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Carbon–Hydrogen Bond Activation of Arenes by a [Bis(oxazolinyl)phenyl]-rhodium(III) Acetate Complex

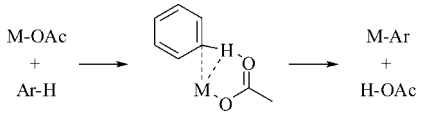
Jun-ichi Ito[a] and Hisao Nishiyama*[a]

Keywords: C–H activation / Arenes / Rhodium / Substituent effects

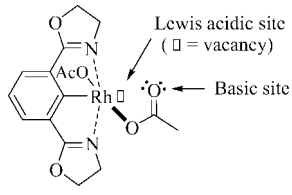
Thermolysis of the rhodium(III) complex [(*dm*-Phebox-*dm*)-$Rh(OAc)_2(H_2O)$] [**1**; *dm*-Phebox-*dm* = 2,6-bis(4,4-dimethyloxazolinyl)phenyl] in various arenes results in the formation of the corresponding aryl complexes [(*dm*-Phebox-*dm*)Rh(Ar)(κ^2-OAc)] [Ar = C_6H_5 (**2**), 3,5-$Me_2C_6H_3$ (**3**), 3,4-$Me_2C_6H_3$ (**4**), C_6H_4Me (**5**), $C_6H_4CF_3$ (**6**), C_6H_4OMe (**7**), C_6H_4COMe (**8**), C_6H_4Cl (**9**)]. The reaction of **1** with monosubstituted benzenes such as toluene, anisole, acetophenone, trifluorotoluene, and chlorobenzene produces a mixture of *meta*- and *para*-activated complexes, the ratio of which depends on the substituents on the benzene ring. The relative rate of the reaction of **1** with monosubstituted benzenes C_6H_5X was determined to be: X = OMe (1.8) > COMe (1.6) > CF_3 (1.2), Cl (1.2) > CH_3 (1). The acetato ligand of **1** appears to be essential for C–H bond activation of arenes as no reaction of the Rh^{III} complex [(*dm*-Phebox-*dm*)$RhCl_2(H_2O)$] is observed in chlorobenzene at 120 °C. The first-order rate constants obtained by thermolysis of **1** in [D_8]toluene at 97.1–116.5 °C yielded the following activation parameters: $\Delta H^{\ddagger}$ = 22(2) kcal mol^{-1}, $\Delta S^{\ddagger}$ = –24(5) cal mol^{-1} K^{-1}. The kinetic isotope effect for the C–H bond activation of toluene by **1** was determined to be k_H/k_D = 5.4 at 100 °C. These data suggest that the rate-determining step involves the C–H bond cleavage with a rigid, cyclic transition structure.

Introduction

Intermolecular C–H bond activation has been considered to be an essential step for functionalization of unreactive hydrocarbons due to their relatively high dissociation energies.[1] Such transformations are attractive from a synthetic point of view due to the possibility of using simple and naturally abundant compounds to provide more useful and complex products.[2] Thus far, a number of studies have focused on the mechanism involving oxidative addition, σ-bond metathesis, 1,2-addition, and electrophilic activation.[3] Recently, electron-deficient Pd complexes bearing acetato ligands have been found to be reactive for inter- and intramolecular C–H bond activation and have been applied to a suitable precursor for catalytic reactions.[4] Furthermore, computational studies of the C–H bond activation by $Pd(OAc)_2$ and related complexes have suggested a mechanism whereby the acetato ligand assists the heterolytic cleavage through a six-membered cyclic transition state, as shown in Scheme 1.[5] Although Rh and Ir complexes have been known to undergo oxidative addition to the electron-rich metal center for some time,[3] only very recently have Periana and co-workers reported the C–H bond cleavage of arenes by the action of the alkoxy ligands of the Ir^{III} complexes [$Ir(acac)_2(OR)L$].[6] Similarly, Davies and co-workers have reported the intramolecular C–H bond activation of {Cp*M} (M = Rh, Ir) species.[7] Such base-assisted C–H bond activation is very attractive as an alternative mechanism to oxidative addition. In this context, the Rh^{III} complexes [(Phebox)$Rh(OAc)_2(H_2O)$] [Phebox = 2,6-bis(oxazolinyl)phenyl],[8] which possess an Rh^{III} center and meridional stereochemistry, could be expected to combine the functions of a Lewis acid for coordination of the substrate and a base to act as a proton acceptor during the C–H bond cleavage step (Scheme 2). The Rh^{III} acetate complex would therefore provide different information regarding the coordination chemistry in the meridional reaction field compared with the structurally related Rh and Ir complexes having a phosphane-based ligand (PCP- and PNP-type li-



Scheme 1.



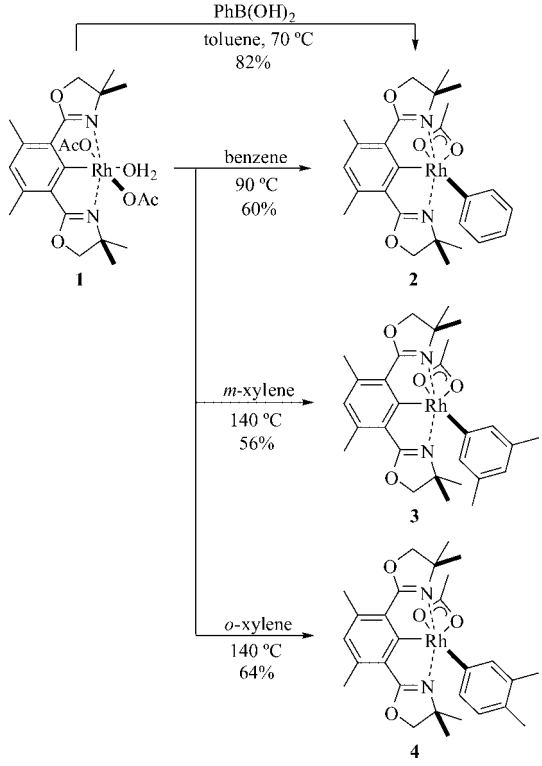
Scheme 2.

[a] Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Chikusa, Nagoya 464-8603, Japan
Fax: +81-52-789-3209
E-mail: hnishi@apchem.nagoya-u.ac.jp

gands).[9] We report herein an intermolecular C–H bond activation reaction of simple arenes to a (Phebox)Rh^{III} acetate complex.

Results and Discussion

When a solution of the Rh^{III} acetate complex [(*dm*-Phebox-*dm*)$Rh(OAc)_2(H_2O)$] [**1**; *dm*-Phebox-*dm* = 2,6-bis(4,4-dimethyloxazolinyl)phenyl][8b] in benzene was heated at 90 °C for 144 h, C–H bond activation took place to produce the novel phenylrhodium(III) complex [(*dm*-Phebox-*dm*)-Rh(Ph)(κ^2-OAc)] (**2**) in 60% isolated yield (Scheme 3). Thermolysis of **1** in *m*- and *o*-xylenes also gave the corresponding arylRh^{III} complexes [(*dm*-Phebox-*dm*)Rh(Ar)(κ^2-OAc)] [Ar = 3,5-$Me_2C_6H_3$ (**3**), 3,4-$Me_2C_6H_3$ (**4**)] in 56% and 64% yields, respectively (Scheme 3). Since products arising from *ortho*-C–H bond activation of xylenes were not detected, the regioselectivity of the reactions must be strongly affected by the steric hindrance in the coordination environment of the Phebox ligand. The authentic phenyl complex **2** could be synthesized in 82% yield by treating **1** with $PhB(OH)_2$.



Scheme 3.

An X-ray analysis of **3** confirmed its structure as an arylRh^{III} complex (Figure 1). The orientation of the aryl ligand is perpendicular to the Phebox plane [C(1)–Rh(1)–C(19) 91.81(9)°]. The difference in angles around the *ipso*-carbon atom of the aryl ligand [C(20)–C(19)–Rh(1) 128.83(17), C(24)–C(19)–Rh(1) 113.55(17)°] indicates that the aryl ring is bent slightly towards the acetato ligand, probably due to steric repulsion with the Phebox ligand. The Rh(1)–C(19) bond length of 1.993(2) Å is comparable to those in other arylRh^{III} complexes.[10] The κ^2-acetato ligand makes the Rh center saturated.

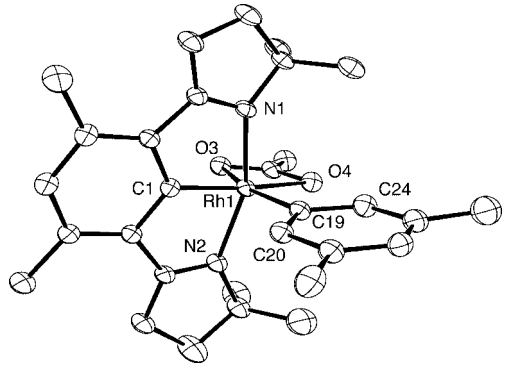
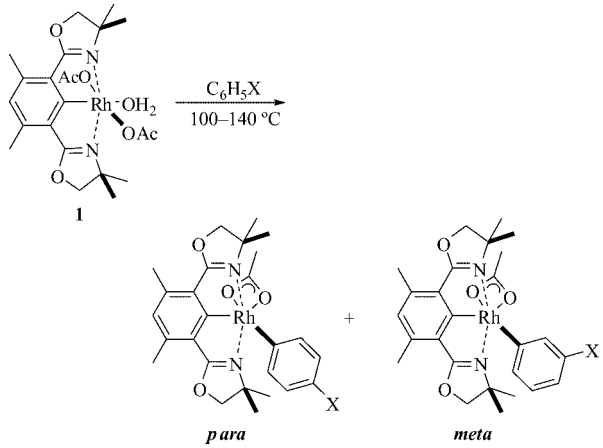


Figure 1. Molecular structure of **3** with ellipsoids at the 40% probability level (one of the molecules in the unit cell has been omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh(1)–C(1) 1.919(2), Rh(1)–C(19) 1.993(2), Rh(1)–O(3) 2.2687(16), Rh(1)–O(4) 2.2673(16), Rh(1)–N(1) 2.0753(18), Rh(1)–N(2) 2.0580(18); N(2)–Rh(1)–N(1) 158.72(7), C(20)–C(19)–Rh(1) 128.83(17), C(24)–C(19)–Rh(1) 113.55(17).

Since the substituent on the benzene ring has been shown to affect the selectivity of C–H bond activation, we examined the reactivity of **1** toward the monosubstituted benzenes C_6H_5X (X = Me, CF_3, OMe, COMe, Cl; Scheme 4). Thermolysis of **1** in toluene resulted in the formation of *para*- and *meta*-tolyl complexes **5p** and **5m** in 64% isolated yield in a 1:1.4 ratio, respectively. We did not detect the *ortho*-C–H activated product, as observed in the reaction of xylenes. We also prepared the authentic tolyl complex **5p** as a single isomer by the reaction of **1** with *p*-tolylboronic acid (Figure 2). A similar C–H bond activation of electron-deficient $C_6H_5CF_3$ took place to produce a 1:7.8 mixture of **6p** and **6m**, respectively, in 76% yield. In the cases of anisole and acetophenone, the formation of *para*- and *meta*-activated complexes was observed. This suggests that precoor-



Scheme 4.

dination of the carbonyl and methoxy groups to the Rh center is not important for the selectivity of the C–H bond activation.[11] Reaction of **1** with C_6H_5Cl produced the *para*- and *meta*-activated complexes **9p** and **9m**. The C–Cl bond-activated complex was not detected in the (Phebox)-Rh system.[12] Selectivity for the *para* position in preference to the *meta* position was observed for electron-rich toluene and anisole, whereas the inverse selectivity was observed for electron-deficient trifluorotoluene and acetophenone. This tendency is due to electrophilic aromatic substitution reactions. It is noteworthy that interconversion between **5p** and **5m** is inhibited, as shown by no observation of isomerization of **5p** in toluene at 120 °C for 24 h.

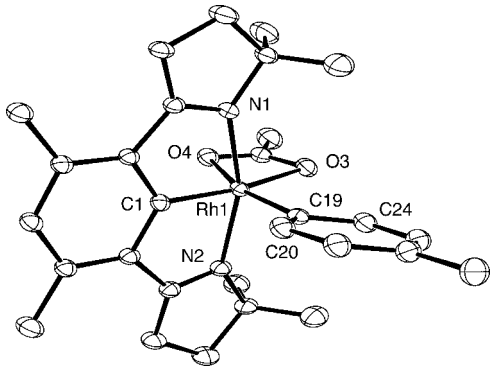


Figure 2. Molecular structure of **5p** with ellipsoids at the 40% probability level (one of the molecules in the unit cell has been omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh(1)–C(1) 1.912(2), Rh(1)–C(19) 2.005(2), Rh(1)–O(3) 2.2843(17), Rh(1)–O(4) 2.2328(18), Rh(1)–N(1) 2.0526(19), Rh(1)–N(2) 2.0592(19); N(1)–Rh(1)–N(2) 159.00(8), C(20)–C(19)–Rh(1) 128.69(19), C(24)–C(19)–Rh(1) 113.81(19).

The substituent effect for C–H bond activation of monosubstituted benzenes was determined by competition reactions between two different aromatic compounds. The relative rate of reaction of **1** with C_6H_5X decreased in the following sequence: OMe (1.8) > COMe (1.6) > CF_3 (1.2), Cl (1.2) > CH_3 (1); no correlation with Hammett's σ values was observed. This result is inconsistent with electrophilic C–H bond activation, where the ρ values have been determined in the cases of $PtCl_6^{2-}$ and [(OEP)RhCl] (OEP = octaethylporphyrinato).[13,14]

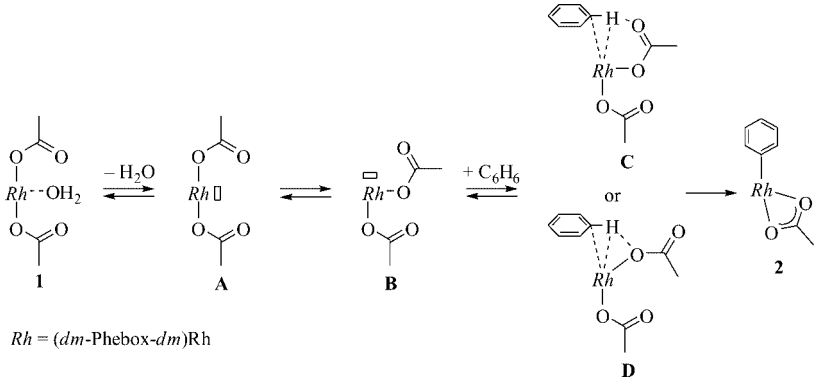
Thermolysis of **1** in a 1:1 mixture of toluene and [D_8]-toluene at 100 °C resulted in formation of the C–H- and C–D-activated complexes **5** and [D_7]**5**. ^{1}H NMR analysis revealed that the kinetic isotope effect is 5.4. This large value suggests that the C–H bond cleavage is the rate-determining step. Additionally, the rate constants obtained in the range of 97.1–116.5 °C yielded the following activation parameters: $\Delta H^{\ddagger} = 22 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24 \pm 5$ cal mol^{-1} K^{-1}. The relatively large and negative value of the activation entropy suggests a rigid transition state.[15]

We also checked the reaction of the Rh^{III} complex [(*dm*-Phebox-*dm*)$RhCl_2(H_2O)$] with chlorobenzene. When a solution of the complex in chlorobenzene was heated at 120 °C for 40 h, no reaction was observed. This result clearly indicates that the acetato ligand in **1** is essential for C–H bond activation.

The proposed mechanism for C–H bond activation of arenes by **1** is illustrated in Scheme 5. We have demonstrated previously that the coordination site of H_2O in [(Phebox)$RhCl_2(H_2O)$] plays the role as the Lewis acidic position.[16] We therefore presume that a coordinatively unsaturated intermediate **A** with a vacant site can be formed by dissociation of H_2O. According to the final geometry of the aryl complexes, isomerization to **B** might be important to accept the arene molecule. The negative activation entropy suggests that the C–H bond of arenes is cleaved though a rate-determining six-centered transition state **C**.[5,7b] However, we cannot rule out mechanisms involving σ-bond metathesis and oxidative hydrogen migration, which require the four-centered transition state **D**.[3,17]

Conclusion

We have found intermolecular C–H bond activation of various arenes by the structurally well-defined Rh^{III} acetate complex **1**, where the acetato ligand acts as a proton acceptor. A large kinetic isotope effect and negative entropy were found in this system. X-ray analysis of **3** has revealed a molecular structure with the aryl ligand at the apical position and a κ^2-acetato ligand. Further detailed mechanistic and derivatization studies of arenes are in progress.



Scheme 5.

Experimental Section

General Procedures: ^{1}H and ^{13}C NMR spectra were obtained at 25 °C with a Varian Mercury 300 spectrometer. ^{1}H NMR chemical shifts are reported relative to the singlet at δ = 7.26 ppm for chloroform or δ = 7.16 ppm for benzene. ^{13}C NMR spectra are reported in terms of chemical shifts relative to the triplet at δ = 77.0 ppm for $CDCl_3$ or δ = 128.0 ppm for C_6D_6 as an internal standard. IR spectra were recorded with a JASCO FT/IR-230 spectrometer. Elemental analysis was performed with a Perkin–Elmer 2400II. [(*dm*-Phebox-*dm*)Rh(OAc)$_2$(H$_2$O)] (**1**) and [(*dm*-Phebox-*dm*)Rh(Cl)$_2$(H$_2$O)] were prepared according to a literature procedure.[8b]

Reaction of 1 with Benzene: Complex **1** (27 mg, 0.050 mmol) was dissolved in benzene (5 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 90 °C for 144 h. After removal of the solvent, the yellow residue was purified by column chromatography on silica gel with ethyl acetate/MeOH (10:1) as eluent to give [(*dm*-Phebox-*dm*)Rh(Ph)(κ^2-OAc)] (**2**; 17 mg, 62%) as a yellow solid. Complex **2** was alternatively synthesized by treatment of **1** (54 mg, 0.10 mmol) with PhB(OH)$_2$ (27 mg, 0.22 mmol) in toluene (2 mL) at 70 °C for 46 h. Workup as described above gave **2** (44 mg, 0.082 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.97 (s, 6 H, Phebox-*Me*), 1.39 (s, 6 H, Phebox-*Me*), 2.07 (s, 3 H, O*Ac*), 2.56 (d, $J_{H,H}$ = 0.6 Hz, 6 H, 3,5-*Me*), 4.23 (d, $J_{H,H}$ = 8.2 Hz, 2 H, Phebox-CH_2), 4.33 (d, $J_{H,H}$ = 8.2 Hz, 2 H, Phebox-CH_2), 6.69–6.79 (m, 6 H, C_6H_5 and 4-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.08, 24.45 (OAc), 27.01, 27.19, 65.18, 81.87, 121.5, 125.3, 126.1, 126.7, 134.1, 139.7, 146.0 (d, $J_{Rh,C}$ = 31.9 Hz, C_{ipso}), 171.0 (d, $J_{Rh,C}$ = 5.2 Hz), 183.5 (OAc), 196.5 (d, $J_{Rh,C}$ = 29.6 Hz) ppm. $C_{26}H_{31}N_2O_4Rh$ (538.44): calcd. C 58.00, H 5.80, N 5.20; found C 58.11, H 5.67, N 5.07.

Reaction of 1 with *m*-Xylene: Complex **1** (54 mg 0.10 mmol) was dissolved in *m*-xylene (10 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 140 °C for 60 h. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate as eluent to give [(*dm*-Phebox-*dm*)Rh(3,5-Me$_2$C$_6$H$_3$)(κ^2-OAc)] (**3**; 32 mg, 56%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 1.00 (s, 6 H, Phebox-*Me*), 1.38 (s, 6 H, Phebox-*Me*), 2.05 (s, 3 H, OAc), 2.06 (s, 6 H), 2.55 (s, 6 H), 4.24 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 4.33 (d, $J_{H,H}$ = 8.4 Hz, 2 H, Phebox-CH_2), 6.32 (s, 1 H, $C_6H_3Me_2$), 6.38 (s, 2 H, $C_6H_3Me_2$), 6.68 (s, 1 H, 4-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.08, 21.52, 24.47 (OAc), 27.06, 27.14, 65.23, 81.84, 123.6, 126.0, 126.7, 131.6, 131.6, 133.9, 139.5, 145.6 (d, $J_{Rh,C}$ = 31.4 Hz, C_{ipso}), 170.9 (d, $J_{Rh,C}$ = 5.7 Hz), 183.3 (OAc), 196.7 (d, $J_{Rh,C}$ = 29.6 Hz) ppm. $C_{28}H_{35}N_2O_4Rh$ (566.49): calcd. C 59.37, H 6.23, N 4.95; found C 59.34, H 6.33, N 4.46.

Reaction of 1 with *o*-Xylene: Complex **1** (27 mg 0.050 mmol) was dissolved in *o*-xylene (2 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 140 °C for 36 h. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate as eluent to give [(*dm*-Phebox-*dm*)Rh(3,4-Me$_2$C$_6$H$_3$)(κ^2-OAc)] (**4**; 24 mg, 86%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 1.01 (s, 6 H, Phebox-*Me*), 1.38 (s, 6 H, Phebox-*Me*), 2.06 (m, 9 H, OAc and $C_6H_3Me_2$), 2.55 (d, $J_{H,H}$ = 0.6 Hz, 6 H), 4.23 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 4.33 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 6.17 (d, $J_{H,H}$ = 7.8 Hz, 1 H, $C_6H_3Me_2$), 6.48 (d, $J_{H,H}$ = 7.8 Hz, 1 H, $C_6H_3Me_2$), 6.68 (m, 1 H, 4-*H*), 6.76 (s, 1 H, $C_6H_3Me_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.05, 19.08, 19.90, 24.52 (OAc), 27.17, 65.19, 81.84, 125.9, 126.7, 126.8 (d, $J_{Rh,H}$ = 1.1 Hz), 129.1, 131.4, 133.0, 134.9 (d, $J_{Rh,C}$ = 1.1 Hz), 139.5 (d, $J_{Rh,C}$ = 1.1 Hz), 141.2 (d, $J_{Rh,C}$ = 32.0 Hz, C_{ipso}), 170.9 (d, $J_{Rh,C}$ = 5.7 Hz), 183.4 (OAc), 196.8 (d, $J_{Rh,C}$ = 29.6 Hz) ppm. $C_{28}H_{35}N_2O_4Rh$ (566.49): calcd. C 59.37, H 6.23, N 4.95; found C 58.75, H 6.19, N 4.28.

Reaction of 1 with Toluene: Complex **1** (27 mg 0.050 mmol) was dissolved in toluene (10 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 115 °C for 144 h. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate as eluent to give [(*dm*-Phebox-*dm*)Rh(C_6H_4Me)(κ^2-OAc)] (**5**; 22 mg, 78%) as a yellow solid. The ^{1}H NMR spectrum of the crude product revealed the formation of **5p** and **5m** in a 1.0:1.4 ratio. Complex **5p** was alternatively synthesized by treatment of **1** (54 mg, 0.10 mmol) with (*p*-C_6H_4Me)B(OH)$_2$ (30 mg, 0.20 mmol) in toluene (2 mL) at 90 °C for 16 h. Workup as described above gave complex **5p** (36 mg, 65%). **5p:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.99 (s, 6 H, Phebox-*Me*), 1.37 (s, 6 H, Phebox-*Me*), 2.06 (s, 3 H, O*Ac*), 2.14, (s, 3 H, C_6H_4Me), 2.55 (s, 3,5-*Me*), 4.23 (d, $J_{H,H}$ = 8.4 Hz, 2 H, Phebox-CH_2), 4.33 (d, $J_{H,H}$ = 8.4 Hz, 2 H, Phebox-CH_2), 6.57 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4Me), 6.61 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4Me), 6.69 (s, 1 H,4-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.09, 20.67 (C_6H_4Me), 24.48 (OAc), 27.11, 27.23, 65.18, 81.87, 122.4–139.6, 140.8 (d, $J_{Rh,H}$ = 31.9 Hz, C_{ipso}), 170.9 ($J_{Rh,C}$ = 5.2 Hz), 183.5 (O*Ac*), 196.7 ($J_{Rh,C}$ = 29.6 Hz) ppm. **5m:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.99 (s, 6 H, Phebox-*Me*), 1.38 (s, 6 H, Phebox-*Me*), 2.06 (s, 3 H, *OAc*), 2.13, (s, 3 H, C_6H_4Me), 2.55 (s, 3,5-Me), 4.23 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 4.33 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 6.27 (d, $J_{H,H}$ = 7.6 Hz, 1 H, C_6H_4Me), 6.50 (d, $J_{H,H}$ = 7.6 Hz, 1 H, C_6H_4Me), 6.60 (t, $J_{H,H}$ = 7.6 Hz, 1 H, C_6H_4Me), 6.69 (s, 1 H), 6.87 (s, 1 H, C_6H_4Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.09, 21.67 (C_6H_4Me), 24.48 (OAc), 27.05, 27.17, 65.21, 81.87, 122.4–139.60, 145.8 (d, $J_{Rh,C}$ = 31.4 Hz, C_{ipso}), 170.9 (d, $J_{Rh,C}$ = 5.2 Hz), 183.5 (OAc), 196.6 (d, $J_{Rh,C}$ = 29.6 Hz) ppm. $C_{27}H_{33}N_2O_4Rh$ (552.47): calcd. C 58.70, H 6.02, N 5.07; found C 58.83, H 5.98, N 4.96.

Reaction of 1 with α,α,α-Trifluorotoluene: Complex **1** (27 mg 0.050 mmol) was dissolved in α,α,α-trifluorotoluene (3 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 100 °C for 140 h. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate as eluent to give [(*dm*-Phebox-*dm*)Rh($C_6H_4CF_3$)(κ^2-OAc)] (**6**; 23 mg, 76%) as a yellow solid. The ^{1}H NMR spectrum of the crude products revealed the formation of **6p** and **6m** in a ratio of 1:7.8. **6p:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.94 (s, 6 H, Phebox-*Me*), 1.39 (s, 6 H, Phebox-*Me*), 2.06 (s, 3 H, O*Ac*), 2.57 (s, 3,5-*Me*), 4.25 (d, $J_{H,H}$ = 8.4 Hz, 2 H, Phebox-CH_2), 4.35 (d, $J_{H,H}$ = 8.4 Hz, 2 H, Phebox-CH_2), 6.74 (s, 1 H, 4-*H*), 6.77–6.97 (4 H, $C_6H_4CF_3$) ppm. **6m:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.94 (s, 6 H, Phebox-*Me*), 1.39 (s, 6 H, Phebox-*Me*), 2.06 (s, 3 H, O*Ac*), 2.57 (s, 3,5-*Me*), 4.25 (d, $J_{H,H}$ = 8.4 Hz, 2 H, Phebox-CH_2), 4.35 (d, $J_{H,H}$ = 8.4 Hz, 2 H, Phebox-CH_2), 6.74 (s, 1 H, 4-*H*), 6.77–6.97 (3 H, $C_6H_4CF_3$), 7.18 (s, 1 H, $C_6H_4CF_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.11, 24.45 (OAc), 26.99, 27.23, 65.23, 81.94, 118.5 (q, $J_{C,F}$ = 4.1 Hz), 124.4 (q, $J_{C,F}$ = 269.9 Hz), 127.0 (q, $J_{C,F}$ = 31.4 Hz), 130.4 (q, $J_{C,F}$ = 2.9 Hz), 134.3, 140.1, 147.4 (d, $J_{Rh,C}$ = 31.9 Hz, C_{ipso}), 171.1 (d, $J_{Rh,C}$ = 5.1 Hz), 184.1 (OAc), 195.6 (d, $J_{Rh,C}$ = 29.1 Hz) ppm. $C_{27}H_{30}F_3N_2O_4Rh$ (606.44): calcd. C 53.47, H 4.99, N 4.62; found C 54.13, H 5.27, N 3.85.

Reaction of 1 with Anisole: Complex **1** (27 mg 0.050 mmol) was dissolved in anisole (3 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 120 °C for 44 h. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate as eluent to give [(*dm*-Phebox-*dm*)Rh(C_6H_4OMe)(κ^2-OAc)] (**7**; 20 mg, 70%) as a yellow solid. The ^{1}H NMR spectrum

of the crude products revealed the formation of **7p** and **7m** in a 1:1 ratio. **7p:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.98 (s, 6 H, Phebox-*Me*), 1.38 (s, 6 H, Phebox-*Me*), 2.05 (s, 3 H, OAc), 2.55 (s, 3,5-Me), 3.64 (s, 3 H, OMe), 4.23 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 4.33 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 6.42 (d, $J_{H,H}$ = 7.8 Hz, 2 H, C_6H_4OMe), 6.60 (d, $J_{H,H}$ = 7.8 Hz, 2 H, C_6H_4OMe), 6.69 (s, 1 H, 4-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.10, 24.47 (OAc), 27.03, 27.23, 55.07 (O*Me*), 65.16, 81.88, 111.5, 126.0, 126.7, 133.3 (d, $J_{Rh,C}$ = 33.1 Hz, C_{ipso}), 133.9, 139.6, 155.6, 170.9 (d, $J_{Rh,C}$ = 5.3 Hz), 183.6 (O*Ac*), 196.6 (d, $J_{Rh,C}$ = 29.0 Hz) ppm. **7m:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.99 (s, 6 H, Phebox-*Me*), 1.38 (s, 6 H, Phebox-*Me*), 2.05 (s, 3 H, OAc), 2.54 (s, 3,5-*Me*), 3.61 (s, 3 H, O*Me*), 4.23 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 4.33 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Phebox-CH_2), 6.01 (m, 1 H, C_6H_4OMe), 6.27 (d, $J_{H,H}$ = 7.8 Hz, 1 H, C_6H_4OMe), 6.69 (t, $J_{H,H}$ = 7.8 Hz, 1 H, C_6H_4OMe), 6.69 (s, 1 H, 4-*H*), 6.77 (d, $J_{H,H}$ = 7.8 Hz, 1 H, C_6H_4OMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.10, 24.47 (OAc), 27.03, 27.23, 54.82 (O*Me*), 65.21, 81.88, 106.5, 120.0, 124.8, 126.2, 126.6, 127.0, 139.7, 148.0 (d, $J_{Rh,C}$ = 31.4 Hz, C_{ipso}), 156.4, 170.9 (d, $J_{Rh,C}$ = 5.2 Hz), 183.6 (O*Ac*), 196.3 (d, $J_{Rh,C}$ = 29.7 Hz) ppm. $C_{27}H_{33}N_2O_5Rh$ (568.47): calcd. C 57.05, H 5.85, N 4.93; found C 56.85, H 5.76, N 4.72.

Reaction of 1 with Acetophenone: Complex **1** (27 mg 0.050 mmol) was dissolved in acetophenone (3 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 140 °C for 24 h. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate as eluent to give [(*dm*-Phebox-*dm*)-Rh(C_6H_4COMe)(κ^2-OAc)] (**8**; 23 mg, 78%) as a yellow solid. The ^{1}H NMR spectrum of the crude products revealed the formation of **8p** and **8m** in a 1:4.5 ratio. **8p:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.95 (s, 6 H, Phebox-*Me*), 1.39 (s, 6 H, Phebox-*Me*), 2.07 (s, 3 H, OAc), 2.44 (s, 3 H, -CO*Me*), 2.57 (s, 3,5-*Me*), 4.24 (d, $J_{H,H}$ = 8.5 Hz, 2 H, Phebox-CH_2), 4.35 (d, $J_{H,H}$ = 8.5 Hz, 2 H, Phebox-CH_2), 6.74 (s, 1 H, 4-*H*), 6.96 (d, $J_{H,H}$ = 8.0 Hz, 2 H), 7.31 (d, $J_{H,H}$ = 8.0 Hz, 2 H) ppm. **8m:** ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 0.95 (s, 6 H, Phebox-*Me*), 1.39 (s, 6 H, Phebox-*Me*), 2.07 (s, 3 H, OAc), 2.39 (s, 3 H, -CO*Me*), 2.57 (s, 3,5-*Me*), 4.24 (d, $J_{H,H}$ = 8.5 Hz, 2 H, Phebox-CH_2), 4.35 (d, $J_{H,H}$ = 8.5 Hz, 2 H, Phebox-CH_2), 6.74 (s, 1 H, 4-*H*), 6.84 (t, $J_{H,H}$ = 7.8 Hz, 1 H, C_6H_4COMe), 7.15 (d, $J_{H,H}$ = 7.8 Hz, 1 H, C_6H_4COMe), 7.23 (s, 1 H, C_6H_4COMe), 7.31 (d, $J_{H,H}$ = 7.8 Hz, 1 H, C_6H_4COMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, room temp.): δ = 19.11, 24.52 (OAc), 26.70 (CO*Me*), 27.06, 27.33, 65.20, 81.92, 121.8, 125.1, 126.5, 126.6, 133.3, 139.5, 140.1, 146.7 (d, $J_{Rh,C}$ = 31.9 Hz, C_{ipso}), 171.1 (d, $J_{Rh,C}$ = 5.7 Hz), 184.0 (OAc), 195.9 (d, $J_{Rh,C}$ = 29.7 Hz), 199.0 (*C*OMe) ppm. $C_{28}H_{33}N_2O_5Rh$ (580.48): calcd. C 57.93, H 5.73, N 4.83; found C 57.68, H 5.60, N 4.64.

Reaction of 1 with Chlorobenzene: Complex **1** (27 mg 0.050 mmol) was dissolved in chlorobenzene (5 mL) in a 20-mL Schlenk tube under argon and the solution was stirred at 120 °C for 50 h. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate as eluent to give [(*dm*-Phebox-*dm*)-Rh(C_6H_4Cl)(κ^2-OAc)] (**9**; 23 mg, 80%) as a yellow solid. The ^{1}H NMR spectrum of the crude products revealed the formation of **9p** and **9m** in a 1:2.2 ratio. **9p:** ^{1}H NMR (300 MHz, C_6D_6, room temp.): δ = 0.78 (s, 6 H, Phebox-*Me*), 1.17 (s, 6 H, Phebox-*Me*), 2.16 (s, 3 H, OAc), 2.48 (s, 6 H, 3,5-*Me*), 3.43 (d, $J_{H,H}$ = 8.7 Hz, Phebox-CH_2), 3.55 (d, $J_{H,H}$ = 8.7 Hz, Phebox-CH_2), 6.49 (s, 1 H, 4-*H*), 6.91 (d, $J_{H,H}$ = 8.3 Hz, 2 H, C_6H_4Cl), 7.08 (d, $J_{H,H}$ = 8.3 Hz, 2 H, C_6H_4Cl) ppm. ^{13}C NMR (75 MHz, C_6D_6, room temp.): δ = 19.35, 25.04 (OAc), 27.10, 27.34, 65.45, 81.90, 122.5–140.0, 145.2 (d, $J_{Rh,C}$ = 32.5 Hz, C_{ipso}), 171.4 (d, $J_{Rh,C}$ = 4.5 Hz), 184.1, 198.3 (d, $J_{Rh,C}$ = 28.0 Hz) ppm. **9m:** ^{1}H NMR (300 MHz, C_6D_6, room temp.): δ = 0.81 (s, 6 H, Phebox-*Me*), 1.16 (s, 6 H, Phebox-*Me*), 2.16 (s, 3 H, OAc), 2.45 (s, 6 H, 3,5-*Me*), 3.40 (d, $J_{H,H}$ = 8.1 Hz, Phebox-CH_2), 3.52 (d, $J_{H,H}$ = 8.1 Hz, Phebox-CH_2), 6.47 (s, 1 H, 4-*H*), 6.61 (t, $J_{H,H}$ = 7.8 Hz, 2 H, C_6H_4Cl), 6.84 (d, $J_{H,H}$ = 7.8 Hz, 2 H, C_6H_4Cl), 6.97 (d, $J_{H,H}$ = 7.8 Hz, 2 H, C_6H_4Cl), 7.46 (s, 1 H, C_6H_4Cl) ppm. ^{13}C NMR (75 MHz, C_6D_6, room temp.): δ = 19.35, 25.04 (OAc), 27.04, 27.34, 65.45, 81.90, 122.5–140.1, 150.4 (d, $J_{Rh,C}$ = 32.6 Hz, C_{ipso}), 171.5 (d, $J_{Rh,C}$ = 5.2 Hz), 184.1, 198.1 (d, $J_{Rh,C}$ = 28.0 Hz) ppm. $C_{26}H_{30}ClN_2O_4Rh$ (572.89): calcd. C 54.51, H 5.28, N 4.89; found C 54.66, H 5.18, N 4.72.

Competition Reaction: Complex **1** (16 mg, 0.030 mmol) was dissolved in a 1:1 molar mixture (4 mL) of toluene and C_6H_5X (X = OMe, COMe, CF_3, or Cl) under argon. The solution was stirred at 100 °C for 24 h and then passed through a short column. The relative ratio of products was determined on the basis of the ^{1}H NMR spectra in $CDCl_3$.

Reaction of 1 with [D$_8$]Toluene/Toluene: Complex **1** (11 mg 0.020 mmol) was dissolved in a 1:1 mixture of [D_8]toluene and toluene (1 mL) in a 20-mL Schlenk tube under argon. The solution was stirred at 100 °C for 40 h and then the solvent was removed under reduced pressure. The ^{1}H NMR spectrum of the resulting residue revealed the formation of [D_7]**3** and **3** in a 5.4:1 ratio.

Monitoring the Reaction of 1 with [D$_8$]Toluene: Complex **1** (16.0 mg, 0.030 mmol) was dissolved in [D_8]toluene (3 mL) under argon. The solution (0.6 mL) was placed into an NMR tube and then the tube was flame-sealed. The four samples were maintained in oil baths at 97.1, 105.0, 111.3, and 116.5 °C. The reaction was monitored by ^{1}H NMR spectroscopy by recording the signal of the methyl group. The rate constants were estimated as $2.48(5)\times10^{-6}$ (97.1 °C), $4.13(5)\times10^{-6}$ (105.0 °C), $7.12(9)\times10^{-6}$ (111.3 °C), and $1.21(1)\times10^{-5}$ s^{-1} (116.5 °C). The Eyring plot gave the following activation parameters: $\Delta H^{\ddagger}$ = 22 ± 2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = –24 ± 5 cal mol^{-1} K^{-1}.

X-ray Diffraction Study: Single crystals of **3** and **5p** suitable for an X-ray diffraction study were obtained from hexane/CH_2Cl_2 solutions at room temperature. The diffraction data were collected with a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). An empirical absorption correction was applied with SADABS. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL. All non-hydrogen atoms of the rhodium complex were refined with anisotropic displacement parameters. All hydrogen atoms were located at calculated positions and refined as rigid groups. Refinement details for **3**: empirical formula: $C_{29.50}H_{38.50}N_2O_4Rh$; M_r = 588.03; temperature: 153(2) K; crystal system: triclinic; space group: $P\bar{1}$; a = 11.2915(5), b = 13.4972(7), c = 19.5574(9) Å, α = 96.8790(10), β = 103.3450(10), γ = 101.8940(10)°, V = 2793.7(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.398 Mg m^{-3}, μ = 0.648 mm^{-1}, F(000) = 1226, crystal size = 0.40 × 0.40 × 0.30 mm, θ range = 1.74–27.53°; index ranges: $-14 \le h \le 14$, $-16 \le k \le 17$, $-25 \le l \le 21$; reflections collected: 19914; independent reflections: 12803 [R(int) = 0.0187], completeness to θ = 27.53°: 99.2%; max/min transmission: 1.000000/0.788581; data/restraints/parameters: 12803/0/673; goodness-of-fit on F^2: 1.030; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0343, $wR2$ = 0.0844; R indices (all data): $R1$ = 0.0438, $wR2$ = 0.0895; largest diff. peak/hole: 0.946/–0.363 e Å^{-3}. Refinement details for **5p**: empirical formula: $C_{27}H_{33}N_2O_4Rh$; M_r = 552.46; temperature: 173(2) K; crystal system: triclinic; space group: $P\bar{1}$; a = 11.3424(5), b = 13.1787(6), c = 17.4623(8) Å, α = 94.8920(10), β = 94.7150(10), γ = 102.4740(10)°, V = 2525.7(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.453 Mg m^{-3}, μ = 0.711 mm^{-1}, F(000) = 1144, crystal size = 0.30 × 0.20 × 0.10 mm, θ range = 1.18–27.51°; index ran-

ges: $-14 \leq h \leq 14$, $-17 \leq k \leq 16$, $-14 \leq l \leq 22$; reflections collected: 18003, independent reflections: 11516 [R(int) = 0.0353], completeness to θ = 27.51°: 99.3%; max/min transmission: 1.000000/0.735363; data/restraints/parameters: 11516/0/629; goodness-of-fit on F^2: 0.983; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0320, $wR2$ = 0.0788; R indices (all data): $R1$ = 0.0407, $wR2$ = 0.0872; largest diff. peak/hole: 0.901 and –0.661 e Å^{-3}. CCDC-623906 and -623907 contain the supplementary crystallographic data for complexes **3** and **5p**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif.

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