Reactivity Studies of Rhodium Porphyrin Radical with Diazo Compounds

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Rh(tmp) reacted with two diazo compounds to give rhodium(III) porphyrin alkyls in high yields under mild conditions. Mechanistic studies showed that Rh(tmp) was coordinated with a diazo compound, which then underwent a rapid hydrogen atom abstraction via carbon−hydrogen bond activation to give Rh(tmp)H. Rh(tmp)H subsequently reacted with a second molecule of the diazo compound in the rate-determining step to give Rh(tmp) alkyl and N_2. The rate law revealed that rate = k[Rh(tmp)][EDA]^2 for ethyl diazoacetate.

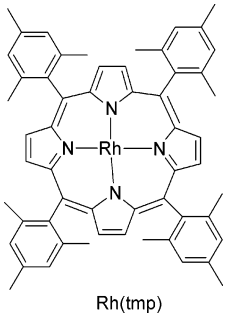
Introduction

Rhodium(II) tetramesitylporphyrin, Rh(tmp) (Figure 1), is a metallo radical and exhibits rich chemistry in both coordination chemistry and bond activations.

Rh(tmp), with its very bulky substituents, is monomeric in solution.[1,2] Mononuclear Rh(II) complexes possess structural and electronic features that make them generally susceptible to ligand substitution reactions. Rh(II) porphyrins are observed to undergo ligand association reactions to form the five-coordinate complexes LRh(tmp).[3] The series of coordination complexes Rh(tmp)L (L = NEt_3, $NHEt_2$, py, 2,6-Me_2py, PEt_3, PPh_3, $AsPh_3$, CNR) have been reported.[4] The adducts Rh(tmp)L disproportionate especially readily to form Rh(tmp)$^-$ and Rh(tmp)L_2^+, when L is a σ strong donor ligand (e.g., py), because L repels and destabilizes the unpaired electron in the d_{z^2} orbital.[5]

The versatile reactivities of Rh(II) have been exemplified in the activation of carbon−hydrogen bonds of the hydrocarbons H−CH_2R,[6,7] removal of an allylic hydrogen atom from methyl methacrylate,[8] abstractions of halogen atoms from a wide variety of organic halides,[9] activation of carbon−nitrogen bonds in alkyl isonitriles,[10] and aliphatic sp^3−sp^3 C−C bond activation of nitroxides[11] and ketones.[12]

Diazo complexes have been used as carbene sources in the transition-metal-catalyzed cyclopropanation of olefins,[13] cyclopropenation of acetylenes,[14] carbene insertion into C−H,[15] Si−H,[16] N−H,[17] and O−H[18] bonds, and formation of ylides.[19,20] Catalytic Rh-mediated polymerizations of carbenes, generated



Rh(tmp)

Figure 1. Structure of Rh(tmp).

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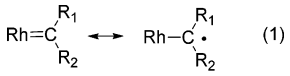
from the reaction of ethyl diazoacetate with a rhodium(I) complex to form highly stereoregular polymers with a high molecular mass, have been reported recently.[21] A detailed investigation of the mechanism of cyclopropanation of alkenes by rhodium(III) porphyrin complexes has been carried out, with an emphasis on the nature and characterization of intermediates and predominant catalytic species in the catalytic cycle.[22] However, until now, the metalloporphyrin carbene complex intermediate has not been obtained and has only been observed and supported by indirect evidence. It is likely that the high activity of the metal carbene intermediate hampers its isolation.

Due to our continuing interest in the reactivity studies of rhodium porphyrin radical,[11,12,23] we sought to synthesize rhodium porphyrin carbene complexes from the reactions of Rh(tmp) with diazo complexes using well-documented methods in both porphyrin and non-porphyrin systems.[24] Rhodium carbene complexes of porphyrin are structurally interesting, as two resonance forms can exist: the rhodium−carbon double bond (**C1**) or the α-rhodium carbon centered radical (**C2**) (eq 1). Such resonance forms have been reported for the the cobalt



(1)

C1 **C2**

analogue.[25] Now we report the unexpected formation of rhodium porphyrin alkyls (Rh(tmp)CH_2R) from the reactions of Rh(tmp) with diazo compounds. Mechanistic studies, including kinetic experiments, were also carried out to gain a better understanding of the reaction pathways.

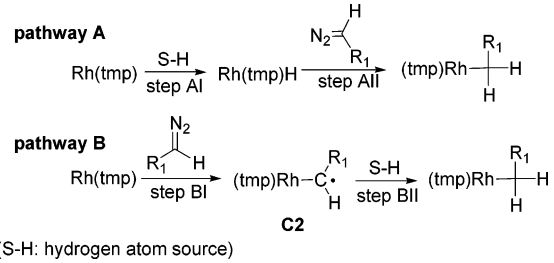
Results and Discussion

Reactions of Rh(tmp) and Diazo Complexes. When Rh(tmp) in benzene solution was mixed with ethyl diazoacetate (EDA) at room temperature, gas evolution, presumably N_2, was observed immediately (eq 2). After 30 min, Rh(tmp)CH_2CO_2-

$$\mathrm{Rh(tmp)} + \underset{\textbf{2a, 3a}}{\mathrm{RCHN_2}} \xrightarrow[\text{room temp, 30 min}]{\text{benzene}} \underset{\textbf{2b} (75\%),\ \textbf{3b} (70\%)}{\mathrm{Rh(tmp)CH_2R}} + \mathrm{N_2} \quad (2)$$

$$\mathrm{R = COOEt\ (\textbf{2a},\textbf{b}),\ Si(CH_3)_3\ (\textbf{3a},\textbf{b})}$$

Scheme 1. Possible Reaction Pathways



(S-H: hydrogen atom source)

Et was unexpectedly isolated in 75% yield. Likewise, Me_3SiCHN_2 dissolved in diethyl ether also gave Rh(tmp)CH_2SiMe_3 in 70% yield.

Independent Synthesis. The structures of the two products were further confirmed by authentic samples prepared by independent synthesis through reduction of Rh(tmp)Cl with $NaBH_4$ followed by alkylation with the appropriate alkyl chlorides (eq 3).

$$\mathrm{Rh(tmp)Cl} \xrightarrow[\text{(2) RCl, 0 °C to room temp, 1 h}]{\text{(1) } NaBH_4\text{, EtOH, } N_2\text{, 50−60 °C to room temp, 1 h}} \mathrm{Rh(tmp)R} \quad (3)$$

$$\mathrm{R = CH_2CO_2Et,\ 85\%;\ R = CH_2Si(CH_3)_3,\ 63\%}$$

Scheme 1 shows two possible reaction pathways, A and B, to account for the incorporation of an extra hydrogen atom into the product from the hydrogen source S−H. In pathway A, Rh(tmp) abstracts a hydrogen atom to give Rh(tmp)H (step AI), which then reacts with a diazo compound to give Rh(tmp)CH_2-CO_2Et (step AII). The second step, AII, was supported by the reaction of Rh(tmp)H with ethyl diazoacetate to give Rh(tmp)-CH_2CO_2Et in 76% yield at room temperature after 15 min (eq 4). In pathway B, the rhodium porphyrin carbon-centered radical

$$\mathrm{Rh(tmp)H + EDA} \xrightarrow[\text{room temp, 15 min}]{\text{benzene}} \underset{76\%}{\mathrm{Rh(tmp)CH_2COOEt}} \quad (4)$$

C2 is formed from the reaction of Rh(tmp) with a diazo compound,[25] with the extrusion of N_2. The intermediate **C2** then abstracts a hydrogen atom to give Rh(tmp) alkyl.

Mechanistic experiments were carried out to distinguish the two pathways. The key is to support or rule out the hydrogen atom abstraction step: the C−H activation by Rh(tmp) (step AI) or hydrogen atom abstraction by α-rhodium alkyl radical (step BII).

There are two possible hydrogen sources: (1) the C−H bonds of diazo alkanes and (2) solvents. (1) Since EDA contains alkyl C−H bonds which can be easily activated by Rh(tmp),[6,7] other aryl diazo compounds were prepared to examine the possibility. While $Ph_2C{=}N_2$[26] reacted with Rh(tmp), a new doublet at −1.99 ppm (J = 3.3 Hz), characteristic of Rh(tmp) alkyl, in the ^{1}H NMR spectrum of the crude reaction mixture was observed. However, no pure compounds were isolated, presumably due to the steric hindrance of two phenyl rings in causing instability of the product during chromatographic isolation. When PhC(O)C$=N_2$C(O)Ph[27] was used as the substrate, a complex mixture formed. Therefore, the hydrogen source from diazo alkanes is not completely ruled out. Presumably, the coordinating diazo substrate can facilitate the C−H activation for both alkyl and aryl C−H bonds. (2) The C−H bonds in the solvent are also a

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Table 1. Trapping Experiments for the Reaction of Rh(tmp) with EDA

entry	trap	BDE,[28] kcal mol^{-1} C−H	BDE,[28] kcal mol^{-1} O−H	BDE,[28] kcal mol^{-1} Si−H	product [amt, %]	disfavored pathway
1	TEMPO				Rh(tmp)CH_2CO_2Et (**2b**) [65]	
2	triethylsilane-*d*			95	Rh(tmp)CH_2CO_2Et (**2b**) [73]	B
3	toluene-d_8	89			Rh(tmp)CH_2CO_2Et (**2b**) [72]	B
4	methanol-d_4	96	105		Rh(tmp)CH_2CO_2Et (**2b**) [70]	B
5	D_2O		119		Rh(tmp)$CHDCO_2Et$ (**2c**) [70]	B

10 equiv. EDA and 100 equiv. trap reference to Rh(tmp) were added.

viable source. For Me_3SiCHN_2, the commercially available reagent was supplied in ether solution. Ether is a coordinating substrate with reactive weak α-C−H bonds ($BDE_{CH_3CH(H)OC_2H_5}$ = 93 kcal mol^{-1})[28] and can serve as a hydrogen atom donor. Since Rh(tmp) was stable in benzene at 80 °C for 2 days,[7a] the C−H bonds in benzene solvent and porphyrin ligand were not possible hydrogen atom sources for pathway AI.

These experiments suggest that the diazo compounds and ether solvent are both possible hydrogen sources. Further trapping experiments are necessary.

It is difficult to find a suitable trap, since Rh(tmp) can activate even the inert C−H bond in methane at room temperature.[6,7] Nevertheless, we attempted to trap the proposed intermediate **C2** in the reactions of Rh(tmp) with EDA.

(1) TEMPO. Since TEMPO was stable toward Rh(tmp) at room temperature,[11] it was used to trap **C2**. However, Rh(tmp)-CH_2CO_2Et was isolated in about 65% yield. It is likely that, if **C2** is formed, it is too bulky to undergo coupling. Therefore, no definitive conclusion could be drawn (Table 1, entry 1).

(2) Silane. Since the triethylsilane did not react with Rh(tmp) at room temperature for about 6 days, Et_3SiD was used to trap the intermediate **C2**. However, only Rh(tmp)CH_2CO_2Et was isolated and no deuterated product was observed. The higher Si−H bond energy of silane (BDE_{Si-H} = 95 kcal mol^{-1})[28] as compared to the C−H bond energy of EDA ($BDE_{CH_3CH-(H)CO_2Et}$ = 93 kcal mol^{-1})[28] accounts for the failed trapping, as the hydrogen abstraction is not exothermic.

(3) Toluene-d_8. Due to the failed trapping of **C2** in the above two experiments, toluene-d_8 was used, despite its known C−H activation with Rh(tmp) to give Rh(tmp)Bn and Rh(tmp)H reported by Wayland.[29] However, Rh(tmp)CH_2CO_2Et was isolated without any deuterium incorporation in 72% yield with toluene-d_8 added. The results suggested that **C2** was not likely generated, since **C2** can abstract a hydrogen atom from the weaker benzylic C−H bond of toluene ($BDE_{C_6H_5CH_2-H}$ = 89 kcal mol^{-1}).[28] Furthermore, the absence of Rh(tmp)Bn product revealed that Rh(tmp) reacted much more quickly with EDA than with toluene. The formation of Rh(tmp)H from EDA by hydrogen abstraction may be a viable process, in view of the better coordination of EDA to facilitate hydrogen atom abstraction.

The above three traps used failed to trap **C2** in pathway B. The alternative pathway may be operating, and coordinating traps were used to support pathway A.

(4) Methanol-d_4. As Rh(tmp) has been reported to react with MeOH at the C−H bond at room temperature,[30] we reasoned that addition of CD_3OD, a coordinating hydrogen atom donor, can generate Rh(tmp)D and subsequently Rh(tmp)$CHDCO_2Et$ in the reaction with EDA. However, only Rh(tmp)CH_2CO_2Et was obtained in 70% yield without any Rh(tmp)CD_2OD being observed. We rationalized that the unsuccessful deuterium incorporation may be due to the coordination of MeOH being weaker than that of EDA as well as the C−H bond being stronger ($BDE_{CH_2(H)OH}$ = 96 kcal mol^{-1})[28] than that of EDA ($BDE_{N_2CHCO_2CH(H)CH_3}$ = 93 kcal mol^{-1}).[28]

(5) D_2O. Finally, inspired by the reported conversion of Rh^{II}(tspp) (tspp = tetra *p*-sulfonatophenyl porphyrinate) by D_2O into Rh^{III}(tspp)D(D_2O) by Wayland,[31] we added D_2O to the reaction of Rh(tmp) with EDA; Rh(tmp)$CHDCO_2Et$ (**2c**) was obtained in 70% yield and characterized by ^{1}H NMR, ^{2}D NMR, and HRMS. In the ^{1}H NMR spectrum of **2c**, the triplet at −4.22 ppm (1 H, J_{H-D} = 3.9 Hz)[32] indicated that one proton had been deuteriated. ^{2}D NMR supported the formation of **2c** with a peak at −8.90 Hz (referenced to the residual deuterium in CH_2Cl_2). D_2O was the deuterium atom source, and the product was proposed to be obtained through pathway A. Three possible pathways to give the product were proposed. (1) Rh(tmp)D was first formed from the reaction of Rh(tmp) and D_2O and then reacted with EDA to give Rh(tmp)$CHDCO_2Et$. In this pathway, the yield of Rh(tmp)$CHDCO_2Et$ should be less than 50%, since equal amounts of Rh(tmp)D and Rh(tmp)OD should be formed. However, a 70% yield of Rh(tmp)$CHDCO_2Et$ was produced. This suggested that the formation of Rh(tmp)D from Rh(tmp)-(D_2O) was unlikely. (2) Deuterium exchange between Rh(tmp)-CH_2CO_2Et (**2b**) and D_2O was ruled out, since no deuterated product was observed by stirring Rh(tmp)CH_2CO_2Et with D_2O for about 5 days. The 1:1 ratio of H to D in Rh(tmp)$CHDCO_2$-Et further ruled out the exchange. (3) Rh(tmp)H was formed from the reaction of Rh(tmp) with EDA. Rh(tmp)H then underwent rapid deuterium exchange with D_2O to give Rh-(tmp)D, which reacted with another EDA molecule to give Rh-(tmp)$CHDCO_2Et$ with H/D in a 1:1 ratio. This possibility is most consistent with the experimental results.

On the basis of the results of the above experiments, we reasoned that pathway A is operating. Rh(tmp)H is most readily formed from coordinating the hydrogen atom donor of a diazo compound to facilitate chelation-assisted C−H activation. The intermediate Rh(tmp)H further reacts with EDA to give Rh(tmp)CH_2CO_2Et.

Kinetic Studies of the Reaction of Rh(tmp) with Ethyl Diazoacetate. Since the reaction of Rh(tmp) with ethyl diazoacetate (EDA) is high-yielding and clean, kinetic experiments were carried out to gain further mechanistic understandings. The kinetic measurements of reaction 5 were performed spectrally

$$\text{Rh(tmp)} + \text{EDA} \rightarrow \text{Rh(tmp)CH}_2\text{CO}_2\text{Et} + \text{N}_2 \qquad (5)$$

by monitoring the absorbance changes accompanying the reaction at 522 nm under the conditions 25.0 °C and initial concentrations (1.48−7.42) × 10^{-5} M Rh(tmp) and (0.56−3.91)

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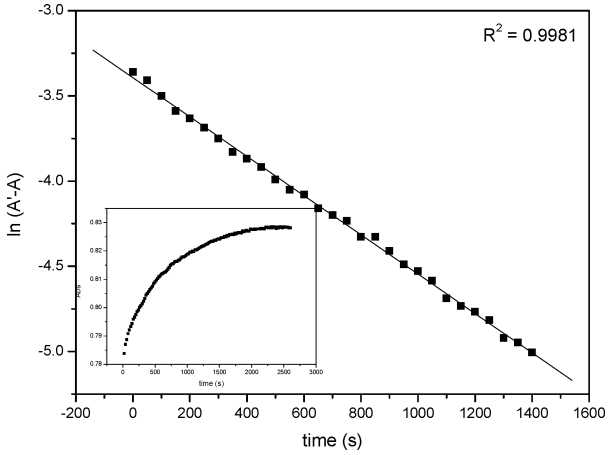


Figure 2. Pseudo-first-order rate plot for Rh(tmp) and EDA at 25.0 °C.

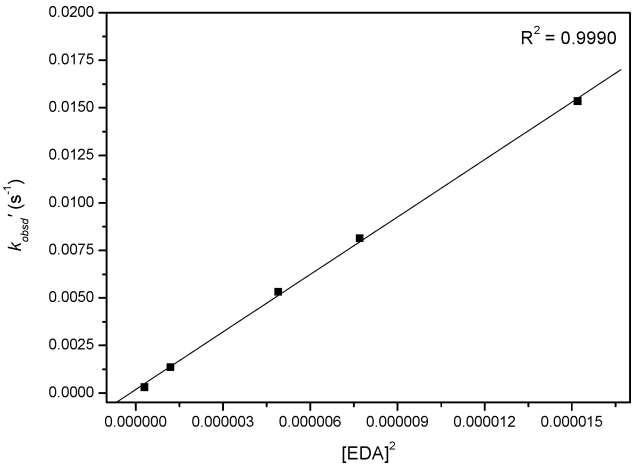


Figure 3. Plot of k_{obs}' vs $[EDA]^2$.

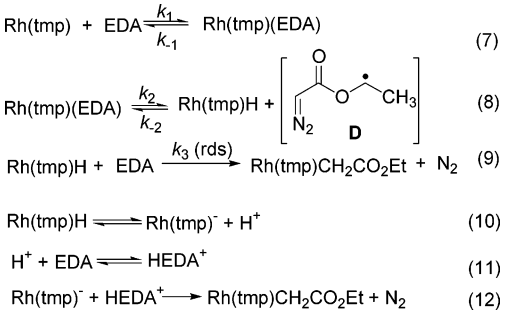
Table 2. Rate Constants of the Reaction of Rh(tmp) and EDA at 25.0 °C

entry	10^5[Rh(tmp)], M	10^3[EDA], M	$10^3 k_{obs}'$	$10^3 k_{obs}$, M^{-2} s^{-1}
1	1.48	1.12	1.45 ± 0.02	1.16 ± 0.02
2	3.71	1.12	1.15 ± 0.01	0.92 ± 0.01
3	7.42	1.12	1.49 ± 0.02	1.19 ± 0.02
4	3.71	2.23	5.32 ± 0.06	1.07 ± 0.01
5	3.71	0.56	0.30 ± 0.01	0.96 ± 0.03
6	3.71	2.79	8.15 ± 0.03	1.05 ± 0.004
7	3.71	3.91	15.35 ± 0.02	1.00 ± 0.001

× 10^{-3} M EDA. A time scan was carried out for at least 4 half-lives. A linear pseudo-first-order plot with slope equal to k_{obs}' is obtained to yield a reaction first order in Rh(tmp), independent of the initial concentrations of Rh(tmp) (Figure 2; Table 2, entries 1−3). Pseudo-first-order rate constants k_{obs}' were plotted against $[EDA]^2$ to yield the linear plot shown in Figure 3. The rate constants of k_{obs}, derived from the slopes of these plots, are summarized in Table 2. Kinetic measurements indicated that the reaction of Rh(tmp) with EDA was an overall third-order reaction with first order in Rh(tmp) and second order in EDA, as shown in eq 6.

$$\text{rate} = k_{obs}[\text{Rh(tmp)}][\text{EDA}]^2 \tag{6}$$

Proposed Mechanism. According to the rate law, the mechanism was derived as shown in eqs 7−12, with reaction 7 attaining a fast equilibrium of the coordination of Rh(tmp) by EDA. A facile hydrogen atom abstraction from chelation-



assisted C−H activation occurred with a coordinated EDA to give Rh(tmp)H and the organic radical **D**. We are not certain about the true identity of **D** and its fate. Hydrogen atom transfer with the traps shown in Table 2 might have occurred for the benzylic hydrogen of toluene. The rate-determining irreversible step shown in reaction 9 occurred with the formation of the rhodium porphyrin alkyl and extrusion of N_2. Two pathways for the insertion of Rh(tmp)H into EDA to give Rh(tmp)CH_2CO_2Et (**2b**) are possible. First, a concerted process operated. Rh(tmp)H was initially coordinated with EDA in a productive cis manner. Extrusion of N_2 then gave Rh(tmp)CH_2CO_2Et (**2b**). Alternatively, an ionic process could occur. Rh(tmp)H, being a weak acid, ionized into $Rh(tmp)^-$ and H^+ (the pK_a value of Rh(tpp)H is equal to 11 with tpp = tetraphenylporphyrinate).[33] EDA then reacted with H^+ to give $N_2{}^+CH_2CO_2Et$ ($EDAH^+$), which further underwent nucleophilic attack by $Rh(tmp)^-$ to give N_2 and Rh(tmp)CH_2CO_2Et (**2b**) (eqs 10−12). Such a

$$\text{Rh(tmp)H} \rightleftharpoons \text{Rh(tmp)}^- + \text{H}^+ \tag{10}$$

$$\text{H}^+ + \text{EDA} \rightleftharpoons \text{HEDA}^+ \tag{11}$$

$$\text{Rh(tmp)}^- + \text{HEDA}^+ \rightarrow \text{Rh(tmp)CH}_2\text{CO}_2\text{Et} + \text{N}_2 \tag{12}$$

$$\begin{aligned} \text{rate} &= k_3[\text{Rh(tmp)H}][\text{EDA}] \\ &= k_3K_2[\text{Rh(tmp)(EDA)}][\text{EDA}] \\ &= k_3K_2K_1[\text{Rh(tmp)}][\text{EDA}]^2 \end{aligned} \tag{13}$$

$$K_1 = k_1/k_{-1},\ K_2 = k_2/k_{-2}$$

$$k_{obs} = k_3K_2K_1$$

mechanism has been proposed for the reaction of CH_2N_2 with RCOOH to give RCOOMe.[34] The above mechanistic studies could not distinguish between these two possibilities. We favor the concerted process for its simplicity (eq 9). This mechanism readily accounts for the second-order dependence of EDA. The first EDA molecule acted as a hydrogen atom donor, and the second molecule acted as an alkylating agent.

Conclusion

In conclusion, Rh(tmp) reacted with diazo complexes to form rhodium(III) porphyrin alkyls. The reaction of Rh(tmp) with

(33) Nelson, A. P.; Dimagno, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 8569−8570.

(34) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley: New York, 2001; Chapter 10.

EDA exhibited an overall third-order reaction. The proposed mechanism involved the chelation-assisted hydrogen atom abstraction from a diazo compound by Rh(tmp) to form Rh(tmp)H as the intermediate. The subsequent formation of a rhodium(III) porphyrin alkyl with nitrogen extrusion from the reaction of Rh(tmp)H with another molecule of the diazo compound was the rate-determining step.

Experimental Section

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used before purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates.

^{1}H NMR spectra were recorded on a Bruker DPX-300 instrument (300 MHz). Chemical shifts were reported with reference to the residual solvent protons in $CDCl_3$ (δ 7.24 ppm) or with tetramethylsilane (δ 0.00 ppm) as the internal standard. Coupling constants (J) were reported in hertz (Hz). Mass spectra were recorded on a Finnigan MAT 95XS mass spectrometer (FAB-MS and ESI-MS). Samples for elemental analysis were prepared by vacuum drying (0.005 mmHg) at 50−60 °C for 2 days.

Reaction of Rh(tmp) and Ethyl Diazoacetate. Ethyl diazoacetate (0.009 mL, 0.088 mmol) was added via a microsyringe to a solution of Rh(tmp) (0.0088 mmol) in benzene (4.0 mL), and the reaction mixture was stirred at room temperature for 30 min under N_2 in the absence of light. The crude product was purified by chromatography on silica gel, with a hexane−CH_2Cl_2 solvent mixture (2:1 to 1:1) as eluent. A red solid of Rh(tmp)CH_2CO_2Et (**2b**; 6.4 mg, 0.0066 mmol, 75%) was obtained. R_f = 0.47 (1:1 hexane−CH_2Cl_2). ^{1}H NMR (C_6D_6, 300 MHz): δ −4.22 (d, 2 H, J = 4.2 Hz), −0.08 (t, 3 H, J = 7.2 Hz), 2.17 (s, 12 H), 2.22 (s, 12 H), 2.26 (q, 2 H, J = 7.2 Hz), 2.45 (s, 12 H), 7.22 (s, 4 H), 8.82 (s, 8 H). ^{13}C NMR (C_6D_6, 100 MHz): −3.73 (d, J_{Rh-C} = 40 Hz), 13.59, 21.45, 21.91, 22.04, 57.57, 120.75, 131.17, 137.71, 138.83, 139.20, 139.59, 143.32, 171.28. HRMS (FAB): calcd for $(C_{60}H_{59}N_4O_2Rh)^+$, m/z 970.3688. found, m/z 970.3687. Anal. Calcd for $C_{60}H_{59}N_4O_2Rh$: C, 74.21; H, 6.12; N, 5.77. Found: C, 74.01; H, 6.23; N, 6.11.

Reaction of Rh(tmp) and (Trimethylsilyl)diazomethane. (Trimethylsilyl)diazomethane (0.044 mL, 2.0 M in ether, 0.088 mmol) was added via a microsyringe to a Rh(tmp) (0.0088 mmol) benzene solution (4.0 mL), and the reaction mixture was stirred at room temperature for 30 min under N_2 in the absence of light. The crude product was purified by chromatography on silica gel, with a solvent mixture of hexane and CH_2Cl_2 (10:1 to 5:1) as eluent. A red solid of Rh(tmp)$CH_2Si(CH_3)_3$ (**3b**; 6.0 mg, 0.0062 mmol, 70%) was obtained. R_f = 0.62 (5:1 hexane−CH_2Cl_2). ^{1}H NMR (C_6D_6, 300 MHz): δ −5.28 (d, 2 H, J = 2.7 Hz), −2.09 (s, 9 H), 1.89 (s, 12 H), 2.18 (s, 12 H), 2.44 (s, 12 H), 7.14 (s, 4 H), 8.74 (s, 8 H). ^{13}C NMR (C_6D_6, 100 MHz) −6.68 (d, J_{Rh-C} = 40 Hz), −1.85, 21.84, 22.21, 22.79, 121.31, 131.75, 138.11, 139.20, 139.26, 139.81, 143.97. HRMS (FAB): calcd for $(C_{60}H_{63}N_4SiRh)^+$, m/z 970.3125; found, m/z 970.3129. Anal. Calcd for $C_{60}H_{63}N_4SiRh$: C, 74.20; H, 6.54; N, 5.77. Found: C, 73.91; H, 6.53; N, 5.59.

Preparation of Ethyl (5,10,15,20-Tetramesitylporphyrinato)-rhodium(III) Acetate, [Rh(tmp)CH_2CO_2Et] (2b).[35] A red suspension of Rh(tmp)Cl (50 mg, 0.038 mmol) in EtOH (50 mL) and a solution of $NaBH_4$ (7 mg, 0.19 mmol) in 0.5 M NaOH (2 mL) were purged with N_2 separately for about 15 min. The $NaBH_4$ solution was added to the suspension of Rh(tmp)Cl via a cannula. The reaction mixture was heated at 55 °C for 1 h under N_2. After the mixture was cooled to room temperature, $ClCH_2CO_2$Et was added via a syringe. A bright red suspension formed immediately and was further stirred for 1 h at room temperature. The reaction mixture was worked up by addition of CH_2Cl_2 and H_2O. The crude product was extracted with CH_2Cl_2 (200 mL), and the extract was washed with H_2O (25 mL × 3), dried over anhydrous $MgSO_4$, filtered, and rotary evaporated to dryness. After purification by column chromatography on silica gel, with a solvent mixture of hexane and CH_2Cl_2 (2:1 to 1:1) as eluent, a bright red solid of Rh(tmp)CH_2CO_2Et (31 mg, 0.032 mmol, 85%) was obtained, which was further purified by recrystallization from CH_2Cl_2/MeOH.

Preparation of ((Trimethylsilyl)methyl)(5,10,15,20-tetramesitylporphyrinato)rhodium(III), [Rh(tmp)CH_2SiMe_3] (3b).[35] A red suspension of Rh(tmp)Cl (50 mg, 0.038 mmol) in EtOH (50 mL) and a solution of $NaBH_4$ (7 mg, 0.19 mmol) in 0.5 M NaOH (2 mL) were purged with N_2 separately for about 15 min. The $NaBH_4$ solution was added to the suspension of Rh(tmp)Cl via a cannula. The reaction mixture was heated at 55 °C for 1 h under N_2. After the mixture was cooled to room temperature, $ClCH_2SiMe_3$ was added via a syringe. A bright red suspension formed immediately and was further stirred for 1 h at room temperature. The reaction mixture was worked up by addition of CH_2Cl_2 and H_2O. The crude product was extracted with CH_2Cl_2 (200 mL), and the extract was washed with H_2O (25 mL × 3), dried over anhydrous $MgSO_4$, filtered, and rotary evaporated to dryness. After purification by column chromatography on silica gel with a solvent mixture of hexane and CH_2Cl_2 (10:1 to 5:1) as eluent, a bright red solid of Rh(tmp)CH_2SiMe_3 (23 mg, 0.024 mmol, 63%) was obtained, which was further purified by recrystallization from CH_2Cl_2/MeOH.

Reaction of Rh(tmp)H and Ethyl Diazoacetate. EDA was added to Rh(tmp)H (20.0 mg, 0.023 mmol) benzene solution and stirred at room temperature for 15 min under N_2 in the absence of light. The crude product was purified by chromatography on silica gel, with a solvent mixture of hexane and CH_2Cl_2 (2:1 to 1:1) as eluent. A red solid of Rh(tmp)CH_2CO_2Et (**2b**) (14.9 mg, 0.015 mmol, 68%) was obtained.

Trapping Experiments using TEMPO. A trapping experiment using TEMPO is described as the typical procedure. TEMPO (136.6 mg, 100 equiv) was added to a benzene solution of Rh(tmp) (0.0088 mmol). Then EDA (9.0 μL, 10 equiv) was added to the mixture and the solution was stirred for 0.5 h at room temperature. After the solvent was removed, the residue was purified by column chromatography. A red solid of **2b** (mg, mmol, 65%) was obtained.

Trapping Experiments using Triethylsilane-*d*. Et_3Si−D (142 μL, 100 equiv) was used. A red solid of **2b** (mg, mmol, 73%) was obtained.

Trapping Experiments using Toluene-d_8. $C_6D_5CD_3$ (94 μL, 100 equiv) was used. A red solid of **2b** (mg, mmol, 72%) was obtained.

Trapping Experiments using Methanol-d_4. CD_3OD (36 μL, 100 equiv) was used. A red solid of **2b** (mg, mmol, 70%) was obtained.

Reaction of Rh(tmp) and Ethyl Diazoacetate with D_2O added. D_2O (18 μL) was added via a microsyringe to a benzene solution of Rh(tmp) (0.0088 mmol) and the reaction mixture was stirred at r.t. for 15 min. Then EDA (0.009 mL, 0.088 mmol) was added via a microsyringe to the reaction mixture and was stirred at r.t. for 30 min under N_2 in the absence of light. The crude product was purified by chromatography on silica gel, with a solvent mixture of hexane and CH_2Cl_2 (2:1 to 1:1) as eluent. A red solid of Rh(tmp)$CHDCO_2$Et (**2c**; 5.9 mg, 0.0062 mmol, 70%) was obtained. R_f = 0.47 (1:1 hexane−CH_2Cl_2). ^{1}H NMR (C_6D_6, 300 MHz): δ −4.22 (~t, 1 H, J = 3.9 Hz), −0.07 (t, 3 H, J = 7.2 Hz), 2.04 (s, 12 H), 2.08 (s, 12 H), 2.22 (q, 2 H, J = 7.2 Hz), 2.46 (s, 12 H), 8.78 (s, 8 H). ^{2}D NMR (CH_2Cl_2, 60 MHz): δ −8.90. HRMS (FAB): calcd for $(C_{60}H_{58}N_4O_2DRh)^+$, m/z 971.3750; found, m/z 971.3772.

Reaction of Rh(tmp)H and Ethyl Diazoacetate with D_2O Added. D_2O (46 μL) was added via a microsyringe to a benzene solution of Rh(tmp)H (20.0 mg, 0.023 mmol), and the reaction

(35) Wayland, B. B.; Sherry, A. E.; Poszmik, G.: Bunn, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 1673−1681.

mixture was stirred at room temperature for 15 min. Then EDA (0.027 mL, 0.23 mmol) was added via a microsyringe to the reaction mixture and was stirred at room temperature for 30 min under N_2 in the absence of light. The crude product was purified by chromatography on silica gel, with a solvent mixture of hexane and CH_2Cl_2 (2:1 to 1:1) as eluent. A red solid of Rh(tmp)$CHDCO_2$-Et (**2c**; 14.9 mg, 0.015 mmol, 68%) was obtained.

Deuterium Exchange of Rh(tmp)H and D_2O. D_2O (12 μL) was added to a benzene solution of Rh(tmp)H (5.0 mg, 0.0046 mmol), and the mixture was stirred for 15 min. Then the benzene was removed and benzene-d_6 was added, and the solution was transferred to a NMR tube under N_2. The NMR spectrum was recorded, and the signal at high field of Rh(tmp)H disappeared. Deuterium exchange had occurred.

Kinetic Studies of the Reaction between [Rh(tmp)] and Ethyl Diazoacetate. Kinetic studies were carried out at a temperature of 25.0 ± 0.2 °C maintained by a constant temperature controlling bath. Rh(tmp)CH_3 (2.5 mg, 0.00225 mmol) was dissolved in benzene in a 2.00 mL volumetric flask, and this solution was then transferred to a flask fitted with a Teflon stopcock and degassed. After photolysis for 10 h at 6−10 °C, a stock solution of Rh(tmp) (1.11×10^{-3} M) was produced. The substrate EDA (0.1674 M) was prepared and degassed. A measured amount of the stock solution of Rh(tmp) was added with benzene in a cuvet-Schlenk UV cell and was thermally equilibrated at 25 °C for 15 min. Then the EDA solution in benzene was added to the mixture quickly, and the sample was time-scanned by UV spectra at 522 nm.

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Supporting Information Available: NMR and HRMS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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