

Supporting Information for

Generation and Spectroscopic Characterization of Ruthenacyclobutane and Ruthenium Olefin Carbene Intermediates Relevant to Ring Closing Metathesis Catalysis

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1. General Information.

1.A. Reagents and General Procedures. Most operations involving ruthenium complexes were performed under a purified argon atmosphere using glove box or vacuum line techniques. Preparations of most organic compounds were done on the air. CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2 , tetrahydrofuran (THF) and pentane were dried over $\text{Na/Ph}_2\text{CO}$, and distilled under reduced pressure. NMR spectra for the ruthenium complexes were recorded at variable temperatures in dry, oxygen free CD_2Cl_2 . Those for organic compounds were run in CDCl_3 and acetone- d_6 , which were used as received.

Ruthenium phosphonium alkylidenes $[(\text{H}_2\text{IMes})(\text{Cl})_2\text{Ru}=\text{C}(\text{H})\text{PCy}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[(\text{H}_2\text{IMes})(\text{Cl})_2\text{Ru}=\text{C}(\text{H})\text{PCy}_3]^+[\text{BF}_4]^-$ and $[(\text{H}_2\text{IMes})(\text{Cl})_2\text{Ru}=\text{C}(\text{H})\text{PCy}_3]^+[\text{OSO}_2\text{CF}_3]^-$ and carbide $(\text{H}_2\text{IMes})(\text{Cl})_2(\text{PCy}_3)\text{Ru}\equiv\text{C}$ were prepared as previously described.¹ Dimethyl diallylmalonate was prepared as described,² except N,N-dimethylformamide (DMF) was used as the solvent instead of THF. 3,3-Diallyl-2,4-pentanedione was prepared in H_2O by modification of a literature procedure.³ $(\text{H}_2\text{IMes})(\text{Cl})_2(\text{py})_2\text{Ru}=\text{CHPh}$ was prepared as described.⁴ Acetylene-1,2- $^{13}\text{C}_2$ (99 atom % ^{13}C , CIL), Lindlar catalyst (5 % Pd on CaCO_3 , 1.6 % Pb poisoned, Strem), triisopropylphosphine (Strem), dimethyl malonate (Aldrich), diethyl diallylmalonate (Aldrich), allyl bromide (Aldrich), 2,4-pentanedione (Aldrich), DMF (anhydrous, 99.8 %, Aldrich), 1,4-dichloro-cis-2-butene (Acros), lithium hydride (Strem), SOCl_2 (Fluka) were used as received. Acenaphthylene (75 %, Aldrich) was sublimed in vacuo at room temperature on an ice-cooled finger to obtain material that

¹ Dubberley, S.R.; Romero, P.E.; Piers, W.E.; McDonald, R.; Parvez, M. *Inorg. Chim. Acta* **2006**, 359, 2658.

² Harrowven, D.C.; May, P.J.; Bradley, M. *Tetrahedron Lett.* **2003**, 44, 503.

³ King, I.F.; Rathore, R.; Lam, J.Y.L.; Guo, Z.R.; Klassen, D.F. *J. Am. Chem. Soc.* **1992**, 114, 3028. Reaction was performed at pH 10 to obtain diallyl.

⁴ Sanford, M.S.; Love, J.A.; Grubbs, R.H. *Organometallics* **2001**, 20, 5314.


was >90 % pure, the remainder being acenaphthene. $\text{B}(\text{C}_6\text{F}_5)_3$ (97 %, Strem) was purified to >99 % purity by sublimation in vacuo at 70 °C. Hydrogen (UHP 5.0, Praxair) was passed over an Oxisorb oxygen scrubber. Ethene (99.9 %, Matheson) was passed over an Oxisorb oxygen scrubber, and added via gastight syringe, assuming ideal gas behaviour, to a pre-cooled (−78 °C, dry ice/acetone bath) 528-PP NMR tube through its septum. Gas additions using ethene-1,2- $^{13}\text{C}_2$ (99 %, Aldrich) were done with a small-scale gas addition setup, using a J-Young NMR tube.

1.B. Instrumentation. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{13}C , ^{13}C gated decoupled, DEPT-135, ^{19}F , ^{31}P NMR experiments were performed on Bruker AC-200, AMX-300 and DRX-400 spectrometers. 2D NMR experiments COSY, NOESY (EXSY) and HMQC were performed on the Bruker DRX-400 spectrometer. Data are given in ppm relative to residual solvent signals for ^1H and ^{13}C spectra. ^{19}F and ^{31}P spectra were referenced to external C_6F_6 and 85% H_3PO_4 respectively. Elemental analyses and high-resolution mass spectrometry were performed at the University of Calgary. Single crystal X-ray analysis was performed by Dr. Masood Parvez on a Nonius Kappa CCD diffractometer (University of Calgary).

2. Experimental Procedures and Characterization Data.

2.A. Organic Compounds.

Synthesis of dimethyl cyclopent-3-ene-1,1-dicarboxylate

 In a glove box, dimethyl diallylmalonate (0.325 g, 1.53 mmol) was placed in a 50 mL 2-necked flask. On the vacuum line, 15 mL of CH_2Cl_2 was condensed into the flask at −78 °C. The solution was warmed to room temperature and $[(\text{H}_2\text{IMes})(\text{Cl})_2\text{Ru}=\text{C}(\text{H})\text{PCy}_3]^+[\text{OSO}_2\text{CF}_3]^-$ (15 mg, 0.016 mmol) was added as a solid through the second neck. The solution developed a light red colour, and evolution of a gas (presumably ethene) was observed. Judging from TLC analysis, all the starting material was consumed within 15 minutes. The volatiles were removed in vacuo, resulting in a brown solid residue. The product was sublimed from this residue in vacuo

at 45 °C onto a water-cooled finger to yield the product as colourless crystals, which were isolated. Yield: 0.267 g (1.43 mmol, 93.2 %).

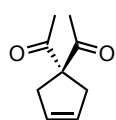
^1H NMR (CD_2Cl_2 , 399.6 MHz, 295 K): δ 5.60 (m, 2H, =CH), 3.70 (s, 6H, CH_3), 2.99 (m, 4H, CH_2).

^1H NMR (CD_2Cl_2 , 399.6 MHz, 213 K): δ 5.57 (m, 2H, =CH), 3.66 (s, 6H, CH_3), 2.94 (m, 4H, CH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 295 K): δ 173.1 (s, C=O), 128.3 (s, =CH), 59.2 (s, O=CCC=O), 53.2 (s, CH_3), 41.4 (s, CH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 213 K): δ 172.6 (s, C=O), 127.8 (s, =CH), 58.0 (s, O=CCC=O), 53.2 (s, CH_3), 40.7 (s, CH_2).

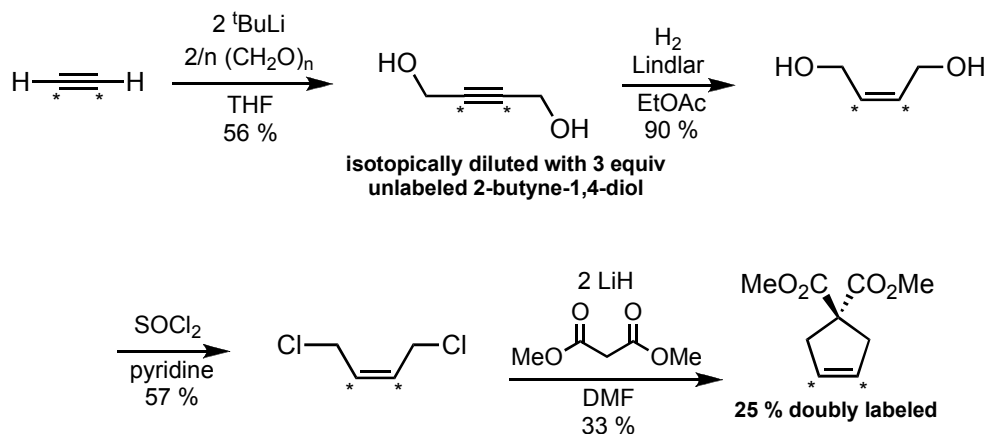
Synthesis of 4,4-diacetylcyclopentene



Synthesized from 3,3-diallyl-2,4-pentanedione using same procedure as above, in 79 % yield.

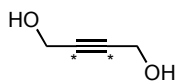
^1H NMR (CD_2Cl_2 , 399.6 MHz, 213 K): δ 5.54 (m, 2H, =CH), 2.78 (m, 4H, CH_2), 2.03 (s, 6H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 213 K): δ 205.8 (br, C=O), 128.0 (s, =CH), 72.4 (s, O=CCC=O), 37.5 (s, CH_2), 26.6 (s, CH_3).



Synthesis of 2-butyne-1,4-diol-2,3- $^{13}\text{C}_2$ ⁵

⁵ Modified procedure based on: Wolf, E.; Spenser, I.D. *J. Org. Chem.* **1995**, 60, 6937.

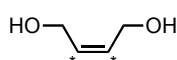


In the glove box, a 250 mL three-necked round bottom flask was charged with 3.10 g (48.4 mmol) of solid ^tBuLi. On the vacuum line, ca. 100 mL of THF was vacuum transferred onto the solids at −78 °C, affording a light yellow suspension. The flask was then cooled down to −97 °C using a methanol/liquid nitrogen bath. Acetylene-1,2-¹³C₂ (500 mL, ca. 20 mmol) was vacuum transferred from a breakseal flask into the reaction flask. Upon diffusion of the acetylene into the THF solution, a white precipitate became visible and the solution became viscous. The mixture was stirred for 1.5 hours at −97 °C, then for 30 minutes at −78 °C, then allowed to warm to room temperature and stirred for 2 more hours. Dry paraformaldehyde (1.65 g, corresponding to 55 mmol of monomer) was added in one portion through a side-neck of the reaction flask. A small rise in temperature could be noticed during the reaction. The mixture was stirred at room temperature overnight, after which the flask was heated to a gentle reflux for 1 hour. Water (1.5 mL, 1.5 g, 83 mmol) was added by syringe and the mixture was refluxed for 15 minutes, after which it was allowed to cool down to room temperature. The product was separated from the precipitated LiOH by filtration (with suction) through a coarse frit, and the precipitate was washed with 3 × 50 mL of THF. The precipitate was dried and crushed up with mortar and pestle, and washed with 3 more 50 mL portions of THF. The THF extracts were combined and the volatiles removed on the rotavap to yield 1.01 g of a yellowish solid, consisting of the title compound contaminated with some BHT (2,6-di-tert-butyl-4-methylphenol, stabilizer in THF). The BHT was sublimed out of the flask in vacuo under warming to ~40 °C to afford spectroscopically pure title compound. Yield: 0.99 g (11.2 mmol, ~56 %).

¹H NMR (acetone-*d*₆, 300 MHz, 300 K): δ 4.2-4.0 (m, 6H, CH₂ + OH).

¹³C{¹H} NMR (acetone-*d*₆, 75.5 MHz, 300 K): δ 84.4 (s, C≡C, enriched), 50.6 (app t, CH₂).

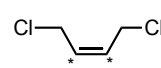
Synthesis of *cis*-2-butene-1,4-diol-2,3-¹³C₂ (25 % doubly labeled)⁵



A mixture of unlabeled 2-butyne-1,4-diol (2.96 g, 34.4 mmol) and 2-butyne-1,4-diol-2,3-¹³C₂ (0.97 g, 11.0 mmol) was dissolved in 150 mL EtOAc and 5.5 mL pyridine in a 250 mL 2-necked flask, and 200 mg Lindlar catalyst (5 % Pd on CaCO₃, 1.6 % Pb poisoned) was added. The mixture was stirred for 1 hour at

room temperature. Hydrogen gas was admitted under (slow) replenishing flow. The reaction was followed regularly by TLC (100 % EtOAc, stained with KMnO_4) and the reaction was stopped when the peak for 2-butyne-1,4-diol ($R_f = 0.40$) had just disappeared. (Possibly due to small amounts of residual BHT, the reaction took 28 hours, and several additions of 100-200 mg portions of catalyst were necessary. Reactions using only unlabeled 2-butyne-1,4-diol were always complete within 3 hours, with only a single portion of catalyst). The solution was then gravity filtered, and the solvent removed on the rotavap at 70 °C to afford a slightly yellow liquid. Yield: 3.95 g (~40.9 mmol, ~90.1 %). Circa 10 % of pyridine was retained in the liquid, but this was not removed because of its usefulness in the next step. The ratio cis-2-butene-1,4-diol:trans-2-butene-1,4-diol:butane-1,4-diol was ca. 89:5:6, as judged from the $^{13}\text{C}\{^1\text{H}\}$ spectrum. MS patterns in GC-MS analyses confirmed that the percentage of doubly labeled material was ca. 25 %. ^1H NMR (acetone- d_6 , 300 MHz, 300 K): δ 5.56 (m, 2H, $=\text{CH} + =^{13}\text{CH}$), 4.12 (m, 4H, CH_2), 3.71 (t, 2H, OH). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 75.5 MHz, 300 K): δ 131.7 (s, $=\text{CH}$, enriched), 58.6 (s, CH_2). Side-products found at δ 131.1 (trans-2-butene-1,4-diol, s, enriched) and 30.6 (butane-1,4-diol, s, enriched).

Synthesis of 1,4-dichloro-cis-2-butene-2,3- $^{13}\text{C}_2$ (25 % doubly labeled)⁶

 The crude cis-2-butene-1,4-diol (1.45 g, ~15.0 mmol) from the previous step was placed in a 50 mL round bottom flask and cooled in an ice bath. SOCl_2 (2.8 mL, 4.6 g, 38 mmol) was added dropwise over a period of ca. 15 minutes, during which gas evolution was observed and the mixture became very dark in colour. The mixture was stirred overnight, then added dropwise to 50 mL of water in order to quench unreacted SOCl_2 . Et_2O (100 mL) was added to extract the product, and 2 more extractions with 50 mL of Et_2O were carried out. The combined extracts were washed with H_2O (2 \times 50 mL), dried over MgSO_4 and filtered. The volatiles were removed on the rotavap to afford the crude product (ca. 90 % pure) as a dark brown liquid. Yield: 1.20 g (~8.6 mmol, ~57 %). The ratio 1,4-dichloro-cis-2-butene:1,4-dichloro-trans-2-butene:1,4-

⁶ Modified procedure based on: Brandsma, L., in *Preparative Acetylenic Chemistry*, 2nd edition, Elsevier: Amsterdam, 1988 (p 199).

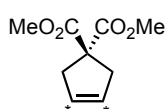
dichlorobutane was ca. 92:3:5, as judged from the $^{13}\text{C}\{^1\text{H}\}$ spectrum. MS patterns in GC-MS analyses confirmed that the percentage of doubly labeled material was ca. 25 %.

^1H NMR (CDCl_3 , 300 MHz, 300 K): δ 5.82 (m, 2H, $=\text{CH} + =^{13}\text{CH}$), 4.10 (m, 4H, CH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.5 MHz, 300 K): δ 129.6 (s, $=\text{CH}$, enriched), 37.9 (s, CH_2).

Side-products found at δ 130.0 (1,4-dichloro-trans-2-butene, s, enriched) and 29.7 (1,4-dichlorobutane, s, enriched).

Synthesis of dimethyl cyclopent-3-ene-1,1-dicarboxylate-3,4- $^{13}\text{C}_2$ (25 % doubly labeled)⁷



Dimethyl malonate (0.8 mL, 0.92 g, 7.0 mmol) was syringed into a dry, argon flushed 100 mL 2-necked flask, followed by 30 mL of anhydrous DMF. The solution was cooled in an ice bath. Lithium hydride (0.145 g, 18.2 mmol) was added through the side-neck of the flask, after which gas evolution became apparent. After 20 minutes at 0 °C, crude 1,4-dichloro-cis-2-butene (0.95 mL, 1.1 g, ~8.1 mmol) from the previous step was added by syringe, and the ice bath was removed. After 40 hours of stirring at room temperature, the mixture was cooled in an ice bath, and 50 mL of Et_2O was added, followed by slow addition of 20 mL of H_2O , during which gas formation was visible. The product was extracted with Et_2O (4×50 mL), the combined extracts were washed with H_2O (2×50 mL), dried over Na_2SO_4 and filtered. Evaporation of the volatiles on the rotavap yielded a dark brown sticky solid. Sublimation in vacuo at 35 °C on a water-cooled finger afforded the pure product as a white crystalline solid. Yield: 0.43 g (2.3 mmol, 33 %). MS patterns in GC-MS analyses confirmed that the percentage of doubly labeled material was ca. 25 %.

^1H NMR (CD_2Cl_2 , 300 MHz, 300 K): δ 5.60 (m, 2H, $=\text{CH} + =^{13}\text{CH}$), 3.70 (s, 6H, CH_3), 2.99 (app s, 4H, CH_2).

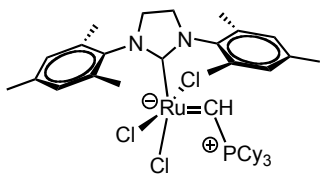
$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75.5 MHz, 300 K): δ 128.3 (s, $=\text{CH}$, enriched), 53.2 (s, CH_3), 41.5 (s, CH_2).

HRMS (TOF EI+): Calcd. for $\text{C}_9\text{H}_{12}\text{O}_4$: 184.0736; Found: 184.0733. Calcd. for $\text{C}_7^{13}\text{C}_2\text{H}_{12}\text{O}_4$: 186.0803; Found: 186.0806.

⁷ Modified procedure based on: Deprés, J.-P.; Greene, A.E. *J. Org. Chem.* **1984**, *49*, 928.

2.B. Ruthenium Complexes.

Synthesis of $(\text{H}_2\text{IMes})(\text{Cl})_3\text{Ru}=\text{CHPCy}_3$ ⁸



$(\text{H}_2\text{IMes})(\text{Cl})_2(\text{PCy}_3)\text{Ru}\equiv\text{C} \cdot \text{CH}_2\text{Cl}_2$ (0.304 g, 0.355 mmol) was put in a 50 mL flask. Dichloromethane (20 mL) was condensed onto the pale yellow solid at $-78\text{ }^\circ\text{C}$. To dissolve all of the carbide, the flask was warmed to room temperature, after which it was cooled down to $-78\text{ }^\circ\text{C}$ again, giving a light yellow solution. Ca. 150 mL (~ 10 -15 equiv) of anhydrous HCl gas was introduced into the flask at $-78\text{ }^\circ\text{C}$ through the vacuum line. This resulted in a red/orange solution, which turned a greenish yellow colour when the reaction mixture was allowed to warm to room temperature. After two hours of stirring all the volatiles were removed in vacuo, leaving a yellow solid. To recrystallize the material, it was dissolved in a mixture of 4 mL of bromobenzene and 2 mL of CH_2Cl_2 , and carefully layered with 6 mL of pentane. After two days of standing at room temperature, the vial was kept in the freezer at $-35\text{ }^\circ\text{C}$ for one day. The mother liquor was separated from the resulting yellow needle-shaped crystals. In order to remove the bromobenzenes of crystallization (3 per [Ru]),⁹ the crystals were treated and washed twice with 5 mL of pentane for 10 minutes. This gave straw-coloured dried out crystals, which were isolated. Yield: 0.232 g (0.287 mmol, 80.9 %).

^1H NMR (CD_2Cl_2 , 399.6 MHz, 298 K): δ 19.77 (d, $^2J_{\text{HP}} = 50\text{ Hz}$, 1H, $\text{Ru}=\text{CH}$), 6.98 (s, 4H, Mes CH), 3.98 (br, 4H, CH_2CH_2), 3.02 (ps q, 3H, Cy CH), 2.45 (br, 12H, Mes ortho CH_3), 2.35 (s, 6H, Mes para CH_3), 1.80-1.62 (m, 15H, Cy CH_2), 1.48-1.12 (m, 15H, Cy CH_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.8 MHz, 298 K): δ 32.6 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75.5 MHz, 300 K): δ 269.2 (br d, $^1J_{\text{CP}} \sim 15\text{ Hz}$, $\text{Ru}=\text{CH}$), 204.6 (d, $^3J_{\text{CP}} = 3\text{ Hz}$, $\text{Ru}-\text{C}(\text{N})_2$), 138.9 (br, Mes quaternary C), 130.2 (br, Mes CH), 52.4 (br, CH_2CH_2), 34.6 (d, $^1J_{\text{CP}} = 36\text{ Hz}$, Cy CH), 27.9 (d, $J_{\text{CP}} = 4\text{ Hz}$, Cy CH_2), 27.3 (d, $J_{\text{CP}} = 12\text{ Hz}$, Cy CH_2), 26.3 (d, $^4J_{\text{CP}} = 1.5\text{ Hz}$, Cy CH_2), 21.6 (s, Mes CH_3), 19.9 (v br, Mes CH_3).

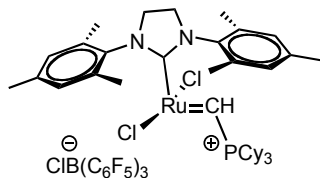
⁸ This compound has been reported, see Macnaughtan, M.L.; Johnson, M.J.A.; Kampf, J.W. *J. Am. Chem. Soc.* **2007**, 129, 7708.

⁹ Determined by X-ray diffraction, structure not reported here. See ref. 8 for structure.

Note: due to fluxionality of NHC ligand, not all resonances for quaternary C's are observed, and several signals are broadened.

Anal. Calcd. for $C_{40}H_{60}Cl_3N_2PRu$: C, 59.51; H, 7.49; N, 3.47. Found: C, 59.45; H, 7.50; N, 3.39.

Generation of $[(H_2IMes)(Cl)_2Ru=CHPCy_3]^+[ClB(C_6F_5)_3]^-$



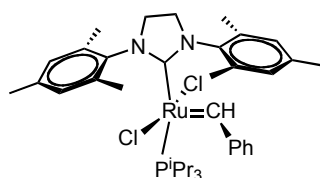
In order to validate the chloride abstraction procedure using $B(C_6F_5)_3$, $(H_2IMes)(Cl)_3Ru=CHPCy_3$ and 1.1 equiv $B(C_6F_5)_3$ were weighed into a vial and dissolved in 0.6 mL CD_2Cl_2 , affording a light brown solution. The 1H and ^{31}P NMR spectral

data were identical to those reported¹⁰ for $[(H_2IMes)(Cl)_2Ru=CHPCy_3]^+[B(C_6F_5)_4]^-$. NMR data for the anion are given below, these data are not repeated for other $ClB(C_6F_5)_3^-$ salts.

^{19}F NMR (CD_2Cl_2 , 282.4 MHz, 300 K): δ -132.6 (m, 6F, ortho CF), -161.9 (br, 3F, para CF), -166.9 (m, 8F, meta CF).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 100.5 MHz, 213 K): δ 147.6 (dm, $^1J_{CF}$ = 242 Hz, CF), 138.7 (dm, $^1J_{CF}$ = 247 Hz, CF), 136.4 (dm, $^1J_{CF}$ = 245 Hz, CF), 122.3 (v br, C_6F_5 quaternary C).

Synthesis of $(H_2IMes)(Cl)_2(P^iPr_3)Ru=CHPh$



$(H_2IMes)(Cl)_2(py)_2Ru=CHPh$ (0.651 g, 0.896 mmol) was put a 100 mL 2-necked flask. Toluene (50 mL) was condensed onto the green solids at $-78^\circ C$, after which the flask was warmed to room temperature. Triisopropylphosphine (0.164 g, 1.02 mmol) was dissolved in 5 mL of toluene and added to the bis(pyridine) complex,

resulting in a colour change from green to dark red. After 30 minutes of stirring at room temperature, the volatiles were removed in vacuo to yield a red residue, which was washed with pentane (2×25 mL). The product was purified by passing it through a plug of silica (eluent 50:50 Et_2O :pentane, material loaded in CH_2Cl_2), from which it elutes as a red band. Removal of the volatiles on the rotavap gave a red solid, which was washed with pentane (2×25 mL), dried in vacuo and isolated. Yield: 0.593 g (0.849 mmol, 90.8

¹⁰ Romero, P.E.; Piers, W.E.; McDonald, R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6161.

%). Ca. 10 mol % of CH_2Cl_2 was retained in the solid, judging from ^1H NMR spectra. This is also consistent with combustion analysis results.

^1H NMR (CD_2Cl_2 , 399.6 MHz, 242 K): δ 18.90 (s, 1H, Ru=CH), 8.95 (app d, 1H, Ph CH), 7.38 (app tt, 1H, Ph para CH), 7.14 (app t, 1H, Ph CH), 7.07 (app t, 1H, Ph CH), ~6.96 (1H, Ph CH, overlapped by 2 Mes CH resonances), 6.95 (s, 1H, Mes CH), 6.94 (s, 1H, Mes CH), 6.69 (s, 1H, Mes CH), 5.74 (s, 1H, Mes CH), 4.14-3.73 (m, 4H, CH_2CH_2), 2.67 (s, 3H, Mes CH_3), 2.48 (s, 3H, Mes CH_3), 2.45 (s, 3H, Mes CH_3), 2.43 (m, 3H, ^iPr CH), 2.28 (s, 3H, Mes CH_3), 2.00 (s, 3H, Mes CH_3), 1.85 (s, 3H, Mes CH_3), 0.69 (dd, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 12$ Hz, 9H, ^iPr CH_3), 0.64 (dd, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 14$ Hz, 9H, ^iPr CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.8 MHz, 242 K): δ 44.1 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 242 K): δ 293.0 (br, Ru=CH), 220.2 (d, $^2J_{\text{CP}} = 75$ Hz, Ru-C(N) $_2$), 150.8 (s, Ph quaternary C), 139.6, 139.1, 138.9, 137.7, 137.0, 136.9, 136.5, 134.4 (all s, Mes quaternary C), 131.8, 130.1 (both br s, Ph CH), 129.9, 129.5, 129.2, 128.7 (all s, Mes CH), 128.4 (br s, Ph CH), 128.3 (s, Ph para CH), 127.5 (br s, Ph CH), 51.9 (d, $^4J_{\text{CP}} = 3$ Hz, CH_2CH_2), 51.4 (d, $^4J_{\text{CP}} = 2$ Hz, CH_2CH_2), 21.4, 21.2, 21.1, 20.9, 20.0, 19.9 (all s, Mes CH_3), 19.1 (s, ^iPr CH_3), 18.6 (s, ^iPr CH_3), 18.5 (d, $^1J_{\text{CP}} = 18$ Hz, ^iPr CH).

Anal. Calcd. for $\text{C}_{37}\text{H}_{53}\text{Cl}_2\text{N}_2\text{PRu} \cdot 0.1 \text{CH}_2\text{Cl}_2$: C, 60.44; H, 7.27; N, 3.80. Found: C, 60.36; H, 7.35; N, 3.77. (Calcd. for $\text{C}_{37}\text{H}_{53}\text{Cl}_2\text{N}_2\text{PRu}$: C, 60.98; H, 7.33; N, 3.84.)

Synthesis of $(\text{H}_2\text{IMes})(\text{Cl})_2(\text{OSO}_2\text{CF}_3)\text{Ru}=\text{CHP}^i\text{Pr}_3$

$(\text{H}_2\text{IMes})(\text{Cl})_2(\text{P}^i\text{Pr}_3)\text{Ru}\equiv\text{C}$ (0.151 g, 0.232 mmol) was placed in a 50 mL flask. Dichloromethane (25 mL) was condensed onto the pale yellow solid at -78°C , after which the flask was warmed to 0°C with an ice bath. In the glove box, triflic acid (0.037 g, 0.25 mmol) was dissolved in 4 mL of dichloromethane. The triflic acid solution was taken up in a syringe and added over ca. 5 minutes to the cooled carbide solution, upon which the colour changed from light yellow to green/brown. After 15 minutes of stirring at 0°C , the volatiles were removed in vacuo to give a green oily residue. Pentane (20 mL) was condensed onto the residue at -78°C , which was sonicated at room temperature into a green powder, after which the volatiles were removed in vacuo. The material was recrystallized by dissolving it in 2 mL of dichloromethane and layering with 2 mL of

pentane and the vial was placed in the $-35\text{ }^{\circ}\text{C}$ freezer. Crystallization was completed after three days; the mother liquor was decanted from the green crystals, which were dried in vacuo. Yield: 0.138 g (0.172 mmol, 74.3 %).

^1H NMR (CD_2Cl_2 , 399.6 MHz, 213 K): δ 18.70 (br d, $^2J_{\text{HP}} = 44\text{ Hz}$, 1H, Ru=CH), 7.03 (app s, 4H, overlapping inequivalent Mes CH), 4.12–3.90 (m, 4H, CH_2CH_2), 2.69 (m, 3H, ^iPr CH), 2.48 (s, 6H, Mes CH_3), 2.31 (app s, 6H, overlapping inequivalent Mes CH_3), 2.27 (s, 6H, Mes CH_3), 1.10 (dd, $^3J_{\text{HH}} = 7\text{ Hz}$, $^3J_{\text{HP}} = 16\text{ Hz}$, 18H, ^iPr CH_3).

^1H NMR (CD_2Cl_2 , 399.6 MHz, 277 K): δ 18.43 (d, $^2J_{\text{HP}} = 40\text{ Hz}$, 1H, Ru=CH), 7.06 (s, 4H, Mes CH), 4.12 (s, 4H, CH_2CH_2), 2.76 (d septet, $^3J_{\text{HH}} = 7\text{ Hz}$, $^2J_{\text{HP}} = 13\text{ Hz}$, 3H, ^iPr CH), 2.39 (s, 12H, Mes CH_3), 2.35 (s, 6H, Mes CH_3), 1.09 (dd, $^3J_{\text{HH}} = 7\text{ Hz}$, $^3J_{\text{HP}} = 16\text{ Hz}$, 18H, ^iPr CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.8 MHz, 213 K): δ 43.4 (v br s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.8 MHz, 277 K): δ 52.5 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 213 K): δ 270.5 (br, Ru=CH), 195.2 (br, Ru-C(N_2)), 139.1, 138.6, 137.3, 136.7, 134.2 (all s, Mes quaternary C), 130.0, 128.9 (both s, Mes CH), 119.0 (q, $^1J_{\text{CF}} = 320\text{ Hz}$, CF_3), 52.3 (CH_2CH_2), 51.8 (CH_2CH_2), 24.5 (d, $^1J_{\text{CP}} = 38\text{ Hz}$, ^iPr CH), 21.0, 20.9, 20.0, 18.0 (all s, Mes CH_3), 17.3 (d, $^2J_{\text{CP}} = 3\text{ Hz}$, ^iPr CH_3). Due to fluxional behavior (reversible triflate dissociation/recoordination), most of the resonances are broadened.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 277 K): δ 266 (br, Ru=CH), 192.8 (br, Ru-C(N_2)), 140.1, 138.4 (both s, Mes quaternary C), 135.5 (br, Mes quaternary C), 130.3 (s, Mes CH), 120.4 (q, $^1J_{\text{CF}} = 320\text{ Hz}$, CF_3), 52.8 (CH_2CH_2), 23.4 (d, $^1J_{\text{CP}} = 38\text{ Hz}$, ^iPr CH), 21.3 (s, Mes CH_3), 19.4 (br s, Mes CH_3), 17.8 (d, $^2J_{\text{CP}} = 3\text{ Hz}$, ^iPr CH_3).

Anal. Calcd. for $\text{C}_{32}\text{H}_{48}\text{Cl}_2\text{F}_3\text{N}_2\text{O}_3\text{PSRu}$: C, 48.00; H, 6.04; N, 3.50. Found: C, 47.68; H, 6.08; N, 3.24.

Generation of $[\text{H}_2\text{C=CHP}^i\text{Pr}_3][\text{ClB}(\text{C}_6\text{F}_5)_3]$

$\text{ClB}(\text{C}_6\text{F}_5)_3$ P^iPr_3 This vinylphosphonium salt was generated by reaction of freshly generated (see above) **1- ^iPr** with 2.2 equiv of ethene at $-78\text{ }^{\circ}\text{C}$, producing the known¹¹

¹¹ Romero, P.E.; Piers, W.E. *J. Am. Chem. Soc.* **2005**, *127*, 5032. See also the current Supporting Information for full ^{13}C NMR data.

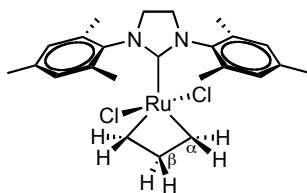
red/purple ruthenacyclobutane (**2**) and the title compound. The reaction is very rapid and was already fully completed when the first NMR spectrum was taken at 213 K.

^1H NMR (CD_2Cl_2 , 399.6 MHz, 213 K): δ 6.76 (dd, $^3J_{\text{HH}} = 13$ Hz, $^3J_{\text{HP}} = 41$ Hz, 1H, $\text{HHC}=\text{CHP}$), 6.33 (app t, $^3J_{\text{HH}} = 19$ Hz, $^3J_{\text{HP}} = 19$ Hz, 1H, $\text{HHC}=\text{CHP}$), 6.04 (app dt, $^3J_{\text{HH}} = 13$ Hz, $^3J_{\text{HH}} = 19$ Hz, $^2J_{\text{HP}} = 19$ Hz, 1H, $\text{HHC}=\text{CHP}$), 2.67 (d septet, $^3J_{\text{HH}} = 7$ Hz, $^2J_{\text{HP}} = 12$ Hz, 3H, $^i\text{Pr CH}$), 1.31 (dd, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 16$ Hz, 18H, $^i\text{Pr CH}_3$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.8 MHz, 213 K): δ 38.1 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 213 K): δ 143.9 (d, $^2J_{\text{CP}} = 2$ Hz, $\text{H}_2\text{C}=\text{CHP}$), 112.9 (d, $^1J_{\text{CP}} = 71$ Hz, $\text{H}_2\text{C}=\text{CHP}$), 20.4 (d, $^1J_{\text{CP}} = 44$ Hz, $^i\text{Pr CH}$), 16.1 (d, $^2J_{\text{CP}} = 3$ Hz, $^i\text{Pr CH}_3$).

Generation of **2**



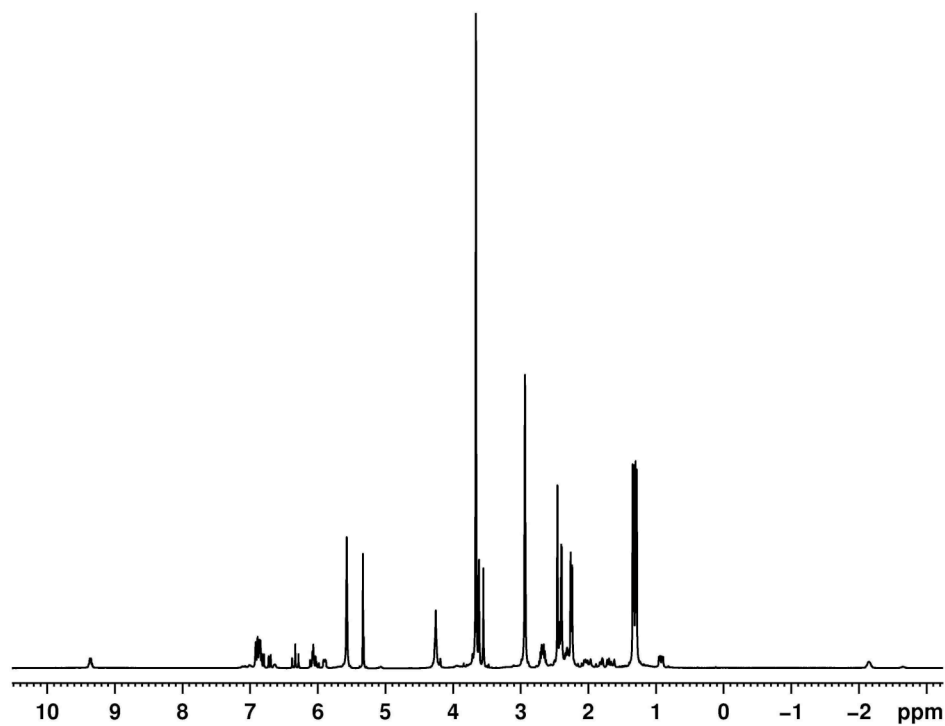
Generated as described above.

^1H NMR (CD_2Cl_2 , 400 MHz, 223 K): δ 6.88 (s, 4H, Mes CH), 6.64 (m, 4H, $\text{C}_\alpha\text{H}_2$), 4.25 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.42 (s, 12H, Mes *o*- CH_3), 2.26 (s, 6H, Mes *p*- CH_3), -2.64 (m, 2H, C_βH_2).

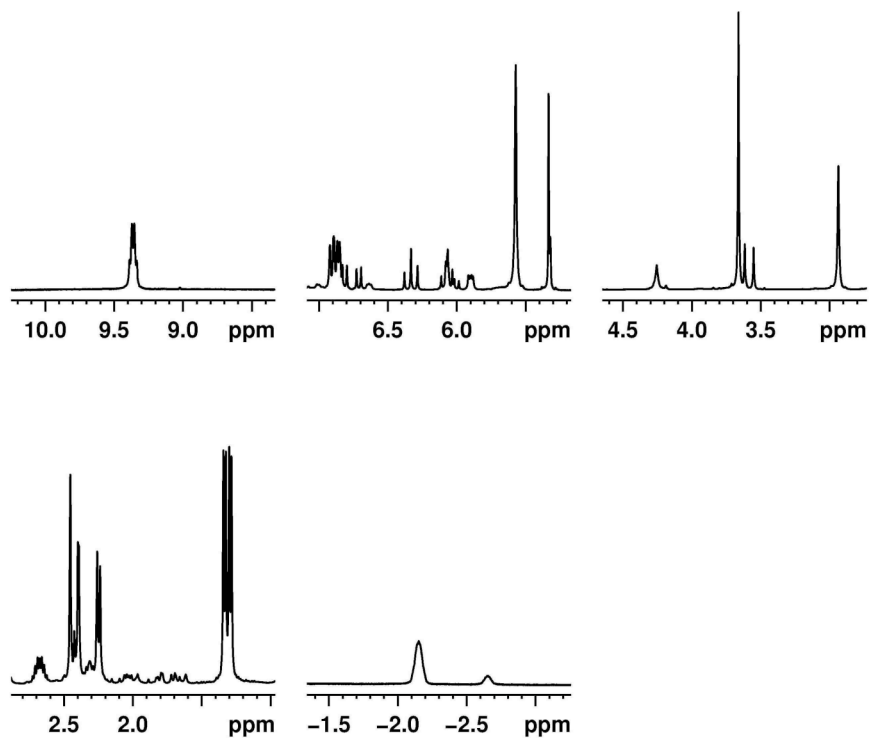
$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz, 223 K): δ 214.2 (s, $\text{RuC}(\text{N})_2$), 139.1, 137.3, 132.1 (all s, Mes quaternary C), 128.9 (s, Mes CH), 94.1 (s, $\text{C}_\alpha\text{H}_2$), 52.2 (s, $\text{NCH}_2\text{CH}_2\text{N}$), 21.0 (s, Mes para CH_3), 19.0 (s, Mes ortho CH_3), 2.2 (s, C_βH_2).

3. NMR plots.

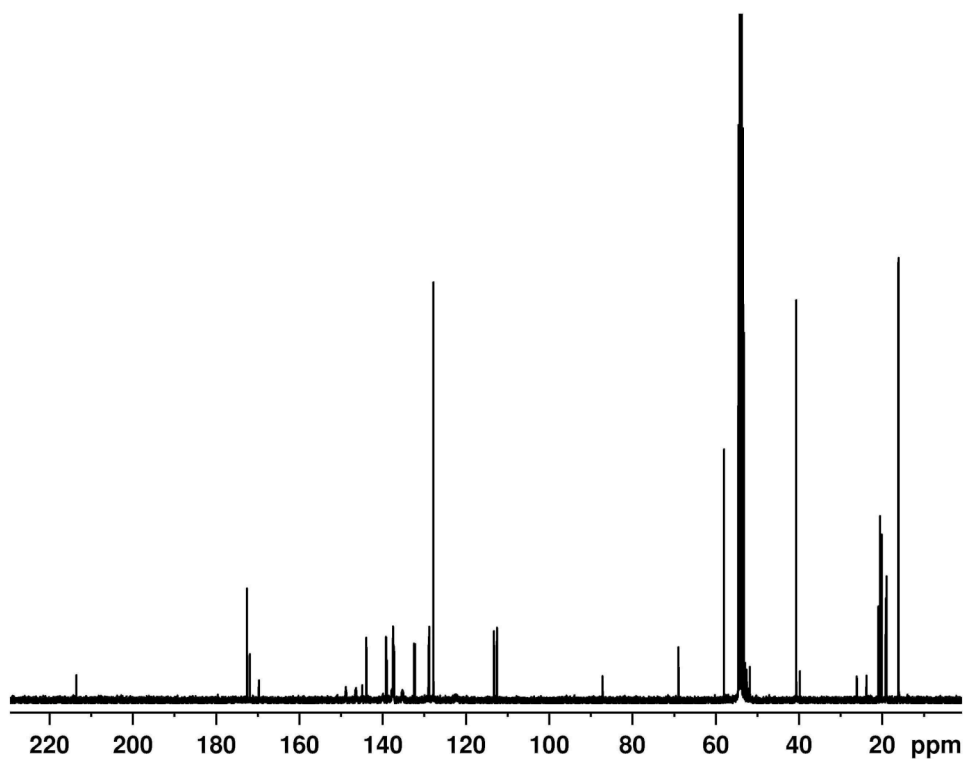
^1H NMR of **3** (CD_2Cl_2 , 399.6 MHz, 213 K):



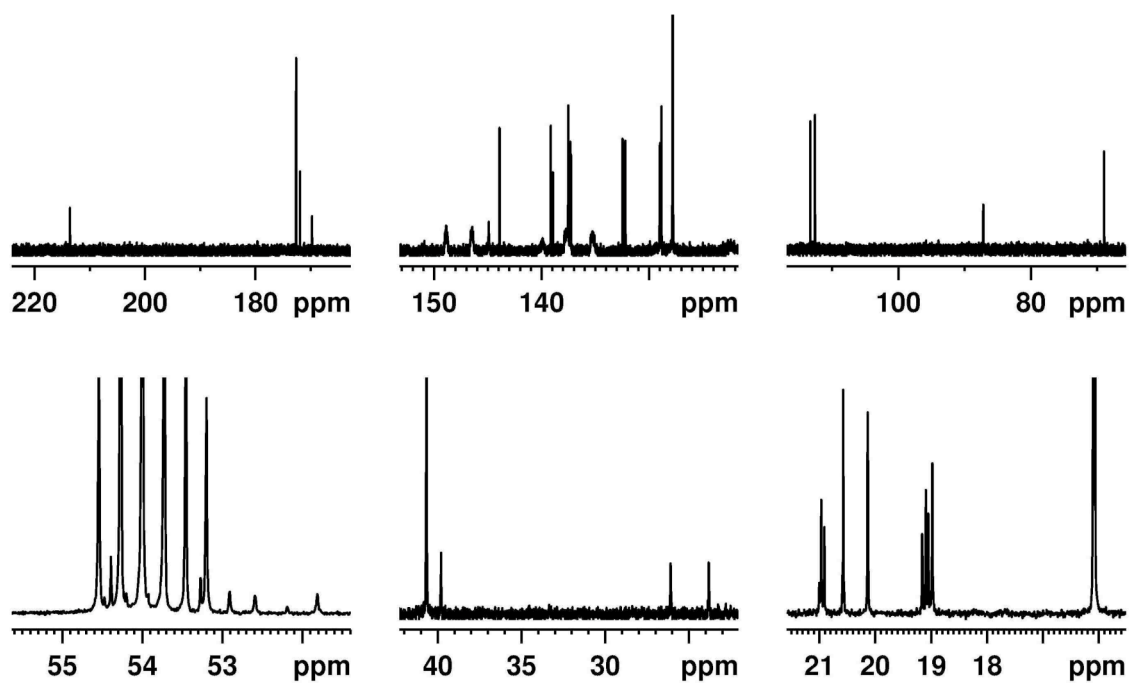
Expansions of ^1H NMR of **3** (CD_2Cl_2 , 399.6 MHz, 213 K), not all at same scale:



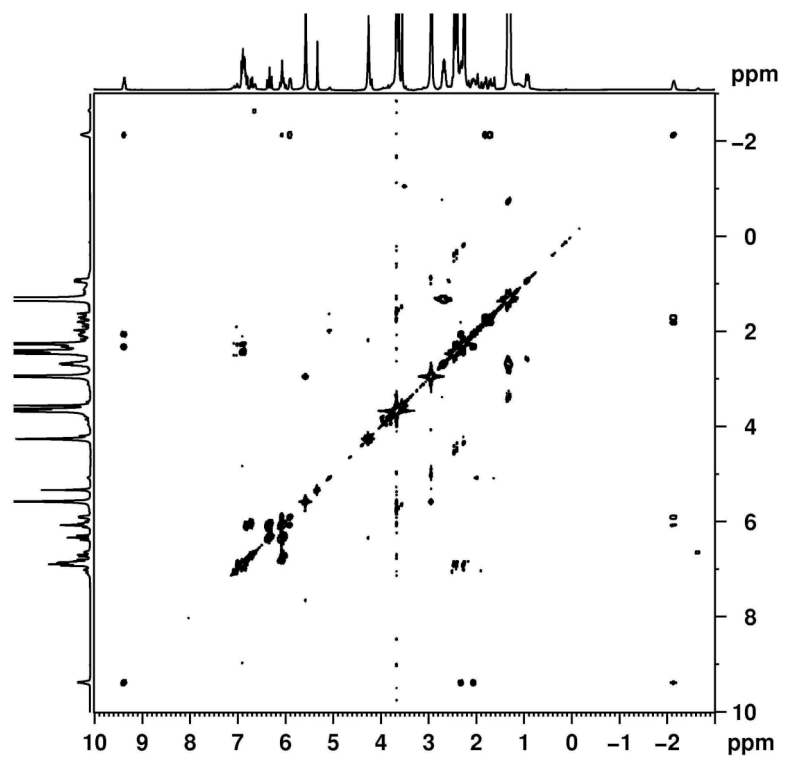
$^{13}\text{C}\{^1\text{H}\}$ NMR of **3** (CD_2Cl_2 , 100.5 MHz, 213 K):



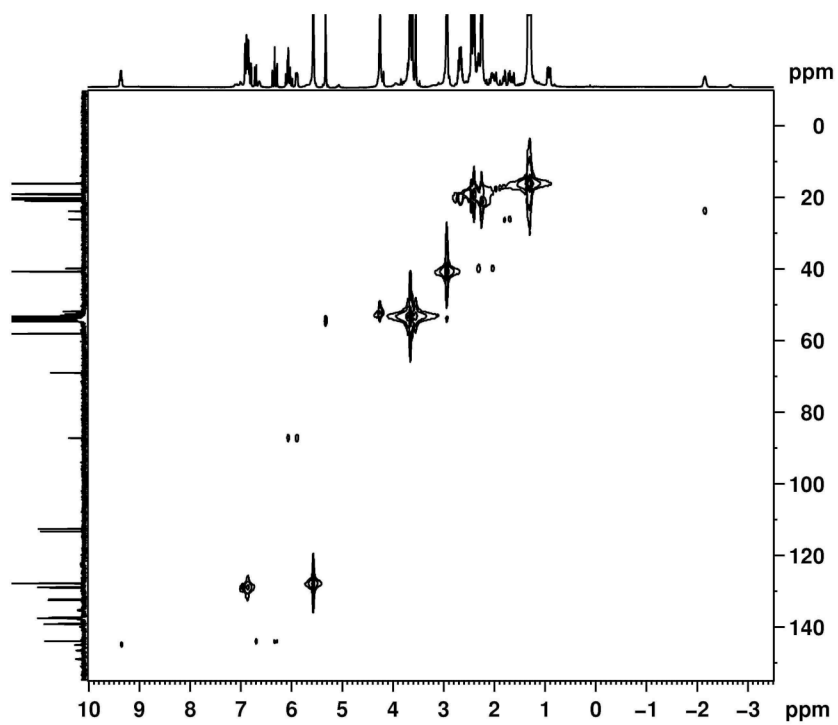
Expansions of $^{13}\text{C}\{^1\text{H}\}$ NMR of **3** (CD_2Cl_2 , 100.5 MHz, 213 K), not all at same scale:



^1H -COSY of **3** (CD_2Cl_2 , 399.6 MHz, 213 K):



HMQC of **3** (CD₂Cl₂, 399.6 MHz, 213 K):



4. Crystal Structure of $(\text{H}_2\text{IMes})(\text{Cl})_3\text{Ru}=\text{CHP}^i\text{Pr}_3 \cdot \text{CH}_2\text{Cl}_2$.¹²

fit, $S = 1.007$. The weighting scheme was based on counting statistics and the final difference Fourier map was essentially featureless with the largest peak being close to the solvent Cl-atoms.

References:

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3. Altomare, A., Cascarano, M., Giacovazzo, C. & Guagliardi, A. (1993). *SIR92*. *J. Appl. Cryst.*, **26**, 343
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4.B. Crystal data and structure refinement.

| | | |
|-----------------------------------|--|-----------------------------|
| Empirical formula | $\text{C}_{31}\text{H}_{28}\text{Cl}_3\text{N}_2\text{PRu} \cdot \text{CH}_2\text{Cl}_2$ | |
| Formula weight | 772.03 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | $a = 23.855(7)$ Å | $\alpha = 90^\circ$ |
| | $b = 16.442(6)$ Å | $\beta = 110.390(15)^\circ$ |
| | $c = 19.947(4)$ Å | $\gamma = 90^\circ$ |
| Volume | 7333(4) Å ³ | |
| Z | 8 | |
| Density (calculated) | 1.399 Mg/m ³ | |
| Absorption coefficient | 0.859 mm ⁻¹ | |
| F(000) | 3200 | |
| Crystal size | 0.14 × 0.14 × 0.10 mm ³ | |
| Theta range for data collection | 2.18 to 27.47° | |
| Index ranges | $-30 \leq h \leq 30, -19 \leq k \leq 21, -25 \leq l \leq 25$ | |
| Reflections collected | 15030 | |
| Independent reflections | 8354 [R(int) = 0.0513] | |
| Completeness to theta = 27.47° | 99.5 % | |
| Absorption correction | Multi-scan method | |
| Max. and min. transmission | 0.9190 and 0.8891 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 8354 / 0 / 382 | |
| Goodness-of-fit on F ² | 1.007 | |
| Final R indices [I > 2sigma(I)] | R1 = 0.0430, wR2 = 0.0952 | |
| R indices (all data) | R1 = 0.0854, wR2 = 0.1133 | |
| Largest diff. peak and hole | 0.508 and -0.872 e Å ⁻³ | |