

Supporting Information for

Metalloradical-Catalyzed Rearrangement of Cycloheptatrienyl to Benzyl

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Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and used after purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Rh(tp)H and Rh₂(tp)₂ were prepared according to literature procedures.¹ Thin-layer chromatography was performed on precoated silica gel 60 F₂₅₄ plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography in air.

^1H NMR spectra were recorded on a Bruker AvanceIII 400 (400 MHz). Spectra were referenced internally to the residual proton resonance in C₆D₆ (δ 7.15 ppm) or CDCl₃ (δ 7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). ^{13}C NMR spectra were recorded on a Bruker AvanceIII 400 (100 MHz) spectrometer and referenced to CDCl₃ (δ 77.10 ppm). Coupling constants (J) are reported in hertz (Hz). Mass spectra (HRMS) were performed on a

ThermoFinnigan MAT 95 XL instrument (FABMS). The kinetic experiments were carried out with an old GC-oven with temperature kept at ± 0.1 °C.

The reactions were carried out in N₂ in the dark with Teflon-stoppered reaction tubes or NMR tubes sealed under vacuum and covered with aluminum foil. Unless otherwise stated, the reactions were duplicated and the yields were the average values when conducted in Teflon-stoppered reaction tubes. They were traced by TLC. Unless otherwise stated, all the reactions were stopped once the starting materials were consumed. Unless otherwise stated, the yields of reactions which carried out in NMR tubes were determined using benzene residue as the internal standard.

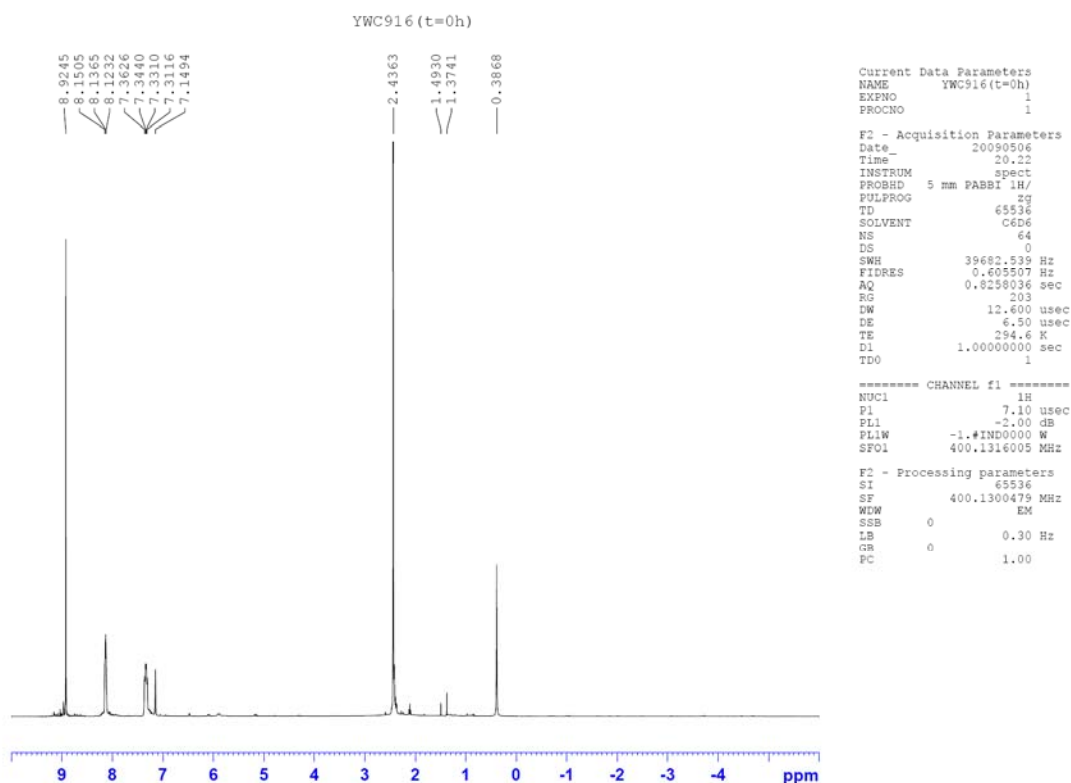
Reaction of Rh₂(ttp)₂¹ and Cycloheptatriene in Benzene-*d*₆. Rh₂(ttp)₂ (3.6 mg, 0.0023 mmol), cycloheptatriene (5 μL) and degassed benzene-*d*₆ (500 μL) were added in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was kept at room temperature. The reaction progress was monitored with ¹H NMR spectroscopy after 5 minutes. Rh(tp)(cycloheptatrienyl) **1** was obtained quantitatively. ¹H NMR (C₆D₆, 400 MHz) δ 2.44 (s, 19), 7.32 (d, 8 H, *J* = 7.4 Hz, *m*-phenyl), 7.35 (d, 4 H, *J* = 7.8 Hz, *o*-phenyl), 8.13 (d, 4 H, *J* = 5.4 Hz, *m*'-phenyl), 8.14 (d, 4 H, *J* = 5.4 Hz, *o*'-phenyl), 8.93 (s, 8 H, pyrrole). ¹³C NMR (C₆D₆, 100 MHz) δ 21.50, 123.47, 131.82, 132.80, 134.22, 134.28, 134.92, 137.11, 140.43, 144.24. HRMS (FABMS) Calcd. for (C₅₅H₄₃N₄Rh)⁺: *m/z* 862.2537. Found: *m/z* 862.2549. Single crystal for X-ray diffraction analysis was grown from CH₂Cl₂/methanol.

Reaction of Rh(tp)H¹ and Cycloheptatriene in Benzene-*d*₆. Rh(tp)H (3.6 mg, 0.0047 mmol), cycloheptatriene (5 μL) and degassed benzene-*d*₆ (500 μL) were added in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was kept at room temperature. The reaction progress was

monitored with ^1H NMR spectroscopy after 5 minutes and 15 minutes. Rh(tp)(cycloheptatrienyl) **1** was obtained quantitatively.

Synthesis of Rh(tp)(cycloheptatrienyl) 1. Rh(tp)H (3.6 mg, 0.0047 mmol) and cycloheptatriene (5 μL) were added into degassed benzene (500 μL) in a Telfon-stoppered tube. The red solution was degassed for three freeze-thaw-pump cycles, purged with N_2 and put into a water bath at 25 $^\circ\text{C}$ for 15 minutes. After the solvent was removed by vacuum distillation, 500 μL degassed benzene- d_6 was then added and the product was found to be air-sensitive and decomposed during column chromatography.

The following shows a ^1H NMR spectrum of Rh(tp)(cycloheptatrienyl) which formed from the reaction between Rh(tp)H and CHT.



Kinetic of Rearrangement reaction of Rh(tp)(cycloheptatrienyl). The experimental procedure of a typical kinetic rearrangement reaction of Rh(tp)(cycloheptatrienyl) (eq S1) was described as follow: Rh(tp)(cycloheptatrienyl) **1** (4.0 mg, 0.0046 mmol) was added into degassed benzene- d_6 (500 μ L) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 $^{\circ}$ C in a thermostated-oven. The reaction was monitored with 1 H NMR spectroscopy and Rh(tp)Bn² was formed. The collected kinetic data were fitted by first-order exponential decay using OriginPro 7.5 software.

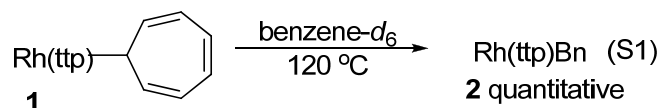


Table S1 summarized the experimental results of various initial concentrations of Rh(tp)(cycloheptatrienyl) (entry 1 vs 2) and various reaction temperatures (entry 1 vs entries 3-5).

Table S1 k_{obs} of the rearrangement of Rh(tp)(cycloheptatrienyl) at different conditions

Entry	$[\mathbf{1}]_0 \times 10^3$ /M	Temp / $^{\circ}$ C	$1/T$ ($\times 10^{-3}$ K^{-1})	$k_{\text{obs}} \times 10^6$ / s^{-1}	Error $\times 10^7$ / s^{-1}	$k \times 10^4$ / $\text{L}^{-1} \text{mol}^{-1}$ s^{-1}
1	6.95	120	2.545	4.75439	3.97540	6.84892
2	13.90	120	2.545	4.69852	3.45935	6.76046
3	6.95	130	2.481	8.76127	8.45695	12.6043
4	6.95	140	2.421	15.4640	34.0559	22.3022
5	6.95	150	2.364	41.0845	57.0695	59.1367

The following shows a typical example of 1st order decay of Rh(tp)(cycloheptatrienyl) (Fig. S1).

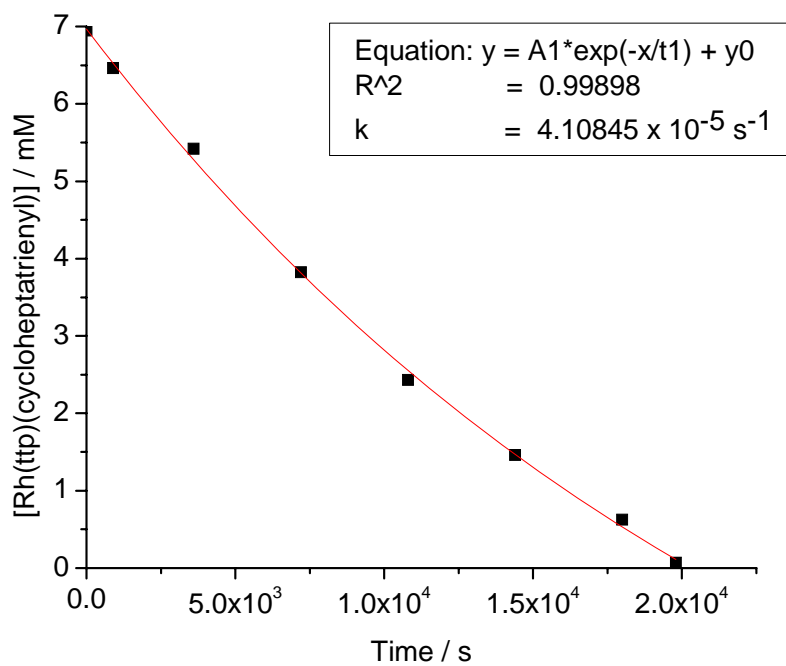


Fig. S1 1st Order decay of Rh(tp)(cycloheptatrienyl) at 150 °C

Determination of Reaction Order and Rate Constant

The rate equation can be expressed as eq S2, where k_{obs} was the observed rate constant of the reaction.

$$\text{Rate} = k [\text{Rh}(\text{tp})(\text{cycloheptatrienyl})]^m \quad (\text{S2})$$

Firstly, the value of m was evaluated. Typical conditions were $[\text{Rh}(\text{tp})(\text{cycloheptatrienyl})]_0 = 6.95 \times 10^{-3} \text{ M}$ to $13.90 \times 10^{-3} \text{ M}$ and $T = 120 \text{ }^\circ\text{C}$. The results were fitted well by a first-order exponential decay function (Table S1, entries 1 and 2). The k_{obs} of $[\text{Rh}(\text{tp})(\text{cycloheptatrienyl})]_0 = 6.95 \times 10^{-3} \text{ M}$ and $13.90 \times 10^{-3} \text{ M}$ were found to be $4.75 \times 10^{-6} \text{ s}^{-1}$ and $4.70 \times 10^{-6} \text{ s}^{-1}$, respectively. As k_{obs} did not change with the initial concentration

of Rh(tp)(cycloheptatrienyl) **1**, the kinetic order of Rh(tp)(cycloheptatrienyl) **1** was confirmed to be one. According to the above results, the rate law can be expressed as rate = $k_{\text{obs}} [\text{Rh}(\text{tp})(\text{cycloheptatrienyl})]$, where $k_{\text{obs}} = 4.75 \times 10^{-6} \text{ s}^{-1}$ at 120 °C. The conversion of **1** to **2** was a first order reaction.

The Eyring equation describes the temperature dependence of reaction rate (eq S3).⁴

$$\ln(k/T) = -\Delta H^\ddagger/(RT) + \ln(\kappa/h) + \Delta S^\ddagger/R \quad (\text{S3})$$

(κ is the Boltzmann constant, R is the ideal gas constant and h is the Planck's constant.)

Therefore, a plot of $\ln(k/T)$ against $1/T$ gives a linear Eyring plot with a slope of $-\Delta H^\ddagger/R$ and a y-intercept of $\ln(\kappa/h) + \Delta S^\ddagger/R$ (Fig. S2, Table S2).⁴

Table S2 $\ln(k/T)$ at different (1/T)

Entry	Temp / °C	1 / T (x 10 ⁻³ K ⁻¹)	k x 10 ⁶ /s ⁻¹	Error x 10 ⁷ /s ⁻¹	ln (k _{obs} /T)
1	120	2.545	4.75439	3.97540	-18.2303
2	130	2.481	8.76127	8.45695	-17.6441
3	140	2.421	15.4640	34.0559	-17.1004
4	150	2.364	41.0845	57.0695	-16.1473

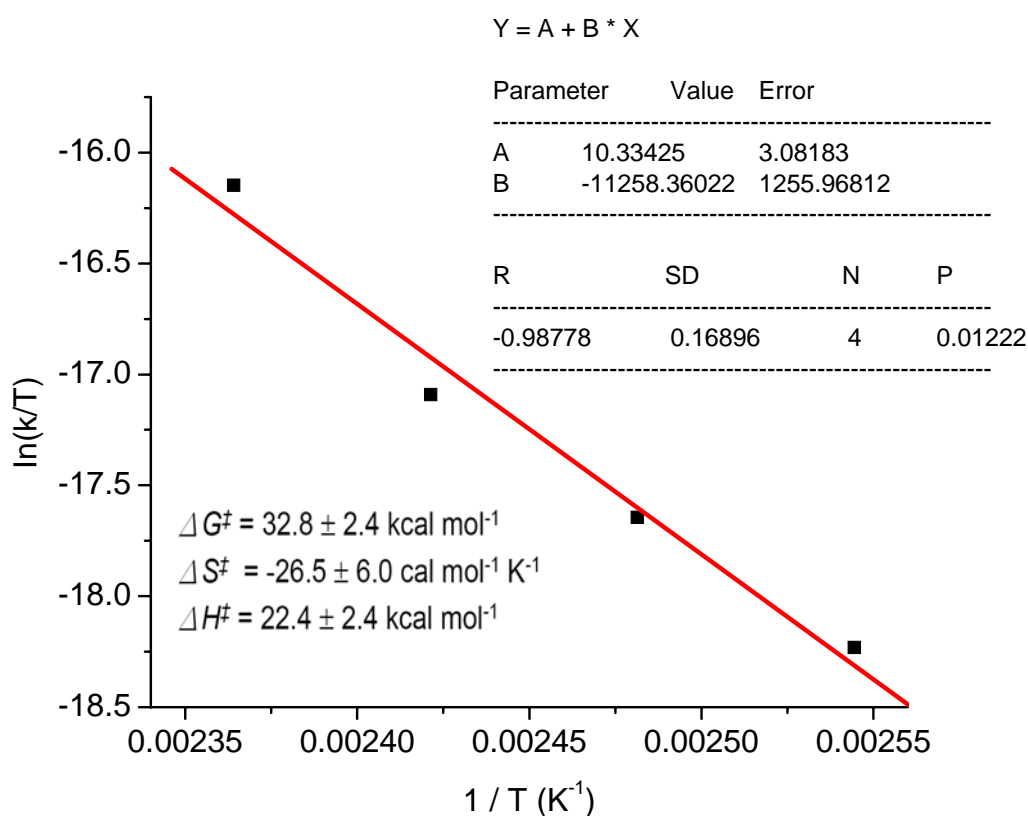


Fig. S2 Eyring Plot of the Conversion of **1** to **2** over the Temperature Range 120-150 °C

Since y-intercept = $\ln(\kappa/h) + \Delta S^\ddagger/R$

$$10.39025 = \ln(1.3807 \times 10^{-23}/6.6261 \times 10^{-34}) + \Delta S^\ddagger/1.9859$$

$$\Delta S^\ddagger = -26.5 \pm 6.0 \text{ cal mol}^{-1} \text{ K}^{-1}$$

And slope = $-\Delta H^\ddagger/R$

$$-11280 = -\Delta H^\ddagger/1.9859$$

$$\Delta H^\ddagger = 22.4 \pm 2.4 \text{ kcal mol}^{-1}$$

Then $\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$

$$\Delta G^\ddagger = 32.8 \pm 2.4 \text{ kcal mol}^{-1}$$

Kinetic of Rearrangement reaction of Rh(tp)(cycloheptatrienyl) with [Rh₂(tp)₂] addition. Rh(tp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) and Rh₂(tp)₂ (0.027 mg, 1.7 x 10⁻⁵ mmol) were added into degassed benzene-*d*₆ (500 μL) in a NMR tube. The red reaction mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. The reaction was monitored with ¹H NMR spectroscopy and the NMR yields were taken.

Table S3 summarized the experimental results of rearrangement reaction of Rh(tp)(cycloheptatrienyl) with the addition of various [Rh₂(tp)₂] (entry 1 vs 2).

Table S3 *k*_{obs} of the rearrangement of Rh(tp)(cycloheptatrienyl) with various [Rh₂(tp)₂]

Entry	[8] ₀ x 10 ³ /M	Additive	<i>k</i> _{obs} x 10 ⁶ /s ⁻¹	Error x 10 ⁷ /s ⁻¹
1	6.95	Rh ₂ (tp) ₂ (3.48 x 10 ⁻⁵ M) ^a	7.33611	2.04693
2	6.95	Rh ₂ (tp) ₂ (3.48 x 10 ⁻⁴ M) ^b	21.5318	12.6614

^a 1 mol%; ^b 10 mol%

Rate extrapolation of CHT to Toluene at 120 °C from literature.

According to the data obtained from literature,³ log (A/s⁻¹) was 13.6 and E was 217.7 kJ mol⁻¹.

By Arrhenius equation,

$$\ln k = -E_a/RT + \ln A$$

$$\text{At } 120 \text{ }^\circ\text{C}, \ln k = -217.7 \times 1000 / (8.314 \times 393) + \ln (10^{13.6})$$

$$\ln k = -35.3$$

$$k = 4.61 \times 10^{-16} \text{ s}^{-1}$$

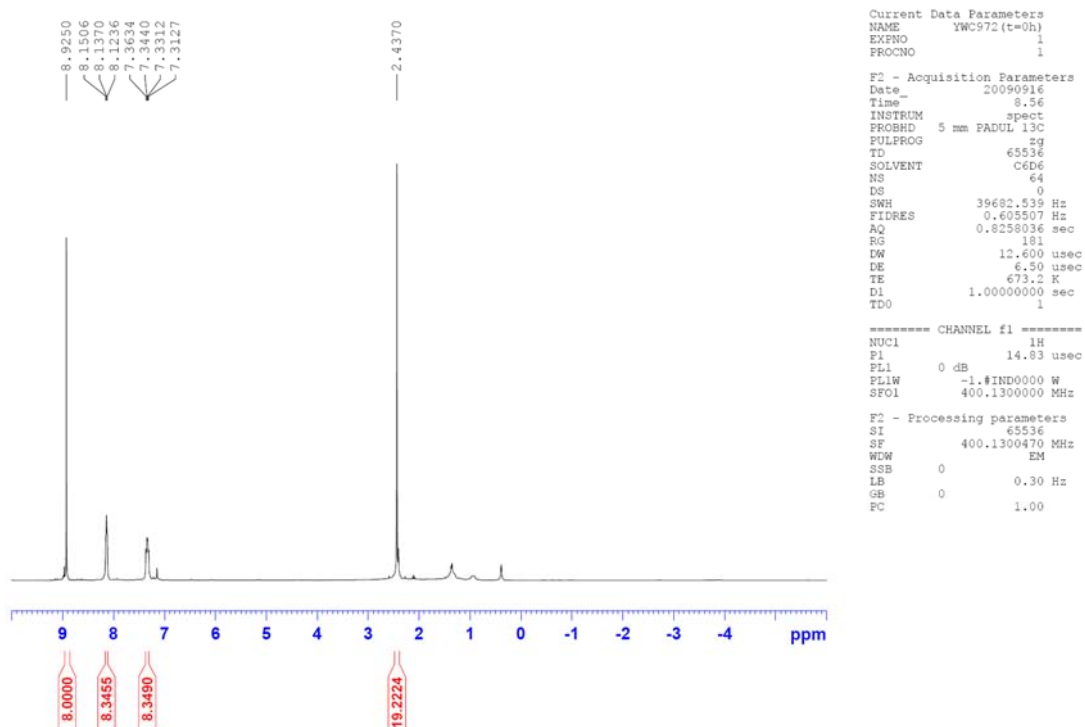
Rate extrapolation of CHT to Toluene at 475 °C.

At 475 °C, $\ln k = -217.7 \times 1000 / (8.314 \times 648) + \ln (10^{13.6})$

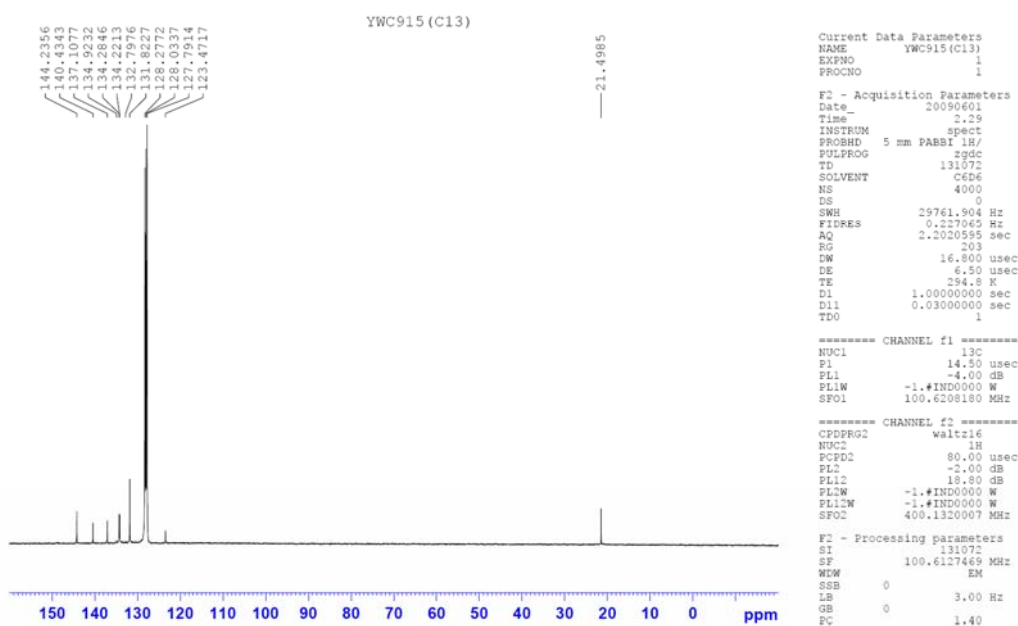
$$\ln k = -9.09$$

$$k = 1.12 \times 10^{-4} \text{ s}^{-1}$$

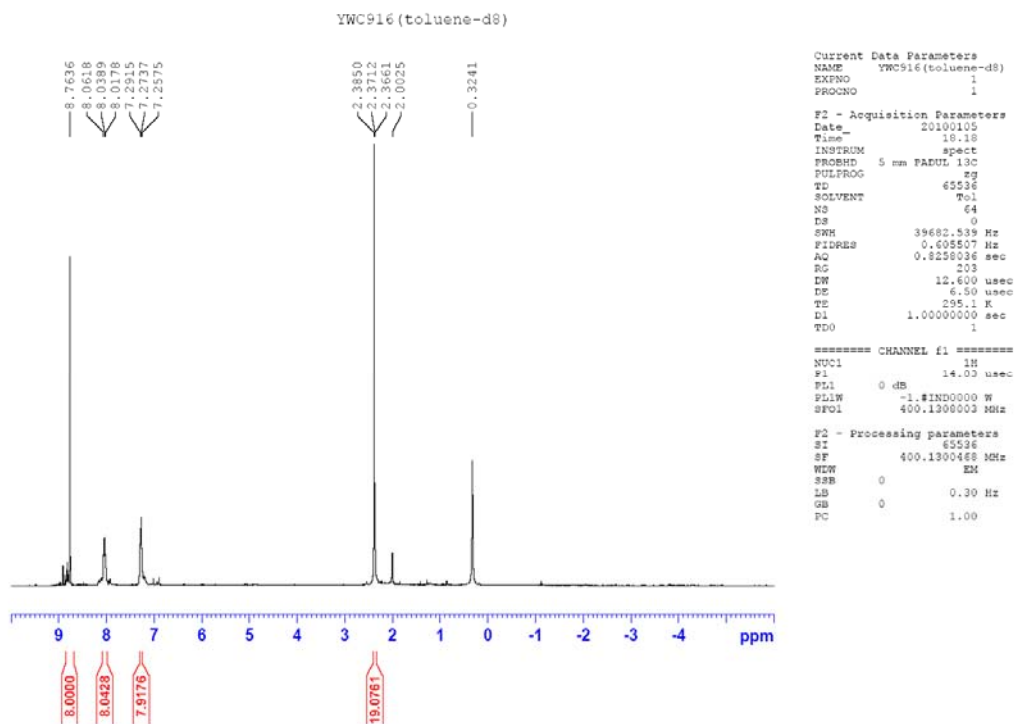
Rh(ttp)(cycloheptatrienyl) **1** ¹H NMR



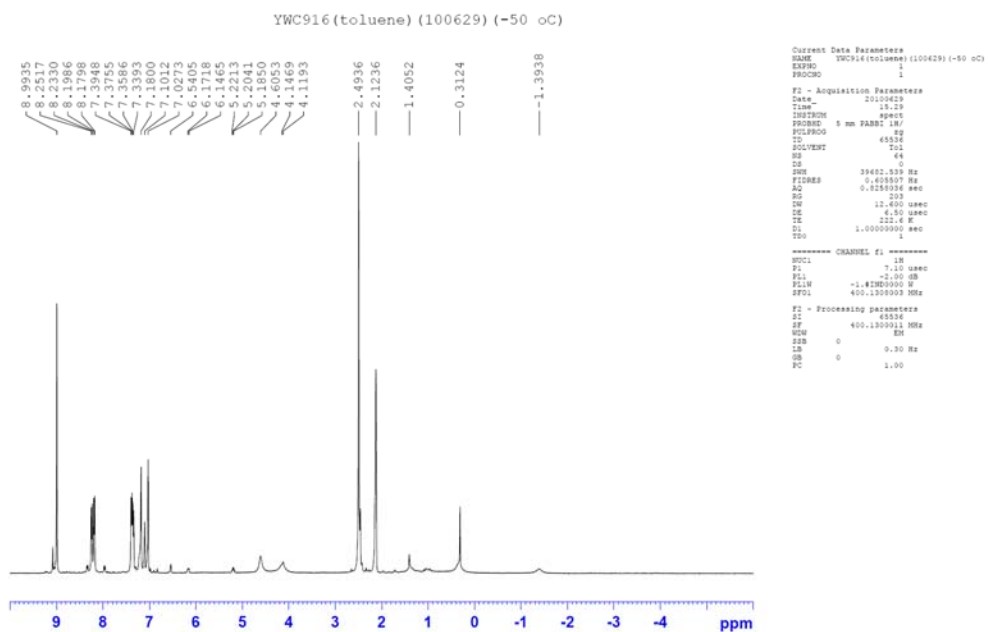
Rh(ttp)(cycloheptatrienyl) **1** ¹³C NMR



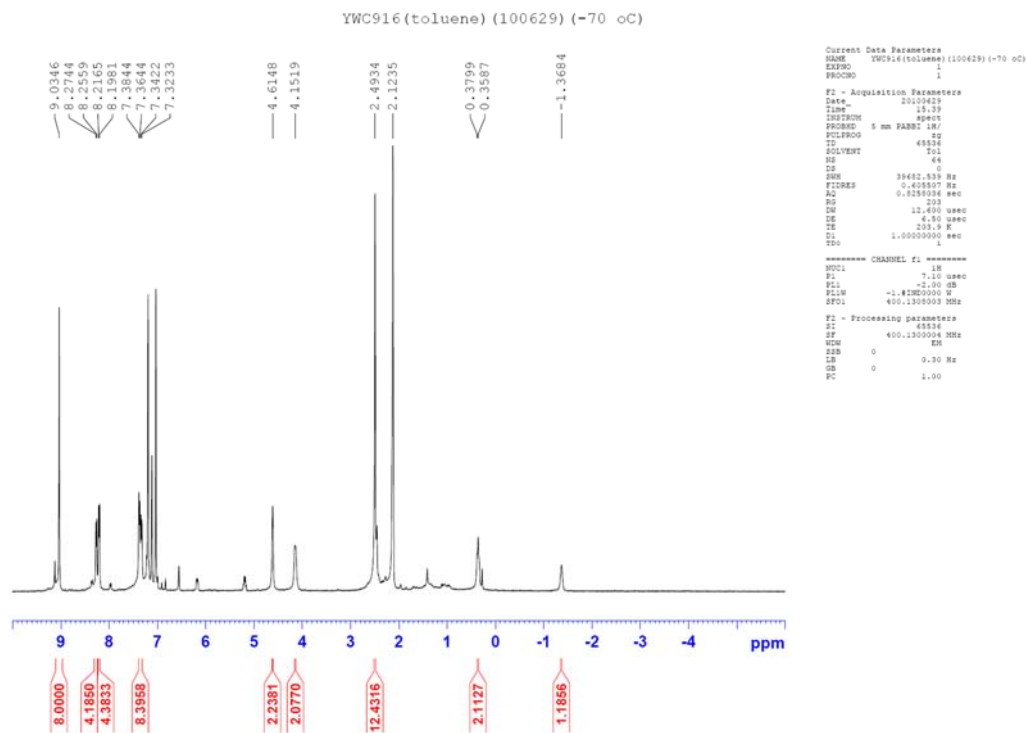
Rh(ttp)(cycloheptatrienyl) **1** (toluene-*d*₈, 25 °C) ¹H NMR



Rh(ttp)(cycloheptatrienyl) **1** (toluene-*d*₈, -50 °C) ¹H NMR



Rh(ttp)(cycloheptatrienyl) **1** (toluene-*d*₈, -70 °C) ¹H NMR



X-ray data and structure

Table S4 Crystal Data and Summary of Data Collection and Refinement for **1**

	Rh(tp)(cycloheptatrienyl) 1
Color, shape	Purple Prism
empirical formula	C ₅₅ H ₄₂ N ₄ Rh
formula wt	861.84
Temp (K)	296(2)
wavelength(Å)	0.71073
cryst syst	monoclinic
Space group	P2 ₁ /n
unit cell dimens	
<i>a</i> (Å)	15.486 (1)
<i>b</i> (Å)	18.711 (1)
<i>c</i> (Å)	16.421 (1)
<i>α</i> (deg)	90
<i>β</i> (deg)	106.763 (1)
<i>γ</i> (deg)	90
Volumn (Å ³)	4555.9 (2)
<i>Z</i>	4
Calcd density (g cm ⁻³)	1.256
abs coeff (mm ⁻¹)	0.415
<i>F</i> (000)	1780
cryst size (mm)	0.50 x 0.40 x 0.30
<i>θ</i> range for data collection (deg)	1.59 to 25.25
Limiting indices	-18 ≤ <i>h</i> ≤ 16
	-22 ≤ <i>h</i> ≤ 22
	-19 ≤ <i>h</i> ≤ 19
no. of rflns collected/ unique	42092/8244 [R(int) = 0.0468]
Completeness to <i>θ</i> = 28	100.0
Absorp corr	Multi-scan
max. and min. transmn	0.7456 and 0.6264
Refinement method	Full-matrix least squares on <i>F</i> ²
no. of data/ restraints / params	8244 / 17 / 550
GOF	1.061
final R indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.0364
	wR ₂ = 0.1030
R indices (all data)	R ₁ = 0.0435
	wR ₂ = 0.1081
Largest diff peak and hole (e Å ⁻³)	0.750 and -0.336

^a $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b $wR_2 = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]} \right\}^{1/2}$. ^c Weighting scheme $w^{-1} = \sigma^2(F_o^2) + (w_1P)^2 + w_2P$ where $P = (F_o^2 + 2F_c^2)/3$.

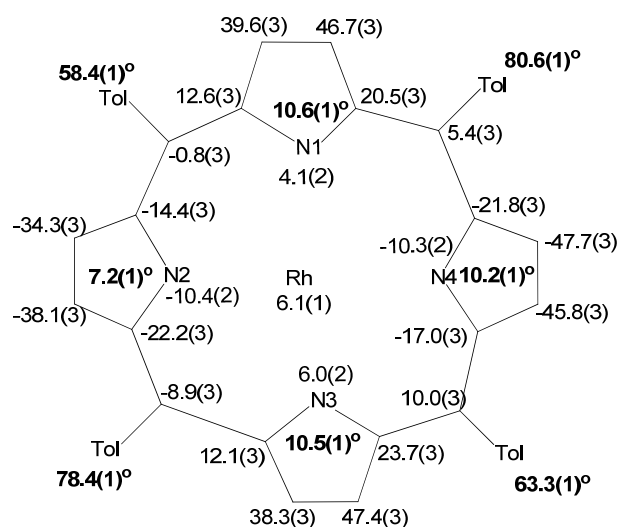


Fig. S3 The conformations of porphyrins in **1** showing the displacement of the core atoms and of Rh from the 24-atom least squares plane of porphyrin core (in pm; positive values correspond to displacement towards the alkyl group). Absolute values of the angles between pyrrole rings and the least-squares 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.

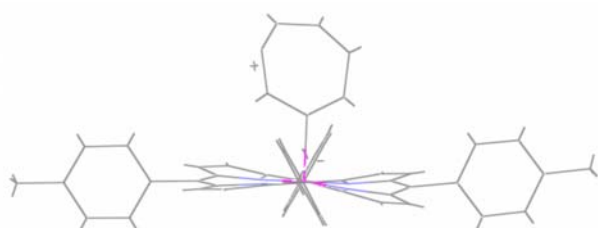


Fig. S4 Wireframe presentation of the molecular structures for **1**.

Table S5 Selected Bond lengths (Å) and Angles (deg) for Rh(tp)(cycloheptatrienyl)

Entry	Rh(tp)R	Rh-C length (Å)	Max. deviation from 24-least sq plane (Å)	Rh- N_{average} (Å)
1	Rh(tp)(cycloheptatrienyl) 1	2.104 (3)	0.477(3)	2.017

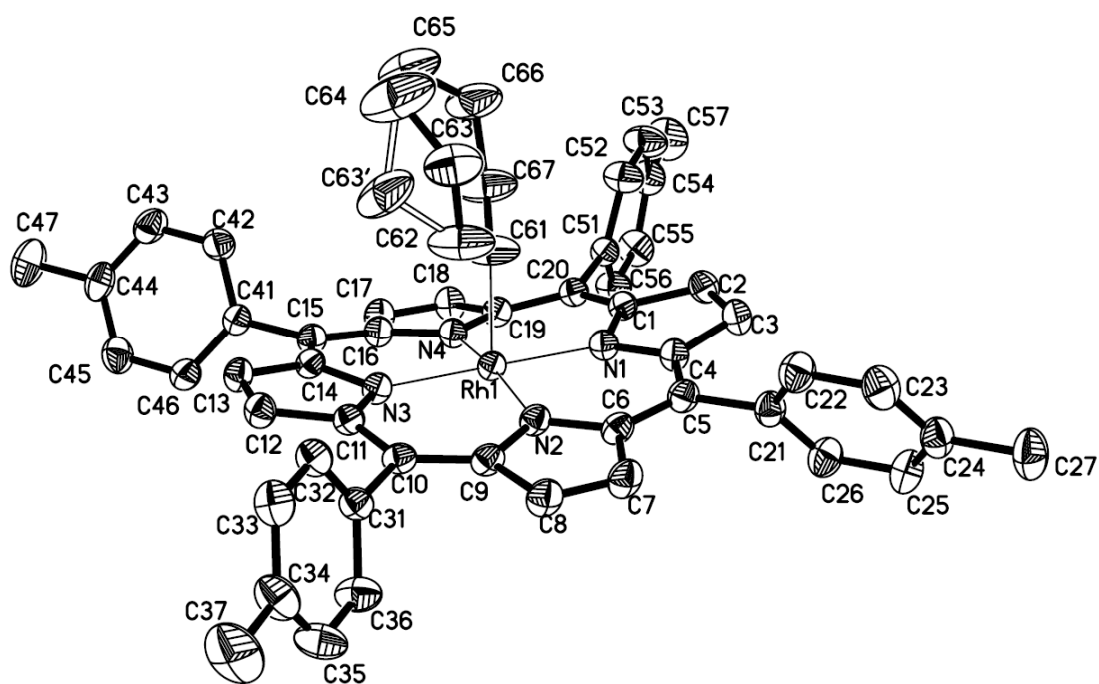


Fig. S5 ORTEP presentation of Rh(tp)(cycloheptatrienyl) (30% probability displacement ellipsoids)

Table S6 Selected Carbon–Carbon Bond lengths (Å) of Rh(tmp)(cycloheptatrienyl)

Entry	Carbon–Carbon Bond	Bond Length (Å)
1	C61–C62	1.458(4)
2	C62–C63	1.425(6)
3	C63–C64	1.492(8)
4	C64–C65	1.442(6)
5	C65–C66	1.459(6)
6	C66–C67	1.449(5)
7	C61–C67	1.444(4)

Estimation of Bond Dissociation Energy of the Rh–C bond of Rh(tmp)(cycloheptatrienyl)⁵

Table S7 BDEs of various organic and organometallic compounds

R group	BDE (kcal mol ⁻¹)		ΔBDE (kcal mol ⁻¹)
	R–H	Rh(tmp)–R	
Et	100.5	48.5	52
Bn	88.5	33	55.5
Cycloheptatrienyl	76.6	26 (Rh–C of 1)	50 (estimated)

The BDEs of Rh(tmp)Et and Rh(tmp)Bn are 48.5 and 33 kcal mol⁻¹, respectively. The BDEs of the analogous C–H bond of ethane and toluene are 100.5 and 88.5 kcal mol⁻¹. The C–H bond of ethane is 52 kcal mol⁻¹ stronger than the Rh–C bond of Rh(tmp)Et. The benzylic C–H bond of toluene is 55.5 kcal mol⁻¹ stronger than the Rh–C bond of Rh(tmp)Bn. The C–H bonds of organic molecules are roughly 50 kcal mol⁻¹ stronger than the Rh–C bond of Rh(tmp)R.

Assuming the Rh–C BDE of Rh(tmp)–R is same as Rh(tpp)–R, as the methylene C–H bond of CHT is $76.6 \text{ kcal mol}^{-1}$, the Rh–C bond of Rh(tpp)(cycloheptatrienyl) is estimated to be 26 kcal mol^{-1} .

Reference

1. (a) B. B. Wayland, S. L. Van Voorhees, C. Wilker, *Inorg. Chem.*, 1986, **25**, 4039. (b) H. Ogoshi, J. Setsune, T. Omura, Z. Yoshida, *J. Am. Chem. Soc.*, 1975, **97**, 6461.
2. K. S. Chan, C. M. Lau, *Organometallics*, 2006, **25**, 260.
3. B. J. Gaynor, R. G. Gilbert, *Int. J. Chem. Kinet.*, 1976, **8**, 695.
4. N. S. Isaacs, *Physical Organic Chemistry*, Longman: Essex, 1987.
5. The BDE of Rh–C bond of Rh(tpp)(cycloheptatrienyl) is estimated BDE 26 kcal mol^{-1} .
(a) The bond dissociation energies (BDEs) of Rh–C of Rh(tmp)Et and Rh(tmp)Bn are 48.5 and 33 kcal mol^{-1} , respectively (tmp = mesitylporphyrinato dianion). See B. B. Wayland, *In Energetics of Organometallic Species*, J. A. Marinho, Ed., NATO Ser. C:367, Kluwer Academic Publisher, Dordrecht, The Netherlands, 69, 1992. (b) The BDE of Rh–H of Rh(tmp)H is 60 kcal mol^{-1} . See Wayland, B. B.; S. Ba, A. E. Sherry, *J. Am. Chem. Soc.*, 1991, **113**, 5305. (c) The BDEs of C–H of ethane is $100.5 \text{ kcal mol}^{-1}$, the benzylic C–H of toluene is $88.5 \text{ kcal mol}^{-1}$ and the methylene See Y. R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, FL, 2007.