EXPERIMENTAL SECTION

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I General Information

All manipulations were performed under an argon atmosphere using standard Schlenk techniques.

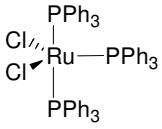
Solvents were purchased from Carlo Erba, SDS or Aldrich. THF and diethyl ether were distilled over Na/benzophenone prior to use. Pentane, heptane, toluene were distilled over a sodium suspension and dichloromethane over calcium hydride.
From the synthesis of the compound **L26**, solvents were dried by a solvent purification system (SPS-M-Braun). The water contents of these solvents were periodically controlled by Karl-Fischer coulometry using a Methrom 756 KF apparatus.

Starting materials were purchased from Aldrich, Fluka or Strem Chemicals and used as received.

^{1}H NMR (300 MHz), ^{31}P $\{^{1}H\}$ NMR (122 MHz) and ^{13}C $\{^{1}H\}$ NMR (75 MHz) spectra were recorded on a Bruker AC 300MHz instrument at room temperature. Deuterated solvent (CD_2Cl_2, $CDCl_3$, CD_3CN, C_6D_6) was purchased from Eurisotop or Aldrich. Chemical shifts are reported in ppm *vs* $SiMe_4$ and were determined by reference to the residual solvent peaks. All coupling constant are given in Hertz.
IR spectra were recorded in the region 4000-450 cm^{-1} on a Perkin-Elmer Spectrum one FT-IR spectrometer (ATR mode, ZnSe diamond).
Mass spectra were collected with an Agilent 6890 N apparatus with Agilent 5975B inert XL EI/CI MSD mass spectrometer.
C, H, N elemental analyses were performed by the ICMUB Université de Bourgogne (Dijon, France) or by the Service Central d'Analyses of CNRS (Vernaison, France).

II Synthesis

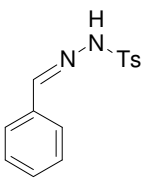
Dichloro-tris(triphenylphosphine) ruthenium (II) **C3**



Hydrated ruthenium trichloride (1.02 g, 3.8 mmol) was dissolved in freshly degassed methanol (250 mL). The reddish brown solution was refluxed for 5 minutes under argon. After cooling, triphenylphosphine (6.1 g, 23.2 mmol) were added. The reaction mixture was again refluxed under argon for 3 hours. The complex was precipitated from the hot solution; on cooling, obtained crystals were filtered, washed with ether several times until no trace of free PPh_3 in solvent was observed. The brown crystals obtained were then dried under vacuum. (3.66 g, 99% yield).

^{31}P {^{1}H} NMR (122 MHz, CD_2Cl_2): 41.12 (br s, PPh_3). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 132.2, 132.1 (*ipso*-C), 132 (d, *o*-C), 128.6, 128.5 (*m*-C, *p*-C).

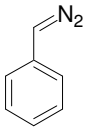
Tosylhydrazone **L6**



A solution of 4.02 g (21.6 mmol) of *p*-tosylhydrazine in 5 mL of acetic acid was was stirred at 70°C until complete dissolution. Then, 2.68 g of benzaldehyde (25.3 mmol) was added. Heating was continued during 2.5 hr. The crude yellow mixture was let overnight at room temperature before the crystalline product was removed by filtration. The product obtained was washed successively with a mixture of acetic acid/water 1:1 and then water. After recrystallization in a minimum amount of acetic acid, the solid was washed again with water and dried under vacuum, yielding **L6** as a yellow needle (3.25 g, 55%).

^{1}H NMR (300 MHz, $CDCl_3$): 8.46 (s, 1H, C<u>H</u>=N), 7.8 (d, 2H, *m*-C<u>H</u> Ar), 7.7 (s, 1H, N<u>H</u>), 7.47 (*m*, 2H, *o*-C<u>H</u> Ar), 7.22 (m, 5H, CH Ar), 2.3 (s, 3H, C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 148.18(<u>C</u>=N), 144.42 (*ipso*-C Ar), 135.38 (*p*-C Ar), 133.36 (*ipso*-C), 130.5 (*p*-C Ar), 129.84 (*o*-C Ar), 128.72 (*o*-C Ar), 128.04 (*m*-C Ar), 127.48 (*m*-C Ar), 21.68 (<u>C</u>H_3).

Phenyldiazomethane **L7**

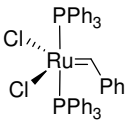


p-tosylhydrazone **L6** (0.58 g, 2.13 mmol) and benzyl triethylammonium chloride (58.3 mg, 0.25 mmol) were dissolved in distilled toluene (75 mL). To this solution,

was added 75 mL of 14 $\%_{wt}$ aqueous sodium hydroxide (12 g NaOH) degassed. The white reaction mixture was warmed at 70°C with vigorous stirring for 2 hours. After cooling, the red organic phase was extracted and dried over Na_2SO_4.

Yield was determined by titrating a 2 mL aliquot with 5.78. 10^{-3} M trifluoroacetic acid in CH_2Cl_2 with the phenyldiazomethane acting as indicator.

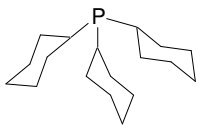
***Benzylidene dichloro bis(triphenylphosphine) ruthenium (II)* C4**



A solution of $[RuCl_2(PPh_3)_3]$ **C3** (1.506 g, 1.53 mmol) in CH_2Cl_2 (12.6 mL) at -78°C was treated with a -78°C freshly degassed solution of phenyldiazomethane **L7** (2 eq.). A spontaneous color change from brown to brown-green and vigorous bubbling was observed. After 5 minutes of stirring at room temperature, the solvent were removed under vacuum. The green residue was then dissolved in CH_2Cl_2 (2 mL) and washed with pentane (3 * 20 mL). The precipitate was then dried, leading to a dark green powder (0.98 g, 79%).

^{31}P $\{^1H\}$ NMR (122 MHz, CD_2Cl_2): 30.42 (PPh_3).

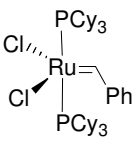
***Tricyclohexylphosphine* L40**



$PCy_3.CS_2$ (7,9 g, 22.3 mmol) and dry ethanol (130 mL) was heated at 80°C for 2.5 hr with argon bubbling. The orange solution was gradually cleared up. The mixture was filtered at room temperature and the white precipitate was then dried under vacuum. 5.1 g of **L40** were obtained as a white powder (82% yield).

^{31}P $\{^1H\}$ NMR (122 MHz, CD_2Cl_2): 10.8 (s, PCy_3). ^{13}C $\{^1H\}$ NMR (75 MHz, CD_2Cl_2): 32.14 (*ipso*-C), 31.91 (*ipso*-C), 31.66 (*o*-C), 31.5 (*o*-C), 28.14 (*m*-C), 28 (*m*-C), 27 (*p*-C).

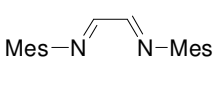
***Benzylidene dichloro bis(tricyclohexylphosphine)ruthenium (II)* C5**



A solution of PCy_3 (235 mg, 0.839 mmol) in CH_2Cl_2 (3.8 mL) was added to a solution of $[RuCl_2(PPh_3)_2(=CHPh)]$ (304 mg, 0.386 mmol) in CH_2Cl_2 (12.5 mL) and stirred at room temperature for 30 minutes. The solvent was removed under vacuum. The residue was dissolved in a minimum amount of CH_2Cl_2 then repeatedly washed with degassed acetone (2* 5 mL). 252 mg of **C5** were obtained as a purple solid (79% yield).

^{31}P {^{1}H} NMR (122 MHz, CD_2Cl_2): 36.23 (s, PCy_3, 98.8%). ^{1}H NMR (300 MHz, CD_2Cl_2): 20.02 (s, 1H, Ru=C<u>H</u>), 8.44 (d, 2H, *o*-C<u>H</u> Ar), 7.54 (d, 1H, *p*-C<u>H</u> Ar), 7.32 (t, 2H, *m*-C<u>H</u> Ar), 2.61-1.19 (m, 66H, PCy_3). ^{13}C {^{1}H} NMR (75 MHz, CD_2Cl_2): 294.62 (s, Ru=<u>C</u>H), 153.06 (s, *ipso*-C Ar), 131.16, 129.47, 129.23 (s, C_6H_5), 32.36 (pseudo-t, *ipso*-C, Cy), 29.96(s, *m*-<u>C</u>H, Cy), 28.21 (pseudo-t, *o*-<u>C</u>H, Cy), 26.92 (s, *p*-<u>C</u>H, Cy).

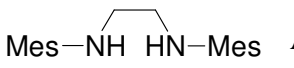
Glyoxal-bis(mesitylimine) **L8**



To a solution of 8.25 mL of 2,4,6-triméthylphénylamine (58.8 mmol) in 325 mL of methanol were added 3.75 mL of a 40%$_{wt}$ aqueous solution of glyoxal (81.7 mmol). The mixture was stirred at room temperature for 24h. The yellow solid precipitated was collected by filtration. The mother liquid was evaporated and the recrystallization of the residue in absolute ethanol, leading to yellow needles. The entire collected product was recrystallized in ethanol then dried under vacuum. 6.3 g of **L8** were obtained (73% yield).

mp: 159°C. ^{1}H NMR (300 MHz, CDCl3): 8.1 (s, 2H, N=C<u>H</u>), 6.91 (s, 4H, *m*-CH), 2.29 (s, 6H, *p*-CH_3), 2.16 (s, 12H, *o*-CH_3). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 163.6 (s, N=<u>C</u>H), 147.6 (s, *ipso*-C), 129.4 (s, *p*-C), 129.1 (s, *m*-C), 126.7 (s, *o*-C), 20.9 (s, *p*-<u>C</u>H_3), 18.3 (s, *o*-<u>C</u>H_3).

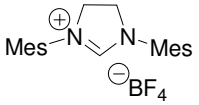
N,N'-dimesitylethylene diamine **L9** (This synthesis was realized by Boumediene, M.)



A suspension of 3.03 g of **L8** (10.3 mmol) in 50 mL of dry ether was treated at 0°C with 0.87 g of $LiAlH_4$ (22.92 mmol). The mixture was stirred for 23h at 23°C. After cooling at 0°C, 20 mL of Et_2O and 20 mL of THF were added to the yellow solution. 20 mL of water was added dropwise then before the mixture was acidified with 13 mL of a 37 %$_{wt}$ aqueous solution of HCl (pH=1). The aqueous phase was extracted twice with 50 mL of THF. To the solution was added, 20 mL of 20 %$_{wt}$ aqueous solution of KOH (pH= 12.5). The aqueous phase was again extracted 4 times by ether (60 mL). The organic layers were collected, dried over $MgSO_4$ and concentrated under vacuum. The brown liquid obtained was purified by flash chromatography on silica column (solvent: heptane/ether, 2:1). 2.1 g of diamine **L9** were obtained (69% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 6.86 (s, 4H, m-C<u>H</u>), 3.34 (br s, 2H, N<u>H</u>), 3.19 (s, 4H, C<u>H$_2$</u>-N), 2.31 (s, 12H, *o*-C<u>H$_3$</u>), 2.26 (s, 6H, *p*-C<u>H$_3$</u>). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 143.7 (s, *ipso*-C), 131.7 (s, *p*-C), 129.9 (s, *m*-C), 129.6 (s, *o*-C), 49.3 (C<u>H$_2$</u>-N), 20.7 (s, *p*-<u>C</u>H$_3$), 18.6 (s, *o*-<u>C</u>H$_3$).

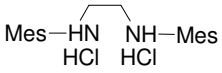
1,3-dimesitylimidazolinium tetrafluoroborate **L10** (This synthesis was realized by Boumediene, M.).



2.1 g of diamine **L9** (7.09 mmol) and 0.77 g of ammonium tetrafluoroborate (7.33 mmol) were dissolved in 1.25 mL of triethylorthoformiate (7.51 mmol). The reaction mixture refluxed for 3 hours. The orange solid obtained was recrystallized from EtOH. 1.53 g of **L10** were obtained as white fine needles (55% yield).

^{1}H NMR (300 MHz, CD_3CN): 8.1 (1H, NC<u>H</u>N), 7.08 (4H, CH Ar), 4.41 (C<u>H$_2$</u>-N), 2.35 (12H, o-C<u>H$_3$</u>), 2.31 (6H, p-C<u>H$_3$</u>). ^{13}C {^{1}H} NMR (75 MHz, CD_3CN): 160.6 (N=<u>C</u>H), 141.8 (*ipso*-C), 136.6 (*p*-C), 131.4 (*m*-C), 130.7 (*o*-C), 52.2 (<u>C</u>H$_2$-N), 21.1 (*p*-<u>C</u>H$_3$), 17.9 (*o*-<u>C</u>H$_3$).

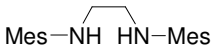
N, N'-dimesitylethylene diamine dihydrochloride **L41**



A suspension of diimine **L8** (3g, 10.26 mmol) in THF (37.5 mL) was treated at 0°C with sodium borohydride (1.56 g, 41.4 mmol). The mixture was stirred for 16h at 23°C. To the mixture were added slowly, 2.14 mL of a 35%$_{wt}$ aqueous solution of HCl at 0°C. The reaction mixture was then stirred for 20 minutes at 0°C and 93.6 mL of 3M HCl was added. The white solid precipitated was filtered, washed with water (60 mL) and subsequently with a mixture of acetone/ether 5:95. The solvent were removed under vacuum, yielding 3.77 g of a white powder (99% yield).

^{1}H NMR (300 MHz, DMSO): 6.98 (s, 4H, *m*-C<u>H</u>), 3.67 (s, 4H, NC<u>H$_2$</u>), 2.45 (s, 12H, *o*-C<u>H$_3$</u>), 2.23 (s, 6H, *p*-C<u>H$_3$</u>). ^{13}C {^{1}H} NMR (75 MHz, DMSO): 137.3 (*p*-C), 132.8 (*o*-C), 131.6 (*m*-C), 130.3 (*ipso*-C), 46.1 (N<u>C</u>H$_2$), 20.3 (*p*-CH3)18.1 (*o*-CH$_3$).

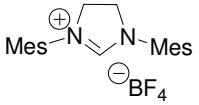
N,N'-dimesitylethylene diamine* L42 *(from L41)



A solution of **L41** (4.46 g, 12.1 mmol) in CH_2Cl_2 (30 mL) was treated by 1.67 g of K_2CO_3. The mixture was stirred for 2 hours at room temperature. The organic phase was then washed with water (3 * 30 mL), separated, dried over $MgSO_4$ before removing all volatiles under vacuum. The product was obtained as a yellow oil (2.52 g, 71% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 6.85 (s, 4H, *m*-C<u>H</u>), 3.18 (br s, 6H, N<u>H</u>, CH_2-N), 2.3 (s, 12H, *o*-C<u>H</u>$_3$), 2.25 (s, 6H, *p*-C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 143.25 (s, *ipso*-C), 131.75 (s, *p*-C), 129.95 (s, *m*-C), 129.65 (s, *o*-C), 49.27 (C<u>H</u>$_2$-N), 20.68 (s, *p*-<u>C</u>H$_3$), 18.56 (s, *o*-<u>C</u>H$_3$).

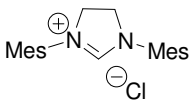
1, 3-dimesitylimidazolinium tetrafluoroborate* L10 *(from L42)



2.52 g of diamine **L42** and 0.9 g of NH_4BF_4 were dissolved in 1.9 mL of triethyl orthoformiate. The reaction mixture was brought to 120°C for 4 hours. The orange solid was recrystallized from ethanol and afforded 2.95 g of **L10** (88% yield).

^{1}H NMR (300 MHz, CD_3CN): 8.11 (1H, NC<u>H</u>N), 7.07 (4H, CH Ar), 4.41 (C<u>H</u>$_2$-N), 2.35 (12H, *o*-C<u>H</u>$_3$), 2.31 (6H, *p*-C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, CD_3CN): 160.51 (N=<u>C</u>H), 141.67 (*ipso*-C), 136.54 (*p*-C), 131.38 (*m*-C), 130.68 (*o*-C), 52.15 (<u>C</u>H$_2$-N), 21 (*p*-<u>C</u>H$_3$), 17.79 (*o*-<u>C</u>H$_3$).

***1,3-dimesityl-4,5-dihydroimidazolium chloride* L43**

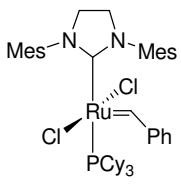


A mixture of 3.5 g of **L43** (9.47 mmol), 28 mL of triethyl orthoformiate (6.6 mmol, 7 eq.), and two drops of formic acid was heated for 5 hours at 120 °C. Upon cooling to room temperature, a white solid precipitated which was collected by filtration, washed with heptane (2 * 60mL) and dried under vacuum. 2.77 g were obtained as a white solid (85% yield).

^{1}H NMR (300 MHz, DMSO): 9.07 (s, 1H, NC<u>H</u>N), 7.09 (s, 4H, *m*-CH), 4.46 (s, 4H, C<u>H</u>$_2$), 2.35 (s, 12H, *o*-CH_3) 2.29 (s, 6H, *p*-CH_3). ^{13}C {^{1}H} NMR (75 MHz, DMSO): 160.3 (N<u>C</u>N),

139.6 (*p*-C), 135.4 (*o*-C), 130.9 (*ipso*-C), 129.44 (*m*-C), 50.91 (N<u>C</u>H$_2$), 20.56 (*p*-<u>C</u>H$_3$), 17.22 (*o*-<u>C</u>H$_3$).

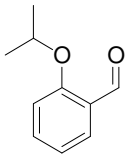
Benzylidene dichloro tricyclohexylphosphine (1,3-dimesityl-imidazolidinylidene) ruthenium (II) **C9**



L10 (343 mg, 0.87 mmol) and 97 mg of potassium *tert*-butoxide (0.86 mmol) were stirred in dry THF for 15 minutes. To this suspension were added toluene (10 mL) and **C5** (600 mg, 0.73 mmol). The reaction mixture was heated at 80°C for 30 minutes. The volatiles were removed under vacuum. The obtained residue was washed with methanol (4 * 8 mL) then dried under vacuum to give **C9** as a pinkish-brown solid (580 mg) in 94% yield.

^{31}P {^{1}H} NMR (122 MHz, CD_2Cl_2): 29.5 (s, PCy_3). ^{1}H NMR (300 MHz, CD_2Cl_2): 19.09 (s, 1H, Ru=C<u>H</u>), 7.36-6.74 (m, 9H, C<u>H</u> Ar), 3.96 (br s, 4H, C<u>H</u>$_2$-N), 2.31-0.97 (m, 51H, C<u>H</u>$_3$ and Cy).

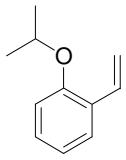
2-isopropoxybenzaldehyde **L11**



A solution of 5.3 mL salicylaldehyde (0.497 mmol) and 8.33 g potassium carbonate in 50 mL de DMF was heated in reflux at 60°C. 8.15 mL of 2-bromopropane (0.868 mmol) was then added. The yellow reaction mixture was stirred at 60°C for 6h. The reaction mixture was filtered and the filtrate was evaporated under vacuum. The crude product was dissolved in 60 mL of Et_2O and washed with 30 mL of water. The aqueous layer was extracted with Et_2O (3×80 mL). The organic layers collected were dried over $MgSO_4$ before removing all volatiles under vacuum. 6.13 g of **L11** were obtained as a pale yellow liquid (75% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 10.48 (s, 1H, C<u>H</u>=O), 7.75 (dd, 1H, *J* = 1.6 Hz; 7.7 Hz, C<u>H</u> Ar), 7.62-7.56 (ddd, 1H, *J* = 1.9 Hz; 7.3 Hz; 8.8 Hz, C<u>H</u> Ar), 7.18-6.99 (m, 2H, C<u>H</u> Ar), 4.79 (sept., 1H, *J* = 6 Hz, C<u>H</u>(CH$_3$)$_2$), 1,41 (d, 6H, *J* = 6 Hz, CH(C<u>H</u>$_3$)$_2$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 190.3 (<u>C</u>=O), 160.75, 135.88, 128.43, 125.85, 120.53, 114.12, 71.22 (<u>C</u>H(CH$_3$)$_2$), 22,12 (<u>C</u>H$_3$).

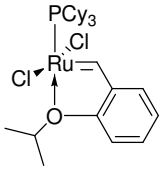
1-isopropoxy-2-vinylbenzene **L12**



10.1 g of methyltriphenylphosphonium iodide (25 mmol) in dry Et_2O (50 mL) were cooled to 0°C. 17 mL of butyllithium (1.6 M in hexane, 25.2 mmol) were slowly added dropwose. The mixture was stirred for 4h. A solution of **L11** (4.09 g, 24.9 mmol) in Et_2O (22 mL) was then added to the orange mixture which was stirred under reflux for 19 hours. After cooling to room temperature, 100 mL of Et_2O were added to precipitate $OPPh_3$. The reaction mixture was filtered and the mother liquid concentrated. The residue was purified by column chromatography on silica gel (solvent: heptane/éther 95:5). 1-isopropoxy-2-vinylbenzene was obtained as an incolorless oil (0.85 g, 21% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.5-7.47 (dd, 1H, C<u>H</u> Ar), 7.2-6.9 (m, 4H, CH Ar), 5.76 (dd,1H, *J* = 1.5 Hz; 17.8 Hz, Ar-CH=C<u>H</u>-H), 5.23 (dd, 1H, *J* = 1.5 Hz; 11.2 Hz, Ar-CH=CH-<u>H</u>), 4,54 (sept., 1H, *J* = 5.9 Hz, C<u>H</u>$(CH_3)_2$), 1.37 (d, 6H, *J* = 6.1 Hz, CH(C<u>H</u>$_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 132.2 (<u>C</u>H=CH_2), 155.3, 128.1, 126.7, 120.7, 114 (<u>C</u> Ar), 114.4 (CH=<u>C</u>H_2), 71 (<u>C</u>H$(CH_3)_2$), 22,3 (<u>C</u>H_3).

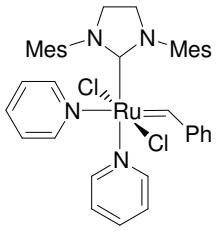
Dichloro (o-isopropoxyphenylmethylene) (tricyclohexylphosphine) ruthenium (II) **C15**



A solution of **Ll2** (115 mg, 0.71 mmol) in CH_2Cl_2 (6.7 mL) was added via cannula to 600 mg of **C5** (0.72 mmol) and CuCl (73 mg, 0.73 mmol). The reaction mixture was stirred at 40°C for 1.5 hr, after which the volatiles were removed in vacuo. The resulting solid residue was purified by silica gel chromatography (CH_2Cl_2) and the brown solid was then recrystallized in CH_2Cl_2/nC_5 1:10 to afford **C15** (245 mg, 56% yield).

^{31}P {^{1}H} NMR (122 MHz, $CDCl_3$): 58.85 (s, PCy_3). ^{1}H NMR (300 MHz, $CDCl_3$): 17.41 (d, J_{PH} = 4.6Hz, 1H, Ru=C<u>H</u>), 7.66 (ddd, 1H, C<u>H</u> Ar), 7.61 (ddd, 1H, C<u>H</u> Ar), 7.06 (m, 2H, C<u>H</u> Ar), 5.28 (m, 1H, OC<u>H</u>$(CH_3)_2$), 2.31-1.28 (m, 33H, C<u>H</u>$_3$, Cy). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 280.6 (Ru=<u>C</u>H), 152.99, 144.09, 129.79, 123.01, 122.67, 113, 52, 75.7, 35.84, 30.24, 26.43, 26.05, 22.24.

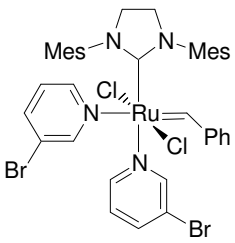
Benzylidene dichloro-(1,3-dimesityl-imidazolidinylidene) bispyridine ruthenium (II) **C72**



78 eq. of pyridine (3.3 mL, 41.3 mmol), drying before with 3Å molecular sieves, were added to a solution of Grubbs 2nd generation catalyst (0.45 g, 0.53 mmol) in toluene(1.1 mL). From the addition of the first drop of pyridine, a color change from pink to grren was observed. The reaction mixture was stirred for 10 minutes, then, it was cannula transferred into 30 mL of cold (-30°C) pentane. The green precipitate was filtered, washed twice with pentane (2 * 10 mL), and dried under vacuum to afford as a green powder (366 mg, 95% yield).

^{1}H NMR (300 MHz, CD_2Cl_2): 19.16 (s, 1H, Ru=C<u>H</u>), 8.62 (br s, 2H, py), 7.81 (br s, 2H, py), 7.6 (d, 2H, C<u>H</u> Ar), 7.48 (t, 1H, *p*-C<u>H</u>), 7.22-6.77 (m, 10H, CH Ar), 4.08 (br d, 4H, C<u>H</u>$_2$-N), 2.6 (br s, 6H, C<u>H</u>$_3$), 2.31 (br s, 6H, C<u>H</u>$_3$), 2.23 (br s, 6H, C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, CD_2Cl_2): 313.02 (Ru=<u>C</u>H), 218.14 (N<u>C</u>N), 152.36, 151.7, 150.25, 130.23, 130.11, 129.63, 128.18, 124.02, 51.96, 51.1, 21.19, 20.54, 18.43.

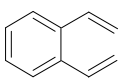
Benzylidene dichloro bis(3-bromopyridine)(1,3-dimesityl-imidazolidinylidene) ruthenium (II) **C73**



C73 was obtained in analogy to **C72**. 3-bromopyridine (10 eq.) was added to a solution of **C9**. The reaction mixture was stirred within minutes. After precipitation with pentane, the product was isolated in 85% yield as a green powder.

^{1}H NMR (300 MHz, CD_2Cl_2): 19.07 (s, 1H, Ru=CH), 8.64 (br d, 2H, 3-Br-py), 8.01 (br s, 2H, 3-Br-py), 7.78-6.79 (13H, Mes C<u>H</u>, C<u>H</u> Ar, 3-Br-py), 4.07 (br s, 4H, C<u>H</u>$_2$-N), 2.57-2.3 (m, 18, C<u>H</u>$_3$).

1,2 divinylbenzene **L13**

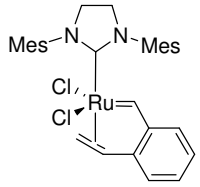


21 mL of lithium ethoxide (1M in EtOH, 21 mmol) was added, with stirring under argon, to a solution of *o*-xylylene-bistriphenylphosphonium bromide (6.65 g, 8.43 mmol) and formaldehyde (88 mg, 29.5 mmol) in absolute ethanol (30 mL). After 3 h, the yellow reaction mixture was concentrated. The resulting residue was dissolved in pentane (40 mL) and washed with water (20 mL). The organic layer was extracted, dried over

anhydrous Na_2SO_4. $OPPh_3$ was removed by flash chromatography on alumina (solvent: pentane). Evaporation of the solvent yielded the product **L13**, as a colorless oil (0.76g, 70%yield).

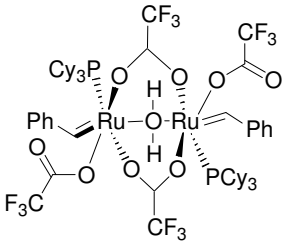
^1H NMR (300 MHz, $CDCl_3$): 7.46-7.26 (dd, 4H, CH Ar), 7.03 (dd, 2H, C<u>H</u>=CH_2), 5.63 (d, 2H, CH=C<u>H</u>$_2$), 5.33 (d, 2H, CH=C<u>H</u>$_2$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$): 136.2 (*ipso*-C), 134.96 (<u>C</u>H=CH_2), 127.93, 126.4 (<u>C</u>H Ar), 116.48 (CH=<u>C</u>H_2).

***Dichloro-(1,3-dimesityl-imidazolidinylidene) (2-vinylbenzene) ruthenium (II)* C76**



To a solution of **C72** (200 mg, 0.27 mmol) in toluene (5 mL) was added 45.4 mg of 1,2 divinylbenzène (0.30 mmol) in toluene (5 mL). The reaction was stirred for 2h at room temperature during which time a green precipitate is formed. The solid was filtered, washed with toluene (2 * 5 mL) and dried under vacuum overnight to give a green powder (150 mg, 92 % yield). ^1H spectrum is represented in Annexe **C**, page 282.

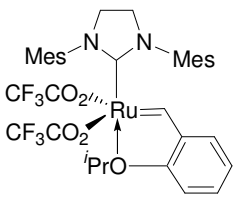
***µ-aquo-benzylidene(tricyclohexylphosphine)bis{(µ-trifluoroacetate)-(trifluoroacetate) ruthenium (II)}* C43**



A solution of 59.3 mg CF_3CO_2Ag (0.27 mmol) in THF (4 mL) was added to a solution of Grubbs 1st generation catalyst **C5** (110 mg, 0.13 mmol) in heptane (80 mL) at 0°C, in 15 minutes. The mixture was stirred for 1 h at 0°C and then it was filtered. The green filtrate was evaporated to dryness to yield a green powder (50 mg, 51% yield).

^{31}P {^1H} NMR (122 MHz, CD_2Cl_2): 42.85 (s, PCy_3). ^1H NMR (300 MHz, CD_2Cl_2): 20.69 (d, 2H, $^3J_{PH}$ = 5.7 Hz, Ru=C<u>H</u>), 11.77 (s, 2H, H_2O), 8.16 (d, $^3J_{HH}$ = 7.5 Hz, 4H, *o*-H Ar), 7.77 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *p*-H Ar), 7.45 (t, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-H Ar), 2.04-1.27 (m, 74H, PCy_3, C_7H_{16}). ^{13}C NMR was not realized due to instability of this complex at room temperature.

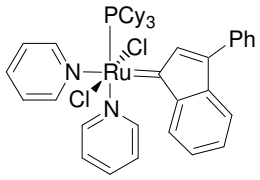
o-isopropoxyphenylmethylene - (1,3-dimesityl-imidazolidinylidene)- bistrifluoroacetate ruthenium (II) **C44**



A solution of 141.8 mg CF_3CO_2Ag (0.64 mmol) in THF (2 mL) was slowly added to the stirred solution of Hoveyda 2nd generation catalyst (200 mg, 0.32 mmol) in THF (10 mL). Stirring was continued for 30 minutes. A color change from green to lilac and the formation of a precipitate were observed. The precipitate was filtered off and the solution evaporated to dryness. The residue was redissolved in CH_2Cl_2 (1 mL), flashed over 5 cm silica gel and evaporated to dryness, giving lilac crystals (145 mg, 58% yield).

^{1}H NMR (300 MHz, CD_2Cl_2): 17.45 (br s, 1H, Ru=C<u>H</u>), 7.43 (m, 1H, *m*-C<u>H</u> Ar), 7.17 (s, 4H, Mes-C<u>H</u>), 7.1-7.08 (dd, 1H, *o*-C<u>H</u> Ar), 6.99 (td, 1H, *p*-C<u>H</u> Ar), 6.7 (d, 1H, *m*-C<u>H</u> Ar), 4.63 (sept., 1H, OC<u>H</u>$(CH_3)_2$), 4.12 (s, 4H, C<u>H</u>$_2$-N), 2.46 (s, 6H, *p*-CH_3), 2.26 (s, 12H, *o*-CH_3), 0.93 (d, 6H, OCH(C<u>H</u>$_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, CD_2Cl_2): 315.37 (Ru=<u>C</u>H), 209.64 (NCN), 159.98 (<u>C</u>=O), 153.61, 143.87 (*ipso*-C), 139.91 (*ipso*-C Mes), 139.26 (*o*-C Mes), 134.85 (*p*-C Mes), 130.79 (*p*-CH Ar), 130.62 (*m*-CH Mes), 123.69, 122.88, 111.47 (CH Ar), 74.95 (O<u>C</u>H$(CH_3)_2$), 51.79 (<u>C</u>H$_2$-N), 21.25 (*p*-CH_3), 20.35 (OCH(<u>C</u>H$_3)_2$), 17.99 (CH_3 Mes).

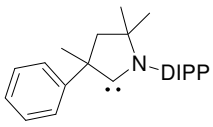
Dichloro-tricyclohexylphosphine-(3-phenyl-indenylidene)-bispyridine **C80**



251 mg of [$RuCl_2(PCy_3)_2$(3-phenylindenylidene)] (0.27 mmol) was dissolved in 0.5 mL of pyridine. The mixture was stirred 30 minutes at room temperature before adding 20 mL of hexanes. The mixture was again stirred 30 minutes at room temperature before cooling at -40 °C. The resulting precipitate was filtered, washed with hexanes (3 * 5 mL), and dried under vacuum to yield brownish red solid (214 mg, 98% yield).

^{31}P {^{1}H} NMR (122 MHz, C_6D_6): 23.9. ^{1}H NMR (300 MHz, CD_2Cl_2): 9.23 (3H), 8.63-7.64 (m, 8H), 6.98-6.21 (m, 7H), 2.43-0.51 (m, 33H, PCy_3).

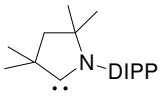
***1-(2,6-diisopropylphenyl)-2,2,4-trimethyl-4-phenyl-pyrrolidinylidene* L26**



A 1/3 mixture of iminium salt **L23** (208 mg, 0.49 mmol) and KHMDS was cooled to -78°C and THF was added (10 mL). The suspension was warmed to room temperature and stirred for 16h. After evaporation of the solvent under vacuum, the solid residue was extracted with cyclohexane (2 x 8 mL). **L26** was obtained as a white solid after removal of solvent and was conserved in a glovebox (95% yield).

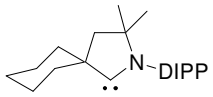
^{1}H NMR (300 MHz, C_6D_6): 7.84-7.26 (m, 8H, CH Ar), 3.18 (sept., 1H, C<u>H</u>$(CH_3)_2$), 2.04 (m, 1H, C<u>H</u>$(CH_3)_2$), 1.8 (s, 2H, C<u>H</u>$_2$-C), 1.51-1.02 (m, 21H, C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 310.5 (N<u>C</u>C), 150.6, 146 (d), 139.95, 127.16, 126.44, 124.21, 124.02, 82.08 (<u>C</u>H$(CH_3)_2$), 64.85, 51.47 (<u>C</u>H$_2$-C), 29.79, 29.44, 28.37, 28.12, 27.23, 26.63, 26.42, 21.94 (CH_3).

***1-(2,6-diisopropylphenyl)-2,2,4,4-tetramethyl-pyrrolidinylidene* L2**



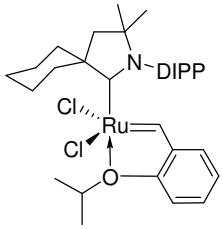
L2 was prepared from **L25,** in the same way as **L26**.

***1-(2,6-diisopropylphenyl)-2,2,-dimethyl-4-cyclohexyl-pyrrolidinylidene* L3**



L3 was prepared from **L24,** in the same way as **L26**.

Dichloro-{1-(2,6-diisopropylphenyl)-2,2-dimethyl-4-cyclohexyl-pyrrolidinylidene)} (o-isopropoxyphenylmethylene) ruthenium (II) C67

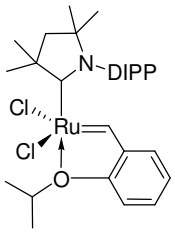


L24 (0.22 g, 0.55 mmol) and 3 eq. of KHMDS (0.33 g, 1.67 mmol) were dissolved at -78°C in THF (10 mL). The reaction mixture was stirring for 16h, then the solvent was evaporated. The solid residue was extracted with toluene (8 mL) and added to a vial containing Hoveyda 1st generation catalyst (49.5 mmol). The brown solution was stirring overnight at room temperature. After removal of solvent, the crude product was purified by flash column chromatography under argon (eluent: toluene/cyclohexane 9: 1). The desired product eluted as

a green band. Evaporation of the appropriate fractions afforded a green solid (73 mg, 22% yield).

^{1}H NMR (300 MHz, C_6D_6): 16.44 (s, 1H, Ru=C<u>H</u>), 7.25-7.22 (m, 1H, CH Ar), 7.16-7.13 (m, 2H, CH Ar), 7.01-6.88 (m, 1H, C<u>H</u> Ar), 6.53 (t, 1H, *p*-C<u>H</u> Ar), 6.31 (d, 1H, CH Ar), 4.54 (sept., 1H, (OC<u>H</u>$(CH_3)_2$), 3.65 (m, 2H, Cy), 3.09 (sept. 2H, C<u>H</u>$(CH_3)_2$), 2.38 (d, 2H, Cy), 1.8 (s, 2H, C<u>H</u>$_2$-C), 1.61 (d, 6H, OCH(C<u>H</u>$_3)_2$), 1.04 (d, 6H, CH(C<u>H</u>$_3)_2$), 0.88 (s, 6H, N-CC<u>H</u>$_3$), 0.81 (d, 6H, CH(C<u>H</u>$_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 291.51 (Ru=<u>C</u>H), 268.47 (N<u>C</u>C), 153.48, 148.98, 143.5, 137.2, 130.36, 129.58, 125.93, 123.75, 121.95, 113.53, 77.49, 75.02, 62.67, 44.43, 35.05, 30.14, 28.74, 27.01, 25.91, 24.43, 23.42, 22.24.
HRMS (FT-ICR) EI+ m/z: 645.2075 [M+].

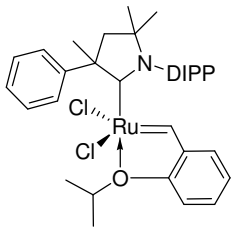
Dichloro-{1-(2,6 diisopropylphenyl)-2,2,4,4-tetramethyl-pyrrolidinylidene}
(*o*-isopropoxyphenylmethylene) ruthenium (II) C65



L25 (0.77 g, 2.16 mmol) and 3 eq. of KHMDS (1.292 g, 6.48 mmol) were dissolved in THF (40 mL) at -78°C. The reaction mixture was stirring for 16h and then the solvent was evaporated. The solid residue was extracted with cyclohexane (50 mL) and dried. A solution of Hoveyda 1st generation catalyst **C15** (1.66 mmol) in toluene (40 mL) was added to the vial containing the carbene. The brown solution was stirring overnight at room temperature. After removal of solvent, the crude product was washed with hexane (2 x 20 mL). The green solid thus obtained was filtered using a cannula filter and dried under vacuum (782 mg, 71% yield).

^{1}H NMR (300 MHz, C_6D_6): 16.44 (d, 1H, Ru=CH), 7.38-7.32 (m, 1H, *p*-CH DIPP), 7.25-7.23 (m, 2H, *m*-CH DIPP), 7.1-7.08 (m, 1H, *p*-C<u>H</u> Ar), 7.01-6.98 (dd, 1H, *o*-C<u>H</u> Ar), 6.63 (t, 1H, m-CH Ar), 6.42 (d, 1H, m-CH Ar), 4.65 (sept., 1H, OC<u>H</u>$(CH_3)_2$), 3.17 (sept., 2H, C<u>H</u>$(CH_3)_2$), 2.25 (s, 6H, C(C<u>H</u>$_3)_2$), 1.77 (s, 2H, CCH2), 1.71 (d, 6H, OCH(C<u>H</u>$_3)_2$), 1.14 (d, 6H, CH(C<u>H</u>$_3)_2$), 0.93 (s, 6H, N-CC<u>H</u>$_3$), 0.91 (d, 6H,CH(C<u>H</u>$_3)_2$).
^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 290.49 (Ru=<u>C</u>H), 268.6 (N<u>C</u>C), 153.5, 149.01, 143.35, 137.23, 130.3, 129.61, 125.94, 123.61, 121.96, 113.47, 77.47, 75.14, 56.49, 51.5, 29.6, 29.28, 28.75, 27, 24.4, 22.18.
HRMS (FT-ICR) EI+ m/z : 605.1767 [M+].

Dichloro-{1-(2,6 diisopropylphenyl)-2,2,4trimethyl-4-phenyl-pyrrolidene}(o-isopropoxyphenylmethylene) ruthenium (II) **C81**

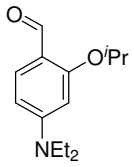


C81 was obtained with the procedure used to prepare **C65** (87% yield).

^{1}H NMR (300 MHz, C_6D_6): 16.59 (s, 1H, Ru=C<u>H</u>), 8.38 (d, *m*-CH Ar), 7.5 (m, 2H, *p*-CH Ar), 7.34-7.23 (m, 4H, CH Ar), 7.08-6.93 (m, 2H, CH Ar), 6.61 (t, 1H, *p*-CH), 6.37 (d, 1H, CH Ar), 4.51 (sept., 1H, OC<u>H</u>$(CH_3)_2$), 3.25 (sept., 2H, C<u>H</u>$(CH_3)_2$), 2.87 (d, 1H, CC<u>H</u>$_2$), 2.49 (s, 3H, C<u>H</u>$_3$), 1.93 (d, 1H, CC<u>H</u>$_2$), 1.52 (d, 3H, C<u>H</u>$_3$), 1.35 (d, 3H, C<u>H</u>$_3$), 1.21 (d, 3H, CH_3), 1.13 (d, 3H, CH_3), 1.05 (m, 9H, CH(C<u>H</u>$_3)_3$), 0.78 (d, 3H, C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 293.71, 266.23, 153.53, 149.17, 148.85, 143.54, 143.03, 137.48, 130.53, 130.38, 129.66, 129.09, 126.19, 125.91, 123.9, 121.77, 113.58, 77.13, 74.77, 63.39, 48.96, 29.18, 28.53, 28.44, 27.76, 26.73, 24.49, 24.38, 22.42, 22.28.

HRMS (FT-ICR) EI+ m/z : 667.1921 [M+]. Anal. Calcd for $C_{35}H_{48}Cl_2NORu$: C, 62.958; H, 6.79; N, 2.098. Found: C, 62.59; H, 6.85; N, 1.99.

4-diethylamino-2-isopropoxybenzaldehyde **L28**

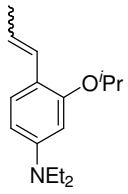


Solid powdered K_2CO_3 (15.42 g, 111.5 mmol) and $CsCO_3$ (4.04 g, 12.4 mmol) were placed in a round bottom flask. A solution of 4-diethylamino-2-hydroxybenzaldehyde (12 g, 62.1 mmol) in dry DMF (145.1 mL) was added. After stirring for 30 minutes 2-iodopropane (9.38 mL, 93.9 mmol) was added to the red solution. The reaction mixture was heated overnight at 50°C. After pouring onto a saturated aqueous solution of K_2CO_3 the reaction mixture was extracted with MTBE. The combined organic layers were washed with 1M solution of NaOH, water and then with brine. The dark red solution was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. **L28** was obtained as a dark red oil (12.45 g, 85.3% yield).

^{1}H NMR (300 MHz, C_6D_6): 10.78 (s, 1H, C<u>H</u>O), 8.17 (d, *J* = 8.5 Hz, 1H, C<u>H</u> Ar), 6.02 (dd, *J* = 8.91, 2.37 Hz, 1H, C<u>H</u> Ar), 5.91 (d, *J* = 2.32 Hz, 1H, C<u>H</u> Ar), 4.26 (sept, *J* = 6.1 Hz, 1H, OC<u>H</u>$(CH_3)_2$), 2.81 (q, *J* = 7.1 Hz, 4H, N(C<u>H</u>$_2$CH$_3)_2$), 1.07 (d, *J* = 6 Hz, 6H, OCH(C<u>H</u>$_3)_2$), 0.78 (t, *J* = 7.1 Hz, 6H, N(CH$_2$C<u>H</u>$_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 186.43 (<u>C</u>HO), 162.93 (<u>C</u>N$(CH_2CH_3)_2$), 153.4 (<u>C</u>OCH$(CH_3)_2$), 130.64 (<u>C</u>CHO), 120.26 (<u>C</u>H Ar), 116.75 (<u>C</u> Ar),

105.1, 95.73 (CH Ar); 70.75 ($O\underline{C}H(CH_3)_2$), 44.55 ($N(\underline{C}H_2CH_3)_2$), 21.91 ($OCH(\underline{C}H_3)_2$), 12.58 ($N(CH_2\underline{C}H_3)_2$).

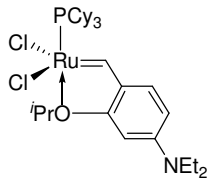
***N, N diethyl-N-{3-isopropoxy-4-[(E,Z)-1-propenyl]phenyl}amine* L27**



To a cold solution (0°C) of dry THF (300 mL) and ethyl(triphenyl)phosphonium bromide (27.39 g, 73.8 mmol) was added NaH (4.22 g, 105.4 mmol) under argon. The reaction mixture was heated at 70°C for two hours. After this period, the solution was cooled to -50°C and a solution of 4-diethylamino-2-isopropoxy-benzaldehyde (12.4 g, 52.7 mmol) in THF (40 mL) was dropwise added to the orange mixture. The reaction mixture was stirred overnight at room temperature. The product was extracted with ethyl acetate then washed with brine and dried over MgSO4. The solution was filtered then concentrated under reduced pressure. The crude product was purified by flash column chromatography with pentane/ethyl acetate (90:10) as eluent to afford **LX** as a yellow oil (13 g, 99.8% yield).

^{1}H NMR (300 MHz, C_6D_6): isomer (E) 7.19 (d, *J* = 8.61 Hz, 1H, CH Ar), 6.55 (dq, *J* = 15.77, 1.8 Hz, 1H, $C\underline{H}$=CH(CH_3)), 6.23 (m, 1H, CH Ar), 5.95 (m, 1H, CH=$C\underline{H}(CH_3)$), 4.4 (sept, *J* = 6Hz, 1H, $OC\underline{H}(CH_3)_2$), 3.27 (q, *J* = 7.1 Hz, 4H, $N(C\underline{H}_2CH_3)_2$), 1.8 (dd, *J* = 7, 1.8 Hz, 3H, CH=CH($C\underline{H}_3$)), 1.28 (d, *J* = 6Hz, 6H, $OCH(C\underline{H}_3)_2$), 1.1 (t, *J* = 7.11 Hz, 6H, $N(CH_2C\underline{H}_3)_2$); isomer (Z) 7.12 (d, *J* = 8.61 Hz, 1H, CH Ar), 6.43 (dq, *J* = 11.7, 1.8 Hz, 1H, $C\underline{H}$=CH(CH_3)), 6.23 (m, 1H, CH Ar), 5.55 (m, 1H, CH=$C\underline{H}(CH_3)$), 4.4 (sept, *J* = 6Hz, 1H, $OC\underline{H}(CH_3)_2$), 3.27 (q, *J* = 7.11 Hz, 4H, $N(C\underline{H}_2CH_3)_2$), 1.8 (dd, *J* = 7, 1.8 Hz, 3H, CH=CH($C\underline{H}_3$)), 1.28 (d, *J* = 6Hz, 6H, $OCH(C\underline{H}_3)_2$), 1.1 (t, *J* = 7.11 Hz, 6H, $N(CH_2C\underline{H}_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 157.49, 148.23, 131.43, 126.63, 120.24 , 122.86 (CH Ar), 116.82 (C Ar), 105.02, 100 (CH Ar); 70.8 ($O\underline{C}H(CH_3)_2$), 44.65 ($N(\underline{C}H_2CH_3)_2$), 22.37 ($OCH(\underline{C}H_3)_2$), 15.13, 12.87 ($N(CH_2\underline{C}H_3)_2$).

***Dichloride (o-isopropoxy-p-diethylamino-phenylmethylene) tricyclohexylphosphine ruthenium* C87**

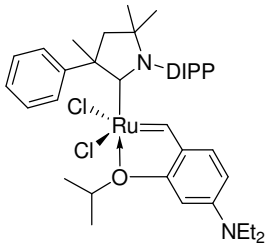


A solution of 496 mg (2 mmol) of **L27** in 40 mL of CH_2Cl_2 was added to a solution of 1.5 g (1.82 mmol) of benzylidene dichloride bis(tricyclohexylphosphine) ruthenium **C15** and 180 mg of CuCl in

5.75 mL of CH_2Cl_2. The resulting solution was stirred at 40°C for two hours. The reaction mixture was concentrated in vacuo and the residue was purified by column chromatography on silica. Elution with cyclohexane/ethyl acetate/triethyl amine (4:1:0.1) removed **C87** as a brown band. Removal of the solvent, three washing of cold hexane (20 mL) and drying under vacuum afforded **C87** as a brown solid (807 mg, 66% yield).

^{1}H NMR (300 MHz, C_6D_6): 17 (d, *J* = 4.3 Hz, 1H, Ru=C<u>H</u>), 7.38 (d, *J* = 8.7 Hz, 1H, C<u>H</u> Ar), 6.04 (m, 2H, C<u>H</u> Ar), 4.89 (sept, *J* = 6.2 Hz, 1H, OC<u>H</u>$(CH_3)_2$), 2.81 (q, *J* = 7.1 Hz, 4H, N($C\underline{H}_2CH_3)_2$), 2.49-1.07 (m, 39H, PCy_3, OCH($C\underline{H}_3)_2$), 0.82 (t, *J* = 7.1 Hz, 6H, N($CH_2C\underline{H}_3)_2$). ^{31}P {^{1}H} NMR (122 MHz, C_6D_6): 62.88. ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 274 (Ru=CH), 156.4, 149.7, 136.96, 124.85, 104.34, 96.91, 74.91 (O<u>C</u>H$(CH_3)_2$), 44.97 (N($\underline{C}H_2CH_3)_2$), 36.45, 36.12, 31.97, 30.65, 30.22, 28.24, 28.1, 26.78, 22.3 (OCH($\underline{C}H_3)_2$), 12.58 (N($CH_2\underline{C}H_3)_2$).
HRMS (FT-ICR) EI+ (CH_2Cl_2) m/z: 636.26 [M-Cl].

Dichloride-{1-(2,6-diisopropylphenyl)-2,2, 4-trimethyl- 4-phenyl- pyrrolidinylidene)} (o-isopropoxy-p-diethylamino-phenylmethylene) ruthenium **C89**



Iminium salt **L23** (374 mg 0.89 mmol) and three equivalents of KHMDS (536 mg, 2.68 mmol) in THF (15 mL) were stirred at room temperature for 16h. After evaporation of the solvent, the solid residue was extracted with cyclohexane (20 mL), and then the CAAC **L26** was obtained after removal of volatiles in vacuum. A solution of **C87** (0.5 g, 0.744 mmol) in toluene (15 mL) was added to **L26**. The reaction mixture was stirred at room temperature until complete disappearance of the initial complex in ^{1}H and ^{31}P NMR (10h). Removal of volatiles in vacuum afforded a brown powder that was dissolved in CH_2Cl_2 (40 mL) before filtration and concentration until 1-2 mL. The complex was obtained as a red brown powder by washing with cold hexane (3*20 mL) and dried under vacuum (435 mg, 79% yield).

^{1}H NMR (300 MHz, C_6D_6): 15.89 (s, 1H, Ru=C<u>H</u>), 8.45 (d, 2H, *m*-C<u>H</u> Ar), 7.55-7.42 (m, 2H, *p*-C<u>H</u> Ar), 7.34 (m, 6H, C<u>H</u> Ar), 6.77 (d, 1H, *o*-C<u>H</u> Ar), 4.64 (sept, 1H, OC<u>H</u>$(CH_3)_2$), 3.4 (sept, 2H, C<u>H</u>$(CH_3)_2$), 2.93 (d, 1H, NCC<u>H</u>$_2$), 2.69 (q, 4H, N($C\underline{H}_2CH_3)_2$), 2.56 (s, 3H, C<u>H</u>$_3$), 2 (d, 1H, NCC<u>H</u>$_2$), 1.65 (d, 3H, CH($C\underline{H}_3)_2$), 1.47 (d, 3H, CH($C\underline{H}_3)_2$), 1.4 (s, 3H, C<u>H</u>$_3$), 1.27 (d, 3H, CH($C\underline{H}_3)_2$), 1.21 (d, 3H, CH($C\underline{H}_3)_2$), 1.18 (d, 3H, CH($C\underline{H}_3)_2$), 1.15 (s, 3H, C<u>H</u>$_3$), 1.1 (d,

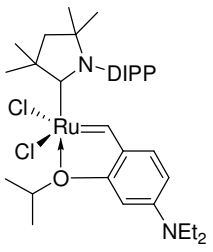
3H, $CH(C\underline{H}_3)_2$), 0.72 (t, 6H, $N(CH_2C\underline{H}_3)_2$). ^{13}C {^1H} NMR (75 MHz, C_6D_6): 289.61 (Ru=$\underline{C}$H), 268.66 (N$\underline{C}$C), 156.63, 150.82, 149.6, 149.26, 143.58, 138.05, 136.16, 130.38, 129.29, 129.21, 103.55, 96.28, 76.43, 73.91, 63.16, 49.25, 44.83, 36.24, 35.43, 32.28, 30.25, 29.2, 28.6, 28.08, 27.75, 27.34, 27.19, 27, 26.85, 24.6, 24.51, 22.6.
HRMS (FT-ICR) EI+ (C_6D_6) m/z: 777.23 [M+K], 738.26 [M], 703.29 [M-Cl], 667.32 [M-HCl_2], 348.26 [**L26**].

One pot synthesis of C89

203 mg of iminium salt **L23** (0.48 mmol) and 3 equivalents of KHMDS (290 mg, 1.45 mmol) in THF (15 mL) were stirred overnight at room temperature. The reaction solution was concentrated under vacuum. The carbene was extracted with cyclohexane (20 mL) and the solvent was removed under vacuum. Then, 67.8 mg of **L27** (0.27 mmol) in dichloromethane (10 mL) was added to 200 mg of **C5** (0.24 mmol) and 24 mg of copper chloride (0.24 mmol). After stirring at 40°C for two hours, the reaction solution was filtered and the solvent was removed under vacuum. The brown residue was dissolved in toluene (10 mL). The resulting solution was added via cannula to the schlenk containing the free carbene. The mixture was stirred for 10 hours and filtered. The volatiles were removed under vacuum and the residue was washed with cold hexane (3*5 mL). 162 mg of **C89** were obtained (90% yield).

Alternative synthesis

Dichloride-{1-(2,6-diisopropylphenyl)-2,2, 4,4-tetramethyl- pyrrolidinylidene)} (o-isopropoxy-p-diethylamino-phenylmethylene) ruthenium **C88**

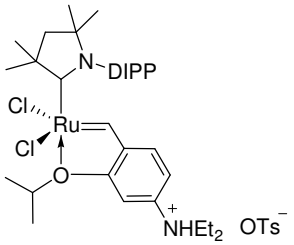


C65 (501 mg, 0.83 mmol) and 5 equivalents of **L27** were placed in a tricol flask and dissolved in toluene (20 mL). The flask was then connected to a condenser and an ethylene line. The reaction mixture was heated at 80°C with ethylene bubbling until complete disappearance of the initial complex is observed by ^1H NMR. The solvent was evaporated under vacuum, the residue was washed with hexane (3*20 mL). The resulting green precipitate was filtered and dried under vacuum to afford the catalyst as a green solid (420 mg, 75%).

^1H NMR (300 MHz, C_6D_6): 15.84 (s, 1H, Ru=C$\underline{H}$), 7.43 (m, 1H, *p*-C$\underline{H}$ Ar), 7.33 (m, 2H, *m*-C$\underline{H}$ Ar), 6.84 (d, *J* = 8.5Hz, 1H, *o*-C$\underline{H}$ Ar), 5.89-5.83 (dd, *J* = 11, 2.6 Hz, 2H, *m*-C$\underline{H}$ Ar), 4.8

(sept, *J* =6.1 Hz, 1H, OC<u>H</u>$(CH_3)_2$), 3.33 (sept, *J* = 6.7 Hz, 2H, C<u>H</u>$(CH_3)_2$), 2.7 (q, *J* = 7Hz, 4H, N($C\underline{H}_2CH_3)_2$), 2.74 (s, 6H, NC($C\underline{H}_3)_2$), 1.87 (s, NCC$\underline{H}_2$, 2H), 1.86 (d, *J* = 6.1 Hz, 6H, OCH($C\underline{H}_3)_2$), 1.21 (d, *J* = 6.6 Hz, 6H, CH($C\underline{H}_3)_2$), 1.07 (d, *J* = 6.4 Hz, 6H, CH($C\underline{H}_3)_2$), 1.04 (s, 6H, NCC($C\underline{H}_3)_2$), 0.75 (t, 6H, N($CH_2C\underline{H}_3)_2$). ^{13}C {^1H} NMR (75 MHz, C_6D_6): 287.06 (Ru=<u>C</u>H), 271.02 (N<u>C</u>C), 156.5, 154.9, 152.2, 150.6, 150.3, 149.4, 148.3, 137.8, 135.89, 129.3, 126.1, 125.8, 103.7, 96.3, 76.8 (O<u>C</u>H$(CH_3)_2$), 74.3 (<u>C</u>H$(CH_3)_2$), 56.2, 51.7 (NC<u>C</u>H_2), 44.9 (N($\underline{C}H_2CH_3)_2$), 29.8, 29.3, 28.8, 27.3, 24.5, 22.3, 12.5 (N($CH_2\underline{C}H_3)_2$).

***Dichloride-{1-(2,6-diisopropylphenyl)-2,2, 4,4-tetramethyl- pyrrolidinylidene)} (o-isopropoxy-p-diethylammonium-phenylmethylene) tosylate ruthenium* C90**



42.8 mg of PTSA.H_2O (0.22 mmol) was added to a solution of complex **C88** (150 mg, 0.22 mmol) in dichloromethane (12 mL). The initially red brown reaction mixture becomes rapidly green. This mixture was stirred for 30 min then evaporated under vacuum. The green residue was washed with hexane and dried under vacuum to afford **C90** as a green solid (169 mg, 90%).

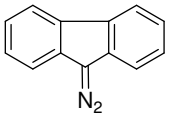
^1H NMR (300 MHz, CD_2Cl_2): 16.27 (s, 1H Ru=C<u>H</u>), 12.20 (br s, 1H N<u>H</u>($CH_2CH_3)_2$), 7.72 (d, *J* = 8.1 Hz, 2H, C<u>H</u> Ar), 7.64 (t, *J* = 7.7 Hz, 1H, *p*-C<u>H</u> Ar), 7.47 (d, *J* = 7.7 Hz, 2H, C<u>H</u> Ar), 7.43 (s, 1H, C<u>H</u> Ar), 7.20 (d, *J* = 7.9 Hz, 2H, C<u>H</u> Ar), 6.97 (s, 2H, C<u>H</u> Ar), 5.15 (sept, *J* = 6.1 Hz, 1H, OC<u>H</u>$(CH_3)_2$), 3.63 (br s, 2H, NC$\underline{H}_2CH_3$), 3.36 (br s, 2H, NC$\underline{H}_2CH_3$), 2.95 (sept, *J* = 6.5 Hz, 2H, C<u>H</u>$(CH_3)_2$), 2.37 (s, 3H, Ar-C$\underline{H}_3$), 2.19 (s, 2H, NCC$\underline{H}_2$), 2.08 (s, 6H, NCC($C\underline{H}_3)_2$), 1.70 (d, *J* = 6.1 Hz, 6H, OCH($C\underline{H}_3)_2$), 1.35 (s, 6H, NC($C\underline{H}_3)_2$), 1.26 (d, *J* = 6.7 Hz, 6H, CH$(CH_3)_2$), 1.17 (t, *J* = 7.2 Hz, 6H, NH($CH_2C\underline{H}_3)_2$), 0.64 (d, *J* = 6.4 Hz, 6H, CH($C\underline{H}_3)_2$).^{13}C {^1H} NMR (75 MHz, CD_2Cl_2): 288.3 (Ru=<u>C</u>H), 265.5 (N<u>C</u>C), 153.7, 148.6, 142.8, 140.7, 136.8, 130.0, 129.2, 126.2, 124.6, 78.7 (O<u>C</u>H$(CH_3)_2$), 77.4 (<u>C</u>H$(CH_3)_2$), 56.5, 51.7 (NC<u>C</u>H_2), 30.0 (NH($\underline{C}H_2CH_3)_2$), 29.3, 28.7, 26.6, 24.4, 22.1, 21.4, 10.5 (NH($CH_2\underline{C}H_3)_2$). HRMS (FT-ICR) EI+ (C_6D_6) m/z: 676.249 [M-(HOTs+H)] EI- (C_6D_6) m/z: 171.01 [OTs].

***Manganese oxide on silica* L44**

$$2\ MnO_4^- + 3\ Mn^{2+} + 2H_2O \xrightarrow[60\,°C]{SiO_2} 5\ MnO_2 + 8H^+$$

To a solution of $KMnO_4$ (3.79 g, 24 mmol) in H_2O (60 mL) was added silica gel (60.4 g Merck, 70-230 mesh) and H_2O was evaporated at 60°C under reduced pressure. The resulting brown powder was added to a vigorously stirred solution of $MnSO_4.4\text{-}5H_2O$ (9.32 g) in H_2O (100 mL) and the mixture was stirred for 1h. The dark brown solid was filtered, washed with H_2O, and dried at 60°C in vacuo (47 g).

***9-diazofluorene* L29**



Fluorenone hydrazone (4 g, 20 mmol) was dissolved in dry ether (60 mL). To the orange solution were added anhydrous sodium sulphate (1 g, 7.3 mmol) and 1 mL of a freshly prepared, concentrated solution of potassium hydroxide in ethanol. Then, mercuric oxide (15 g, 69.4 mmol) was added and the mixture was stirred 6h in the dark. The red solution was filtered; the residue was washed with ether. The washing were combined with the ethereal solution which was then concentrated under reduce pressure. Red needles were obtained (2.89 g, 73% yield).

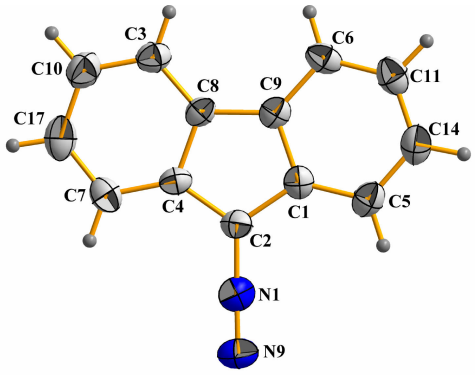
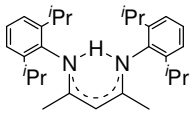


Figure 1 : *ORTEP diagram of a molecule of **L29** with the thermal ellipsoids at the 30% probability level.*

mp_{exp}: 96°C (94-95°C[1]). IR: 2049 cm^{-1} (C=N). GC-MS m/z: 328 [(**L29**)$_2$-N_4].

^1H NMR (300 MHz, C_6D_6): 7.73-7.7 (dm, 2H, H_7, H_5), 7.13-7.1 (dm, 2H, H_{17}, H_{10}), 7.-7.1 (dt, 2H, H_{14}, H_{11}), 7.04-6.93 (dt, 2H, H_3, H_6). ^{13}C {^1H} NMR (75 MHz, C_6D_6): 141.87 (C_2), 141.5, 138.78, 133.35, 131.9, 129.38, 127.15, 124.75, 121.21, 120.19, 119.61.

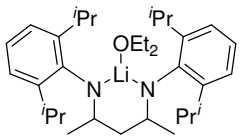
***β-diimine* L37**



Concentrated HCl (4 mL, 48 mmol) was added to a solution of 2,4-pentanedione (5 mL, 49 mmol) and 2,6-diisopropylaniline (21.2 mL, 110 mmol) in ethanol (200 mL). The pinkish reaction mixture was heated at reflux for 3 days and then concentrated to a brown residue. The crude product was dissolved in methylene chloride (75 mL) then a saturated solution of sodium carbonate (60g in 200 mL H_2O) was added. After stirring vigorously for 15 minutes, the organic layer was extracted. Evaporation of solvent and recrystallization from methanol afforded **L37** as a white crystalline solid (14.41 g, 71% yield).

^{1}H NMR (300 MHz, C_6D_6): 12.47 (br s, 1H, N<u>H</u>), 7.14 (m, 6H, 2,6-^{i}Pr$_2$C$_6$<u>H</u>$_3$), 4.89 (s, 1H, H$_\beta$), 3.32 (sept, 4H, C<u>H</u>(CH$_3$)$_2$), 1.67 (s, 6H, α-CH$_3$), 1.22 (d, 12H, CH(C<u>H</u>$_3$)$_2$), 1.17 (d, 12H, C<u>H</u>(CH$_3$)$_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 161.54 (C$_\alpha$), 142.81 (*ipso*-C), 141.28 (*o*-C), 125.88 (*p*-C), 123.61 (*m*-C), 94.3 (C$_\beta$), 28.66, 24.51, 23.46 (<u>C</u>H(CH$_3$)$_2$), 20.8 (*α*-CH$_3$).
GC-MS m/z: 418.34 (calc. 418.335).

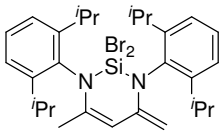
***Lithien β-diketiminato* L38**



A solution of methyllithium (17 mL, 1.26 M in diethyl ether) was added dropwise to a stirred solution of **L37** (10g, 23.9 mmol) in n-hexane (48 mL) at -78°C. The yellow reaction mixture was warmed to room temperature and was stirred for 4 h. After filtration, the filtrate was concentrated. Storage of the filtrate overnight, at -78°C, afforded colorless crystals of **L38** (11.6 g, 97%).

^{1}H NMR (300 MHz, C_6D_6): 7.19-7.07 (m, 6H, 2,6-^{i}Pr$_2$C$_6$<u>H</u>$_3$), 5.02 (s, 1H, H$_\beta$), 3.46-3.32 (sept, 4H, C<u>H</u>(CH$_3$)$_2$), 2.81-2.74 (q, 4H, O(C<u>H</u>$_2$CH$_3$)$_2$), 1.91 (s, 6H, CH$_3$), 1.28 (d, 12H, CH(C<u>H</u>$_3$)$_2$), 1.22 (d, 12H, CH(C<u>H</u>$_3$)$_2$), 0.48 (t, 6H, O(CH$_2$C<u>H</u>$_3$)$_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 163.91, 149.88 (N<u>C</u>-2,6-^{i}Pr$_2$C$_6$H$_3$), 140.91, 123.39, 123.12 (<u>C</u>H); 93.03 (C$_\beta$), 63.55 (O(<u>C</u>H$_2$CH$_3$)$_2$), 28.15 (<u>C</u>H(CH$_3$)$_2$), 24.31, 23.82, 23.45 (CH(<u>C</u>H$_3$)$_2$), 13.54 (O(CH$_2$<u>C</u>H$_3$)$_2$).

***Silyl dibromide* L39**

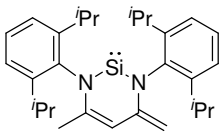


To a cooled (-60°C) solution of compound **L38** (1.22 g, 2.44 mmol) and N, N, N', N'-tetramethylethylenediamine (0.37 mL, 2.44 mmol) in diethyl

ether (14.3 mL) was dropwise added $SiBr_4$ (0.3 mL, 2.44 mmol) with stirring. The reaction mixture was slowly warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue extracted with n-hexane (35.7 mL). Filtration and subsequent concentration afforded, after 24 h of cooling at -30°C, yellow crystals of **L39** (1.07 g, 73% yield).

^{1}H NMR (300 MHz, C_6D_6): 7.3-7.21 (m, 6H, 2,6-^{i}Pr$_2$C$_6$H$_3$), 5.5 (s, 1H, H_β), 4.07 (s, 1H, NCCH_2), 3.84 (sept, 2H, CH(CH$_3$)$_2$), 3.55 (sept, 2H, CH(CH$_3$)$_2$), 3.44 (s, 1H, NCCH_2), 1.5 (s, 3H, NCCH_3), 1.45 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.43 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.38 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 149.1 (NC-2,6-^{i}Pr$_2$C$_6$H$_3$), 148.93, 146.43, 140.5, 136.06, 133.96, 129.11, 128.7, 125.55, 124.81; 108.79 (C_β); 90.78 (NCCH$_2$); 29.14, 28.99 (CH(CH$_3$)$_2$); 26.31, 25.54, 24.77, 24.51 (CH(CH_3)$_2$); 21.65 (NCCH$_3$). ^{29}Si {^{1}H} NMR (79.46 MHz): -53.

***Silylene* L36**



A cooled (-60°C) solution of **L38** (674 mg, 1.1 mmol) in THF (9.5 mL) was transferred in a cooled (-60°C) schlenk containing KC_8 (392 mg, 2.9 mmol). After 3 h stirring at -60°C, the reaction mixture was warmed to room temperature. Volatiles were removed in vacuo and the dark residue extracted with n-hexane (20 mL). Filtration and subsequent concentration afforded, after 5 h at -50°C, yellow crystals of **L36** (391 mg, 79% yield).

^{1}H NMR (300 MHz, C_6D_6): 7.22-6.98 (m, 6H, 2,6-^{i}Pr$_2$C$_6$H$_3$), 5.4 (s, 1H, H_β), 3.88 (s, 1H, NCCH_2), 3.62 (sept, 2H, CH(CH$_3$)$_2$), 3.44 (sept, 2H, CH(CH$_3$)$_2$), 3.28 (s, 1H, NCCH_2), 1.31 (s, 3H, NCCH_3), 1.30 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.28 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.24 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.12 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(CH_3)$_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 147.9 (NC-2,6-^{i}Pr$_2$C$_6$H$_3$), 147.8, 139.5, 137.3, 137.2, 128.5, 124.7, 124.1, 108.5 (C_β); 85.2 (NCCH$_2$); 28.6, 28.5 (CH(CH$_3$)$_2$); 25.4, 25.3, 24.6, 23.3 (CH(CH_3)$_2$); 21.4 (NCCH$_3$).

III Crystallographic data and structure refinement details

A suitable crystal was mounted on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Intensities were collected at 295, 208 and 120K by means of the COLLECT software[2]. Reflection indexing, Lorentz-polarization correction, peak integration, and background determination were carried out with DENZO[3]. Frame scaling and unit-cell parameters refinement were made with SCALEPACK[3]. An analytical absorption correction was applied using the modeled faces of the crystal[4]. The structures were solved by direct methods with SIR97[5]. The remaining non-hydrogen atoms were located by successive difference Fourier map analyses. H-atoms were placed geometrically and included in the refinement using soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93-0.98 Å and O-H = 0.82 Å) and isotropic atomic displacement parameters (U(H) in the range 1.2-1.5 times $U_{eq.}$ of the adjacent atom). In the last cycles of the refinement, the hydrogen atoms were refined using a riding mode. The structure refinement was carried out with CRYSTALS.21.

Compound	**C81**	**C89**	**C88**	**C90**
Formula	$C_{35}H_{44}Cl_2NORu$	$C_{39}H_{54}Cl_2N_2ORu$	$C_{34}H_{52}Cl_2N_2ORu$	$C_{34}H_{53}Cl_2N_2ORu{\cdot}C_7H_7O_3S$
Formula weight	666.72	738.85	676.78	848.98
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P12$_1$/n1*	*P-1*	*P2$_1$/c*	*P2$_1$/c*
a (Å)	9.4526(2)	9.9220 (10)	13.6527 (7)	15.1095 (3)
b (Å)	17.4474(3)	10.7100 (10)	14.2599 (7)	10.5586 (2)
c (Å)	19.7965(5)	19.256 (2)	17.9830 (10)	27.7712 (6)
α (°)		83.876 (8)		
β (°)	98.9298 (11)	88.147 (8)	102.040 (5)	91.340 (2)
γ (°)		68.777 (9)		
Volume (Å^3)	3225.33 (12)	1896.5 (3)	3424.0 (3)	4429.27 (15)
Z	4	2	4	4
Density$_{calc}$ (g cm^{-3})	1.373	1.294	1.313	1.273
μ (Mo Kα) (mm^{-1})	0.68	0.59	0.64	0.56
F(000)	1388	776	1424	1784
Crystal size (mm)		0.14 × 0.03 × 0.02	0.21 × 0.16 × 0.12	0.12 × 0.06 × 0.05
Data collection				
Temperature (K)	150	293	293	293
Theta min - max		2.6 – 26.7	2.7 - 29.2	2.7 – 29.2
Index ranges [h, k, l]	-12/12, -22/20, -26/26	-11/12,-9/12,-23/23	-18/18, -19/19, -24/23	-18/20, -14/11, -37/35
Tot., Uniq. Data, R(int)	14868, 7678, 0.035	11261, 1599, 0	32979, 8364 0.049	42041, 10641, 0.032
Observed. Refl. [I>2σ(I)]	6118	2399	6038	7465
Refinement		Full-matrix least-squares on F^2		
Data / restraints / parameters	7658 / 0 / 361	6236 / 1 / 406	8345 / 23 / 379	10615 / / 460
Goodness-of-fit on F^2	0.95	0.88	0.99	0.90
R[I>2σ(I)]	0.068	0.072	0.037	0.042
wR2[I>2σ(I)]	0.178	0.232	0.105	0.084
Largest diff. peak and hole	4.76 and -2.97 e.Å^{-3}	1.64 and -1.28 e.Å^{-3}	0.98 and –0.84 e.Å^{-3}	0.74 and -1.17 e.Å^{-3}

Compound	**C87**	**L29**
Formula	$C_{32}H_{54}Cl_2NOPRu$	$C_{13}H_8N_2$
Formula weight	671.73	192.22
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$
a (Å)	10.4995 (4)	10.98
b (Å)	16.6280 (10)	5.52
c (Å)	19.8800 (10)	16.38
α (°)	75.071 (5)	
β (°)	86.996 (4)	94.06
γ (°)	88.182 (4)	
Volume (Å^3)	3348.4 (3)	990.80927 (7)
Z	4	4
Density$_{calc}$ (g cm^{-3})	1.332	1.289
μ (Mo Kα) (mm^{-1})	0.70	0.08
F(000)	1416	400
Crystal size	0.09 × 0.08 × 0.02	
Data collection		
Temperature (K)	293	293
Theta min - max	2.7 – 29.2	3.7 – 29.5
Index ranges [h, k, l]	-12/13, -7/20, -14/25	-14/9, -5/5, -21/6
Tot., Uniq. Data, R(int)	9660, 7931, 0.035	1938, 1343, 0.026
Observed. Refl. [$I>2\sigma(I)$]	5042	729
Refinement	Full-matrix least-squares on F^2	
Data / restraints / parameters	7912 / 26 / 685	1340 / 19 / 272
Goodness-of-fit on F^2	0.81	0.87
R[I>2σ(I)]	0.041	0.034
wR2[I>2σ(I)]	0.086	0.089
Largest diff. peak and hole	1.04 and -0.59 e.Å^{-3}	

IV Ethenolysis of methyl oleate (batch reaction procedure)

All catalytic reactions were carried out in a magnetically stirred (~ 1600 rpm) 50 mL stainless steel autoclave.

The evacuated reactor was heated to 23°C. Methyl oleate and dodecane were degassed by freeze pumping thaw prior to use. 19. 25 mL of a solution containing methyl oleate (1.15 mL, 3.3 mmol), dodecane (0.25 mL, 1.1 mmol, internal standard) and docosane (80 mg, 0.25 mmol, internal standard) in toluene (20 mL) was charged in the autoclave. The ruthenium catalyst was then dissolved in toluene (10 mL). 2 mL of the catalyst solution (0.1 % mol Ru) was introduced in one portion to the reactor.

The reactor was pressurized to the desire pressure during 1 min and heated via computerized temperature controller to the desire temperature. The reaction was monitored by sampling via a shutoff valve through a tube inserted into the reaction mixture. The sample was quenched with excess butyl vinyl ether.

After 1.5 h, the autoclave was cooled down at room temperature. At t = 2h, the reaction mixture was collected in a recipient containing butyl vinyl ether.
Aliquot of liquid effluent was filtered on celite then analyzed through gas chromoatography.

Conversions and selectivity were determined on an Agilent Technologies 6890 Plus instrument using a BPX70 column (50 m x 0.32 x 0.25 µm film thickness) and a flame ionization detector (FID).

The following conditions were used: inlet temperature of 280°C and detector temperature of 300°C were used with the following temperature ramp (39 min):
Starting temperature, 80°C; ramp rate 1, 3°C/min to 100°C ; ramp rate 2, 5°C/min to 150°C ; ramp 3, 10°C/min to 220 °C ; hold time 1, 15 min.

Catalytic runs were performed for 2h at 50°C, 10 bar ethylene in 21.5 mL of toluene, 0.13% mol Ru (unless otherwise stated).

V Self-metathesis of methyl oleate (representative procedure)

A 50 mL two-necked round bottom flask was fitted with a reflux condenser, and connected to argon. Methyl oleate (3.5 mmol) wich was degassed before use by freeze pumping thaw was added to the reaction vessel and the reaction was heated to the desired temperature. 2 mL of catalyst solution (3.5 mmol in toluene) was then added. At the end of the reaction (t=2h), excess of butyl vinyl ether was introduced. After cool down the flask at room temperature, 0.25 mL of dodecane (1.1 mmol, internal standard) was added. Aliquot of the liquid was filtered and analyzed by gas chromatography.

VI Appendix

Appendix A: Ethenolysis of methyl oleate, literature data

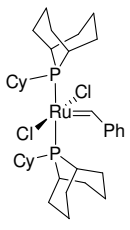
Appendix B: Summary of synthesized complexes

Appendix C: RMN ^{1H} spectrum of complex C76

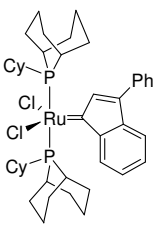
Appendix A: Ethenolysis of methyl oleate, literature data

Ref.	Catalysts	Conditions	metal /substrat	Conversion (%)	Selectivity (%)	TON
6	WCl_6-Me_4Sn	2 bar, 70°C, 20h	50	57		
6	WCl_6-Me_4Sn	2 bar, 20°C, 20h	50	67	63	
6	Re_2O_7-Al_2O_3	2 bar, 70°C, 20h	50	68	57	
7	WCl_6-Me_4Sn	50 bar, 5h	1/20	66	97	
7	WCl_6-Me_4Sn	2 bar, 5h	1/20	62	76	
7	Re_2O_7-Al_2O_3	50 bar, 5h	1/20	91	99	
7	Re_2O_7-Al_2O_3	2 bar, 5h	1/20	84	87	
8	$RuCl_2(PCy_3)_2$(=CH-CH=CPh_2) **C2**	6.9 bar, 20°C, 12h	1/152	94	47.3	
9	$RuCl_2(PCy_3)_2$(=CHPh) **C5**	10 bar, 50°C, 2h	1/4 000	58-74		2320-2960
10	**C5**	10 bar, 60°C, 2h	1/3 333	14	91	4247
11	**C5**	4.1 bar, 30°C, 20h	1/ 100 000	18	95	15400
12	**C5**	4,1 bar, 30°C, 3h	1/4 500	48		
13	**C5**	10 bar, 40°C, 2h	1/10 000	58	93	5400
14	**C5**	10 bar, 60°C, 30 min	1/10 000	54	89	4800
15	**C5**	1 bar, 70°C, 3h30	1/40	45	91	
10	$RuCl_2$(SIMes)(PCy_3)(=CHPh) **C9**	10 bar, 60°C, 2h	1/3 333	37	58	7153
13	**C9**	10 bar, 40°C, 2h	1/10 000	64	44	2800
14	**C9**	10 bar, 60°C, <15 min	1/10 000	64	44	2800
12	$RuCl_2(PCy_3)$(=CH-O-^{i}PrC_6H_4) **C15**	4,1 bar, 30°C, 3h	1/4 500	57		
13	**C15**	10 bar, 40°C, 30 min	1/10 000	51	94	4800
15	**C15**	1 bar, 70°C, 3h30	1/40	91	97	
15	**C15**	1 bar, 20°C, 1h	1/40	93	100	

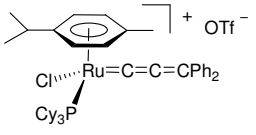
Ref.	Catalysts	Conditions	metal /substrat	Conversion (%)	Selectivity (%)	TON
13	$RuCl_2$(SIMes)(=CH-O-^{i}PrC_6H_4) **C22**	10 bar, 60°C, 30 min	1/10 000	60	33	2000
10	$RuCl_2$(Cy-phoban)$_2$(=CHPh) **C47**	10 bar, 60°C, 2h	1/3 333	43	98	14047
16	**C47**	10 bar, 55°C,	1/3 333	36		
17	$RuCl_2$(Cy-phoban)$_2$(3-Ph-indenylidene) **C75**	10 bar, 50°C, 2h	1/20 000	64	97	12450
14	$RuCl_2$(SIMes)(py)$_2$(=CHPh) **C72**	10 bar, 40°C, 15 min	1/10 000	50		329
15	$RuCl_2PCy_3$(p-cymene) $(=C=C=CPh_2)^+$ OTf^- **C45**	1 bar, 70°C, 3h30	1/40	25	78	
15	0.5 $RuCl_2$(p-cymene) + SIMesH.Cl +Cs_2CO_3	1 bar, 70°C, 3h30	1/40	97	37	
14	$RuCl_2$(SIMes)(PCy_3)(=CH-$PCy_3^+BF_4^-$) **C97**	10 bar, 60°C, 4h	1/10 000	77	66	5200
14	**C97**	10 bar, 40°C, 20h	1/10 000	71	59	4200
14	$RuCl_2$(**L2**)(PCy_3)(=CH-$PCy_3^+BF_4^-$) **C98**	10 bar, 40°C, 22h	1/10 000	60	90	5440
13	$RuCl_2$(**L2**)(=CH-O^{i}Pr-C_6H_4) **C65**	10 bar, 40°C, 22h	1/10 000	61	92	5600
13	**C65**	10 bar, 40°C, 20h	1/20 000	61	93	11400
13	$RuCl_2$(**L3**)(=CH-O^{i}Pr-C_6H_4) **C67**	10 bar, 40°C, 6h	1/10 000	46	94	4200
14	$RuCl_2$(CAAC)(=CH-O^{i}Pr-C_6H_4) **C66**	10 bar, 40°C, <30min	1/10 000	73	73	5300
14	**C66**	10 bar, 40°C, <30min	1/100 000	42	83	35000



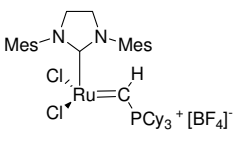
C47



C75



C45



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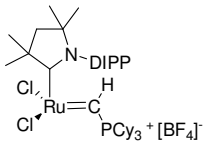

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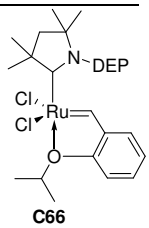
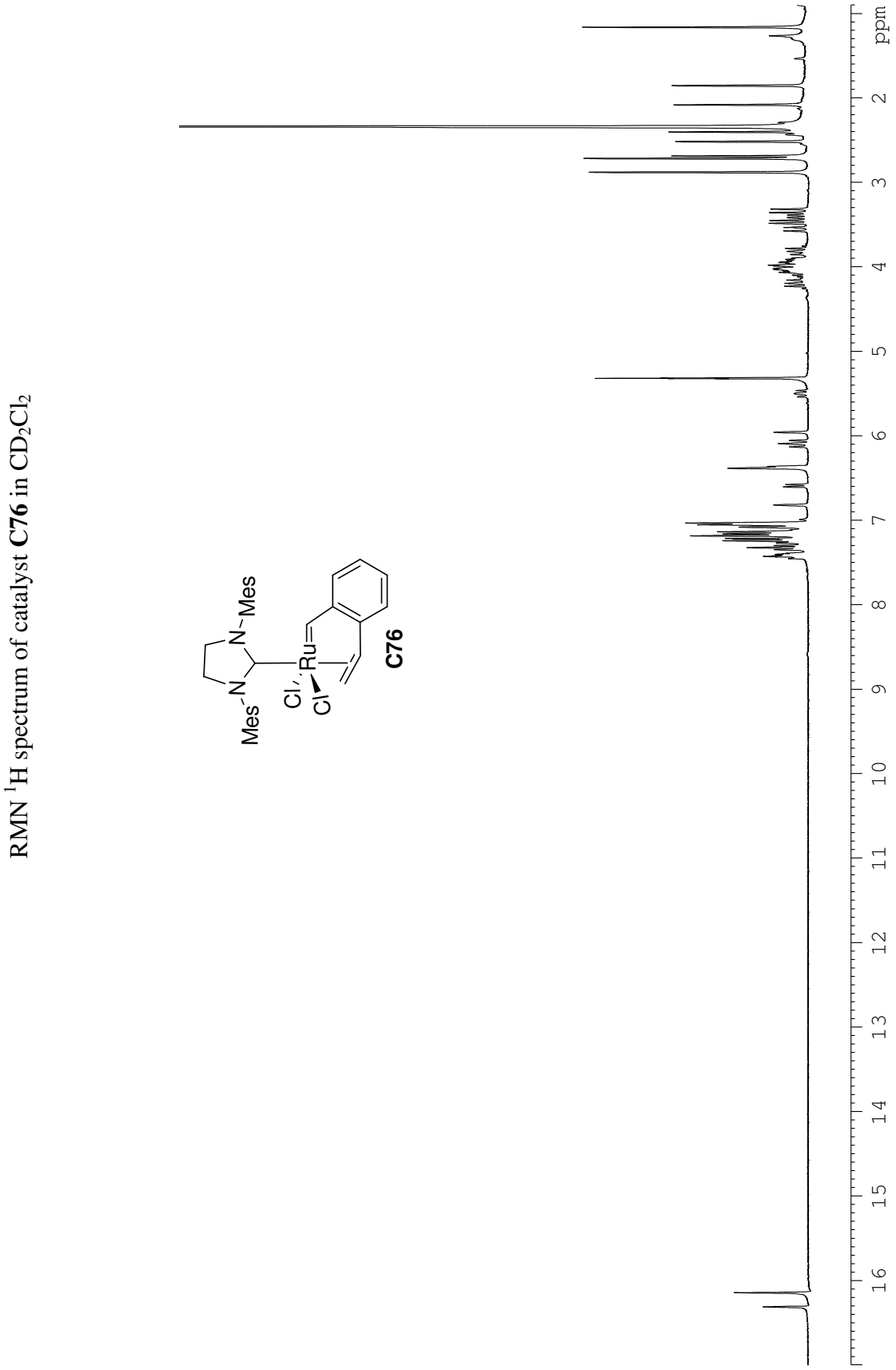


C66

Mes = 2,4,6- trimethylphenyl
DIPP = 2,6-diisopropylphenyl
DEP = 2,6-diethylphenyl

Appendix B: Summary of synthesized complexes

Appendix C: RMN ^{1}H spectrum of complex C76



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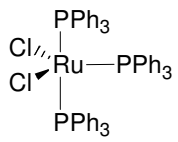
Appendix B: Summary of synthesized complexes



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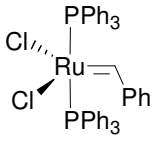

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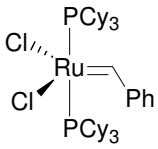
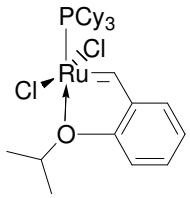
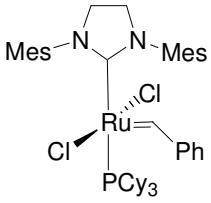


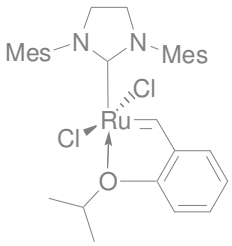
C5



C15



C9



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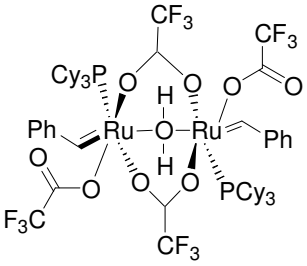

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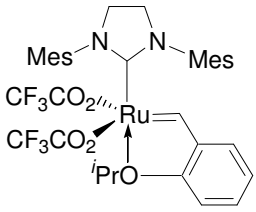

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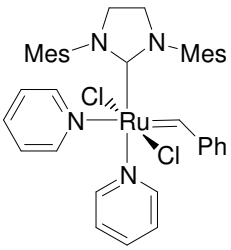

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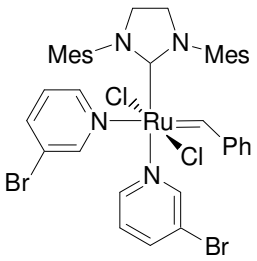

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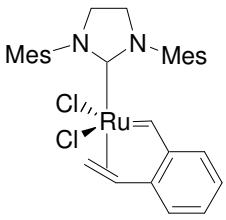
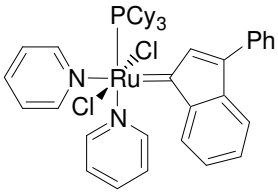
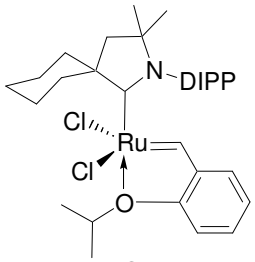


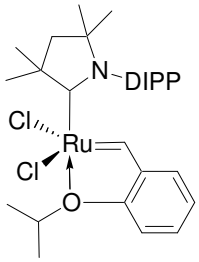
C76



C80



C67



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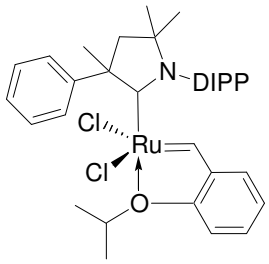

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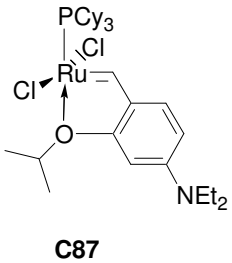
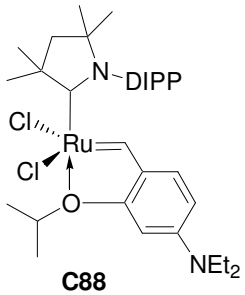
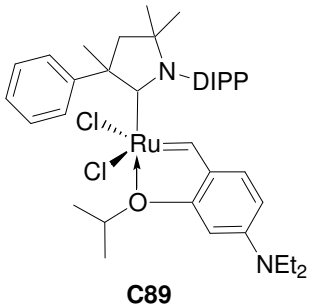


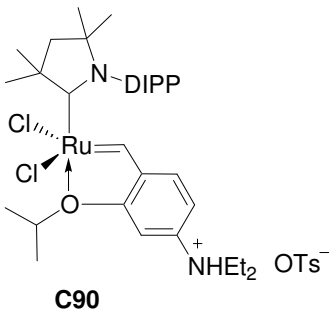
C87



C88



C89



C90

Mes = 2,4,6-trimethylphenyl DIPP = 2,6-diisopropylphenyl