Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Ligand Effect on the Rhodium Porphyrin Catalyzed Hydrogenation of [2.2]Paracyclophane with Water: Key Bimetallic Hydrogenation

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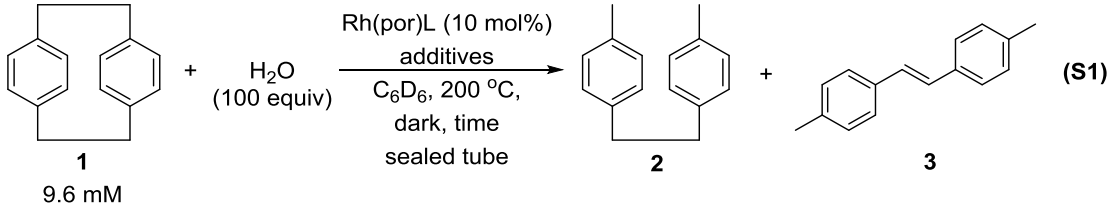
Contents

1. Summary of Porphyrin Ligand and Axial Ligand Effect on the Rhodium Porphyrin Catalyzed Hydrogenation of [2.2]Paracyclophane (1) with Water

Table S1

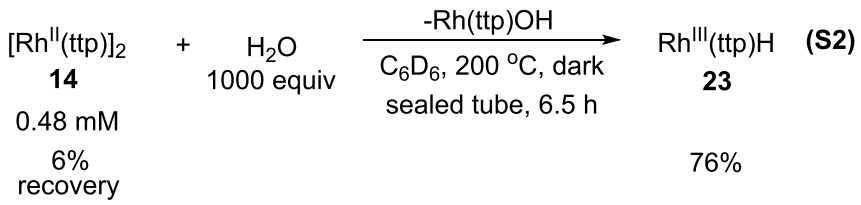


Entry	por ligand / por	axial ligand / L	Catalyst	time / h	**2**[a] / %	**3**[a] / %	Mass Balance[a] / %	$Rh^{III}(por)H$[a] / %
1	ttp	Me	**12**	54	79	10	89	30
2	tap	Me	**13**	54	69	10	79	43
3	ttp	Rh^{II}(ttp)	**14**	47	79	14	93	38
4	tmp	Me	**15**	168	55	13	68	18
5	tmp	/	**16**	83	78	19	97	43
6	ttp	Cl (KOH)[b]	**17**	48	65	13	78	31
7	ttp	CH_2CH_2Ph	**18**	51	74	11	85	24
8	ttp	^{i}Pr	**19**	50	68	10	78	41
9	ttp	CH_2CH_2OH	**20**	49	75	12	87	17
10	ttp	Bn	**21**	47	75	10	85	27
11	ttp	Me (PPh_3)[c]	**22**	53	79	9	88	21
12	ttp	H	**23**	40	79	15	94	45

[a] NMR yield. [b] 1 equiv of KOH w.r.t. **1** added. [c] 1 equiv of PPh_3 w.r.t. Rh(ttp)Me (**12**) added. ttp = 5,10,15,20-tetratolylporphyrin, tap = 5,10,15,20-tetraanisylporphyrin, tmp = 5,10,15,20-tetramesitylporphyrin.

2. Reaction Time Profile

Table S2. Reaction Time Profile for the Oxidative Addition of water with $[Rh^{II}(ttp)]_2$ (14)



Time / h	$[Rh^{II}(ttp)]_2$ / mM	$Rh^{III}(ttp)H$ / mM	Mass Balance / mM
0	0.48	0	0.96
0.08	0.28	0.16	0.72
0.4	0.18	0.35	0.71
1.0	0.13	0.52	0.78
2.2	0.06	0.64	0.76
3.2	0.04	0.70	0.79
4.2	0.04	0.70	0.78
6.4	0.03	0.73	0.78

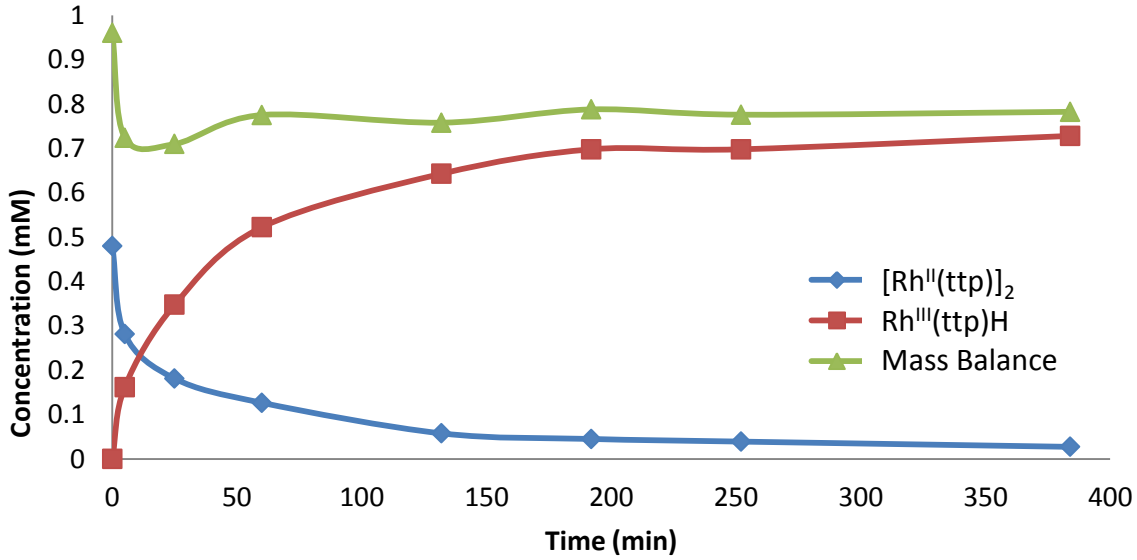
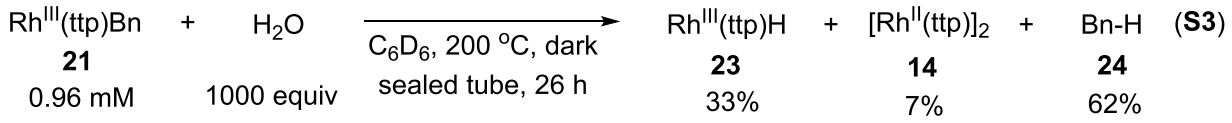


Figure S1. Reaction Time Profile for the Oxidative Addition of Water with $[Rh^{II}(ttp)]_2$ (14)

Table S3. Reaction Time Profile for the Hydrolysis of Rh^{III}(ttp)Bn (21) with Water



Time / h	Rh^{III}(ttp)Bn / mM	Rh^{III}(ttp)H / mM	$[Rh^{II}(ttp)]_2$ / mM	Mass Balance / mM	Bn-H / mM
0	0.96	0	0	0.96	0
0.3	0.86	0.06	0.02	0.96	0.03
0.8	0.77	0.07	0.03	0.89	0.08
1.8	0.45	0.05	0.03	0.55	0.10
5.2	0.32	0.08	0.04	0.48	0.22
13	0.15	0.15	0.04	0.38	0.47
26	0.03	0.32	0.04	0.44	0.60

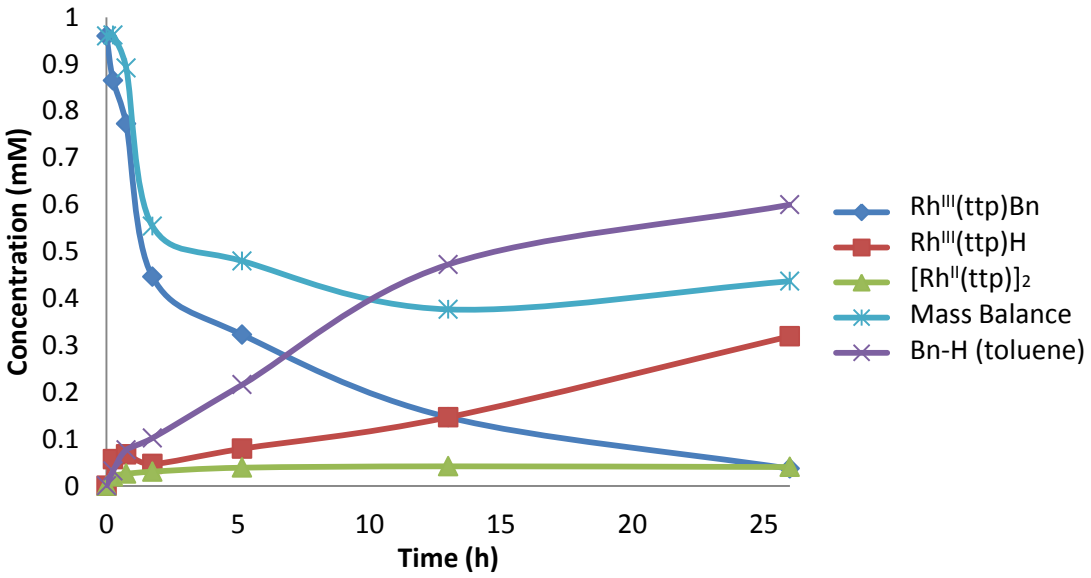
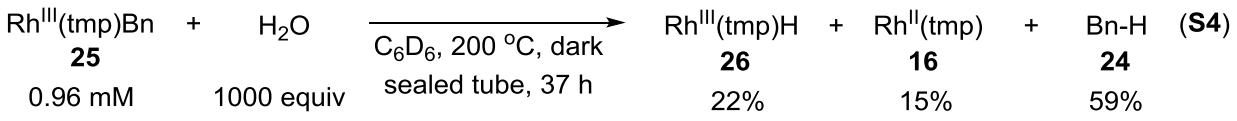


Figure S2. Reaction Time Profile for the Hydrolysis of Rh^{III}(ttp)Bn (21) with Water

Table S4. Reaction Time Profile for the Hydrolysis of Rh^{III}(tmp)Bn (25) with Water



Time / h	Rh^{III}(tmp)Bn / mM	Rh^{III}(tmp)H / mM	Rh^{II}(tmp) / mM	Mass Balance / mM	Bn-H / mM
0	0.96	0	0	0.96	0
0.5	0.92	~0	~0	0.92	0.03
2.5	0.75	0.06	0.07	0.88	0.13
4.5	0.52	0.06	0.08	0.67	0.18
12.5	0.24	0.10	0.12	0.47	0.34
26	0.08	0.17	0.17	0.42	0.49
31	0.05	0.20	0.15	0.40	0.51
35	0.04	0.20	0.15	0.39	0.53
37	0.03	0.21	0.14	0.38	0.56

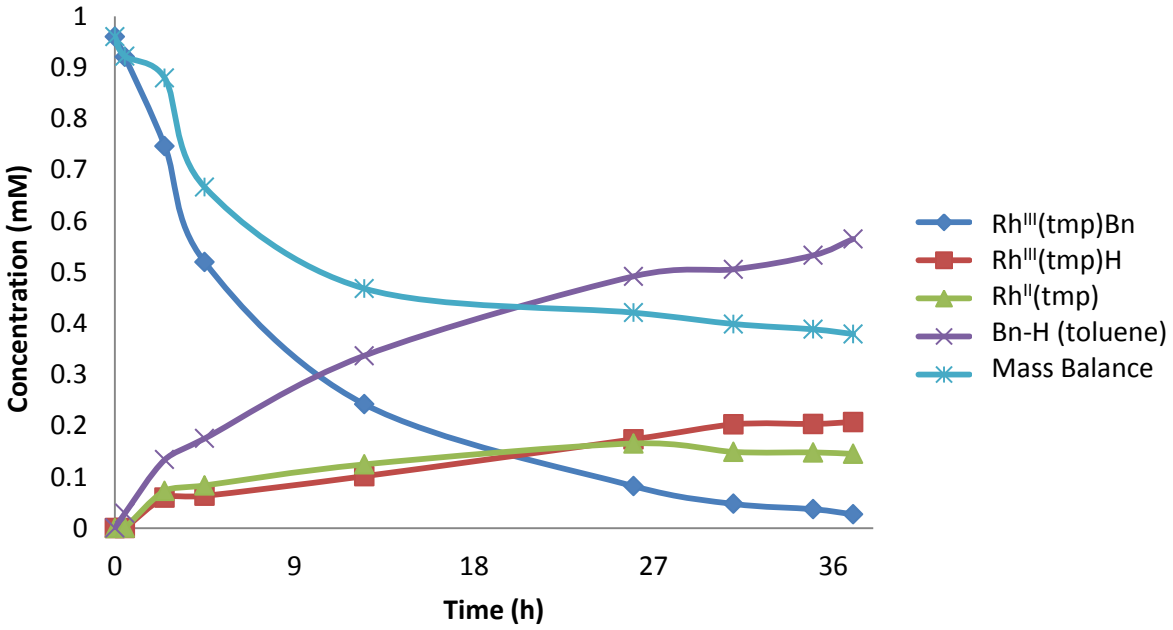
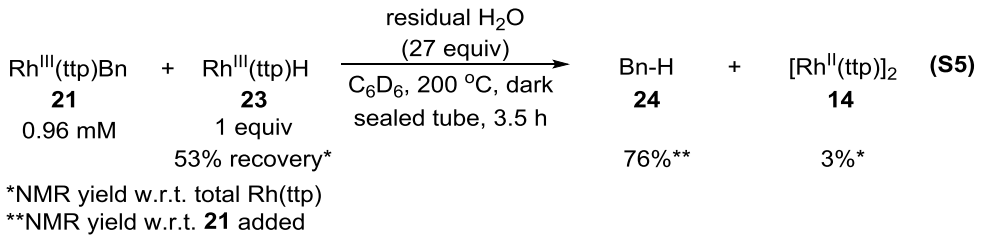


Figure S3. Reaction Time Profile for the Hydrolysis of Rh^{III}(tmp)Bn (25) with Water

Table S5. Reaction Time Profile for the Bimetallic Reductive Elimination of Toluene (24) from Rh^{III}(ttp)H (23) and Rh^{III}(ttp)Bn (21)



Time / h	Rh^{III}(ttp)Bn / mM	Rh^{III}(ttp)H / mM	$[Rh^{II}(ttp)]_2$ / mM	Mass Balance / mM	Bn-H / mM
0	0.96	0.96	0.07	2.05	0
0.08	0.83	0.71	0.07	1.69	0.07
0.3	0.73	0.72	0.10	1.65	0.18
0.4	0.54	0.89	0.11	1.66	0.30
0.9	0.32	0.95	0.10	1.46	0.48
1.4	0.19	0.96	0.07	1.29	0.59
1.9	0.15	1.06	0.04	1.29	0.59
2.8	0.08	1.06	0.04	1.21	0.68
3.7	0.03	1.08	0.03	1.17	0.73

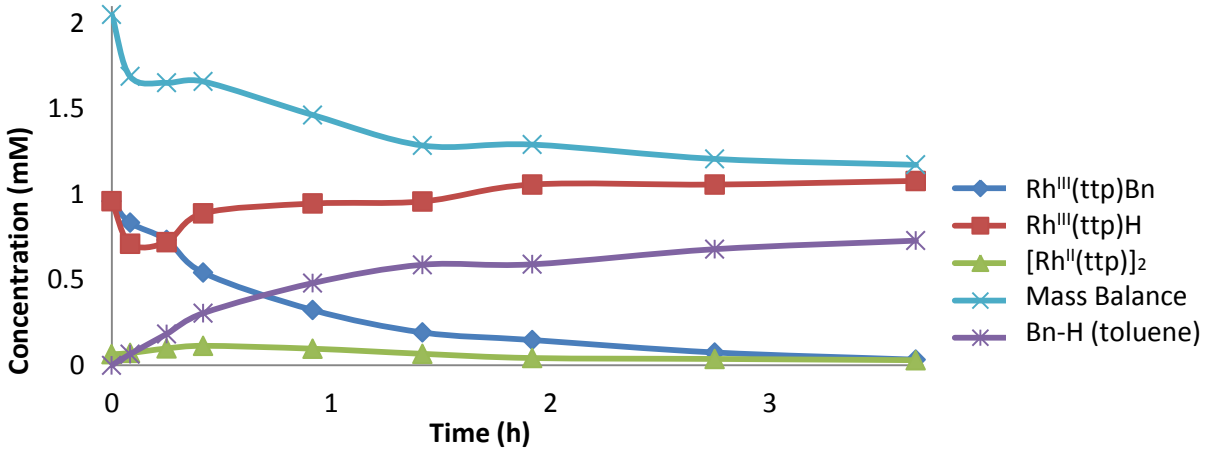
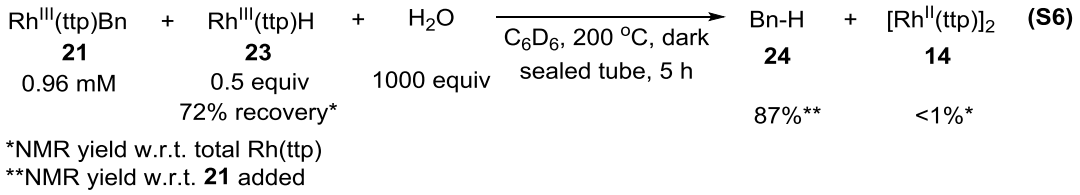


Figure S4. Reaction Time Profile for the Bimetallic Reductive Elimination of Toluene (24) from Rh^{III}(ttp)H (23) and Rh^{III}(ttp)Bn (21)

Table S6. Reaction Time Profile for the Hydrogenolysis of Rh^{III}(ttp)Bn (21) with water and 0.5 Equiv Rh^{III}(ttp)H (23)



Time / h	Rh^{III}(ttp)Bn / mM	Rh^{III}(ttp)H / mM	$[Rh^{II}(ttp)]_2$ / mM	Mass Balance / mM	Bn-H / mM
0	0.96	0.48	0	1.44	0
0.5	0.84	0.51	0	1.35	0.22
1.0	0.54	0.58	0.02	1.16	0.41
2.0	0.24	0.76	0.02	1.04	0.56
2.6	0.17	0.83	0.03	1.06	0.67
3.1	0.13	0.87	0.03	1.06	0.72
3.6	0.08	0.94	0.03	1.08	0.78
4.6	0.05	1.01	0	1.06	0.82
5.1	0.03	1.04	0	1.08	0.83

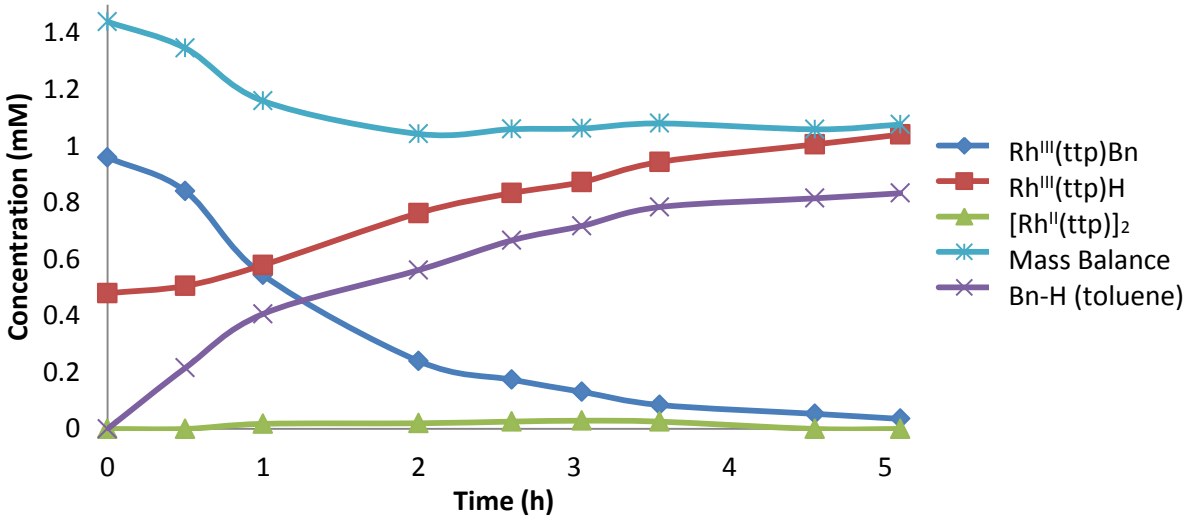
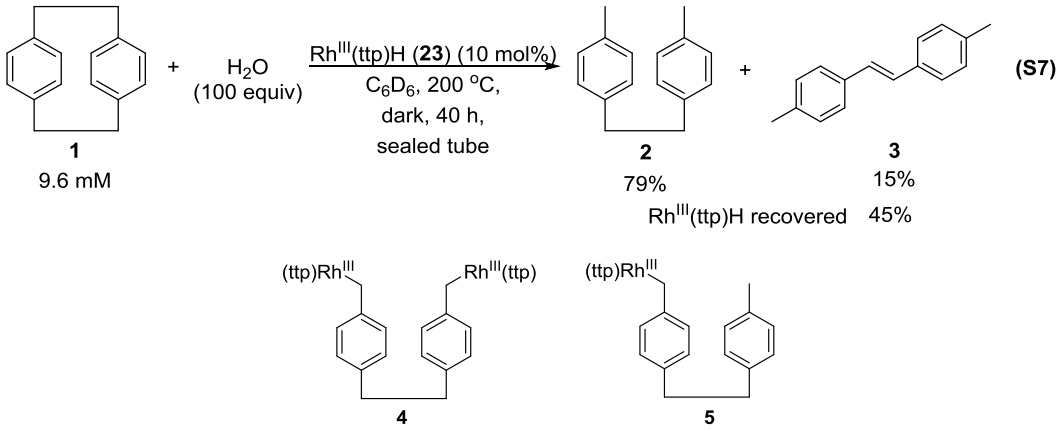


Figure S5. Reaction Time Profile for the Hydrogenolysis of Rh^{III}(ttp)Bn (21) with water and 0.5 Equiv Rh^{III}(ttp)H (23)

Table S7. Reaction Time Profile for Rhodium benzyl Intermediates 4 and 5 Over Time for 10 mol% Rh(ttp)H (23) Catalysis (Table 1/S1, entry 12)



Time / h	**4** / %	**5** / %	Ratio **4/5**	$[Rh^{II}(ttp)]_2$ / %	$Rh^{III}(ttp)H$ / %	Total Rh(ttp) Mass Balance / %
0	0	0	/	8	100	108
0.16	11	18	0.61	13	55	97
2.2	28	40	0.70	0	0	67
4.0	18	25	0.72	0	0	42
18	5	17	0.29	0	0	22
25	5	19	0.26	0	0	24
35	4	20	0.20	0	0	25
38	0	10	0	0	35	45
40	0	3	0	0	45	48

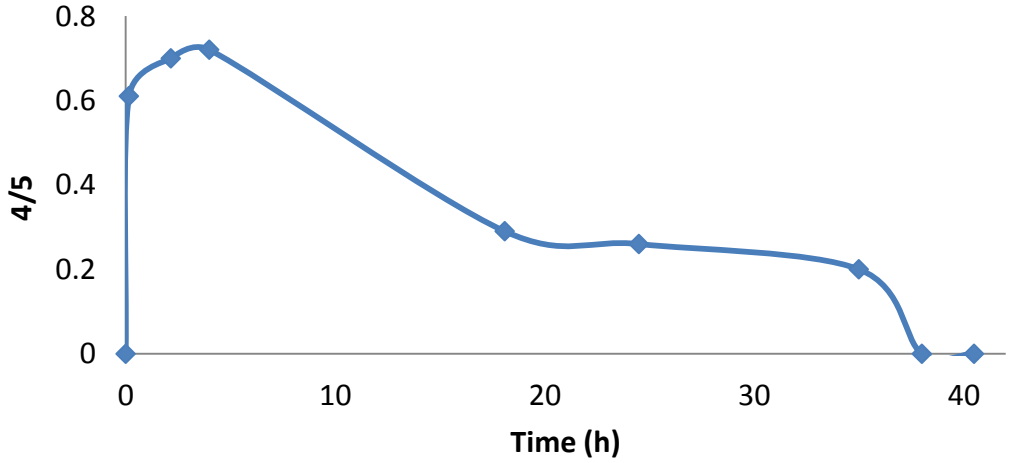
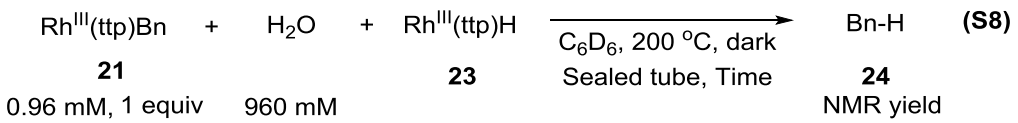


Figure S6. Plot of Ratio of Rhodium Benzyl Intermediates (4/5) Over Time

3. Estimation of Reaction Rate for Hydrolysis and Bimetallic Reductive Elimination

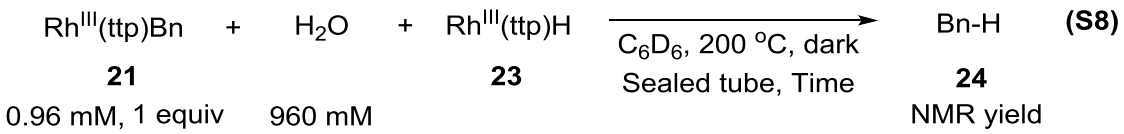


(S8)

Hydrolysis and BMRE are proposed to be the two parallel hydrogenation pathways since Rh^{III}(ttp)H (**23**) and $[Rh^{II}(ttp)]_2$ (**14**) were observed in the hydrolysis of Rh^{III}(ttp)Bn (**21**) with water (eq S3 and Figure S2). Furthermore, **23**, either added or build-up from **14** in the presence of excess water, could promote the hydrogenation of **21** via BMRE and shorten the reaction time from 26 h to 3.5 h (Table S8 and Figure S7).

The contribution from BMRE (k_1) and hydrolysis (k_2) in the hydrogenolysis of **21** was estimated with the initial rate of Bn-H (**24**) formation (<20% consumption of **21**) against [Rh^{III}(ttp)H] with assumed rate = k_1[**21**][Rh^{III}(ttp)H] + k_2'[**21**], where $k_2' = k_2[H_2O]$; [H_2O] = 960 mM; [**21**] = 0.96 mM and [**23**] = 0 – 0.96 mM (Table S8 and Figure S8). The solubility of water in benzene is reported to be ~2 M at 200 °C.[1] The values of k_1 and k_2' were found to be 0.71 ± 0.02 and 0.11 ± 0.01 mM^{-1} h^{-1} respectively. The ratio of $k_1/k_2' = 6.7 \pm 0.1$ is consistent with the BMRE being a more effective hydrogenolysis step than hydrolysis.

Table S8. Rh^{III}(ttp)H (23) Dependent Hydrogenolysis of Rh^{III}(ttp)Bn (21) with Water



entry	Rh^{III}(ttp)H / mM	Time / h	Rh^{III}(ttp)H recovered[a] / mM	Bn-H[b] / %	Initial rate of Bn-H formation / mM h^{-1}
1	0	26	0.32	62	0.10
2	0.096	22	0.25	75	0.18
3	0.48	5	1.0	87	0.41
4[c]	0.96	3.5	1.1	76	0.76

[a] $[Rh^{II}(ttp)]_2$ (**14**) was recovered in <0.04 mM. [b] NMR yield w.r.t. **21** added. [c] Amount of Residual water ~27 equiv estimated by NMR.

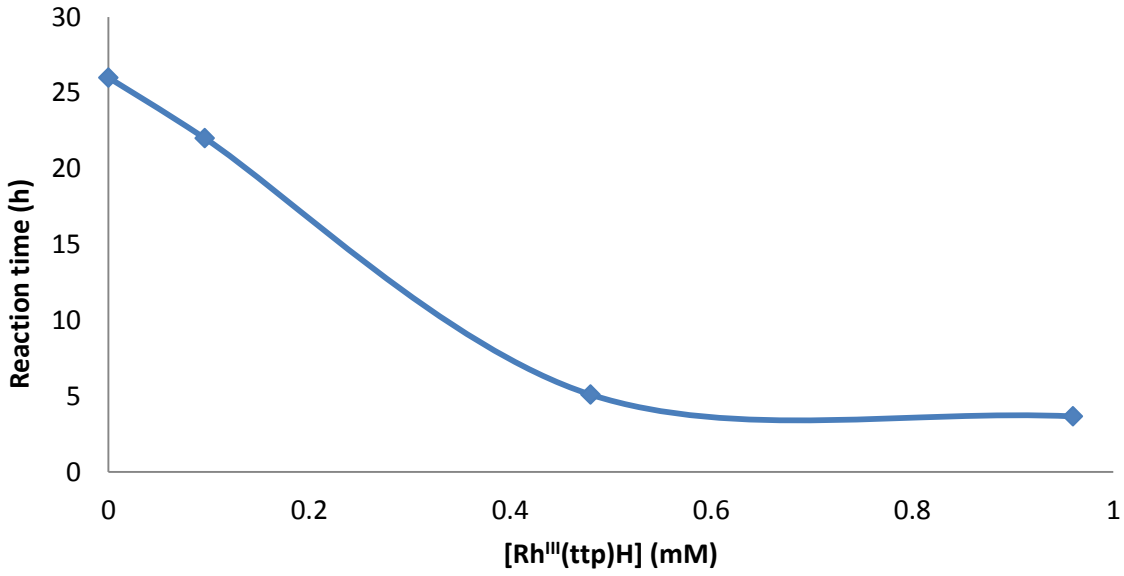


Figure S7. Plot of Reaction Time for the Hydrogenolysis of Rh^{III}(ttp)Bn (21) against Rh^{III}(ttp)H (23) Loading

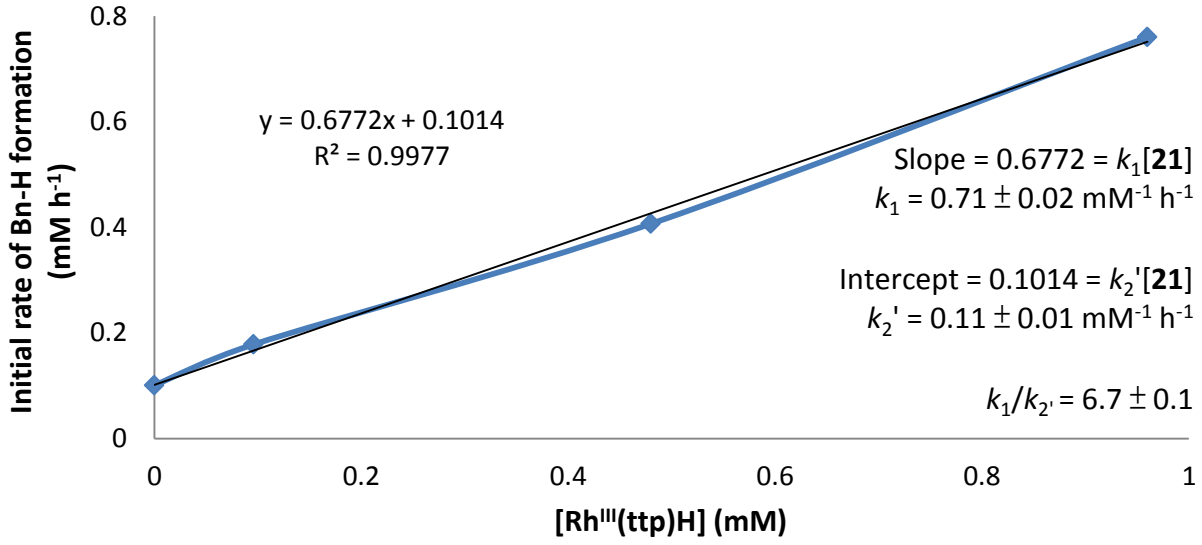


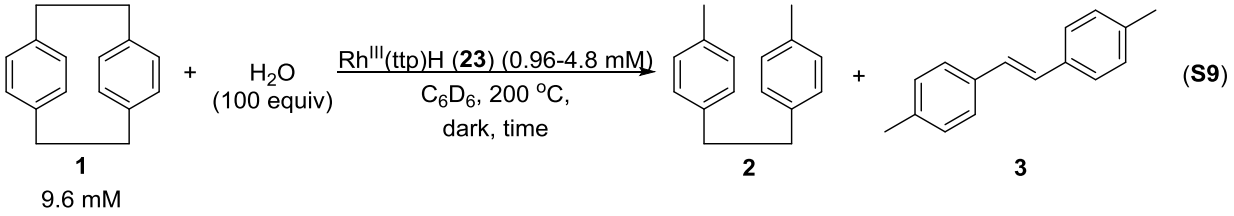
Figure S8. Plot of Initial Rate of Toluene (24) Formation against [Rh^{III}(ttp)H] (23)

4. Kinetics Experiment Section

The reaction order of Rh^{III}(ttp)H (**23**) was examined with initial rate measurements with conditions which [Rh^{III}(ttp)H] = 0.96 – 2.4 mM and [**1**] = 9.6 mM at 200 ^{o}C (Table S9-S10 and Figure S9-11).

The reaction order of **23** was also examined with the normalized time scale which utilize plots of [substrate] against [catalyst]^{n} (where n = reaction order) over the entire reaction time profiles monitored by ^{1}H NMR. (Figure 3 and Table S11)

Table S9. Determination of reaction order of Rh^{III}(ttp)H (23) By Initial Rate Measurement



Entry	n / mM	time / h	**2** / %	**3** / %	**2** + **3** / %	Rh^{III}(ttp)H recovered / %	Initial Rate of Consumption of **1** / mM h^{-1}	Initial Rate of Formation of **2** / mM h^{-1}
1	0.96	40	79	15	94	45	-0.43 ± 0.04	0.38 ± 0.01
2	1.9	32	77	11	88	26	-0.9 ± 0.1	0.75 ± 0.03
3	2.4	28	79	13	92	29	-1.1 ± 0.2	0.97 ± 0.01
4	9.6	10	71	24	95	28	/	/

Table S10. Determination of reaction order of Rh^{III}(ttp)H (23) By Initial Rate Measurement with log-log Plot

Entry	n / mM	log n	log (-Initial Rate of Consumption of **1**)	log (Initial Rate of Formation of **2**)
1	0.96	-0.018	-0.36_7	-0.42_0
2	1.9	0.28	-0.045_8	-0.12_5
3	2.4	0.38	0.041_4	-0.013_2
4	9.6	/	/	/

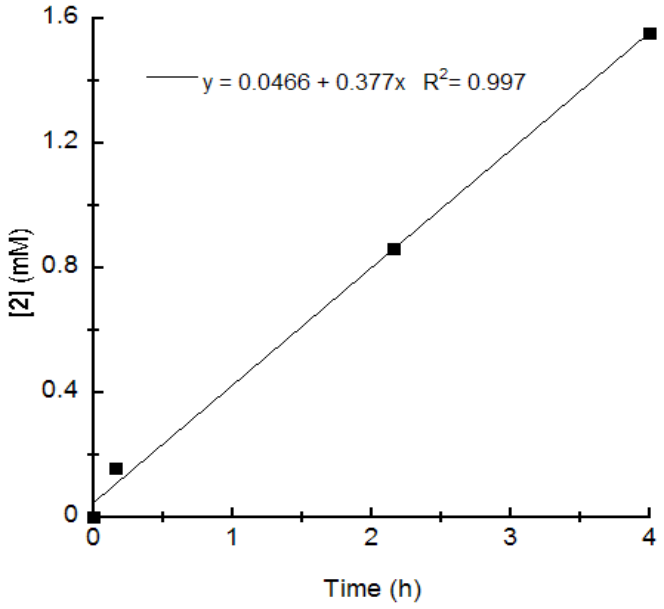


Figure S9. Plot of Initial Rate of Formation of [**2**] against Time with [Rh^{III}(ttp)H] = 0.96 mM and [**1**] = 9.6 mM at 200 °C (Table S9, entry 1)

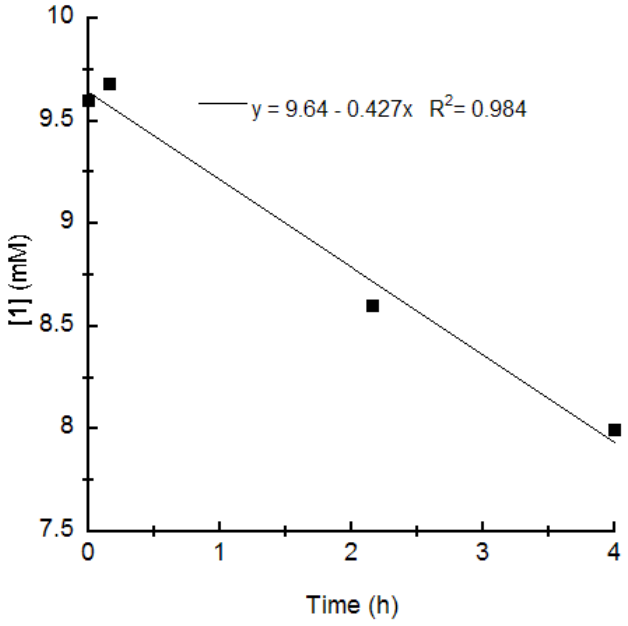


Figure S10. Plot of Initial Rate of Consumption of [**1**] against Time with [Rh^{III}(ttp)H] = 0.96 mM and [**1**] = 9.6 mM at 200 ^{o}C (Table S9, entry 1)

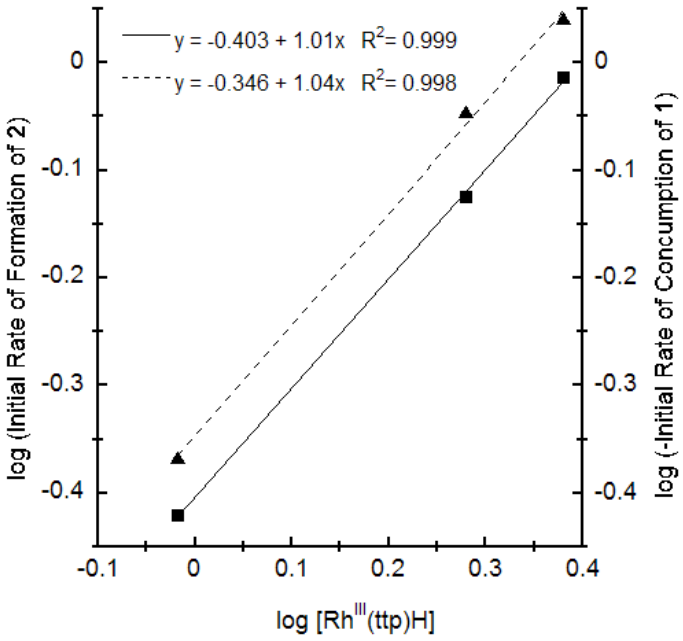


Figure S11. Plot of log (-Initial Rate of Consumption of [**1**]) (▲) and log (Initial Rate of Formation of **2**) (■) against log [Rh^{III}(ttp)H]

Table S11. Determination of reaction order of Rh^{III}(ttp)H (23) By Normalized Time Scale Method

[cat] = 0.96 mM Rh^{III}(ttp)H (**23**)

t / h	[**1**] / mM	t[cat]^0 / h	t[cat]$^{0.5}$ / mM$^{0.5}$ h	t[cat]^1 / mM h	t[cat]^2 / mM^2 h
0	9.6	0	0	0	0
0.16	9.7	0.16	0.16	0.15	0.15
2.2	8.6	2.2	2.1	2.1	2.0
4.0	8.0	4.0	3.9	3.8	3.7
18	2.8	18	18	17	17
25	2.0	25	24	24	23
35	0.69	35	34	34	32
38	0.46	38	37	36	35
40	0.26	40	40	39	37

[cat] = 1.9 mM Rh^{III}(ttp)H (**23**)

t / h	[**1**] / mM	t[cat]^0 / h	t[cat]$^{0.5}$ / mM$^{0.5}$ h	t[cat]^1 / mM h	t[cat]^2 / mM^2 h
0	9.6	0	0	0	0
0.25	9.3	0.25	0.34	0.48	0.92
0.58	9.1	0.58	0.80	1.1	2.1
4.0	7.0	4.0	5.5	7.7	15
14	2.0	14	19	27	52
32	0.20	32	44	61	118

[cat] = 2.4 mM Rh^{III}(ttp)H (**23**)

t / h	[**1**] / mM	$t[cat]^0$ / h	$t[cat]^{0.5}$ / $mM^{0.5}$ h	$t[cat]^1$ / mM h	$t[cat]^2$ / mM^2 h
0	9.6	0	0	0	0
0.16	8.8	0.16	0.25	0.38	0.92
2.2	7.1	2.2	3.3	5.2	12
4.0	4.3	4.0	6.2	9.6	23
18	1.0	18	28	43	104
25	0.51	25	38	59	141
27	0.23	27	41	64	152
28	0.13	28	43	67	161

[cat] = 9.6 mM Rh^{III}(ttp)H (**23**)

t / h	[**1**] / mM	$t[cat]^0$ / h	$t[cat]^{0.5}$ / $mM^{0.5}$ h	$t[cat]^1$ / mM h	$t[cat]^2$ / mM^2 h
0	9.6	0	0	0	0
0.75	5.5	0.75	2.3	7.2	69
1.1	4.6	1.1	3.4	11	101
3.7	1.4	3.7	11	36	340
4.5	1.0	4.5	14	43	414
6.5	0.51	6.5	20	62	599
7.7	0.34	7.7	24	73	705
9.7	0.13	9.7	30	93	889

5. Estimation of Free Energy Change of C-C σ-bond Hydrogenation of 1 with water

SPARTAN '16 Quantum Mechanics Driver: (Win/64b) Release 2.0.0

Job type: Frequency calculation.

Method: RHF

Basis set: 3-21G

Table S12 Optimization of Coordinates for [2.2]Paracyclophane (1), 4,4'-Dimethylbibenzyl (2), Water and Oxygen

H_2O

Number of basis functions: 13

Number of electrons: 10

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
1 O	O1	0.0000000	0.0000000	-0.3800314
2 H	H1	0.0000000	0.7806339	0.1900157
3 H	H2	0.0000000	-0.7806339	0.1900157

O_2

Number of basis functions: 18

Number of electrons: 16 (2 unpaired)

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
1 O	O1	0.0000000	0.0000000	0.6197905
2 O	O2	0.0000000	0.0000000	-0.6197905

[2.2]Paracyclophane (**1**)

Number of basis functions: 176

Number of electrons: 112

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
1 H	H1	1.4994550	2.1216346	1.2165486
2 C	C1	1.5247468	1.1858953	0.6910877
3 C	C4	1.5247468	-1.1858953	-0.6910877
4 C	C2	1.5247416	1.1858066	-0.6912641
5 C	C6	1.3799705	0.0000949	1.3953465
6 C	C5	1.5247416	-1.1858066	0.6912641
7 C	C3	1.3799705	-0.0000949	-1.3953465
8 H	H2	1.4994459	2.1214740	-1.2168590
9 H	H5	1.4994459	-2.1214740	1.2168591
10 H	H4	1.4994550	-2.1216346	-1.2165486
11 H	H7	-1.4994459	2.1214740	1.2168590
12 C	C7	-1.5247416	1.1858066	0.6912641
13 C	C8	-1.5247416	-1.1858066	-0.6912641
14 C	C9	-1.5247468	1.1858953	-0.6910877
15 C	C10	-1.3799705	-0.0000949	1.3953465
16 C	C11	-1.5247468	-1.1858953	0.6910877
17 C	C12	-1.3799705	0.0000949	-1.3953465
18 H	H8	-1.4994550	2.1216346	-1.2165486
19 H	H10	-1.4994550	-2.1216346	1.2165486
20 H	H12	-1.4994459	-2.1214740	-1.2168590
21 C	C13	0.8094701	0.0002887	2.7998030
22 H	H13	1.1451671	-0.8735977	3.3445903
23 H	H14	1.1448190	0.8744768	3.3443320
24 C	C14	-0.8094701	-0.0002887	2.7998030
25 H	H6	-1.1451671	0.8735977	3.3445903
26 H	H15	-1.1448190	-0.8744768	3.3443320
27 C	C15	0.8094701	-0.0002887	-2.7998030
28 H	H17	1.1448190	-0.8744768	-3.3443320
29 H	H18	1.1451671	0.8735977	-3.3445903
30 C	C16	-0.8094701	0.0002887	-2.7998030
31 H	H3	-1.1451671	-0.8735977	-3.3445903
32 H	H19	-1.1448190	0.8744768	-3.3443320

4,4’-Dimethylbibenzyl (**2**)

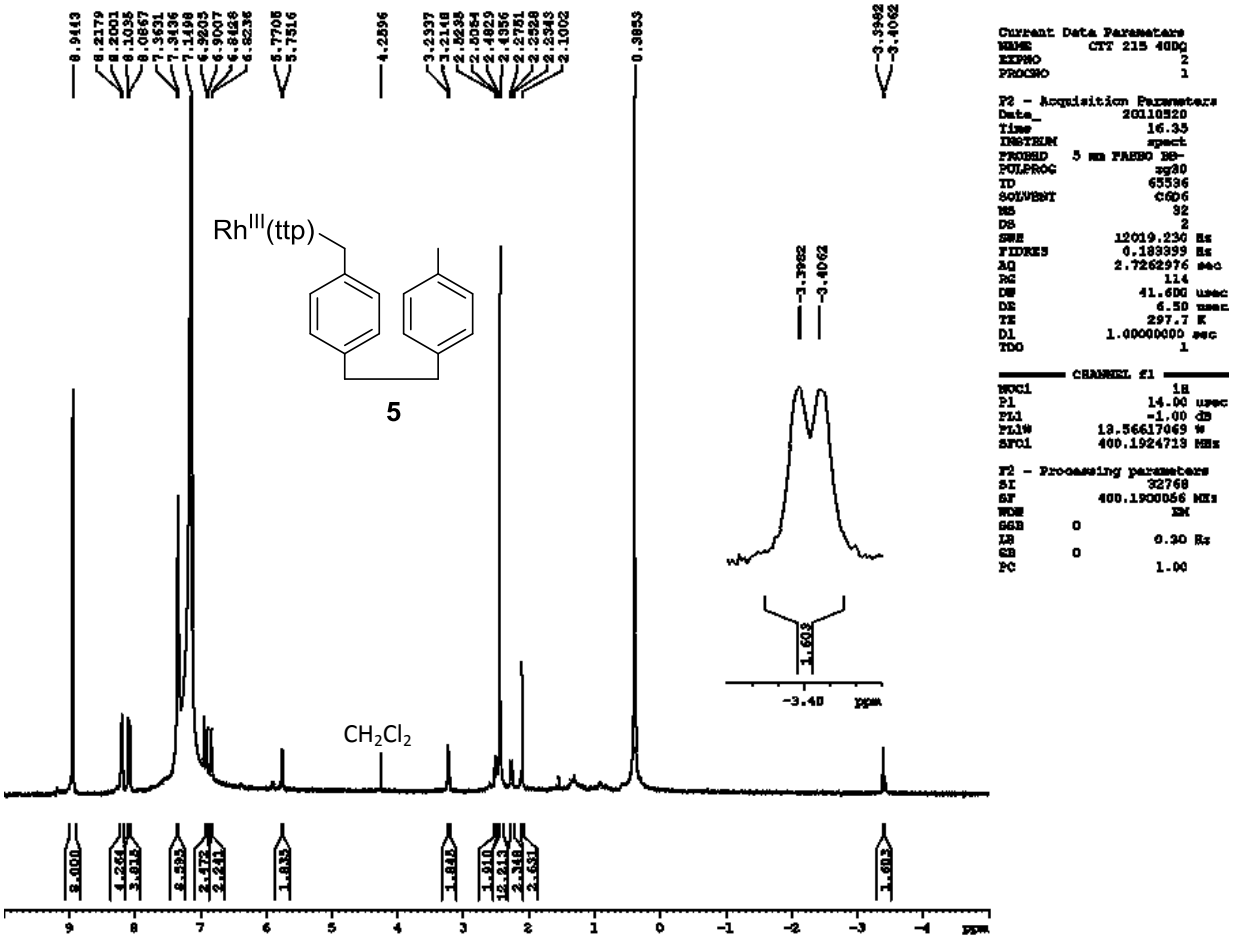
Number of basis functions: 180

Number of electrons: 114

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
1 H	H1	-2.1098318	1.4953854	-1.9437206
2 C	C1	-2.2540993	0.9387364	-1.0375454
3 C	C4	-2.6021912	-0.4682445	1.3006913
4 C	C2	-3.3291251	0.0701862	-0.9320353
5 C	C6	-1.3634383	1.1006049	0.0094139
6 C	C5	-1.5236828	0.3991890	1.1942318
7 C	C3	-3.4910992	-0.6310236	0.2545297
8 H	H6	-0.5358102	1.7736859	-0.0981541
9 H	H3	-4.3208901	-1.3031302	0.3637877
10 H	H4	-2.7537559	-1.0148377	2.2125999
11 H	H7	4.3208901	1.3031302	0.3637877
12 C	C7	3.4910992	0.6310236	0.2545297
13 C	C8	1.3634383	-1.1006049	0.0094139
14 C	C9	3.3291251	-0.0701862	-0.9320353
15 C	C10	2.6021912	0.4682445	1.3006913
16 C	C11	1.5236828	-0.3991890	1.1942318
17 C	C12	2.2540993	-0.9387364	-1.0375454
18 H	H9	2.7537559	1.0148377	2.2125999
19 H	H11	2.1098318	-1.4953854	-1.9437206
20 H	H12	0.5358102	-1.7736859	-0.0981541
21 C	C13	-4.2902879	-0.1270159	-2.0892562
22 H	H2	-3.9640105	-0.9501219	-2.7182145
23 H	H13	-4.3457066	0.7630932	-2.7045531
24 H	H14	-5.2879922	-0.3533295	-1.7318473
25 C	C14	4.2902879	0.1270159	-2.0892562
26 H	H8	5.2879922	0.3533295	-1.7318473
27 H	H15	3.9640105	0.9501219	-2.7182145
28 H	H16	4.3457066	-0.7630932	-2.7045531
29 C	C15	-0.5472953	0.5527302	2.3429000
30 H	H17	-1.0896380	0.5027802	3.2818153
31 H	H18	-0.0655870	1.5222003	2.2953569
32 C	C16	0.5472953	-0.5527302	2.3429000
33 H	H5	1.0896380	-0.5027802	3.2818153
34 H	H20	0.0655869	-1.5222003	2.2953569

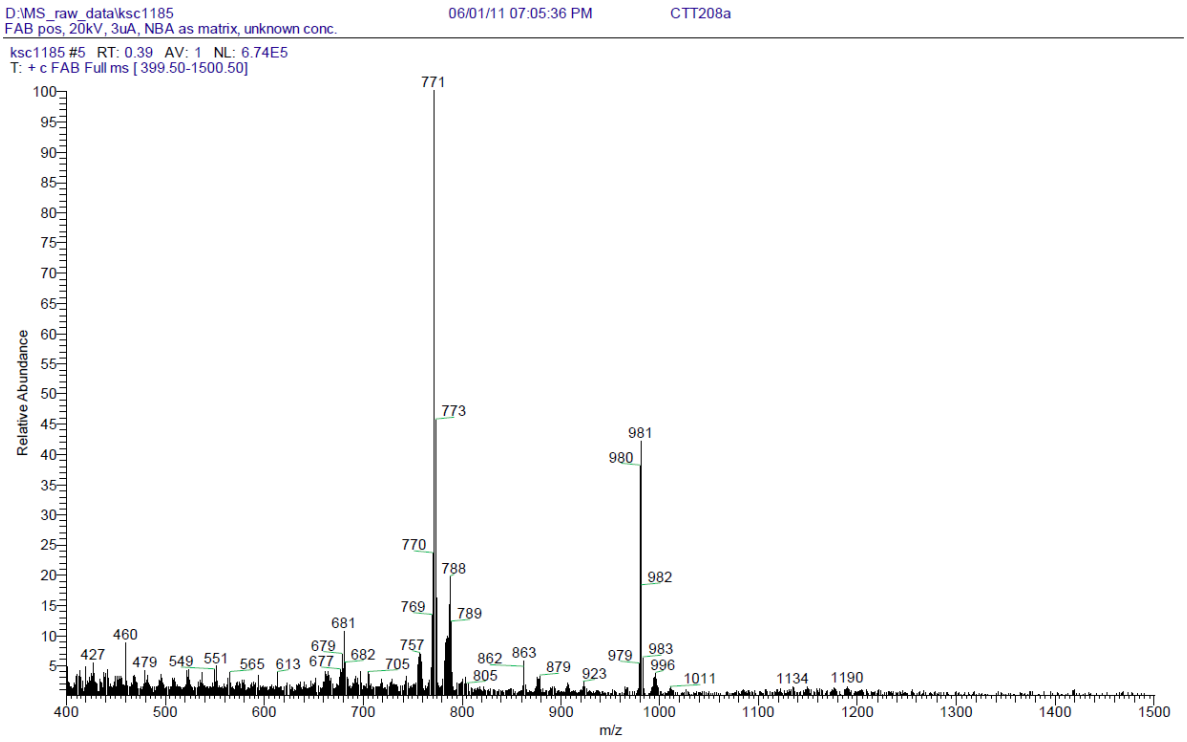
6. NMR Spectra

^{1}H NMR Spectrum of **5** (C_6D_6, 400 MHz)

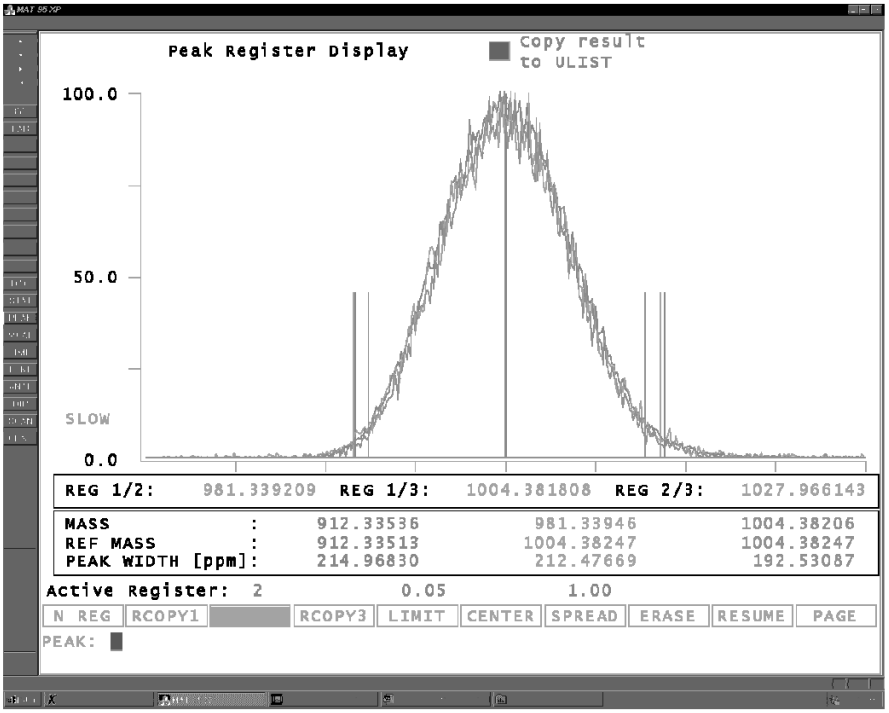


7. Mass Spectra

Mass Spectra of 5



Accurate Mass Measurement



Molecular formula
$C_{64}H_{53}N_4Rh$
$[M+H]^+$ (theoretical)
= 981.3398

8. References

(1) M. Góral, B. Wiśniewska-Gocłowska and A. Mączyński, *J. Phys. Chem. Ref. Data*, 2004, **33**, 1159.