Activation of Aldehydic Carbon−Hydrogen Bonds under Aerobic Conditions by Masked Rhodium(III) Porphyrin Cation

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Rh^{III}(ttp)CH_2CH_2OH activated the aldehydic carbon−hydrogen bonds of functionalized aryl and enolizable aldehydes to give high yields of Rh(ttp)COR at 50 °C under both anaerobic and aerobic conditions. The Rh(ttp)(C_2H_4)OH intermediate was proposed to form via β-hydroxy elimination. The reactions exhibited rate and yield enhancement upon the addition of Ph_3P, suggesting ligand-promoted β-elimination. The nonlinear free energy relationship of the Hammett plot suggested a multistepwise reaction with the rate-determining step (binding or activation) dependent on the electronic effect of para substituents of aryl aldehydes.

Carbon−hydrogen bond activation (CHA) is an important area of research in organometallic chemistry. Examples of carbon−hydrogen bond activation by high-valent late-transition-metal complexes, such as rhodium(III)[2−4] and iridium(III),[5,6] have been much less reported than their lower valent metal complexes. These reaction systems raise interesting mechanistic issues. A few mechanistic possibilities exist, such as oxidative addition,[7] σ-bond metathesis,[8] and (base-promoted) heterolysis,[9] and these are often not easily defined. Only in the successful isolation of high-valent metal(V) intermediates can the oxidative addition be firmly established.[7] Furthermore, the reactivities and selectivities of some of the cationic complexes depend on the nature of counteranions.[2,10] Therefore, further examples and studies would aid to explore the rich chemistry in high-valent late-transition-metal complexes in bond activation.

We have reported earlier that the high-valent Rh^{III}(ttp)Cl (ttp = tetra-4-tolylporphyrinate) and alkyls undergo selective aldehydic CHA with both aryl and aliphatic aldehydes.[11] This newly discovered five-coordinated square-pyramidal Rh(III) system for CHA, however, requires a fairly high temperature of 200 °C and suffers from the disadvantage of solvent-free conditions, with excess reagent serving as the solvent. Functional group compatibility is also limited. Rh(ttp)OTf,[2,11] with a more labile counteranion, has also been found to react more quickly than Rh(ttp)Cl. A cationic rhodium porphyrin intermediate for the CHA has been suggested, and the roles of anions appear to be important.[11]

Our recent proposed β-amino elimination[12] of Rh(ttp)CH_2-CH_2NH_2 to give a Rh(ttp) cationic intermediate at 80 °C has led us to develop a mild, convenient synthesis of a reactive cationic rhodium porphyrin via β-heteroatom elimination.[13] Therefore, we have taken advantage of the reported β-hydroxyl elimination reaction of Rh(oep)CH_2CH_2OH (oep = octaethylporphyrinate) to give Rh(oep)(CH_2CH_2)OH by Wayland[14] as a convenient masked cationic rhodium porphyrin (eq 1). We

$$\underset{\mathbf{I}}{\mathrm{LRh(por)CH_2CH_2X}} \xrightarrow{\beta\text{-heteroatom elimination}} \underset{\mathbf{II}}{\mathrm{LRh(por)(CH_2CH_2)X}} \quad (1)$$

$$\mathrm{L = Ph_3P,\ none;\ por = oep,\ ttp;\ X = NH_2,OH}$$

now report that Rh(ttp)CH_2CH_2OH underwent successful sequential β-hydroxyl elimination and selective aldehydic CHA with aryl and alkyl aldehydes under mild, aerobic, and ligand-promoted conditions in THF with broad functional group compatibility.

Results and Discussion

Discovery of the Reaction Protocol. Rh(ttp)CH_2CH_2OH (**2**) was conveniently prepared in a high yield of 90% by the reaction

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Table 1. Effect of Concentration of Aldehyde and Air in CHA

entry	FG	time (h)	atmosphere	yield (%)
1	H	72	N_2	15[a] (**3**)
2	H	48	N_2	62[b] (**3**)
3	H	60	air	81[b] (**3**)
4	F	72	N_2	28[a] (**4**)
5	F	60	N_2	65[b] (**4**)
6	F	24	air	74[b] (**4**)

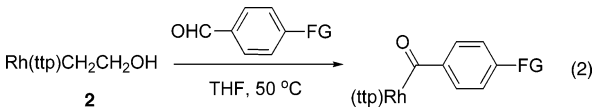
[a] 10 equiv of ArCHO. [b] 100 equiv of ArCHO.

Table 2. Effect of Phosphine Ligand in Aerobic CHA

entry	FG	time (h)[a]	yield (%)[a]
1	H	5 [60]	76 [81] (**3**)
2	F	7 [24]	65 [74] (**4**)
3	Cl	16 [48]	82 [67] (**5**)
4	CF_3	48 [36]	35 [44] (**6**)
5	CN	60 [48]	46 [46] (**7**)
6	Me	7 [24]	75 [51] (**8**)
7	^{t}Bu	36 [36]	71 [51] (**9**)
8	OMe[b]	24 [24]	83 [83] (**10**)
9	NMe_2	72 [72]	54 [42] (**11**)
10	NO_2	72	none
11	Br	72	none

[a] Average of at least of two runs. Results without Ph_3P are given in brackets. [b] Yield was obtained at 80 °C.

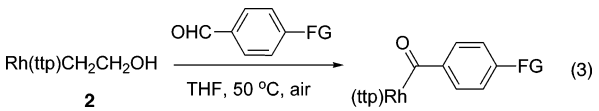
of Rh(ttp)Cl (**1**) with $NaBH_4/BrCH_2CH_2OH$. Initially, Rh(ttp)-$(CH_2CH_2)OH$ in THF reacted with PhCHO (10 equiv) in 72 h at 50 °C under N_2 to give Rh(ttp)COPh (**3**) in 15% yield (Table 1, entry 1; eq 2). Though the yield was low, the reaction



(2)

was more successful than the high-temperature aldehydic CHA with Rh(ttp)Cl. Furthermore, no reduction product of Rh(ttp)-CH_2Ph was observed.[11] A more selective protocol was thus identified. When PhCHO was increased from 10 to 100 equiv, a higher yield of **3** was obtained in 62% (Table 1, entry 2). Presumably, a higher concentration of PhCHO favored the selective formation of **3** with less side product formed. More notably, when the reaction was run in air, an even higher yield of **3**, 81%, was obtained in a slightly longer time of 60 h (Table 1, entry 3).[11] The same concentration and air effects were also observed in the reactions with 4-fluorobenzaldehyde (Table 1, entries 4−6).

With the new CHA reaction protocol conducted in air, Rh-(ttp)CH_2CH_2OH (**2**) is more reactive and more functional group compatible than Rh(ttp)Cl (Table 2; eq 3).[11] With 100 equiv of



(3)

ArCHO used, most reactions with aryl aldehydes required less than 72 h at 50 °C to give 42−81% of Rh(ttp)COAr (Table 2). In contrast with the case for Rh(ttp)Cl, no CHA at the benzylic, ^{t}Bu, and methoxy positions was observed (Table 2, entries 6−8). 4-Chloro-, 4-cyano-, and 4-dimethylamino-substituted benzaldehydes all smoothly reacted (Table 2, entries 3, 5, and 9). Anisaldehyde, though, required a higher temperature of 80 °C and did not undergo any carbon−oxygen cleavage to give Rh(ttp)Me. Other functional groups such as nitro and bromo were not compatible (Table 2, entries 10 and 11). This broader functional group compatibility is likely due, at least partially, to the lower temperature required to generate reactive cationic rhodium porphyrin complexes.

Table 3. CHA of Aliphatic Aldehydes by Rh(ttp)CH_2CH_2OH (2)

entry	R	time (h)	yield (%)
1	C_2H_5	0.5	80 (**12**)
2		6	90 (**12**)[a]
3	^{t}Bu	36	none[b]
4		48	none[a,b]

[a] 1.2 equiv of PPh_3. [b] No reaction.

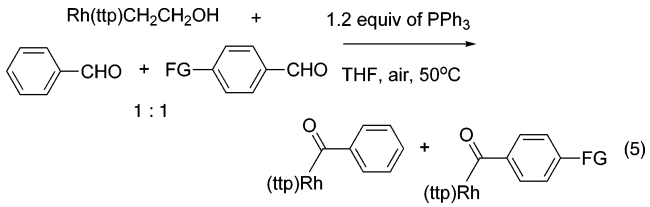
Effect of Ph_3P. We envisioned that the β-heteroatom elimination could be promoted by the addition of a ligand to give a more stabilized rhodium porphyrin cation (**II** in eq 1). We were delighted to find out that addition of Ph_3P (1.2 equiv) enhanced the rates with little difference in product yields of the aerobic aldehydic CHA in most substrates (Table 2, entries 1−3 and 6). The products were isolated after column chromatography to be free of Ph_3P coordination, presumably due to the strong trans effect of ArCO groups. Any aerobic oxidation of Ph_3P into $Ph_3P{=}O$ was not detrimental, as $Ph_3P{=}O$ was a less effective ligand. Added $Ph_3P{=}O$ was found to give Rh(ttp)-COPh either more slowly or to lower the yields under nitrogen (46 h, 62%) and in air (16 h, 67%).

Aliphatic Aldehyde. Apart from aromatic aldehydes, Rh-(ttp)CH_2CH_2OH **2** also reacted successfully with non-hindered aliphatic aldehydes (100 equiv) in aerobic conditions (Table 3; eq 4). Propanal reacted with Rh(ttp)CH_2CH_2OH (**2**) to give a

$$\underset{\mathbf{2}}{\mathrm{Rh(ttp)CH_2CH_2OH}} + \mathrm{RCHO} \xrightarrow[50\ ^\circ\mathrm{C,\ time}]{\mathrm{THF}} \mathrm{RCORh(ttp)} \tag{4}$$

good yield of the aldehydic CHA product EtCORh(ttp) (**12**; 80% yield) within 30 min. No CHA at the α-CH of the carbonyl group was observed, in contrast with the reaction of enolizable carbonyl with Rh(oep)ClO_4 (oep = octaethylporphyrinato).[15] Therefore, propanal was more reactive than PhCHO. It is likely that the sterically less hindered propanal can bind to the rhodium easily and thus facilitates the reaction rate. When 1.2 equiv of PPh_3 was added, the reaction time increased from 0.5 to 6 h. Presumably, after the addition of Ph_3P, (ttp)Rh$(Ph_3P)(CH_2{=}CH_2)OH$ (**13**) is formed but is less reactive toward a more electron-rich aliphatic aldehyde. Unfortunately, the sterically very hindered ^{t}BuCHO did not react at all.

Mechanistic Studies. In order to gain some mechanistic understandings of the electronic effect of CHA, the Hammett plot was constructed from a series of competition experiments using a 1:1 mixture of excess 4-substituted benzaldehyde and PhCHO with Rh(ttp)CH_2CH_2OH (**2**) at 50 °C in THF in aerobic conditions (Table 4; eq 5). All reactions were monitored by



(5)

TLC analysis to ensure complete consumption of Rh(ttp)CH_2-

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Table 4. Competition Experiments of Aldehydic CHA

entry	*p*-FG	σ_p[a]	log *k* (H_{FG}/H_H)
1	$N(Me)_2$	−0.32	−0.2183
2	^tBu	−0.15	−0.2001
3	Me	−0.14	−0.1348
4	F	0.15	−0.0529
5	Cl	0.34	0.3099
6	CF_3	0.53	0.0946
7	CN	0.71	−0.1978

[a] σ_p: para-substituent constant.

CH_2OH **2**. Furthermore, the relative ratios of the products did not change with time. Figure 1 shows that a nonlinear free energy relationship was observed from the Hammett plot using the substituent constant σ_p.[16] As the para substituent became more electron withdrawing, the rate increased (Me to F and Cl). More electron poor substituents (Cl to CF_3 and CN), however, lowered the rate with an inversion of rate being observed. Therefore, the rate-determining step of the reactions likely changes with the para substituents of aryl aldehydes.

Scheme 1 illustrates a plausible mechanism for the CHA reactions. Rh(ttp)CH_2CH_2OH initially forms the coordination complex (Ph_3P)Rh(ttp)CH_2CH_2OH (**13**) with Ph_3P (eq 6). Then **13** undergoes β-hydroxyl elimination to give the Rh−ethene complex **14**.[14] In the presence of Ph_3P, a higher equilibrium concentration of Rh(ttp)OH would result. The rate would then be enhanced. Ligand substitution of **14** with an aldehyde occurs to displace the ethene, and its rate and binding constants are facilitated by an electron-rich aldehyde to form the more stable complex **15**. Either the aldehydic oxygen or the CO π bond can donate an electrons to the cationic rhodium center. Both are facilitated by electron-donating substitutents at the aldehydes. The resultant Rh(ttp) aldehyde complex **15** forms the acyl-rhodium porphyrin product via aldehydic CHA, which may be faster for an electron-poor aldehyde if oxidative addition is operating. The inversion in the Hammett plot likely arises due to the change of rate-determining step from the aldehydic CHA step (k_4) for an electron-donating aldehyde to the binding step (k_3) for an electron-withdrawing aldehyde.[17]

Scheme 1

$$\underset{\mathbf{2}}{\text{Rh(ttp)CH}_2\text{CH}_2\text{OH}} + \text{L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{13}}{\text{(L)Rh(ttp)CH}_2\text{CH}_2\text{OH}} \quad (6)$$

$$\text{(L)Rh(ttp)CH}_2\text{CH}_2\text{OH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{14}}{[\text{(L)(ttp)Rh}(\text{C}_2\text{H}_4)]^+\text{OH}^-} \quad (7)$$

$$[\text{(L)(ttp)Rh}(\text{C}_2\text{H}_4)]^+\text{OH}^- + \text{ArCHO} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\mathbf{15}}{[\text{(L)Rh(ttp)(ArCHO)}]^+\text{OH}^-} + \text{C}_2\text{H}_4 \quad (8)$$

$$[\text{(L)Rh(ttp)(ArCHO)}]^+\text{OH}^- \xrightarrow{k_4} \text{ArCORh(ttp)} + \text{L} + \text{H}_2\text{O} \quad (9)$$

$$\text{L} = \text{PPh}_3$$

In the absence of structural data, the detailed structures of the intermediates remain speculative. An alternative mechanism involving a covalent rhodium porphyrin hydroxide[18] is also reasonable. **14** could also exist as a covalent, cis (Ph_3P)Rh(ttp)OH−ethene complex and react with an aldehyde to give a seven-coordinated *cis*-(Ph_3P)Rh(ttp)OH−aldehyde complex (cis OH and aldehyde) before yielding the acyl product.

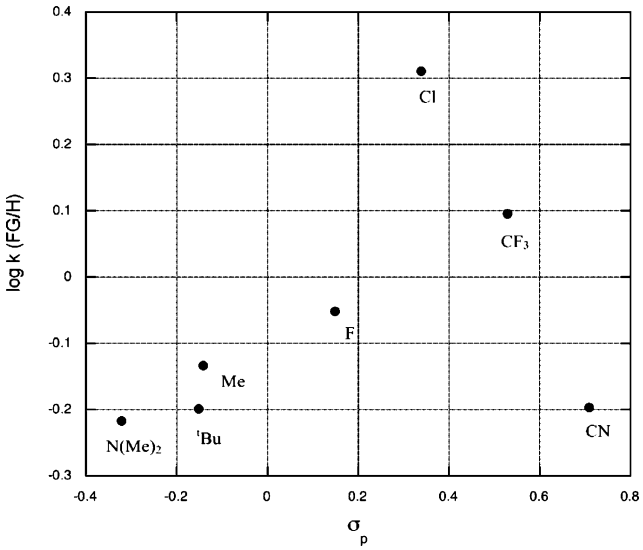

Figure 1. Hammett plot of CHA of aryl aldehydes with Rh(ttp)CH_2CH_2OH (**2**).

Regardless of the ionic or covalent nature of the Rh−OH bond, the hydroxide group is very important,[18−19] as Rh(ttp)OTf did not react with PhCHO at 50 °C in 2 days.[11] It is likely that the CHA step is likely a heterolysis[9] or its closely related σ-bond metathesis.[8] Oxidative addition[4] appears to be less likely, since a less common Rh(V) intermediate is required. Furthermore, Rh(ttp)OTf with a less coordinating anion would be expected to undergo oxidative addition more quickly, due to steric preference.

Rh(ttp)H is not likely to be an intermediate, even though Rh(ttp)H reacts with PhCHO at 200 °C to give Rh(ttp)COPh in 35% yield.[11] First, β-hydride elimination of Rh(ttp)CH_2CH_2OH to give Rh(ttp)H is likely noncompetitive at 50 °C, especially in the presence of added ligand.[20] Addition of a ligand such as Ph_3P or pyridine has been reported to inhibit the rate of 1,2-rearrangement of Rh(por) (por = porphyrinate) alkyls via the suppressed β-hydride elimination.[21] Furthermore, Rh(ttp)H reacted with neat PhCHO to give only a trace of Rh(ttp)COPh at 50 °C in 48 h. The reactivity of Rh(ttp)H is therefore too low to be a viable intermediate to directly react with PhCHO at this temperature.

We do not fully understand the effect of air on rate and yield enhancement. As Rh^{II}(tmp) (tmp = tetrakismesitylporphryinate) did not react with PhCHO in benzene, metalloradical activation by Rh(II) porphyrin is less probable. One possible rationalization could be the (co)presence of a minor pathway to generate small amounts of Rh(ttp)H by β-hydride elimination from Rh(ttp)CH_2CH_2OH. Because Rh(ttp)H does not react with PhCHO at 50 °C, it reacts with oxygen to give the more reactive (Ph_3P)-

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Rh(ttp)OH or $(Ph_3P)Rh(ttp)OOH$ (versus $(Ph_3P)Rh(ttp)(C_2H_4)OH$)[22,23] for subsequent CHA.

In summary, we have discovered that $Rh(ttp)CH_2CH_2OH$ served as a masked rhodium porphyrin hydroxide and underwent selective aldehydic CHA with aryl and nonbulky alkyl aldehydes under mild conditions. Further studies are ongoing.

Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Tetrahyrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Benzonitrile was distilled from anhydrous P_2O_5. Benzaldehyde was purified by vacuum distillation. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70−230 and 230−400 mesh) was used for column chromatography. Rh(ttp)Cl[11,24] and Rh(ttp)R[25] were prepared according to the literature.

^{1}H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in C_6D_6 (δ 7.15 ppm) and $CDCl_3$ (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 DPX 300 (75 MHz) or Varian Innova 400 (100 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.15 ppm). Coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Thermofinnigan MAT 95 XL instrument (FABMS).

Preparation of Starting Materials. (5,10,15,20-Tetratolylporphyrinato)(2-hydroxyethyl)rhodium(III), Rh(ttp)CH$_2$CH$_2$OH (2). A suspension of Rh(ttp)Cl[11] (100 mg, 0.11 mmol) in THF (50 mL) and a solution of $NaBH_4$ (40 mg, 1.08 mmol) in aqueous NaOH (0.1 M, 2 mL) were purged with N_2 for 15 min. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The solution mixture was heated at 50 °C under N_2 for 1 h to give a brown suspension. The solution was then cooled to 0 °C under N_2 and $BrCH_2CH_2OH$ (0.8 mL, 10.8 mmol) was added via a syringe. A reddish orange suspension was formed. The reaction mixture was then worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried (anhydrous $MgSO_4$), filtered, and rotary evaporated off to dryness. The reddish orange residue was purified by column chromatography over silica gel (250−400 mesh), with a mixture of hexane and CH_2Cl_2 (1/1) as eluent. The major orange fraction was collected to give a reddish orange solid (**2**; 86 mg, 0.099 mmol, 90%), which was further purified by recrystallization from CH_2Cl_2/CH_3OH. R_f = 0.34 (1/1 hexane/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −4.97 (dt, 2 H, $^2J_{Rh-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.0 Hz), −2.74 (t, 1 H, J = 6.5 Hz), −2.20 to −2.14 (m, 2 H), 2.70 (s, 12 H), 7.52 (d, 8 H, J = 8.4 Hz), 7.99 (dd, 4 H, J = 2.1, 8.4 Hz), 8.05 (dd, 4 H, J = 2.1, 8.4 Hz), 8.75 (s, 8 H). HRMS (ESI): calcd for $(C_{50}H_{41}N_4ORh)^+$, m/z 816.2330; found, m/z 816.2343. Anal. Calcd for $C_{50}H_{41}N_4ORh$: C, 73.52; H, 5.06; N, 6.86. Found: C, 73.03; H, 5.15; N, 6.71.

Reactions of Aromatic Aldehydes with Rh(ttp)CH$_2$CH$_2$OH (2). (5,10,15,20-Tetratolylporphyrinato)(benzoyl)rhodium(III), C$_6$H$_5$CORh(ttp) (3). General Procedure. Method A. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of benzaldehyde (124 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 60 h to yield **3** (8.5 mg, 0.0097 mmol, 81%). R_f = 0.42 (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (d, 2 H, J = 7.5 Hz), 2.70 (s, 12 H), 5.98 (t, 2 H, J = 7.6 Hz), 6.41 (t, 1 H, J = 7.2 Hz), 7.53 (d, 8 H, J = 8.2 Hz), 7.95 (dd, 4 H, J = 2.1, 8.1 Hz), 8.04 (dd, 4 H, J = 2.1, 8.1 Hz), 8.76 (s, 8 H). HRMS (FABMS): calcd for $(C_{55}H_{41}N_4ORh)^+$, m/z 876.2330; found, m/z 876.2303. IR (KBr, cm^{-1}): ν(C═O) 1716 (s). Anal. Calcd for $C_{55}H_{41}N_4ORh$: C, 75.34; H, 4.71; N, 6.39. Found: C, 75.09; H, 4.61; N, 6.37.

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 100 equiv of benzaldehyde (124 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 5 h to yield **3** (8.0 mg, 0.0091 mmol, 76%).

(5,10,15,20-Tetratolylporphyrinato)(4-fluorobenzoyl)rhodium(III), 4-FC$_6$H$_5$CORh(ttp) (4).[11] Method A. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of 4-fluorobenzaldehyde (130 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 24 h to yield **4** (8.0 mg, 0.0089 mmol, 74%). R_f = 0.54 (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (dd, 2 H, J = 3.2, 8.7 Hz), 2.71 (s, 12 H), 5.65 (t, 2 H, J = 8.7 Hz), 7.53 (d, 4 H, J = 6.0 Hz), 7.55 (d, 4 H, J = 6.3 Hz), 7.95 (dd, 4 H, J = 1.8, 6.0 Hz), 8.03 (dd, 4 H, J = 1.8, 6.0 Hz), 8.77 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.69, 112.21 (d, $^1J_{C-F}$ = 21.6 Hz), 114.51 (d, $^1J_{Rh-C}$ = 20.9 Hz), 118.93 (d, $^2J_{C-F}$ = 10.8 Hz), 122.90, 127.62, 131.28, 131.77, 133.96, 134.12, 137.48, 139.17, 143.17. HRMS (FABMS): calcd for $(C_{55}H_{40}N_4OFRh)^+$, m/z 894.2236; found, m/z 894.2256. IR (KBr, cm^{-1}): ν(C═O) 1711 (s).

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 4-fluorobenzaldehyde (130 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 7 h to yield **4** (7.0 mg, 0.0078 mmol, 65%).

(5,10,15,20-Tetratolylporphyrinato)(4-chlorobenzoyl)rhodium(III), 4-ClC$_6$H$_5$CORh(ttp) (5).[11] Method A. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of 4-chlorobenzaldehyde (172 mg, 1.20 mmol) in THF (1.0 mL) at 50 °C for 48 h. The solvent was then removed, and **5** was isolated by column chromatography on silica gel with hexane/CH_2Cl_2 (4/1). A red solid of **5** was obtained (8.5 mg, 0.0080 mmol, 67%). R_f = 0.70 (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (d, 2 H, J = 8.1 Hz), 2.71 (s, 12 H), 5.95 (d, 2 H, J = 8.1 Hz), 7.53 (d, 4 H, J = 6.6 Hz), 7.55 (d, 4 H, J = 6.6 Hz), 7.93 (dd, 4 H, J = 2.1, 7.5 Hz), 8.04 (dd, 4 H, J = 2.1, 7.5 Hz), 8.79 (s, 8 H). HRMS (FABMS): calcd for $(C_{55}H_{40}N_4OClRh)^+$, m/z; found, m/z. IR (KBr, cm^{-1}): ν(C═O) 1703 (s). Anal. Calcd for $C_{55}H_{40}ClN_4ORh$: C, 72.49; H, 4.42; N, 6.15; Found C, 72.49; H, 4.45; N, 6.15.

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 4-chlorobenzaldehyde (172 mg, 1.20 mmol) in THF (1.0 mL) at 50 °C for 16 h to yield **5** as a red solid (9.0 mg, 0.0098 mmol, 82%).

(5,10,15,20-Tetratolylporphyrinato)(4-α,α,α-trifluoromethylbenzoyl)rhodium(III), 4-CF$_3$C$_6$H$_5$CORh(ttp) (6).[11] Method A. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of 4-α,α,α-trifluoromethylbenzaldehyde (167 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 36 h to yield **6** (5.7 mg, 0.0053 mmol, 44%). R_f = 0.54 (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (d, 2 H, J = 8.1 Hz), 2.71 (s, 12 H), 6.24 (d, 2 H, J = 8.1 Hz), 7.53 (d, 8 H, J = 6.6 Hz), 7.92 (dd, 4 H, J = 2.1, 6.6 Hz), 8.04 (dd, 4 H, J = 2.1, 6.6 Hz), 8.79 (s, 8 H). HRMS (FABMS): calcd for $(C_{56}H_{40}N_4OF_3Rh)^+$, m/z 944.2204; found, m/z 944.2220. IR (KBr, cm^{-1}): ν(C═O) 1691 (s). Anal. Calcd for $C_{56}H_{40}N_4F_3ORh$: C, 71.19; H, 4.27; N, 5.93. Found: C, 70.84; H 4.22; N, 5.74.

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 4-α,α,α-trifluoromethylbenzaldehyde (167 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 48 h to yield **6** (4.0 mg, 0.0042 mmol, 35%).

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(5,10,15,20-Tetratolylporphyrinato)(4-cyanobenzoyl)rhodium(III), 4-CNC_6H_5CORh(ttp) (7). Method A. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of 4-cyanobenzaldehyde (161 mg, 1.20 mmol) in THF (1.0 mL) at 50 °C for 48 h. The solvent was then removed, and 4-CNC_6H_5CORh(ttp) (**7**) was isolated by column chromatography on silica gel with hexane/CH_2Cl_2 (4/1) as eluent. A red solid was obtained (5.0 mg, 0.0054 mmol, 46%). $R_f = 0.42$ (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (d, 2 H, $J = 8.7$ Hz), 2.71 (s, 12 H), 6.29 (d, 2 H, $J = 8.7$ Hz), 7.54 (d, 4 H, $J = 8.1$ Hz), 7.57 (d, 4H, $J = 8.4$ Hz), 7.91 (dd, 4 H, $J = 2.3$, 7.8 Hz), 8.03 (dd, 4 H, $J = 2.3$, 7.8 Hz), 8.80 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.68, 109.40, 117.39, 118.07 ($^1J_{Rh-C} = 18.8$ Hz), 123.04, 127.74, 129.73, 131.74, 133.98, 134.06, 137.68, 138.90, 139.07, 134.11. HRMS (FABMS): calcd for $(C_{56}H_{40}N_5ORh)^+$, *m*/*z* 901.2288; found, *m*/*z* 901.2282. IR (KBr, cm^{-1}): ν(C═O) 1639 (s), ν(C≡N) 2305 (s).

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 4-cyanobenzaldehyde (161 mg, 1.20 mmol) in THF (1.0 mL) at 50 °C for 60 h to yield **7** as a red solid (5.0 mg, 0.0055 mmol, 46%).

(5,10,15,20-Tetratolylporphyrinato)(4-methylbenzoyl)rhodium(III), 4-$CH_3C_6H_5CO$Rh(ttp) (8).[11] **Method A.** Rh(ttp)CH_2CH_2-OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of 4-methylbenzaldehyde (144 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 24 h. **8** was obtained (5.4 mg, 0.0061 mmol, 51%). $R_f =$ 0.45 (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87 (s, 3 H), 2.34 (d, 2 H, $J = 7.9$ Hz), 2.70 (s, 12 H), 5.75 (d, 2 H, $J = 7.9$ Hz), 7.53 (d, 8 H, $J = 7.8$ Hz), 7.92 (dd, 4 H, $J = 1.8$, 6.9 Hz), 8.05 (dd, 4 H, $J = 1.8$, 6.9 Hz), 8.75 (s, 8 H). HRMS (FABMS): calcd for $(C_{56}H_{43}N_4ORh)^+$, *m*/*z* 890.2486; found, *m*/*z* 890.2472. IR (KBr, cm^{-1}): ν(C═O) 1704 (s). Anal. Calcd for $C_{56}H_{43}N_4ORh$: C, 75.50; H, 4.87; N, 6.29. Found: C, 75.13; H, 4.91; N, 6.50.

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 4-methylbenzaldehyde (144 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 7 h to yield **8** (8.0 mg, 0.0090 mmol, 75%).

(5,10,15,20-Tetratolylporphyrinato)(4-*tert*-butylbenzoyl)rhodium(III), 4-^{t}BuC_6H_5CORh(ttp) (9).[11] **Method A.** Rh(ttp)CH_2CH_2-OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of 4-tert-butylbenzaldehyde (150 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 24 h to yield **9** (5.4 mg, 0.0061 mmol, 51%). $R_f = 0.43$ (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95 (s, 9 H), 2.42 (d, 2 H, $J = 7.8$ Hz), 2.70 (s, 12 H), 5.97 (d, 2 H, $J =$ 7.8 Hz), 7.96 (d, 8 H, $J = 7.8$ Hz), 7.96 (dd, 4 H, $J = 1.8$, 6.9 Hz), 8.04 (dd, 4 H, $J = 1.8$, 6.9 Hz), 8.74 (s, 8 H). HRMS (FABMS): calcd for $(C_{59}H_{49}N_4ORh)^+$, *m*/*z* 932.2956; found, *m*/*z* 932.2974. IR (KBr, cm^{-1}): ν(C═O) 1710 (s). Anal. Calcd for $C_{59}H_{49}N_4$-ORh: C, 75.96; H, 5.29; N, 6.00. Found: C, 75.96; H, 5.49; N, 5.60.

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 4-methylbenzaldehyde (150 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 7 h to yield **9** (8.0 mg, 0.0085 mmol, 71% yield).

(5,10,15,20-Tetratolylporphyrinato)(4-methoxylbenzoyl)rhodium(III), 4- $MeOC_6H_5CO$Rh(ttp) (10).[11] **Method A.** Rh(ttp)CH_2-CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with anisaldehyde (115 μL, 1.20 mmol) in THF (1.0 mL) at 80 °C for 24 h to yield **10** (9.0 mg, 0.010 mmol, 83%). as a red solid. $R_f = 0.52$ (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (d, 2 H, $J =$ 8.5 Hz), 2.70 (s, 12 H), 3.45 (s, 3 H), 5.47 (d, 2 H, $J = 8.5$ Hz), 7.53 (d, 8 H, $J = 8.1$ Hz), 7.95 (d, 4 H, $J = 6.9$ Hz), 8.04 (d, 4 H, $J = 6.9$ Hz), 8.76 (s, 8 H). HRMS (FABMS): calcd for $(C_{56}H_{43}N_4O_2Rh)^+$, *m*/*z* 906.2422; found, *m*/*z* 906.2436. IR (KBr, cm^{-1}): ν(C═O) 1704 (s). Anal. Calcd for $C_{56}H_{43}N_4ORh$: C, 74.17; H, 4.78; N, 6.17. Found: C, 73.92; H, 4.70; N, 5.93.

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with anisaldehyde (115 μL, 1.20 mmol) in THF (1.0 mL) at 80 °C for 24 h to yield **10** (9.0 mg, 0.010 mmol, 83%).

(5,10,15,20-Tetratolylporphyrinato)(4-(Dimethylamino)benzoyl)rhodium(III), 4-$(NMe_2)C_6H_5CO$Rh(ttp) (11). Method A. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) was mixed with 100 equiv of 4-(dimethylamino)benzaldehyde (182 mg, 1.20 mmol) in THF (1.0 mL) at 50 °C for 3 days. The solvent was then removed and 4-$(NMe_2)C_6H_5CO$Rh(ttp) (**11**) was isolated by column chromatography on silica gel with hexane/CH_2Cl_2 (5/1) as eluent, followed by CH_2Cl_2. A brick red solid was obtained (5.0 mg, 0.0050 mmol, 42%). $R_f = 0.30$ (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (d, 2 H, $J = 8.5$ Hz), 2.60 (s, 6 H), 2.70 (s, 12 H), 5.24 (d, 2 H, $J = 8.7$ Hz), 7.51 (d, 4 H, $J = 5.7$ Hz), 7.53 (d, 4 H, $J = 5.7$ Hz), 7.95 (dd, 4 H, $J = 2.1$, 7.2 Hz), 8.06 (dd, 4 H, $J = 2.1$, 7.2 Hz), 8.74 (s, 8 H). ^{13}C NMR (100 MHz, CD_8O): δ 24.43, 43.09, 111.78 (δ, $^1J_{Rh-C} = 7.1$ Hz), 112.58, 122.19, 127.74, 125.63, 130.74, 130.87, 133.07, 134.61, 137.37, 137.99, 140.67, 143.72, 146.73. HRMS (FABMS): calcd for $(C_{57}H_{46}N_5ORh)^+$, *m*/*z* 919.2752; found, *m*/*z* 919.2763.

Method B. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with mixed 4-(dimethylamino)benzaldehyde (182 mg, 1.20 mmol) in THF (1.0 mL) at 50 °C for 3 days to yield **15** (6.0 mg, 0.0065 mmol, 54%).

(5,10,15,20-Tetratolylporphyrinato)(ethylformyl)rhodium(III), CH_3CH_2CORh(ttp) (12).[11] **Method A.** Rh(ttp)CH_2CH_2OH (10 mg, 0.012 mmol) was mixed 100 equiv of propanal (87 μL, 1.20 mmol) in THF (2.0 mL) at 50 °C for 30 min. The solvent was then removed and **12** was isolated by column chromatography on silica gel with hexane/CH_2Cl_2 (4/1) as eluent, followed by CH_2-Cl_2. A brick red solid was obtained (8.0 mg, 0.0096 mmol, 80% yield). $R_f = 0.52$ (1/1 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.14 (q, 2 H, $J = 7.5$ Hz), −1.69 (t, 3 H, $J =$ 7.2 Hz), 2.70 (s, 12 H), 7.26 (d, 8 H, $J = 7.8$ Hz), 8.05 (d, 8 H, $J = 6.3$ Hz), 8.80 (s, 8 H). HRMS (FABMS): calcd for $(C_{51}H_{41}N_4$-$ORh)^+$, *m*/*z* 828.2335; found, *m*/*z* 828.2330. IR (KBr, cm^{-1}): ν-(C═O) 1717 (s). Anal. Calcd for $C_{51}H_{41}N_4ORh$: C, 73.91; H, 4.99; N, 6.76. Found: C, 73.88; H, 5.04; N, 6.71.

Method B. Rh(ttp)CH_2CH_2OH (10 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 100 equiv of propanal (87 μL, 1.20 mmol) in THF (1.0 mL) at 50 °C for 6 h to yield **12** (6 mg, 0.011 mmol, 90% yield).

Competition Reactions between Benzaldehyde and Para-Substituted Benzaldehydes using Rh(ttp)CH_2CH_2OH. A typical procedure was described as follows. Rh(ttp)CH_2CH_2OH (10.0 mg, 0.012 mmol) and 1.2 equiv of PPh_3 (3.8 mg, 0.014 mmol) were mixed with 100 equiv of benzaldehyde and 100 equiv of para-substituted benzaldehyde in THF (1.0 mL) at 50 °C. The reaction was monitored by the TLC analysis. After the reaction was complete, the ^{1}H NMR spectrum of the crude reaction mixture was taken. The relative rate was then calculated from the integration of the β-protons of the porphyrin signals in the ^{1}H NMR by duplicate runs.

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Supporting Information Available: NMR spectra for complexes **4**, **7**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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