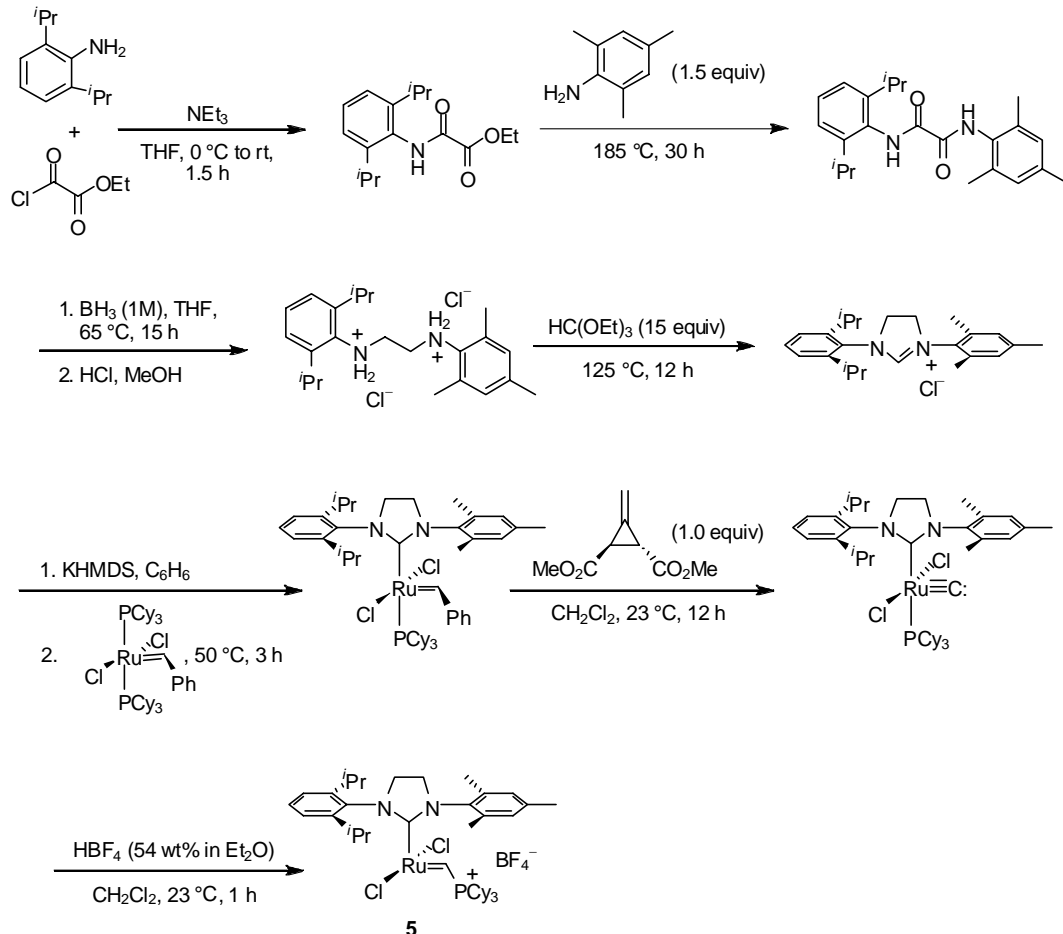
**I.B. Instrumentation.** Nuclear magnetic resonance (NMR) spectra were obtained using Varian Mercury-300, Varian Inova-500, and Bruker Avance-500 NMR spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl<sub>3</sub>: δ 7.26; CD<sub>2</sub>Cl<sub>2</sub>: δ 5.32). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl<sub>3</sub>: δ 77.2; CD<sub>2</sub>Cl<sub>2</sub>: δ 54.0). Chemical shifts for phosphorous are reported in parts per million downfield from H<sub>3</sub>PO<sub>4</sub> (δ = 0 ppm). Chemical shifts for fluorine are reported in parts per million relative to CFCl<sub>3</sub> (δ = 0 ppm). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants in Hertz (Hz), and assignment. Mass spectroscopic data were obtained at the Caltech Mass Spectrometry Facility. X-ray crystallographic data was obtained utilizing a Bruker SMART 1000 CCD diffractometer.

<sup>1</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

<sup>2</sup> Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6161-6165.

## II. General Experimental Procedures.

### II.A. Preparation of catalyst 5.

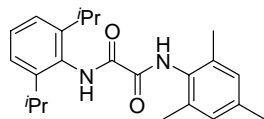


**Ethyl 2-(2,6-diisopropylphenylamino)-2-oxoacetate.** To a 200-mL, flame-dried flask under an atmosphere of argon: 2,6-diisopropylaniline (7.0 mL, 37 mmol, 1.0 equiv) and freshly distilled triethylamine (10.3 mL, 74.0 mmol, 2.0 equiv) were dissolved in anhydrous tetrahydrofuran (62 mL). The flask was then immersed in an ice bath and cooled to  $\sim 0$  °C. Ethyl chloroacetate (4.5 mL, 41 mmol, 1.1 equiv) was then added dropwise (neat) over a five-minute period. Once the addition was complete, the reaction was stirred for 5 minutes at 0 °C, and then allowed to proceed at ambient temperature for 1.5 h. A white precipitate (triethylamine hydrochloride) was observed to form over the course of the reaction. Reaction progress was monitored via TLC (10% ethyl acetate in hexanes;  $R_f$ (starting material) = 0.53,  $R_f$ (product) = 0.11; UV TLC visualization). Upon completion, the reaction was partitioned between diethyl ether (50 mL) and aqueous hydrochloric acid solution (1N, 50 mL). Organics were washed with aqueous hydrochloric acid solution (1N, 2 x 50 mL), saturated aqueous sodium bicarbonate solution (50 mL), and brine (50 mL). The organic layer was then dried over anhydrous magnesium sulfate, filtered, and concentrated to afford a white solid in 99% yield (10.2 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$  8.41 (1H, br, NH), 7.38 (1H, m, DIPP *p*-H),<sup>3</sup> 7.25 (2H, m, DIPP *m*-H), 4.49 (2H, q,  $J$  = 7.2 Hz,

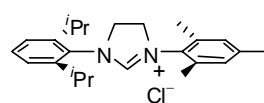
<sup>3</sup> DIPP = 2,6-diisopropylphenyl

CH<sub>3</sub>CH<sub>2</sub>O-), 3.05 (2H, sep,  $J = 6.8$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.53 (3H, t,  $J = 7.2$  Hz, CH<sub>3</sub>CH<sub>2</sub>O-), 1.25 (12H, d,  $J = 6.9$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 20 °C) δ 161.1, 156.0, 145.8, 129.4, 128.9, 123.7, 63.6, 28.8, 23.6, 13.96; HRMS(FAB+)  $m/z$ : 278.1752 [M+H].

***N*<sup>1</sup>-(2,6-diisopropylphenyl)-*N*<sup>2</sup>-mesityloxalamide.** A 50-mL, flame-dried Schlenk flask was charged with ethyl 2-(2,6-diisopropylphenylamino)-2-oxoacetate (10.5 g, 37.9 mmol, 1.0 equiv) and 2,4,6-trimethylaniline (8.0 mL, 57 mmol, 1.5 equiv). The flask was sealed under an atmosphere of argon and then heated to 185 °C for 24 h. Upon cooling to ambient temperature, the product was observed to precipitate out of solution. The resulting solids were triturated with pentane to afford a white solid, which was dried *in vacuo* to afford the desired product in 32% yield (4.44 g).<sup>4</sup> TLC conditions: 20% ethyl acetate in hexanes,  $R_f$ (starting material) = 0.18,  $R_f$ (product) = 0.42, KMnO<sub>4</sub> TLC visualization; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 8.87 (1H, br s, NH), 8.81 (1H, br s, NH), 7.37 (1H, m, DIPP *p*-H), 7.24 (2H, m, DIPP *m*-H), 6.97 (2H, s, mesityl *m*-H), 3.07 (2H, sep,  $J = 6.8$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.31 (3H, s, mesityl *p*-CH<sub>3</sub>), 2.23 (6H, s, mesityl *o*-CH<sub>3</sub>), 1.21 (12H, d,  $J = 6.9$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 160.2, 158.9, 146.7, 138.2, 135.4, 130.5, 129.5, 129.4, 124.2, 29.5, 23.9, 21.2, 18.6; HRMS(FAB+)  $m/z$ : 367.2390 [M+H].



**1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium chloride.**

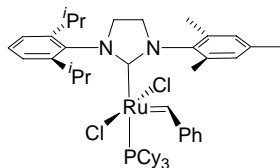


*N*<sup>1</sup>-(2,6-diisopropylphenyl)-*N*<sup>2</sup>-mesityloxalamide (2.5 g, 6.8 mmol, 1.0 equiv) was added to a flame-dried, thick-walled Schlenk flask under an atmosphere of argon. Borane (1.0 M in tetrahydrofuran; 48 mL, 48 mmol, 7.0 equiv) was then added dropwise via syringe. Vigorous bubbling was observed. Once the gas evolution had subsided, the flask was sealed, placed behind a blast shield, and heated to 65 °C for 15 h. Upon cooling to ambient temperature, the flask was unsealed, and anhydrous methanol (~60 mL) was slowly added via pipette until all gas evolution had ceased. The volatiles were then removed *in vacuo*, and additional methanol (3 x 30 mL) was sequentially added and removed under reduced pressure to ensure that the excess borane had been successfully removed as B(OMe)<sub>3</sub>. Concentrated hydrochloric acid solution (~7 mL) was added in conjunction with the third methanol addition to convert the product to its dihydrochloride salt. This was isolated as a white foam upon removal of the volatiles *in vacuo* (99% crude yield; HRMS(FAB+)  $m/z$ : 339.2717 [M-2HCl+H]). Anhydrous triethylorthoformate (17 mL, 100 mmol, 15 equiv) was then added to the diamine salt in one portion. The flask was capped with a water-cooled reflux condenser under an atmosphere of argon and heated to 125 °C with stirring. After 12 h, the reaction was allowed to cool to ambient temperature, during which time the product was observed to precipitate out of solution. Additional product was precipitated via the addition of pentane (~25 mL). The resulting solids were isolated via filtration and purified by rinsing with pentane (3 x 5 mL) and diethyl ether (3 x 5 mL) to afford the imidazolium salt as a pale pink solid in 99% yield (2.56 g, 98% yield over 2 steps). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 10.15 (1H, s, <sup>+</sup>N=CH-N), 7.49 (1H, t,  $J = 7.9$  Hz, DIPP *p*-H), 7.30 (2H, d,  $J = 7.7$  Hz, DIPP *m*-H), 7.03 (2H, s, mesityl *m*-H), 4.48 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>N), 2.99 (2H, sep,  $J = 6.8$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.40 (6H, s, mesityl *o*-CH<sub>3</sub>), 2.33 (3H, s, mesityl *p*-CH<sub>3</sub>), 1.36 (6H, d,  $J = 6.6$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (6H, d,  $J = 6.6$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,

<sup>4</sup> Note: in some cases, impurities may remain in the product mixture following trituration. However, these impurities are tolerated during imidazolium salt formation, and can be readily removed during the subsequent diethyl ether wash to afford analytically pure product (>98%).

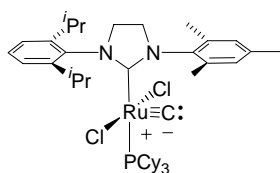
CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 161.4 (s, <sup>+</sup>N=CH-N), 146.8, 141.2, 135.6, 131.7, 130.9, 130.5, 130.3, 125.4, 54.6, 52.3, 29.7, 25.5, 24.0, 21.4, 18.3; HRMS(FAB+) m/z: 349.2638 [M].

**(1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolyl)(PCy<sub>3</sub>)(Cl)<sub>2</sub>**



**Ru=CHPh.** 1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium chloride (240 mg, 0.623 mmol, 1.5 equiv) and potassium hexamethyldisilazide (KHMDs; 133 mg, 0.665 mmol, 1.6 equiv) were combined in a Schlenk flask in the glovebox. Benzene (17 mL) was then added in one portion, and the reaction was stirred for 15 minutes, resulting in the formation of a cloudy, salmon-colored mixture. (PCy<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh (342 mg, 0.416 mmol, 1.0 equiv) was then added in one portion, using additional benzene (1.0 mL) to complete the addition. The Schlenk flask was sealed and removed from the box. The reaction mixture was heated to 50 °C for 3 h, during which time the reaction mixture was observed to change from dark purple to pink/brown in color. Upon cooling to ambient temperature, the reaction mixture was concentrated under reduced pressure to ~4 mL. The product was then purified via flash chromatography on silica gel (3.5 x 20 cm silica, 4% diethyl ether in hexanes, R<sub>f</sub> = 0.28 (10% diethyl ether in hexanes, UV TLC visualization) to afford the desired product as a brownish pink solid in 56% isolated yield (208 mg).<sup>5</sup> <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C; compound exists as a 2.4:1 mixture of rotamers: the major rotamer is denoted by \*) δ 19.37 (1H, s, Ru=CHPh), 19.10 (1H, s, Ru=CHPh\*); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 295.7 (Ru=CHPh\*), 221.4 (d, J = 78.2 Hz, NCN\*); <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 30.5 (PCy<sub>3</sub>\*), 28.0 (PCy<sub>3</sub>); HRMS(FAB+) m/z: 890.3737 (M+H-H<sub>2</sub>).

**(1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolyl)(PCy<sub>3</sub>)(Cl)<sub>2</sub>**



**Ru≡C.** To a 25 mL flask: 2,3-dicarbomethoxymethylenecyclopropane<sup>6</sup> (25 mg, 0.145 mmol, 1.0 equiv) was dissolved in 3 mL of dichloromethane in the glovebox. (1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolyl)(PCy<sub>3</sub>)(Cl)<sub>2</sub>Ru=CHPh (129 mg, 0.145 mmol, 1.0 equiv) was then added in one portion with stirring. Additional dichloromethane (1.0 mL) was used to complete the addition. The flask was capped and allowed to stir at ambient temperature for 5 h. During this time, the reaction mixture was observed to change from brownish pink to pale yellow. Upon reaction completion, the flask was transferred out of the glovebox, and the volatiles were removed *in vacuo*. A water-cooled reflux condenser was then attached to the flask, and the apparatus was placed under vacuum (100 mTorr) and heated to 50 °C for 1.5 h to remove the styrene and fumarate byproducts. The resulting residue was further purified via flash chromatography on silica gel (2.5 x 20 cm silica, 50% dichloromethane in hexanes, R<sub>f</sub> = 0.58, UV TLC visualization) to afford analytically pure carbide as a pale yellow solid (114 mg, 97%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 7.34 (1H, m, DIPP *p*-H), 7.26-7.23 (2H, m, DIPP *m*-H), 6.87 (2H, s, mesityl *m*-H), 4.16-3.98 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>N), 3.46 (2H, sep, J = 6.7 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.52 (6H, s, mesityl *o*-CH<sub>3</sub>), 2.34-2.16 (3H, m, Cy), 2.23 (3H, s, mesityl *p*-CH<sub>3</sub>), 1.82 (6H, br, Cy), 1.68-1.56 (9H, br m, Cy), 1.27 (6H, d, J = 7.2 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (6H, d, J = 6.6 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.26-1.03 (15H, br m, Cy); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) δ 475.8 (Ru≡C), 213.9 (d, J = 86.0

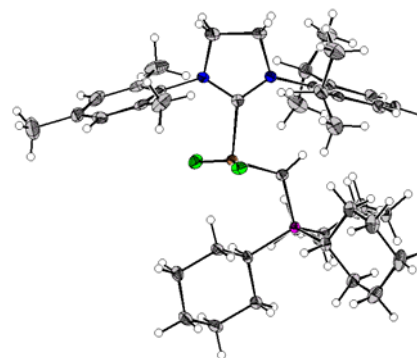
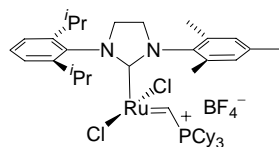
<sup>5</sup> Note: this ruthenium complex will rapidly decompose on silica in the presence of dichloromethane. Use only benzene or diethyl ether when solvating under ambient conditions.

<sup>6</sup> Feist's acid (3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid) is commercially available from ACROS (\$10/mmol in the 2006 catalog). Methyl ester formation was performed according to: Hsiao, C.-N.; Hannick, S. M. *Tetrahedron Lett.* **1990**, *31*, 6609-6612.

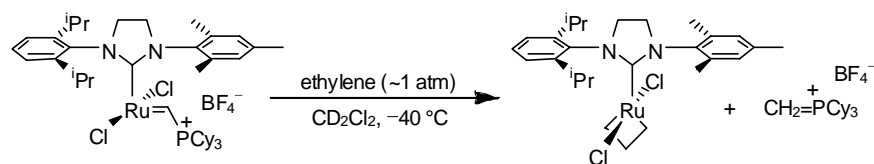
Hz, NCN), 148.6, 139.2, 139.0, 138.6, 135.7, 129.7, 129.5, 124.8, 54.4 (d,  $J = 2.3$  Hz), 52.3 (d,  $J = 4.0$  Hz), 31.6 (d,  $J = 19.6$  Hz), 29.9, 28.6, 28.4 (d,  $J = 10.9$  Hz), 26.9, 26.2, 23.8, 21.2, 20.2;  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$  35.8; HRMS(FAB+)  $m/z$ : 813.3405 (M+H-H<sub>2</sub>).

### [(1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolyl)(PCy<sub>3</sub>)(Cl)<sub>2</sub>Ru=CH(PCy<sub>3</sub>)](BF<sub>4</sub>) (5).

(1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolyl)(PCy<sub>3</sub>)(Cl)<sub>2</sub>Ru=CH(PCy<sub>3</sub>)](BF<sub>4</sub>) (100 mg, 0.123 mmol, 1.0 equiv) was added to a flame-dried flask under an atmosphere of argon. Anhydrous dichloromethane (9 mL) was then added in one portion, followed by tetrafluoroboric acid (HBF<sub>4</sub>; 54 wt% in diethyl ether; 17  $\mu\text{L}$ , 0.123 mmol, 1.0 equiv). A yellow to dark brown color change was immediately observed. The reaction was allowed to stir at ambient temperature for 1 h. The volatiles were then removed *in vacuo*. The resulting brown residue was washed with anhydrous pentane (2 x 5 mL), decanting the solvent from each wash via cannula under an atmosphere of argon. The remaining brown powder was allowed to dry under vacuum (10 mTorr) for 3 h to afford analytically pure product in 96% yield (106 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$  17.56 (1H, d,  $J = 37.2$ , Ru=CH(PCy<sub>3</sub>)), 7.57 (1H, m, DIPP *p*-H), 7.39 (2H, m, DIPP *m*-H), 7.08 (2H, s, mesityl *m*-H), 4.36-4.18 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>N), 3.26 (2H, br, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.43 (6H, s, mesityl *o*-CH<sub>3</sub>), 2.38 (3H, s, mesityl *p*-CH<sub>3</sub>), 2.40-2.32 (3H, m, Cy), 1.80 (6H, br, Cy), 1.75 (3H, br, Cy), 1.27 (12H, d,  $J = 6.8$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.34-1.12 (21H, m, Cy);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 20 °C, 3300 scans)  $\delta$  259.6 (br, Ru=CH(PCy<sub>3</sub>)), 188.9 (br, NCN), 148.8, 140.9, 138.7, 131.4, 130.7, 125.8, 56.1, 53.1, 30.9 (d,  $J = 37.2$  Hz), 29.3, 28.5, 26.6 (d,  $J = 12.2$  Hz), 25.4, 24.0, 21.4, 19.6;  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$  52.5;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$  -153.4; HRMS(FAB+)  $m/z$ : 813.3400 (M+H-H<sub>2</sub>-BF<sub>4</sub>); crystallographic data can be obtained on request, free of charge, from the Cambridge Crystallographic Database (CCDC #612852; crystal grown from dichloromethane/pentane utilizing the diffusion method).<sup>7</sup>



### II.B. Reaction of 5 with ethylene.

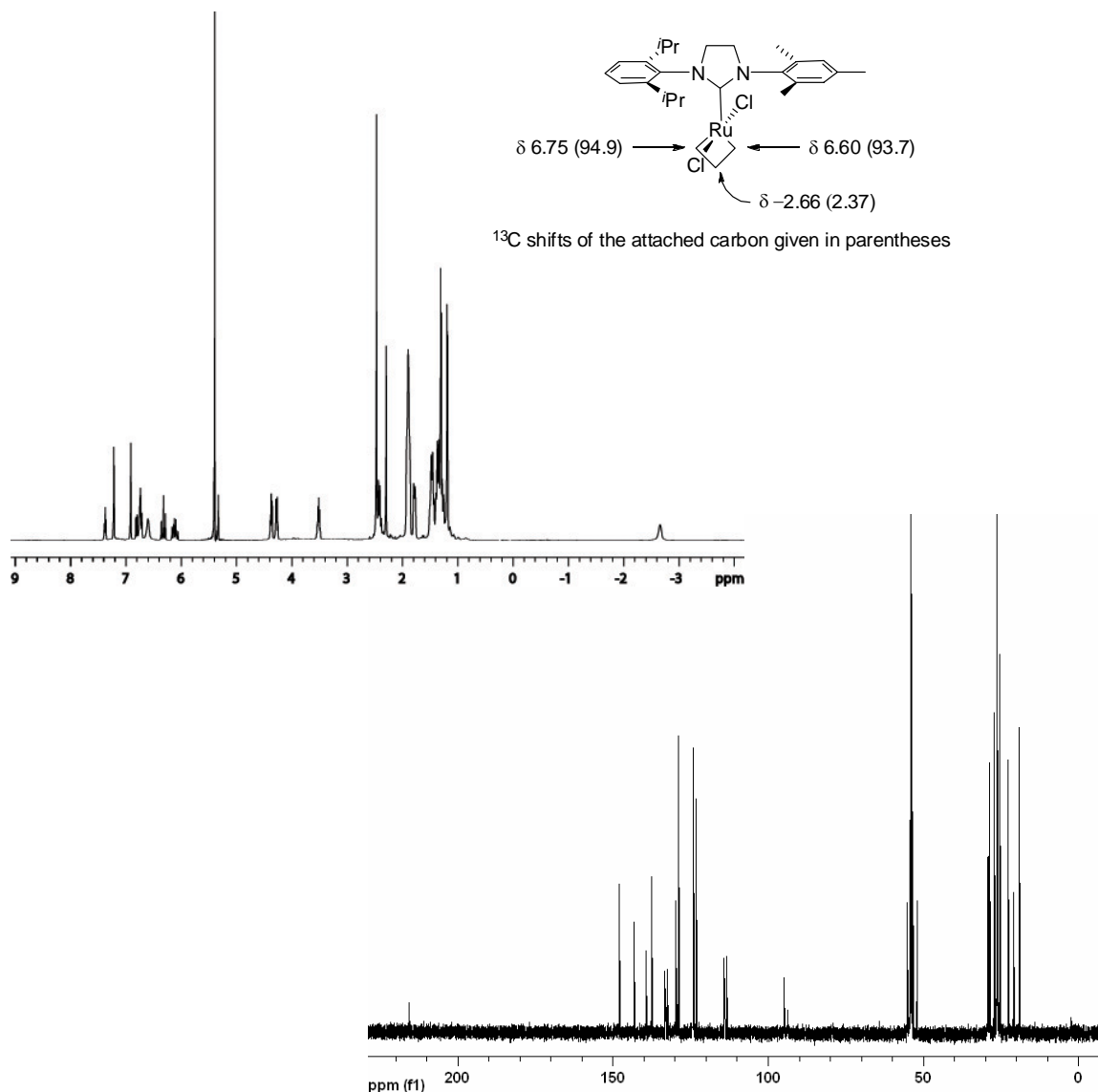


To a J-Young tube in the glovebox: [(1-(2,6-diisopropylphenyl)-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolyl)(PCy<sub>3</sub>)(Cl)<sub>2</sub>Ru=CH(PCy<sub>3</sub>)](BF<sub>4</sub>) (5; 17.5 mg, 0.021 mmol, 1.0 equiv) was dissolved in  $\text{CD}_2\text{Cl}_2$  (600  $\mu\text{L}$ ), forming a homogeneous brown solution. The tube was sealed with a Teflon stopper, removed from the box, and attached to a Schlenk line. The tube was then cooled to -78 °C, placed under vacuum (100 mTorr), and backfilled with an atmosphere of ethylene. The tube was sealed, shaken, and allowed to warm to -40 °C. Reaction progress was monitored via VT-NMR at -40 °C. Complete conversion to metallacycle (>95%) was observed

<sup>7</sup> CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; <http://www.ccdc.cam.ac.uk>.

after 1.5 h.<sup>8</sup> <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -40 °C) δ 7.83 (1H, m, DIPP *p*-H), 7.22 (2H, m, DIPP *m*-H), 6.92 (2H, s, mesityl *m*-H), 6.75 (2H, br, RuCH<sub>2</sub>-), 6.60 (2H, br, RuCH<sub>2</sub>-), 4.37 (2H, m, (DIPP)NCH<sub>2</sub>CH<sub>2</sub>N(Mes)),<sup>9</sup> 4.27 (2H, m, (DIPP)NCH<sub>2</sub>CH<sub>2</sub>N(Mes)), 3.52 (2H, sep, *J* = 6.6 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.48 (6H, s, mesityl *o*-CH<sub>3</sub>), 2.34 (3H, s, mesityl *p*-CH<sub>3</sub>), 1.31 (6H, d, *J* = 6.4 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (6H, d, *J* = 6.9 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), -2.66 (2H, br, metallacycle β-H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -40 °C)<sup>10</sup> δ 215.6 (NCN), 148.1 (Ar), 139.4 (Ar), 137.6 (Ar), 133.0 (Ar), 132.4 (Ar), 129.9 (DIPP C<sup>4</sup>), 129.1 (mesityl C<sup>3</sup> and C<sup>5</sup>), 124.1 (DIPP C<sup>3</sup> and C<sup>5</sup>), 94.9 (metallacycle α-carbon), 93.7 (metallacycle α-carbon), 55.3 ((DIPP)NCH<sub>2</sub>CH<sub>2</sub>N(Mes)), 52.2 ((DIPP)NCH<sub>2</sub>CH<sub>2</sub>N(Mes)), 28.7 (-CH(CH<sub>3</sub>)<sub>2</sub>), 27.4 (-CH(CH<sub>3</sub>)<sub>2</sub>), 22.7 (-CH(CH<sub>3</sub>)<sub>2</sub>), 21.1 (mesityl *p*-CH<sub>3</sub>), 19.3 (mesityl *o*-CH<sub>3</sub>), 2.4 (metallacycle β-carbon).

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -40 °C):

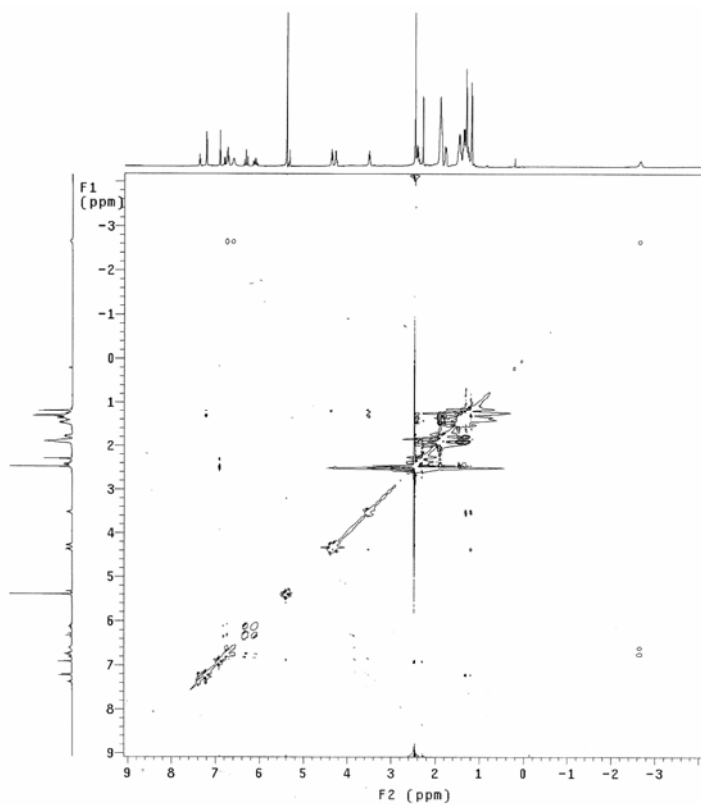


<sup>8</sup> Spectroscopic values for the vinyl phosphonium byproduct match those reported in: Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032-5033.

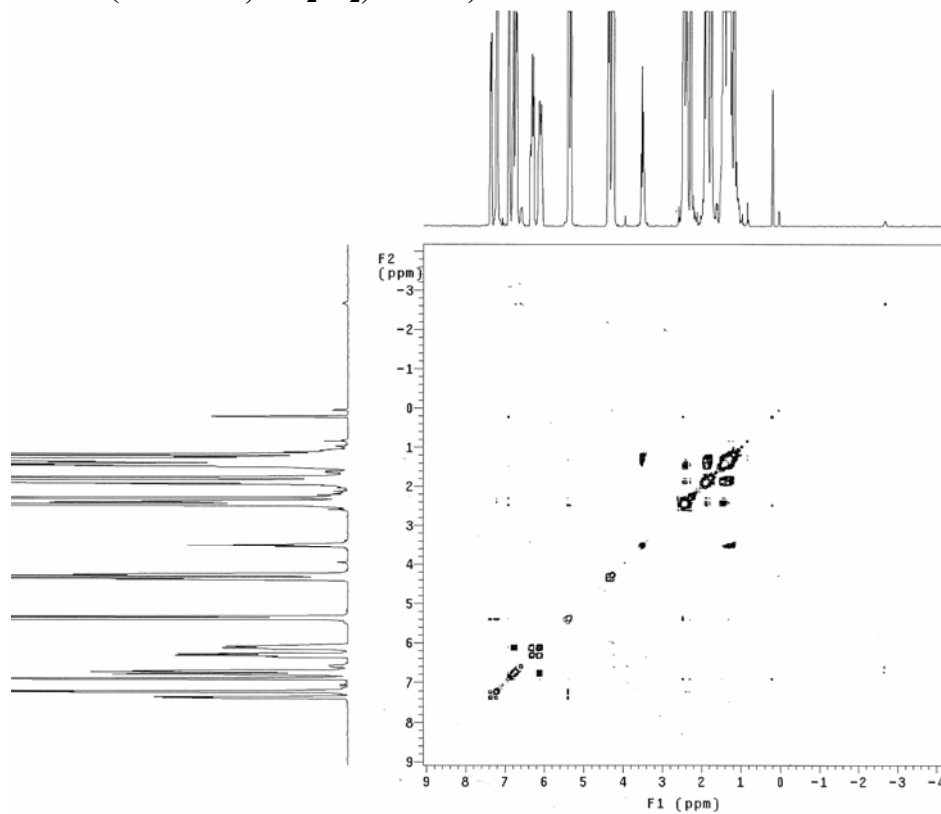
<sup>9</sup> Mes = mesityl

<sup>10</sup> Assignments determined via HMQC.

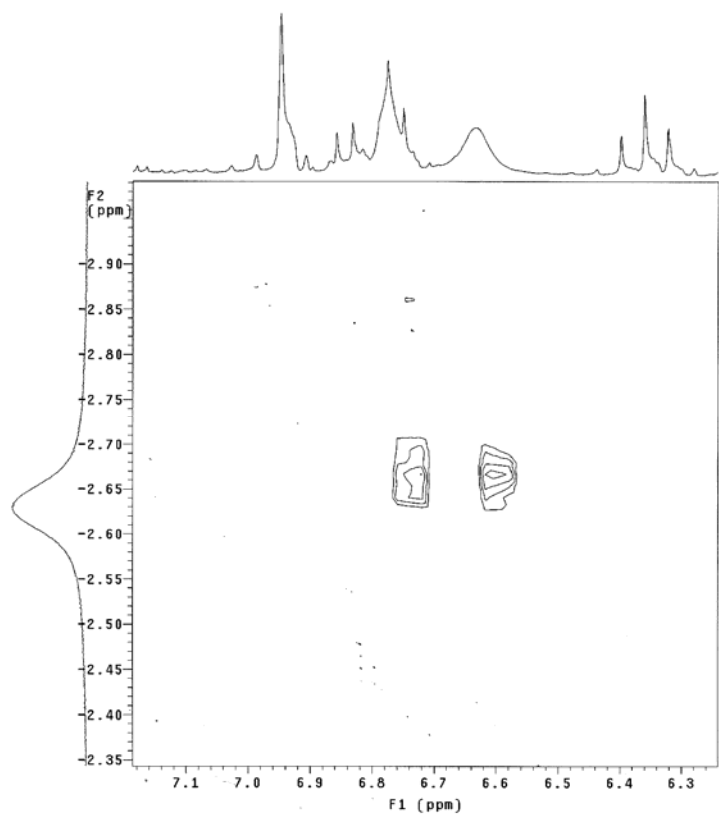
**2D-ROESY (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -40 °C; mix = 0.13 s):**



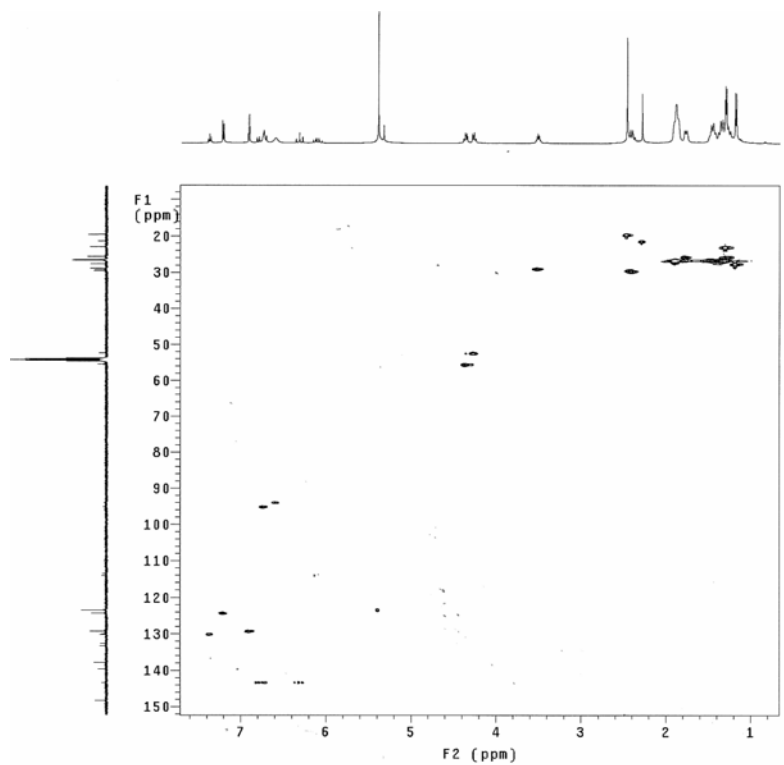
**COSY (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -40 °C):**



**COSY (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -40 °C; metallacycle region):**

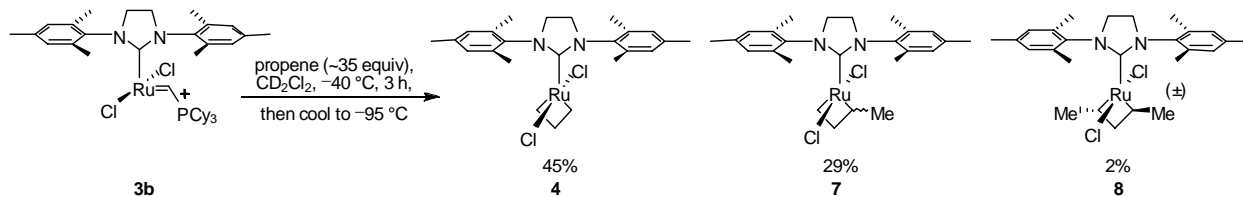


**HMQC (CD<sub>2</sub>Cl<sub>2</sub>, -40 °C):**

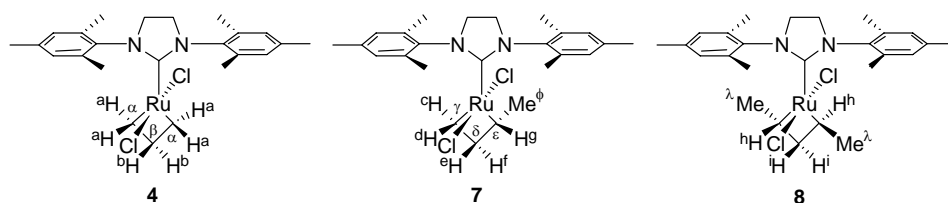




### II.C. Reaction of [(IMesH<sub>2</sub>)Cl<sub>2</sub>Ru=CH(PCy<sub>3</sub>)](BF<sub>4</sub>) with propene.



[(IMesH<sub>2</sub>)Cl<sub>2</sub>Ru=CH(PCy<sub>3</sub>)](BF<sub>4</sub>) (**3b**; 18.0 mg, 0.021 mmol, 1.0 equiv) was added to a J-Young tube in the glovebox. CD<sub>2</sub>Cl<sub>2</sub> (600 μL) was then added, and the tube was sealed, shaken, and removed from the box. Propene (0.735 mmol, 35 equiv) was added to the NMR tube via the Schlenk technique referenced in Section I.A.<sup>11</sup> The tube was then sealed, shaken, and allowed to warm to -40 °C. Reaction progress was monitored via VT-NMR at -40 °C. The complete conversion (>95%) of starting material was observed after 3.0 h, with 45% conversion to metallacycle **4** (the spectroscopic values for **4** match those reported previously<sup>2</sup>).<sup>12</sup> The reaction was removed from the NMR and immersed in a -78 °C cold bath for transport to the U.C. Irvine NMR facility, where it was placed into a Bruker Avance-500 NMR spectrometer cooled to -40 °C. Once it had been established that no decomposition had occurred, the reaction was further cooled to -95 °C. At this temperature, metallacycle **4** remains present in 45% conversion. Two new metallacycle species are also clearly visible: **7** (29% conversion) and **8** (2% conversion). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C)<sup>13</sup> δ 7.85 (2H, br, **H<sup>h</sup>** metallacycle **8**), 7.76 (1H, br, **H<sup>g</sup>** metallacycle **7**), 6.65 (1H, br, **H<sup>c</sup>** metallacycle **7**), 6.60 (4H, br, **H<sup>a</sup>** metallacycle **4**), 6.05 (1H, br, **H<sup>d</sup>** metallacycle **7**), 0.89 (3H, d, *J* = 5.4 Hz, RuCH(CH<sub>3</sub>) metallacycle **7**), 0.72 (6H, d, *J* = 5.6 Hz, RuCH(CH<sub>3</sub>) metallacycle **8**), -2.11 (1H, br, **H<sup>f</sup>** metallacycle **7**), -2.35 (2H, br d, *J* = 8.1 Hz), **H<sup>i</sup>** metallacycle **8**), -2.63 (2H, br, **H<sup>b</sup>** metallacycle **4**), -2.84 (1H, br, **H<sup>e</sup>** metallacycle **7**); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C)<sup>14</sup> δ 120.2 (**C<sup>e</sup>** metallacycle **7**), 93.9 (**C<sup>α</sup>** metallacycle **4**), 89.3 (**C<sup>γ</sup>** metallacycle **7**), 9.0 (**C<sup>δ</sup>** metallacycle **7**), 1.7 (**C<sup>β</sup>** metallacycle **4**).



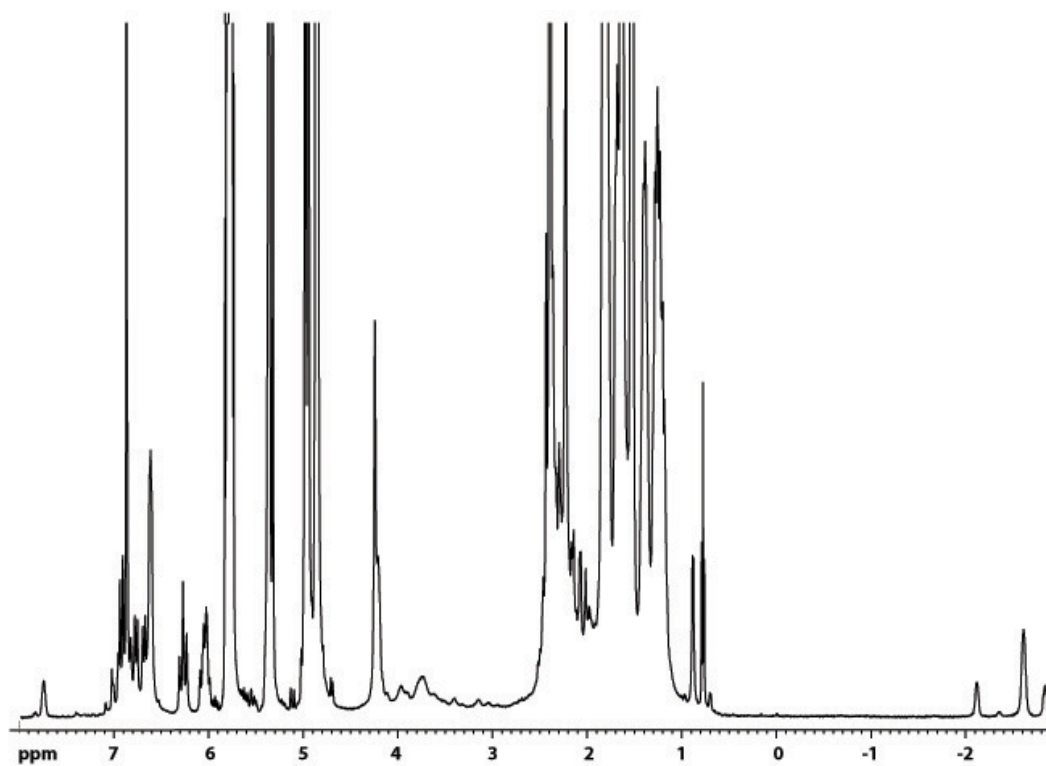
<sup>11</sup> The addition of 35 equivalents of propene ensures that the reaction does not freeze upon cooling to -95 °C. In addition, the presence of excess propene serves to minimize the amount of starting catalyst that is converted to a bis-ruthenium sideproduct, in which only one of the rutheniums is metathesis active.

<sup>12</sup> Conversions were determined utilizing anthracene (0.014 M, 0.5 equiv) as an internal standard.

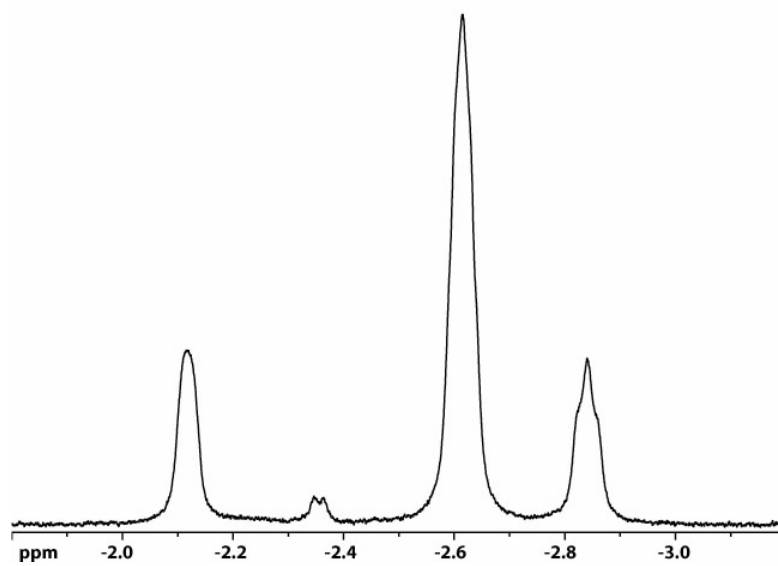
<sup>13</sup> Shifts corresponding to the NHC ligand of each species cannot be definitively assigned, as no 2D crosspeaks were observed to enable identification.

<sup>14</sup> The <sup>13</sup>C chemical shifts for metallacycle **8** could not be conclusively assigned due to low conversion. In addition, noise was found to occlude the chemical shift region for C<sup>φ</sup> and C<sup>λ</sup> in the HMQC, preventing assignment. See Section II.D. for the assignment of C<sup>φ</sup> and C<sup>λ</sup> using 3-<sup>13</sup>C-labeled propene.

**$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-95\text{ }^\circ\text{C}$ ):**

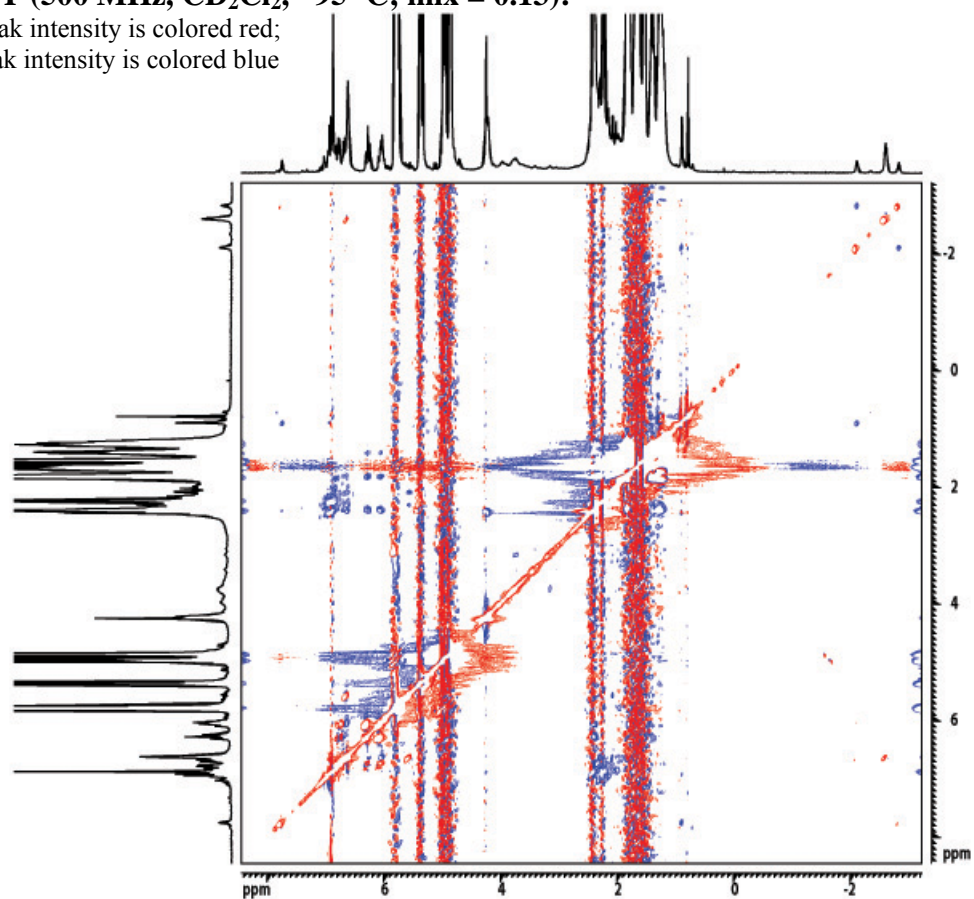


**$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-95\text{ }^\circ\text{C}$ ; metallacycle  $\beta$ -hydrogen region):**

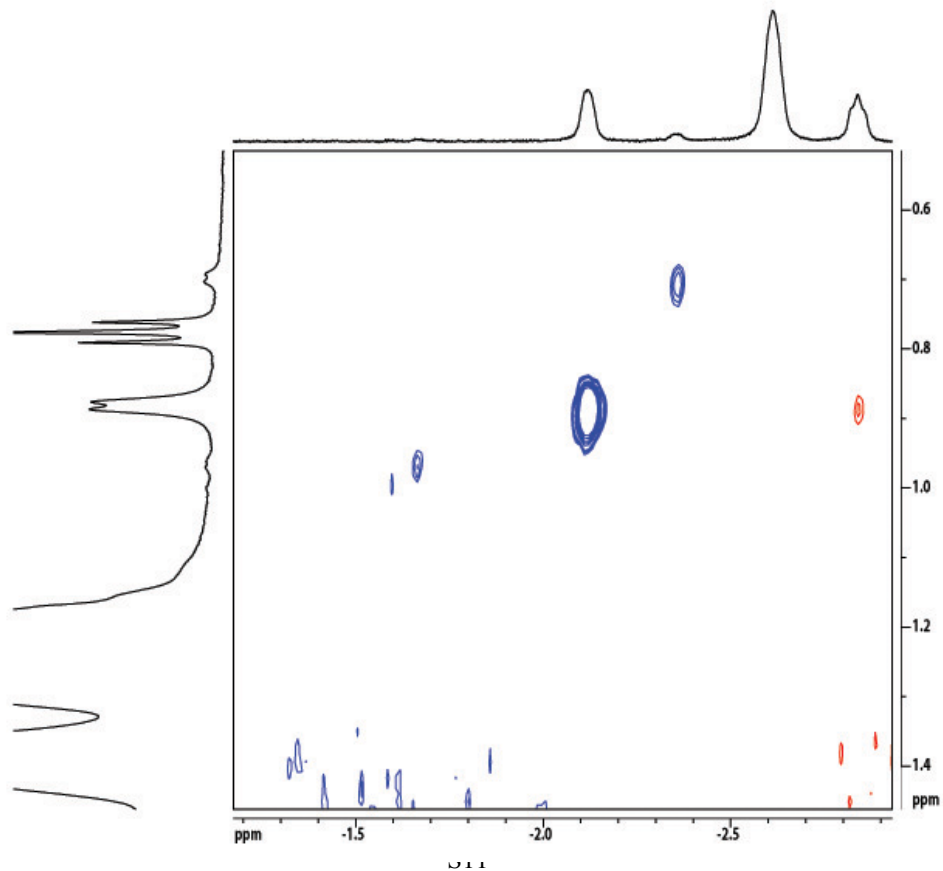


**2D-ROESY (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C; mix = 0.13):**

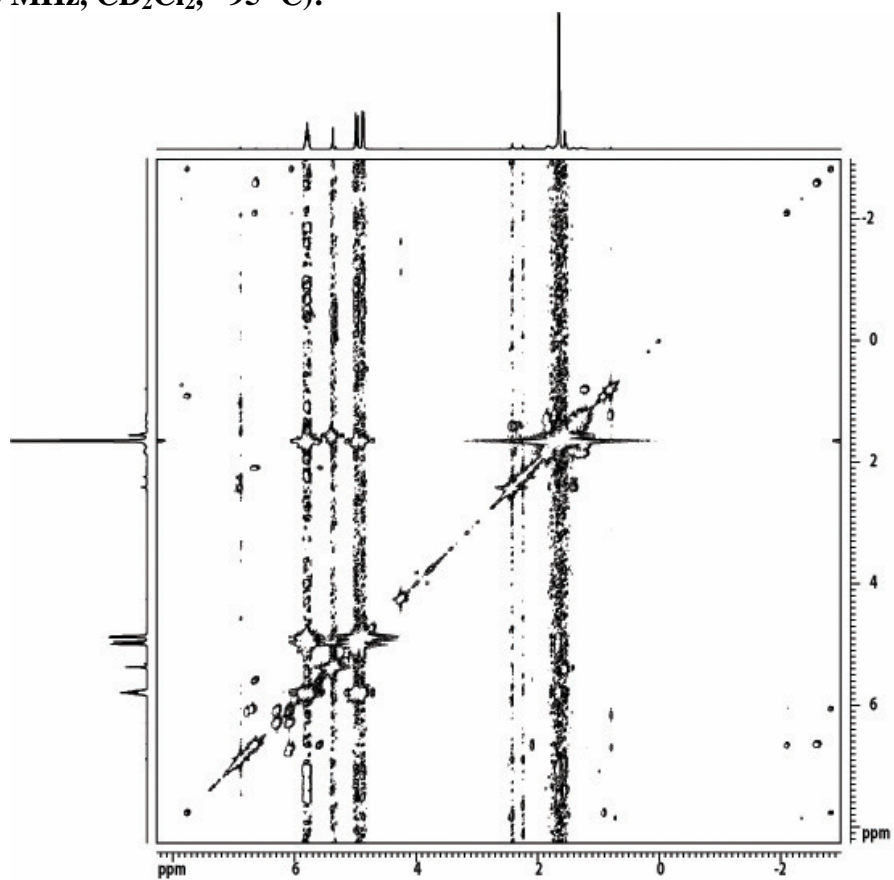
\*negative peak intensity is colored red;  
positive peak intensity is colored blue



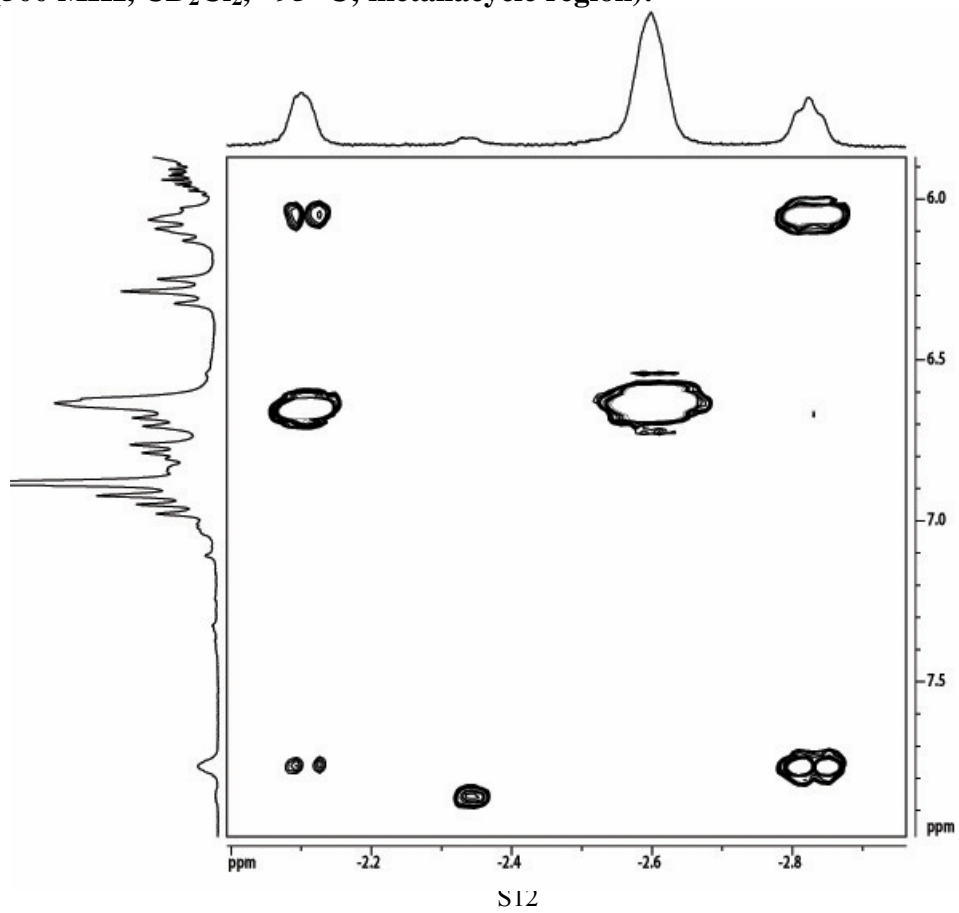
**2D-ROESY (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C; mix = 0.13; metallacycle region):**



COSY (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C):

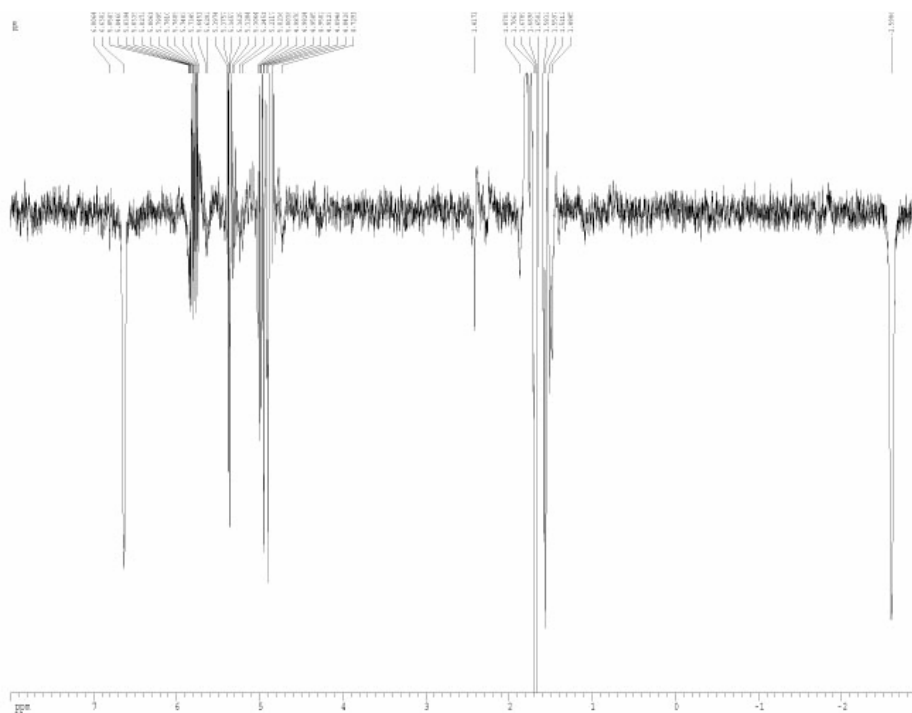


COSY (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C; metallacycle region):

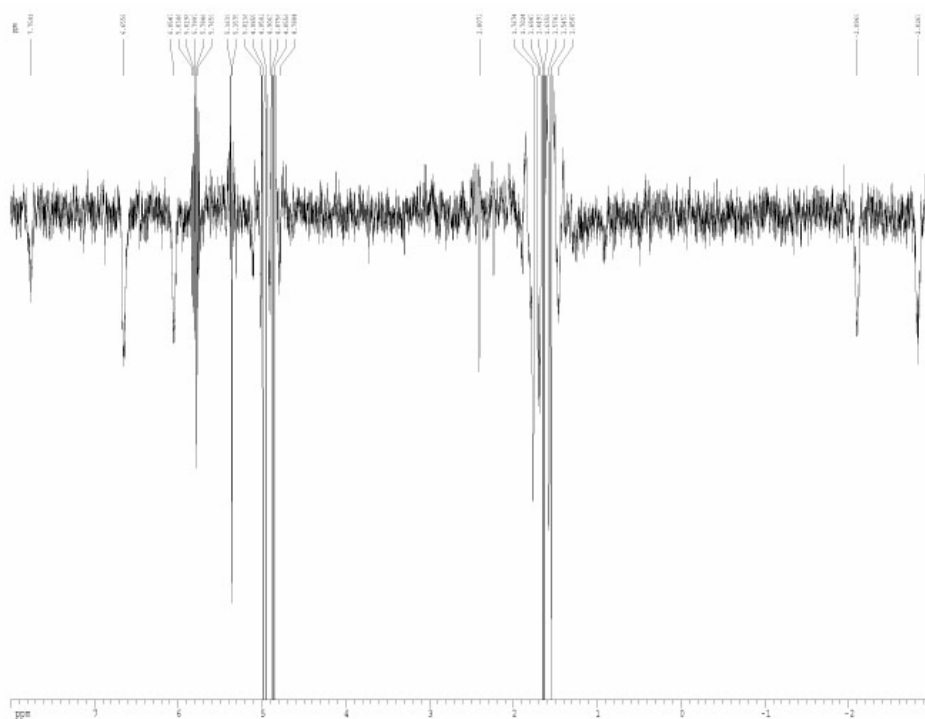




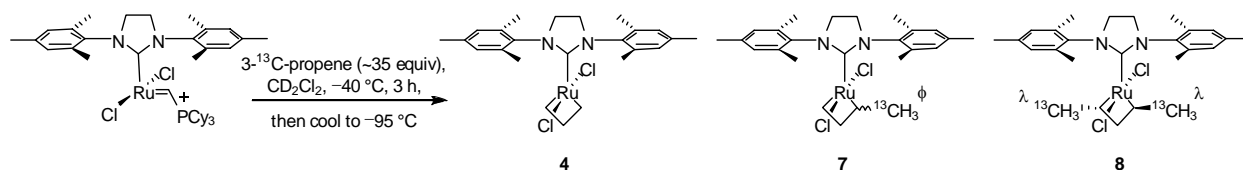
**NOE Experiment (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C; -2.66 peak irradiated, irradiation = 0.5 s):**



**NOE Experiment (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C; -2.84 peak irradiated, irradiation = 0.5 s):**

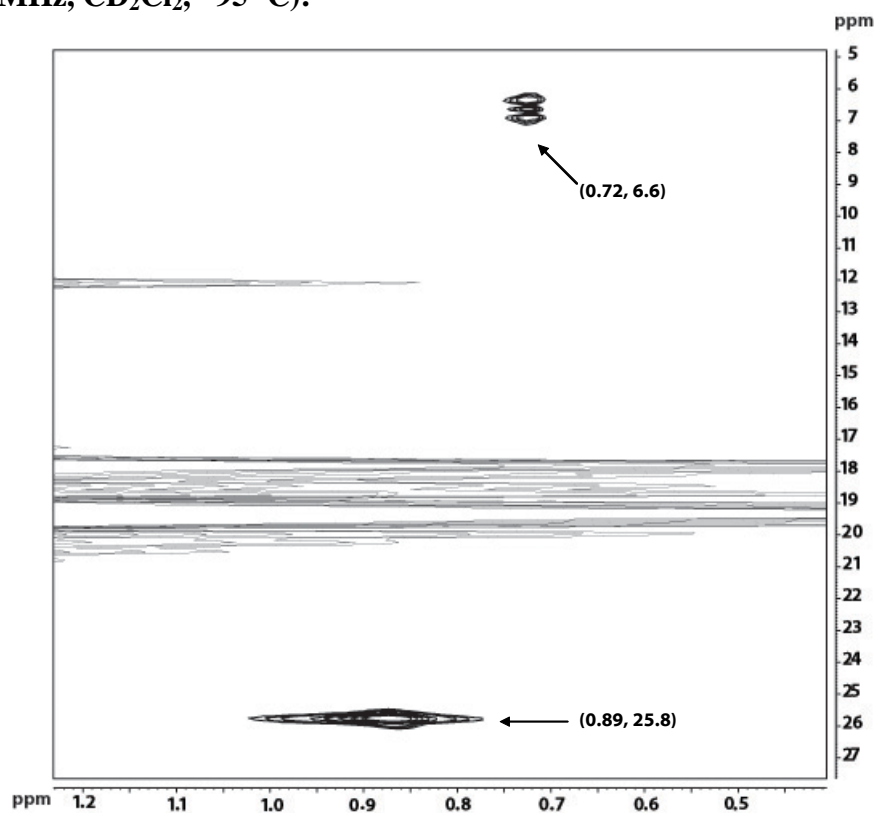


**II.D. Reaction of [(IMesH<sub>2</sub>)Cl<sub>2</sub>Ru=CH(PCy<sub>3</sub>)](BF<sub>4</sub>) with 3-<sup>13</sup>C-labeled propene (identification of C<sup>ϕ</sup> and C<sup>λ</sup>).**



Isotopically enriched metallacycles **7** and **8** were generated utilizing the same general procedure as outlined in Section II.C., with the exception that 3-<sup>13</sup>C-labeled propene was used in place of unlabeled propene. Analysis of the reaction mixture via <sup>1</sup>H NMR found two of the metallacycle peaks to demonstrate distinct <sup>1</sup>J<sub>C-H</sub> couplings: <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C) δ 0.89 (3H, dd, *J* = 5.4 Hz, <sup>1</sup>J<sub>C-H</sub> = 127.8 Hz, RuCH(CH<sub>3</sub><sup>ϕ</sup>)), 0.72 (6H, dd, *J* = 5.6 Hz, <sup>1</sup>J<sub>C-H</sub> = 120.3 Hz, RuCH(CH<sub>3</sub><sup>λ</sup>)). Utilizing a HMQC experiment, it was found that <sup>13</sup>C had incorporated into the methyl groups of propene, butene, and metallacycles **7** and **8**: <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C) δ 25.8 (RuCH(CH<sub>3</sub><sup>ϕ</sup>)), 6.6 (RuCH(CH<sub>3</sub><sup>λ</sup>)).

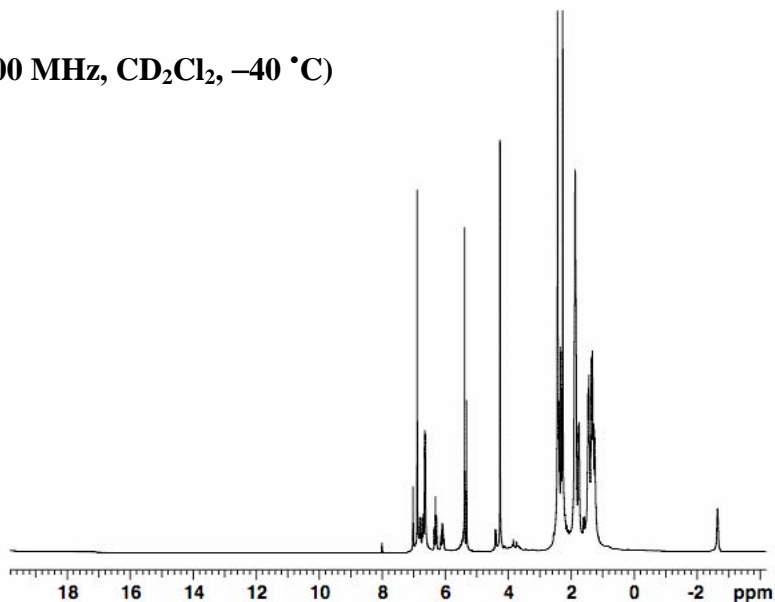
**HMQC (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -95 °C):**



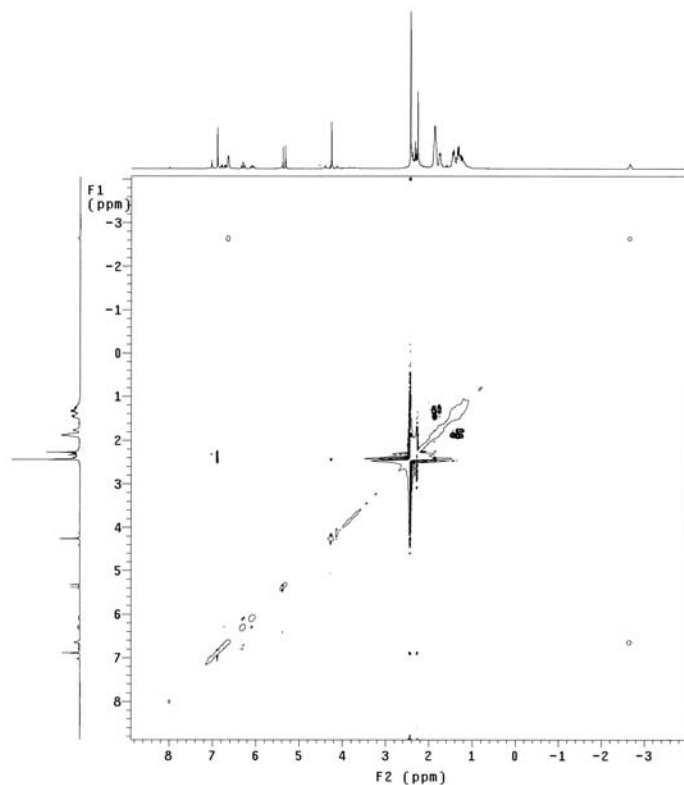
### II.E. Analysis of Metallacycle **4** via 2D-NMR for Exchange Crosspeaks.

To a J-Young tube in the glovebox:  $[(\text{IMesH}_2)\text{Cl}_2\text{Ru}=\text{CH}(\text{PCy}_3)](\text{BF}_4)$  (**3b**; 18.0 mg, 0.021 mmol, 1.0 equiv) was dissolved in  $\text{CD}_2\text{Cl}_2$  (600  $\mu\text{L}$ ), forming a homogeneous brown solution. The tube was sealed with a Teflon stopper, removed from the box, and attached to a Schlenk line. The tube was then cooled to  $-78\text{ }^\circ\text{C}$ , placed under vacuum (100 mTorr), and backfilled with an atmosphere of ethylene. The tube was sealed, shaken, and allowed to warm to  $-40\text{ }^\circ\text{C}$ . Reaction progress was monitored via VT-NMR at  $-40\text{ }^\circ\text{C}$ . Complete conversion ( $>95\%$ ) to metallacycle **4** was observed after 3 h.<sup>8</sup>

#### $^1\text{H}$ NMR (500 MHz, $\text{CD}_2\text{Cl}_2$ , $-40\text{ }^\circ\text{C}$ )

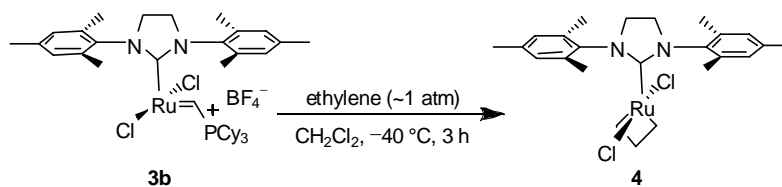


#### 2D-ROESY (500 MHz, $\text{CD}_2\text{Cl}_2$ , $-40\text{ }^\circ\text{C}$ ; mix = 0.13)



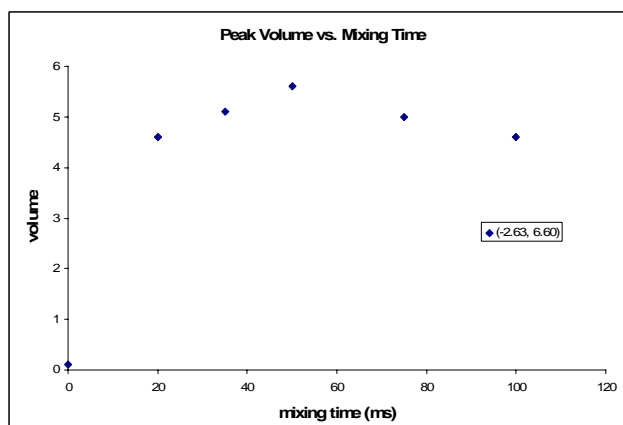


## II.F. Dynamic NMR Behavior of Metallacycle **4** in CD<sub>2</sub>Cl<sub>2</sub> at -40 °C.

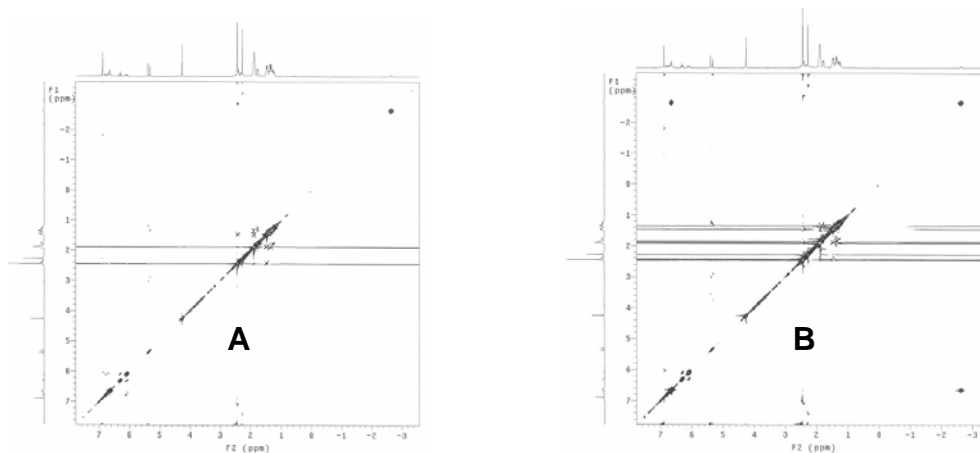


Metallacycle **4** was generated using the same experimental procedure as listed in Section II.E. Upon reaction completion, a series of 2D-NOESY experiments were performed at various mixing times (10  $\mu\text{s}$ , 20 ms, 35 ms, 50 ms, 75 ms, and 100 ms). A plot of the peak volume at (-2.63, 6.60) relative to mixing time was used to identify the linear region of NOE buildup to lie in the region below 50 ms.<sup>15</sup>

mix (ms)	volume
0.00001	0.1
20	4.6
35	5.1
50	5.6
75	5.0
100	4.6



The dynamics of interconversion between the  $\alpha$ - and  $\beta$ -positions of metallacycle **4** were determined by quantifying the off-diagonal NOESY exchange peaks in the region of minimal spin diffusion (20-50 ms). This technique is commonly referred to as EXSY, and is well-known.<sup>16</sup> Results for the 20 ms NOESY experiment are listed below:



500 MHz <sup>1</sup>H NOESY experiments at -40 °C in CD<sub>2</sub>Cl<sub>2</sub>. Negative peak intensity is solid black. (A) mixing time = 10  $\mu\text{s}$ ; (B) mixing time = 20 ms. Peak intensities are listed clockwise, starting at the high-field resonance: A = 18.2, 0.1, 9.1, 0.1; B = 10.6, 4.6, 5.1, 4.7.

<sup>15</sup> Linear regions in plots of peak intensity vs. time are generally attributed to mixing times where spin diffusion is minimal. See: Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, 2<sup>nd</sup> Ed.; Wiley-VCH: New York, 2000; Chapter 4.

<sup>16</sup> The *EXSY CALC* software package and instructions for crosspeak analysis can be obtained at: <http://www.mestrec.com>.

Peak volumes were entered into *EXSY CALC* to afford the following rate constants:

mixing time	$k_f$ ( $s^{-1}$ )	$k_r$ ( $s^{-1}$ )	ratio
20 ms	26	53	0.49

These values were found to correlate with Matlab calculations employing Zolnai's Full Matrix Analysis (FMA) method.<sup>17,18</sup> The value of  $k_f$  ( $26 \pm 2 s^{-1}$ ) was then input into the following expression to provide an estimate of the Gibbs free energy of activation ( $\Delta G^\ddagger$ ) at  $-40^\circ C$  (233 K) to be  $12.18 \pm 0.04$  kcal/mol.

$$\Delta G^\ddagger = RT[\ln(k_B/h) - \ln(k/T)]$$

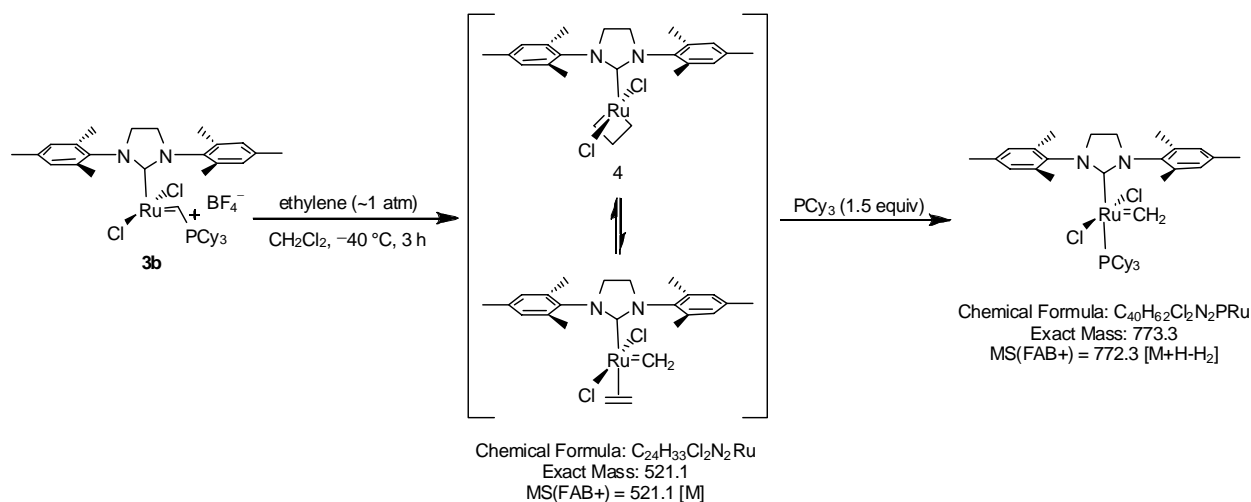
$$h = 6.626075 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$k_B = 1.380658 \times 10^{-23} \text{ J/K}$$

$$R = 1.987 \times 10^{-3} \text{ kcal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T = 233 \text{ K}$$

## II.G. Mass Spectroscopy Investigation for the Presence of 4.



To a 25-mL, 2-neck, round-bottom flask:  $[(\text{IMesH}_2)\text{Cl}_2\text{Ru}=\text{CH}(\text{PCy}_3)](\text{BF}_4)$  (**3b**; 18.0 mg, 0.021 mmol, 1.0 equiv) was dissolved in  $\text{CD}_2\text{Cl}_2$  (600  $\mu\text{L}$ ) under an atmosphere of argon, forming a homogeneous brown solution. The flask was then cooled to  $-78^\circ C$ , placed under vacuum (100 mTorr), and backfilled with an atmosphere of ethylene. The reaction was then allowed to warm to  $-40^\circ C$  with stirring. After 3 h, the reaction mixture was diluted with anhydrous dichloromethane ( $-78^\circ C$ ; 10 mL). A 3- $\mu\text{L}$  aliquot was then added to a chilled FAB probe (approx.  $-60^\circ C$ ) coated with a 2-nitrophenyl octyl ether matrix. Spectroscopic analysis using FAB+ afforded  $m/z = 521.1$  [M], as well as 539.0 [M+H<sub>2</sub>O], which was presumably due to the presence of condensation on the probe. The subsequent addition of tricyclohexylphosphine (8.8 mg, 0.031 mmol, 1.5 equiv) to the remaining reaction mixture afforded quantitative conversion to  $(\text{IMesH}_2)\text{Cl}_2(\text{PCy}_3)\text{Ru}=\text{CH}_2$ , the characterization of which matched reported literature values (HRMS(FAB+)  $m/z$ : 772.2981 [M+H-H<sub>2</sub>]).<sup>19</sup>

<sup>17</sup> *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 611-621.

<sup>18</sup> See also: Anderson, D. R.; Hickstein, D. D.; O'Leary, D. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 8386-8387.

<sup>19</sup> Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543-6554.