Supporting Information

Unsymmetrical Ru-NHC Catalysts: A Key for the Selective Tandem Ring Opening - Ring Closing Alkene Metathesis (RO-RCM) of Cyclooctene.

Santosh Kavitake,[a] Manoja K. Samantaray, [a] Richard Dehn,[b] Michael Limbach,[b,c] Jörg A. Schachner,[c] Erwan Jeanneau,[d] Christophe Copéret,*[,a,e] Chloé Thieuleux*[,a].

[a] Université de Lyon, C2P2, UMR 5265 (CNRS -CPE Lyon – Université Lyon 1), 43 Bd. du 11 Novembre 1918, 69616 Villeurbanne Cedex France, [b] BASF SE, Basic Chemicals Research, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany, [c] CaRLa – Catalysis Research Laboratory, Im Neuenheimer Feld 584, 69120 Heidelberg, Germany, [d] Centre de Diffractométrie Henri Longchambon - Université Lyon 1, 43, Bd du 11 Novembre 1918 F-69616 Villeurbanne, France, [e]ETH Zürich, Department of Chemistry, Wolfgang-Pauli-Str. 10, CH-8093 Zurich, Switzerland

email: ccoperet@inorg.chem.ethz.ch; thieuleux@cpe.fr

General Information. All experiments for introduction of metal complex and catalytic performances were carried out under Ar using standard Schlenk techniques, using freshly distilled and degassed solvents. Toluene was freshly distilled over NaK under Ar in presence of benzophenone ketyl. $[K(N(SiMe_3)_2]$ (0.5M in toluene and Grubbs I catalyst $(Cl_2(PCy_3)_2Ru(=CHPh))$ were bought from Sigma-Aldrich.

Nuclear Magnetic Resonance Spectroscopy. Liquid state NMR spectra were recorded using a Bruker AC 300.

Gas Chromatography: Gas phase analyses (metathesis of cyclooctene) were performed on a Hewlett Packard 7890 A series II GC apparatus equipped with a FID detector and a HP5 column (30m X 0.25 mm).

Experimental procedures:

Synthesis of unsymmetrical homogeneous complexes:

Synthesis of RuPr. To a solution of 1-mesityl-3-propylimidazolium iodide (0.5 g, 1.4 mmol) in 5 mL of toluene was added 2.8 mL (1.4 mmol) of a 0.5 M toluene solution of $[K(N(SiMe_3)_2]$. A white precipitate was formed, after stirring for 20 min, then a solution of $Cl_2(PCy_3)_2Ru(=CHPh)$ (0.98 g, 1.2 mmol) in 10 mL of toluene was added. The reaction mixture, was stirred for 3 h and then filtered over Celite. The solvent was removed under vacuum and the residual solid product was crystallized in toluene and pentane to give 0.64 g of **RuPr**. ^1H NMR (CD_2Cl_2, 300 MHz): δ (ppm)= 19.26 (s, 1H), 7.9 (br, 1H), 7.45 (t, 1H, *J* = 7.5 Hz), 7.3 (d, 1H, *J* = 1.8 Hz), 7.16 (m, 2H), 6.88 (d, 1H, *J* =1.8Hz), 6.3 (br, 2H), 4.7 (t, 2H, *J* = 7.5 Hz), 2.4-2.2 (m, 6H), 1.96 (s, 6H), 1.94 (s, 3H), 1.66 (m, 16H), 1.17-1.39 (m, 18H), ^{31}P NMR (CD_2Cl_2, 300MHz): δ (ppm)= 33.7 (s, 1P). ^{13}C NMR (CD_2Cl_2, 75 MHz): 187.5 (C_{NHC}=Ru, J_{P-C} = 82 Hz), 152.2 C_{ar}, 139.3 C_{ar}, 137.2 C_{ar}, 136.9 C_{ar}, 131 C_{ar}, 129.4 C_{ar}, 129.0 C_{ar}, 128.8 $C_{ar,}$ 124.4 $C_{NHC,}$ 121.8 $C_{NHC,}$ 53.1 (CH_2-N), 32.5 (d, J_{P-C} *= 16.5 Hz, ipso*-C_{Cy}), 30.4 (*meta*-C_{Cy}), 28.7 (d, J_{P-C} *= 9.75 Hz ortho*-C_{Cy}), 27.5 (*para*-C_{Cy}), 24.8 (-CH_2), 21.6 (Ar-CH_3), 18.9 (Ar-CH_3) , 12.2 (-CH_3) . HRMS (ESI+): m/z 735.3150 $[M]^+$ *i.e* calculated 735.3150

Synthesis of RuBn. To 1-mesithyl-3-benzylimidazolium chloride (0.3 g, 0.96 mmol) in 5 mL of toluene was added 1.92 mL (0.96mmol) of a 0.5 M toluene solution of $[K(N(SiMe_3)_2]$. After stirring for 20 min, a solution of $Cl_2(PCy_3)_2Ru(=CHPh)$ (0.67 g, 0.82 mmol) in 10 mL of toluene was added. The reaction mixture was stirred for 3 h and filtered over celite. The solvent was removed under vacuum, and the residual solid product was crystallized in toluene and pentane giving 0.46 g of **RuBn**.

^1H NMR (CD_2Cl_2, 300 MHz): δ (ppm)= 19.21 (s, 1H), 7.96 (br, 1H), 7.72 (dd, 1H, *J* = 1.8 Hz), 7.47 (t, 2H, *J* = 7.5 Hz), 7.16 (t, 2H, *J* = 7.5 Hz), 6.98 (d, 1H, *J* =1.8Hz), 6.86 (d, 1H, *J* =1.8Hz), 6.37 (br, 2H), 5.9 (s, 2H), 2.4-2.2 (m, 4H), 2.0 (s, 3H), 1.98 (s, 6H), 1.62 (m, 16H), 1.11-1.36 (m, 14H), ^{31}P NMR (CD_2Cl_2, 300MHz): δ (ppm)= 36.9 (s, 1P). ^{13}C NMR (CD_2Cl_2, 75 MHz): 187.5 (C_{NHC}=Ru, $J_{P\text{-}C}$ = 82 Hz), 152.2 C_{ar}, 138.8 C_{ar}, 136.5 $C_{ar,}$ 136.3 C_{ar}, 135.8 C_{ar}, 130.6 C_{ar}, 129.7 C_{ar}, 129.2 C_{ar}, 129.0 C_{ar}, 128.9 C_{ar}, 128.5 $C_{ar,}$128.3 $C_{ar,}$124.4 $C_{NHC,}$ 121.9 $C_{NHC,}$ 55.3 (CH_2-N), 31.7 (d, $J_{P\text{-}C}$ = *16.5 Hz, ipso*-C_{Cy}), 29.9 (*meta*-C_{Cy}), 28.07 (d, $J_{P\text{-}C}$ = *9.8 Hz ortho*-C_{Cy}), 26.9 (*para*-C_{Cy}), 21.07 (Ar-CH_3), 18.3 (Ar-CH_3). HRMS (ESI+): m/z 783.3149 $[M\text{-}Cl]^+$ *i.e* calculated 783.3151

Catalytic tests:

All metathesis experiments were carried out under an inert atmosphere, in a glove-box. Toluene was dried over NaK and distilled under nitrogen prior to use. Cyclooctene (*cis*-cyclooctene) was purchased from Aldrich, distilled over Na prior to use. Catalysts Grubbs second generation catalyst was purchased from Aldrich and catalyst (Nolan) was synthesized according to the literature procedures.

GC response factors using internal standard:

GC response factors were determined for cyclooctene (C8) & dimer (C16) with respect to eicosane (E) as an internal standard. Standard solutions were prepared with different concentrations of cyclooctene & dimer keeping the eicosane concentration constant at 8.14 mM. The molar ratio of each solution was plotted against the ratio of area percentage data. The corrosponding factor was determined by fitting the data to a linear trendline.

Gas phase analyses (metathesis) were performed on a Agilent Technologies 7890A GC apparatus equipped with a FID detector and a HP5 Fame column (30m X 0.32mm) and an automated sampler.

Split ratio of GC was set to 50:1. , Sample injection 1 microliter with 10 microliter syringe.

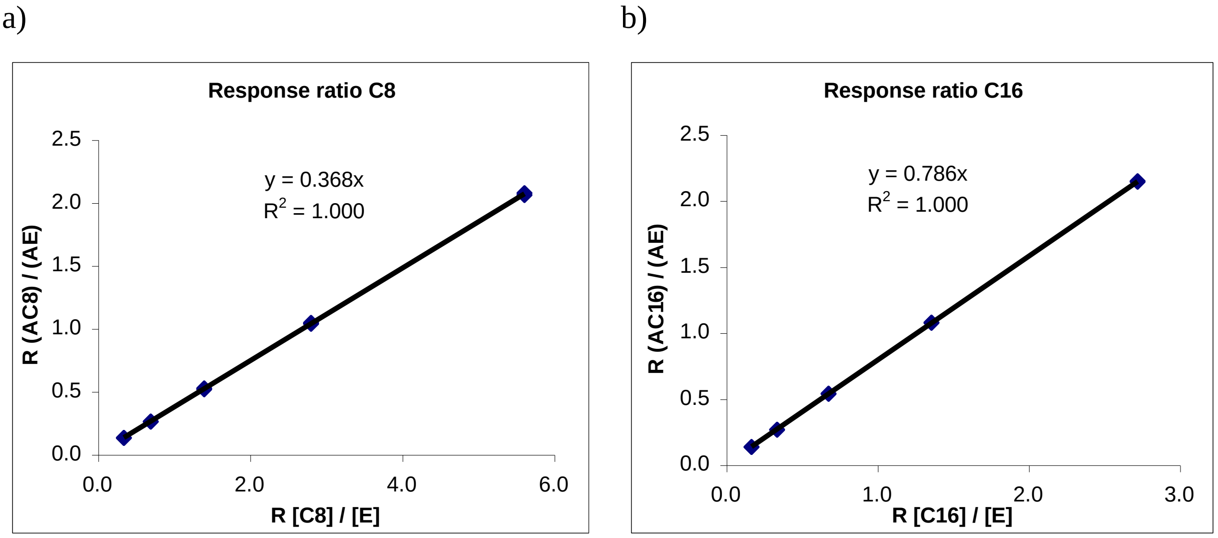


Figure S 1: a) Response ratio of C8 /E **b)** Response ratio of C16/ E. [C8] = Concentration of C8 in mM, [C16] = Concentration of C16 in mM, [E] = Concentration of eicosane in mM, (AC8) = Area of of C8, (AC16) = Area of C16. (AE) = Area of eicosane

Cyclooctene metathesis experiments with homogeneous Ru-complexes

(*Ratio Cyclooctene/ Ru of c.a. 10,000).*

Representative procedure: (G-II, N-II, RuPr, **RuBn):** Eicosane was dissolved in ~20mM toluene solution of cyclooctene. Sample was taken for GC analysis as a reference.Homogeneous Ru-catalyst was dissolved in toluene so as to obtain the initial stock solution. An aliquot of this stock solution was added to the above solution of cyclooctene, at room temperature. The progress of the metathesis reaction was monitored by sampling at suitable intervals. (The samples were immediately quenched by an excess of ethyl acetate). The samples were analysed by GC with a HP5 column.

Selectivity and mass balance are defined as follows:

Selectivity in product i (S_i).= (number of mole of cyclooctene converted in product i) / (total number of cyclooctene converted).

Mass balance = (sum of number of mole of cyclooctene converted in all the products) / (total number of cyclooctene converted).

Plots for the catalytic performances of homogeneous catalysts in RO-RCM of cyclooctene

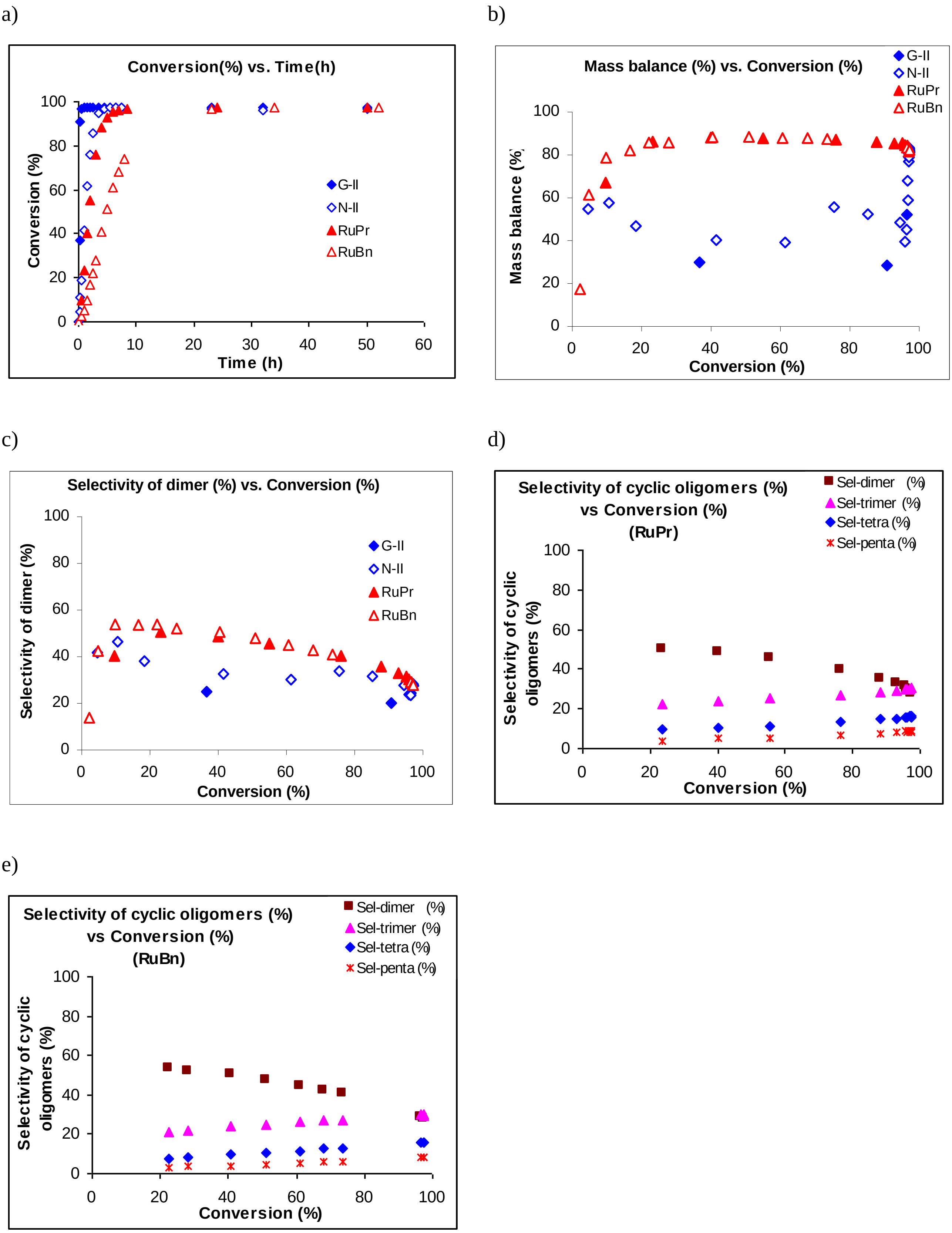
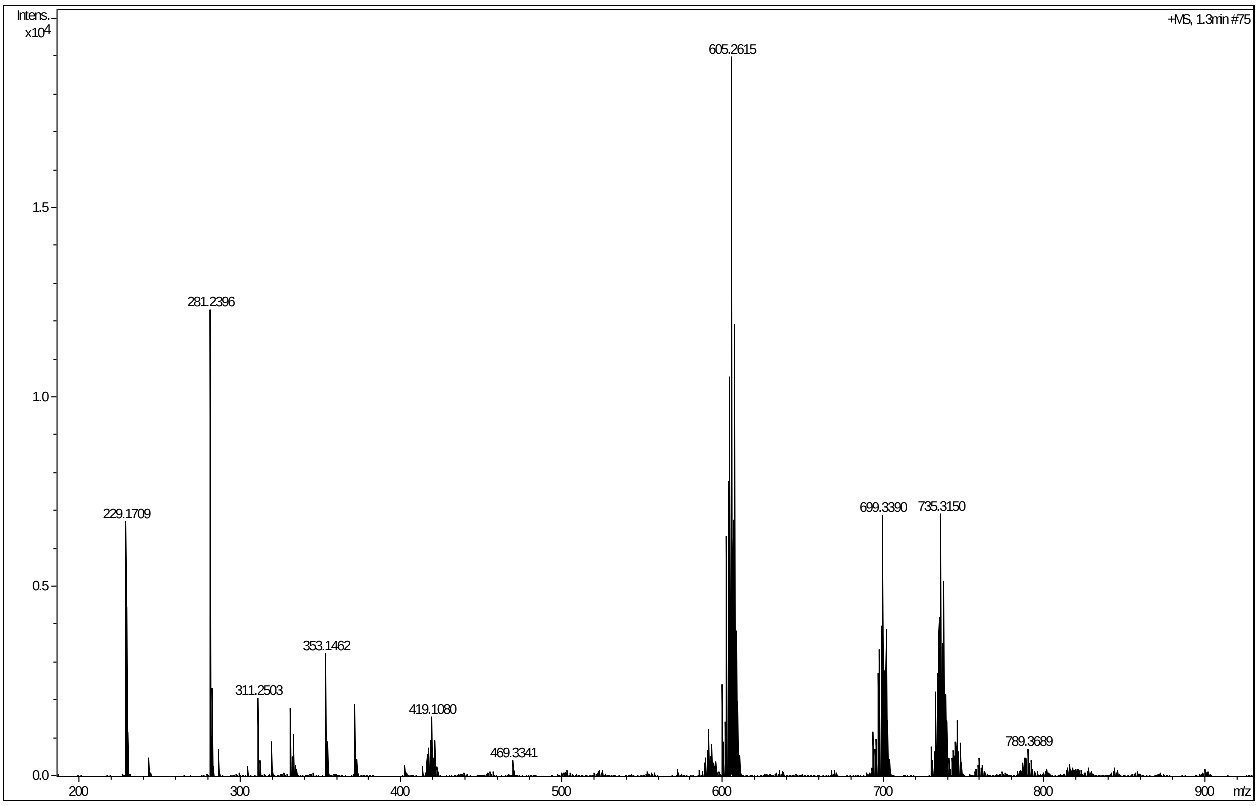


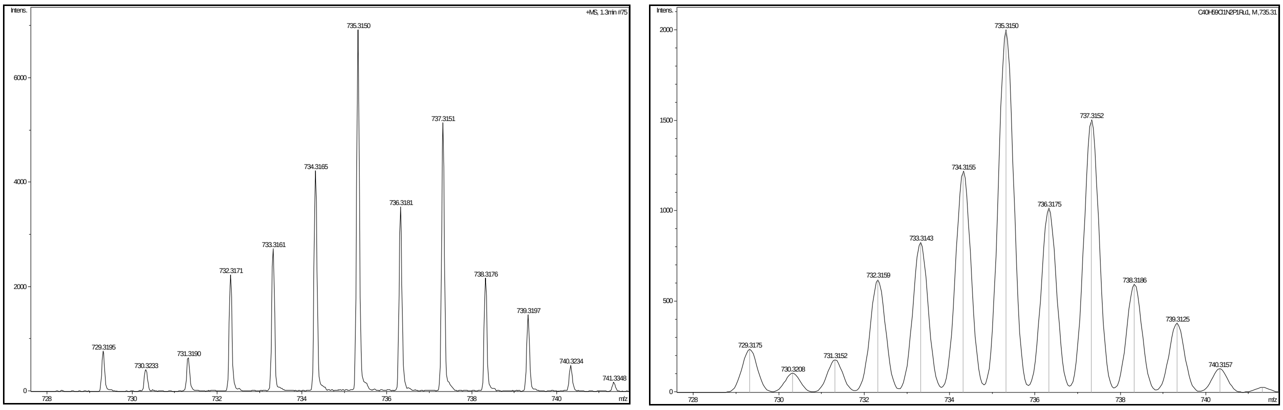
Figure S2: a) Conversion *vs.* Time for all the catalysts; **b)** Mass balance *vs.* Conversion for all the catalysts; **c)** Selectivity of dimer *vs.* Conversion for all the catalysts; **d)** Selectivity of cyclic oligomers *vs.* conversion, at constant mass balance for **RuPr**; **e)** Selectivity of cyclic oligomers *vs.* conversion, at constant mass balance for **RuBn**.

Characterisation of Homogeneous complexes RuPr and RuBn

1) RuPr

a) High resolution mass spectrum (ESI+) of **RuPr**





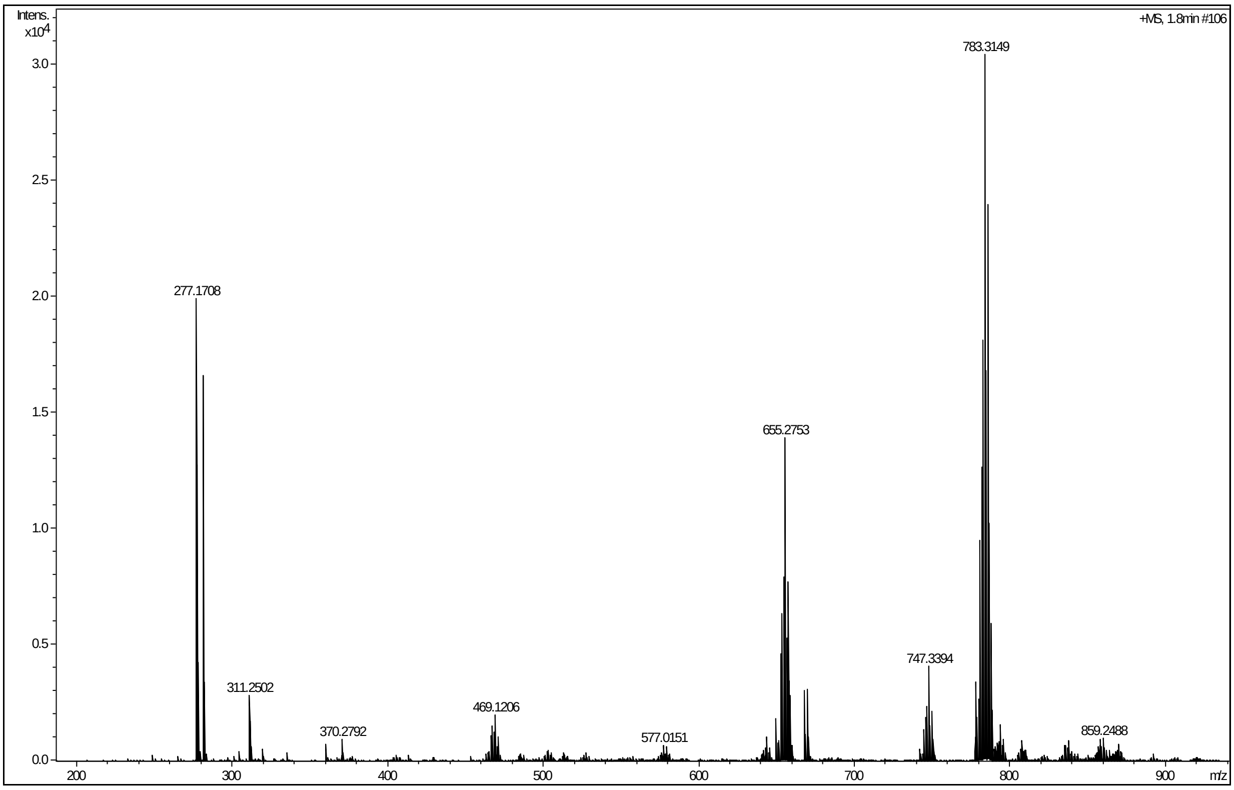
b) Experimental molecule ion spectrum

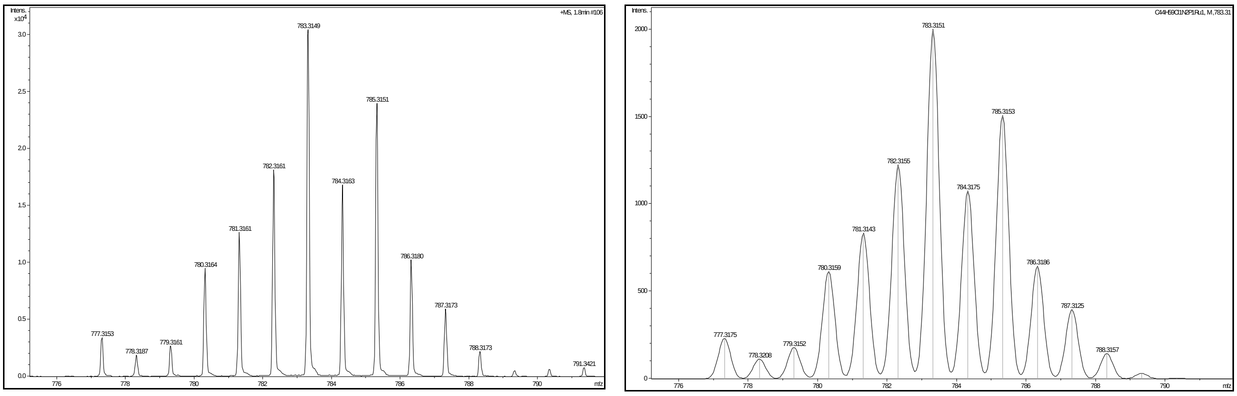
c) Simulated spectrum.

Figure S 3: a) High resolution mass spectrum (ESI+) of **RuPr.** b) Experimental molecule ion spectrum. c) Simulated spectrum.

2) RuBn

a) High resolution mass spectrum (ESI+) of **RuBn**

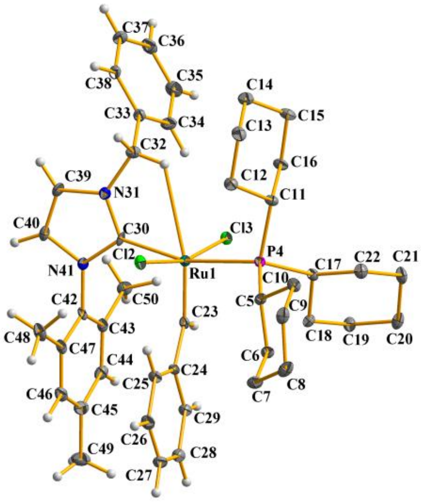



b) Experimental molecule ion spectrum

c) Simulated spectrum.

Figure S 4: a) High resolution mass spectrum (ESI+) of **RuBn.** b) Experimental molecule ion spectrum. c) Simulated spectrum.

3) X-ray structure of RuBn



Crystal data

$C_{44}H_{59}Cl_2N_2PRu$	$Z = 2$
$M_r = 818.91$	$F(000) = 860$
Triclinic, $P\bar{1}$	$D_x = 1.348$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
$a = 9.5221$ (6) Å	Cell parameters from 23423 reflections
$b = 13.8865$ (7) Å	$\theta = 3.3$–29.6°
$c = 17.1831$ (9) Å	$\mu = 0.59$ mm^{-1}
$\alpha = 96.169$ (4)°	$T = 110$ K
$\beta = 104.967$ (5)°	Block, dark brown
$\gamma = 109.769$ (5)°	0.25 × 0.18 × 0.09 mm
$V = 2017.7$ (2) Å^3	

Data collection

Xcalibur, Atlas, Gemini ultra diffractometer	10138 independent reflections
Radiation source: Enhance (Mo) X-ray Source	8696 reflections with $I > 2.0\sigma(I)$
graphite	$R_{int} = 0.082$
Detector resolution: 10.4685 pixels mm^{-1}	$\theta_{max} = 29.7°$, $\theta_{min} = 3.4°$
Absorption correction: analytical *CrysAlis PRO*, Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 CrysAlis171 .NET) (compiled Aug 27 2010,11:50:40) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)	$h = -13 \rightarrow 13$
$T_{min} = 0.903$, $T_{max} = 0.954$	$k = -19 \rightarrow 18$
39857 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.068$	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ···+ A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 0.102E + 04 0.159E + 04 828. 218.
$wR(F^2) = 0.168$	$(\Delta/\sigma)_{max} = 0.001$
S = 0.98	$\Delta\rangle_{max} = 1.75$ e Å^{-3}
10138 reflections	$\Delta\rangle_{min} = -1.98$ e Å^{-3}
452 parameters	Extinction correction: Larson (1970), Equation 22
0 restraints	Extinction coefficient: 52 (9)

Geometric parameters (Å, º)

Ru1—Cl2	2.3968 (10)	C22—H221	0.973
Ru1—Cl3	2.3959 (10)	C23—C24	1.471 (5)
Ru1—P4	2.4202 (11)	C23—H231	0.933
Ru1—C23	1.830 (4)	C24—C25	1.401 (6)
Ru1—C30	2.067 (3)	C24—C29	1.411 (6)
P4—C5	1.858 (4)	C25—C26	1.378 (6)
P4—C11	1.861 (4)	C25—H251	0.933
P4—C17	1.858 (4)	C26—C27	1.397 (7)
C5—C6	1.540 (6)	C26—H261	0.936
C5—C10	1.542 (6)	C27—C28	1.389 (7)
C5—H51	0.980	C27—H271	0.933
C6—C7	1.530 (6)	C28—C29	1.378 (6)
C6—H61	0.972	C28—H281	0.932
C6—H62	0.965	C29—H291	0.934
C7—C8	1.526 (7)	C30—N31	1.357 (5)
C7—H71	0.973	C30—N41	1.359 (5)
C7—H72	0.970	N31—C32	1.471 (6)
C8—C9	1.530 (7)	N31—C39	1.381 (5)
C8—H82	0.975	C32—C33	1.508 (6)
C8—H81	0.973	C32—H322	0.972
C9—C10	1.533 (6)	C32—H321	0.977
C9—H91	0.968	C33—C34	1.386 (6)
C9—H92	0.964	C33—C38	1.392 (6)

C10—H102	0.976	C34—C35	1.388 (7)
C10—H101	0.972	C34—H341	0.928
C11—C12	1.527 (6)	C35—C36	1.388 (8)
C11—C16	1.537 (6)	C35—H351	0.935
C11—H111	0.986	C36—C37	1.377 (8)
C12—C13	1.523 (6)	C36—H361	0.930
C12—H122	0.978	C37—C38	1.390 (7)
C12—H121	0.974	C37—H371	0.928
C13—C14	1.531 (7)	C38—H381	0.929
C13—H131	0.965	C39—C40	1.335 (7)
C13—H132	0.968	C39—H391	0.927
C14—C15	1.516 (7)	C40—N41	1.402 (5)
C14—H142	0.973	C40—H401	0.934
C14—H141	0.972	N41—C42	1.451 (5)
C15—C16	1.525 (6)	C42—C43	1.401 (6)
C15—H151	0.969	C42—C47	1.381 (6)
C15—H152	0.963	C43—C44	1.386 (6)
C16—H161	0.968	C43—C50	1.482 (6)
C16—H162	0.978	C44—C45	1.388 (7)
C17—C18	1.537 (6)	C44—H441	0.933
C17—C22	1.536 (6)	C45—C46	1.398 (8)
C17—H171	0.978	C45—C49	1.503 (7)
C18—C19	1.526 (6)	C46—C47	1.401 (7)
C18—H182	0.980	C46—H461	0.934
C18—H181	0.972	C47—C48	1.505 (7)
C19—C20	1.525 (6)	C48—H481	0.961
C19—H191	0.972	C48—H482	0.967
C19—H192	0.973	C48—H483	0.960
C20—C21	1.526 (7)	C49—H492	0.958
C20—H201	0.973	C49—H491	0.956
C20—H202	0.970	C49—H493	0.958
C21—C22	1.532 (6)	C50—H502	0.961
C21—H211	0.974	C50—H501	0.965
C21—H212	0.972	C50—H503	0.958
C22—H222	0.972		
Cl2—Ru1—Cl3	165.56 (4)	C21—C20—H202	108.8
Cl2—Ru1—P4	91.92 (4)	H201—C20—H202	109.0
Cl3—Ru1—P4	89.70 (4)	C20—C21—C22	112.3 (4)
Cl2—Ru1—C23	104.50 (13)	C20—C21—H211	108.5
Cl3—Ru1—C23	89.39 (13)	C22—C21—H211	108.1
P4—Ru1—C23	99.06 (13)	C20—C21—H212	109.5

Cl2—Ru1—C30	82.97 (11)	C22—C21—H212	109.2
Cl3—Ru1—C30	91.20 (11)	H211—C21—H212	109.2
P4—Ru1—C30	162.38 (12)	C17—C22—C21	109.9 (4)
C23—Ru1—C30	98.55 (17)	C17—C22—H222	109.5
Ru1—P4—C5	115.12 (14)	C21—C22—H222	108.9
Ru1—P4—C11	108.41 (14)	C17—C22—H221	110.1
C5—P4—C11	103.47 (19)	C21—C22—H221	109.6
Ru1—P4—C17	114.65 (14)	H222—C22—H221	108.8
C5—P4—C17	110.44 (19)	Ru1—C23—C24	135.4 (3)
C11—P4—C17	103.43 (19)	Ru1—C23—H231	112.7
P4—C5—C6	111.9 (3)	C24—C23—H231	111.9
P4—C5—C10	119.1 (3)	C23—C24—C25	125.9 (4)
C6—C5—C10	109.1 (3)	C23—C24—C29	116.8 (4)
P4—C5—H51	105.1	C25—C24—C29	117.3 (4)
C6—C5—H51	105.5	C24—C25—C26	121.2 (5)
C10—C5—H51	105.0	C24—C25—H251	118.7
C5—C6—C7	109.8 (3)	C26—C25—H251	120.0
C5—C6—H61	108.5	C25—C26—C27	120.6 (5)
C7—C6—H61	109.3	C25—C26—H261	119.2
C5—C6—H62	109.4	C27—C26—H261	120.2
C7—C6—H62	110.5	C26—C27—C28	119.2 (4)
H61—C6—H62	109.2	C26—C27—H271	120.6
C6—C7—C8	111.3 (4)	C28—C27—H271	120.2
C6—C7—H71	109.5	C27—C28—C29	120.2 (5)
C8—C7—H71	109.1	C27—C28—H281	119.5
C6—C7—H72	108.8	C29—C28—H281	120.3
C8—C7—H72	109.2	C24—C29—C28	121.5 (4)
H71—C7—H72	108.9	C24—C29—H291	119.2
C7—C8—C9	111.2 (4)	C28—C29—H291	119.3
C7—C8—H82	109.1	Ru1—C30—N31	123.2 (3)
C9—C8—H82	109.1	Ru1—C30—N41	132.0 (3)
C7—C8—H81	108.5	N31—C30—N41	104.1 (3)
C9—C8—H81	109.4	C30—N31—C32	125.2 (4)
H82—C8—H81	109.5	C30—N31—C39	111.6 (4)
C8—C9—C10	112.6 (4)	C32—N31—C39	123.2 (4)
C8—C9—H91	108.5	N31—C32—C33	112.6 (4)
C10—C9—H91	108.8	N31—C32—H322	107.3
C8—C9—H92	108.9	C33—C32—H322	108.8
C10—C9—H92	109.0	N31—C32—H321	109.7
H91—C9—H92	109.0	C33—C32—H321	109.4
C5—C10—C9	109.9 (4)	H322—C32—H321	108.9
C5—C10—H102	109.1	C32—C33—C34	121.2 (4)

C9—C10—H102	109.0	C32—C33—C38	120.0 (4)
C5—C10—H101	110.2	C34—C33—C38	118.8 (4)
C9—C10—H101	109.9	C33—C34—C35	120.4 (5)
H102—C10—H101	108.8	C33—C34—H341	119.6
P4—C11—C12	110.5 (3)	C35—C34—H341	120.0
P4—C11—C16	112.6 (3)	C34—C35—C36	120.2 (5)
C12—C11—C16	110.9 (4)	C34—C35—H351	119.5
P4—C11—H111	107.3	C36—C35—H351	120.3
C12—C11—H111	108.0	C35—C36—C37	120.0 (5)
C16—C11—H111	107.4	C35—C36—H361	120.4
C11—C12—C13	112.2 (4)	C37—C36—H361	119.6
C11—C12—H122	108.8	C36—C37—C38	119.7 (5)
C13—C12—H122	108.9	C36—C37—H371	120.1
C11—C12—H121	108.0	C38—C37—H371	120.2
C13—C12—H121	109.6	C33—C38—C37	120.9 (4)
H122—C12—H121	109.3	C33—C38—H381	119.6
C12—C13—C14	110.2 (4)	C37—C38—H381	119.5
C12—C13—H131	110.1	N31—C39—C40	107.0 (4)
C14—C13—H131	108.8	N31—C39—H391	125.9
C12—C13—H132	109.6	C40—C39—H391	127.1
C14—C13—H132	108.7	C39—C40—N41	106.6 (4)
H131—C13—H132	109.5	C39—C40—H401	127.6
C13—C14—C15	109.8 (4)	N41—C40—H401	125.8
C13—C14—H142	110.5	C40—N41—C30	110.7 (4)
C15—C14—H142	109.7	C40—N41—C42	122.4 (4)
C13—C14—H141	109.6	C30—N41—C42	126.6 (3)
C15—C14—H141	109.2	N41—C42—C43	117.2 (4)
H142—C14—H141	108.1	N41—C42—C47	119.2 (4)
C14—C15—C16	111.7 (4)	C43—C42—C47	123.5 (4)
C14—C15—H151	108.5	C42—C43—C44	117.0 (4)
C16—C15—H151	109.4	C42—C43—C50	121.6 (4)
C14—C15—H152	108.9	C44—C43—C50	121.4 (4)
C16—C15—H152	109.2	C43—C44—C45	122.4 (5)
H151—C15—H152	109.1	C43—C44—H441	118.3
C11—C16—C15	111.2 (4)	C45—C44—H441	119.4
C11—C16—H161	109.1	C44—C45—C46	118.2 (5)
C15—C16—H161	109.0	C44—C45—C49	120.7 (5)
C11—C16—H162	109.1	C46—C45—C49	121.1 (5)
C15—C16—H162	109.2	C45—C46—C47	121.9 (5)
H161—C16—H162	109.3	C45—C46—H461	118.9
P4—C17—C18	114.1 (3)	C47—C46—H461	119.2
P4—C17—C22	115.5 (3)	C46—C47—C42	117.0 (4)

C18—C17—C22	111.3 (4)	C46—C47—C48	121.8 (4)
P4—C17—H171	103.7	C42—C47—C48	121.3 (4)
C18—C17—H171	104.4	C47—C48—H481	109.4
C22—C17—H171	106.6	C47—C48—H482	110.4
C17—C18—C19	110.7 (4)	H481—C48—H482	108.8
C17—C18—H182	108.6	C47—C48—H483	110.1
C19—C18—H182	109.0	H481—C48—H483	108.7
C17—C18—H181	108.6	H482—C48—H483	109.3
C19—C18—H181	110.0	C45—C49—H492	110.1
H182—C18—H181	109.9	C45—C49—H491	111.3
C18—C19—C20	111.5 (4)	H492—C49—H491	108.3
C18—C19—H191	108.7	C45—C49—H493	110.5
C20—C19—H191	109.9	H492—C49—H493	108.1
C18—C19—H192	108.4	H491—C49—H493	108.5
C20—C19—H192	109.2	C43—C50—H502	110.7
H191—C19—H192	109.0	C43—C50—H501	110.1
C19—C20—C21	111.1 (4)	H502—C50—H501	108.8
C19—C20—H201	109.4	C43—C50—H503	110.2
C21—C20—H201	109.9	H502—C50—H503	108.7
C19—C20—H202	108.6	H501—C50—H503	108.3