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Regio-selective metalloradical catalyzed carbon–oxygen bond cleavage of epoxides with rhodium porphyrin hydride

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ABSTRACT

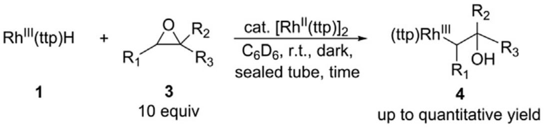
The carbon-oxygen bond activation (COA) of epoxides with rhodium(II) and rhodium (III) porphyrins have been examined. Rh^{III}(ttp)H (**1**) (ttp = 5,10,15,20-tetratolylporphyrinato dianion) was found to cleave the less sterically hindered carbon-oxygen bond of epoxides selectively at room temperature under neutral conditions to generate the stoichiometric COA product rhodium porphyrin β-hydroxyl alkyls in moderate to good yields.

1. Introduction

Epoxides are synthetically important building blocks. Due to the high ring strain in epoxides [1], the epoxide carbon-oxygen bond activation (COA) has been achieved with both organic reagents and transition metal complexes through a number of approaches. The COA of epoxides with nucleophilic transition metal complexes generally cleaves the sterically less hindered C–O bond via an S_N2 pathway [2]. In contrast, electrophilic transition metal complexes serve as Lewis acid catalysts to promote the rearrangement [3] and the nucleophilic ring opening of epoxides [4]. The more substituted C–O bond can be cleaved in the process, driven by the formation of more stable carbocation. The oxidative addition of isobutylene oxide with $Rh^{I}(PMe_3)_3Br$ [5a-5c] and that of tetracyanoethylene oxide with low valent Pt^0 complexes such as $Pt^0(AsPh_3)$, $Pt^0(PPh_3)_4$ and $Pt^0[P(p\text{-}CH_3C_6H_4)_3]_3$ are reported to yield isolatable metallaoxetanes [5d-5e]. In addition, the radical C–O bond cleavage of epoxides with titanocene(III) complexes, most notably Cp_2TiCl (Cp = cyclopentadienyl anion), have been utilized to generate functionalized alcohols [6].

Our group is interested in the bond activation of small molecules with rhodium porphyrins. We have previously reported the COA of methanol with Rh^{III}(ttp)H at 150 °C to give $Rh^{III}(ttp)CH_3$ via a σ-bond metathesis pathway [7]. In addition, the nucleophilic substitution of phenyl alkyl ethers Ph-*O*-R (R = CH_3 and benzyl) with in situ generated $Rh^{I}(ttp)^{-}$ anion was achieved at 150 °C in basic conditions to give the COA product rhodium porphyrin alkyls Rh^{III}(ttp)R [8]. Recently, Rh^{II}(tmp) (tmp = 5,10,15,20-tetramesitylporphyrinato dianion) has been reported to undergo carbon-carbon bond activation (CCA) with mono-substituted cyclopropanes at 25 °C under neutral reaction conditions to yield $Rh^{III}(tmp)CH_2CH_2CH_2R'$ (R' = –C(O)Ph, –C(O)CH_3, –CN, -Ph, –CO_2Et) up to 52% yield [9].

The COA of epoxides with nucleophilic $Rh^{I}(por)^{-}$ in basic conditions has been reported to generate the Rh^{III}(por) β-hydroxyalkyl complexes in moderate yield at 25 °C [2e-2g]. The reactivity between epoxides and other reactive rhodium porphyrin species $[Rh^{II}(por)]_2$ metalloradical and Rh^{III}(por)H has yet to be explored. Therefore, we sought to achieve the selective COA of epoxides with rhodium porphyrin under mild, neutral conditions as in the CCA of cyclopropanes. Herein, we report the $[Rh^{II}(ttp)]_2$ (**2**) catalyzed regio-selective stoichiometric COA of epoxides with Rh^{III}(ttp)H (**1**) at room temperature (eq 1).



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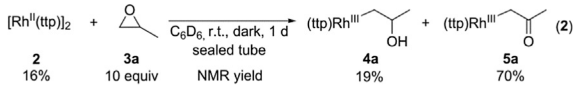
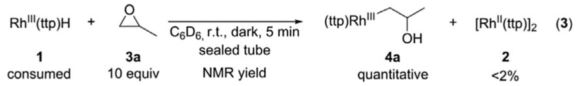
2. Results and discussion

2.1. Reactivity of epoxides with $[Rh^{II}(ttp)]_2$ and $Rh^{III}(ttp)H$

Propylene oxide (**3a**, 10 equiv) was found to react with $[Rh^{II}(ttp)]_2$ (**2**) in benzene-d_6 in a sealed NMR tube to yield the COA product $Rh^{III}(ttp)CH_2CH(OH)CH_3$ (**4a**) and the dehydrogenation product $Rh^{III}(ttp)CH_2COCH_3$ (**5a**) in 19% and 70% yields, respectively at r. t. in 1 d (eq 2). $Rh^{III}(ttp)CH_2CH(OH)CH_3$ (**4a**) was suspected to originate from the hydrogen atom abstraction from hydrogen sources presence in the reaction mixture. To test the hypothesis, $Rh^{III}(ttp)H$ (**1**), which is a good hydrogen atom source with bond dissociation energy (BDE) of $Rh^{III}(ttp){-}H \approx 60\ \mathrm{kcal\ mol^{-1}}$ [10], reacted with **3a** under similar reaction conditions to yield $Rh^{III}(ttp)CH_2CH(OH)CH_3$ (**4a**) quantitatively in 5 min (eq 3). **2** was generated in about 2% yield. The reversible thermal reductive elimination of $Rh^{III}(ttp)H$ (**1**) was responsible for the presence of $[Rh^{II}(ttp)]_2$ (**2**) at room temperature [10a,11]. The preliminary result showed that $Rh^{III}(ttp)H$ (**1**) exhibited higher reactivity and better product selectivity than that of $[Rh^{II}(ttp)]_2$ (**2**) in the COA of epoxides.





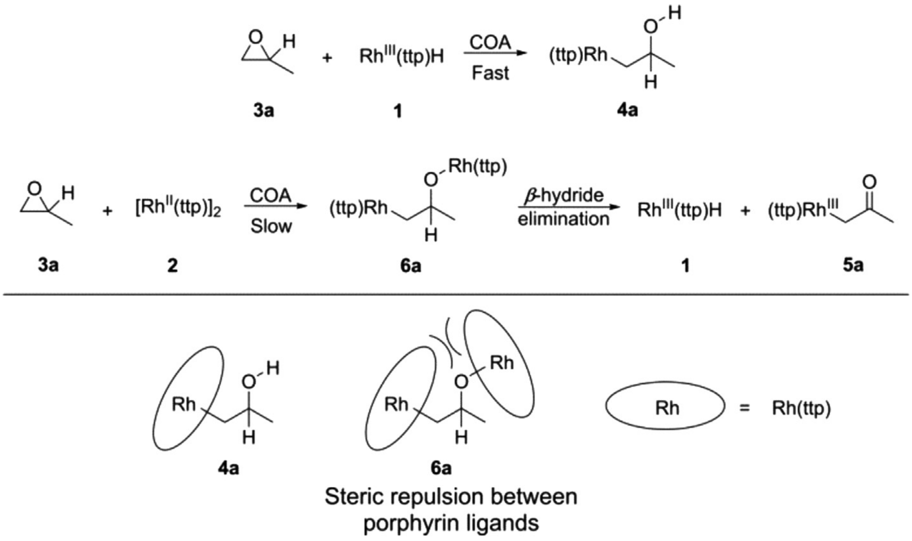
The slower reaction rate of epoxide with $[Rh^{II}(ttp)]_2$ (**2**) is attributed to the steric repulsion arise upon the 1,2-metalloradical addition. Wayland reported that the rhodium porphyrin metalloradical 1,2-insertion into acrylates was sensitive to both the steric hindrance between the porphyrin ligands and the bridging alkyl group [12]. The less sterically bulky $[Rh^{II}(oep)]_2$ (oep = octaethylporphyrinato dianion) reacted with methyl acrylate to yield the 2 carbon alkyl bridged complex $(oep)Rh^{III}CH_2CH(CO_2Me)Rh^{III}(oep)$ selectively; the reaction with the more bulky $Rh^{II}(tmp)$ mainly gave the 4 carbon alkyl bridged complex $(tmp)Rh^{III}CH_2CH(CO_2Me)CH(CO_2Me)CH_2Rh^{III}(tmp)$ in equilibrium to minimize the steric repulsion between the two rhodium porphyrins [12]. Likewise, the $[Rh^{II}(ttp)]_2$ mediated COA of propylene oxide suffers from unfavorable steric repulsion between the porphyrin ligands in $Rh^{III}(ttp)CH_2CH(CH_3)ORh^{III}(ttp)$ (**6a**), the $[Rh^{II}(ttp)]_2$ 1,2-insertion rate was therefore reduced (Scheme 1). In addition, the rhodium porphyrin alkoxy intermediate $Rh^{III}(ttp)CH_2CH(CH_3)ORh^{III}(ttp)$ (**6a**) would undergo facile β-hydride elimination to give $Rh^{III}(ttp)H$ (**1**) and $Rh^{III}(ttp)CH_2COCH_3$ (**5a**), thus eliminating the steric repulsion between the two Rh(ttp) moieties (Scheme 1). Lastly, the $Rh^{III}(ttp)H$ (**1**) generated could be utilized to afford $Rh^{III}(ttp)CH_2CH(OH)CH_3$ (**4a**) and a mixture of **4a** and **5a** was formed eventually. As a result of the faster reaction rate and higher product selectivity, further experiments employed $Rh^{III}(ttp)H$ (**1**) to explore the COA of epoxides.

2.2. Substrate scope of epoxide COA

The COA of mono and di-substituted alkyl epoxides with $Rh^{III}(ttp)H$ (**1**) are successful. Propylene oxide (**3a**), isobutylene oxide (**3b**) and cyclohexene oxide (**3c**) reacted with **1** rapidly to yield $Rh^{III}(ttp)CH_2CH(OH)CH_3$ (**4a**), $Rh^{III}(ttp)CH_2C(OH)(CH_3)_2$ (**4b**) and $Rh^{III}(ttp)(c\text{-hexyl})(2\text{-OH})$ (**4c**) in quantitatively yields, respectively at r. t. (Table 1, entries 1–3).

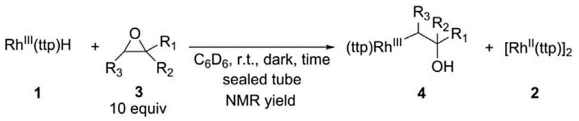
The COA of epoxides with $Rh^{III}(ttp)H$ (**1**) is sensitive to steric hindrance and the reaction rate is reduced significantly with phenyl substituted epoxides. $Rh^{III}(ttp)H$ (**1**) reacted with styrene oxide (**3d**) at r. t. for 3 d to give the COA product $Rh^{III}(ttp)CH_2CH(OH)Ph$ (**4d**) in 83% yield together with the dehydrogenation product $Rh^{III}(ttp)CH_2COPh$ (**5d**) in 15% yield (Table 1, entry 4). 2,2-Diphenyloxriane (**3e**) reacted slowly with $Rh^{III}(ttp)H$ (**1**) at r. t. to give $Rh^{III}(ttp)CH_2C(OH)Ph_2$ (**4e**) in 46% yield with $[Rh^{II}(ttp)]_2$ (**2**) recovered in 52% yield in 16 d (Table 1, entry 5). However, the sterically more hindered *trans*-stilbene oxide (**3f**) did not react with $Rh^{III}(ttp)H$ (**1**) at r. t., $Rh^{III}(ttp)H$ (**1**) and $[Rh^{II}(ttp)]_2$ (**2**) were recovered in 57% and 37% yields, respectively in 3 d (Table 1, entry 6).

The COA of epoxides with rhodium porphyrins in some cases yielded the epoxide isomerization co-product. The COA of propylene oxide (**3a**) with $Rh^{III}(ttp)H$ (**1**) gave acetone in 2% yield in 5 min w.r.t Rh(ttp) added. The amount of acetone increased to 25% yield when the reaction mixture was allowed to stand for 20 h in the dark (eq 4 and Table 1, entry 1). Similarly, the reaction between styrene oxide (**3d**) and $Rh^{III}(ttp)H$ (**1**) gave acetophenone in 16% yield w.r.t Rh(ttp) added in 3 d (Table 1, entry 4).



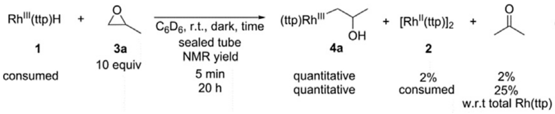
Scheme 1. Proposed Mechanism for the Epoxide COA with $Rh^{III}(ttp)H$ and $[Rh^{II}(ttp)]_2$.

Table 1
COA of Epoxides with $Rh^{III}(ttp)H$.



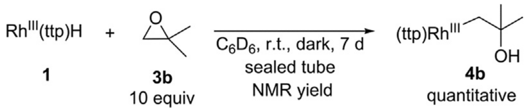
Entry	R_1	R_2	R_3		Time	2/%	$[Rh^{II}(ttp)]_2$[f]/%	Total yield/%
1[a]	Me	H	H	(**3a**)	5 min	100 (**4a**)	<2	~100
2	Me	Me	H	(**3b**)	5 min	100 (**4b**)	<2	~100
3	H	c-hexyl		(**3c**)	5 min	100 (**4c**)	0	~100
4[b,c]	Ph	H	H	(**3d**)	3 d	83 (**4d**)	0	98
5[d]	Ph	Ph	H	(**3e**)	16 d	46 (**4e**)	52	98
6[e]	Ph	H	Ph	(**3f**)	3 d	0 (**4f**)	37	94

[a] Acetone formed in 2% yield w.r.t. Rh(ttp).
[b] Acetophenone formed in 16% yield w.r.t. Rh(ttp).
[c] $Rh^{III}(ttp)CH_2COPh$ (**5d**) formed in 15% yield.
[d] Diphenylacetaldehyde formed in 42% yield w.r.t. Rh(ttp).
[e] $Rh^{III}(ttp)H$ was recovered in 57% yield.
[f] Yield of $[Rh^{II}(ttp)]_2$ formed w.r.t. Rh(ttp) added.



(4)

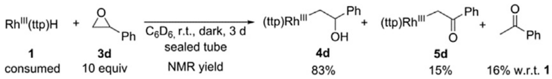
We rationalize that $Rh^{III}(ttp)CH_2CH(OH)CH_3$ (**4a**) and $Rh^{III}(ttp)CH_2CH(OH)Ph$ (**4d**) undergo a consecutive β-hydride elimination [13] to yield the corresponding enols, which then tautomerize into ketones (Scheme 2). The β-hydride elimination of the water soluble rhodium porphyrin β-hydroxyalkyl $Rh^{III}(tspp)CH_2CH(OD)R$ (tspp = tetra(p-sulfonatophenyl)porphyrinato dianion) is also known to yield the corresponding ketones under thermal conditions [14]. In contrast, $Rh^{III}(ttp)CH_2C(OH)(CH_3)_2$ (**4b**), which does not bear any β-hydrogens, remained stable in the reaction mixture for 7 d (eq 5 and Table 1, entry 2).



(5)

The COA of 2,2-diphenyloxriane (**3e**) with $Rh^{III}(ttp)H$ (**1**) gave diphenylacetaldehyde in 42% yield in 16 d (Table 1, entry 5). The isomerization of **3e** to diphenylacetaldehyde catalyzed by Lewis acids is well documented in the literature [3e,15]. Scheme 3 illustrates the proposed mechanism for the Lewis acid promoted isomerization of **3e** catalyzed by $Rh^{III}(ttp)H$ (**1**) and $Rh^{III}(ttp)CH_2C(OH)Ph_2$ (**4e**).

The COA of styrene oxide (**3d**) with $Rh^{III}(ttp)H$ (**1**) gave the dehydrogenation product $Rh^{III}(ttp)CH_2COPh$ (**5d**) in 15% yield at r. t. in 3 d (eq 6 and Table 1, entry 4). $Rh^{III}(ttp)CH_2COPh$ (**5d**) was not generated from $Rh^{III}(ttp)H$ (**1**) and acetophenone at r. t. The carbon hydrogen bond activation (CHA) of acetophenone with $Rh^{III}(ttp)H$ (**1**) is known to operate only at a high temperature of 200 °C to give $Rh^{III}(ttp)CH_2COPh$ (**5d**) in quantitative yield via $[Rh^{II}(ttp)]_2$ (**2**) intermediate (eq 7) [16].



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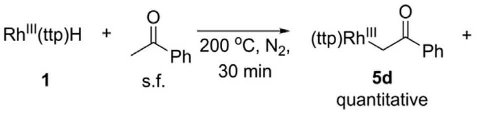
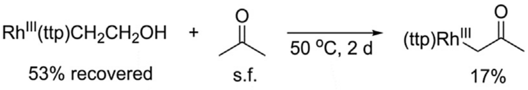


(7)

In addition, the COA product $Rh^{III}(ttp)CH_2CH(OH)Ph$ (**4d**) is unlikely a productive intermediate to **5d** at r. t. Previous reports indicated the CHA of acetone with β-hydroxyl alkyl complexes $Rh^{III}(ttp)CH_2CH_2OH$ was slow 50 °C to give the dehydrogenation product $Rh^{III}(ttp)CH_2COCH_3$ in 17% yield in 2 d (eq 8) [17]. Based on the current data, $Rh^{III}(ttp)CH_2COPh$ (**5d**) is proposed to originate from the COA of styrene oxide (**3d**) with the small amount of $[Rh^{II}(ttp)]_2$ present in $Rh^{III}(ttp)H$ as illustrated in Scheme 1.



(8)

2.3. *Proposed mechanism for the COA of epoxides*

Scheme 4 illustrates the $[Rh^{II}(ttp)]_2$ (**2**) catalyzed $Rh^{III}(ttp)H$ (**1**) insertion pathway for the regio-selective COA of epoxides. The thermal reductive elimination of $Rh^{III}(ttp)H$ **(1)** generates a small amount of $[Rh^{II}(ttp)]_2$ (**2**) in equilibrium [10a,11]. The homolysis of the weak $(ttp)Rh^{II}{-}Rh^{II}(ttp)$ (BDE ≈ 12 kcal mol^{-1}) produces the monomeric $Rh^{II}(ttp)$ metalloradical [10]. The $Rh^{II}(ttp)$ metalloradical cleaves the less hindered C—O bond of epoxides to generate the oxygen centered radical intermediate **7**. **7** is rapidly trapped with $Rh^{III}(ttp)H$ to give the COA product **4** and regenerate the $Rh^{II}(ttp)$ metalloradical.

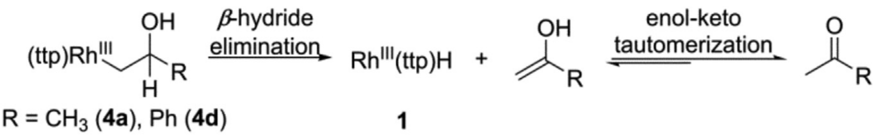
3. Conclusion

In summary, we have achieved the regio-selective C—O bond cleavage of epoxides at the less substituted C—O bond. $[Rh^{II}(ttp)]_2$ metalloradical catalyzed the 1,2-insertion of epoxides with $Rh^{III}(ttp)H$ at room temperature under neutral conditions to give the rhodium porphyrin β-hydroxyl alkyls complexes in moderate to good yields.

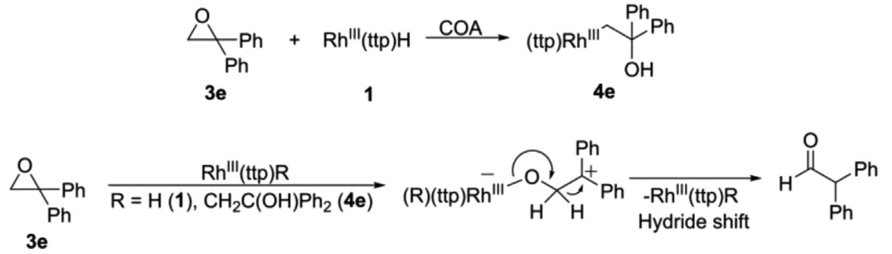
4. Experimental section

All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) was purified by sublimation before used. $H_2(ttp)$ [18], $[Rh^{II}(ttp)]_2$ (**2**) [19] and $Rh^{III}(ttp)H$ (**1**) [20], *trans*-stilbene oxide (**3f**) [21], 2,2-diphenyloxirane (**3e**) [22], were prepared according to literature.

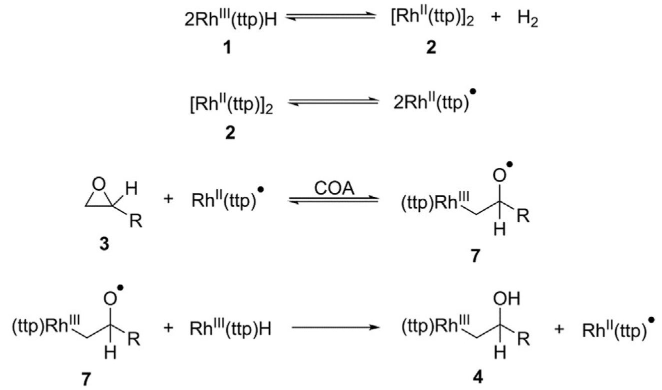
^1H NMR spectra were recorded on a Bruker AV-400 (400 MHz) spectrometer. Spectra were referenced to the residual proton resonance in C_6D_6 (δ 7.15 ppm) or $CDCl_3$ (δ 7.26 ppm) or with



Scheme 2. Proposed Mechanism for the Formation of Ketone Co-Products.



Scheme 3. Proposed Mechanism for the Lewis Acid Catalyzed Isomerization of 4e.



Scheme 4. Proposed Mechanism for the COA of Epoxide with Rh^{III}(ttp)H.

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). ^{13}C NMR spectra were record on a Bruker AVIII-700 (175 MHz) spectrometer and were referenced to $CDCl_3$ (δ 77.1 ppm). MALDI-TOF MS spectra were recorded on a Bruker Autoflex speed MALDI-TOF with DCTB as matrix and PPG-1000 as internal standard. ESI MS were recorded on a Thermo QEF MS in the positive ion mode.

All reactions in 0.5 ml benzene-d_6 were carried out in a flame-sealed NMR tube in vacuum with the reaction mixture degassed with three freeze(77 K)-pump(0.005 mmHg)-thaw cycles, then wrapped with aluminum foil to protect from exposure to room light before ^{1}H NMR measurements. Benzene stock solutions of [Rh^{II}(ttp)]$_2$ (**2**) and Rh^{III}(ttp)H (**1**) were prepared separately, transferred to the reaction vessel under N$_2$. Benzene-d_6 stock solution of epoxides were prepared separately and transferred to the reaction vessel.

4.1. Experimental procedures

4.1.1. Reaction of [Rh^{II}(ttp)]$_2$ with of propylene oxide

[Rh^{II}(ttp)]$_2$ (**2**, 1.5 mg, 0.00097 mmol) and propylene oxide (**3a**, 1.4 μl, 0.019 mmol) were added into a sealed tube in 0.50 ml of C_6D_6. The brown mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was wrapped with aluminum foil and allowed to stand in dark for 1 d. The reaction progress was monitored by ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Rh^{III}(ttp) $CH_2CH(OH)CH_3$ (**4a**) and Rh^{III}(ttp)CH_2COCH_3 (**5a**) were formed in 19% and 70% yields, respectively. [Rh^{II}(ttp)]$_2$ (**2**) was recovered in 16% yield. Compound **4a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ −4.90 to −4.97 (m, 2H), −4.15 (s, 1H), −2.34 (m, 1H), −1.45 (d, J = 6.3 Hz, 2H), 2.70 (s, 12H), 7.54 (d, J = 7.9 Hz, 8H), 8.02 (d, J = 7.1 Hz, 4H), 8.06 (d, J = 7.0 Hz, 4H), 8.77 (s, 8H). ^{1}H NMR (C_6D_6, 400 MHz) δ −4.48 to −4.57 (m, 2H), −3.72 (s, 1H), −1.93 (m, 1H), −1.38 (d, J = 6.4 Hz, 2H), 2.40 (s, 12H), 7.24 (d, J = 7.6 Hz, 4H), 7.34 (d, J = 7.4 Hz, 4H), 8.06 (d, J = 7.0 Hz, 4H), 8.16 (d, J = 6.8 Hz, 4H), 8.98 (s, 8H). ^{13}C NMR ($CDCl_3$, 175 MHz) δ 19.2, 21.9, 22.1 (d, $^1J_{Rh\text{-}C}$ = 28.5 Hz), 65.7, 122.9, 127.8, 132.1, 132.2, 133.9, 134.4, 137.7, 139.2, 143.6. HRMS (MALDI) calcd. for $(C_{51}H_{43}N_4ORh)^+$: m/z 830.2492. Found: m/z 830.2485. Compound **5a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ −4.63 (d, $^2J_{Rh\text{-}H}$ = 3.9 Hz, 2H), −1.80 (s, 3H), 2.70 (s, 12H), 7.54 (d, J = 6.6 Hz, 8H), 8.02 (d, J = 7.3 Hz, 4H), 8.08 (d, J = 7.4 Hz, 4H), 8.78 (s, 8H).

4.1.2. Reaction of Rh^{III}(ttp)H with propylene oxide

Rh^{III}(ttp)H (**1**, 1.5 mg, 0.0019 mmol) and propylene oxide (**3a**, 1.4 μl, 0.019 mmol) were added into a sealed tube in 0.50 ml of C_6D_6. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was wrapped with aluminum foil and allowed to stand in dark at room temperature. The reaction progress was monitored by ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Rh^{III}(ttp)$CH_2CH(OH)CH_3$ (**4a**) was formed in quantitative amount in 5 min.

4.1.3. Reaction of Rh^{III}(ttp)H with isobutylene oxide

Rh^{III}(ttp)H (**1**, 1.5 mg, 0.0019 mmol) and isobutylene oxide (**3b**, 1.7 μl, 0.019 mmol) were added into a sealed tube in 0.50 ml of C_6D_6. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was wrapped with aluminum foil and allowed to stand in dark for 5 min. The reaction progress was monitored by ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Rh^{III}(ttp)$CH_2C(OH)(CH_3)_2$ (**4b**) was formed in quantitative amount. Compound **4b**: ^{1}H NMR (C_6D_6, 400 MHz) δ −4.41 (d, $^2J_{Rh\text{-}H}$ = 2.9 Hz, 2H), −3.87 (s, 1H), −1.84 (s, 6H), 2.40 (s, 12H), 7.26 (d, J = 7.7 Hz, 4H), 7.33 (d, J = 7.4 Hz, 4H), 8.12 (d, J = 8.4 Hz, 4H), 8.15 (d, J = 8.6 Hz, 4H), 8.98 (s, 8H). ^{13}C NMR ($CDCl_3$, 175 MHz) δ 21.7, 25.8, 27.5 (d, $^1J_{Rh\text{-}C}$ = 29.2 Hz), 71.0, 123.0, 127.6, 127.6, 131.9, 133.6, 134.1, 137.5, 138.9, 143.6. HRMS (ESI) calcd. for $(C_{52}H_{45}N_4ORh)^+$: m/z 844.2648. Found: m/z 844.2720.

4.1.4. Reaction of Rh^{III}(ttp)H with cyclohexene oxide

Rh^{III}(ttp)H (**1**, 1.5 mg, 0.0019 mmol) and cyclohexene oxide (**3c**, 2.0 μl, 0.019 mmol) were added into a sealed tube in 0.50 ml of C_6D_6. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was wrapped with aluminum foil and allowed to stand in dark for 5 min. The reaction progress was monitored by ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Rh^{III}(ttp)(c-hexyl)(2-OH) (**4c**) was formed in quantitative amount. Compound **4c**: ^{1}H NMR (C_6D_6, 400 MHz) δ −4.01 to −4.11 (m, 1H), −3.85 to −3.87 (m, 1H), −3.63 to −3.69 (m, 1H), −3.58 (s, 1H), −1.74 to −1.77 (m, 1H), −1.11 to −1.67 (m, 1H), −0.75 to −0.79 (m, 3H), −0.19 (m, 1H), −0.08 (m, 1H), 2.40 (s, 12H), 7.28 (d, J = 7.5 Hz, 4H), 7.32 (d, J = 7.5 Hz, 4H), 8.13 (d, J = 7.7 Hz, 4H), 8.16 (d, J = 7.8 Hz, 4H), 8.96 (s, 8H). ^{1}H NMR ($CDCl_3$, 700 MHz) δ −4.39 to −4.45 (m, 1H, H$_a$), −4.33 to −4.35 (m, 1H, H$_b$), −4.19 (m, 1H,

H_c), −4.13 to −4.17 (m, 1H, H_d), −2.13 to −2.16 (m, 1H, H_e), −1.22 to −1.28 (m, 1H, H_f), −1.06 to −1.11 (m, 1H, H_g), −0.80 to −0.86 (m, 1H, H_h), −0.66 (m, 1H, H_i), −0.31 (m, 1H, H_j), 0.03 to 0.05 (m, 1H, H_k), 2.68 (s, 12H), 7.53 (d, $J = 7.0$ Hz, 8H), 8.01 (d, $J = 8.0$ Hz, 8H), 8.73 (s, 8H). ^{13}C NMR ($CDCl_3$, 175 MHz) δ 21.7, 22.8, 25.6, 30.1, 33.4, 43.8 (d, $^1J_{\text{Rh-C}} = 32.4$ Hz), 72.6, 123.0, 127.5, 127.6, 132.0, 133.5, 134.3, 137.5, 138.9, 143.4. HRMS (ESI) calcd. for $(C_{54}H_{47}N_4ORh + Na)^+$: *m*/*z* 893.2697. Found: *m*/*z* 893.2700.

The ^1H NMR signals of the methylene resonances of **4c** could be assigned on the basis of the COSY, HSQC and ROESY experiments. The relative stereochemistry was assigned based on the ROESY experiment. The ROESY experiment showed correlation between H_a, H_e and H_h which indicated that these 3 protons are on the same side of the cyclohexane ring in a 1,3-diaxial orientation. Similarly, ROESY correlation between H_d, H_f and H_g put these 3 protons on the opposite side of the ring in a 1,3-diaxial orientation. In combination with the HSQC spectra which correlates specific protons attached on a carbon, the Rh(ttp) and the OH group were therefore located next to each other with trans stereochemistry.

4.1.5. *Reaction of Rh^{III}(ttp)H with styrene oxide*

Rh^{III}(ttp)H (**1**, 1.5 mg, 0.0019 mmol) and styrene oxide (**3d**, 2.0 μl, 0.019 mmol) were added into a sealed tube in 0.50 ml of C_6D_6. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was wrapped with aluminum foil and allowed to stand in dark for 3 d. The reaction progress was monitored by ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken. Rh^{III}(ttp)$CH_2CH(OH)Ph$ **(4d)** and Rh^{III}(ttp)CH_2COPh (**5d**) were formed in 83% and 15% yields, respectively. Compound **4d**: ^1H NMR (C_6D_6, 400 MHz) δ −2.99 to −3.04 (m, 2H), −2.02 to −2.09 (m, 1H), −1.68 (dd, $J = 4.2$ Hz, $J = 9.6$ Hz, 1H), −1.10 to −1.17 (dt, $^2J_{\text{H-H}} = 3.8$ Hz, $^3J_{\text{H-H}} = 11.3$ Hz, 1H), 2.44 (s, 12H), 3.42 (d, $J = 7.4$ Hz, 2H), 6.01 (dt, $J = 32.2$ Hz, $J = 6.5$ Hz, 2H), 6.49 (t, $J = 7.2$ Hz, 1H), 7.34 (d, $J = 6.3$ Hz, 8H), 8.08 (dd, $J = 7.6$ Hz, $J = 2.0$ Hz, 4H), 8.13 (dd, $J = 7.6$ Hz, $J = 2.0$ Hz, 4H), 8.92 (s, 8H). ^{13}C NMR ($CDCl_3$, 175 MHz) δ 21.7, 28.6 (d, $^2J_{\text{Rh-C}} = 28.4$ Hz), 59.1, 121.2, 122.9, 124.6, 126.4, 126.6, 126.8, 127.6, 131.8, 131.9, 133.9, 134.0, 137.4, 139.2, 140.2, 143.4. HRMS (ESI) calcd. for $(C_{56}H_{45}N_4ORh + Na)^+$: *m*/*z* 915.2541. Found: *m*/*z* 915.2530. Compound **5d**: ^1H NMR (C_6D_6, 400 MHz) δ −3.86 (d, $^2J_{\text{Rh-H}} = 4.0$ Hz, 2H), 2.44 (s, 12H), 4.90 (d, $J = 7.4$ Hz, 2H), 6.42 (t, $J = 7.7$ Hz, 2H), 6.80 (t, $J = 7.3$ Hz, 1H), 7.32 (d, $J = 7.8$ Hz, 4H), 7.35 (d, $J = 7.8$ Hz, 4H), 8.05 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 4H), 8.18 (dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 4H), 8.95 (s, 8H).

4.1.6. *Reaction of Rh^{III}(ttp)H with 2,2-diphenyloxirane*

Rh^{III}(ttp)H (**1**, 1.5 mg, 0.0019 mmol) and 2,2-diphenyloxirane (**3e**, 3.8 mg, 0.019 mmol) were added into a sealed tube in 0.50 ml of C_6D_6. The orange mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was wrapped with aluminum foil and allowed to stand in dark for 16 d. The reaction progress was monitored by ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken. Rh^{III}(ttp)$CH_2C(OH)Ph_2$ (**4e**) was formed in 46% yield. [Rh^{II}(ttp)]$_2$ (**2**) was recovered in 52% yield. Compound **4e**: ^1H NMR (C_6D_6, 400 MHz) δ −3.62 (d, $^2J_{\text{Rh-H}} = 3.0$ Hz, 2H), −3.47 (s, 1H), 2.42 (s, 12H), 5.20 (d, $J = 7.6$ Hz, 4H), 6.30 (t, $J = 7.6$ Hz, 4H), 6.46 (t, $J = 7.2$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 8.0H), 8.08 (dd, $J = 7.5$ Hz, $J = 2.1$ Hz, 4H), 8.12 (dd, $J = 8.6$ Hz, $J = 2.1$ Hz, 4H), 8.94 (s, 8H). ^{13}C NMR ($CDCl_3$, 175 MHz) δ 21.7, 22.9 (d, $^2J_{\text{Rh-C}} = 30.0$ Hz), 76.6, 122.9, 123.6, 125.3, 126.7, 127.5, 127.6, 132.0, 134.1, 134.3, 137.4, 139.0, 143.5, 143.5. HRMS (ESI) calcd. for $(C_{62}H_{49}N_4ORh)^+$: *m*/*z* 968.2956. Found: *m*/*z* 968.2952.

4.1.7. *Reaction of Rh^{III}(ttp)H with trans-stilbene oxide*

Rh^{III}(ttp)H (**1**, 1.5 mg, 0.0019 mmol) and *trans*-stilbene oxide (**3f**, 3.8 mg, 0.019 mmol) were added into a sealed tube in 0.50 ml of C_6D_6. The brown mixture was degassed for three freeze-thaw-pump cycles (77 K, 0.005 mmHg) and then flame sealed. The tube was wrapped with aluminum foil and allowed to stand in dark for 3 d. The reaction progress was monitored by ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken. Rh^{III}(ttp)H (**1**) and [Rh^{II}(ttp)]$_2$ (**2**) were recovered in 57% and 37% yields, respectively.

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Appendix A. Supplementary data

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