Base-Promoted Carbon Hydrogen Bond Activation of Alkanes with Rhodium(III) Porphyrin Complexes

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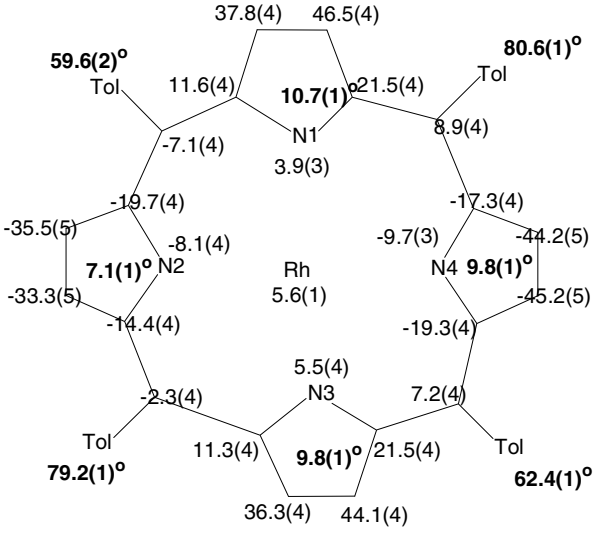
X-ray data and structure

Table 1. Crystal Data and Summary of Data Collection and Refinement for 2a, 2b, and 2e

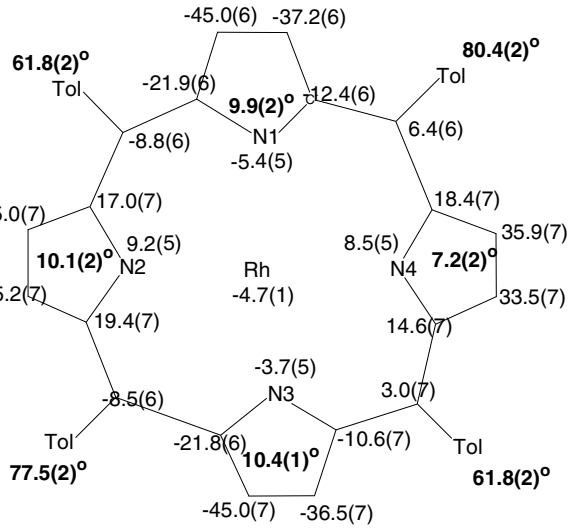
	2a	**2b**	**2e**
Color, shape	Purple Prism	Purple Prism	Purple Prism
empirical formula	$C_{54}H_{47}N_4Rh{\cdot}CH_2Cl_2$	$C_{53}H_{45}N_4Rh{\cdot}CH_3CH_2OH$	$C_{56}H_{51}N_4Rh$
formula wt	939.79	886.91	882.92
Temp (K)	293 (2)	293 (2)	293 (2)
wavelength(Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	P1
unit cell dimens			
a (Å)	15.509 (2)	15.579 (2)	10.578 (2)
b (Å)	18.651 (2)	18.482 (2)	14.575 (3)
c (Å)	16.266 (2)	16.155 (2)	16.226 (4)
α (deg)	90	90	65.745 (4)
β (deg)	106.993 (2)	107.516 (2)	77.764 (4)
γ (deg)	90	90	82.348 (4)

Volumn (Å^3)	4499.6 (9)	4436.1 (10)	2225.8 (9)
Z	4	4	2
Calcd density (g cm^{-3})	1.387	1.328	1.317
abs coeff (mm^{-1})	0.541	0.430	0.426
F(000)	1944	1848	920
cryst size (mm)	0.40 x 0.30 x 0.20	0.50 x 0.30 x 0.20	0.50 x 0.40 x 0.30
θ range for data collection (deg)	1.60 to 28.04	1.72 to 25.00	1.53 to 28.08
limiting indices	-20 = h = 18	-18 = h = 18	-13 = h = 13
	-24 = k = 24	-21 = k = 19	-19 = k = 18
	-21 = l =20	-19 = l =19	-21 = l = 12
no. of rflns collected/ unique	30232/10856 [(R (int) = 0.0414)	23310/7800 [R (int) = 0.0479]	15187/10539 [R (int) = 0.0239]
complete ness to θ = 28	99.6	99.8	97.3
absorp corr	SADABS	SADABS	SADABS
max. and min. transmn	1.0000 and 0.836682	1.0000 and 0.660829	1.0000 and 0.616130
refineme nt method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
no. of data/ restraints/ params	10856 / 2 / 559	7800 / 14 / 550	10539 / 10 / 568
GOF	1.025	1.069	1.036
final R indices [*I*>2*s* (*I*)]	R_1 = 0.0572	R_1 = 0.0677	R_1 = 0.0449
	$_wR_2$ = 0.1511	$_wR_2$ = 0.1861	$_wR_2$ = 0.1124
R indices (all data)	R_1 = 0.0945	R_1 = 0.1032	R_1 = 0.0616
	$_wR_2$ = 0.1784	$_wR_2$ = 0.2249	$_wR_2$ = 0.1245
largest diff peak and hole (e Å^3)	1.597 and -1.788	2.976 and -0.711	0.774 and -0.421

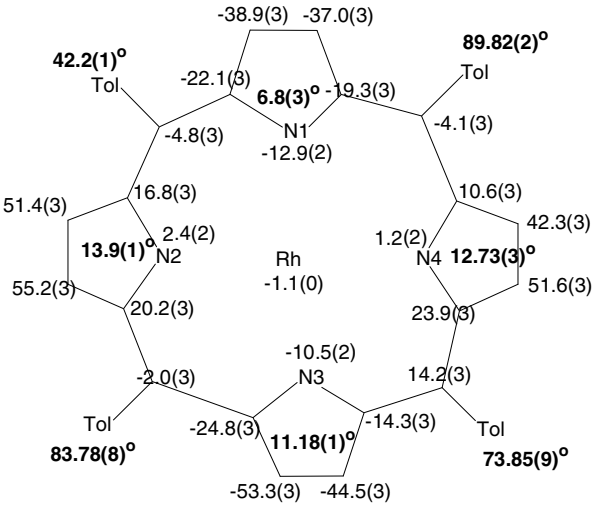
[a] $R_1 = \sum\left(||F_0|-|F_c||\right)/\sum|F_0|$. [b] ${}_wR_2 = \left\{\sum\left[{}_w\left(F_0^2 - F_c^2\right)^2\right]/\sum\left[{}_w\left(F_0^2\right)^2\right]\right\}^{1/2}$. [c] Weighting scheme $w^{-1} = \sigma^2(F_0^2) + (w_1P)^2 + w_2P$ where $P = (F_0^2 + 2F_c^2)/3$.



2a



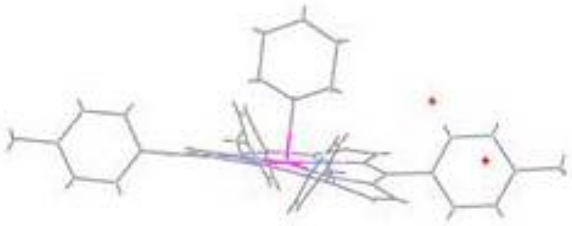
2b



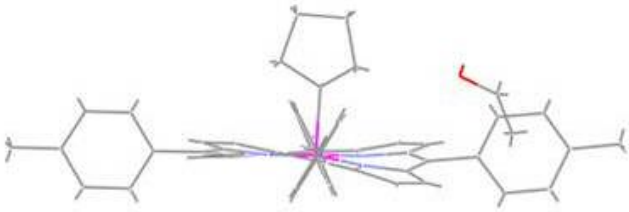
2e

Figure 1. The conformations of porphyrins showing the displacement of the core atoms and of Rh from the 24-atom least squares plane of porphyrin core (in pm; negative values correspond to displacement towards the alkyl group). Absolute values of the angles between pyrrole rings and the least-squares plane, and angles between pyrrole rings and the least-squares plane, and angles between phenyl substituents and the least-squares plane, are shown in bold.

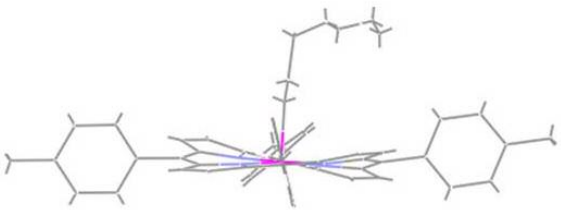
Figure 2. Wireframe presentation of the molecular structure for **2a, 2b, 2e,** respectively.



2a



2b

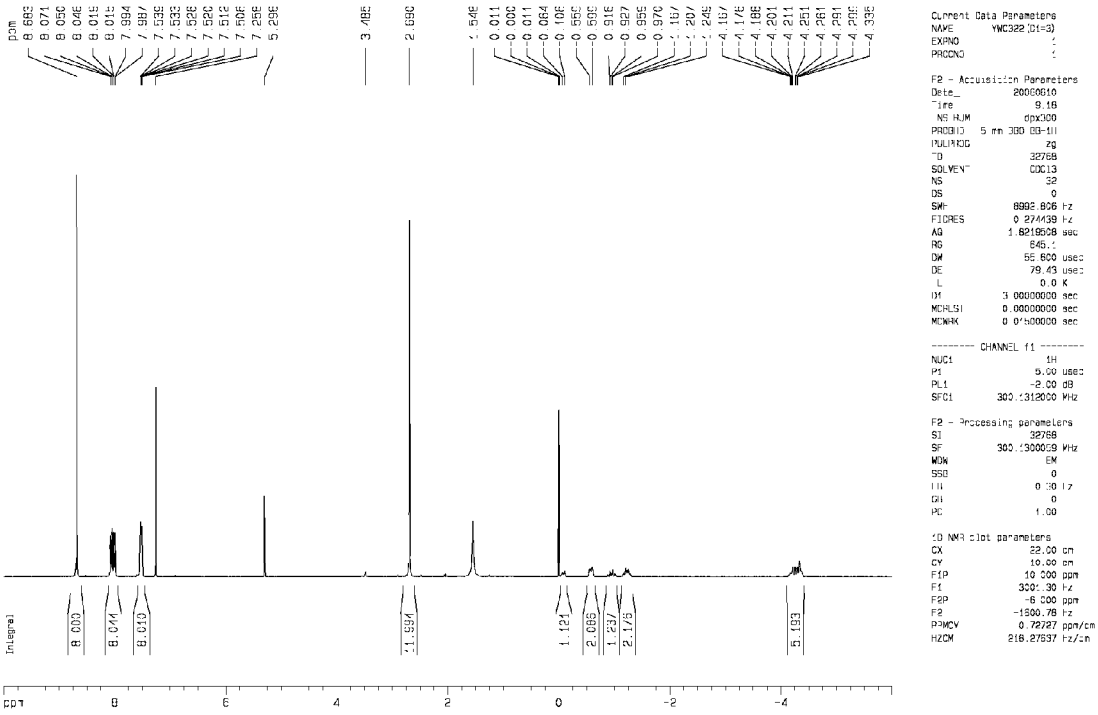


2e

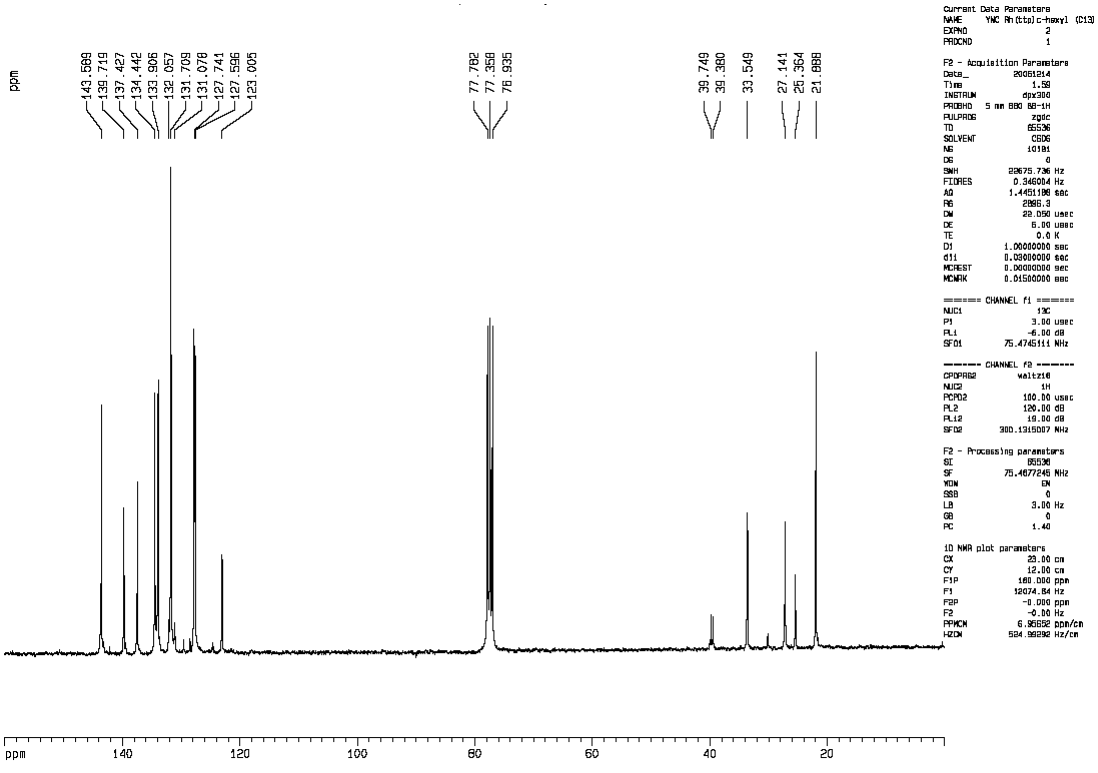
Spectra

Rh(ttp)(*c*-hexyl) (**2a**)

^{1}H NMR

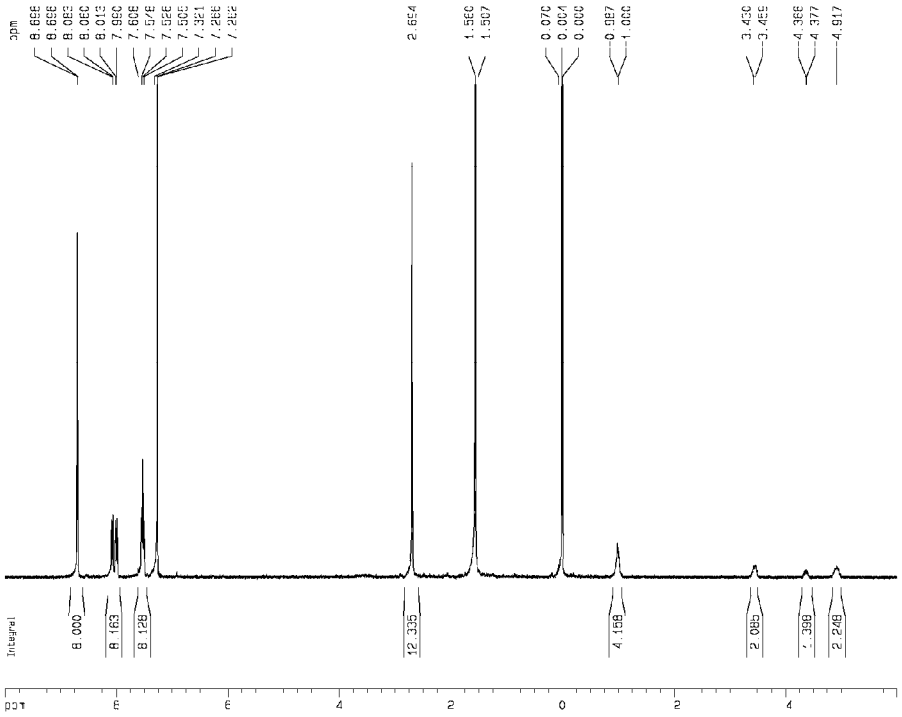


^{13}C NMR

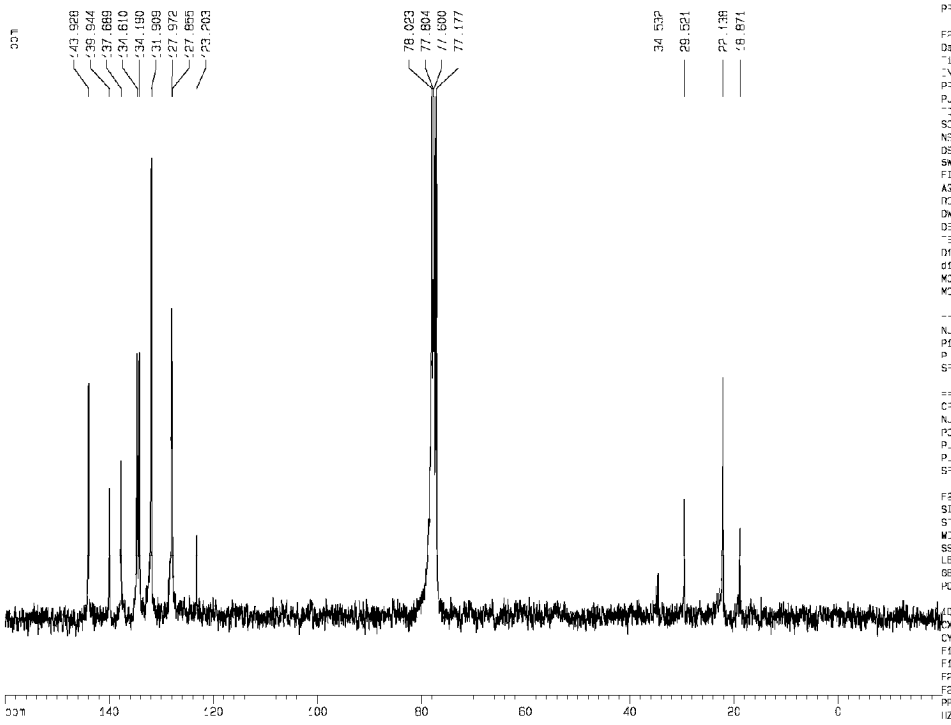


Rh(ttp)(*c*-pentyl) (**2b**)

^{1}H NMR

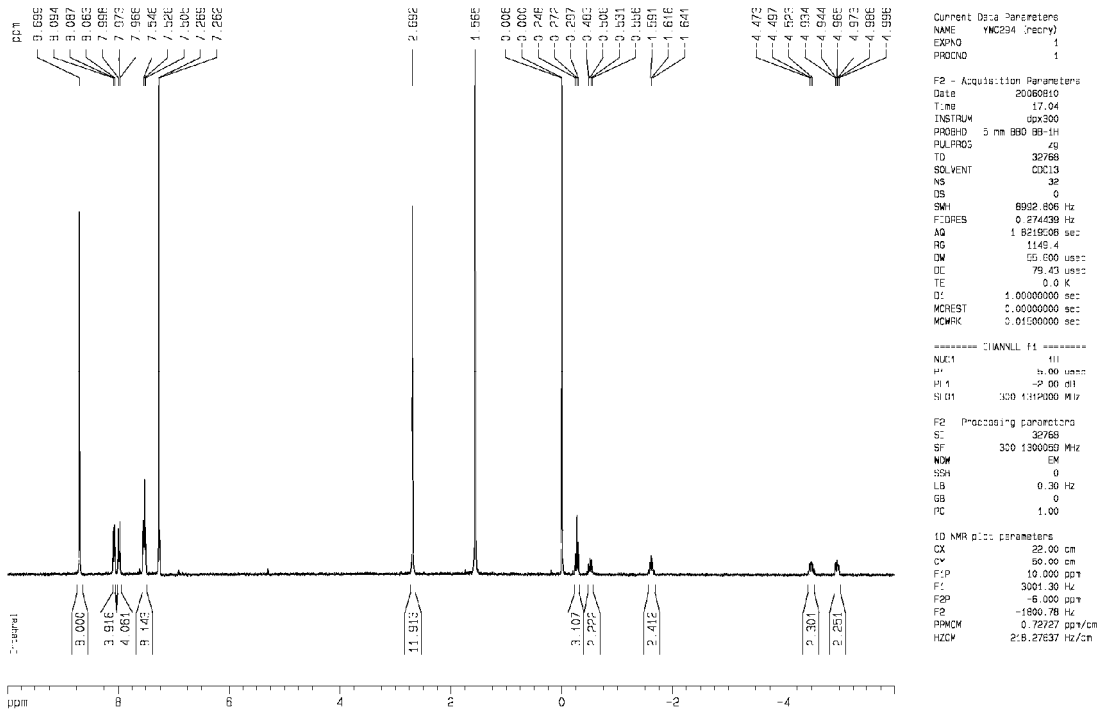


^{13}C NMR

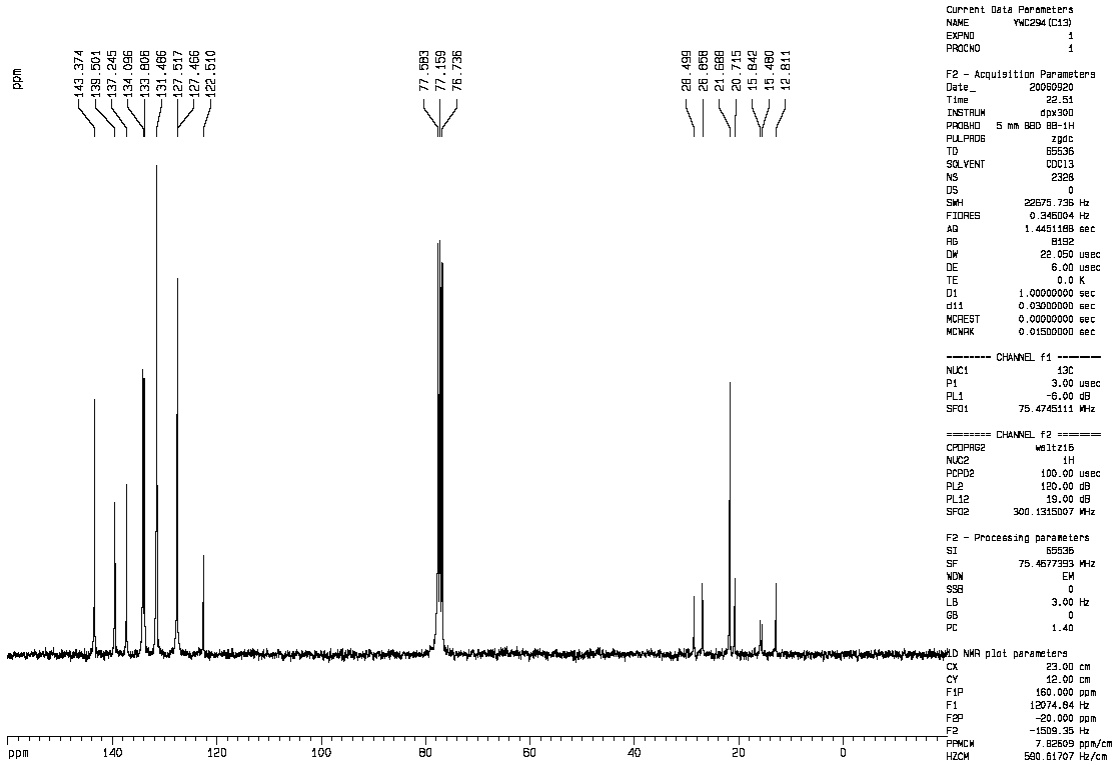


Rh(ttp)(*n*-pentyl) (**2c**)

^{1}H NMR

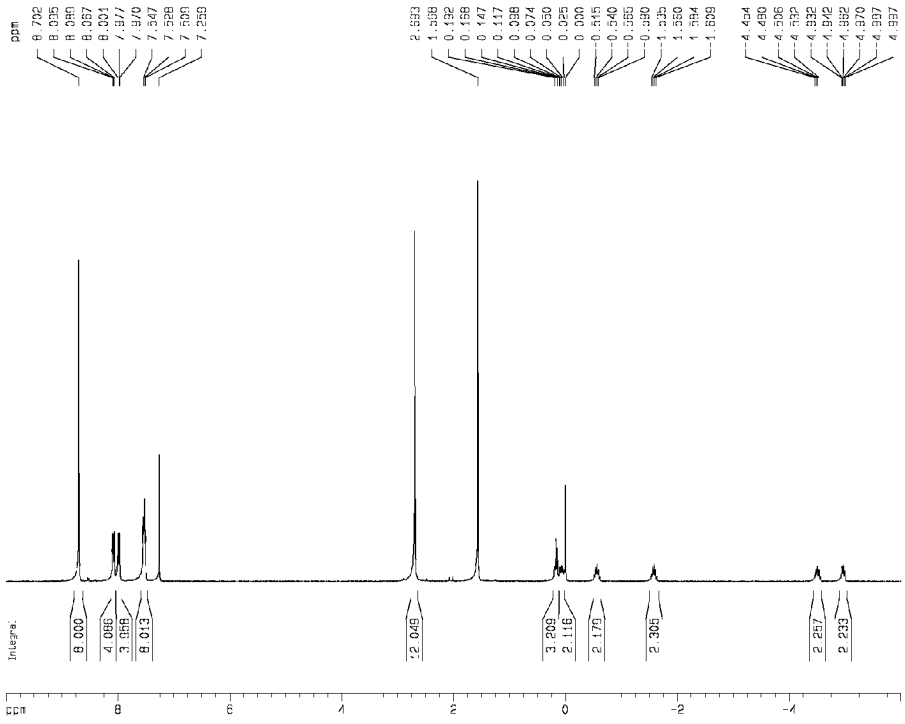


^{13}C NMR



Rh(ttp)(*n*-hexyl) (**2d**)

^{1}H NMR

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PROCNO                   1

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PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH              6devil 806 Hz
FIDRES         0.274439 Hz
AQ             1.8219008 sec
RG                  64x.1
DW                 55.600 usec
DE                 79.43 usec
TE                  0.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.00 usec
PL1                 -2.00 dB
SFO1          300.1312000 MHz

F2 - Processing parameters
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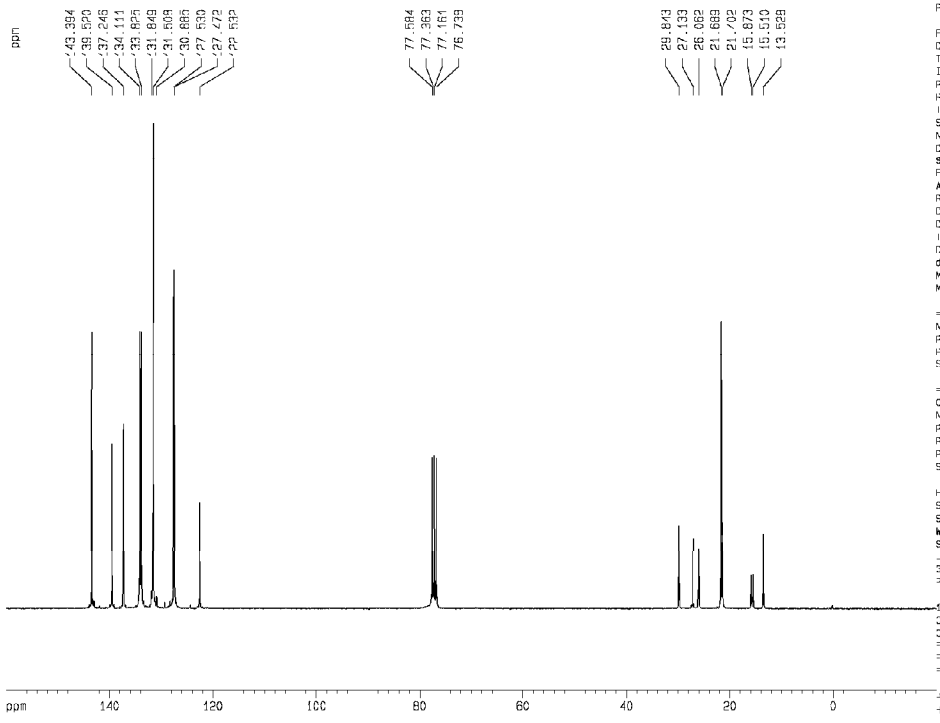
SF          300.1300056 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.00 cm
CY                  16.00 cm
F1P                10.000 ppm
F1                 3001.30 Hz
F2P                -6.000 ppm
F2                 1800.75 Hz
PPMCM              0.72727 ppm/cm
HZCM             218.27637 Hz/cm
```

^{13}C NMR

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PROCNO                   1

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PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                 13716
DS                     0
SWH          22675.738 Hz
FIDRES         0.346004 Hz
AQ             1.4451188 sec
RG                1825.5
DW                22.050 usec
DE                 6.00 usec
TE                  0.0 K
D1             1.00000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   3.00 usec
PL1                -6.00 dB
SFO1          75.4748411 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                120.00 dB
PL12                19.00 dB
SFO2          300.1315007 MHz

F2 - Processing parameters
SI                  65536
SF          75.4677406 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  23.00 cm
CY                  12.00 cm
F1P               180.000 ppm
F1              13074.64 Hz
F2P               -20.000 ppm
F2              -1509.55 Hz
PPMCM             7.82609 ppm/cm
HZCM            590.61767 Hz/cm
```
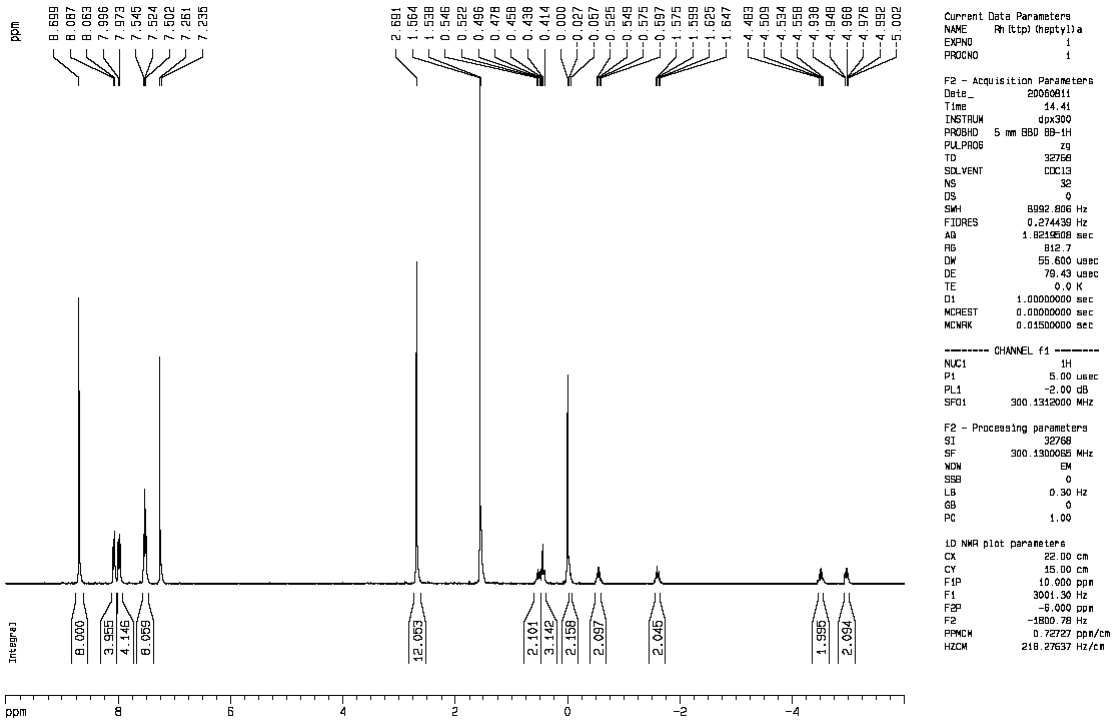

Rh(ttp)(*n*-heptyl) (**2e**)

^{1}H NMR

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Current Data Parameters
NAME      Rh(ttp)(heptyl)a
EXPNO                    1
PROCNO                   1

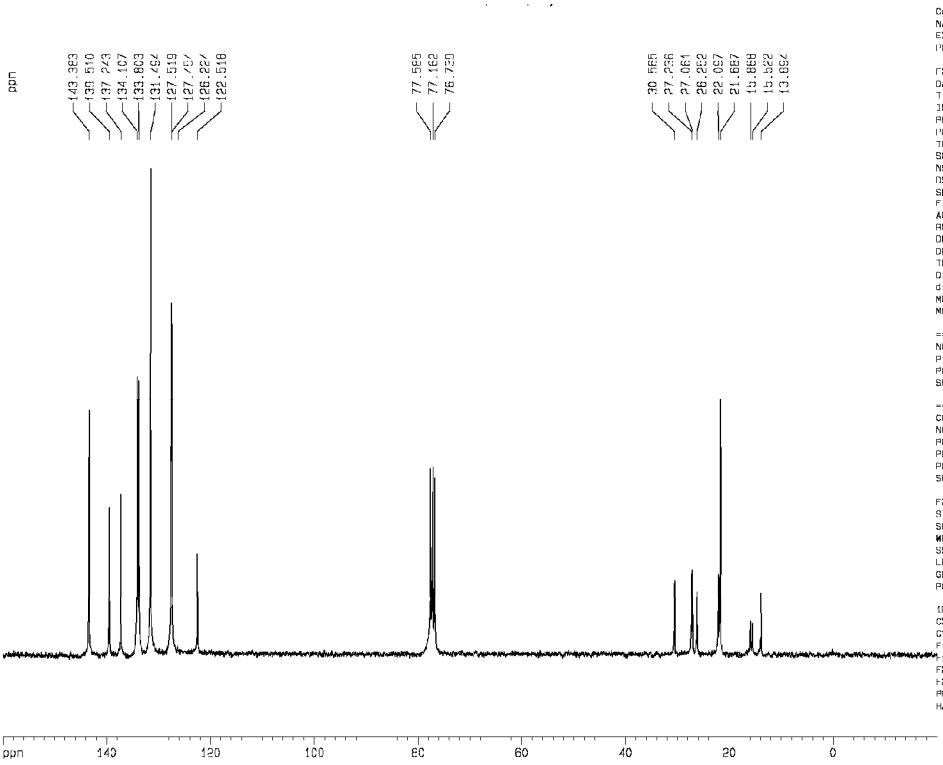
F2 - Acquisition Parameters
Date_           20060811
Time               14.41
INSTRUM           dpx300
PROBHD  5 mm BBO BB-1H
PULPROG              zg
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            8992.806 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                812.7
DW                55.600 usec
DE                70.43 usec
TE                 0.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

-------- CHANNEL f1 --------
NUC1                  1H
P1                  5.00 usec
PL1                -2.00 dB
SFO1         300.1312000 MHz

F2 - Processing parameters
SI                32768
SF          300.1300085 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.00 cm
CY                15.00 cm
F1P               10.000 ppm
F1              3001.30 Hz
F2P               -5.000 ppm
F2              -1500.78 Hz
PPMCM          0.72727 ppm/cm
HZCM         218.27637 Hz/cm
```

^{13}C NMR

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Current Data Parameters
NAME      Rh(ttp)Hept-1 (C13)
EXPNO                    2
PROCNO                   1

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PULPROG              zgpg
TD                65536
SOLVENT           CDCl3
NS                 2832
DS                    0
SWH           22675.736 Hz
FIDRES         0.345884 Hz
AQ             1.4451189 sec
RG                4096
DW                22.050 usec
DE                 6.00 usec
TE                 0.0 K
D1             1.00000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.00 usec
PL1                -6.00 dB
SFO1         75.4746111 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 usec
PL2                120.00 dB
PL12                19.00 dB
SFO2         300.1315007 MHz

F2 - Processing parameters
SI                65536
SF          75.4677403 MHz
WDW                  EM
SSB                   0
LB                 3.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                23.00 cm
CY                12.00 cm
F1P              160.000 ppm
F1             12074.84 Hz
F2P              -20.000 ppm
F2             -1509.36 Hz
PPMCM          7.86609 ppm/cm
HZCM         593.81707 Hz/cm
```
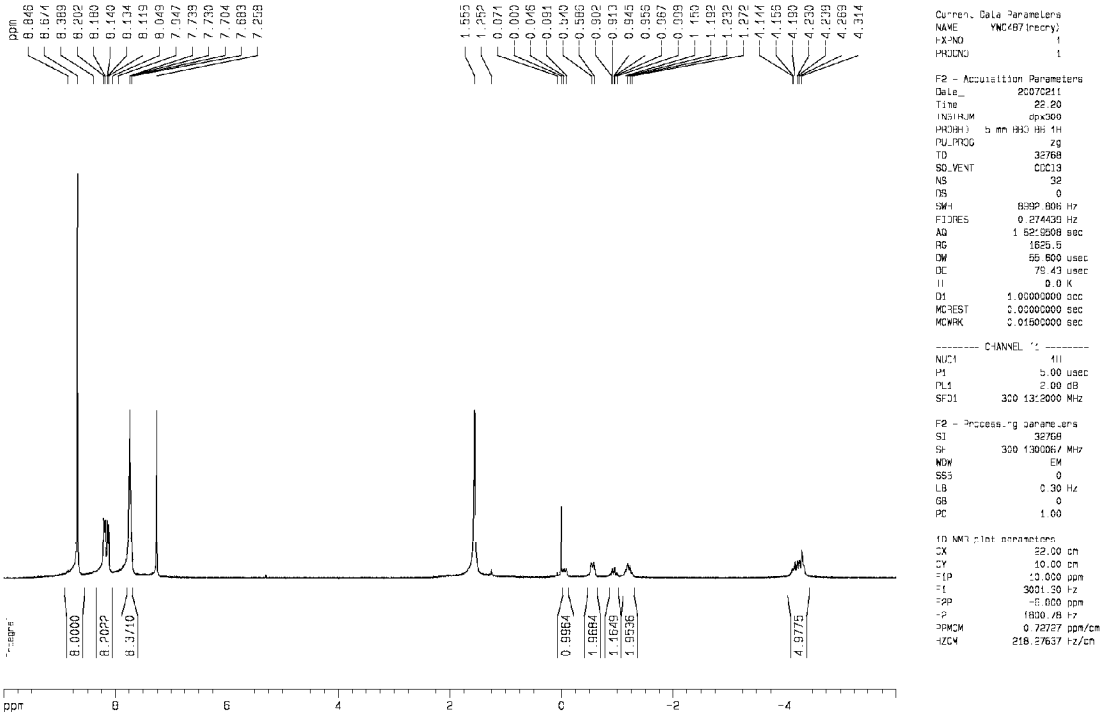
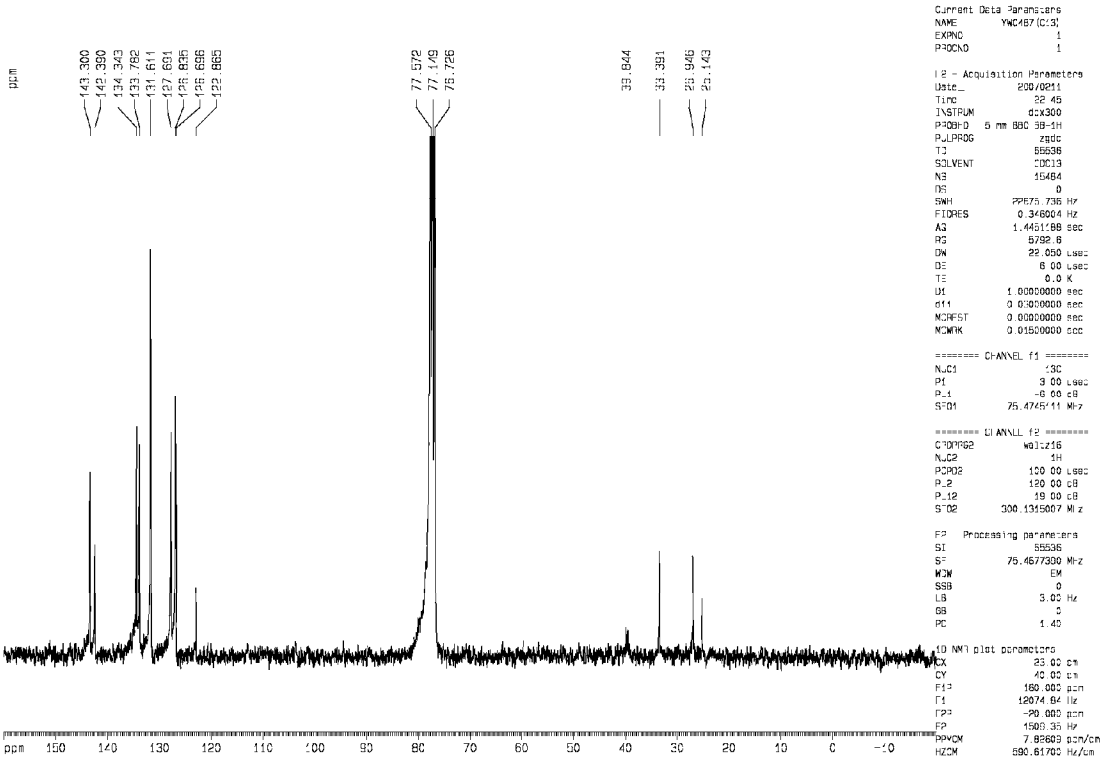

Rh(tpp)(*c*-hexyl) (**4a**)

^{1}H NMR

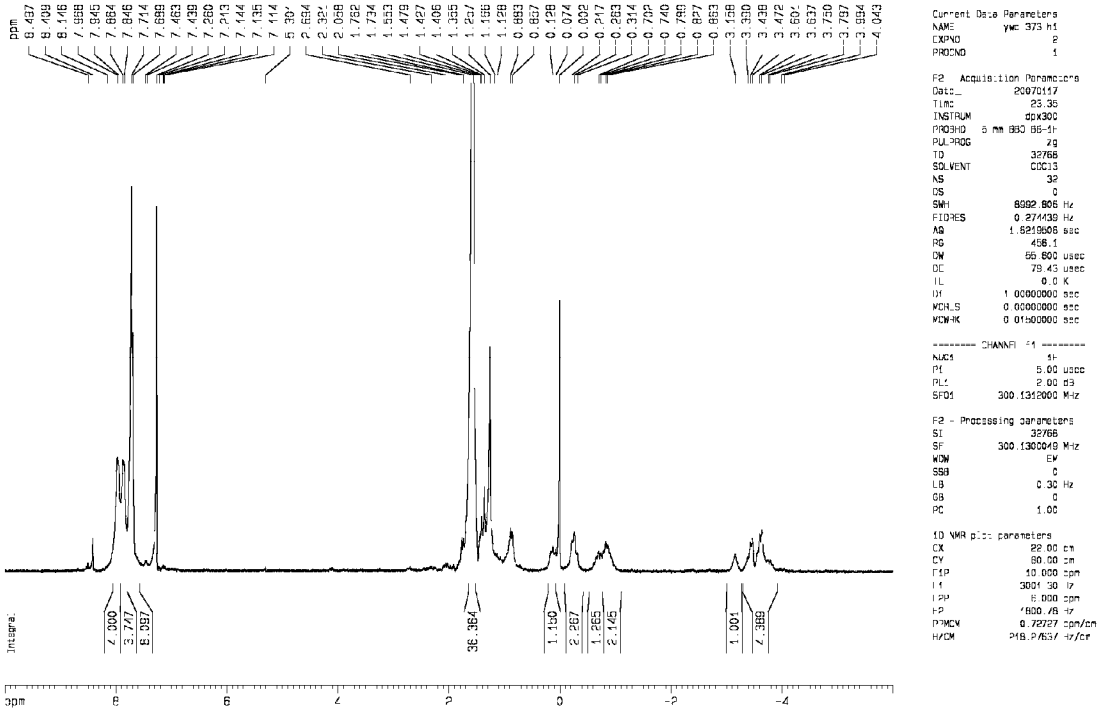


^{13}C NMR

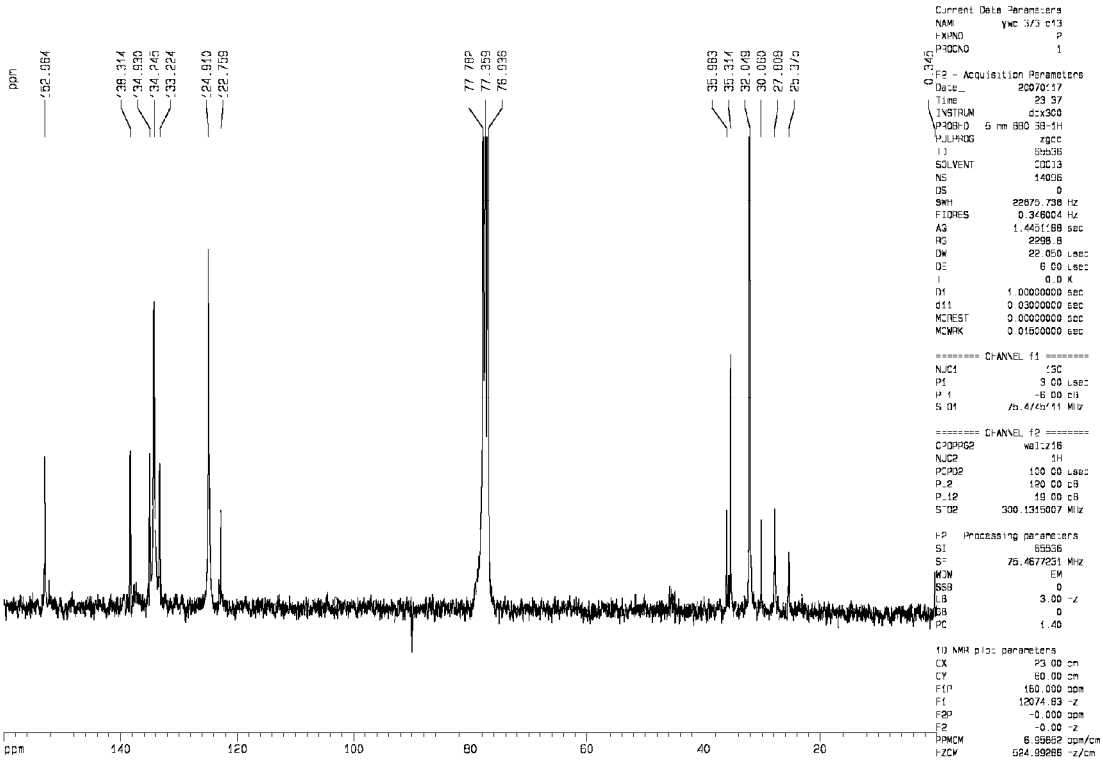


Rh(bocp)(*c*-hexyl) **(4b)**

^{1}H NMR

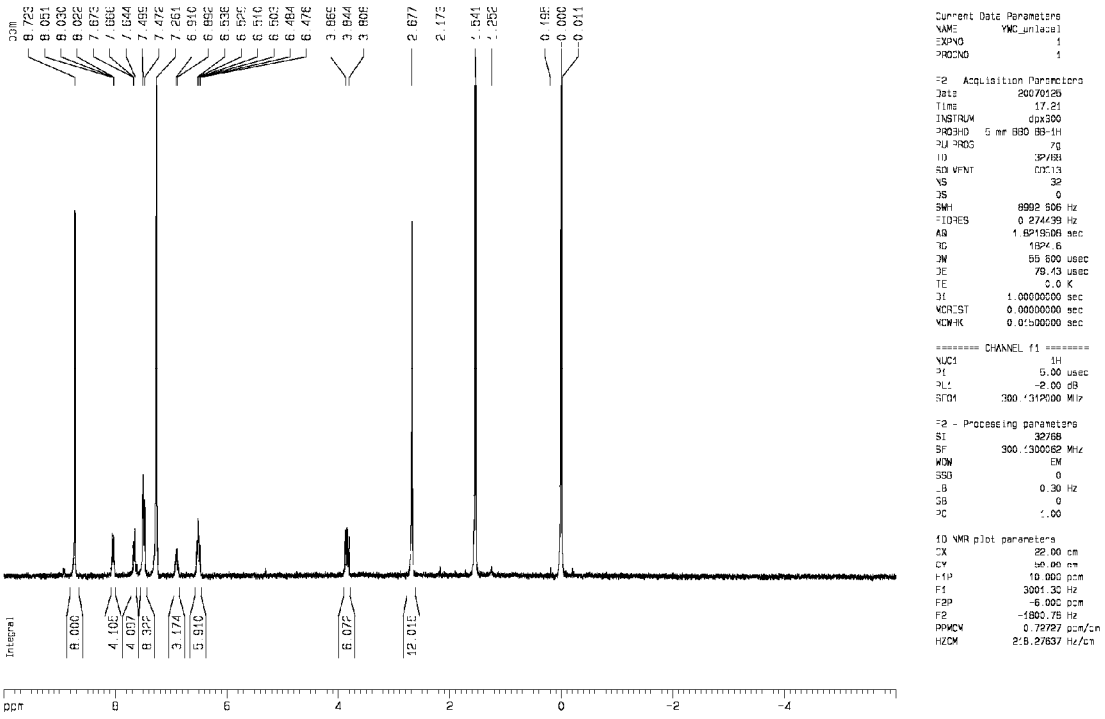


^{13}C NMR



Rh(ttp)Cl(Ph_3) (**2f**)

^{1}H NMR



^{13}C NMR

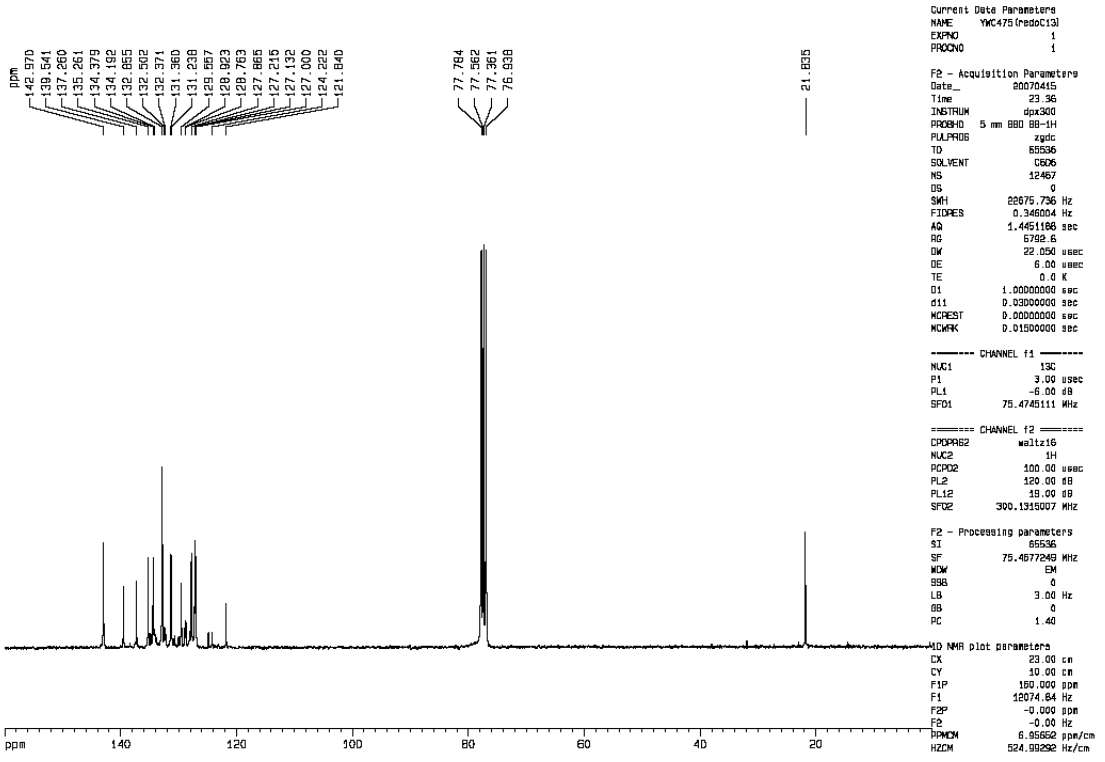
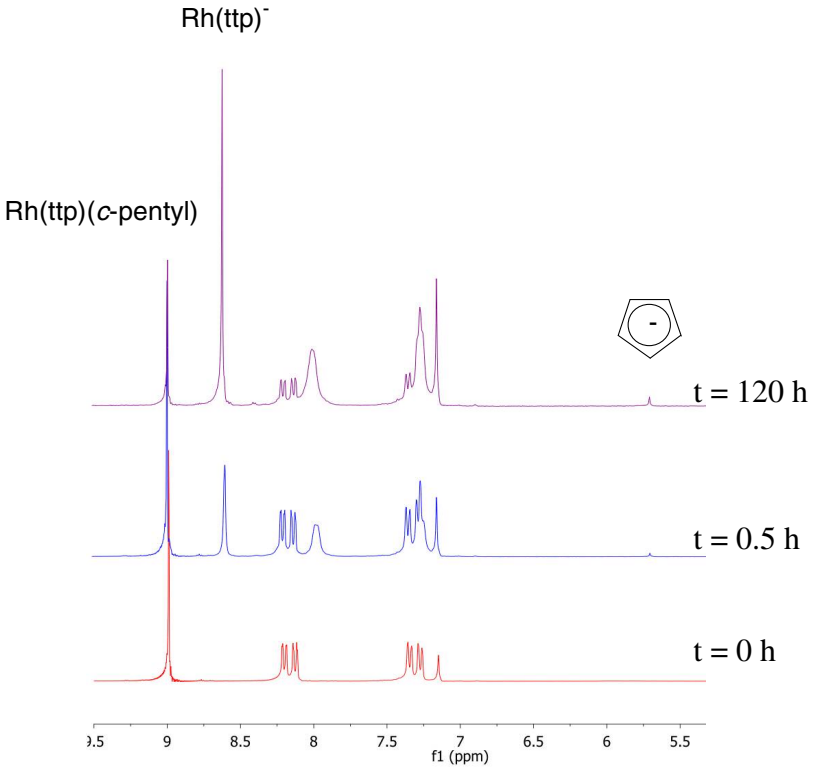


Figure 5. ^{1}H NMR spectra of the reaction Rh(ttp)(*c*-pentyl) with K_2CO_3 in Benzene-d_6



Scheme 4. Proposed Mechanism of Rh(ttp)(*c*-pentyl) Reaction

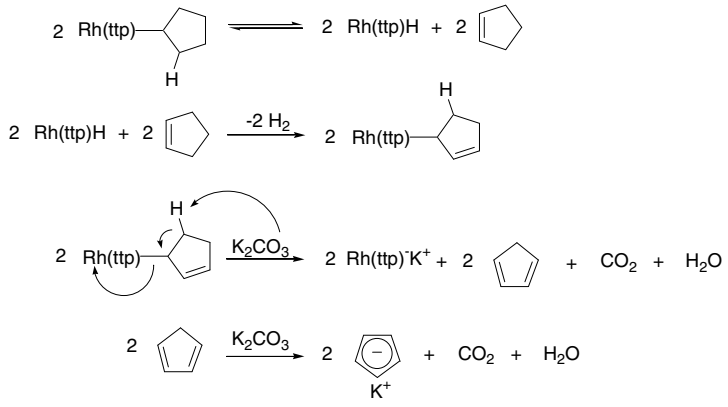
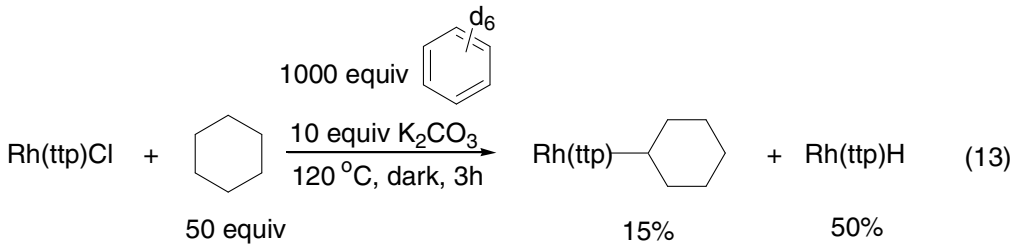


Table 10. Reaction Time Profile of Rh(ttp)Cl and Cyclohexane with K_2CO_3



		Yield (%)				
Entry	Time (h)	Rh(ttp)Cl	$[Rh(ttp)]_2$	Rh(ttp)H	Rh(ttp)(*c*-hexyl)	Total
1	0	100	0	0	0	100
2	0.5	71	20	0	0	91
3	1	44	22	32	0	98
4	2	24	17	51	5	97
5	3	14	8	50	15	87
6	12	0	0	56	11	67
7	36	0	0	53	8	61
8	96	0	0	52	9	61