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Base-Promoted Selective Activation of Benzylic Carbon-Hydrogen Bonds of Toluenes with Rhodium(III) Porphyrin Chloride: Synthetic Scopes and Mechanism

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Toluenes underwent base-promoted selective benzylic carbon-hydrogen bond activation (CHA) with rhodium porphyrin chlorides (Rh(por)Cl). In the absence of nucleophilic base, both aryl and benzylic rhodium porphyrins were formed. In the presence of nucleophilic base, the selectivity, rates and functional group compatibilities of benzylic activation reactions were enhanced. K_2CO_3 was found to be the optimal base to achieve the best yields. Ortho-, meta- and para-substituted toluenes in the presence of K_2CO_3 yielded the corresponding rhodium porphyrin benzyls in high yields both in solvent-free conditions and in benzene solvent. Mechanistically, in the absence of nucleophilic base, a cationic rhodium(III) porphyrin species together with some rhodium(II) porphyrin are the most likely intermediates to account both the aryl and benzylic CHA. In the presence of a base, Rh(por)OH is generated by ligand substitution with Rh(por)Cl and rapidly undergoes reduction to give rhodium(II) porphyin dimer and H_2O_2. The key rhodium porphyrin intermediates for benzylic CHA were found to be rhodium(II) porphyrin dimer and hydrides as observed by ^{1}H NMR spectroscopy, which underwent parallel benzylic CHA reactions with the rhodium(II) porphyrin dimer being the more reactive intermediate.

Keywords: Benzylic; Carbon-hydrogen bond activation; Toluene; Rhodium(III); Porphyrin.

INTRODUCTION

Recent interests in carbon-hydrogen bond activation (CHA) by transition metal complexes (M) both in stoichiometric and catalytic applications in organic synthesis have ushered intensive research for functional group compatible, mild and selective processes.[1] Late transition metal complexes are more appealing than their early transition metal counterparts due to broader functional group compatibilities.[2] Often, the rates and yields of these CHA reactions are enhanced significantly in the presence of bases, which can play the role in abstracting the acidic hydrogens of the C-H bonds, especially upon coordination to the metal centers.[3]

We have been interested in the chemistries of alkyl,[4] aryl,[5] benzylic[6] and aldehydic[7] carbon-hydrogen bond activation, and silicon-hydrogen activation[8] with both rhodium(III) and iridium(III) porphyrin chlorides complexes.[9] These types of metalloporphyrins are unique due to the apparent steric difficulty of cis-coordination of a substrate to a five coordinate metalloporphyrin complex in the course of activation and the relative electronic inaccessibility of an oxidative addition intermediate that requires a formal M(V) oxidation state. We have also recently discovered that a nucleophilic base can accelerate the rate and enhance the selectivities of these types of bond activation reactions.[4,6,9b] To identify the synthetic scopes and gain further mechanistic understanding of the base-promoted benzylic CHA by rhodium(III) porphyrin chloride, we have undertaken an extensive study and now report the results.

Scheme I Base-Promoted Benzylic CHA

$$\mathrm{M} + \mathrm{H{-}Bn} \xrightarrow{\text{Base}} \mathrm{M{-}Bn}$$

RESULTS AND DISCUSSION

Temperature Dependent CHA Selectivity

Initially, rhodium(III) tetrakis(4-tolyl)porphyrin chloride (Rh(ttp)Cl) was found to react with toluene in solvent-free conditions at 120 °C in 3 days to give a mixture of 3-tolyl and 4-tolyl as well as benzylic rhodium porphyrin complexes (Table 1, entry 2). Prolonged heating at 120 °C for 7 days produced similar product yields and poor selectivities (Table 1, entry 3). The absence of Rh(ttp)(2-tolyl) is likely due to the steric hindrance of an adjacent methyl group of toluene. To our surprise, the reaction at 200 °C generated only Rh(ttp)Bn in 65% yield (Table 1, entry 4).

Special Issue Dedicated to Prof. Yu Wang in Honor of Her 70th Birthday

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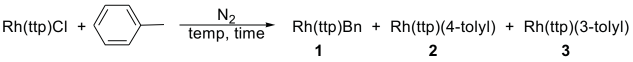
Table 1. Temperature Effect on CHA of Toluene with Rh(ttp)Cl

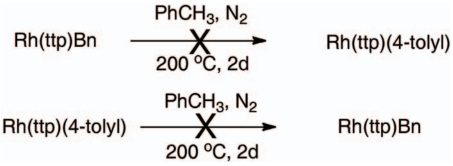


Entry	Temp /°C	Time /d	Yield /%[a]		
			1	2	3
1	60	3	No rxn		
2	120	3	26	26	13
3	120	7	28	14	14
4	200	1	65		

[a] Estimated from the integration of the reaction mixture after chromatography by ^{1}H NMR spectroscopy.

The selective formation of the apparently less stable Rh(ttp)Bn was favored at high temperature, as Rh-Ar has a stronger Rh-C bond.[10] Since both Rh(ttp)(4-tolyl) and Rh(ttp)Bn were stable in toluene at an elevated temperature of 200 °C for 2 days without any interconversion (Scheme II), BnCHA and ArCHA products are not formed from consecutive, but from concurrent pathways. The lack of interconversion between Rh(ttp)(4-tolyl) and Rh(ttp)Bn likely originates from the absence of a kinetically accessible cis-coordination site and the steric hindrance of these large benzyl and tolyl groups. Since Rh(ttp)Cl did not react at 60 °C in 3 days (Table1, entry 1), the K_2CO_3-promoted BnCHA required at least 120 °C in 30 min.

Scheme II No Interconversion of Rh Complexes



Base-Promoting Effect

With the reported base-promoted CHA by transition metal complexes,[3] we then explored the effect of added ligands and bases. Coordinating ligands, such as Ph_3P and pyridine, did not produce any CHA products due to formation of coordination complexes that shut down the CHA reaction completely. Indeed, (Ph_3P)Rh(ttp)Cl was isolated in 52% yield. The non-coordinating base 2,6-di-*tert*-butylpyridine (30 equiv) proved to be a somewhat effective but non selective promoter, as Rh(ttp)Bn and Rh(ttp)(4-tolyl) were obtained in 46 and 18% yields, respectively, after 3 days at 120 °C.

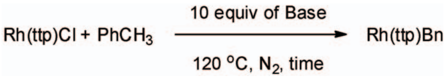
Further enhancements in selectivity, rate, and yields in BnCHA were observed with the addition of other inorganic nucleophilic bases (Table 2). Stronger bases such NaOH, KOH, K_3PO_4, K_2CO_3, NaOPh and $KHCO_3$ (10 equiv) were in general very effective promoter to yield Rh(ttp)Bn selectively in high yields in 30 to 600 minutes with K_2CO_3 being the most effective one both in terms of rate enhancement and highest product yield (Table 2, entris 1-7). Weaker bases such as NaOAc, KOAc and $(CH_3)_3CCO_2Na$ were also effective but required longer reaction times (Table 2, entries 8 to 10). However, when $NaHSO_4$ was added, only Rh(ttp)(4-tolyl) and Rh(ttp)(3-tolyl) was formed (Table 2, entry 11). The absence of Rh(ttp)Bn is likely due to the non-nucleophilic nature of HSO_4^- to stabilize the more cationic Rh(ttp)HSO_4 that favors an electrophilic aromatic substitution. Indeed, a cationic Rh porphyrin, such as Rh(oep)ClO_4 is reported to undergo S_EAr with arenes.[11]

Besides the basicity, the size of cation and possibly the apparent solubility of bases also affect the rates of BnCHA. The rate of BnCHA was slower when NaOH was added compared with KOH (Table 2, entries 1 and 2), similar to the reactivity of NaOAc versus KOAc (Table 2, entries 8 and 9). Also, Na_2CO_3 was observed to be less soluble in the reaction mixture compared with K_2CO_3. Therefore K_2CO_3 was found to be the optimal base.

K_2CO_3 Loading

The loading of K_2CO_3 was further optimized. Both 1 and 5 equivalents of K_2CO_3 required extended reaction time of more than 4 hours and produced lower yields of

Table 2. Base Effect on BnCHA



Entry	Base	pKa of conjugated acid[12]	Time /min	Yields /%
1	NaOH	13.8	45	79
2	KOH	13.5	60	94
3	K_3PO_4	12.3	60	77
4	Na_2CO_3	10.3	600	79
5	K_2CO_3	10.3	30	97
6	NaOPh	9.90	60	93
7	$KHCO_3$	6.35	600	94
8	NaOAc	4.76	60	84
9	KOAc	4.76	45	84
10	$(CH_3)_3CCOO^-Na^+$	4.76	60	74
11	$NaHSO_4$	1.99	480	42[a]

[a] as a mixture of Rh(ttp)(4-tolyl) (**2**) and Rh(ttp)(3-tolyl) (**3**).

Rh(ttp)Bn (Table 3, entries 1 and 2). 10 to 100 equivalents of K_2CO_3 were equally efficient. A lower loading of K_2CO_3 gave a slower reaction with a lower yield and a higher loading (up to 100 equivalents) resulted in little improved reaction efficiency. Therefore, 10 equivalents of K_2CO_3 were therefore employed for further studies.

Table 3. Loading Effect of K_2CO_3

$$\text{Rh(ttp)Cl} + \text{BnH} \xrightarrow[\text{K}_2\text{CO}_3\text{, time}]{120\ ^\circ\text{C, N}_2} \text{Rh(ttp)Bn}$$

Entry	Equiv of K_2CO_3	Time /min	Yields /%
1	1	840	69
2	5	240	77
3	10	30	97
4	20	30	97
5	100	30	96

Scope of Substrates

To examine the substrate scope of toluene, the optimized base-promoted reaction conditions were applied to various substituted toluenes. Generally, high yields of rhodium porphyrin benzyls were obtained in the presence of K_2CO_3 or NaOH (Table 4). The basic reaction conditions were also more functional group compatible (Columns A and B versus C). Even the coordinating CN and redox active NO_2 groups were amenable (Table 4, columns A, entries 7 and 8; 12 and 13). We do not understand the very slow reaction and lower yield observed for 4-fluorotoluene (Table 4, entry 6) presumably some C-F cleavage might have occurred.[13] More sterically hindered toluenes (*ortho* and *meta* positions) were also applicable in the base-promoted BnCHA but required longer times (Table 4, entries 10 and 11). Slightly lower yields of Rh(ttp)FG-Bn were obtained for the ortho-substituted toluenes (Table 4, entries 11-13) and were attributed to steric hindrance.

The stronger base, NaOH, produced lower product yields in most substrates with similar rates compared to that of K_2CO_3. Since Rh(ttp)Bn was found to be stable towards KOH in toluene or benzene at 120 °C for 1 day, we reasoned that some of the intermediates generated might be base-labile to undergo decomposition. Rh(ttp)H is a possible intermediate and can be converted into Rh(ttp)$^-$ by proton abstraction in the presence of a stronger base and then likely undergoes thermal decomposition. This aspect will be discussed in details in the mechanistic studies section.

Porphyrin Effect

Both electron-rich and -deficient rhodium porphyrin chlorides were examined (Table 5). The reactivity follows the order of electron-deficient rhodium porphyrin chlorides: bocp > ttp > tdbpp. (bocp = 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(*p*-*tert*-butylphenyl)porphyrinato dianion, tdbpp = 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato dianon). The product yields of Rh(por)Bn were all high with a slightly lower yield for

Table 4. Base Effect of Solvent-free Benzylic CHA of Toluenes

$$\text{Rh(ttp)Cl} + \text{4-FG-BnH} \xrightarrow[120\ ^\circ\text{C, N}_2\text{, time}]{\text{10 equiv of Base}} \text{Rh(ttp)(4-FG-Bn)}$$

Entry	FG	A (K_2CO_3)		B (NaOH)		C (No base)	
		Time/min	Yield (%)	Time/min	Yield (%)	Time/d	Yield (%)
1	4-OMe	30	**1a** (92)	30	**1a** (98)	2	**1a** (78)
2	4-^{t}Bu	45	**1b** (98)	45	**1b** (82)	2	**1b** (84)
3	4-Me	45	**1c** (90)	45	**1c** (77)		
4	H	30	**1** (97)	45	**1** (79)	3	**1** (26)[a]
5	4-F	240	**1d** (64)	240	**1d** (60)	3	**1d** (72)
6	4-CHO	15	**1e** (39)[b]				
7	4-CN	60	**1f** (83)			3	No rxn
8	4-NO_2	30	**1g** (98)	45	**1g** (75)	1	Decompo.
9	3,5-Me_2	60	**1h** (67)	45	**1h** (55)	3	**1h** (35)
10	3-Me	120	**1i** (81)				
11	2-Me	90	**1j** (73)				
12	2-CN	90	**1k** (81)				
13	2-NO_2	90	**1l** (84)				

[a] **2** and **3** were also obtained in 26% and 13% respectively.

[b] **1c** was also obtained in 31%.

Table 5. Porphyrin Effect on Benzylic CHA

$$\mathrm{Rh(por)Cl} + \mathrm{BnH} \xrightarrow[\mathrm{NaOH\ (10\ equiv)}]{120\ ^{o}\mathrm{C},\ N_2,\ \mathrm{time}} \mathrm{Rh(por)Bn}$$

Entry	Por	Time /min	Yields /%
1	tdbpp	120	89
2	ttp	45	94
3	bocp	15	86

Rh(bocp)Bn. The faster rate for Rh(bocp)Cl might be due to the faster ligand substitution with NaOH. (See mechanistic studies below.)

In Benzene Solvent

The reactions were also successful in benzene solvent with 10 equivalents of various 4-substituted toluenes used but with slightly lower efficiency. (Table 6) Longer reaction times of 90 minutes were required and slightly lower product yields were obtained.

X-ray Structures

The collection and processing parameters of single-crystal data for complexes **1h-k** are given in the Supporting Information (CCDC 923670-923673). The X-ray structure of **1b** and **1d** have been reported previously.[18] Table 7 lists selected bond lengths and angles. The bond lengths of Rh-C_α and the bond angles of Rh-C_α-C_β are similar to the reported bond lengths of Rh-C_α and bond angles of Rh-C_α-C_β in Rh(ttp)Bn (2.064 Å and 115.8°)[7] and the Rh-C_α-C_β angles are not affected by the substituents (Table 7). As a representative, Figure 1 shows the molecular structure of Rh(ttp)(3,5-Me_2-Bn) (**1h**) (30% thermal ellipsoids).

Mechanistic Studies

No Base. In the absence of base, 3- and 4-tolyl Rh(ttp) complexes, typical of S_EAr sustitution products, formed and this suggests the generation of a cationic $Rh(ttp)^+$ likely in the form of ion pair as an intermediate for the ArCHA reactions. Since these aryl complexes do not convert into the benzyl complex even at 200 °C, independent parallel pathways exist for the aryl and benzyl CHA reactions. We suggest that Rh(ttp)H and $Rh_2(ttp)_2$ are viable intermediates in the BnCHA as they are known intermediate in CHA.[4,14] Indeed independent experiments of Rh(ttp)H and $Rh_2(ttp)_2$ with toluene, both gave Rh(ttp)Bn in high yields of 68% and 70%, respectively in 1 h and support their possible intermediacy (Scheme III).

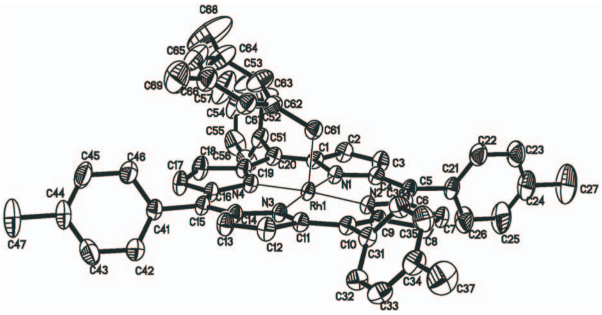


Fig. 1. ORTEP drawing of Rh(ttp)(3,5-Me_2-Bn) (1h) (30% probability displacement ellipsoids).

Table 6. Benzylic CHA of Toluenes in Benzene Solvent

$$\mathrm{Rh(ttp)Cl} + \mathrm{4\text{-}FG\text{-}BnH} \xrightarrow[K_2CO_3\ \mathrm{(10\ equiv)}]{120\ ^{o}\mathrm{C},\ \mathrm{PhH},\ N_2,\ \mathrm{time}} \mathrm{Rh(ttp)(4\text{-}FG\text{-}Bn)}$$

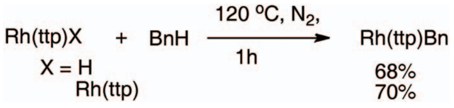
Entry	FG	Time /h	Yields[a] /%
1	4-OMe	1.5	76
2	4-^{t}Bu	2	65
3	4-Me	2	68
4	H	1.5	75
5	4-F	7	55
6	4-CN	2	68
7	4-NO_2	1.5	70
8	3,5-Me_2	2.5	54
9	3-Me	5	64
10	2-Me	5	64
11	2-CN	4	77
12	2-NO_2	4	71

[a] isolated yields.

Table 7. Selected Bond Lengths and Bond Angles of Rh(ttp)Bn Complexes

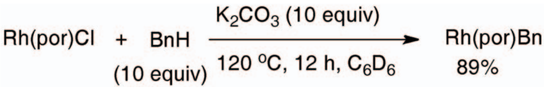
Entry	FG	Rh-C_α length /Å	Rh-C_α-C_β bond angle /deg
1	4-^{t}Bu, **1b**	2.079(6)	116.3(4)
2	4-F, **1d**	2.072(5)	115.8(3)
3	3,5-Me_2, **1h**	2.057(4)	115.4(3)
4	3-Me, **1i**	2.056(9)	116.2(6)
5	2-Me, **1j**	2.066(8)	118.1(6)
6	2-CN, **1k**	2.053(6)	115.1(4)

Scheme III Benzylic CHA with Rh^{II} and $Rh^{III}H$



Base Enhancement. To gain some insight into the high yielding base-promoted BnCHA, the reaction of toluene (10 equiv) with Rh(ttp)Cl in benzene-d_6 with 10 equiv of K_2CO_3 in a sealed NMR tube was monitored in the course of 12 h by ^1H NMR spectroscopy (For reaction progess, see Figure S7 and Table S2). Initially, Rh(ttp)Cl slowly disappeared with the formation of $Rh_2(ttp)_2$ and then Rh(ttp)H which are both slowly converted to Rh(ttp)Bn. $Rh_2(ttp)_2$ and Rh(ttp)H are therefore likely intermediates.[15] In fact, $Rh_2(ttp)_2$ can exist in small amount with Rh(ttp)H in benzene or can equilibrate with Rh(ttp)H in benzene under an atmosphere of H_2.[14,16] Indeed, Rh(ttp)H at 120 °C after 2 hours gave about 2% of $Rh_2(ttp)_2$ (Table 8, entries 1 and 2).

Scheme IV Benzylic CHA in benzene



$$\underset{}{\mathrm{Rh(por)Cl}} + \underset{(10\ \mathrm{equiv})}{\mathrm{BnH}} \xrightarrow[120\ ^{\circ}\mathrm{C},\ 12\ \mathrm{h},\ C_6D_6]{K_2CO_3\ (10\ \mathrm{equiv})} \underset{89\%}{\mathrm{Rh(por)Bn}}$$

The base-promoted conversion of Rh(ttp)H into $Rh_2(ttp)_2$ was observed as well. K_2CO_3 in benzene promoted the conversion of Rh(ttp)H into $Rh_2(ttp)_2$ in 6% very slowly at 120 °C after 1 hour (Table 8, entries 3 and 4). Therefore, Rh(ttp)H undergoes slow conversion into and likely in equilibration with $Rh_2(ttp)_2$ under both thermal and basic reaction conditions as the hydrogenation of $Rh_2(ttp)_2$ into Rh(ttp)H is known.[17] We do not understand the detailed mechanism of this base-promoted dehydrogenation of Rh(ttp)H at this stage and will be a subject of further study.

Since independent reactions of Rh(ttp)H and $Rh_2(ttp)_2$ with toluene with K_2CO_3 added gave Rh(ttp)Bn in high yields of 68% and 70%, respectively in 1 h (Scheme III). Both $Rh_2(ttp)_2$ and Rh(ttp)H are the viable intermediates. As Rh(ttp)H and $Rh_2(ttp)_2$ are shown to equilibrate (Table 8), we have to examine whether only one or both activate(s) the C-H bond by their relative reactivity.

The relative reactivities of $Rh_2(ttp)_2$, Rh(ttp)H and Rh(ttp)Cl in BnCHA in the presence of K_2CO_3 (10 equiv) were measured by the amount of Rh(ttp)Bn formed in the first 15 minutes of the reaction (Table 9). The relative reactivities are about: 12 ($Rh_2(ttp)_2$) : 1 (Rh(ttp)H) : 1 (Rh(ttp)Cl). $Rh_2(ttp)_2$ is the most reactive species (Table 9). As the reactivity difference is not very large, we still could not conclude that both are direct intermediates. We turned our focus to the magnitude of kinetic isotope effect to probe the nature of the transition states in the reactions with Rh(ttp)Cl, Rh(ttp)H and $Rh_2(ttp)_2$.

Isotope Effect

The observed isotope effects $(k_H/k_D)_{obs}$ for the BnCHA of toluene with Rh(ttp)Cl were measured by competition experiments with an equimolar mixture of solvent toluene and toluene-d_8. At 120 °C, without any base, $(k_H/k_D)_{obs}$ were measured to be 6.6 for ArCHA (indistinguishable between para and meta) and 4.1 for BnCHA. The isotope ratios were calculated from the integration of the benzylic and aryl protons. With K_2CO_3 added, $(k_H/k_D)_{obs}$ was found to be 4.0. No benzyl exchange occurred under the same basic conditions in one hour, as Rh(ttp)Bn did not react with toluene-d_8 to give any Rh(ttp)Bn-d_7. These values suggested that the CHA steps were involved in or prior to the rate-determining step in the reactions. Furthermore, when NaOH was added, $(k_H/k_D)_{obs}$ was found to be 4.3. Both the $(k_H/k_D)_{obs}$ values in the K_2CO_3 and NaOH experiments were similar. Therefore, the nature of a base has no significant effect on the nature of transition state in the BnCHA steps.

Table 8. K_2CO_3-Promoted Conversion of Rh(ttp)H to $Rh_2(ttp)_2$

$$2\mathrm{Rh(ttp)H} \xrightarrow[120\ ^{\circ}\mathrm{C},\ C_6D_6]{K_2CO_3} \mathrm{Rh_2(ttp)_2}$$

Entry	K_2CO_3	Time /h	Yield of Rh(ttp)H /%	Yield of $Rh_2(ttp)_2$ /%	Total yields /%
1	---	0	100	nil	100
2	---	2	97	2	99
3	10 equiv	0	100	nil	100
4	10 equiv	1	81	6	87

Table 9. Reactivity on Benzylic CHA of Rhodium Porphyrin Complexes

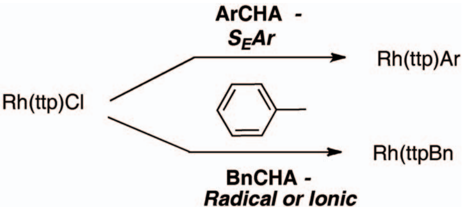
$$\mathrm{Rh(ttp)X} + \mathrm{BnH} \xrightarrow[120\ ^{\circ}\mathrm{C},\ 15\ \mathrm{min},\ C_6D_6]{K_2CO_3\ (10\ \mathrm{equiv})} \mathrm{Rh(ttp)Bn}$$

Entry	X	[Rh(ttp)X] /M	$[PhCH_3]$ /M	[Rh(ttp)Bn] : [Rh(ttp)X] at 15 min
1	Cl	0.01	0.1	0.18
2	H	0.01	0.1	0.12
3	Rh(ttp)	0.005	0.1	2.10

ArCHA

With the help of the KIE and the formation of both Rh(ttp)Ar (Ar = 3- and 4-tolyl), we reason that the ArCHA operates by an S_EAr mechanism (Scheme V). It is possible that initially Rh(ttp)Cl ionizes into a $Rh(ttp)^+$ which is then coordinated by the π-orbitals of toluene. Subsequently, the ArCHA occurs with a rate-limiting aromatic C-H cleavage step. The BnCHA, however, goes through different mecha-

Scheme V Aromatic and Benzylic CHA of Toluene with Rh(ttp)Cl

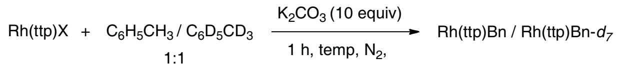


nisms either via coordination of the benzylic C-H to $Rh(ttp)^+$ followed by subsequent Cl^- deprotonation to yield Rh(ttp)Bn via an ionic pathway as we previously proposed.[18] Alternatively, some extent of ligand substitution with water to yield Rh(ttp)OH can happen to yield $Rh_2(ttp)_2$ and Rh(ttp)H. (See discussion below.)

Temperature Effect on KIE

We focused our effort on the nature of the transition states of K_2CO_3-promoted BnCHA as the reactions are much more selective and broader in scope. The values of temperature dependent KIE from 120 to 200 ^{0}C obtained from the BnCHA of toluene with Rh(ttp)Cl, $Rh_2(ttp)_2$, and Rh(ttp)H in the presence of K_2CO_3 (10 equiv) are very revealing (Table 10). For Rh(ttp)Cl and Rh(ttp)H (Table 10, entries 1-4 and 7-8), the KIEs unusually increased with temperature and is significant with a fairly large change in magnitude. For $Rh_2(ttp)_2$, the opposite trend and a large difference were also observed. Both a change of mechanism or a change of major reaction pathway for parallel reactions for three rhodium porphyrin complexes can account the trends. We argue for the latter proposal since it is more consistent with the equilibrating mixture of Rh(ttp)H and $Rh_2(ttp)_2$ as possible intermediates.

Table 10. Temperature Dependent Kinetic Isotope Effect of K_2CO_3-promoted BnCHA



$$\underset{}{Rh(ttp)X} + \underset{1:1}{C_6H_5CH_3 / C_6D_5CD_3} \xrightarrow[\text{1 h, temp, } N_2,]{K_2CO_3\text{ (10 equiv)}} Rh(ttp)Bn / Rh(ttp)Bn\text{-}d_7$$

Entry	Rh(ttp)X	Temp /^{o}C	$(k_H/k_D)_{obs}$[a]	Total yields /%
1	Rh(ttp)Cl	120	4.0 ± 0.1[b]	91%
2	Rh(ttp)Cl	150	4.5 ± 0.1	88%
3	Rh(ttp)Cl	180	4.8 ± 0.1	88%
4	Rh(ttp)Cl	200	5.4 ± 0.1	85%
5	$Rh_2(ttp)_2$	120	6.7 ± 0.2[c]	74%
6	$Rh_2(ttp)_2$	200	5.8 ± 0.1	68%
7	Rh(ttp)H	120	4.1 ± 0.1	71%
8	Rh(ttp)H	200	5.3 ± 0.1	68%

[a] Determined by ^{1}H NMR. [b] 4.0 from mass spectrometry.
[c] 6.7 from mass spectrometry.

Proposed Mechanism

Based on the above findings and our latest understandings of rhodium porphyrin chemistries, Scheme VI illustrates the reaction pathways that is different from our previous one.[18] Initially, Rh(ttp)Cl undergoes a ligand substitution with KOH or K_2CO_3 to give $Rh(ttp)CO_3K$ (or Rh(ttp)OK after decarboxylation or Rh(ttp)OH after protonation of Rh(ttp)OK with residual water in solvent or reagent), which is then reduced to yield the metal-metal bonded dimer of Rh^{II}_2 $(ttp)_2$ as we have reported earlier. Rh^{II}_2 $(ttp)_2$ having a fairly weak Rh-Rh bond of about 16 kcal/mol, can dissociate into the $Rh^{II}(ttp)$ monomer as a metalloradical in solution.

Rh^{II}(por) Bimetalloradical Pathway. $Rh^{II}_2(ttp)_2$ or more correctly $Rh^{II}(ttp)$ then undergoes a bimetalloradical BnCHA with toluene to give Rh(ttp)Bn and Rh(ttp)H. Both $Rh^{II}_2(ttp)_2$ and Rh(ttp)H now exist in solution. Rh(ttp)H can undergo thermal or base-promoted dehydrogenation to yield some $Rh^{II}_2(ttp)_2$. The concentration of $Rh^{II}_2(ttp)_2$ depends on temperature and base used. A stronger base may competitive depronate the weakly acidic Rh(ttp)H to form $Rh(ttp)^-$ which precipitates in solution and undergoes thermal decomposition. We rationalize that two parallel BnCHA reactions[19] with $Rh_2(ttp)_2$ and Rh(ttp)H exist and can account the increasing KIEs with temperature. The KIE value of 6.7 for $Rh_2(ttp)_2$ at 120 ^{o}C (Table 10, entry 5) supports the bimetalloradical activation with $Rh^{II}(ttp)$ having a linear transition state (TS) in the cleavage of the benzylic C-H bond (Scheme V, Figure 2a). Such bimetalloradical activation mechanism of toluene by rhodium(II) porphyrin has been well-established by Wayland and coworkers to have a KIE value of 6.5 at 80 ^{o}C.[17] The lower KIE value of 5.6 at 200 ^{o}C is attributed to the Arrhenius behavior with a smaller energy level difference of ground and transition states at a higher temperature (Table 10, entry 6).[20]

Rh^{III}(por)H Sigma Bond Metathesis. For the BnCHA with Rh(ttp)H at 120 ^{o}C, the observed KIE value of 4.1 (Table 3, entry 7), is consistent with a bent TS[20] associated with a sigma bond metathesis process (Scheme VI, Figure 2b) since the proposed TS of the reaction of Rh(ttp)Me with toluene to give methane and Rh(ttp)Bn is elucidated to be a bent one based on the observed KIE of 2.7 at 150 ^{o}C. The slightly higher KIE at 120 ^{o}C can be accounted by the parallel metalloradical pathway as a small

Scheme VI Parallel Base-Promoted BnCHA of Toluene

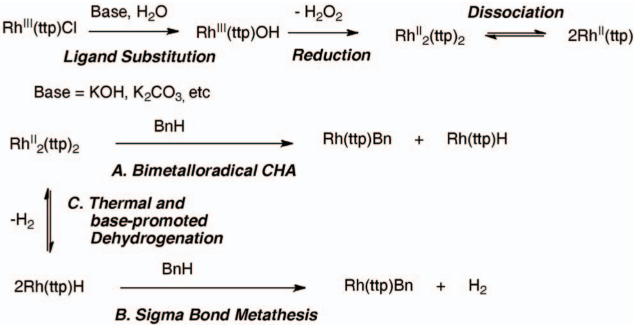


Table 11. Competition Experiments of Electronic Effect on BnCHA

$$\underset{}{\text{Rh(ttp)Cl}} + \underset{1:\ 1}{\text{4-FG-BnH / BnH}} \xrightarrow[K_2CO_3\ (10\ \text{equiv})]{120\ ^{o}C,\ PhH,\ N_2,\ 1h} \text{Rh(ttp)(4-FG-Bn) / Rh(ttp)Bn}$$

Entry	*p*-FG	σ_p[a]	log *k*(H_{FG}/H_H)
1	OMe	-0.27	0.60
2	^{t}Bu	-0.15	-0.55
3	F	1.5	0.39
4	CHO	0.47	0.66
5	CN	0.71	0.81
6	NO_2	0.81	0.87

[a] σ_p: para-substituent constant.

amount of $Rh^{II}{}_2(ttp)_2$ is present. At 200 °C with K_2CO_3 added, a much higher KIE of 5.3 was measured (Table 3, entry 8) and can be reasoned with a larger contribution of parallel bimetalloradical CHA with a higher concentration of $Rh_2(ttp)_2$.

Hammett Studies

In order to gain some mechanistic understandings of the toluene electronic effect of CHA, the Hammett plot was constructed from a series of competition experiments using an equimolar mixture of 4-substituted (FG) toluene and toluene in reacting with Rh(ttp)Cl and K_2CO_3 (10 equiv) at 120 °C in 1 h in benzene (Table 11). The ratios were kinetic ones, as no Rh(ttp)(4-F-Bn) **1d** was formed when Rh(ttp)Bn **1** was reacted with 4-fluorotoluene in benzene with 10 equiv of K_2CO_3 at 120 °C for 1 h. Figure 3 shows that a nonlinear free energy relationship in the Hammett plot using the substituent constant σ_p.[21] As the para substituent became more electron donating, the rate decreased (NO_2 to CN, CHO, F and ^{t}Bu). The more electron-rich substituent (OMe), however, yielded a higher rate resulting in a rate inversion point. We interpret that the BnCHA reaction does not operate in a single step that depends on the substituent electronic effect. Rather, both Rh(ttp)H and $Rh_2(ttp)_2$ exert different electronic influence on the parallel activation reactions.

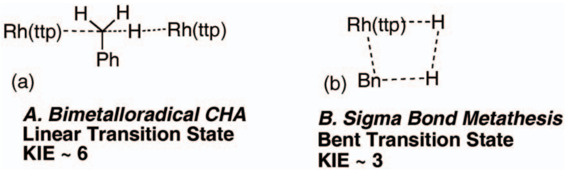


Fig. 2. Transition State Structures for Benzylic CHA.

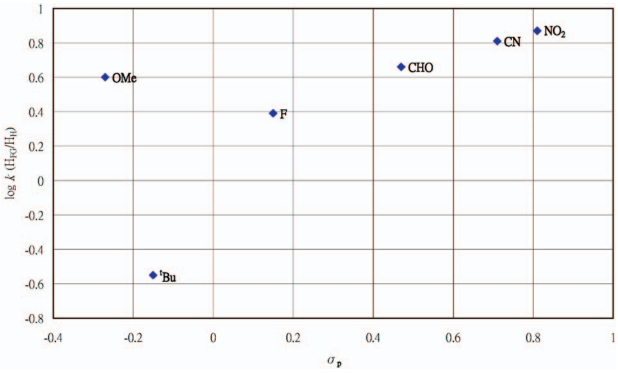


Fig. 3. Hammett plot of BnCHA of Toluenes with Rh(ttp)Cl.

CONCLUSIONS

In summary, nucleophilic base such as K_2CO_3 was found to enhance the BnCHA of toluenes both in rate, functional comaptiblity and yield. The enhancements are due to the more facile ligand substituion of Rh(ttp)Cl with hydroxide to yield Rh(ttp)OH and then Rh^{II}(ttp). Rh^{II}(ttp) activate the benzylic C-H bonds of toluenes in a bimetalloradical mechanism to give Rh(ttp)Bns and Rh(ttp)H. Rh(ttp)H can also undergo a slower sigma bond metathesis type BnCHA. The thermal and/or base-promoted dehydrogenation of Rh(ttp)H back to a small amount of $Rh^{II}{}_2(ttp)_2$ can rationalize the equilibrating mixture of Rh^{II} and Rh^{III}H and the temperature dependent KIEs with the unusual increasing KIEs with temperature for Rh^{III}H.

EXPERIMENTAL

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Benzene and toluene were distilled from sodium. Thin layer chromatography was performed on pre-coated silica gel 60 F_{254} plates.

Silica gel (Merck, 70-230 mesh) were used for column chromatography.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 at 300 MHz and 75 MHz respectively. Chemical Shifts were referenced with the residual solvent protons in C_6D_6 (δ = 7.15 ppm), $CDCl_3$ (δ = 7.26 ppm) or tetramethylsilane (δ = 0.00 ppm) in ^{1}H NMR spectra and $CDCl_3$ (δ = 77.16 ppm) in ^{13}C NMR spectra as the internal standards. Chemical shifts (δ) were reported as part per million (ppm) in (δ) scale downfield from TMS. Coupling constants (J) were reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a ThermoFinnigan MAT 95 XL mass spectrometer. Fast atom bombardment spectra were performed with 3-nitrobenzyl alcohol (NBA) as the matrix. All samples for combustion analyses were recrystallized from CH_2Cl_2/MeOH and vacuum dried at room temperature for at least 2 days before submission.

The synthesis of Rh(ttp)Cl, Rh(ttp)H and $Rh_2(ttp)_2$ follows a literature method.[22,23]

Reaction of Rh(ttp)Cl with Toluene. Rh(ttp)Cl (30.0 mg, 0.037 mmol) and toluene (1.5 mL) were degassed in a Telfon-stoppered tube for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 3 d with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). Three CHA products **1**, **2** and **3** with the same R_f = 0.55 (hexane/CH_2Cl_2 = 1:1) were collected in one portion (24.9 mg) and the ratio was determined by ^{1}H NMR analysis from the integration of the benzylic and aromatic protons as Rh(ttp)Bn (**1**)[13] (26%), Rh(ttp)(4-tolyl) (**2**) (26%), and Rh(ttp)(3-tolyl) (**3**) (13%). The complexes **2** and **3** were further synthesized independently.[24]

Synthesis of (5,10,15,20-tetratolylporphyrinato)(4-tolyl)rhodium(III), [Rh(ttp)(4-tolyl)] (2). Rh(ttp)Cl (20.0 mg, 0.025 mmol) was mixed with (4-tolylmagnesium bromide (0.25 mmol) in THF (1.5 mL) at 120 °C under N_2 for 30 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-tolyl) (**2**) (20.0 mg, 0.023 mmol, 93%) as a red solid. R_f = 0.55 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.17 (d, 2 H, J = 6.9 Hz), 1.08 (s, 3 H), 2.69 (s, 12 H), 4.61 (d, 2 H, J = 8.4 Hz), 7.52 (t, 8 H, J = 6.0 Hz), 8.01 (d, 4 H, J = 8.7 Hz), 8.05 (d, 4H, J = 8.6 Hz), 8.75 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.15, 21.68, 120.79 (d, $^1J_{Rh-C}$ = 37.6 Hz), 122.98, 125.06, 127.13, 127.54, 128.36, 129.52, 131.75, 133.94, 134.30, 137.38, 139.27, 143.20. HRMS (FABMS): Calcd. for $(C_{55}H_{43}N_4Rh)^+$: m/z 862.2537. Found: m/z 862.2578. Anal Calcd. for $C_{55}H_{43}N_4Rh$: C, 76.56; H, 5.02; N, 6.49. Found C, 76.09; H, 5.06; N, 6.45.

Synthsis of (5,10,15,20-tetratolylporphyrinato)(3-tolyl)rhodium(III), [Rh(ttp)(3-tolyl)] (3). Rh(ttp)Cl (20.0 mg, 0.025 mmol) was mixed with (3-tolylmagnesium bromide (0.25 mmol) in THF (1.5 mL) at 120 °C under N_2 for 30 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(3-tolyl) (**3**) (14.0 mg, 0.016 mmol, 65%) as a red solid. R_f = 0.55 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (s, 1 H), 0.13 (d, 1 H, J = 8.0 Hz), 2.69 (s, 12 H), 4.64 (t, 1 H, J = 7.5 Hz), 5.04 (d, 1 H, J = 6.8 Hz), 7.53 (t, 8 H, J = 5.9 Hz), 8.02 (dd, 4 H, J = 2.2, 8.6 Hz), 8.07 (dd, 4 H, J = 2.4, 7.9 Hz), 8.75 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.36, 21.88, 121.60, 123.19, 123.55, 125.93, 127.75, 129.77, 131.92, 132.98, 134.12, 134.51, 137.58, 139.51, 143.41. HRMS (FABMS): Calcd for $(C_{55}H_{43}N_4Rh)^+$: m/z 862.2537. Found: m/z 862.2508.

General Procedure for the Reactions of Rh(ttp)Cl with Toluene and Various Ligands/Bases

Addition of 1 equiv of PPh_3. Rh(ttp)Cl (30.0 mg, 0.037 mmol), PPh_3 (9.7 mg, 0.037 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 3 d with the reaction tube covered by aluminum foil. No CHA product was observed.

Addition of 30 equiv of Pyridine. Rh(ttp)Cl (30.0 mg, 0.037 mmol), pyridine (90 μL, 88.2 mg, 1.12 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 3 d with the reaction tube covered by aluminum foil. No CHA product was observed.

Addition of 30 equiv of 2,6-Di-*tert*-butylpyridine. Rh(ttp)Cl (30.0 mg, 0.037 mmol), 2,6-di-tert-butylpyridine (251 μL, 214.3 mg, 1.12 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 3 d with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (14.8 mg, 0.017 mmol, 46%) and Rh(ttp)(4-tolyl) (**2**) (5.8 mg, 0.0067 mmol, 18%).

Addition of 10 equiv of NaOH. Rh(ttp)Cl (30.0 mg, 0.037 mmol) and 10 equiv of NaOH (14.9 mg, 0.37 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 45 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (25.3 mg, 0.035 mmol, 79%).

Addition of 10 equiv of KOH. Rh(ttp)Cl (30.0 mg, 0.037 mmol), 10 equiv of KOH (20.9 mg, 0.37 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 1 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (30.1 mg, 0.035 mmol, 94%).

Addition of 10 equiv of K_3PO_4. Rh(ttp)Cl (30.0 mg, 0.037 mmol) and 10 equiv of K_3PO_4 (85.6 mg, 0.37 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 1 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (24.7 mg, 0.029 mmol, 77%).

Addition of 10 equiv of Na_2CO_3. Rh(ttp)Cl (20.0 mg, 0.025 mmol) and 10 equiv of Na_2CO_3 (26.5 mg, 0.25 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 10 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (17.0 mg, 0.020 mmol, 79%).

Addition of 10 equiv of K_2CO_3. Rh(ttp)Cl (30.0 mg, 0.037 mmol), 10 equiv of K_2CO_3 (51.1 mg, 0.37 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 30 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (30.2 mg, 0.035 mmol, 94%).

Addition of 10 equiv of NaOPh. Rh(ttp)Cl (20.0 mg, 0.025 mmol), 10 equiv of NaOPh (29 mg, 0.25 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 1 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (20.0 mg, 0.023 mmol, 93%).

Addition of 10 equiv of $KHCO_3$. Rh(ttp)Cl (30.0 mg, 0.037 mmol), $KHCO_3$ (37.2 mg, 0.37 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 1 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (30.1 mg, 0.035 mmol, 77%).

Addition of 10 equiv of NaOAc. Rh(ttp)Cl (20.0 mg, 0.025 mmol), NaOAc (20 mg, 0.25 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 1 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (18.0 mg, 0.021 mmol, 84%).

Addition of 10 equiv of KOAc. Rh(ttp)Cl (20.0 mg, 0.025 mmol), KOAc (25 mg, 0.25 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 45 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (18.0 mg, 0.021 mmol, 84%).

Addition of 10 equiv of $(CH_3)_3CCOO^-Na^+$. Rh(ttp)Cl (20.0 mg, 0.025 mmol), $(CH_3)_3CCOO^-Na^+$ (31 mg, 0.25 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 1 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (16.0 mg, 0.019 mmol, 74%).

Addition of 10 equiv of $NaHSO_4$. Rh(ttp)Cl (20.0 mg, 0.025 mmol), $NaHSO_4$ (30 mg, 0.25 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 8 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give the mixture of Rh(ttp)(4-tolyl) (**2**) and Rh(ttp)(3-tolyl) (**3**) (9.0 mg, 0.010 mmol, 42%).

Addition of 10 equiv of K_2CO_3 in Benzene as Solvent. Rh(ttp)Cl (30.0 mg, 0.037 mmol), 10 equiv of K_2CO_3 (51.1 mg, 0.37 mmol), toluene (40 μL, 3.4 mg, 0.37 mmol) and benzene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 ^oC under N_2 for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Bn (**1**) (24.0 mg, 0.028 mmol, 75%).

General Procedure for the Reactions of Rh(ttp)Cl with Various Substituted Toluenes

Reactions of Rh(ttp)Cl with 4-Methylanisole. Rh(ttp)Cl (30.0 mg, 0.037 mmol), 10 equiv of K_2CO_3 (51.1 mg, 0.37 mmol) were mixed with 4-methylanisole (1.5 mL) at 120 °C under N_2 for 30 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-OMe-Bn) (**1a**) (30.5 mg, 0.034 mmol, 92%) as a red solid. $R_f = 0.35$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.77 (d, 2 H, $J = 3.6$ Hz), 2.70 (s, 12 H), 2.92 (d, 2 H, $J = 8.4$ Hz), 3.43 (s, 3 H), 5.42 (d, 2 H, $J = 8.4$ Hz), 7.54 (d, 8 H, $J = 7.8$ Hz), 7.98 (dd, 4 H, $J = 2.1$, 7.4 Hz), 8.07 (dd, 4 H, $J = 2.4$, 7.2 Hz), 8.67 (s, 8 H). HRMS (FABMS): Calcd for $(C_{56}H_{45}N_4ORh)^+$: *m/z* 892.2643. Found: *m/z* 892.2589. Anal Calcd. for $C_{56}H_{45}N_4ORh$: C, 75.33; H, 5.10; N, 6.27. Found C, 74.87; H, 5.27; N, 5.99.

Addition of 10 equiv of 4-Methylanisole in Benzene as Solvent. Rh(ttp)Cl (30.0 mg, 0.037 mmol), K_2CO_3 (51.1 mg, 0.37 mmol) and 4-methylanisole (47 μL, 45.4 mg, 0.37mmol) and benzene (1.5 mL) were heated at 120 °C with for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-OMe-Bn) (**1a**) (25.2 mg, 0.028 mmol, 76%).

Reactions of Rh(ttp)Cl with 4-*tert*-Butyltoluene. Rh(ttp)Cl (30.0 mg, 0.037 mmol), 10 equiv of K_2CO_3 (51.1 mg, 0.37 mmol) was mixed with 4-*tert*-butyltoluene (1.5 mL) at 120 °C under N_2 for 45 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-^{t}Bu-Bn) (**1b**) (33.4 mg, 0.036 mmol, 98%) as a red solid. $R_f = 0.75$ (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.79 (d, 2 H, $J = 3.6$ Hz), 0.96 (s, 9 H), 2.70 (s, 12 H), 2.93 (d, 2 H, $J = 8.1$ Hz), 5.89 (d, 2 H, $J = 8.4$ Hz), 7.54 (t, 8 H, $J = 6.0$ Hz), 8.04 (t, 8 H, $J = 7.9$ Hz), 8.65 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.00 (d, $^1J_{\text{Rh-C}} = 26.6$ Hz), 21.91, 31.01, 34.48, 122.75, 113.30, 124.47, 127.60, 131.68, 134.13, 134.23, 137.41, 139.76, 143.49, 146.20. HRMS (FABMS): Calcd for $(C_{59}H_{51}N_4Rh)^+$: *m/z* 918.3163. Found: *m/z* 918.3139. Anal Calcd. for $C_{59}H_{51}N_4Rh$: C, 77.11; H, 5.59; N, 6.09. Found C, 76.66; H, 5.65; N, 5.91.

Addition of 10 equiv of 4-*tert*-Butyltoluene in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and 4-*tert*-butyltoluene (43 μL, 37 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-^{t}Bu-Bn) (**1b**) (15.0 mg, 0.016 mmol, 74%).

Reaction of Rh(ttp)Cl with *p*-Xylene. Rh(ttp)Cl (30.0 mg, 0.037 mmol), K_2CO_3 (51.1 mg, 0.37 mmol) and *p*-xylene (1.5 mL) were heated at 120 °C for 45 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-Me-Bn) (**1c**) (29.3 mg, 0.033 mmol, 90%) as a red solid. $R_f = 0.65$ (hexane:CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.77 (d, 2H, $J = 3.6$ Hz), 1.68 (s, 3 H), 2.70 (s, 12 H), 2.87 (d, 2 H, $J = 7.8$ Hz), 5.66 (d, 2 H, $J = 7.8$ Hz), 7.54 (dd, 8 H, $J = 2.1$, 6.8 Hz), 7.96 (dd, 4 H, $J = 2.1$, 7.1 Hz), 8.07 (dd, 4 H, $J = 2.1$, 7.7 Hz), 8.67 (s, 8 H). HRMS (FABMS): Calcd for $(C_{56}H_{45}N_4Rh)^+$: *m/z* 876.2694. Found: *m/z* 876.2667. Anal Calcd. for $C_{56}H_{45}N_4Rh$: C, 76.70; H, 5.17; N, 6.39. Found C, 76.64; H, 5.28; N, 6.06.

Addition of 10 equiv of *p*-Xylene in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and *p*-xylene (31 μL, 26.5 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-Me-Bn) (**1c**) (15.0 mg, 0.017 mmol, 68%).

Reactions of Rh(ttp)Cl with 4-Fluorotoluene. Rh(ttp)Cl (30.0 mg, 0.037 mmol), K_2CO_3 (51.1 mg, 0.37 mmol) and 4-fluorotoluene (1.5 mL) were heated at 120 °C under N_2 for 4 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-F-Bn) (**1d**) (20.9 mg, 0.024 mmol, 64%) as a red solid. $R_f = 0.60$ (hexane/ CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.83 (d, 2 H, $J = 3.9$ Hz), 2.70 (s, 12 H), 2.89 (dd, 2 H, $J = 2.7$, 5.7 Hz,), 5.55 (t, 2 H, $J = 8.7$ Hz), 7.55 (t, 8 H, $J = 6.6$ Hz), 7.98 (dd, 4 H, $J = 2.1$, 8.0 Hz), 8.06 (d, 4 H, $J = 1.2$, 8.0 Hz), 8.68 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.43 (d, $^1J_{\text{Rh-C}} = 27.3$ Hz), 21.89, 112.96 (d, $^1J_{\text{C-F}} = 20.9$ Hz), 122.83, 126.08, 126.18, 127.78, 131.83, 134.16, 134.21, 137.52, 139.61, 143.45. HRMS (FABMS): Calcd for $(C_{55}H_{42}FN_4Rh)^+$: *m/z* 880.2443. Found: *m/z* 880.2426. Anal Calcd. for $C_{55}H_{42}FN_4Rh$: C, 74.61; H, 5.07; N, 6.39. Found C, 74.99; H, 4.81; N, 6.36.

Addition of 10 equiv of 4-Fluorotoluene in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25

mmol) and 4-fluorotoluene (28 μL, 28 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-F-Bn) (**1d**) (12.0 mg, 0.014 mmol, 55%).

Reactions of Rh(ttp)Cl with *p*-Tolualdehyde. Rh(ttp)Cl (30.0 mg, 0.037 mmol), 10 equiv of K_2CO_3 (51.1 mg, 0.37 mmol) were mixed with *p*-tolualdehyde (1.5 mL) at 120 °C under N_2 for 15 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-CHO-Bn) (**1e**)[7] (12.9 mg, 0.014 mmol, 39%) as a red solid. $R_f = 0.30$ (hexane/CH_2Cl_2 = 1:1). ^1H NMR ($CDCl_3$, 300 MHz) δ -3.81 (d, 2 H, $J = 3.9$ Hz), 2.70 (s, 12 H), 2.97 (d, 2 H, $J = 7.5$ Hz), 6.35 (d, 2 H, $J = 7.2$ Hz), 7.55 (d, 8 H, $J = 6.3$ Hz), 7.95 (d, 4 H, $J = 7.8$ Hz), 8.05 (d, 4 H, $J = 7.2$ Hz), 8.70 (s, 8 H), 9.43 (s, 1 H). Rh(ttp)(4-Me-Bn) (**1c**) (10.1 mg, 0.012 mmol, 31%) was also obtained.

Addition of 10 equiv of *p*-Tolualdehyde in Benzene as Solvent. Rh(ttp)Cl (30.0 mg, 0.037 mmol), K_2CO_3 (51.1 mg, 0.37 mmol) and *p*-tolualdehyde (43 μL, 44.7 mg, 0.37mmol) and benzene (1.5 mL) were heated at 120 °C with for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-CHO-Bn) (**1e**) (27.0 mg, 0.028 mmol, 75%) and Rh(ttp)(4-Me-Bn) (**1c**) (only observed in NMR of the crude reaction mixture).

Reactions of Rh(ttp)Cl with 4-Methylbenzonitrile. Rh(ttp)Cl (30.0 mg, 0.037 mmol), K_2CO_3 (51.1 mg, 0.37 mmol) and 4-methylbenzonitrile (1.5 mL) were heated at 120 °C for 1 h. with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-CN-Bn) (**1f**) (27.4 mg, 0.031 mmol, 83%) as a red solid. $R_f = 0.30$ (hexane/ CH_2Cl_2 = 1:1). ^1H NMR ($CDCl_3$, 300 MHz) δ -3.87 (d, 2 H, $J = 3.9$ Hz), 2.71 (s, 12 H), 2.90 (d, 2 H, $J = 8.4$ Hz), 6.11 (d, 2 H, $J = 8.1$ Hz), 7.57 (t, 8 H, $J = 8.4$ Hz), 7.93 (dd, 4 H, $J = 1.5$, 8.3 Hz), 8.03 (dd, 4 H, $J = 1.2$, 7.7 Hz), 8.90 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.27 (d, $^1J_{Rh\text{-}C} = 28.0$ Hz), 21.89, 106.25, 120.01, 122.98, 124.92, 127.89, 129.69, 132.04, 134.12, 134.29, 137.32, 139.32, 143.39. HRMS (FABMS): Calcd for $(C_{56}H_{42}N_5Rh)^+$: *m/z* 887.2490. Found: *m/z* 887.2487.

Addition of 10 equiv of 4-Methylbenzonitrile in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and 4-methylbenzonitrile (30 μL, 28 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-CN-Bn) (**1f**) (15.0 mg, 0.017 mmol, 68%).

Reactions of Rh(ttp)Cl with 4-Nitrotoluene. Rh(ttp)Cl (30.0 mg, 0.037 mmol), K_2CO_3 (51.1 mg, 0.37 mmol) and 4-nitrotoluene (1.5 mL) were heated at 120 °C for 30 min with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-NO_2-Bn) (**1g**) (33.0 mg, 0.036 mmol, 98%) as a red solid. $R_f = 0.40$ (hexane/ CH_2Cl_2 = 1:1). ^1H NMR ($CDCl_3$, 300 MHz) δ -3.84 (d, 2 H, $J = 3.9$ Hz), 2.71 (s, 12 H), 2.90 (d, 2 H, $J = 8.7$ Hz), 6.69 (d, 2 H, $J = 8.7$ Hz), 7.56 (t, 8 H, $J = 7.5$ Hz), 7.95 (d, 4 H, $J = 7.1$ Hz), 8.05 (d, 4 H, $J = 7.5$ Hz), 8.71 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.50 (d, $^1J_{Rh\text{-}C}$ = 28.4 Hz), 21.88, 31.28, 121.32, 123.09, 124.79, 127.91, 132.11, 134.11, 134.21, 137.76, 139.27, 143.42, 150.74. HRMS (FABMS): Calcd for $(C_{55}H_{42}N_5O_2Rh)^+$: *m/z* 907.2388. Found: *m/z* 907.2430.

Addition of 10 equiv of 4-Nitrotoluene in Benzene as Solvent. Rh(ttp)Cl (30.0 mg, 0.037 mmol), K_2CO_3 (51.5 mg, 0.37 mmol) and 4-nitrotoluene (51.1 mg, 0.37 mmol) and benzene (1.5 mL) were heated at 120 °C with for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(4-NO_2-Bn) (**1g**) (23.6 mg, 0.026 mmol, 70%).

Reactions of Rh(ttp)Cl with Mesitylene. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (51.1 mg, 0.37 mmol) and mesitylene (1.5 mL) were heated at 120 °C for 1 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(3,5-Me_2-Bn) (**1h**) (15.0 mg, 0.017 mmol, 67%) as a red solid. $R_f = 0.55$ (hexane/ CH_2Cl_2 = 1:1). ^1H NMR ($CDCl_3$, 300 MHz) δ -3.81 (d, 2 H, $J = 3.9$ Hz), 1.56 (s, 6 H), 2.56 (s, 2 H), 2.70 (s, 12 H), 6.08 (s, 1 H), 7.54 (t, 8 H, $J = 6.6$ Hz), 8.00 (dd, 4 H, $J = 1.8$, 7.5 Hz), 8.05 (dd, 4 H, $J = 2.1$, 8.6 Hz), 8.68 (s, 8 H). HRMS (FABMS): Calcd for $(C_{57}H_{47}N_4Rh)^+$: *m/z* 890.2850. Found: *m/z* 890.2824. Anal Calcd. for $C_{57}H_{47}N_4Rh$: C, 76.84; H, 5.32; N, 6.29. Found C, 76.71; H, 5.31; N, 6.17.

Addition of 10 equiv of Mesitylene in Benzene as Sol-

vent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and mesitylene (47 μL, 45.4 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 2.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(3,5-Me_2-Bn) (**1h**) (12.0 mg, 0.013 mmol, 54%).

Reaction of Rh(ttp)Cl with *m*-Xylene. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and *m*-xylene (1.5 mL) were heated at 120 °C for 2 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(3-Me-Bn) (**1i**) (17.7 mg, 0.020 mmol, 81%) as a red solid. $R_f = 0.51$ (hexane:CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.79 (d, $J = 3.9$ Hz, 2 H), 1.58 (s, 3 H), 2.63 (s, 1 H), 2.64 (s, 1 H), 2.70 (s, 12 H), 2.80 (d, $J = 8.1$ Hz, 1 H), 5.77 (t, $J = 7.7$ Hz, 1 H), 6.32 (d, $J = 7.8$ Hz, 1 H), 7.53 (d, $J = 5.7$ Hz, 4 H), 7.55 (d, $J = 5.7$ Hz, 4 H), 8.00 (dd, $J = 2.6, 5.9$ Hz, 4 H), 8.06 (dd, $J = 2.4, 5.1$ Hz, 4 H), 8.67 (s, 8 H). HRMS (FABMS): Calcd for $(C_{56}H_{45}N_4Rh)^+$: *m/z* 876.2694. Found: *m/z* 876.2682. Anal Calcd. for $C_{56}H_{45}N_4Rh$: C, 76.70; H, 5.17; N, 6.39. Found: C, 76.42; H, 5.09; N: 6.37.

Addition of 10 equiv of *m*-Xylene in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and *m*-xylene (31 μL, 26.5 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(3-Me-Bn) (**1i**) (14.0 mg, 0.016 mmol, 64%).

Reaction of Rh(ttp)Cl with *o*-Xylene. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and *o*-xylene (1.5 mL) were heated at 120 °C for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(2-Me-Bn) (**1j**) (16 mg, 0.018 mmol, 73%) as a red solid. $R_f = 0.66$ (hexane:CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.57 (d, $J = 3.6$ Hz, 2 H), -0.91 (s, 3 H), 2.56 (d, $J = 7.5$ Hz, 1 H), 2.70 (s, 12 H), 5.66 (t, $J = 7.5$ Hz, 1 H), 5.72 (d, $J = 7.8$ Hz, 1 H), 6.31 (t, $J = 7.2$ Hz, 1 H), 7.53 (d, $J = 3.3$ Hz, 4 H), 7.54 (d, $J = 1.8$ Hz, 4 H), 7.96 (dd, $J = 1.7, 7.7$ Hz, 4 H), 8.05 (dd, $J = 2.1, 7.4$ Hz, 4 H), 8.67 (s, 8 H). HRMS (FABMS): Calcd for $(C_{56}H_{45}N_4Rh)^+$: *m/z* 876.2694. Found: *m/z* 876.2703. Anal Calcd. for $C_{56}H_{45}N_4Rh$: C, 76.70; H, 5.17; N, 6.39. Found: C, 76.60; H, 5.11; N: 6.33.

Addition of 10 equiv of *o*-Xylene in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and *o*-xylene (30 μL, 26.5 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(2-Me-Bn) (**1j**) (14 mg, 0.016 mmol, 64%).

Reaction of Rh(ttp)Cl with 2-Methylbenzonitrile. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and 2-methylbenzonitrile (1.5 mL) were heated at 120 °C for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(2-CN-Bn) (**1k**) (29.3 mg, 0.033 mmol, 81%) as a red solid. $R_f = 0.66$ (hexane:CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.56 (d, $J = 4.2$ Hz, 2 H), 2.62 (d, $J = 7.5$ Hz, 1 H), 2.70 (s, 12 H), 5.98 (t, $J = 7.7$ Hz, 1 H), 6.17 (d, $J = 7.5$ Hz, 1 H), 6.40 (t, $J = 7.4$ Hz, 1 H), 7.54 (d, $J = 7.5$ Hz, 4 H), 7.59 (d, $J = 7.5$ Hz, 4 H), 8.05 (d, $J = 7.8$ Hz, 4 H), 8.08 (d, $J = 7.8$ Hz, 4 H), 8.73 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ -5.2 (d, $^1J_{Rh-C} = 28.7$ Hz), 21.69, 106.76, 115.11, 122.76, 123.58, 126.09, 127.58, 129.61, 130.58, 131.80, 134.06, 137.32, 139.35, 143.46, 145.54. HRMS (FABMS): Calcd for $(C_{56}H_{42}N_5Rh)^+$: *m/z* 887.2490. Found: *m/z* 887.2478. Anal Calcd. for $C_{56}H_{42}N_5Rh$: C, 76.70; H, 5.17; N, 6.39. Found: C, 76.60; H, 5.11; N: 6.33.

Addition of 10 equiv of 2-Methylbenzonitrile in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and 2-methylbenzonitrile (30 μL, 29.3 mg, 0.25 mmol) and benzene (1.5 mL) were heated at 120 °C with for 4 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(2-CN-Bn) (**1k**) (17.0 mg, 0.019 mmol, 77%).

Reaction of Rh(ttp)Cl with 2-Nitrotoluene. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and 2-nitrotoluene (1.5 mL) were heated at 120 °C for 1.5 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(2-CN-Bn) (**1l**) (19.1 mg, 0.021 mmol, 84%) as a red solid. $R_f = 0.30$ (hexane:CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -3.19 (br, 2 H), 2.51 (d, $J = 6.9$ Hz, 1 H), 2.71 (s, 12 H), 5.87 (t, $J = 7.5$ Hz, 1 H), 6.40 (t, $J = 7.4$ Hz, 1

H), 6.61 (d, $J = 8.0$ Hz, 1 H), 7.53 (d, $J = 7.8$ Hz, 4 H), 7.59 (d, $J = 7.8$ Hz, 4 H), 8.01 (dd, $J = 1.4, 7.7$ Hz, 4 H), 8.12 (dd, $J = 1.5, 7.5$ Hz, 4 H), 8.74 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ -2.83 (d, $^1J_{Rh\text{-}C} = 28.4$ Hz), 21.55, 122.51, 123.47, 123.75, 127.37, 127.49, 128.99, 129.88, 131.61, 133.88, 137.17, 138.34, 139.17, 143.25. HRMS (FABMS): Calcd for $(C_{55}H_{42}N_5O_2Rh)^+$: *m/z* 907.2388. Found: *m/z* 907.2396.

Addition of 10 equiv of 2-Nitrotoluene in Benzene as Solvent. Rh(ttp)Cl (20.0 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and 2-nitrotoluene (34.5 mg, 0.25mmol) and benzene (1.5 mL) were heated at 120 °C with for 4 h with the reaction tube covered by aluminum foil. The solvent was then removed in vacuum and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)(2-CN-Bn) (**1l**) (16 mg, 0.018 mmol, 71%).

NMR Tube Experiment: Reaction of Rh(ttp)Cl with Toluene. Rh(ttp)Cl (8 mg, 0.010 mmol), toluene (11 μL, 0.10 mmol), K_2CO_3 (14 mg, 0.10 mmol) and benzene-d_6 (0.50 mL) were degassed for three freeze-thaw-pump cycles in a Telfon screw capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminium foil and heated at 120 °C in an oil bath. In the course of reaction, the amount of Rh(ttp)Cl was decreasing, both Rh(ttp)H and $Rh_2(ttp)_2$ were observed during the reaction. After 12 h, Rh(ttp)Bn (89%, NMR yield) was observed.

NMR Tube Experiment: Dehydrogenation of Rh(ttp)H

Thermal Dehydrogenation. Rh(ttp)H (3 mg, 0.004 mmol) and benzene-d_6 (0.50 mL) were degassed for three freeze-thaw-pump cycles in a Telfon screw capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminium foil and heated at120 °C in an oil bath. After 2 h, $Rh_2(ttp)_2$ (2%, NMR yield) was observed and Rh(ttp)H (97%, NMR yield) was remained.

Base-Promoted Dehydrogenation. Rh(ttp)H (3 mg, 0.004 mmol), K_2CO_3 (5.4mg, 0.040mmol) and benzene-d_6 (0.50 mL) were degassed for three freeze-thaw-pump cycles in a Telfon screw capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminium foil and heated at 120 °C in an oil bath. After 1 h, $Rh_2(ttp)_2$ (6%, NMR yield) was observed and Rh(ttp)H (81%, NMR yield) was remained.

Isotope Effects. A premixed equimolar solvent mixture of toluene/toluene-d_8 (total volume = 1.5 mL) and Rh(ttp)Cl (30.0 mg, 0.037 mmol) were degassed for three freeze-thaw-pump cycles in the Telfon-stopped tube. The tube was covered by aluminum foil and heated to 120 °C under N_2 for 3 d. The isotope ratio of **1** to **1-*d*$_7$** was determined to be 4.1 (benzylic CHA, integration of benzylic proton = 1.610, the integration of pyrrole signal was set as 8.000) and the isotope ratio of **2** and **3** to **2-*d*$_7$** and **3-*d*$_7$** to be 6.6 (integration of aromatic proton = 2.607 with the integration of pyrrole signal was set as 8.000) by integration of ^{1}H NMR. The results were the average of at least two runs of experiments. Those isotope ratios were confirmed by FABMS and measured to be 4.1.

Addition of 10 equiv of K_2CO_3. Rh(ttp)Cl (30.0 mg, 0.037 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.5 mL) and K_2CO_3 (51.1 mg, 0.37 mmol) were degassed for three freeze-thaw-pump cycles in the Telfon-stopped tube. The tube was covered by aluminum foil and heated to 120 °C under N_2 for 1 h. The isotope ratio of **1** to **1-*d*$_7$** was determined to be 4.0 (benzylic CHA) by integration of ^{1}H NMR (Integration of benzylic proton (1.598) was used to calculate the ratio with the integration of pyrrole signal set as 8.000). The results were the average of at least two runs. The isotope ratio was also measured by FABMS to be 4.0.

Temperature Dependent on Isotope Effect with Rh(ttp)Cl

Kinetic Isotope Effect at 150 °C. Rh(ttp)Cl (30.0 mg, 0.037 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.5 mL) and K_2CO_3 (51.1 mg, 0.37 mmol) were degassed for three freeze-thaw-pump cycles in the Telfon-stopped tube. The tube was covered by aluminum foil and heated to 150 °C under N_2 for 1 h. The isotope ratio of **1** to **1-*d*$_7$** was determined to be 4.5 (benzylic CHA) by integration of ^{1}H NMR (Integration of benzylic proton (1.636) was used to calculate the ratio with the integration of pyrrole signal set as 8.000). The results were the average of at least two runs.

Kinetic Isotope Effect at 180 °C. Rh(ttp)Cl (30.0 mg, 0.037 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.5 mL) and K_2CO_3 (51.1 mg, 0.37 mmol) were degassed for three freeze-thaw-pump cycles in the Telfon-stopped tube. The tube was covered by aluminum foil and heated to 180 °C under N_2 for 1 h. The isotope ratio of **1** to **1-*d*$_7$** was determined to be 4.8 (benzylic CHA) by integration of ^{1}H NMR (Integration of benzylic proton (1.652) was used to calculate the ratio with the integration of pyrrole signal set as 8.000). The results were the average of at least two runs.

Kinetic Isotope Effect at 200 °C. Rh(ttp)Cl (30.0 mg, 0.037 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.5 mL) and K_2CO_3 (51.1 mg, 0.37 mmol) were degassed for three freeze-thaw-pump cycles in the Telfon-stopped tube. The tube was covered by aluminum foil and heated to 200 °C under N_2 for 1 h. The isotope ratio of **1** to **1-*d*$_7$** was determined to be 5.4 (benzylic CHA) by integration of ^{1}H NMR (Integration of benzylic proton (1.670) was used to calculate the ratio with the integration of pyrrole signal set as 8.000). The results were the average of at least two runs.

Attempted H/D exchange. Rh(ttp)Bn (10.0 mg, 0.012 mmol), 10 equiv of K_2CO_3 (16.0 mg, 0.12 mmol) and toluene-d_8 (1.5 mL) were degassed for three freezethaw-pump cycles and heated at 120 °C under N_2 for 1 h with the reaction tube covered by aluminum foil to give only recovered Rh(ttp)Bn (8.0 mg, 0.0093 mmol, 80%).

Temperature Dependent on Isotope Effect with Rh(ttp)H

Kinetic Isotope Effect at 120 °C. Rh(ttp)H (6 mg, 0.008 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.0 mL) and K_2CO_3 (11 mg, 0.080 mmol) were heated at 120 °C under N_2 for 1 h. The isotope ratio of **1** to **1-*d*₇** was determined to be 4.1 (benzylic CHA) by integration of ^1H NMR (Integration of benzylic proton (1.614) was used to calculate the ratio with the integration of pyrrole signal set as 8.000).

Kinetic Isotope Effect at 200 °C with Addition of K_2CO_3. Rh(ttp)H (6 mg, 0.008 mmol), a premixed equimolar solvent mixture of toluene/ toluene-d_8 (1.0 mL) and K_2CO_3 (11 mg, 0.080 mmol) were heated at 200 °C under N_2 for 1 h. The isotope ratio of **1** to **1-d_7** was determined to be 5.3 (benzylic CHA) by integration of ^1H NMR (Integration of benzylic proton (1.684) was used to calculate the ratio with the integration of pyrrole signal set as 8.000).

Temperature Dependent on Isotope Effect with $Rh_2(ttp)_2$

Kinetic Isotope Effect at 120 °C with Addition of K_2CO_3. $Rh_2(ttp)_2$ (6 mg, 0.004 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.0 mL) and K_2CO_3 (5.4 mg, 0.040 mmol) were heated at 120 °C under N_2 for 1 h. The isotope ratio of **1** to **1-d_7** was determined to be 6.7 (benzylic CHA) by integration of ^1H NMR (Integration of benzylic proton (1.711) was used to calculate the ratio with the integration of pyrrole signal set as 8.000). The results were the average of at least two runs. The isotope ratio was also measured by FABMS to be 6.7.

Kinetic Isotope Effect at 200 °C with Addition of K_2CO_3. $Rh_2(ttp)_2$ (8 mg, 0.005 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.0 mL) and K_2CO_3 (7.2 mg, 0.052 mmol) were heated at 200 °C under N_2 for 1 h. The isotope ratio of **1** to **1-d_7** was determined to be 5.6 (benzylic CHA) by integration of ^1H NMR (Integration of benzylic proton (1.699) was used to calculate the ratio with the integration of pyrrole signal set as 8.000).

Competition Experiments of 4-Substituted Toluene. Rh(ttp)Cl (30.0 mg, 0.037 mmol), a premixed equimolar solvent mixture of toluene (39.0 μL, 0.37 mmol) and 4-methylanisole (47.0 μL, 0.37 mmol) and K_2CO_3 (51.1 mg, 0.37 mmol) in benzene (2.0 mL) as the solvent were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 1 h in a Teflon-stoppered tube. After the reaction was complete, the ^1H NMR spectrum of the crude reaction mixture was taken. The ratio of $k(H_{FG}/H_H)$ was calculated from the ratio of the benzylic protons with reference to the pyrrole proton in the ^1H NMR spectrum from at least two runs. A series of experiments was carried out using various functionalized toluenes of 4-*tert*-butyltoluene (64.0 μL, 0.37 mmol), 4-fluorotoluene (41.0 μL, 0.37 mmol), *p*-tolualdehyde (44.0 μL, 0.37 mmol), 4-methylbenzonitrile (44.0 μL, 0.37 mmol), and 4-nitrotoluene (51.1 mg, 0.37 mmol). The ratios of $k(H_{FG}/H_H)$ were calculated from the integration of the benzylic protons in ^1H NMR spectra. The results were the average of at least two runs of experiments.

Attempted exchange

Rh(ttp)Bn (10.0 mg, 0.012 mmol), 10 equiv of K_2CO_3 (16.0 mg, 0.12 mmol) and 4-fluorotoluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 1 h to give only Rh(ttp)Bn (8.0 mg, 0.0093 mmol, 80%).

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SUPPORTING INFORMATION

Text, tables, and figures of crystallographic data for complexes **1h**-**k**, ^1H and ^{13}C NMR spectra for **1a**-**k**. This material is available free of charge via the Internet at http://onlinelibrary.wiley.com. CCDC 923670-923673 contains the supplementary crystallographic data of **1h**-**k**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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