Syntheses of Acyl Rhodium Porphyrins by Aldehydic Carbon−Hydrogen Bond Activation with Rh(III) Porphyrin Chloride and Methyl

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Rhodium(III) porphyrin chloride reacted with aryl aldehydes in solvent-free conditions to give acyl rhodium porphyrins. Selective aldehydic without any aromatic carbon−hydrogen bond activation (CHA) was observed. At lower temperature, reduction and side products were found. Alkanals reacted poorly. On the other hand, Rh(III) porphyrin methyl reacted more cleanly with both aryl and alkyl aldehydes. These reactions provided a facile, convenient synthesis of acyl rhodium porphyrins. These activations are unique CHA by high-valent Rh(III) species. Preliminary mechanistic experiments suggested that the rhodium(III) porphyrin chloride initially formed a cationic rhodium(III) porphyrin via chloride dissociation and then underwent oxidative addition or heterolysis to yield the product. On the other hand, rhodium(III) porphyrin methyl underwent either oxidative addition or σ bond metathesis.

Carbon−hydrogen bond activation (CHA) by cationic and related low-valent late transition metal complexes has emerged as an exciting area of research with potential industrial applications.[1,2] Numerous catalytic applications in organic synthesis have appeared for the direct functionalization of hydrocarbons. The catalytic conversions of methane into methyl derivatives mark one of the milestones.[3−5] An advantage of late transition metal complexes over early transition ones is the broader functional group tolerance in substrates.

The CHA of aldehydes with transition metal complexes gives acyl metal complexes. Acyl transition metal complexes are important compounds and proposed intermediates formed in the hydroacylation of alkenes[6] and alkynes.[7] Most complexes reported are low-valent ones, and the activations occur through classical oxidative addition pathways. One typical example is the reaction of the Wilkinson type complex ($Rh^{I}(R_3P)_3Cl$) with aldehydes.[8] The activation of aldehydes by high-valent rhodium(III) complexes to form acyl rhodium complexes is much less well-known.[9]

Table 1. Optimization of CHA of PhCHO with Rh(ttp)Cl

entry	temp/°C	time	% yield of Rh(ttp)COPh, **2a**	% yield of Rh(ttp)Bn, **3**
1	130	1 day	none	none
2	150	1 day	38%	5%
3		1.5 days	51%	28%
4	180	2 days	43%	17%
5	200	0.5 h	28%	18%
6		1 day	79%	none

In extending our previous success of CHA of PhCN solvent in refluxing conditions with Rh(ttp)Cl (ttp = tetrakis-4-tolylporphyrinatio dianion) to give metacyanophenyl rhodium porphyrins,[10] we have discovered that aldehydes reacted with both Rh(ttp)Cl and Rh(ttp)Me in solvent-free conditions selectively at the aldehydic carbon−hydrogen bond. These reactions provide convenient syntheses of Rh(ttp)COR and illustrate a unique type of CHA by high-valent rhodium(III) complexes.

Results and Discussion

The reactions of Rh(ttp)Cl (**1**) with PhCHO revealed that the solvent, temperature, and extent were crucial in controlling product selectivity and yield (Table 1, eq 1). As Rh(ttp)Cl was found to react with various solvents, such as 1,2,4-trichlorobenzene, dibutyl ether, and NMP above 150 °C, solvent-free conditions, i.e., PhCHO as a reagent and solvent, were used. At 200 °C in 1 day, Rh(ttp)Cl gave Rh(ttp)COPh (**2a**) in 79% yield in the absence of light under nitrogen. Selective activation of the aldehydic carbon−hydrogen bond occurred without any aromatic CHA. Below 150 °C, little reaction occurred. At 150 °C, the CHA product Rh(ttp)COPh (**2a**) and the "reduction

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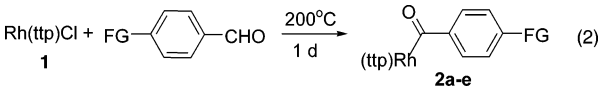
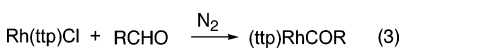
Table 2. Activation of Aryl Aldehydes with Rh(ttp)Cl



entry	FG	time	% yield of Rh(ttp)COAr, **2**	% yield of Rh(ttp)R
1	H	1 day	**2a** 79%	
2	F	1 day	**2b** 45%	
3	Me	1 h	**2c** 20%	(4-$CHOC_6H_4CH_2$)Rh(ttp), **4** (4%)
4		1 day	**2c** 57%	
5	^{t}Bu	1 h	**2d** 17%	(4-$CHOC_6H_4CH(Me)_2$)Rh(ttp), **5** (2%)
6		1 day	**2d** 38%	
7	CF_3	1 day	**2e** 50%	
8	OMe	1 day		MeRh(ttp), **6** (11%)

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



entry	R	temp (°C)	time (h)	Rh(ttp)COR (yield %)
1	C_2H_5	100	48	**7a** (3)
2	C_7H_{15}	200	24	**7b** (0)
3	^{t}Bu	200	48	**7c** (10)

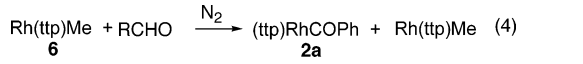
product" Rh(ttp)Bn (**3**) were formed nearly at the same time. **3** slowly disappeared on further heating with slight increase in the yield of **2a**. A similar pattern was observed at 180 and 200 °C. At 200 °C in 1 day, the total yields of the products were 79% with the same yield obtained at 150 °C in 1.5 days. Synthetically, the synthesis of thermally stable Rh(ttp)COPh (**2a**) was optimized to occur at 200 °C in 1 day.

When the optimized reaction conditions were applied to various 4-susbstitued aryl aldehydes, moderate to good yields of Rh(ttp)COAr were obtained in 1 day at 200 °C (Table 2, eq 2). Substrates bearing alkyl carbon−hydrogen bonds such as 4-MeC_6H_4CHO and 4-$^tBuC_6H_4CHO$ gave mainly 4-MeC_6H_4-CORh(ttp) (**2c**) and 4-$^tBuC_6H_4CORh(ttp)$ (**2d**), respectively. Small amounts of alkyl CHA products (4-$CHOC_6H_4CH_2$)Rh(ttp) (**4**) and (4-$CHOC_6H_4C(Me)_2CH_2$)Rh(ttp) (**5**) were observed only initially and nearly simultaneously with aldehydic CHA products in about 1 h. Competitive aliphatic and benzylic CHA therefore occurred. Upon prolonged heating, **4** and **5** disappeared with increasing yields of the corresponding rhodium complexes **2c** and **2d**. Apparently, **4** and **5** likely underwent further CHA with excess aryl aldehydes to afford corresponding acyl complexes similar to that of Rh(ttp)Bn (**3**) with PhCHO. Little substrate electronic effect on rate was noted. Surprisingly, the most electron rich 4-methoxylphenyl aldehyde produced no acyl rhodium complex but only 11% yield of Rh(ttp)Me (**6**), in which the Me group likely comes from the MeO group of anisoyl aldehyde. A limitation for the preparation of anisoyl complex exists.

For aliphatic aldehydes, Rh(ttp)Cl reacted inefficiently to give only either mixtures of products or lower yields of acyl rhodium porphyrins (Table 3, eq 3). Presumably, other carbon−hydrogen bonds, especially those at the α-carbonyl positions, form enolizable carbonyls, which compete to give complex mixtures.[11] More efficient synthesis is desirable.

We reasoned that the electron-rich Rh(ttp)Me would be more difficult to reduce to Rh(ttp)Bn, and cleaner CHA would then be expected. In fact, the more negative reduction potential of Rh(ttp)Me ($E_{1/2} = -1.43$ V) than that of Rh(ttp)Cl ($E_{1/2} = -1.01$ V) supports the rationale.[12] To our delight, Rh(ttp)Me reacted much faster with PhCHO in solvent-free conditions to give a slightly higher yield of Rh(ttp)COPh.

Table 4. Optimization of CHA of PhCHO with Rh(ttp)Me



entry	temp (°C)	time (h)	**2a** (yield %)	**6** recovered (%)
1	100	48	12	40
2	200	0.5	82	0

The optimal temperature of aldehydic CHA of prototypical PhCHO with Rh(ttp)Me (**6**) was found to be 200 °C (Table 4, eq 4). At 100 °C in 2 days, only 12% yield of CHA product was obtained and 40% yield of Rh(ttp)Me was recovered. At 200 °C, fast and complete reaction occurred. PhCHO reacted with Rh(ttp)Me (**6**) to afford PhCORh(ttp) (**2a**) in 82% yield within 0.5 h. No Rh(ttp)Bn (**3**) was formed.

Rh(ttp)Me also underwent aldehydic CHA with other aryl aldehydes at a faster rate, with broader functional group compatibility and cleaner product formation than Rh(ttp)Cl (Table 5, eq 5). In general, most reactions required less than 1 day to complete. Fluoro-, chloro-, and trifluoromethyl groups are compatible. Even the electron-rich 4-anisoylaldehyde yielded 56% of anisoyl rhodium porphyrin without any other CHA or side product. Unfortunately, 4-*N*,*N*-dimethylbenzaldehyde gave complex, unidentified products. In most of these reactions, clean products were formed with little side products.

It is also gratifying that aliphatic aldehydes reacted with Rh(ttp)Me to give moderate yields of Rh(ttp)COR (Table 6, eq 6). Selective aldehydic CHA occurred even with enolizable aldehyde.

The IR stretching ν(C═O) of the benzoyl rhodium complexes appears between 1690 and 1720 cm^{-1}. On the other hand, the carbonyl frequencies in RCORh(oep)[13] range from 1684 to 1709 cm^{-1} (oep = octaethylporphyrinato) and are lower than that in RCORh(ttp). Likely, the Rh to CO back π-bonding is stronger with the more electron rich oep ligand, resulting in lower carbonyl stretching frequencies.

X-ray Data. Single-crystal analyses were carried out for compounds **2**, **3**, and **4**. Crystal data, collection, and processing parameters are listed in the Supporting Information. Notably, the para-substitutents on the benzaldehyde do not affect the bond lengths between Rh−C(O) as they are all similar to the Rh−C(O) (1.988(5) Å) in (oep)RhC(O)NH($C_8H_3(CH_3)_2$) reported by Wayland (Table 7).[14] Moreover, the bond angles are not affected by the para-substitutents. All rhodium atoms do not lie in the porphyrin plane but deviate from the plane defined by the 24-atom least-squares plane (Supporting Information).

Mechanism: Rh(ttp)Cl. We postulate that Rh(ttp)Cl reacts as an electrophile in CHA (Scheme 1)[10,15] analogous to its electrophilic aromatic substitution with PhCN to give meta-cyanophenyl rhodium porphyrin. Such electrophilic aromatic substitution has also been reported with Rh(oep)OTf.[15] Rh(ttp)Cl initially dissociates to give a cationic, electrophilic Rh(ttp) species likely as an ion-pair ($Rh(ttp)^+Cl^-$). Coordination of

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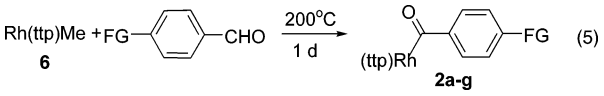
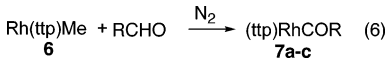
Table 5. CHA of Para-Substituted Benzaldehydes by Rh(ttp)Me



entry	FG	time (h)	yield (%)
1	H	0.5	**2a** (82)
2	F	8	**2b** (76)
3	Cl	24	**2f** (53)
4	CF_3	16	**2e** (54)
5	Me	16	**2c** (73)
6	^{t}Bu	48	**2d** (39)
7	OMe	16	**2g** (56)
8	NMe_2	60	**2h** (0)

Table 6. CHA of Aliphatic Aldehydes by Rh(ttp)Me

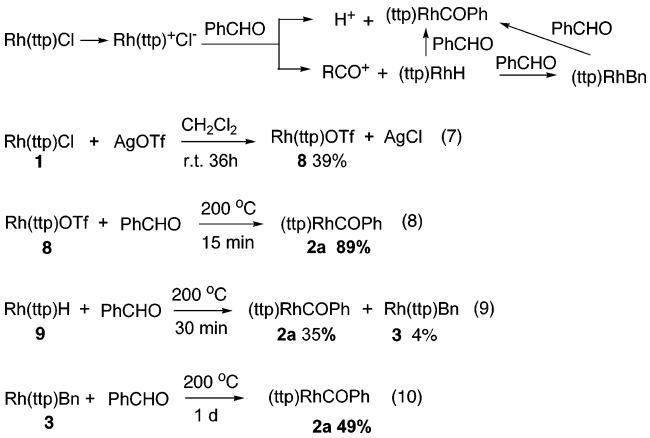


entry	R	temp (°C)	time (h)	yield (%)
1	C_2H_5	100	24	**7a** (60)
2	C_7H_{15}	200	48	**7b** (41)
3	^{t}Bu	200	48	**7c** (37)

Table 7. Selected Bond Lengths and Bond Angles of Compounds 2a, 2b, and 2e

FG	H, **2a**	F, **2b**	CF_3, **2e**
bond length (Rh−CO)	1.950(5) Å	1.976(7) Å	1.941(7) Å
bond angle (Rh−C(O)−C_{aryl})	117.8(4)°	117.1(5)°	118.3(5)°

Scheme 1. Mechanism of Aldehydic CHA with Rh(ttp)Cl



aldehydic oxygen of PhCHO directs the aldehydic CHA to give Rh(ttp)COPh and HCl. Rh(ttp)OTf (**8**) was therefore independently synthesized from metathesis of Rh(ttp)Cl and AgOTf (eq 7)[15] and indeed underwent faster aldehydic CHA than Rh(ttp)Cl to give 89% yield of Rh(ttp)COPh (**2a**) at 200 °C in 15 min (eq 8).

$Rh(ttp)^+Cl^-$ can also be reduced by PhCHO to give Rh(ttp)H and an acylium ion in a parallel manner with the direct CHA. Rh(ttp)H then reacts with PhCHO to give Rh(ttp)COPh, which can be further reduced by Rh(ttp)H to give Rh(ttp)Bn. Supporting evidence has been obtained by an independent experiment. Rh(ttp)H was synthesized by the reductive protonation of Rh(ttp)Cl with $NaBH_4$/HOAc.[16] At 200 °C in half an hour, Rh(ttp)H reacted with PhCHO to give both 35% of Rh(ttp)COPh and 4% of Rh(ttpp)Bn (eq 9).[17]

Finally, Rh(ttp)Bn undergoes CHA with PhCHO to give Rh(ttp)COPh, like that of Rh(ttp)Me with PhCHO. Indeed, Rh(ttp)Bn reacted with PhCHO at 200 °C in 1 day to give Rh(ttp)COPh in 49% yield (eq 10).

Mechanism: Rh(ttp)Me. Since the Rh−Me bond in Rh(ttp)Me is strong (about 57 kcal/mol)[18] and is unlikely to undergo facile and complete homolysis at 200 °C within a few hours, homolysis is unlikely. Concerted pathways are more reasonable. We propose that Rh(ttp)Me undergoes either classical oxidative addition or σ bond metathesis[19] with PhCHO. The oxidative addition demands a Rh(V) intermediate complex, which exists but is less common. The σ bond metathesis does not require a formal Rh(V) species.[9,20,21] They are, however, mechanistically very difficult to distinguish unless a stable intermediate is isolated. At this stage, we cannot rule out one from the other, and to firmly establish the detailed pathway, further experiments are necessary.

In summary, we have discovered a facile synthesis of Rh(ttp)COR from the reactions of Rh(ttp)Cl and Rh(ttp)Me with aldehydes in solvent-free conditions. The reactions involve selective aldehydic CHA with high-valent Rh(III) species. Preliminary mechanistic experiments suggest Rh(tttp)Cl likely activates aldehydes in an electrophilic manner with the parallel formation of Rh(ttp)COPh and Rh(ttp)H. Rh(ttp)H further activates PhCHO consecutively to yield Rh(ttp)COPh. The mechanism of CHA of PhCHO with Rh(ttp)Me is different from that of Rh(ttp)Cl and likely operates through oxidative addition or σ bond methathesis.

Experimental Section

General Procedures. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Benzonitrile was distilled from anhydrous P_2O_5. 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.

^{1}H NMR spetra 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) or $CDCl_3$ (δ 7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm). ^{13}C NMR spectra were recorded on a Bruker DPX 300 (75 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.10 ppm). Coupling constants (J) were reported in hertz (Hz). High-resolution mass spectra (HRMS) were performed on a Thermofinnigan MAT 95 XL (FABMS).

Preparation of Starting Materials. 5,10,15,20-Tetratolyporphyrinato)rhodium(III) Chloride, Rh(ttp)Cl (1).[10a] H_2ttp (350 mg, 0.51 mmol) and $RhCl_3 \cdot xH_2O$ (209 mg, 1.00 mmol) were refluxed in PhCN (30 mL) in air for 3 h. After removal of solvent, the mixture was purified by column chromatography on silica gel

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eluting with CH_2Cl_2. **1** was then dried under vacuum at 80 °C to remove the coordinated PhCN. Purplish red solid **1** was obtained after recrystallization from CH_2Cl_2/MeOH (368 mg, 0.39 mmol, 76% yield). $R_f = 0.30$ (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.71 (s, 12 H), 7.54 (d, 8 H, $J = 8.1$ Hz), 8.07 (d, 4 H, $J = 6.9$ Hz), 8.12 (d, 4 H, $J = 6.9$ Hz), 8.94 (s, 8 H).

(5,10,15,20-Tetratolyporphyrinato)(methyl)rhodium(III), Rh(ttp)Me (6).[22] A suspension of Rh(ttp)Cl (98 mg, 0.11 mmol) in EtOH (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 separately. A solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated at 50 °C under N_2 for 1 h to give a brown solution. The solution was then cooled to 0 °C under N_2, and methyl iodide (0.7 mL, 10.8 mmol) was added via a syringe. A reddish orange suspension was formed. After stirring at room temperature for another 15 min under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2 and washed with H_2O. The combined organic extract was dried (anhydrous $MgSO_4$), filtered, and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250−400 mesh), eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). The major orange fraction was collected and gave **6** as a reddish orange solid (73 mg, 0.095 mmol, 86% yield), which was further purified by recrystallization from CH_2Cl_2/CH_3OH. $R_f = 0.72$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ −5.83 (d, 3 H, $J = 3.0$ Hz), 2.96 (s, 12 H), 7.52 (d, 8 H, $J = 8.1$ Hz), 8.00−8.09 (m, 8 H), 8.72 (s, 8 H). HRMS (FABMS): calcd for $(C_{49}H_{39}N_4Rh)^+$ *m*/*z* 786.2224, found *m*/*z* 786.2242.

Reactions of Aromatic Aldehydes with Rh(ttp)Cl (1). (5,10,15, 20-Tetratolyporphyrinato)(benzoyl)rhodium(III), C_6H_5CORh(ttp) (2a), and (5,10,15,20-Tetratolyporphyrinato)(benzyl)rhodium(III), $C_6H_5CH_2$Rh(ttp) (3): General Procedure. Method A1. Rh(ttp)Cl (47 mg, 0.054 mmol) was dissolved in benzaldehyde (2.0 mL) and formed a bright red reaction mixture. The bright red reaction mixture was heated at 150 °C under N_2 in the dark for 1.5 days, after which the mixture turned dark red. Excess benzaldehyde was removed, and the dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). Two fractions were collected. Red, solid C_6H_5CORh(ttp) (**2a**) was collected as major product (24 mg, 0.028 mmol, 52% yield). $R_f = 0.42$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (dd, 2 H, $J = 1.2$, 8.1 Hz), 2.70 (s, 12 H), 5.98−6.00 (m, 2 H), 6.40 (t, 1 H, $J = 7.8$ Hz), 7.53−7.56 (m, 8 H), 7.95−8.07 (m, 8 H), 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 $C_{55}H_{41}N_4ORh\cdot H_2O$: C, 73.82; H, 4.62; N, 6.26. Found: C, 73.66; H, 4.64; N, 5.90. A single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/MeOH. An orange-red solid, $C_6H_5CH_2$Rh(ttp) (**3**), was collected as minor product (13 mg, 0.015 mmol, 28% yield). $R_f = 0.52$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.80 (d, 2 H, $J = 3.6$ Hz), 2.67 (s, 12 H), 2.94 (d, 2 H, $J = 6.5$ Hz), 5.84−5.89 (m, 2 H), 6.38 (t, 1 H, $J = 7.4$ Hz), 7.45−7.56 (m, 8 H), 7.98−8.08 (m, 8 H), 8.67 (s, 8 H).

Method A2. Rh(ttp)Cl (47 mg, 0.054 mmol) was added into benzaldehyde (2.0 mL). The bright red reaction mixture was heated at 200 °C under N_2 in the dark for 1 day only and **2a** was isolated (24 mg, 0.043 mmol, 79% yield).

Method B. Rh(ttp)CH_3 (30 mg, 0.038 mmol) was mixed with benzaldehyde (1.0 mL) in a Telfon screw-capped flask under nitrogen at 200 °C in the dark for 30 min. Only the red solid (**2a**) was obtained as the major product (20 mg, 0.027 mmol, 70% yield).

(5,10,15,20-Tetratolyporphyrinato)(4-fluorobenzoyl)rhodium(III), 4-FC_6H_5CORh(ttp) (2b). Method A2. Rh(ttp)Cl (47 mg, 0.054 mmol) was mixed with 4-fluorobenzaldehyde (2.0 mL) at 200 °C under N_2 in the dark for 1 day. The dark red crude product was purified by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). 4-FC_6H_5CORh(ttp) (**2b**) was obtained as a red solid (22 mg, 0.024 mmol, 45% yield). $R_f = 0.54$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (dd, 2 H, $J = 5.4$, $J = 8.4$ Hz), 2.71 (s, 12 H), 5.68 (t, 2 H, $J = 8.7$ Hz), 7.53 (t, 8 H, $J = 6.1$ Hz), 7.95−7.977 (m, 4 H), 8.03−8.07 (m, 8 H), 8.78 (s, 8 H). 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). Anal. Calcd for $C_{55}H_{40}N_4ORhF\cdot 3H_2O$: C, 70.13; H, 4.28; N, 5.95. Found: C, 70.39; H, 4.50; N, 5.84. A single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/MeOH.

Method B. Rh(ttp)CH_3 (30 mg, 0.038 mmol) was mixed with 4-fluorobenzaldehyde (1.0 mL) in a Telfon screw-capped flask under nitrogen at 200 °C in the dark for 8 h to yield **4** as a red solid (26 mg, 0.029 mmol, 76% yield).

(5,10,15,20-Tetratolyporphyrinato)(4-chlorobenzoyl)rhodium(III), 4-ClC_6H_5CORh(ttp) (2f). Method B. Rh(ttp)CH_3 (30 mg, 0.038 mmol) was mixed with 4-chlorobenzaldehyde (938 mg) in a Telfon screw-capped flask under nitrogen at 200 °C in the dark for 8 h to yield 4-ClC_6H_5CORh(ttp) (**2f**) as a red solid (16 mg, 0.020 mmol, 53% yield). $R_f = 0.70$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (d, 2 H, $J = 8.1$ Hz), 2.71 (s, 12 H), 5.94 (d, 2 H, $J = 8.1$ Hz), 7.53 (t, 8 H, $J = 6.6$ Hz), 7.90−7.93 (m, 4 H), 8.03−8.06 (m, 4 H), 8.79 (s, 8 H). IR (KBr, cm^{-1}): ν(C═O) 1703 (s). Anal. Calcd for $C_{55}H_{40}ClN_4ORh\cdot H_2O$: C, 71.08; H, 4.56; N, 6.03. Found: C, 70.68; H, 4.35; N, 5.97.

(5,10,15,20-Tetratolyporphyrinato)(4-α,α,α-trifluoromethylbenzoyl)rhodium(III), 4-$CF_3C_6H_5CO$Rh(ttp) (2e). Method A2. Rh(ttp)Cl (47 mg, 0.054 mmol) was dissolved in 4-α,α,α-trifluoromethylbenzaldehyde (2.0 mL) and heated at 200 °C under N_2 in the dark for 1 day. Excess 4-α,α,α-trifluoromethylbenzaldehyde was removed, and the dark red crude products were then purified by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). One fraction was collected. A reddish purple solid, 4-$CF_3C_6H_5CO$Rh(ttp) (**2f**) (26 mg, 0.021 mmol, 38% yield), was obtained. $R_f = 0.54$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (d, 2 H, $J = 8.1$ Hz), 2.71 (s, 12 H), 6.25 (d, 2 H, $J = 8.1$ Hz), 7.53 (d, 8 H, $J = 7.8$ Hz), 7.90−7.93 (m, 4 H), 8.03−8.06 (m, 4 H), 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 $C_{56}H_{40}N_4F_3ORh\cdot H_2O$: C, 69.86; H, 4.19; N, 5.82. Found: C, 69.96; H 4.26; N, 5.73.

Method B. Rh(ttp)CH_3 (30 mg, 0.038 mmol) was mixed with 4-α,α,α-trifluoromethylbenzaldehyde (1.0 mL) in a Telfon screw-capped flask under nitrogen at 200 °C in the dark for 2 days to yield **5** as a reddish purple solid (14 mg, 0.015 mmol, 39% yield).

(5,10,15,20-Tetratolyporphyrinato)(4-methylbenzoyl)rhodium(III), 4-$CH_3C_6H_5CO$Rh(ttp) (2c) and (5,10,15,20-Tetratolyporphyrinato)(4-formylbenzyl)rhodium(III), 4-$CHOC_6H_5CH_2$Rh(ttp) (4). Method A2. Rh(ttp)Cl (47 mg, 0.054 mmol) was dissolved in 4-methylbenzaldehyde (2.0 mL) and heated at 200 °C under N_2 in the dark for 2 h. Then excess 4-methylbenzaldehyde was removed, and the dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). A red solid, 4-$CH_3C_6H_5CO$Rh(ttp) (**2c**) (14 mg, 0.016 mmol, 30% yield), was collected. $R_f = 0.45$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87 (s, 3 H), 2.35 (d, 2 H, $J = 8.1$ Hz), 2.70 (s, 12 H), 5.76 (d, 2 H, $J = 8.1$ Hz), 7.53 (d, 8 H, $J = 8.1$ Hz), 7.92−7.95 (m, 4 H), 8.05−8.08 (m, 4 H), 8.76 (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 $C_{56}H_{43}N_4ORh\cdot H_2O$: C, 73.28; H, 4.72; N, 6.10. Found: C, 73.50; H, 4.70; N, 5.98. An orange-red solid, 4-$CHOC_6H_5CH_2$Rh(ttp) (**4**) (26 mg, 0.030 mmol, 55% yield), was collected. $R_f = 0.35$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.80 (d, 2 H, $J = 3.0$ Hz), 2.70 (s, 12 H), 2.97 (d, 2 H, $J = 7.8$ Hz), 6.35 (d, 2 H,

(22) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461−6466.

J = 7.8 Hz), 7.53−7.56 (m, 8 H), 7.94−8.08 (m, 8 H), 8.70 (s, 8 H), 9.44 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.81 (d, J_{Rh-C} = 27 Hz), 22.0, 24.0, 123.2, 125.2, 128.0, 132.0, 132.2, 134.2, 134.4, 137.8, 139.8, 143.6, 192.3. HRMS (FABMS): calcd for $(C_{56}H_{45}N_4Rh)^+$ *m*/*z* 890.2486, found *m*/*z* 890.2482. IR (KBr, cm^{-1}): ν(C═O) 1693 (s).

Method B. Rh(ttp)CH_3 (30 mg, 0.038 mmol) was mixed with 4-methylbenzaldehyde (1.0 mL) in a Telfon screw-capped flask under nitrogen at 200 °C in the dark for 16 h to yield **12a** (6 mg, 0.021 mmol, 54% yield).

(5,10,15,20-Tetratolyporphyrinato)(4-*tert*-butylbenzoyl)rhodium(III), 4-^{t}BuC_6H_5CORh(ttp) (2d), and (5,10,15,20-Tetratolyporphyrinato)(4-formylphenyl-1,1-dimethylethyl)rhodium(III), 4-CHOC_6H_4(Me)$_2CH_2$Rh(ttp) (5). Method A2. Rh(ttp)Cl (47 mg, 0.054 mmol) was dissolved in 4-*tert*-butylbenzaldehyde (2.0 mL) and heated at 200 °C under N_2 in the dark for 1 h. Then excess 4-*tert*-butylbenzaldehyde was removed, and the dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). Red solids of 4-^{t}BuC_6H_5-CORh(ttp) (**2d**) (9 mg, 0.0092 mmol, 17% yield) were collected. R_f = 0.43 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95 (s, 9 H), 2.42 (d, 2 H, J = 8.3 Hz), 2.70 (s, 12 H), 5.96 (d, 2 H, J = 8.3 Hz), 7.52 (d, 8 H, J = 8.1 Hz), 7.95−7.98 (m, 4 H), 8.04−8.07 (m, 4 H), 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 $C_{59}H_{49}N_4ORh\cdot 2H_2O$: C, 73.13; H, 5.51; N, 5.78. Found: C, 73.25; H, 5.22; N, 5.69. Another orange fraction, 4-CHOC_6H_4(Me)$_2CH_2$Rh(ttp) (**5**), was also collected (3 mg, 0.0011 mmol, 2% yield). R_f = 0.69 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.79 (d, 2 H, J = 3.0 Hz), 1.25 (s, 9 H), 2.70 (s, 12 H), 2.92 (d, 2 H, J = 9.0 Hz), 5.87 (d, 2 H, J = 9.0 Hz), 7.52−7.56 (m, 8 H), 8.01 (t, 8 H, J = 7.5 Hz), 8.65 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.0 (d, J_{Rh-C} = 28 Hz), 22.1, 31.2, 122.9, 123.5, 124.6, 127.8, 127.9, 131.8, 134.3, 134.4, 137.6, 138.3, 139.9, 143.6, 194.5. HRMS (FABMS): calcd for $(C_{59}H_{49}N_4ORh)^+$ *m*/*z* 932.3288, found *m*/*z* 932.2956. IR (KBr, cm^{-1}): ν(C═O) 1704 (s).

Method B. Rh(ttp)CH_3 (30 mg, 0.038 mmol) was mixed with 4-*tert*-butylbenzaldehyde (1.0 mL) in a Telfon screw-capped flask under nitrogen at 200 °C in the dark for 16 h to yield **2d** (26 mg, 0.028 mmol, 73% yield).

(5,10,15,20-Tetratolyporphyrinato)(4-methoxylbenzoyl)rhodium(III), 4-MeOC_6H_5CORh(ttp) (2g). Method B. Rh(ttp)CH_3 (30 mg, 0.038 mmol) was dissolved in anisaldehyde (1.0 mL) in a Telfon screw-capped flask under nitrogen at 200 °C in the dark for 16 h to yield 4-MeOC_6H_5CORh(ttp) (**2g**) (21 mg, 0.021 mmol, 56% yield) as a red solid. R_f = 0.52 (hexane/CH_2Cl_2 = 1:1). ^{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), 7.95−8.08 (m, 8 H), 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 $C_{56}H_{43}N_4ORh\cdot 2H_2O$: C, 71.33; H, 5.02; N, 5.94. Found: C, 71.71; H, 4.72; N, 5.77.

Reaction of Aliphatic Aldehydes with Rh(ttp)Cl (1). (5,10,15,20-Tetratolyporphyrinato)(ethylformyl)rhodium(III), CH_3CH_2-CORh(ttp) (7a). General Procedure. Method A. Rh(ttp)Cl (47 mg, 0.054 mmol) was dissolved in propanal (2.0 mL) and heated at 100 °C under N_2 in the dark for 2 days. Then excess propanal was removed. The dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). A red solid, CH_3CH_2CORh(ttp) (**7a**) (1 mg, 0.0016 mmol, 3% yield), was collected. R_f = 0.52 (hexane/CH_2Cl_2 = 1:1). ^{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 $(C_{51}H_{41}N_4ORh)^+$ *m*/*z* 828.2335, found *m*/*z* 828.2330. IR (KBr, cm^{-1}): ν(C═O) 1717 (s). Anal. Calcd for $C_{51}H_{41}N_4ORh\cdot 2H_2O$: C, 70.83; H, 5.24; N, 6.48. Found: C, 70.46; H, 4.81; N, 6.21.

Method B. Rh(ttp)Me (30 mg, 0.038 mmol) was added into propanal (1.0 mL). The bright red reaction mixture was heated at 100 °C under N_2 in the dark for 1 day. Excess propanal was removed. The dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). Bright red solid **7b** was collected (19 mg, 0.023 mmol, 60% yield).

5,10,15,20-Tetratolyporphyrinato)(hexylformyl)rhodium(III), $CH_3(CH_2)_5$CORh(ttp) (7b). Method B. Rh(ttp)Me (30 mg, 0.038 mmol) was added into heptanal (1.0 mL). The bright red reaction mixture was heated at 200 °C under N_2 in the dark for 3 days. Excess heptanal was removed. The dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). Bright red solids of $CH_3(CH_2)_5$CORh(ttp) (**7b**) were collected (14 mg, 0.016 mmol, 41% yield). R_f = 0.67 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.12 (t, 2 H, J = 7.2 Hz), −1.40 (p, 2 H, J = 9.0 Hz), −0.88 (q, 2 H, J = 9.0 Hz), 0.47 (d, 2 H, J = 5.7 Hz), 0.53 (m, 2 H), 0.86 (d, 3 H, J = 7.2 Hz), 2.70 (s, 12 H), 7.57 (d, 8 H, J = 7.3 Hz), 8.01−8.09 (m, 8 H), 8.79 (s, 8 H). HRMS (FABMS): calcd for $(C_{55}H_{49}N_4ORh)^+$ *m*/*z* 884.2953, found *m*/*z* 884.2956. IR (KBr, cm^{-1}): ν(C═O) 1716 (s). Anal. Calcd for $C_{55}H_{49}N_4ORh\cdot 2H_2O$: C, 71.57; H, 6.00; N, 6.07. Found: C, 71.61; H, 5.60; N, 6.05.

(5,10,15,20-Tetratolyporphyrinato)(*tert*-butylformyl)rhodium(III), ^{t}BuCORh(ttp) (7c). Method A. Rh(ttp)Cl (47 mg, 0.054 mmol) was dissolved in *tert*-butylaldehyde (2.0 mL) and heated at 200 °C under N_2 in the dark for 1 day. Then excess *tert*-butylaldehyde was removed, and the dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). Red solids of ^{t}BuCORh(ttp) (**7c**) (11 mg, 0.013 mmol, 24% yield) were collected. R_f = 0.52 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.36 (s, 9 H), 2.70 (s, 12 H), 7.53 (d, 8 H, J = 9.0 Hz), 7.96−8.05 (m, 8 H), 8.70 (s, 8 H). HRMS (FABMS): calcd for $(C_{53}H_{45}N_4ORh)^+$ *m*/*z* 857.2700, found *m*/*z* 857.2721. IR (KBr, cm^{-1}): ν(C═O) 1732 (s). Anal. Calcd for $C_{53}H_{49}N_4ORh\cdot H_2O$: C, 72.75; H, 5.42; N, 6.41. Found: C, 72.61; H, 5.60; N, 6.05.

Method B. Rh(ttp)Me (30 mg, 0.038 mmol) was added into *tert*-butylaldehyde (1.0 mL). The bright red reaction mixture was heated at 200 °C under N_2 in the dark for 3 days. Excess solvent was removed. The dark red crude products were then isolated by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (4:1). Bright red solid **7c** was collected (16 mg, 0.018 mmol, 48% yield).

(5,10,15,20-Tetratolyporphyrinato)rhodium(III) Trifate, Rh(ttp)OTf (8).[15] Rh(ttp)Cl (50 mg, 0.057 mmol) and the silver triflate (25.6 mg, 0.11 mmol) were put into the dried CH_2Cl_2 (100 mL) and stirred for 1.5 days at room temperature. The color of the mixture changed from red to reddish brown after 1.5 days. Then the product was isolated on silica gel eluting with CH_2Cl_2/EA (9:1). **4** was collected as orange solids (22 mg, 0.023 mmol, 40% yield). R_f = 0.32 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.70 (s, 12 H), 7.48−7.61 (m, 8 H), 7.98−8.05 (m, 8 H), 8.76 (s, 8 H). HRMS (FABMS): calcd for $(C_{49}H_{36}N_4RhO_3F_3S)^+$ *m*/*z* 771.1990, found *m*/*z* 771.1998.

Reaction of Rh(ttp)OTf with PhCHO. Rh(ttp)OTf (**15**) (10 mg, 0.010 mmol) was dissolved in benzaldehyde (1.0 mL) and heated at 200 °C under N_2 in the dark. After 15 min, C_6H_5CORh(ttp) (**2**) (7.8 mg, 0.0089 mmol, 89% yield) was obtained.

(5,10,15,20-Tetratolyporphyrinato)rhodium(III) Hydride, Rh(ttp)H (9).[16] A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in MeOH (50 mL) and a solution of $NaBH_4$ (17 mg, 0.45 mmol) in aqueous NaOH (0.1 M, 2 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated at 50 °C under N_2 for 1 h to give a brown solution. The solution was then cooled to 0 °C under N_2, and 0.1 M HCl (40 mL) was added

via a syringe. A brick red suspension was formed. After stirring at room temperature for another 15 min under N_2, the brick red precipitate was collected after filtration and washing with water (2 × 10 mL). The brick red residue for **9** was obtained (80 mg, 0.10 mmol, 92% yield) and vacuum-dried. ^{1}H NMR (C_6D_6, 300 MHz): δ −40.12 (d, 1 H, J_{Rh-H} = 43.5 Hz), 2.42 (s, 12 H), 7.16 (d, 4 H, J = 8.2 Hz), 7.35 (d, 4 H, J = 8.2 Hz), 7.95 (d, 4 H, J = 8.1 Hz), 8.22 (d, 4 H, J = 8.1 Hz), 9.03 (s, 8 H).

Reaction of Rh(ttp)H with PhCHO. Rh(ttp)H (**9**) (20 mg, 0.026 mmol) was dissolved in PhCHO (1.0 mL) to form a dark red solution and was then heated at 200 °C for 30 min. Both C_6H_5-CORh(ttp) (**2a**) (8.0 mg, 0.0091 mmol, 35% yield) and $C_6H_5CH_2$-Rh(ttp) (**3**) (1.0 mg, 0.0010 mmol, 4% yield) were obtained after chromatography.

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Supporting Information Available: Text, tables, and figure of crystallographic data for complexes **2a**, **2b**, and **2e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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