Bimetallic Ru-Ir/Rh Complexes for Catalytic Allyl Alcohol Reduction to Propylene

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Contents

1. General considerations

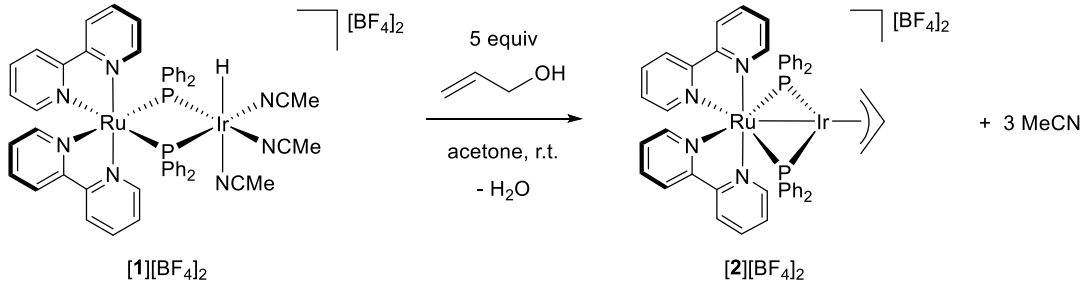
All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line techniques, employing dry solvents and glassware unless otherwise noted. Complexes $[(RuP_2)IrH(NCMe)_3][BF_4]_2$ ([**1**][BF_4]$_2$) and $[(RuP_2)Rh(cod)][OTf]$ ([**4**][OTf]) were prepared as described previously.[1] Organic solvents (acetone, acetonitrile, DMSO, CH_2Cl_2, diethyl ether) were purchased from Kanto or Wako as dehydrated forms (water < 10 ppm) and degassed before use. Deuterated solvents ($CDCl_3$, DMSO-d_6, CD_3CN, acetone-d_6, CD_3NO_2) were degassed and dried over molecular sieves that were vacuum dried overnight at 300 °C. Other chemicals were purchased from commercial vendors and used as received.

NMR spectra were obtained on a Varian VNMR400 or a JEOL ECS400 spectrometers. GC chromatograms were obtained on a Shimadzu GC-8A equipped with a thermal conductivity detector (TCD) and a molecular sieve 5A packed column (for analysis of H_2 and O_2) and on a Shimadzu GC-2025 equipped with a flame ionization detector (FID) and a Rt-Q-BOND capillary column (for analysis of organic substrates). Electrochemical reactions were carried out using an ECstat-101 potentiostat (EC Frontier Co., Ltd.). Elemental analysis was performed on a Parkin Elmer 2400 II at the Division of Instrumental Analysis, Okayama University Advanced Science Research Center.

2. Experimental details

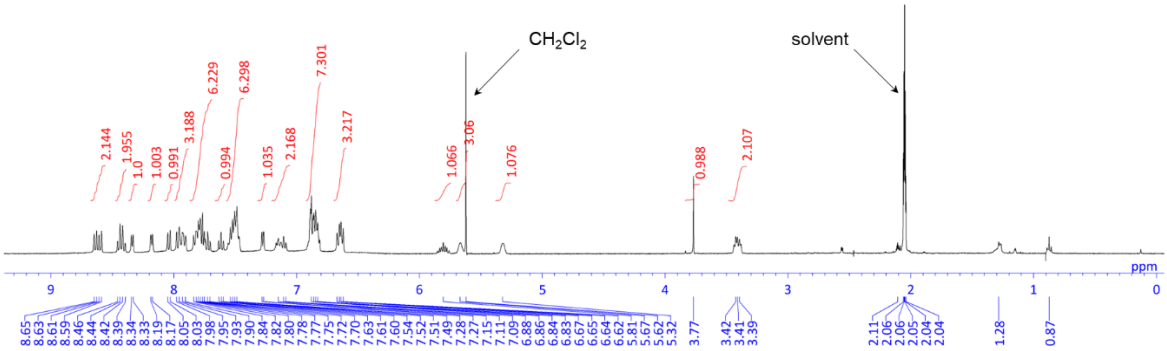
2.1. Synthesis and Stoichiometric Reactions of New Complexes

2.1.1. Synthesis of $[(RuP_2)Ir(\eta^3\text{-}C_3H_5)][BF_4]_2$ ([**2**][BF_4]$_2$)

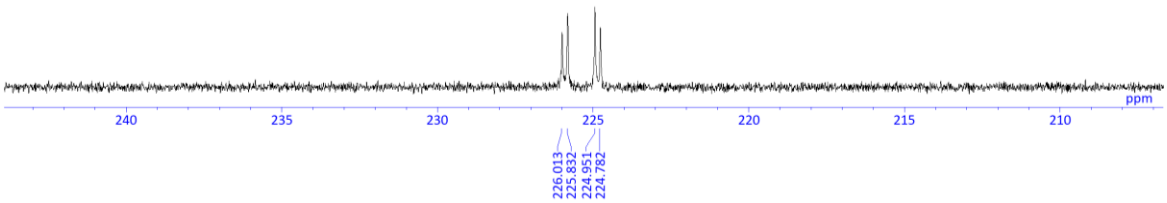


Complex [**1**][BF_4]$_2$ (50 mg, 0.039 mmol) was placed in a 20-mL Schlenk tube and dissolved in 3 mL of acetone. Allyl alcohol (13.4 μL, 0.196 mmol) was added to the solution, and the mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo, and the residue was recrystallized from a CH_2Cl_2-hexane (5 mL/10 mL) two-layer mixture to afford reddish brown crystals of [**2**][BF_4]$_2$·CH_2Cl_2, which were collected by filtration and dried in

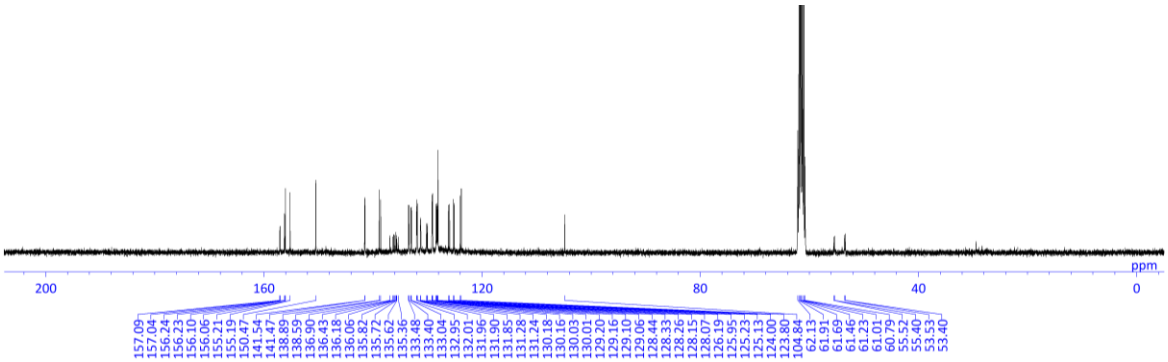
vacuo Yield 42.7 mg, 0.033 mmol, 86%. Anal. Calcd (%) for $C_{47}H_{41}B_2F_8IrN_4P_2Ru{\cdot}CH_2Cl_2$: C, 45.20; H, 3.40; N, 4.39; found C, 45.27; H, 3.63; N, 4.71. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.63 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar), 8.61 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar), 8.43 (q, $^3J_{HH}$ = 8 Hz, 2H, Ar), 8.33 (d, $^3J_{HH}$ = 4 Hz, 1H, Ar), 8.18 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar), 8.04 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar), 7.94 (m, 3H, Ar), 7.77 (m, 6H, Ar), 7.61 (t, $^3J_{HH}$ = 6 Hz, 1H, Ar), 7.51 (m, 6 H, Ar), 7.27 (d, $^3J_{HH}$ = 4 Hz, 1H, Ar), 7.11 (m, 2H, Ar), 6.85 (m, 7H, Ar), 6.64 (q, $^3J_{HH}$ = 8 Hz, 3H, Ar), 5.81 (m, 1H, π-allyl central), 5.67 (m, 1H, π-allyl syn), 5.67 (m, 1H, π-allyl syn), 3.41 (m, 2H, π-allyl anti). ^{31}P{^{1}H} NMR (162 MHz, acetone): δ 225.9 (d, $^2J_{PP}$ = 28 Hz), 224.8 (d, $^2J_{PP}$ = 28 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_3NO_2): δ 157.09, 157.04, 156.23, 156.10, 156.06, 155.21, 155.19, 150.48, 150.47, 141.54, 141.47, 138.89, 138.59, 136.67 (d, J = 47.2 Hz), 135.95 (d, J = 46.2 Hz), 135.84 (d, J = 44.2 Hz), 135.59 (d, J = 46.2 Hz), 133.44 (d, J = 8.0 Hz), 133.00 (d, J = 9.0 Hz), 131.99 (d, J = 5.0 Hz), 131.88 (d, J = 5.0 Hz), 131.28 (d, J = 1.5 Hz), 131.23 (d, J = 1.5 Hz), 130.17 (d, J = 2.0 Hz), 130.02 (d, J = 2.0 Hz), 129.18 (d, J = 4.0 Hz), 129.08 (d, J = 4.0 Hz), 128.39 (d, J = 11.0 Hz), 128.21 (d, J = 11.0 Hz), 128.07, 126.19, 125.95, 125.23, 124.00, 123.80 ,104.84, 55.46 (d, J = 12.0 Hz), 53.47 (d, J = 13.1 Hz).



^{1}H NMR spectrum of [**2**][BF_4]$_2$ (400 MHz, acetone-d_6). The peak at 5.32 ppm corresponds to one molecule of CH_2Cl_2 per [**2**][BF_4]$_2$ contained in the crystalized sample.

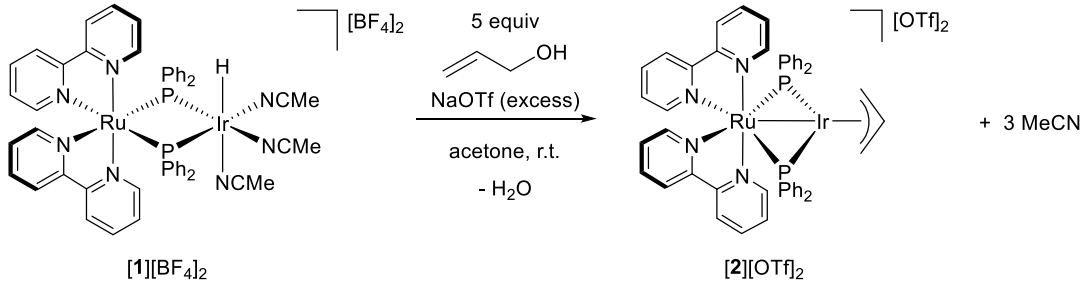


^{31}P{^{1}H} NMR spectrum of [**2**][BF_4]$_2$ (162 MHz, acetone)

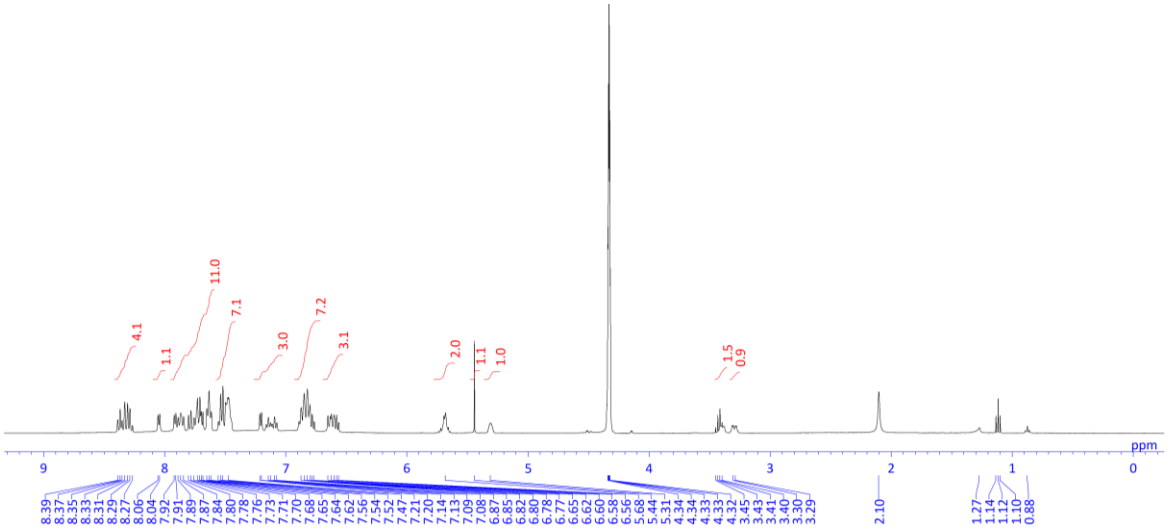


$^{13}C\{^{1}H\}$ NMR spectrum of [**2**][BF_4]$_2$ (100 MHz, CD_3NO_2)

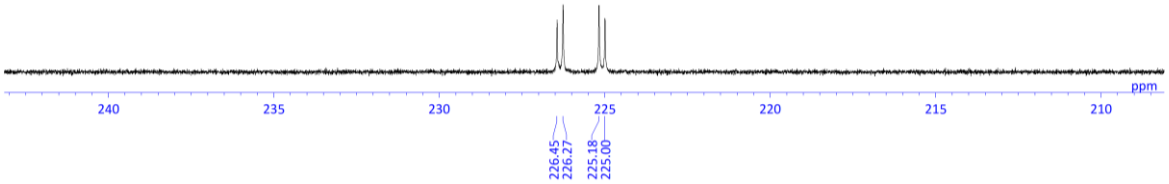
2.1.2. Synthesis of [(RuP_2)Ir(η^3-C_3H_5)][OTf]$_2$ ([**2**][OTf]$_2$)



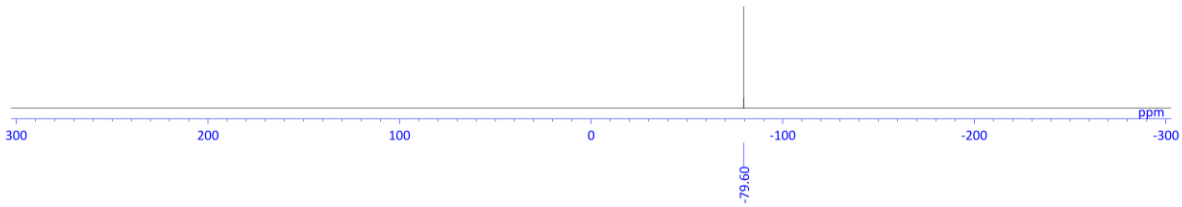
Complex [**1**][BF_4]$_2$ (50 mg, 0.039 mmol) was placed in a 20-mL Schlenk tube and dissolved in 3 mL of acetone. Allyl alcohol (13.4 μL, 0.196 mmol) was added to the solution, and the mixture was stirred for 2 h. The mixture was treated with sodium trifluoromethanesulfonate (134 mg, 0.779 mmol) and further stirred for 1 h. The solvent was then removed in vacuo, and the residue was extracted with CH_2Cl_2. The extract was concentrated to ca. 5 mL and layered with hexane (10 mL), giving reddish brown crystals of [**2**][OTf]$_2$·CH_2Cl_2, which were collected by filtration and dried in vacuo. Yield 45.2 mg, 0.033 mmol, 86%. Anal. Calcd (%) for $C_{49}H_{41}F_6IrN_4O_6P_2RuS_2$: C, 44.75; H, 3.14; N, 4.26; found C, 44.18; H, 3.10; N, 4.44. ^{1}H NMR (400 MHz, CD_3NO_2): δ 8.39-8.27 (m, 4H, Ar), 8.05 (d, $^3J_{HH}$ = 8 Hz, Ar), 7.92 (d, $^3J_{HH}$ = 4 Hz, Ar), 7.87 (m, 2H, Ar), 7.80-7.62 (m, 8H, Ar), 7.56-7.45 (m, 7H, Ar), 7.21 (d, $^3J_{HH}$ = 4 Hz, Ar), 7.14 (m, 1H, Ar), 7.09 (m, 1H, Ar), 6.87-6.77 (m, 7H, Ar), 6.65-6.56 (m, 3H, Ar), 5.68 (m, 2H, π-allyl), 5.31 (m, 1H, π-allyl), 3.40 (m, 1H, π-allyl), 3.29 (m, 1H, π-allyl). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3NO_2): δ 226.3 (d, $^2J_{PP}$ = 29 Hz), 225.1 (d, $^2J_{PP}$ = 29 Hz). ^{19}F NMR (375 MHz, CD_3NO_2): δ -79.60.



^{1}H NMR spectrum of [**2**][OTf]$_2$ (400 MHz, CD_3NO_2).

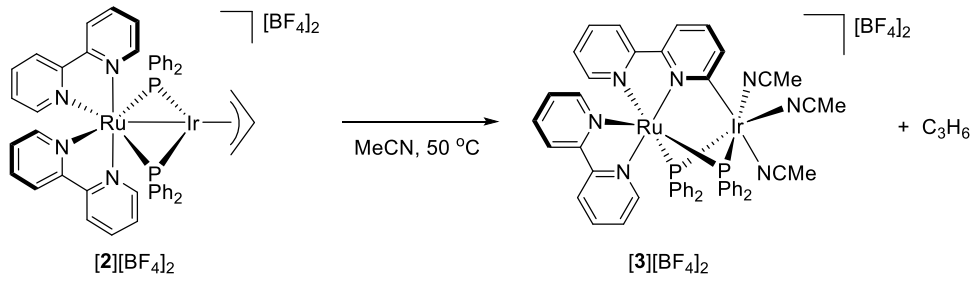


^{31}P{^{1}H} NMR spectrum of [**2**][OTf]$_2$ (162 MHz, CD_3NO_2).



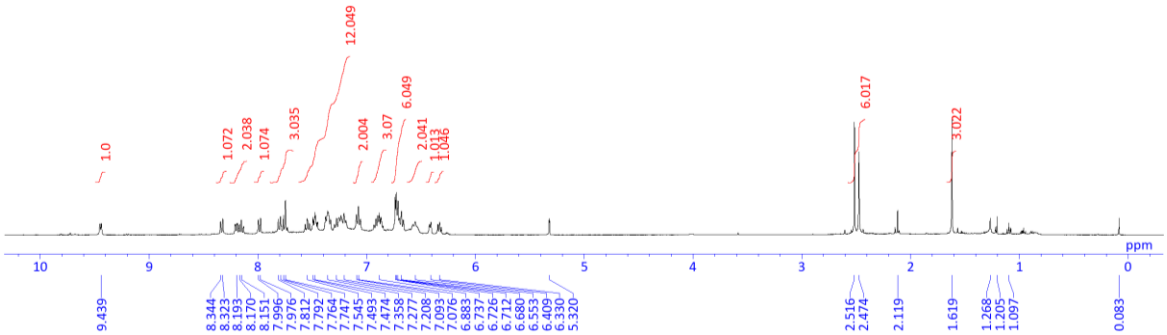
^{19}F NMR spectrum of [**2**][OTf]$_2$ (375 MHz, CD_3NO_2).

2.1.3. Synthesis of [(bpy)Ru(μ-$C_{10}H_7N_2$)(μ-PPh_2)$_2$Ir(NCMe)$_3$][BF_4]$_2$ ([**3**][BF_4]$_2$)

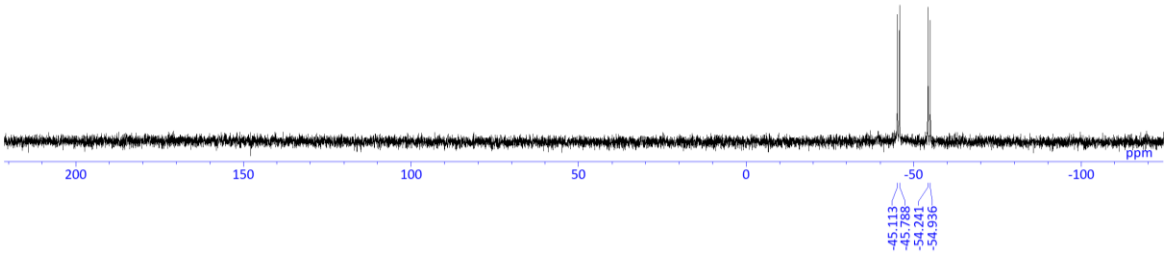


[**2**][BF_4]$_2$ [**3**][BF_4]$_2$

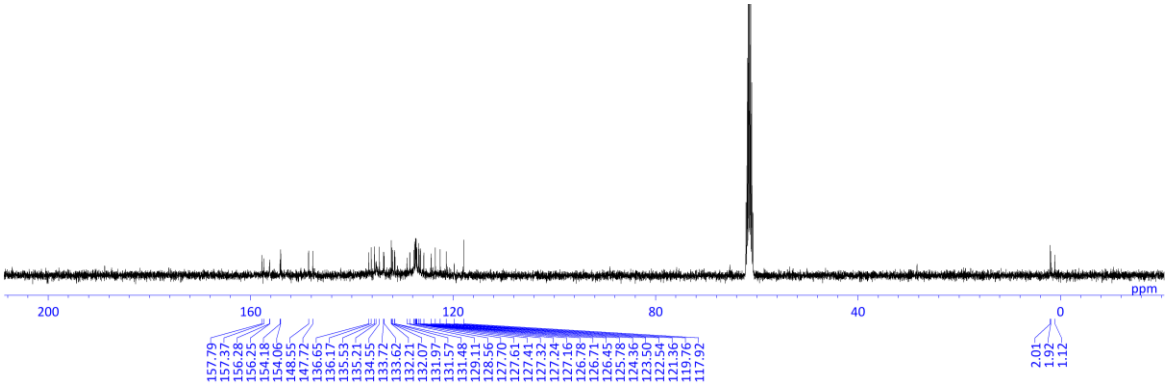
Complex [**1**][BF_4]$_2$ (50 mg, 0.039 mmol) was dissolved in acetone (2 mL), and allyl alcohol (13.4 µL, 0.196 mmol) was added. The solution was stirred at 50 °C for 2 h to generate [**2**][BF_4]$_2$ in situ. Volatiles were removed in vacuo, and the residue was dissolved in acetonitrile (2 mL). The solution was stirred at 50 °C for 2 h and evaporated to dryness under reduced pressure. Washing the residue with diethyl ether afforded [**3**][BF_4]$_2$ as a red solid. Yield 49 mg, 0.032 mmol, 83%. Anal. Calcd (%) for $C_{50}H_{44}B_2F_8IrN_7P_2Ru$: C, 47.22; H, 3.49; N, 7.71; found C, 46.69; H, 3.61; N, 7.43. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.44 (d, $^3J_{HH}$ = 5.6 Hz, 1H, aryl), 8.34 (d, $^3J_{HH}$ = 8.0 Hz, 1H, aryl), 8.19 (d, $^3J_{HH}$ = 7.2 Hz, 1H, aryl), 8.15 (t, $^3J_{HH}$ = 8.0 Hz, 1H, aryl), 7.98 (d, $^3J_{HH}$ = 8.0 Hz, 1H, aryl), 7.8-7.7 (m, 3H, aryl), 7.5-7.2 (m, 12H, aryl), 7.09 (t, $^3J_{HH}$ = 7.2 Hz, 2H, aryl), 6.9-6.8 (m, 3H, aryl), 6.8-6.7 (m, 6H, aryl), 6.55 (m, 2H, aryl), 6.41 (d, $^3J_{HH}$ = 5.6 Hz, 1H, aryl), 6.33 (t, $^3J_{HH}$ = 6.4 Hz, 1H, aryl), 2.52, 2.48, 1.62 (s, 3H each, MeCN). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ -46.8 (d, $^2J_{PP}$ = 111 Hz), -55.7 (d, $^2J_{PP}$ = 111 Hz). ^{31}P{^{1}H} NMR (162 MHz, acetone): δ -45.5 (d, $^2J_{PP}$ = 111 Hz), -54.6 (d, $^2J_{PP}$ = 111 Hz). ^{13}C{1H} NMR (100 MHz, CD_3NO_2): 157.79, 157.37, 156.28, 156.25, 154.18, 154.06, 148.55, 147.72, 136.65, 136.17, 135.53, 135.21, 134.55, 133.72, 133.62, 132.21, 132.07, 131.97, 131.57, 131.48, 129.11, 128.56, 127.70, 127.61, 127.41, 127.32, 127.24, 127.16, 126.78, 126.71, 126.45, 125.78, 124.36, 123.50, 122.54, 121.36, 119.76, 117.92, 2.01, 1.92, 1.12. Single crystals suitable for X-ray analysis were grown from MeCN-Et_2O.



^{1}H NMR spectrum of [**3**][BF_4]$_2$ (400 MHz, CD_2Cl_2).

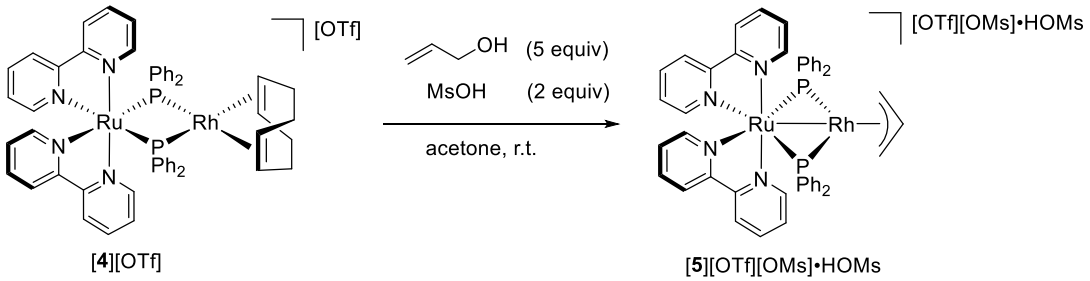


^{31}P{^{1}H} NMR spectrum of [**3**][BF_4]$_2$ (162 MHz, acetone).

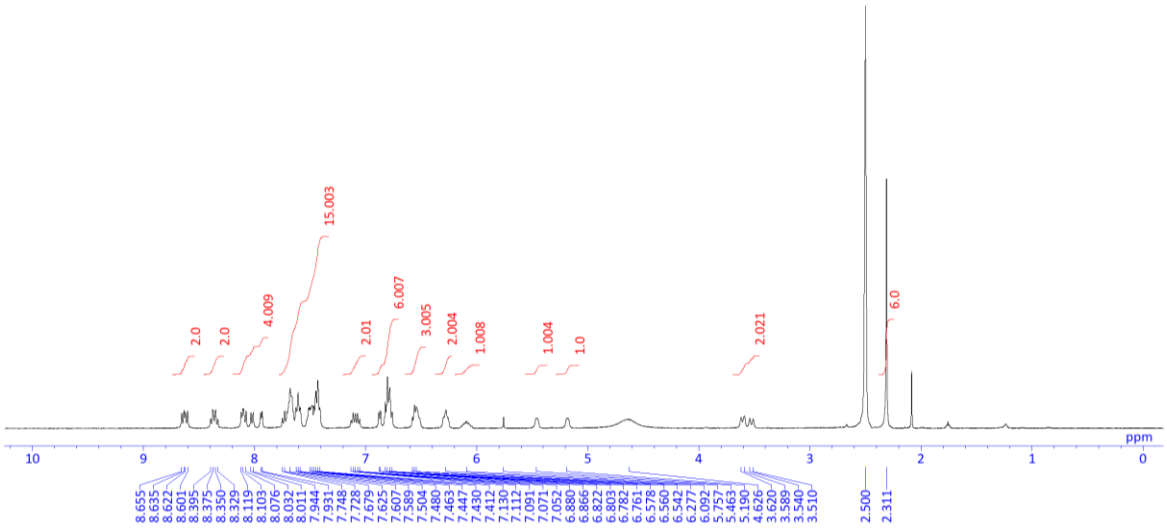


$^{13}C\{^{1}H\}$ NMR spectrum of [**3**][BF_4]$_2$ (100 MHz, CD_3NO_2)

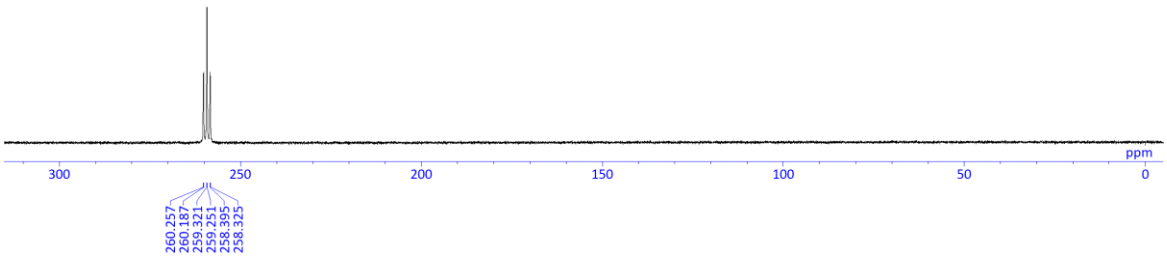
2.1.4. Synthesis of [(RuP_2)Rh(η^3-C_3H_5)][OTf][OMs]·HOMs ([**5**][OTf][OMs]·HOMs)



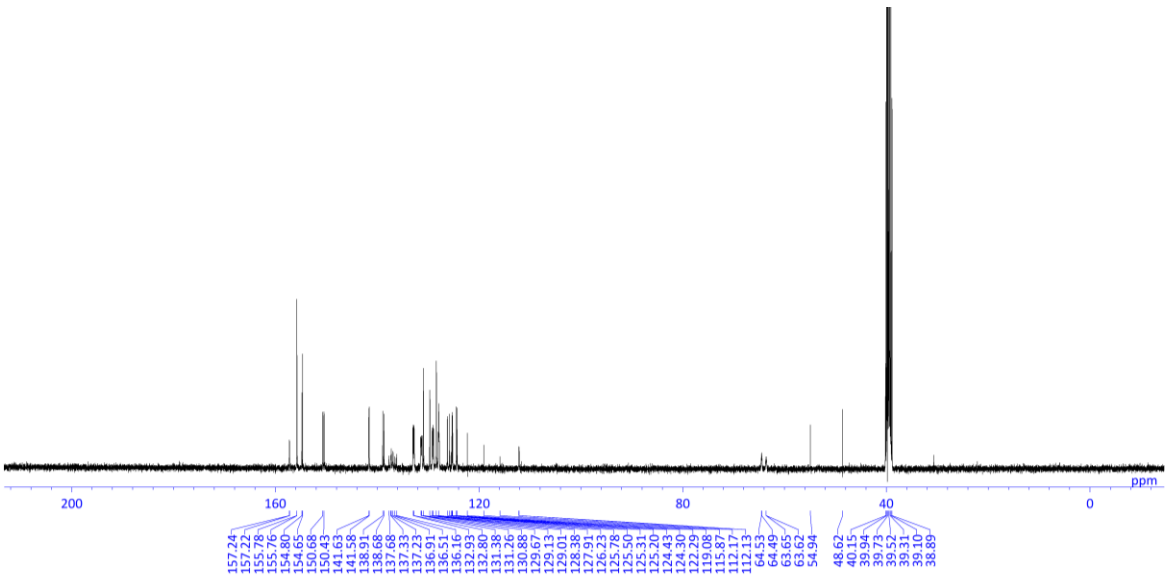
[**4**][OTf] (200 mg, 0.18 mmol) was dissolved in acetone (8 mL). Allyl alcohol (60 µL, 0.90 mmol) and HOMs (23 µL, 0.45 mmol) was added to the solution. The resulting mixture was stirred overnight, during which period the mixture turned orange and a yellow solid precipitated. The solid was collected by filtration, washed successively with acetone (3×2 mL) and diethyl ether (3×3 mL), and dried in vacuo. Yield 93 mg, 0.073 mmol, 41%. Anal. Calcd (%) for $C_{50}H_{48}F_3N_4O_9P_2RhRuS_3$: C, 47.36; H, 3.82; N, 4.42; found C, 47.00; H, 3.75; N, 4.41. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.63 (m, 2H, aryl), 8.35 (m, 2H, aryl), 8.1-7.9 (m, 4H, aryl), 7.8-7.4 (m, 15H, aryl), 7.09 (m, 2H, aryl), 6.87-6.72 (m, 6H, aryl), 6.56 (m, 3H, aryl), 6.28 (m, 2H, aryl), 6.09 (m, 1H, π-allyl central), 5.46 (m, 1H, π-allyl syn), 5.19 (m, 1H, π-allyl syn), 4.63 (br, OH), 3.60 (m, 1H, π-allyl anti), 3.53 (m, 1H, π-allyl anti), 2.31 (s, 6H, CH_3SO_3). $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ 259.8 (dd, $^{1}J_{PRh}$ = 152 Hz, $^{2}J_{PP}$ = 11 Hz), 258.8 (dd, $^{1}J_{PRh}$ = 150 Hz, $^{2}J_{PP}$ = 11 Hz). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ 157.24, 157.22, 155.78, 155.76, 154.80, 154.65, 150.68, 150.43, 141.63, 141.58, 138.91, 138.68, 137.68, 137.33, 137.23, 136.91, 136.51, 136.16, 132.93 (m), 132.80 (m), 131.38 (m), 131.26 (m), 130.88, 129.67, 129.13 (m), 129.01 (m), 128.38, 127.91 (m), 126.23, 125.78, 125.31, 125.20, 124.43, 124.30, 120.70 (q, $^{1}J_{CF}$ = 321 Hz, CF_3), 112.13 (m), 64.51 (m), 63.64 (m), 54.94 (CH_2Cl_2), 48.62.



^{1}H NMR spectrum of [**5**][OTf][OMs]·HOMs (400 MHz, DMSO-d$_6$).

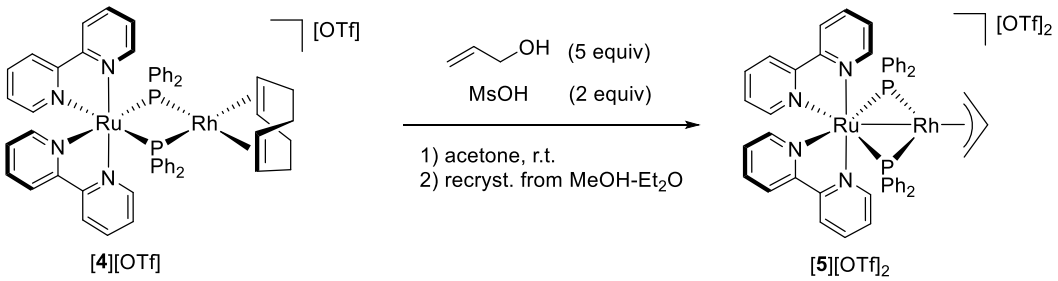


^{31}P{^{1}H} NMR spectrum of [**5**][OTf][OMs]·HOMs (162 MHz, DMSO-d$_6$).

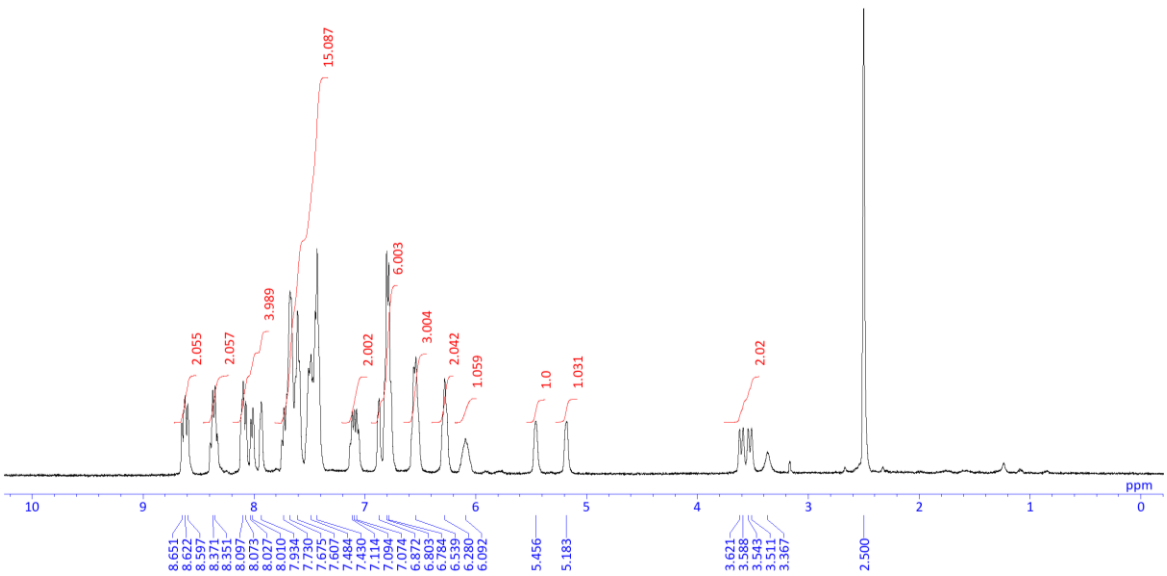


^{13}C{^{1}H} NMR spectrum of [**5**][OTf][OMs]·HOMs (100 MHz, DMSO-d$_6$).

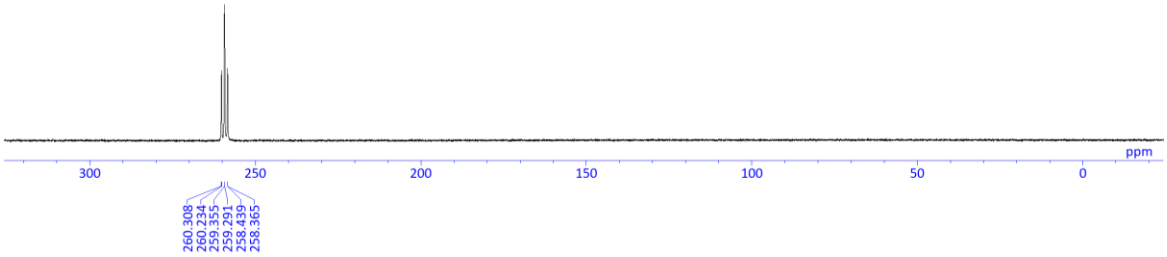
2.1.5. Synthesis of $[(RuP_2)Rh(\eta^3\text{-}C_3H_5)][OTf]_2$ ([**5**][OTf]$_2$)



Allyl alcohol (60 μL, 0.90 mmol) and HOMs (23 μL, 0.45 mmol) was added to a solution of [**4**][OTf] (200 mg, 0.18 mmol) in acetone (8 mL). The resulting mixture was stirred overnight, during which period the mixture turned orange and a yellow solid precipitated. The solid was collected by filtration, washed successively with acetone (3×2 mL) and diethyl ether (3×3 mL), and dried in vacuo. The resulting solid was dissolved in MeOH (5 mL), and the solution was layered with Et_2O (10 mL). The reddish-brown plates that deposited were collected by filtration and dried in vacuo. Yield 57 mg, 0.047 mmol, 26%. Anal. Calcd (%) for $C_{49}H_{41}F_6N_4O_6P_2RhRuS_2$: C, 48.01; H, 3.37; N, 4.57; found C 47.78, H 3.18, N 4.51. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.62 (m, 2H, aryl), 8.36 (m, 2H, aryl), 8.1-7.9 (m, 4H, aryl), 7.8-7.4 (m, 15H, aryl), 7.09 (m, 2H, aryl), 6.9-6.7 (m, 6H, aryl), 6.54 (m, 3H, aryl), 6.28 (m, 2H, aryl), 6.09 (m, 1H, π-allyl central), 5.46 (m, 1H, π-allyl syn), 5.18 (m, 1H, π-allyl syn), 3.61 (m, 1H, π-allyl anti), 3.53 (m, 1H, π-allyl anti). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d$_6$): δ 259.8 (dd, $^1J_{PRh}$ = 153 Hz, $^2J_{PP}$ = 11 Hz), 259.7 (dd, $^1J_{PRh}$ = 149 Hz, $^2J_{PP}$ = 11 Hz).

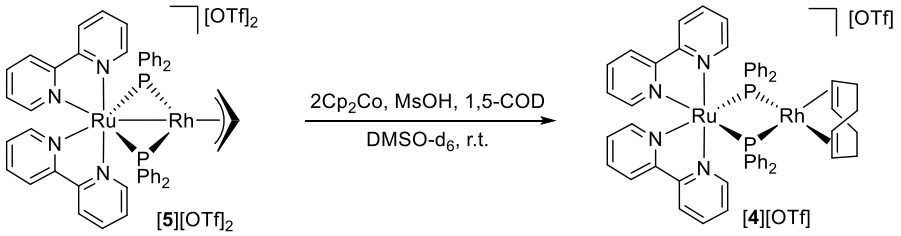


^{1}H NMR spectrum of [**5**][OTf]$_2$ (400 MHz, DMSO-d$_6$).

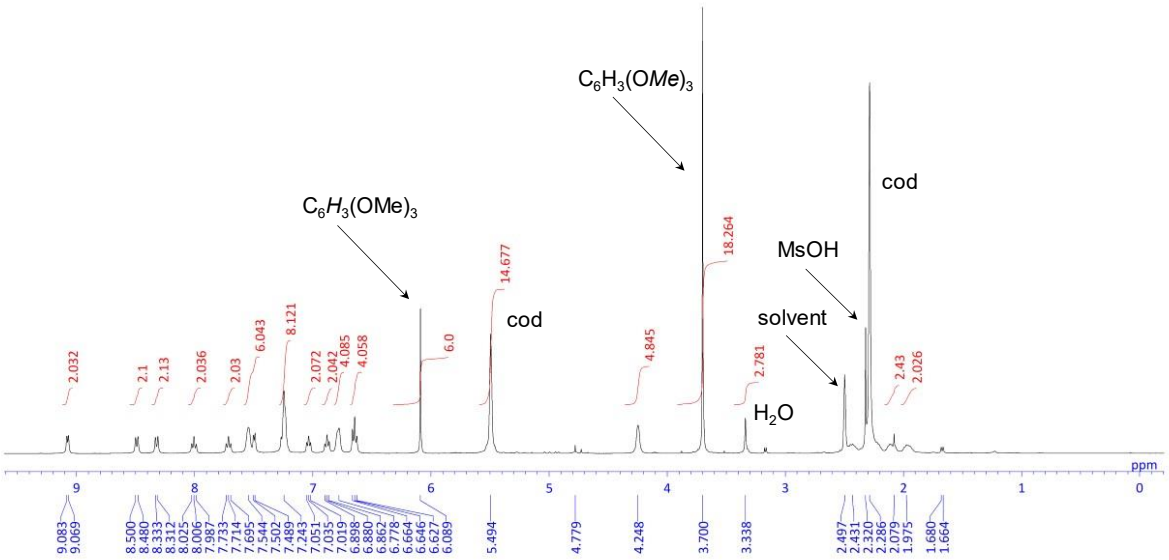


$^{31}P\{^{1}H\}$ NMR spectrum of [**5**][OTf]$_2$ (162 MHz, DMSO-d$_6$).

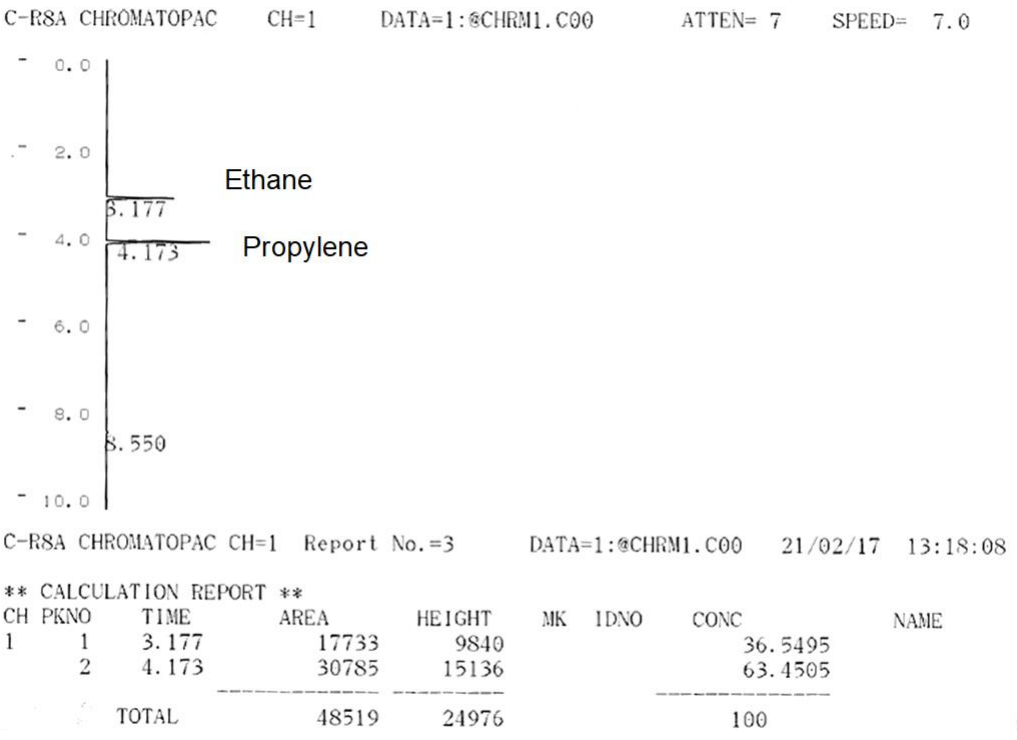
2.1.6. Reduction of [**5**][OTf]$_2$ with Cp_2Co in the presence of MsOH



To a solution of [**5**][OTf]$_2$ (24.5 mg, 0.020 mmol) in DMSO-d$_6$ (0.4 mL) was added MsOH (1.3 µL, 0.020 mmol), 1,5-cyclooctadiene (12.3 µL, 0.10 mmol), and 1,3,5-trimethoxybenzene (6.7 mg, 0.040 mmol as an internal standard). The resulting solution was then treated with Cp_2Co (8.0 mg, 0.040 mmol) dissolved in DMSO-d$_6$ (0.5 mL). After the solution was stirred for 5 min, ethane (1.0 mL as an internal standard) was injected into the reaction vessel and the amount of propylene (65% yield) in the headspace was quantified by GC analysis. The content of the reaction solution was analyzed by ^{1}H NMR spectroscopy, which showed the formation of [**4**][OTf] in 90% yield.



^{1}H NMR spectrum of the reaction mixture (400 MHz, DMSO-d_6).

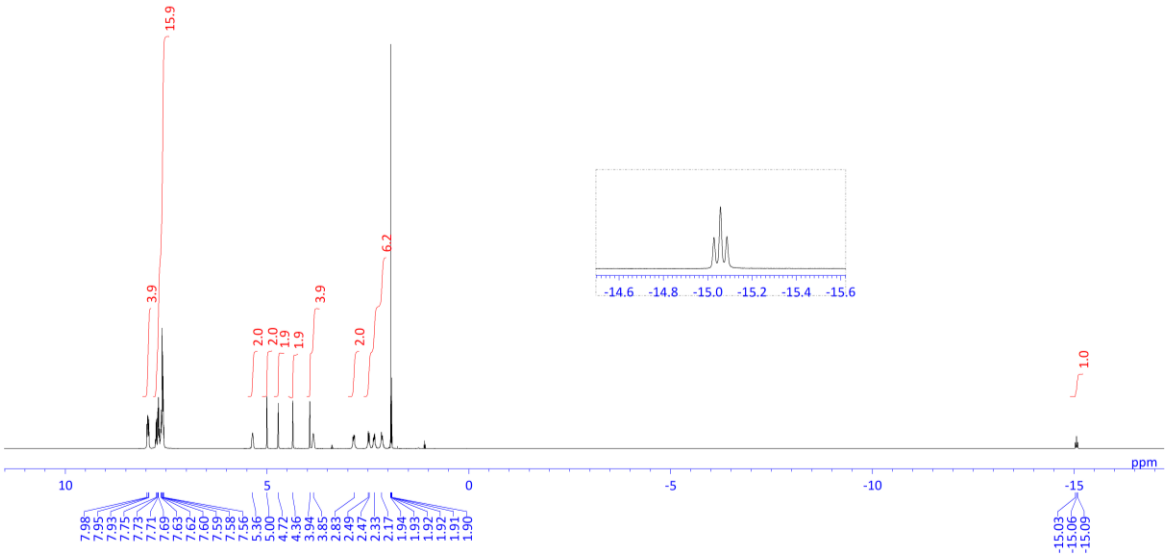


GC chromatogram of the headspace gas.

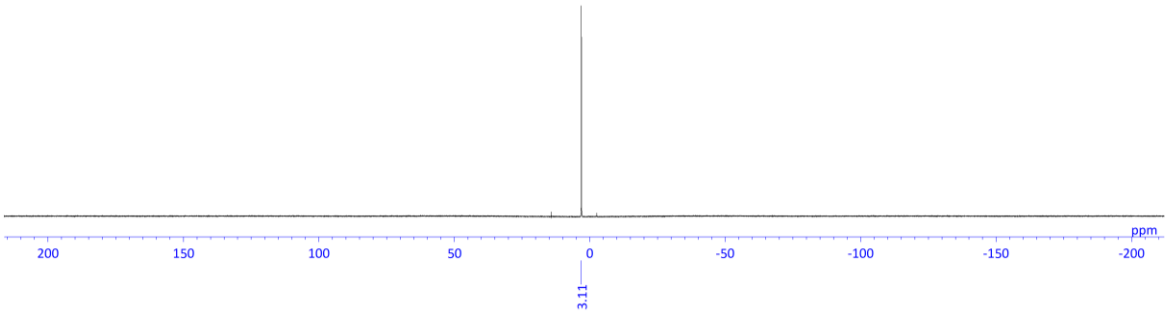
2.1.7. Synthesis of $[IrH(cod)(MeCN)(dppf)][BF_4]_2$

In a Schlenk tube, $[Ir(cod)_2][BF_4]$[2a] (33.2 mg, 0.07 mmol) and dppf (37.8 mg, 0.07 mmol) were dissolved in CH_2Cl_2 (5 mL). The dark red solution was stirred for 2 h at room temperature. The solution was concentrated to ca. 1.5 mL and then diluted with hexane (15 mL). A red solid that formed was collected by filtration, washed twice with 4 mL of hexane, and dried in vacuo. Yield 40 mg, .043 mmol, 61%. The formation of $[Ir(cod)(dppf)][BF_4]$ was confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.[2b] ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (m, 4H, Ph), 7.58 (m, 6H, Ph), 4.37 (m, 4H, cyclopentadienyl), 4.28 (m, 4H, cyclopentadienyl), 4.05 (m, 4H, cod), 2.18 (m, 4H, cod), 1.88 (m, 4H, cod). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 15.1.

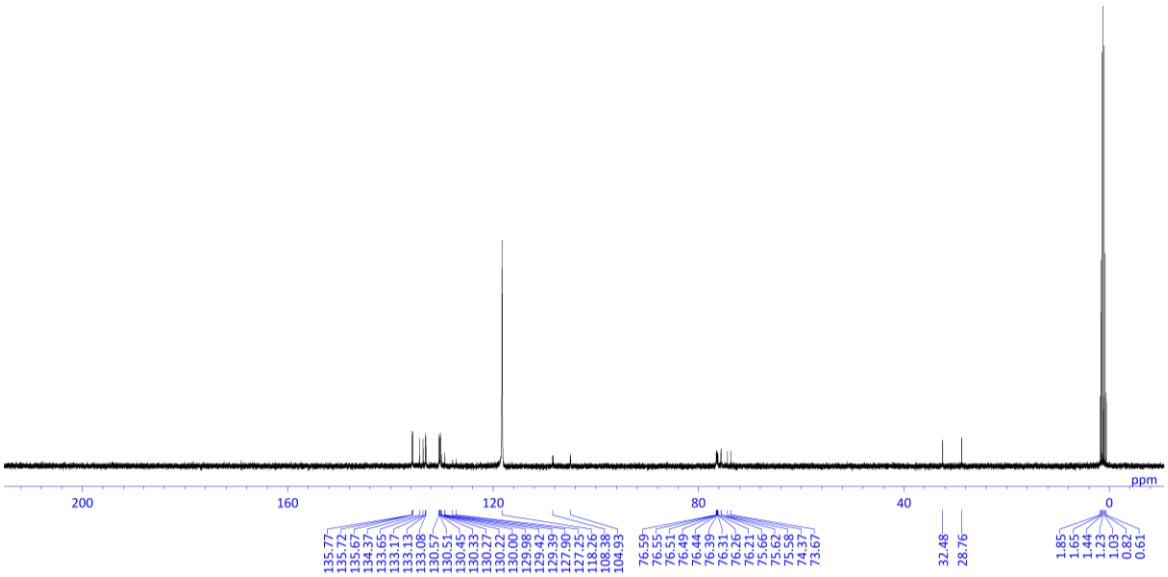
To a solution of $[Ir(cod)(dppf)][BF_4]$ (57.0 mg, 0.061 mmol) in MeCN (4 mL) was added 42% aqueous solution of HBF_4 (19 µL, 0.12 mmol). The solution turned from red to yellow and was stirred at room temperature for 3.5 h. Then, the solution was concentrated to ca. 1 mL, filtered, and layered with diethyl ether (4 mL). After the two layers mixed completely, the orange crystals that deposited were collected by filtration and dried in vacuo. Yield 46.3 mg, 0.043 mmol, 71%. The compound was characterized by NMR spectroscopy and single-crystal X-ray diffraction (see below). ^1H NMR (400 MHz, CD_3CN): δ 7.95 (m, 2H, Ph), 7.75-7.56 (m, 16H, Ph), 5.36 (m, 2H, cod), 5.00, 4.72, 4.36, 3.94 (m, 2H each, C_5H_4), 3.85 (m, 2H, cod), 2.83, 2.48, 2.33, 2.17 (m, 2H each, cod). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ 3.1 (s). 13C{1H} NMR (100 MHz, CD_3CN): δ 135.72 (m, Ph), 134.37 (m, Ph), 133.65 (m, Ph), 130.51 (m, Ph), 130.27 (m, Ph), 129.70 (m, Ph), 127.58 (m, Ph), 108.38 (m, cod), 104.93 (m, cod), 76.55 (m, C_5H_4), 76.44 (m, C_5H_4), 76.26 (m, C_5H_4), 74.10 (m, C_5H_4), 34.28 (cod), 28.76 (cod), -15.06 (t, $^2J_{PH}$ = 12 Hz, Ir-H).



^1H NMR spectrum of $[IrH(cod)(MeCN)(dppf)][BF_4]_2$ (400 MHz, CD_3CN).



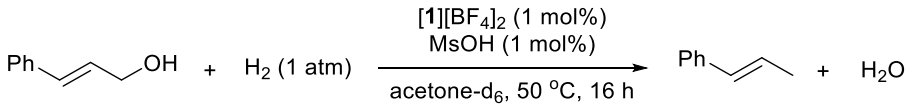
$^{31}P\{^{1}H\}$ NMR spectrum of $[IrH(cod)(MeCN)(dppf)][BF_4]_2$ (162 MHz, CD_3CN).



$^{13}C\{^{1}H\}$ NMR spectrum of $[IrH(cod)(MeCN)(dppf)][BF_4]_2$ (100 MHz, CD_3CN).

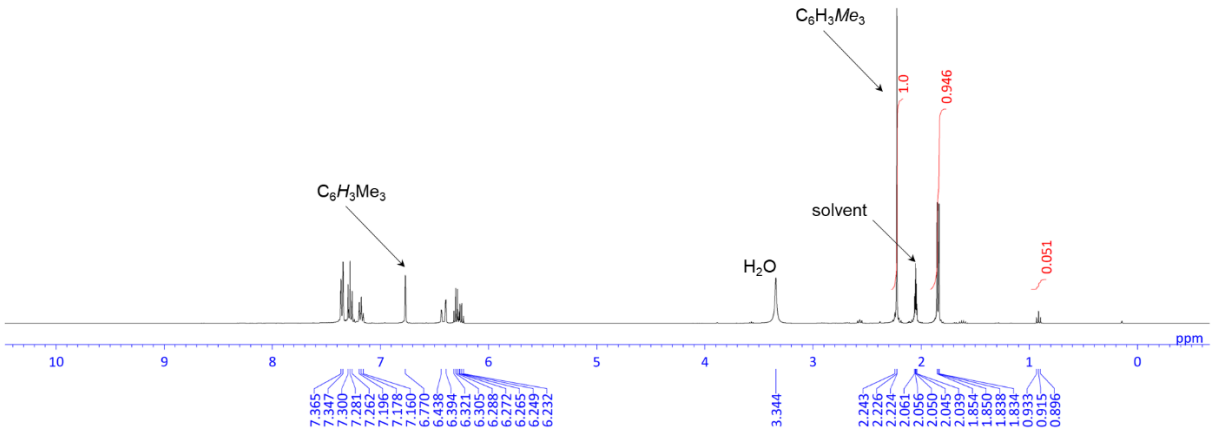
2.2. Catalytic Reactions

2.2.1. Catalytic hydrogenolysis of cinnamyl alcohol.



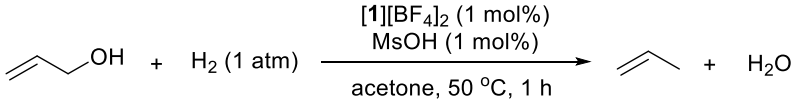
A 20-mL Schlenk tube was charged with [**1**][BF_4]$_2$ (4.3 mg, 0.0033 mmol), cinnamyl alcohol (44.7 mg, 0.33 mmol), acetone-d_6 (1 mL), and a stir bar. To the resulting solution was added MsOH (1.0 M in H_2O, 3.3 μL, 0.0033 mmol) and mesitylene (15.3 μL, 0.11 mmol as an internal standard). The Schlenk tube was sealed with a Teflon stopper, and the reaction solution was degassed by a freeze-pump-thaw cycle. The Schlenk tube was then filled with H_2, and the

reaction solution was stirred at 50 °C for 16 h. Analysis by ^{1}H NMR spectroscopy showed that *trans*-*β*-methylstyene was formed in 95% yield.



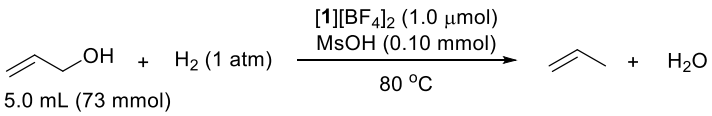
^{1}H NMR spectrum for the catalytic hydrogenolysis of cinnamyl alcohol (400 MHz, acetone-d_6)

2.2.2. Catalytic hydrogenolysis of allyl alcohol.



The catalyst [**1**][BF_4]$_2$ (12.8 mg, 0.010 mmol) was weighed in a Schlenk tube, dissolved in 3 mL of acetone, and the solution treated with allyl alcohol (68 μL, 1.0 mmol) and MsOH (1.0 M in H_2O, 10 μL, 0.010 mmol). The Schlenk tube was sealed with a rubber septum, and the reaction solution was degassed by freeze-pump-thaw cycling. The Schlenk tube was then filled with H_2, and 5 mL of ethane (internal standard) was added through the septum using a gas-tight syringe. After the reaction solution was stirred at specified temperature for a specified period, a 200-μL portion of the headspace gas was analyzed by GC-FID to quantify the amount of propylene produced.

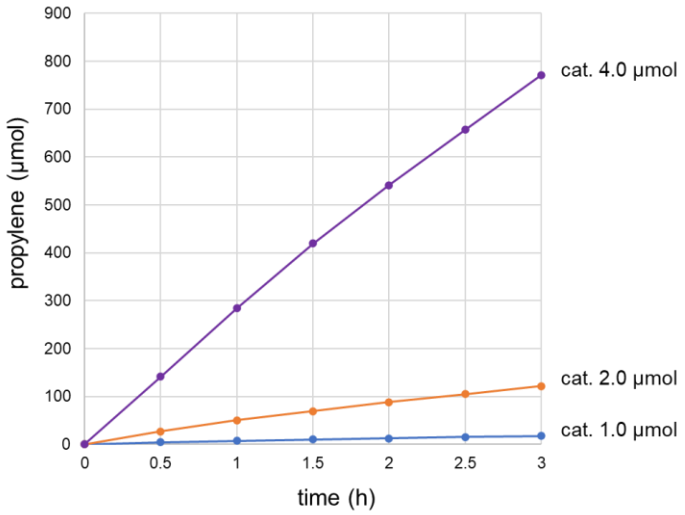
2.2.3. Catalytic hydrogenolysis of neat allyl alcohol.

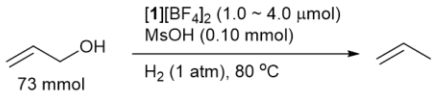


A Schlenk tube of 114-mL inner volume was charged with allyl alcohol (4.5 mL) and a stir bar. Separately, a solution of [**1**][BF_4]$_2$ (12.8 mg, 0.010 mmol) and MsOH (64 μL, 1.00 mmol) in 5.0 mL of allyl alcohol was prepared, and a 0.50-mL portion of this catalyst solution was taken and mixed with the allyl alcohol in the Schlenk tube. Then, the vessel was sealed with a rubber septum, and the reaction solution was degassed by freeze-pump-thaw cycling. The reaction vessel was then filled with H_2, and 5 mL of ethane (internal standard) was added

through the septum using a gas-tight syringe. After the reaction solution was stirred at 80 °C for a specified period, a 200-μL portion of the headspace gas was analyzed by GC-FID to quantify the amount of propylene produced.

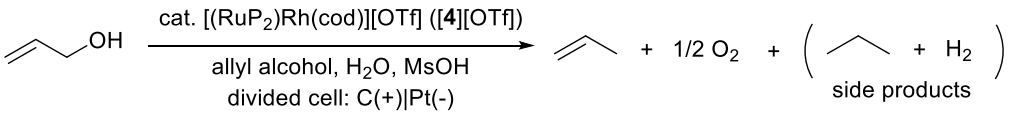
2.2.4. Hydrogenolysis of allyl alcohol at different catalyst loadings





	cat. 1.0 μmol	cat. 2.0 μmol	cat. 4.0 μmol
time (h)	C_3H_6 (μmol)	C_3H_6 (μmol)	C_3H_6 (μmol)
0	0	0	0
0.5	4.5	27.3	141.8
1	7.6	50.4	284.3
1.5	10.5	69.7	419.6
2	13.0	88.3	541.2
2.5	15.3	104.8	657.0
3	17.4	121.5	771.5

2.2.5. Catalytic electrochemical deoxygenation.



The reaction was performed in an H-type electrolysis cell equipped with a proton exchange membrane separator (Nafion N-117), a carbon felt cathode (12 mm diameter, 5 mm thickness, 850 cm^2 surface area), a platinum plate anode (13×12×0.3 mm), and a silver wire pseudo reference electrode (1.2 mm diameter). The cathodic compartment was charged with [**4**][OTf] (12 mg, 0.010 mmol), allyl alcohol (5 mL), distilled water (5 mL), and MsOH (64 μL, 1.0 mmol). The anodic cell contained distilled water (10 mL) and MsOH (64 mL, 1.0 mmol). The electrolyte solution in each cell was magnetically stirred and electrolyzed at a constant potential (-1.2 V) for 1 h. The gases produced in the cathodic cell were propylene, propane, and H_2. O_2 was evolved from the anode. These gases were quantified by GC using methane as an internal standard.

3. X-ray Crystallography

Single crystals of each compound were prepared as described in the synthetic procedures and were immersed in Fomblin Y perfluorinated polyether fluid. A well-shaped crystal of each sample was scooped into a Hampton 18-mm Mounted CryoLoop. All measurements were performed on a Rigaku R-AXIS Rapid imaging plate detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The frame data were processed using Rigaku PROCESS-AUTO,[3] and the reflection data were corrected for absorption with ABSCOR.[4] The structures were solved and refined by the SHELX programs (SHELXT and SHLEXL)[5] using the OLEX2 interface.[6] Unless otherwise mentioned, all non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed at calculated positions and treated as riding models.

In the crystal structure of [**2**][OTf]$_2$, the central π-allyl carbon atom exhibited site disorder, occupying two approximately C_2 symmetric positions, and was consequently modeled as split atoms. The occupancies of these atoms were refined and subsequently fixed. Equivalent displacement parameters (EADP) restraints were applied to this pair of split atoms. Due to uncertainty about their deviation from the plane defined by the allylic carbon atoms, hydrogen atoms on the π-allyl unit were not placed. Additionally, the asymmetric unit contained one molecule of co-crystallized dichloromethane.

In the crystal structure of [**3**][BF_4], one of the three MeCN ligands was severely disordered. The terminal methyl carbon of this MeCN ligand became very flat when anisotropic refinement was attempted, so it was refined isotropically. Additionally, one of the BF_4^- anions showed disorder and was modeled using split atoms with isotropic displacement factors. A co-crystallized diethyl ether molecule in the asymmetric unit also exhibited disorder and was refined isotropically.

The crystal structure of [**5**][OTf]$_2$ exhibited site disorder in the central π-allyl carbon, similar to that found in [**2**][OTf]$_2$. The same split atom treatment was applied to address this disorder. As in [**2**][OTf]$_2$, hydrogen atoms on the π-allyl unit in [**5**][OTf]$_2$ were not placed. Additionally, one of the OTf^- anions showed disorder and was modeled using split atoms with isotropic displacement factors. A co-crystallized methanol molecule was found in the asymmetric unit, which was hydrogen-bonded to a OTf^- anion.

Selected crystallographic data are summarized in Tables S1 and S2, and plots of thermal ellipsoids for the solved structures are depicted on the pages following the table. Further details are provided in the crystallographic information files (CCDC 2347094, 2347095, 2347096, and 2367600).

Table S1. Crystallographic data

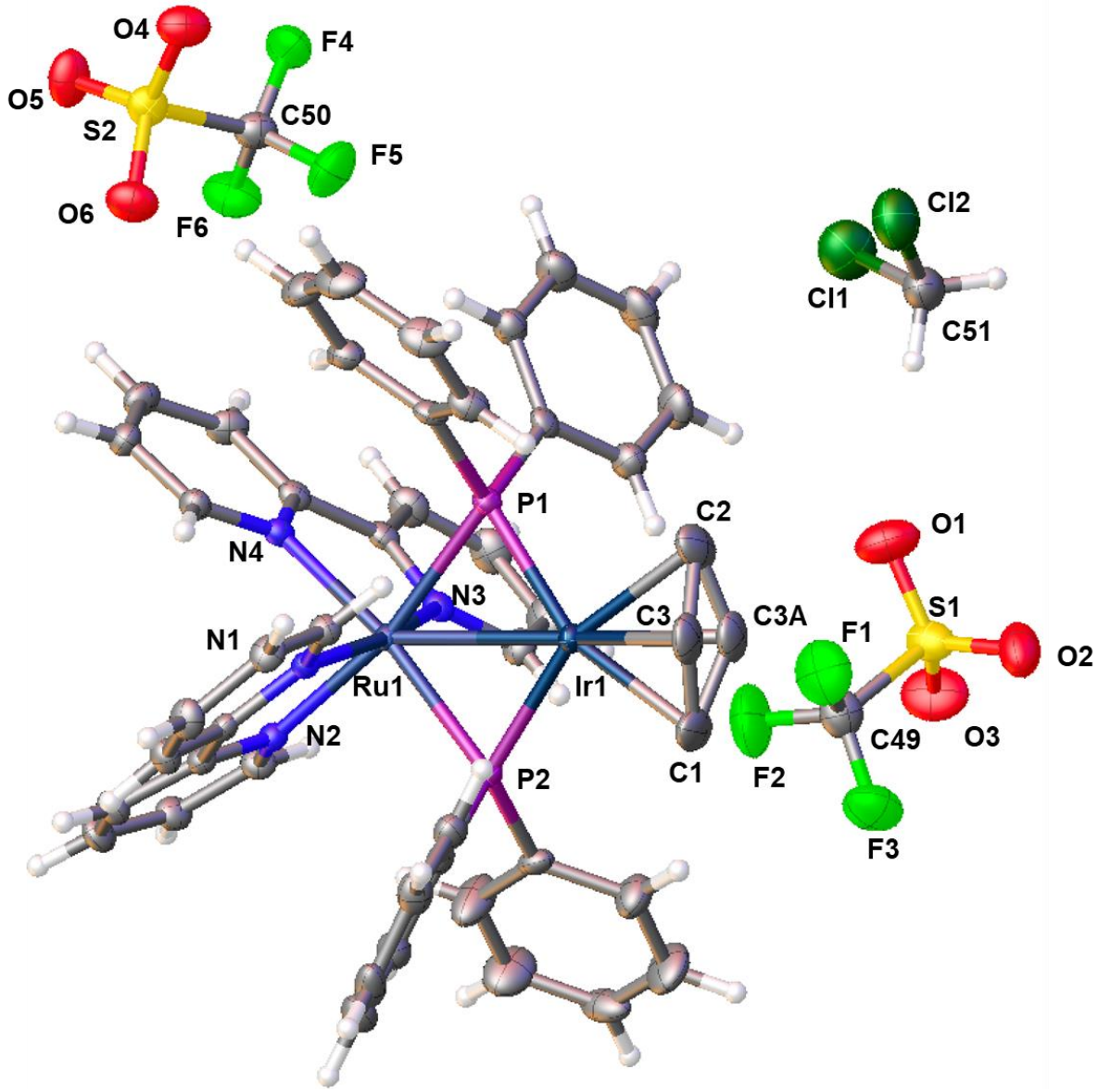
	[**2**][OTf]$_2$	[**3**][BF$_4$]$_2$	[**5**][OTf]$_2$
formula	$C_{50}H_{41}Cl_2F_6N_4O_6P_2S_2IrRu$	$C_{57}H_{44}B_2F_8N_4OP_2IrRu$	$C_{50}H_{41}F_6N_4O_7P_2S_2RhRu$
M	1398.15	1371.87	1253.93
T/K	173(2)	173 (2)	173 (2)
size (mm)	0.30 × 0.10 × 0.02	0.40 × 0.20 × 0.03	0.50 × 0.30 × 0.04
crystal system	triclinic	monoclinic	triclinic
space group	*P*-1	$P2_1/n$	*P*-1
Z	2	4	2
a (Å)	13.0650(4)	10.5215(5)	12.8700(6)
b (Å)	14.1192(5)	24.1984(11)	13.8567(6)
c (Å)	15.0990(6)	22.4372(11)	14.2225(7)
α (deg)	79.524(6)	90.0000	99.607(7)
β (deg)	69.725(5)	93.811(7)	95.647(7)
γ (deg)	87.357(6)	90.0000	92.404(7)
V (Å^3)	2568.70(19)	5700.0(4)	2484.3(2)
D_{calc} (g/cm^3)	1.808	1.599	1.676
μ (mm^{-1})	3.212	2.732	0.863
reflns collected	24941	33382	23068
unique reflns	11646	12980	11096
GOF on F^2	1.052	1.098	1.064
R1 [$I > 2\sigma(I)$][a]	0.0321	0.0754	0.0454
wR2 (all data)[b]	0.0700	0.2211	0.1203
CCDC number	2347094	2347095	2347096

[a] $R1 = (\Sigma \, ||Fo| - |Fc|| \,) / \Sigma \, |Fo|$, [b] $wR2 = [\{\Sigma \, (w(Fo^2 - Fc^2)^2 \,)\} / \Sigma \, w(Fo^2)^2]^{1/2}$

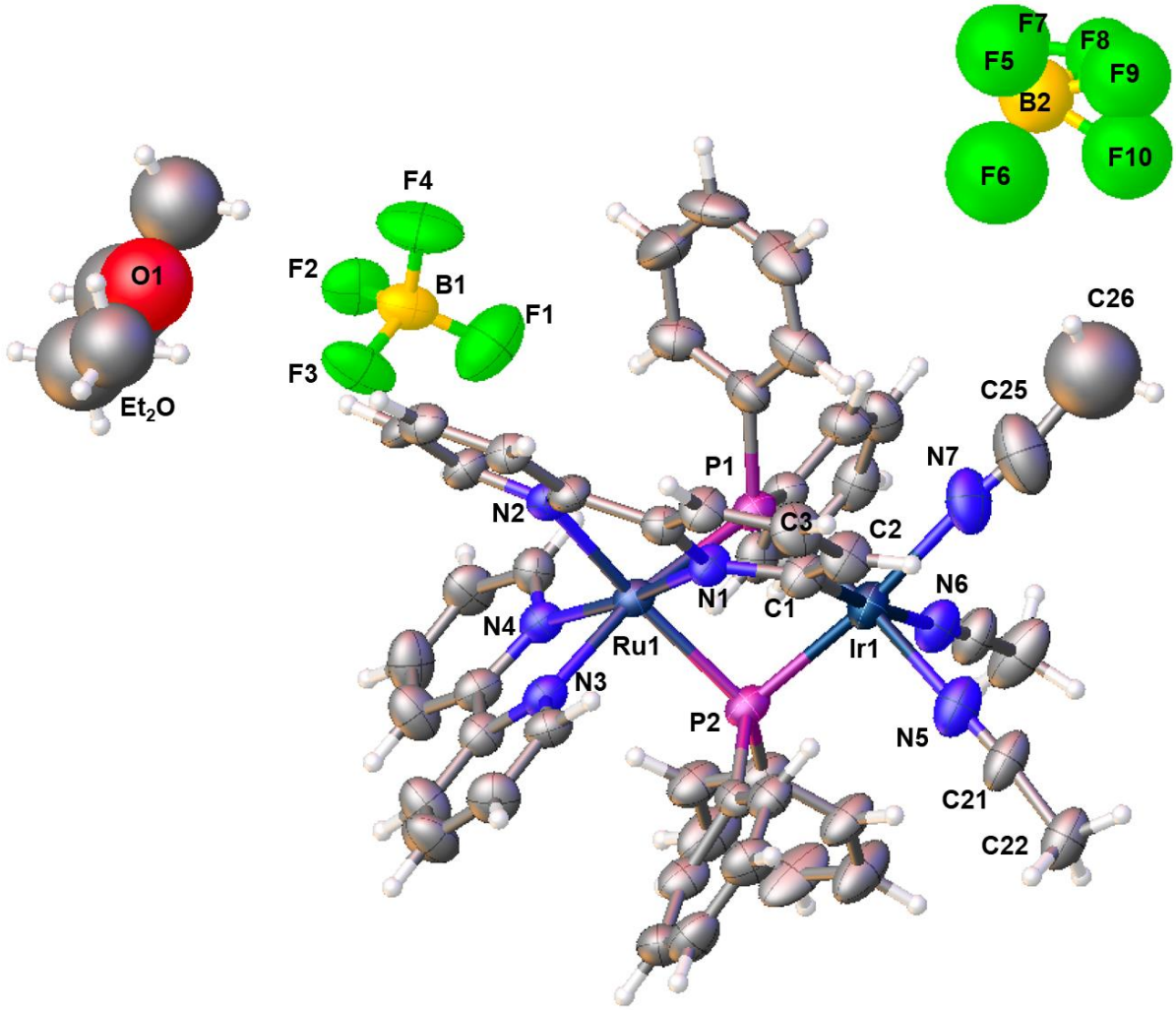
Table S2. Crystallographic data

	[IrH(dppf)(MeCN)][BF_4]$_2$
formula	$C_{50}H_{41}Cl_2F_6N_4O_6P_2S_2IrRu$
M	1193.57
T/K	153(2)
size (mm)	0.40 × 0.30 × 0.03
crystal system	triclinic
space group	*P*-1
Z	2
a (Å)	10.3466(5)
b (Å)	13.4938(6)
c (Å)	19.4429(8)
α (deg)	99.672(7)
β (deg)	102.510(7)
γ (deg)	106.984(7)
V (Å^3)	2455.5(2)
D_{calc} (g/cm^3)	1.614
μ (mm^{-1})	3.138
reflns collected	23696
unique reflns	11124
GOF on F^2	1.058
R1 [$I > 2\sigma(I)$][a]	0.0217
wR2 (all data)[b]	0.0509
CCDC number	2367600

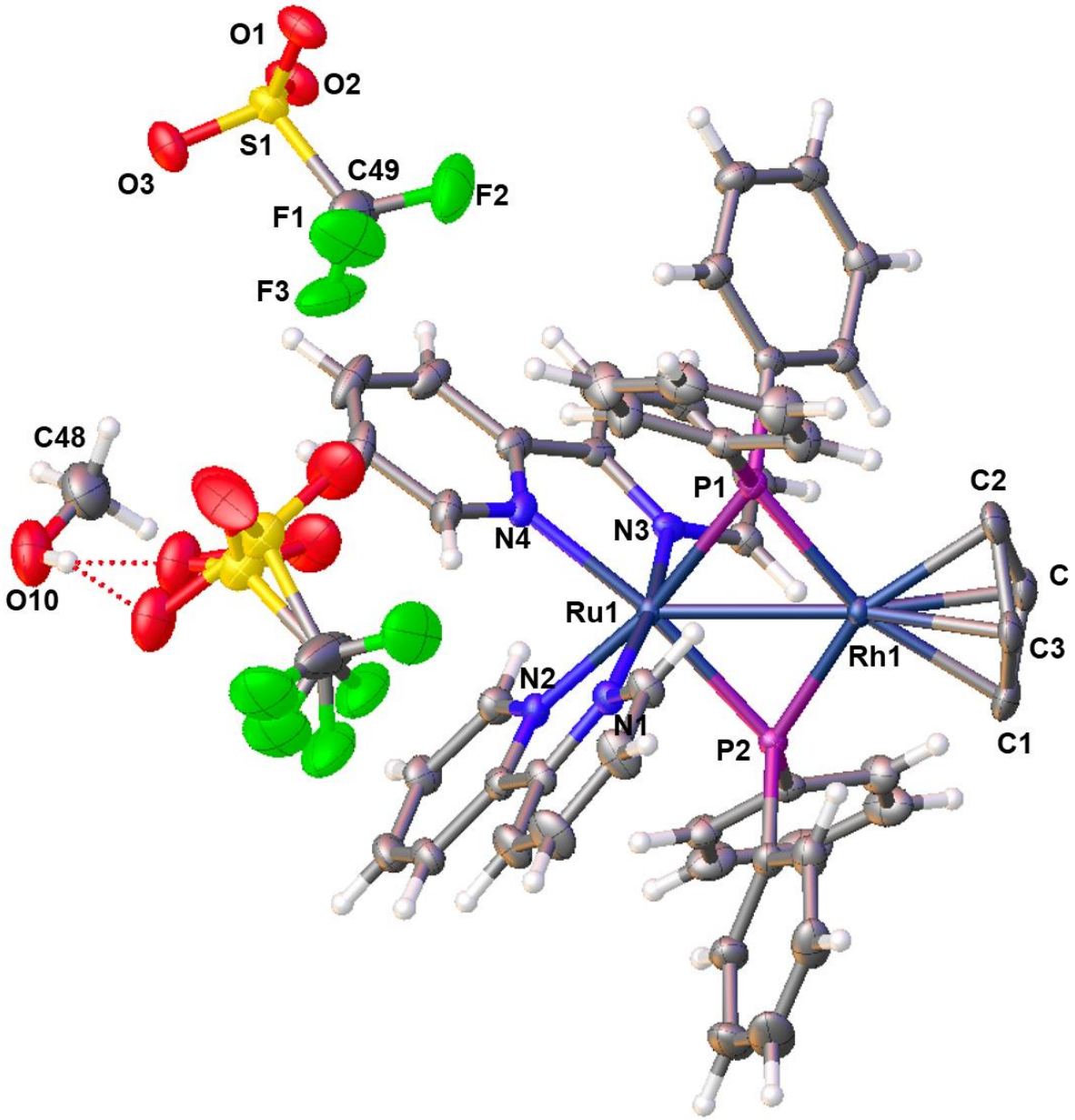
[a] $R1 = (\Sigma \, ||Fo| - |Fc|| \,) / \Sigma \, |Fo|$, [b] $wR2 = [\{\Sigma \, (w(Fo^2 - Fc^2)^2 \,)\} / \Sigma \, w(Fo^2)^2]^{1/2}$



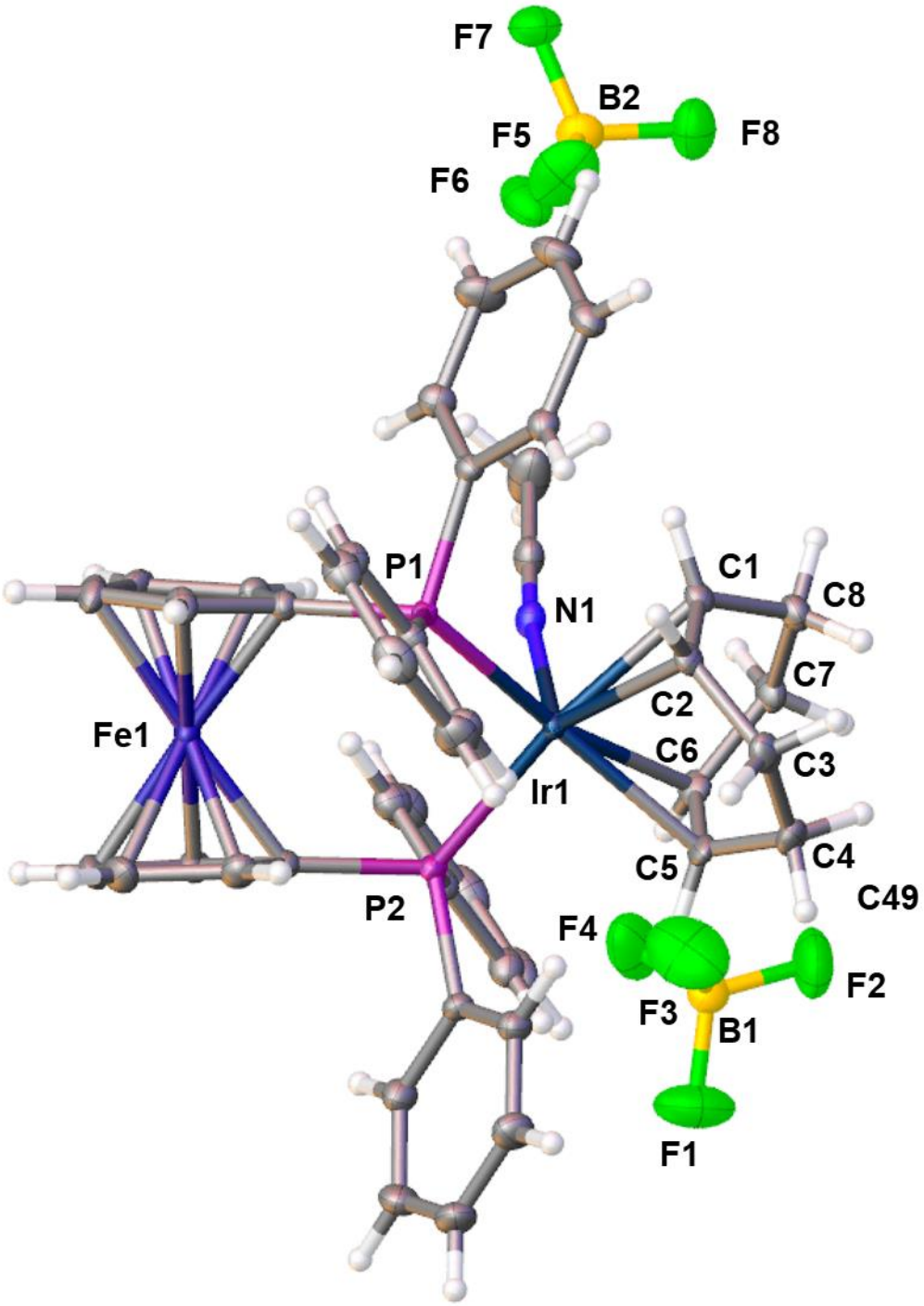
Thermal ellipsoid plot for the crystal structure of [**2**][OTf]$_2$ at 50% probability level



Thermal ellipsoid plot for the crystal structure of [**3**][BF_4]$_2$ at 50% probability level



Thermal ellipsoid plot for the crystal structure of [**5**][OTf]$_2$ at 50% probability level



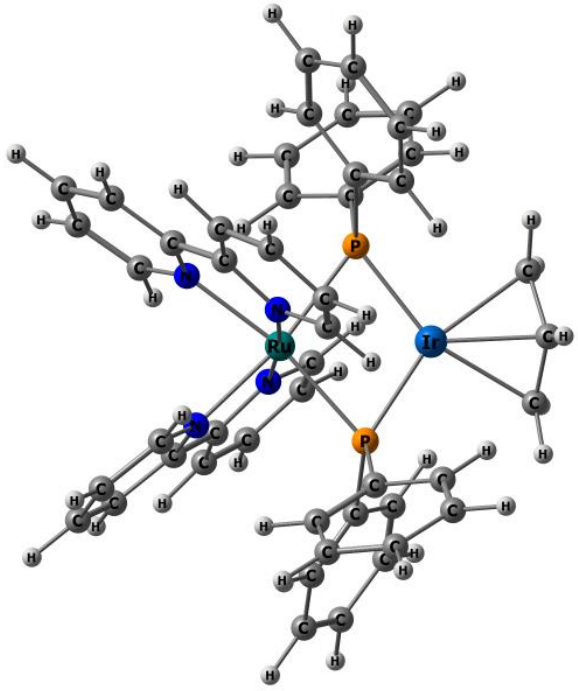
Thermal ellipsoid plot for [IrH(dppf)(MeCN)][BF_4]$_2$ at 50% probability level. Co-crystallized solvent molecules (three MeCN molecules) are omitted for clarity. The hydrogen atom on the iridium center was not found in the difference Fourier map and was not included.

4. Computational details

4.1. Methods

All calculations were done with the Gaussian 09[7] program using the B97-D dispersion corrected functional.[8] Iridium and ruthenium atoms were described with SDD effective core potentials and the associated basis sets,[9] while the 6-31G(d) basis set[10] was used for all other atoms. Geometry optimizations were performed without any symmetry constraints in the gas phase, and the stationary points were checked by frequency calculations to confirm all positive frequencies. Plots of molecular orbitals were generated with Gaussview 6.1.[11]

4.2. Atomic coordinates for $[(RuP_2)Ir(\eta^3\text{-}C_3H_5)]^{2+}$



Ir	-0.096328000000	0.247199000000	-2.052656000000
Ru	0.068130000000	-0.109348000000	0.709608000000
P	1.701521000000	0.703839000000	-0.798449000000
P	-1.752912000000	-0.500752000000	-0.723245000000
C	2.857173000000	2.961765000000	0.521956000000
H	3.053351000000	2.316738000000	1.377151000000
C	4.332307000000	-0.083974000000	-0.055976000000
H	4.346357000000	0.758311000000	0.634420000000
C	1.999139000000	3.302457000000	-1.732687000000
H	1.508951000000	2.905849000000	-2.621996000000

C	-3.743495000000	-3.721490000000	-2.302559000000
H	-4.324783000000	-3.919688000000	-3.204275000000
C	3.212276000000	-0.310051000000	-0.885617000000
C	3.231910000000	-1.383501000000	-1.802038000000
H	2.369487000000	-1.539117000000	-2.452106000000
C	4.351018000000	-2.223150000000	-1.880748000000
H	4.366160000000	-3.040987000000	-2.603271000000
C	5.457116000000	-2.003117000000	-1.042276000000
H	6.332063000000	-2.651405000000	-1.110972000000
C	5.446598000000	-0.931462000000	-0.133172000000
H	6.313346000000	-0.744909000000	0.503268000000
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H	2.169303000000	5.311180000000	-2.517714000000
C	2.961989000000	5.167015000000	-0.503746000000
H	3.241404000000	6.220137000000	-0.450471000000
C	-2.430492000000	-2.185851000000	-0.936652000000
C	-3.234697000000	0.517339000000	-0.448366000000
C	-3.319479000000	1.793167000000	-1.042641000000
H	-2.505709000000	2.128191000000	-1.688950000000
C	-3.557600000000	-4.734828000000	-1.345830000000
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C	2.249644000000	2.441745000000	-0.640688000000
C	-4.441774000000	2.600206000000	-0.810198000000
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H	-3.343132000000	-1.665049000000	-2.839796000000
C	-4.285751000000	0.050570000000	0.371709000000
H	-4.237105000000	-0.951342000000	0.802682000000
C	-5.400957000000	0.866233000000	0.608558000000
H	-6.217072000000	0.502077000000	1.235013000000
C	-5.478952000000	2.141074000000	0.020216000000
H	-6.356030000000	2.766963000000	0.192395000000
C	3.211099000000	4.317813000000	0.587564000000
H	3.685267000000	4.711418000000	1.488367000000
C	-2.254825000000	-3.203246000000	0.021272000000
H	-1.674010000000	-3.003254000000	0.917758000000
C	-2.815835000000	-4.473411000000	-0.182787000000
H	-2.678118000000	-5.255378000000	0.566247000000
N	-0.885570000000	1.716038000000	1.161440000000

N	-1.143000000000	-0.608527000000	2.408409000000
C	-1.855924000000	-2.051413000000	4.202506000000
H	-1.795143000000	-3.026009000000	4.685735000000
C	-2.369761000000	4.017688000000	1.822534000000
H	-2.946643000000	4.905193000000	2.082582000000
C	-2.697788000000	0.207870000000	4.056155000000
H	-3.309322000000	1.016649000000	4.450089000000
C	-2.683023000000	-1.032325000000	4.701483000000
H	-3.294850000000	-1.195647000000	5.588968000000
C	-1.906214000000	0.408416000000	2.909572000000
C	-1.456080000000	4.031390000000	0.762085000000
H	-1.292044000000	4.922380000000	0.156813000000
C	-2.546168000000	2.826567000000	2.533075000000
H	-3.273687000000	2.779518000000	3.340316000000
C	-0.759755000000	2.860953000000	0.451979000000
H	-0.099273000000	2.811871000000	-0.403267000000
C	-1.101052000000	-1.793295000000	3.056462000000
H	-0.436609000000	-2.540622000000	2.627087000000
C	-1.793495000000	1.690224000000	2.194829000000
N	1.024069000000	-1.967855000000	0.510549000000
N	1.554305000000	-0.030116000000	2.238601000000
C	3.209743000000	-1.275892000000	3.461972000000
H	3.790675000000	-2.185752000000	3.597234000000
C	2.485218000000	-4.370774000000	0.365907000000
H	3.050590000000	-5.301365000000	0.316153000000
C	2.597408000000	0.953460000000	4.171628000000
H	2.686935000000	1.806867000000	4.843133000000
C	2.289181000000	-1.170287000000	2.402535000000
C	1.697608000000	0.997257000000	3.104132000000
H	1.072484000000	1.865041000000	2.903522000000
C	0.801217000000	-2.866129000000	-0.477972000000
H	0.064291000000	-2.575692000000	-1.218468000000
C	1.487703000000	-4.078712000000	-0.572386000000
H	1.247018000000	-4.763845000000	-1.384625000000
C	2.766892000000	-3.424664000000	1.356487000000
H	3.568347000000	-3.605969000000	2.069292000000
C	2.030283000000	-2.230559000000	1.413341000000
C	3.369286000000	-0.206934000000	4.349523000000
H	4.080720000000	-0.280541000000	5.172415000000

C	0.988545000000	0.487404000000	-3.998976000000
H	1.837348000000	1.170453000000	-4.056629000000
C	-1.416266000000	0.112421000000	-3.851199000000
H	-2.426165000000	0.522005000000	-3.785478000000
C	-0.332521000000	1.012684000000	-4.087704000000
H	-0.505923000000	2.091580000000	-4.154080000000
H	-1.348628000000	-0.923995000000	-4.200474000000
H	1.194872000000	-0.536007000000	-4.331878000000

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