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Ligand effect on the rhodium porphyrin catalyzed hydrogenation of [2.2]paracyclophane with water: key bimetallic hydrogenation[†]

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Received 2nd June 2017, Accepted 5th July 2017 DOI: 10.1039/c7dt02002c Rhodium porphyrin catalyzed hydrogenation of the aliphatic carbon–carbon σ -bond of [2.2]paracyclophane with water has been examined with a variety of tetraarylporphyrins and axial ligands. Mechanistic investigations show that Rh^{III}(ttp)H, which can be derived from the reaction of [Rh^{II}(ttp)]₂ with water without a sacrificial reductant, plays an important role in promoting bimetallic reductive elimination to give the hydrogenation product.

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Introduction

Carbon–carbon σ -bond activation (CCA) is the process of breaking down aliphatic C–C bonds in long chain hydrocarbons into smaller fragments or cyclic compounds into linear ones.¹ Catalytic CCA provides possible solutions to the degradation of unusable bio-waste² and upgrades the energy content in fuels³ if coupled with hydrogenation. However, reported examples of transition metal mediated catalytic CCA in homogeneous medium have remained scattered⁴ owing to the prohibitively high kinetic barrier for metal centers to approach the aliphatic C–C σ -bonds.⁵ Though the kinetic barrier of CCA is high, catalytic C–C σ -bond hydrogenation with hydrogen is thermodynamically favorable.⁶

Hydrogen is by far the most common hydrogenating agent used in the hydrocracking of fossil fuels into fuels³ and hydrogenation of unsaturated substrates.⁷ However, hydrogen is potentially explosive.⁸ Water represents an ideal alternative as a hydrogenating agent owing to its non-explosive nature and economical attractiveness. The utilization of water as the transfer hydrogenating agent remains challenging.⁹

Our group is interested in the CCA reactions with group 9 metalloporphyrins.¹⁰ Recently, we have reported the rhodium and iridium porphyrin catalyzed C–C σ -bond hydrogenation of [2.2]paracyclophane (1) with water as the transfer hydrogenating agent without the addition of a co-reductant (Scheme 1).¹¹ Rhodium porphyrin metalloradical Rh^{II}(ttp) (ttp = 5,10,15,20-tetratolylporphyrin) is capable of cleaving the C(sp³)–C(sp³)



 σ -bond of 1 to give rhodium benzyl intermediate 4.^{11*a*} The hydrolysis of 4 with water yields 5 and the hydrogenation product 4,4'-dimethylbibenzyl (2).

We have also explored the catalysis with $Ir^{III}(ttp)R [R = Me (6),$ ⁱPr (7) and H (8)] pre-catalysts and discovered that 8 is the most active catalyst; the formation of the dehydrogenation product *trans*-4,4'-dimethylstilbene (3) is suppressed and the yields of 2 are almost quantitative.^{11b} Mechanistic studies reveal that the hydrogenation of 9 to 10 and 10 to 2 is achieved *via* a faster parallel bimetallic reductive elimination pathway (BMRE) with 8 than a direct hydrolysis pathway with water.

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These encouraging results prompted us to examine the porphyrin ligand and axial ligand effects on the rhodium porphyrin catalyzed hydrogenation of **1** with water in order to improve the catalytic efficiency, with closer examination of the hydrolysis and bimetallic reductive elimination steps of the rhodium porphyrin benzyl intermediates in the proposed catalytic cycle.¹¹ Herein, we present our findings.

Results and discussion

The free energy change for the hydrogenation of **1** with water was computed at 25 °C and 200 °C using Spartan'16 with Hartree–Fock Method/3-21G to be -11.3 kcal mol⁻¹ and -9.5 kcal mol⁻¹, respectively (Table 1). The thermodynamic estimation confirms that the hydrogenation of **1** with water is viable.

Various rhodium porphyrins successfully catalyzed the hydrogenation of **1** with H₂O to give **2** in 55–79% yields (Table 2 and Fig. 1).¹² Electronically different *para*-substituted *meso*-aryl rhodium porphyrins Rh^{III}(ttp)Me (**12**) and Rh^{III}(tap) Me (**13**) (tap = 5,10,15,20-tetraanisylporphyrin) gave **2** in 79% and 69% yield, respectively, in 54 h (Table 2, entries 1 and 2). The difference in catalytic efficiency with **12** and **13** was minimal since the substituents were located in the remote *para* aryl positions. Even with the [Rh^{II}(ttp)]₂ (**14**), which generates the monomeric Rh^{II}(ttp) radical most readily under thermal conditions ($K_{200 \text{ } \text{ C}} \sim 19$),^{13a} similar catalytic efficiency to **12** was observed (Table 2, entry 3 *vs*. entry 1).

The sterically bulky porphyrin ligand was found to hamper the catalytic efficiency significantly. The use of the bulky Rh^{III}(tmp)Me (15) (tmp = 5,10,15,20-tetramesitylporphyrin) catalyst yielded 55% of 2 in 168 h (Table 2, entry 4). Rh^{II}(tmp) (16) was used to eliminate the induction period of the catalysis and yielded 78% of 2 in 83 h (Table 2, entry 5). The slow reaction with 15 and 16 can be accounted for by the steric sensitivity of the highly ordered termolecular transition state in bimetalloradical CCA (eqn (1)),^{11*a*} and BMRE, which is the

Table 1 Estimation of the free energy change of the C–C $\sigma\text{-bond}$ hydrogenation of 1 with water

	+ H ₂ O	\rightarrow	+ 1/20 ₂
Temperature (°C)	$\Delta H_{ m rxn}$ (kcal mol ⁻¹)	$\frac{\Delta S_{\rm rxn}}{({\rm cal\ mol}^{-1}\ {\rm K}^{-1})}$	$\Delta G_{ m rxn}$ (kcal mol ⁻¹)
25 200	-13.9 -14.3	-8.6 -10.0	-11.3 -9.5

The values were computed with Spartan'16 with the Hartree–Fock method/3-21G basis set in the gas state after geometry optimization using a similar method.

Table 2Porphyrin ligand and axial ligand effect on the rhodium porphyrin catalyzed hydrogenation of 1 with water

$\begin{array}{c c} \hline & & \\ &$						
Por	Axial ligand (L)	Catalyst	Time (h)	$2^{a,b}$ (%)	Rh(por)H ^b (%)	
ttp	Ме	12	54	79	30	
tap	Ме	13	54	69	43	
ttp	Rh ^{II} (ttp)	14	47	79	38	
tmp	Me	15	168	55	18	
tmp	_	16	83	78	43	
ttp	$Cl (KOH)^{c}$	17	48	65	31	
ttp	CH ₂ CH ₂ Ph	18	51	74	24	
ttp	ⁱ Pr	19	50	68	41	
ttp	CH_2CH_2OH	20	49	75	17	
ttp	Bn	21	47	75	27	
ttp	$Me (PPh_3)^d$	22	53	79	21	
ttp	Н	23	40	79	45	
	Por ttp tap ttp ttp ttp ttp ttp ttp ttp ttp	+ H_2O $H_$	$\begin{array}{c} & \begin{array}{c} & & \\ & & $	$\begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \\ & H_2O\\ & 100 \ equiv \end{array} \end{array} \xrightarrow{\begin{array}{c} Bh(por)L \ (10 \ mol\%) \\ \hline additives \\ \hline C_6D_6, 200 \ ^\circ C, \\ dark, time \\ sealed tube \end{array} \xrightarrow{\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

 a <20% of 3 was formed in each entry. b NMR yield. c 1 equiv. of KOH w.r.t. 1 added. d 1 equiv. of PPh₃ w.r.t. Rh^{III}(ttp)Me (12) added. ttp = 5,10,15,20-tetratolylporphyrin, tap = 5,10,15,20-tetraanisylporphyrin, tmp = 5,10,15,20-tetramesitylporphyrin.



Fig. 1 Structures of rhodium porphyrin complexes.

reverse of bimetalloradical carbon-hydrogen bond activation, reported earlier by Wayland and co-workers.¹³



Various rhodium porphyrin precursors bearing different axial ligands for $[Rh^{II}(ttp)]_2$ (14) were also examined (Scheme 2). 14 generated from (1) ligand substitution of Rh^{III}(ttp)Cl (17) with KOH (Table 2, entry 6),¹⁴ (2) β -hydride elimination of Rh^{III}(ttp)CH₂CH₂Ph (18) and Rh^{III}(ttp)ⁱPr (19) (Table 2, entries 7 and 8),¹⁵ (3) β -hydroxyl elimination of Rh^{III}(ttp)CH₂CH₂OH (20) (Table 2, entry 9),¹⁶ and (4) hydrolysis of the Rh–C bond in Rh^{III}(ttp)Bn (21) (Table 2, entry 10) underwent dissociation in rapid equilibrium by homolysis of the weak Rh–Rh bond¹⁷ to yield 2 in 65–75% in about 50 h. Rh^{III}(ttp)Me(PPh₃) (22), *in situ* generated from Rh^{III}(ttp)Me (12) and PPh₃ (1 equiv.), did not improve the catalytic efficiency since over 99% of 12 remained uncoordinated at 200 °C



Scheme 2 Generation of Rh^{II}(ttp) metalloradicals from pre-catalysts.

(Table 2, entry 11).¹⁸ The similar reactivities for different rhodium porphyrin precursors suggest that the induction period is similarly fast at 200 °C.

Previous work on the iridium porphyrin catalyzed hydrogenation of 1 with water has shown that Ir^{III}(ttp)H (8) promotes the catalytic efficiency compared to other iridium porphyrin alkyls 6 and 7 pre-catalysts through BMRE (Scheme 1).^{11b} We believe that Rh^{III}(ttp)H (23) would exhibit similar enhancement in catalytic efficiency. To our delight, 23 was found to promote the catalytic efficiency, yielding 79% of 2 in 40 h (Table 2, entry 12). It is also noteworthy that all catalyses yielded Rh^{III}(por)H eventually (Table 2). The increase in loading of 23 was found to enhance the catalysis rate (Table 3). The use of 20 mol% of 23 yielded 77% of 2 in 32 h (Table 3, entry 2). Further increase of 23 to 25 mol% yielded 79% of 2 in 28 h (Table 3, entry 3). With 1 equiv. of 23, the reaction time was shortened to 10 h to give 2 in 71% yield (Table 3, entry 4).

Thus, the role of Rh^{III}(ttp)H (23) is prominent in the catalytic hydrogenation of 1. We investigated how 23, either added or *in situ* generated, promoted the catalytic hydrogenation of 1. Experiments on the individual steps in the proposed catalytic cycle (Scheme 3), which included oxidative addition of water with $[Rh^{II}(ttp)]_2$ (14), hydrolysis of rhodium porphyrin benzyls and bimetallic reductive elimination between Rh^{III}(ttp)Bn (21) and 23, were conducted.

The continuous generation of Ir^{III}(ttp)H (8) has been proposed to be the key for the faster catalytic hydrogenation of 1.^{11b}

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Entry	23 (<i>n</i> mol%)	Time (h)	$2^{a}\left(\% ight)$	3 ^{<i>a</i>} (%)	$2+3^a$ (%)	23 recovered ^{<i>a</i>} (%)	
1	10	40	79	15	94	45	
2	20	32	77	11	88	26	
3	25	28	79	13	92	29	
4	100	10	71	24	95	28	

^a NMR yield.



Scheme 3 Proposed catalytic cycle for the hydrogenation of 1 with water catalyzed with rhodium porphyrins.

Group 9 transition metalloporphyrin complexes were reported to react with water to give the corresponding metal hydrides.¹⁹ Indeed, the oxidative addition of 14 with water was found to be facile at 200 °C to yield 76% of 23 and 6% of unreacted 14 in 6.5 h (eqn (2)).



The hydrolysis of Rh^{III}(por)alkyls has been shown as a possible hydrogenolysis pathway to yield alkanes.^{11a,14b} Previously, we have reported that the hydrolysis of Rh^{III}(ttp)Bn (21), as a model compound for metalloporphyrin benzyl intermediates 4 and 5, at 200 °C yielded Rh^{III}(ttp)H (23), $[Rh^{II}(ttp)]_2$ (14) and toluene (24) in 33%, 7% and 62%, respectively, in 26 h (Table 4, entry 1). The formation of 23 suggests that a concurrent BMRE of 23 and 21 to give 24 is operating. The hydrolysis of Rh^{III}(tmp)Bn (25) was found to be slower than that of 21 to yield Rh^{III}(tmp)H (26), Rh^{II}(tmp) 16 and 24 in 22%, 15% and 59%, respectively, in 37 h (Table 4, entry 3). The hydrolysis of 25 was incomplete at 26 h to yield 26, 16 and 24 in 18%, 17% and 51%, respectively. 25 was recovered in 9% yield (Table 4, entry 2). Thus, sterically hindered porphyrin reduced the rate of hydrogenolysis of Rh^{III}(por)Bn.

As a model compound to examine the BMRE step, Rh^{III}(ttp)Bn (21) (1 equiv.) was then allowed to react with Rh^{III}(ttp)H (23) at 200 °C without added H₂O. In 3.5 h, 23 and toluene (24) were yielded in 53% and 76%, respectively (Table 5, entry 4).

Table 4 Hydrogenolysis of Rh^{III}(por)Bn with water

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						
Entry	por	Time (h)	Rh ^{III} (por)Bn recovered ^a (%)	Rh ^{III} (por)H ^a (%)	Rh ^{II} (por) ^a (%)	24^{a} (%)
1 2 3	ttp tmp tmp	26 26 37	<3 9 <3	33 18 22	7 17 15	62 51 59

^{*a*} NMR yield w.r.t. total Rh^{III}(por)Bn added.

Table 3 Rh^{III}(ttp)H (23) catalysis loading effect

Table 5 Hydrogenolysis of $Rh^{III}(ttp)Bn$ (21) with water and $Rh^{III}(ttp)H$ (23)

Rh ^{ll}	^{II} (ttp)Bn + H	₂ O + Rh ^{III} (†	ttp)H $\overline{C_e D_e, 200 {}^{\circ}C_{\cdot}}$ dark.	Bn-H
0.96 m	21 M.1 equiv 1000	2 equiv nee	23 time, sealed tube	
			1	
Entry	n (equiv.)	Time (h)	23 recovered ^{a,b} (%)	24^{c} (%)
1	0	26	33	62
2	0.1	22	31	75
3	0.5	5	72	87
4^d	1.0	3.5	53	76

^a NMR yield w.r.t. total Rh(ttp). ^b [Rh^{II}(ttp)]₂ (14) was yielded in <8%.</p>
^c NMR yield w.r.t. 21 added. ^d Amount of residual water ~27 equiv. estimated by NMR.

Furthermore, the hydrogenolysis of **21** with water was also promoted with the addition of 0.1 and 0.5 equiv. of **23** to yield **24** in about 80% in a shorter time of 22 h and 5 h, respectively (Table 5, entries 2 and 3). Thus, BMRE is a faster hydrogenolysis pathway than hydrolysis. The rate of BMRE is estimated to be about 7 times that of hydrolysis.²⁰ The slower rate of hydrogenolysis of Rh^{III}(tmp)Bn (25) is in line with the major hydrogenolysis pathway of BMRE being suppressed with the sterically more bulky tmp ligand and the slower catalysis rate observed for Rh^{III}(tmp)Me (15) over Rh^{III}(ttp)Me (12) (Table 2, entry 1 *vs.* 4).

To gain further insight into the role of $Rh^{III}(ttp)H$ (23) in the catalysis, kinetic studies by the initial rate method were conducted to follow the conversion of **1**. ([$Rh^{III}(ttp)H$] = 0.96–2.4 mM, [**1**] = 9.6 mM, and *T* = 200 ± 0.2 °C) Both the initial rate of consumption of **1** and the formation of **2** increased linearly with [$Rh^{III}(ttp)H$]; this indicates that the catalysis had first order dependence on [$Rh^{III}(ttp)H$] (Fig. 2).

Moreover, the reaction was determined to be first order on [Rh^{III}(ttp)H] (23) with the normalized time scale method.²¹ [1] was monitored with ¹H NMR and plotted against *t*[Rh^{III}(ttp)H]ⁿ



Fig. 2 Plot of $[Rh^{III}(ttp)H]$ against the initial rate of consumption of **1** (**A**) and the initial rate of formation of **2** (**B**) with $[Rh^{III}(ttp)H] = 0.96-2.4 \text{ mM}$ and [**1**] = 9.6 mM.



Fig. 3 Determination of the reaction order of $[Rh^{III}(ttp)H]$ (23) with the normalized time scale method – plots of [1] against $t[Rh^{III}(ttp)H]^n$, where t = time and n = reaction order.

(*t* = time and *n* = reaction order). The process was repeated for different loadings of ($[Rh^{III}(ttp)H] = 0.96-2.4 \text{ mM}$) (Table 5) and a series of plots were obtained (Fig. 3). The reaction order was then determined visually with the best overlaying of [1] against *t* [$Rh^{III}(ttp)H]^n$ plots at different catalyst loadings and values of *n*.

The results from kinetic studies were used to determine the turnover limiting step (TOL) for the catalysis. The 2nd order on [Rh^{II}(tmp)] in its stoichiometric CCA with 1 rules out that the CCA is the TOL step (eqn (1))^{11*a*} as the catalysis has first order dependence on [Rh^{III}(ttp)H]. While the thermal decomposition of Rh^{III}(por)OH (complete at 120 °C within 1 h)^{14*a*} and the oxidative addition of [Rh^{III}(ttp)]₂ (14) with water (eqn (2)) (almost complete in 6.5 h at 200 °C) are faster than the hydrolysis of Rh^{III}(ttp)Bn (21) (Scheme 3 and eqn (2)) and not rate limiting. The direct hydrolysis of Rh^{III}(ttp)H] and is a parallel hydrogenation pathway with the BMRE.

Based on our current understanding, rhodium benzyl intermediates 4 and 5 are the resting species and the first order kinetics on Rh^{III}(ttp)H (23) is consistent with the BMRE reported for rhodium porphyrin hydride and rhodium porphyrin alkyls.¹³ The relative amount of 4 over 5 was monitored and found to decrease over time.²² The faster conversion of 4 might be attributed to the sterically more bulky structure in promoting hydrogenolysis through hydrolysis.

Based on the previous findings on the rhodium and iridium porphyrin catalyzed hydrogenation of **1** and the above recent findings, Scheme 3 shows the proposed catalytic cycle. Initially, $Rh^{II}(ttp)$ can be generated from the hydrolysis of the $Rh^{III}(ttp)$ alkyl pre-catalyst to give $Rh^{III}(ttp)OH$ (Scheme 2), which then yields $Rh^{II}(ttp)$, H_2O and oxygen.^{17*a*} Subsequently, bi-metalloradical CCA of **1** with $Rh^{II}(ttp)$ gives **4**. Two parallel

hydrogenolysis processes, (a) a slower hydrolysis of $Rh^{III}(ttp)R$ and (b) a faster BMRE of $Rh^{III}(ttp)R$ and $Rh^{III}(ttp)H$ (23) all convert intermediates 4 and 5 to the hydrogenation product 2. The rate of hydrogenolysis of rhodium benzyl intermediates and catalytic efficiency were reduced with the sterically hindered porphyrin ligand. Further work on sterically less hindered porphyrin ligands is ongoing.

Conclusions

In summary, porphyrin ligand effects and axial ligand effects for the rhodium porphyrin catalyzed hydrogenation of **1** with water were investigated. The electronic effect of tetraarylporphyrins and axial ligands on the catalysis was minor. Sterically bulky porphyrin ligands were found to reduce the catalytic efficiency. Current findings suggested that hydrogenolysis but not CCA was likely the turnover limiting step. Rh^{III}(ttp)H is the most active catalyst by providing a faster bimetallic reductive elimination than hydrolysis to give the hydrogenation products from Rh^{III}(ttp)benzyl intermediates (**4**, **5** and **21**).

Experimental

Materials and methods

All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. ¹H NMR spectra were recorded on a Bruker AV-400 (400 MHz) spectrometer. Spectra were referenced 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). Coupling constants (J) are reported in hertz (Hz). All rhodium porphyrin complexes Rh(por)Cl,²³ Rh(por)R (por = ttp, tap and tmp); (R = Me, Bn, -CH₂CH₂OH, -CH₂CH₂Ph and ⁱPr),²⁴ Rh^{III}(ttp)H²⁵ and [Rh^{II}(ttp)]₂²⁶ used were prepared according to the literature. High resolution mass spectra (HRMS) were recorded on a Thermofinnigan MAT 95 XL mass spectrometer. Fast atom bombardment was performed with 3-nitrobenzyl alcohol (NBA) as the matrix.

Ligand effect investigation on rhodium porphyrin catalyzed hydrogenation of [2.2]paracyclophane (1) with water

Catalytic hydrogenation of 1 with H_2O (100 equiv.) catalyzed by Rh^{III}(ttp)Me (12) (10 mol%). 12 (0.38 mg, 0.00048 mmol) was added into a sealed tube in stock solution, and the solvent was removed under vacuum to obtain an anhydrous starting material. 8.6 µL H_2O (0.48 mmol) and 1 (1.0 mg, 0.0048 mmol) in 0.50 ml C_6D_6 were added to the tube. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was heated in the dark at 200 °C for a specified period of time and the reaction progress was monitored by ¹H NMR. In 54 h, 4,4'-dimethylbibenzyl (2), *trans*-4,4'-dimethylstilbene (3) and Rh^{III}(ttp)H (23) were yielded in 79%, 10% and 30%, respect-

ively. The characterization of the previously unreported rhodium benzyl intermediate 5 is included. $R_{\rm f} = 0.71$ (hexane/ CH₂Cl₂ = 1 : 1). ¹H NMR (C₆D₆, 400 MHz) δ –3.40 (s, 2 H), 2.10 (s, 3 H), 2.25 (t, J = 8.1 Hz, 2 H), 2.44 (s, 12 H), 2.50 (t, J = 8.2 Hz, 2 H), 3.22 (d, J = 7.6 Hz, 2 H), 5.76 (d, J = 7.7 Hz, 2 H), 6.83 (d, J = 7.7 Hz, 2 H), 6.91 (d, J = 7.9 Hz, 2 H), 7.35 (d, J = 7.8 Hz, 8 H), 8.10 (d, J = 6.6 Hz, 4 H), 8.21 (d, J = 7.2 Hz, 4 H), 8.94 (s, 8 H). HRMS calcd for (C₆₄H₅₃N₄Rh + H)⁺: *m*/*z* 981.3398. Found: *m*/*z* 981.3392.

With 10 mol% Rh^{III}(tap)Me (13). 13 (0.41 mg, 0.00048 mmol) was added with other reagents and procedures similar to Rh^{III}(ttp)Me (12) catalysis were carried out. In 54 h, 2, 3 and Rh^{III}(tap)H were yielded in 69%, 10% and 43%, respectively.

With 5 mol% $[Rh^{II}(ttp)]_2$ (14). 14 (0.38 mg, 0.00024 mmol) was added with other reagents and procedures similar to $Rh^{III}(ttp)Me$ (12) catalysis were carried out. In 47 h, 2, 3 and 23 were yielded in 79%, 14% and 38%, respectively.

With 10 mol% Rh^{III}(tmp)Me (15). 15 (0.43 mg, 0.00048 mmol) was added with other reagents and procedures similar to Rh^{III}(ttp)Me (12) catalysis were carried out. In 168 h, 2, 3 and Rh^{III}(tmp)H (26) were yielded in 55%, 13% and 18%, respectively.

With 10 mol% Rh^{II}(tmp) (16). 16 (0.43 mg, 0.00048 mmol) was added with other reagents and procedures similar to Rh^{III}(ttp)Me (12) catalysis were carried out. In 83 h, 2, 3 and 26 were yielded in 78%, 19% and 43%, respectively.

With 10 mol% Rh(ttp)Cl (17)/KOH. 17 (0.39 mg, 0.00048 mmol) and KOH (0.27 mg, 0.0048 mmol) were added with other reagents and procedures similar to $Rh^{III}(ttp)Me$ (12) catalysis were carried out. In 49 h, 2, 3 and 23 were yielded in 65%, 13% and 31%, respectively.

With 10 mol% $Rh^{III}(ttp)CH_2CH_2Ph$ (18). 18 (0.42 mg, 0.00048 mmol) was added with other reagents and procedures similar to $Rh^{III}(ttp)Me$ (12) catalysis were carried out. In 51 h, 2, 3 and 23 were yielded in 74%, 11% and 24%, respectively.

With 10 mol% Rh^{III}(ttp)ⁱPr (19). 19 (0.39 mg, 0.00048 mmol) was added with other reagents and procedures similar to Rh^{III}(ttp)Me (12) catalysis were carried out. In 50 h, 2, 3 and 23 were yielded in 68%, 10% and 41%, respectively.

With 10 mol% $Rh^{III}(ttp)CH_2CH_2OH$ (20). 20 (0.40 mg, 0.00048 mmol) was added with other reagents and procedures similar to $Rh^{III}(ttp)Me$ (12) catalysis were carried out. In 49 h, 2, 3 and 23 were yielded in 75%, 12% and 17%, respectively.

With 10 mol% Rh^{III}(ttp)Bn (21). 21 (0.41 mg, 0.00048 mmol) was added with other reagents and procedures similar to Rh^{III}(ttp)Me (12) catalysis were carried out. In 47 h, 2, 3 and 23 were yielded in 75%, 10% and 27%, respectively.

With 10 mol% Rh(ttp)Me(PPh₃) (22). 22 (0.38 mg, 0.00048 mmol) and PPh₃ (0.126 mg, 0.00048 mmol) were added with other reagents and procedures similar to Rh^{III}(ttp)Me (12) catalysis were carried out. In 53 h, 2, 3 and 23 were yielded in 79%, 9% and 21%, respectively.

With 10 mol% Rh^{III}(ttp)H (23). 23 (0.37 mg, 0.00048 mmol) was added with other reagents and procedures similar to Rh^{III}(ttp)Me (12) catalysis were carried out. In 40 h, 2, 3 and 23 were yielded in 79%, 15% and 45%, respectively.

With 20 mol% $Rh^{III}(ttp)H$ (23). 23 (0.74 mg, 0.00096 mmol) was added with other reagents and procedures similar to $Rh^{III}(ttp)Me$ (12) catalysis were carried out. In 32 h, 2, 3 and 23 were yielded in 77%, 11% and 26%, respectively.

With 25 mol% $Rh^{II}(ttp)H$ (23). 23 (0.93 mg, 0.0012 mmol) was added with other reagents and procedures similar to $Rh^{III}(ttp)Me$ (12) catalysis were carried out. In 28 h, 2, 3 and 23 were yielded in 79%, 13% and 29%, respectively.

With 100 mol% $Rh^{III}(ttp)H$ (23). 23 (3.7 mg, 0.0048 mmol) was added with other reagents and procedures similar to $Rh^{III}(ttp)Me$ (12) catalysis were carried out. In 10 h, 2, 3 and 23 were yielded in 71%, 24% and 28%, respectively.

Reaction of $[Rh^{II}(ttp)]_2$ (14) with water

14 (0.38 mg, 0.00024 mmol) in benzene stock solution was transferred to a sealed tube *via* an air tight syringe under N₂. The solvent was removed under vacuum. H₂O (8.6 μ L, 0.48 mmol) was purged with N₂ for 15 minutes and then transferred to the same tube under N₂. Subsequently, 0.50 ml degassed C₆D₆ was added. The brown mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was heated in the dark at 200 °C for a specified period of time and the reaction progress was monitored by ¹H NMR. In 6.5 h, Rh^{III}(ttp)H (23) was yielded in 76% and 6% yield of 14 was recovered.

Reaction of Rh^{III}(ttp)Bn (21) with water

21 (0.41 mg, 0.00048 mmol), H_2O (8.6 µL, 0.48 mmol) and 0.50 ml C_6D_6 were added to a sealed tube. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was heated in the dark at 200 °C for a specified period of time and the reaction progress was monitored by ¹H NMR. In 26 h, Rh^{III}(ttp)H (23), [Rh^{II}(ttp)]₂ (14) and toluene (24) were yielded in 33%, 7% and 62%, respectively.

Reaction of Rh^{III}(tmp)Bn (25) with water

25 (0.47 mg, 0.00048 mmol), H_2O (8.6 µL, 0.48 mmol) and 0.50 ml C_6D_6 were added to a sealed tube. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was heated in the dark at 200 °C for a specified period of time and the reaction progress was monitored by ¹H NMR. In 37 h, Rh^{III}(tmp)H (26), Rh^{II}(tmp) (16) and 24 were yielded in 22%, 15% and 59%, respectively.

Reaction of Rh^{III}(ttp)Bn (21) with Rh^{III}(ttp)H (23)

With $Rh^{III}(ttp)H$ (23) (1 equiv.). 21 (0.41 mg, 0.00048 mmol) was transferred to a sealed tube. 23 (0.37 mg, 0.00048 mmol) in 0.50 ml degassed C_6D_6 stock solution was transferred to the tube *via* an air tight syringe under N₂. The reddish orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. Residual H₂O was estimated by ¹H NMR to be 27 equiv. w.r.t. 21. The tube was heated in the dark at 200 °C for a specified period of time and the reaction progress was monitored by ¹H NMR. In 3.5 h,

 $[Rh^{II}(ttp)]_2$ (14) and toluene (24) were yielded in 3% and 76%, respectively. 23 was recovered in 53% yield w.r.t. total Rh(ttp).

With $Rh^{III}(ttp)H$ (23) (0.5 equiv.) and H_2O (1000 equiv.). 21 (0.41 mg, 0.00048 mmol) was transferred to a sealed tube. 23 (0.19 mg, 0.00024 mmol) in 0.50 ml degassed C_6D_6 stock solution was transferred to the tube *via* an air tight syringe under N₂. H_2O (8.6 µL, 0.48 mmol) was purged with N₂ for 15 minutes and then transferred to the same tube under N₂. The reddish orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was heated in the dark at 200 °C for a specified period of time and the reaction progress was monitored by ¹H NMR. In 5 h, 14 and 24 were yielded in <1% and 87%, respectively. 23 was recovered in 72% yield w.r.t. total Rh(ttp).

With Rh^{III}(ttp)H (23) (0.1 equiv.) and H_2O (1000 equiv.). 21 (0.41 mg, 0.00048 mmol) was transferred to a sealed tube. 23 (0.04 mg, 0.00005 mmol) in 0.50 ml degassed C_6D_6 stock solution was transferred to the tube *via* an air tight syringe under N_2 . H_2O (8.6 µL, 0.48 mmol) was purged with N_2 for 15 minutes and then transferred to the same tube under N_2 . The reddish orange mixture was degassed for three freezethaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was heated in the dark at 200 °C for a specified period of time and the reaction progress was monitored by ¹H NMR. In 22 h, 14 and 24 were yielded in 4% and 75%, respectively. 23 was recovered in 31% yield w.r.t. total Rh(ttp).

Conflict of interest

There is no conflict of interest to declare.

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