# **ORGANOMETALLICS**

# Base-Promoted Vinyl Carbon-Bromine Bond Cleavage by Group 9 Metalloporphyrin Complexes

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**Supporting Information** 

**ABSTRACT:** Base-promoted vinyl carbon-bromine bond cleavage of styryl bromide by group 9 metalloporphyrin complexes was achieved to give the metal(III) porphyrin styryls M(ttp)(styryl) (ttp = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion). Mechanistic studies suggest that  $[M^{II}(ttp)]_2$ (M = Rh, Ir) cleaves the vinyl C-Br bond via an additionelimination mechanism. The much less reactive Co<sup>II</sup>(ttp)



undergoes a radical recombination with styryl radical which is generated by the hydroxide reduction of styryl bromide to give a radical anion with subsequent C–Br cleavage.

# INTRODUCTION

Vinyl halides are useful materials in organic synthesis, and the C–C bond formations of vinyl halides with alkyl halides,<sup>1a</sup> heteroaromatic halides,<sup>1a</sup> aryl halides,<sup>1b,c</sup> heteroarenes,<sup>1d</sup> alkynes,<sup>1c,e</sup> and amides<sup>1c,f</sup> have been reported. Moreover, the stereoselective conversion of vinyl halides to the corresponding hydrocarbons is an important synthetic procedure.<sup>1g-j</sup>

The comprehensive  $C(sp^2)$ -halogen bond cleavage of aryl halides by group 9 metalloporphyrin complexes has been reported by us. Iridium<sup>2</sup> and rhodium<sup>3</sup> porphyrin complexes cleave the aryl-halogen (ArX; X = I, Br) bond via an ipsosubstitution mechanism to give Ir(ttp)Ar and Rh(ttp)Ar (ttp = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion) in good to high yields. We have proposed that, in the presence of base, Ir(ttp)(CO)Cl and Rh(ttp)Cl undergo ligand substitution with OH<sup>-</sup> to generate M(ttp)OH (M = Ir, Rh) followed by reductive dimerization to give  $[M^{II}(ttp)]_2$ .  $M^{II}(ttp)$  metalloradicals, which exist in equilibria with  $[M^{II}(ttp)]_2$ , attack the ipso carbon of ArX to give the M(ttp)-cyclohexadienyl radical intermediates. The radical intermediates then eliminate a halogen atom to give Ir(ttp)Ar and Rh(ttp)Ar.

Cobalt(II) porphyrins, however, cleave the aryl-bromine bond by a distinctly different mechanism, via a key bromine atom transfer.<sup>4</sup> Co<sup>II</sup>(ttp) abstracts the bromine atom from ArBr through halogen atom transfer to give an aryl radical and Co(ttp)Br. The aryl radical then combines with another Co<sup>II</sup>(ttp) to form Co(ttp)Ar.

To expand the substrate scope and gain a more comprehensive understanding of  $C(sp^2)$ -halogen bond cleavage,  $C(sp^2)$ -bromine bond activation of styryl bromide by iridium, rhodium, and cobalt porphyrin complexes have been investigated.

# RESULTS AND DISCUSSION

Base-Promoted Vinyl C–Br Cleavage by Ir(ttp)(CO)Cl. Initially,  $\beta$ -bromostyrene (2) reacted with Ir(ttp)(CO)Cl (1a) in the absence of  $K_2CO_3$  in benzene at 180 °C in 92 h but no Ir(ttp)(styryl) (3) was formed (Table 1, entry 1). Ir(ttp)(CO)

 Table 1. Optimization of Base-Promoted Vinyl C-Br

 Cleavage by an Iridium Porphyrin Complex

Ir <sup>III</sup> (ttp)(C <b>1a</b>	CO)CI +	Ph Br 2 2 equiv	K <sub>2</sub> C N <sub>2</sub> /air, temp,	O <sub>3</sub> time, C <sub>6</sub> H <sub>6</sub>	H ► Ph	H 3 13.9 Hz
entry	amt of	K <sub>2</sub> CO <sub>3</sub> /equiv	temp/°C	$N_2/air$	time/h	yield/% <sup>a</sup>
1 <sup>b</sup>		0	180	$N_2$	92	0
2 <sup>c</sup>		10	180	$N_2$	45	78
3 <sup>c</sup>		20	180	$N_2$	20	97
4 <sup><i>c</i></sup>		20	150	$N_2$	60	93
5 <sup>d</sup>		20	180	air	20	70
6 <sup>c</sup>		20	180	air	45	93

<sup>*a*</sup>Isolated yield. <sup>*b*</sup>A 46% yield of Ir(ttp)(CO)Br (1b) and a 33% yield of Ir(ttp)(CO)Cl (1a) were isolated. <sup>*c*</sup>Ir(ttp)(CO)Br was observed by TLC in the course of the reaction and was completely consumed upon prolonged heating to give Ir(ttp)(styryl) (3). <sup>*d*</sup>A 24% yield of Ir(ttp)(CO)Cl was recovered.

Cl in 33% yield was recovered and  $Ir(ttp)(CO)Br^{2a}$  (1b) in 46% yield was also isolated. Some extent of bromide transfer from  $\beta$ -bromostyrene occurred, likely via partial hydrolysis of Ir(ttp)(CO)Cl with water to give Ir(ttp)OH and then  $Ir^{II}(ttp)$ .

When 10 equiv of  $K_2CO_3$  was added, a 78% yield of Ir(ttp)(styryl) (3) was obtained in 45 h (Table 1, entry 2). A higher  $K_2CO_3$  loading of 20 equiv shortened the reaction time to 20 h for completion with a 97% yield of Ir(ttp)(styryl) obtained (Table 1, entry 3).

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When a lower temperature of 150 °C was employed, the product yield was still high but the reaction time of 60 h was very long (Table 1, entries 3 and 4). The C–Br bond cleavage was also successfully carried out in air. However, the reaction was incomplete in 20 h and required 45 h to complete to give a 93% yield of Ir(ttp)(styryl) (3) (Table 1, entries 3, 5, and 6). Therefore, the optimized reaction conditions required 20 equiv of  $K_2CO_3$  and 2 equiv of  $\beta$ -bromostyrene at 180 °C under N<sub>2</sub>.

The stereochemistry of Ir(ttp)(styryl) (3; J = 13.9 Hz) was assigned to be trans on the basis of the similarity of the vicinal coupling constants for the reported Rh(oep)(styryl) ( $J_{trans} =$ 13.0 Hz,  $J_{cis} = 7.5$  Hz)<sup>5</sup> (oep = 2,3,7,8,12,13,17,18octaethylporphyrinato dianion) and Rh(ttp)(styryl) (5) discussed below.

**Base-Promoted Vinyl C–Br Cleavage by Rh(ttp)Cl.** Without any  $K_2CO_3$  in air, C–Br cleavage of  $\beta$ -bromostyrene with Rh(ttp)Cl (**4a**) was incomplete after 24 h with only a 12% yield of Rh(ttp)(styryl) (**5**) formed (Table 2, entry 1). With

# Table 2. Optimization of Base-Promoted Vinyl C-Br Cleavage by a Rhodium Porphyrin Complex

Rh <sup>Ⅲ</sup> (ttp)Cl ⊣	Ph Br	K <sub>2</sub> CO <sub>3</sub> <sub>2</sub> /air, 150 °C, time,	► Ph ´	H Rh <sup>III</sup> (ttp) H
4a	<b>2</b> 2 equiv		J =	<b>5</b> = 13.0 Hz
antur	amt of K CO /oau	in NI /ain	time o /h	riald /0/a
entry	and of $K_2 CO_3/equ$	$1v = 1v_2/arr$	time/n	yieid/ %
1 <sup>b</sup>	0	air	24	12
2 <sup>c</sup>	2	air	14	74
3 <sup>c</sup>	5	air	3	75
4 <sup>c</sup>	10	air	2	72
5 <sup>°</sup>	10	$N_2$	4	68

<sup>*a*</sup>Isolated yield. <sup>*b*</sup>Incomplete reaction. <sup>*c*</sup>Rh(ttp)Br (4b) was observed by TLC in the course of the reaction, and it was completely consumed upon prolonged heating to give Rh(ttp)(styryl) (5).

the addition of 2 equiv of  $K_2CO_3$ , the yield of Rh(ttp)(styryl) increased significantly to 74% in 14 h (Table 2, entry 2). When  $K_2CO_3$  was increased to 5 equiv, the reaction time decreased to 3 h to give a 75% yield of Rh(ttp)(styryl) (Table 2, entries 2 and 3). A higher loading of  $K_2CO_3$  (10 equiv) showed little enhancement (Table 2, entry 4). Hence, 5 equiv of  $K_2CO_3$  was optimal.

When the reaction was carried out in N<sub>2</sub>, in contrast to the Ir case, the reaction time doubled to 4 h (Table 2, entries 4 and 5). Therefore, the optimized reaction conditions required 5 equiv of  $K_2CO_3$  and 2 equiv of  $\beta$ -bromostyrene at 150 °C in air.

The trans geometry of Rh(ttp)(styryl) (**5**; J = 13.0 Hz) was established by a vicinal coupling constant identical with that of *trans*-Rh(oep)sytyrl ( $J_{trans} = 13.0$  Hz,  $J_{cis} = 7.5$  Hz).<sup>5</sup> Furthermore, X-ray crystal structure of Rh(ttp)(styryl) (Figure S1 in the Supporting Information) further ascertained the trans geometry.

**Base-Promoted Vinyl C–Br Cleavage by Co(ttp).** Co<sup>II</sup>(por) (por = porphyrinato diaion) is the least reactive and reducing among  $M^{II}(por)$  (M = Ir, Rh, Co).<sup>6</sup> We were curious to find out whether the readily available, air-stable Co<sup>II</sup>(por) could react with  $\beta$ -bromostyrene. Without KOH added, Co<sup>II</sup>(ttp) (6) did not react with a higher loading of  $\beta$ bromostyrene (2) of 10 equiv even after heating at 120 °C for 20 h in benzene solvent with Co<sup>II</sup>(ttp) recovered in 94% yield (Table 3, entry 1). Indeed, Co<sup>II</sup>(ttp) alone is not reactive

Table 3. Optimization of Base-Promoted	Vinyl	C–Br
Cleavage by a Cobalt Porphyrin		

Co <sup>ll</sup> (ttp)	+ Ph Br	KOH <sup>t</sup> BuOH N <sub>2</sub> /air, temp, tim	e, C <sub>6</sub> H <sub>6</sub> ►	H Ph	∫Co <sup>III</sup> (ttp)
6	<b>2</b> 10 equiv			<b>7</b> J = 11	.8 Hz
entry	amt of KOH/equiv	amt of <sup>t</sup> BuOH/equiv	temp/°C	$N_2/air$	yield/% <sup>a</sup>
1 <sup>b</sup>	0	50	120	$N_2$	0
2 <sup>c</sup>	10	50	120	$N_2$	34
3 <sup>c</sup>	10	50	120	air	30 <sup>d</sup>
4 <sup><i>c</i></sup>	10	0	120	$N_2$	28 <sup>d</sup>
5 <sup>c</sup>	10	50	90	$N_2$	5 <sup>d</sup>
6 <sup>c</sup>	10	50	150	$N_2$	25
$7^{c,e,f}$	10	50	150	$N_2$	13 <sup>d</sup>
8 <sup>c,f</sup>	10	50	180	$N_2$	20 <sup>d</sup>
a	, , , , h. a		( ) ( )		

<sup>*a*</sup>Isolated yield. <sup>*b*</sup>A 94% yield of Co(ttp) (6) was recovered. <sup>*c*</sup>Incomplete reaction. <sup>*d*</sup>Yield estimated from <sup>*i*</sup>H NMR of crude mixture. <sup>*e*</sup>The reaction time was 5 days. <sup>*f*</sup>Stilbene was detected by GC-MS analysis.

enough to cause any C-Br activation. When 10 equiv of KOH was added, Co(ttp)(styryl) (7) was isolated in 34% yield (Table 3, entry 2). The reaction was also compatible in air, though with a slightly lower product yield of 30% (Table 3, entry 3). Addition of <sup>t</sup>BuOH, likely as a phase transfer agent, is beneficial, as a lower product yield of 28% was obtained without <sup>t</sup>BuOH (Table 3, entries 2 and 4). The optimal temperature was found to be 120 °C to give the highest yield of Co(ttp)(styryl) in the same reaction time of 20 h, as 90, 150, and 180 °C were proved to be inferior (Table 3, entries 2 and 5-8). Co(ttp)(styryl) likely underwent some thermal decomposition at higher temperature like that of Co(ttp)Ph, which begins to undergo thermal decomposition at 150 °C.<sup>4</sup> Indeed, prolonged reaction at 150 °C for 5 days gave a lower yield (Table 3, entry 7). Therefore, the optimized reaction conditions required 10 equiv of  $\beta$ -bromostyrene, 10 equiv of KOH, and 50 equiv of <sup>t</sup>BuOH at 120 °C under N<sub>2</sub>.

Both isomers of Co(oep)styryls have been reported by Ogoshi with reported coupling constants for the cis and trans vicinal protons of 4.0 and 12.0 Hz, respectively.<sup>7</sup> Co(ttp)-(styryl) (7) with J = 11.8 Hz was therefore assigned to be the trans isomer.

Mechanistic Studies. Four M(ttp) (M = Ir, Rh) species, M<sup>I</sup>(ttp)<sup>-</sup>, M<sup>II</sup>(ttp), M<sup>III</sup>(ttp)H, and M<sup>III</sup>(ttp)OH, have been reported to exist in equilibria under basic conditions.<sup>2,3,8-10</sup> For the case of cobalt porphyrin species, which is the least reactive and reducing among  $M^{II}(por)^6$  (M = Ir, Rh, Co), Co<sup>III</sup>(por)-OH with a weaker Co(por)-OH bond<sup>11</sup> is likely to be very unstable. The stronger M(ttp)-OH (M = Rh, Ir) decomposes at 120 °C to give  $H_2O_2$  and  $[M^{II}(ttp)]_2$ .<sup>2,9</sup> The intermediacy of M(por)H is also not considered by the stoichiometry of the reaction, as no hydrogen is introduced into the products. Thus, we only considered the pathways with  $[M^{II}(ttp)]_2$  and M<sup>I</sup>(ttp)<sup>-</sup>. With the known 1,2-metalloradical additions of  $[M^{II}(\text{oep})]_2$  (M = Ir, Rh) to alkenes to give the 1,2-dimetalloalkenes (eqs 1 and 2),<sup>12–14</sup>  $\beta$ -bromostyrene with a weak C=C bond (~40 kcal/mol<sup>15</sup>) may react likewise. While  $Co^{II}(ttp)$  alone did not react at all even at 120 °C (Table 3, entry 1),  $[M^{II}(ttp)]_2$  (M = Rh, Ir) reacted quickly to give *trans*-M(ttp)styryls and M(ttp)Br at room temperature within 25

min in approximately 1:1 ratios.  $[M^{II}(ttp)]_2$  species are much more reducing than  $Co^{II}(ttp)$ . Furthermore, no PhBr and stilbene were detected in the crude reaction mixture (Table 4), suggesting that no bromine atom and styryl radical are formed to couple with benzene solvent.

Table 4. Reactivity of $[M^{II}(ttp)]_2$ with $\beta$ -Bromostyrene							
$1/2[M^{II}(ttp)]_2 + Ph \longrightarrow Br \xrightarrow{C_6D_6, N_2} M^{III}(ttp)Br + Ph \longrightarrow M^{III}(ttp)Br$							
		<b>2</b> 2 equiv					
yield/% <sup>b</sup>							
entry	Μ	M(ttp)Br	M(ttp)(styryl)	total M(ttp) species/%			
1 <sup><i>a</i></sup>	Ir	39 (1c)	59 (3)	98			
2 <sup><i>a</i></sup>	Rh	47 ( <b>4b</b> )	53 ( <b>5</b> )	100			

<sup>*a*</sup>No PhBr and stilbene were detected by GC-MS analysis. <sup>*b*</sup>Determined from the ratio of integration of pyrrole peaks of  $M^{III}(ttp)Br$  with  $M^{III}(ttp)(styryl)$ .

**Possible Mechanisms.** On the basis of the above results and the established mechanism of Ar–X bond activation by  $M(por)L/K_2CO_3$  (M = Ir, L = (CO)Cl; M = Rh, L = Cl),<sup>2–4</sup> five plausible mechanisms for vinyl C–Br cleavage by group 9 M(ttp) species are proposed: (a) anionic mechanism, (b) direct bromine transfer, (c) metalloradical substitution, (d) addition–elimination, and (e) electron transfer (Scheme 1).

Pathway a is an anionic mechanism.  $M^{I}(ttp)^{-}$  undergoes nucleophilic substitution with  $\beta$ -bromostyrene. Initially,  $M^{I}(ttp)^{-}$ , formed by the reaction of  $M^{II}(ttp)$  with  $OH^{-,9,16}_{-,16}$ attacks the somewhat electron poor  $\pi$  bond to give a stabilized benzyl anion intermediate. Further elimination can yield the

### Scheme 1. Possible Mechanisms for Base-Promoted Vinyl C–Br Cleavage with Group 9 Metalloporphyrin Complexes



 $\overset{\text{(b) Election Hansler}}{\underset{Ph}{\overset{Br}{\longrightarrow}}} \left[ \begin{array}{c} Ph \overset{\text{(b)}}{\overset{Ph}{\longrightarrow}} Ph \overset{\text{(c)}}{\overset{Ph}{\longrightarrow}} Ph \overset{\text{(c)}}{$ 

 $M^{III}(ttp)$ styryls and a bromide. No  $M^{III}(ttp)$ Br coproduct should be formed. However, in the reactions without base (Table 1, entry 1, and Table 2, entry 1),  $M^{III}(ttp)$ Br (M = Ir, Rh) was still observed. This pathway is not reasonable.

Pathway b involves a bromine atom abstraction from  $\beta$ bromostyrene by  $M^{II}(ttp)$  radical to give the vinyl radical and  $M^{III}(ttp)$ Br. The vinyl radical then combines with another  $M^{II}(ttp)$  radical or equivalent  $[M^{II}(ttp)]_2$  to form  $M^{III}(ttp)$ -(styryl). Stilbene will be formed from the leakage reaction of the vinyl radical with benzene solvent. However, no stilbene was observed by GC-MS analysis in the reaction mixture of  $\beta$ bromostyrene with both  $[Ir^{II}(ttp)]_2$  and  $[Rh^{II}(ttp)]_2$  (Table 4), only in that of Co<sup>II</sup>(ttp) (Table 3, entries 7 and 8). Therefore, the direct bromine transfer mechanism is ruled out for Rh(ttp) and Ir(ttp) species but likely operates for Co(ttp).

Pathway c is a metalloradical chain substitution.  $M^{II}(ttp)$ radical attacks  $\beta$ -bromostyrene to generate the benzylic radical. Subsequent  $\beta$ -bromine elimination gives  $M^{III}(ttp)(styryl)$  and a bromine atom. The bromine atom can react with  $[M^{II}(ttp)]_2$  to form  $M^{III}(ttp)Br$  and regenerate another M(ttp) in a chain reaction process. In a radical leakage channel, Br gives some PhBr from the radical substitution with benzene solvent. Careful analysis of the reaction mixtures revealed no PhBr for all group 9 metalloporphyrins. We thus disfavor this mechanism.

Pathway d is addition–elimination.  $M^{II}(ttp)$  radical adds to the C=C of  $\beta$ -bromostyrene, forming the bi- $M^{III}(ttp)$  complex intermediate. Elimination occurs that gives  $M^{III}(ttp)(styryl)$ and  $M^{III}(ttp)Br$  via  $\beta$ -bromine elimination<sup>17</sup> in a 1:1 ratio. From the reaction of  $\beta$ -bromostyrene with both [ $Ir^{II}(ttp)$ ]<sub>2</sub> and [ $Rh^{II}(ttp)$ ]<sub>2</sub>, the ratios of  $M^{III}(ttp)Br$  to  $M^{III}(ttp)(styryl)$  are approximately 1:1, which is mostly consistent with the addition–elimination mechanism (Table 4).

Pathway e is the hydroxide reduction of styryl bromide to give styryl radical anion and then styryl radical for the C–Br cleavage. Vinyl C–Br cleavage with Co(ttp) does not likely proceed via the same mechanism as Ir(ttp)(CO)Cl and Rh(ttp)Cl, owing to the absence of reaction of  $Co^{II}(ttp)$  with styryl bromide without KOH and/or the formation of stilbene coproduct in the reactions (Table 3, entries 1, 7, and 8). Bromine atom transfer (pathway b)<sup>4</sup> or electron transfer process (pathway e) may be a more reasonable mechanism for the C–Br bond cleavage by  $Co^{II}(ttp)$  with KOH added, to be discussed below.

**Proposed Mechanisms.** On the basis of the experimental results, Scheme 2 depicts the proposed reaction mechanism for the base-promoted vinyl C–Br bond cleavage.  $M^{III}(ttp)L$  (M = Ir, L = (CO)Cl; M = Rh, L = Cl) is first converted to  $M^{III}(ttp)OH$  through ligand substitution of  $M^{III}(ttp)L$  with OH<sup>-</sup>.  $M^{III}(ttp)OH$  then undergoes reductive dimerization to give  $[M^{III}(ttp)]_2$ , which is in equilibrium with the  $M^{II}(ttp)$  radical.<sup>18</sup> The  $M^{III}(ttp)$  radical then cleaves the vinyl C–Br





bond through an addition–elimination to generate  $M^{III}(ttp)$ (styryl) and  $M^{III}(ttp)Br$ .  $M^{III}(ttp)Br$  can be converted back to  $M^{III}(ttp)OH$  through ligand substitution with  $OH^-$ .  $H_2O_2$  generated from the reductive dimerization of  $M^{III}(ttp)OH$  further decomposes to  $H_2O$  and  $O_2$  through an alkaline-catalyzed process.<sup>19</sup> We could not distinguish with certainty a chain or nonchain concerted mechanism. From the absence of PhBr coproduct, bromine atom must react with  $[M^{II}(ttp)]_2$  very rapidly and have a very short lifetime. In the extreme case, this pathway is the nonchain pathway d. The nearly 1:1 ratios of the reactions shown in Table 4 favor pathway d over c. The role of  $OH^-$  is as both a ligand and a single-electron reductant.<sup>2,8,19,20</sup>

 $\text{Co}^{II}(\text{ttp})$  can in principle cleave the vinyl C–Br bond by bromine atom abstraction similarly to the reported Ar–Br bond activation<sup>4,19</sup> to give Co<sup>III</sup>(ttp)Br and styryl radical. Styryl radical then recombines with Co<sup>III</sup>(ttp) to form Co<sup>III</sup>(ttp)-(styryl). This mechanism is analogous to the well-known halogen atom transfer mechanism by analogous Co<sup>II</sup>(CN)<sub>5</sub><sup>3–</sup> chemistry with alkyl halides.<sup>21</sup> KOH then reduces Co(ttp)Br via the intermediate Co(ttp)OH to give Co<sup>III</sup>(ttp) and H<sub>2</sub>O<sub>2</sub> for further reaction.<sup>2,8</sup> However, the absence of any product in the reaction without base highly disfavors this mechanism (Table 3, entry 1).

We thus propose a more reasonable electron transfer mechanism (pathway e). KOH can reduce styryl bromide by a one-electron process, in either an outer-sphere manner<sup>22</sup> or a Co(ttp)-mediated inner-sphere process,<sup>23</sup> into a styryl radical anion. Subsequently, the styryl radical anion undergoes C–Br bond cleavage to yield a styryl radical and a bromide. The styryl radical is trapped rapidly by the metalloradical Co<sup>II</sup>(ttp) to give Co<sup>III</sup>(ttp)(styryl). No Co(ttp)Br is formed. Though stilbene, formed from the styryl radical with benzene solvent, was only detected at 150 °C or above (Table 3, entries 7 and 8), its formation can be interpreted only by the thermal decomposition of Co(ttp)(styryl); the absence of any reaction without KOH strongly disfavors pathways b–d but supports pathway e. KOH behaves as a reducing agent but not as a ligand to form Co(ttp)OH, and Co(ttp) acts as a radical trap.

The distinct mechanistic difference of vinyl C–Br bond cleavage by Ir and Rh versus that by Co is rationalized by the lower reducing ability of  $\text{Co}^{II}(\text{ttp})$ .<sup>6</sup>  $\text{Co}^{II}(\text{ttp})$  therefore does not undergo the 1,2-addition to the alkene to form the much weaker Co–C bonded intermediate (pathways b–d discussed above). Instead,  $\text{Co}^{II}(\text{ttp})$  acts as a styryl radical trap to yield  $\text{Co}^{III}(\text{ttp})(\text{styryl})$ .

**Competition between Vinyl and Aryl C–Br Cleavage.** To examine the relative reactivities of  $\beta$ -bromostyrene and bromobenzene, an equimolar mixture of excess  $\beta$ -bromostyrene (2) and bromobenzene (8; 10 equiv) reacted with Ir(ttp)(CO) Cl (1a) and Rh(ttp)Cl (4a), respectively. After the complete consumption of M(ttp)L (M = Ir, L = (CO)Cl; M = Rh, L = Cl), M(ttp)(styryl) species were obtained as the exclusive products in good yields of 89 and 73%, respectively (Table 5). The weaker  $\pi^{15}$  and C–Br bonds in styryl bromide (C–Br bond of  $\beta$ -bromostyrene 65.1 kcal/mol<sup>15</sup>) in comparison to the Ar–Br bond (Ph-Br bond 80.4 kcal/mol<sup>15</sup>) account for the higher reactivity of styryl bromide.  $\beta$ -Bromostyrene is therefore much more reactive or more easily reduced.

# CONCLUSION

Table 5. Competition	between `	Vinyl an	d Aryl	C–Br	Bond
Cleavage with M(ttp)L	,				

M(ttp)L	+ Ph ABr +	- PhBr —	K <sub>2</sub> CO <sub>3</sub> N <sub>2</sub> , temp, time, C <sub>6</sub> H	► F	Ph M(ttp)
	<b>2</b> 10 equiv	<b>8</b> 10 equiv			
entry	M(ttp)L	temp/°C	amt of K <sub>2</sub> CO <sub>3</sub> /equiv	time/h	isolated yield/%
1	Ir(ttp)(CO)Cl (1a)	180	20	39	89 (3)
2	Rh(ttp)Cl (4a)	120	10	18	73 (5)

 $Co^{II}(ttp)$  in basic media.  $[M^{II}(ttp)]_2$  (M = Ir, Rh) was proposed to be the intermediate to cleave the vinyl C–Br bond via an addition–elimnination mechanism. In addition,  $\beta$ bromostyrene exhibits reactivity higher than that of bromobenzene with Ir<sup>III</sup>(ttp)(CO)Cl and Rh<sup>III</sup>(ttp)Cl. This indicates the higher reactivity of the vinyl C–Br bond in comparison to the arvl C–Br bond.

#### EXPERIMENTAL SECTION

**General Procedures.** Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Benzene was distilled from sodium and stored in a Teflon-screw-capped tube under nitrogen prior to use. All reactions were carried out in the absence of light by wrapping the reaction vessels with aluminum foil.  $Ir^{III}(ttp)(CO)Cl(1a)$ ,<sup>2</sup> Rh<sup>III</sup>(ttp)Cl(4a),<sup>2</sup> Co<sup>II</sup>(ttp)(6),<sup>4</sup> [ $Ir^{II}(ttp)$ ]<sub>2</sub>,<sup>2</sup> and [Rh<sup>II</sup>(ttp)]<sub>2</sub><sup>24</sup> were prepared according to the literature procedures. Thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Silica gel (Merck, 70–230 and 230–400 mesh) or alumina (90 active neutral, 70–230 mesh) with the addition of H<sub>2</sub>O (v/v 10/1) was used for column chromatography in air.

<sup>1</sup>H NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in CDCl<sub>3</sub> ( $\delta$  7.26 ppm) or in C<sub>6</sub>D<sub>6</sub> ( $\delta$  7.15 ppm) as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). <sup>13</sup>C NMR spectra were recorded on a Bruker AV700 (176 MHz) spectrometer with reference to CDCl<sub>3</sub> ( $\delta$  77.1 ppm) as an internal standard. High-resolution mass spectrometry (HRMS) was performed on a Thermofinnigan MAT 95 XL instrument in FAB mode (3-nitrobenzyl alcohol (NBA) as the matrix and CH<sub>2</sub>Cl<sub>2</sub> as the solvent) and an ESI instrument (MeOH/CH<sub>2</sub>Cl<sub>2</sub> 1/1 as the solvent).

GC-MS analyses were conducted on a GCMS-QP2010 Plus system using an Rtx-5MS column (30 m  $\times$  0.25 mm). Details of the GC program are as follows. The column oven temperature and injection temperature were 80.0 and 250 °C. Helium was used as the carrier gas. The flow control mode was chosen as linear velocity (36.3 cm/s) with a pressure of 62.8 kPa. The total flow, column flow, and purge flow were 13.7, 0.97, and 3.0 mL/min, respectively. Split mode injection with a split ratio of 10.0 was applied. After injection, the column oven temperature was kept at 80 °C for 2 min and was then elevated to a rate of 30 °C/min for 5.5 min up to 250 °C. The temperature of 250 °C was kept for 5 min.

**Optimization of Vinyl C–Br Cleavage by Ir(ttp)(CO)Cl.** *Reaction of Ir(ttp)(CO)Cl with*  $\beta$ -Bromostyrene without  $K_2CO_3$ . Ir(ttp)(CO)Cl (10.0 mg, 0.011 mmol) and  $\beta$ -bromostyrene (2.8  $\mu$ L, 0.022 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 180 °C for 92 h. Benzene solvent was removed by vacuum distillation. Excess  $\beta$ -bromostyrene was removed by washing the reaction mixture with hexane. Ir(ttp)(CO)Br (4.9 mg, 0.005 mmol, 46%) and Ir(ttp)(CO)Cl (3.4 mg, 0.003 mmol, 33%) were obtained.

Reaction of Ir(ttp)(CO)CI with  $\beta$ -Bromostyrene and 10 Equiv of  $K_2CO_3$ . Ir(ttp)(CO)Cl (1a; 10.0 mg, 0.011 mmol),  $K_2CO_3$  (15.0 mg, 0.108 mmol), and  $\beta$ -bromostyrene (2; 2.8  $\mu$ L, 0.022 mmol) were added to benzene (1.0 mL). The mixture was degassed for three

freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 180 °C for 45 h. Benzene solvent was removed by vacuum distillation. The reaction mixture was worked up by extraction with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The combined organic extract was dried with MgSO<sub>4</sub>, filtered ,and rotary evaporated. Excess  $\beta$ -bromostyrene was removed by washing the reaction mixture with hexane, and the dark red solid Ir(ttp)(styryl) (3; 8.3 mg, 0.008 mmol, 78%) was obtained. Ir(ttp)(styryl):  $R_f = 0.49$  (hexane/CH<sub>2</sub>Cl<sub>2</sub> 1/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  –0.46 (d, J = 13.7 Hz, 1 H), –0.18 (d, J = 14.1 Hz, 1 H), 2.68 (s, 12 H), 5.03 (d, J = 6.2 Hz, 2 H), 6.30 (d, J = 7.2 Hz, 3 H), 7.52 (d, J = 5.2 Hz, 8 H), 8.03 (t, J = 5.2, 5.2 Hz, 8 H), 8.59 (s, 8 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 176 MHz)  $\delta$  21.7, 123.4, 123.8, 124.1, 126.9, 127.6, 128.2, 131.5, 133.7, 134.2, 135.5, 137.4, 138.8, 143.0; HRMS (FABMS) calcd for (C<sub>56</sub>H<sub>43</sub>IrN<sub>4</sub>)+ m/z 964.3116, found m/z 964.3112.

Reaction of Ir(ttp)(CO)CI with  $\beta$ -Bromostyrene and 20 Equiv of  $K_2CO_3$ . Ir(ttp)(CO)Cl (1a; 10.0 mg, 0.011 mmol),  $K_2CO_3$  (29.9 mg, 0.216 mmol), and  $\beta$ -bromostyrene (2; 2.8  $\mu$ L, 0.022 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 180 °C for 20 h. Benzene solvent was removed by vacuum distillation. The reaction mixture was worked up by extraction with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The combined organic extract was dried with MgSO<sub>4</sub>, filtered, and rotary evaporated. Excess  $\beta$ -bromostyrene was removed by washing the reaction mixture with hexane, and the dark red solid Ir(ttp)(styryl) (3; 10.3 mg, 0.011 mmol, 97%) was obtained.

Reaction of Ir(ttp)(CO)CI with  $\beta$ -Bromostyrene at 150 °C. Ir(ttp)(CO)Cl (1a; 10.0 mg, 0.011 mmol), K<sub>2</sub>CO<sub>3</sub> (29.9 mg, 0.216 mmol) and  $\beta$ -bromostyrene (2; 2.8  $\mu$ L, 0.022 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 150 °C for 60 h. Benzene solvent was removed by vacuum distillation. The reaction mixture was worked up by extraction with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The combined organic extract was dried with MgSO<sub>4</sub>, filtered, and rotary evaporated. Excess  $\beta$ -bromostyrene was removed by washing the reaction mixture with hexane, and the dark red solid Ir(ttp)(styryl) (3; 9.9 mg, 0.010 mmol, 93%) was obtained.

Reaction of Ir(ttp)(CO)Cl with  $\beta$ -Bromostyrene in Air. Ir(ttp)(CO) Cl (1a; 10.0 mg, 0.011 mmol), K<sub>2</sub>CO<sub>3</sub> (29.9 mg, 0.216 mmol), and  $\beta$ bromostyrene (2; 2.8  $\mu$ L, 0.022 mmol) were added to benzene (1.0 mL). The mixture was heated to 180 °C for 20 h. Benzene solvent was removed by vacuum distillation. The reaction mixture was worked up by extraction with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The combined organic extract was dried with MgSO<sub>4</sub>, filtered, and rotary evaporated. Excess  $\beta$ bromostyrene was removed by washing the reaction mixture with hexane. The dark red solid Ir(ttp)(styryl) (3; 7.4 mg, 0.007 mmol, 70%) and Ir(ttp)(CO)Cl (1a; 2.0 mg, 0.002 mmol, 20%) were obtained.

Reaction of Ir(ttp)(CO)Cl with  $\beta$ -Bromostyrene in Air. Ir(ttp)-(CO)Cl (1a; 10.0 mg, 0.011 mmol), K<sub>2</sub>CO<sub>3</sub> (29.9 mg, 0.216 mmol), and  $\beta$ -bromostyrene (2; 2.8  $\mu$ L, 0.022 mmol) were added to benzene (1.0 mL). The mixture was heated to 180 °C for 45 h. Benzene solvent was removed by vacuum distillation. The reaction mixture was worked up by extraction with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The combined organic extract was dried with MgSO<sub>4</sub>, filtered, and rotary evaporated. Excess  $\beta$ bromostyrene was removed by washing the reaction mixture with hexane, and the dark red solid Ir(ttp)(styryl) (3; 9.9 mg, 0.010 mmol, 93%) was obtained.

**Optimization of Vinyl C–Br Cleavage by Rh(ttp)Cl.** *Reaction of Rh(ttp)Cl with β-Bromostyrene without K*<sub>2</sub>CO<sub>3</sub>. Rh(ttp)Cl (4a; 10.0 mg, 0.012 mmol) and β-bromostyrene (2; 3.3 µL, 0.024 mmol) were added to benzene (1.0 mL). The mixture was heated to 150 °C for 24 h, and the reaction was incomplete. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) solvent mixture as eluent. The red solid product Rh(ttp)(styryl) (5; 1.2 mg, 0.001 mmol, 12%) was collected. Rh(ttp)(styryl):  $R_f$  = 0.82 (hexane/CH<sub>2</sub>Cl<sub>2</sub> 1/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ –0.46 (d, *J* = 13.0 Hz, 1 H), -0.29 (d, *J* = 13.0 Hz, 1 H), 2.70 (s, 12 H), 4.96 (d, *J* = 7.0 Hz, 2 H), 6.31 (m, 3 H), 7.53 (t, *J* = 6.4 Hz, 8 H), 8.06 (dd, *J* = 7.5 Hz, 8 H), 8.78 (s, 8 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 176 MHz) δ 21.7, 118.7,

118.9, 122.7, 123.6, 124.5, 127.0, 127.3, 127.5, 127.6, 131.7, 133.9, 134.3, 137.4, 139.3, 143.1; HRMS (FABMS) calcd for  $(C_{56}H_{43}N_4Rh)^+$  m/z 874.2537, found m/z 874.2538.

Reaction of Rh(ttp)Cl with  $\beta$ -Bromostyrene and 2 Equiv of K<sub>2</sub>CO<sub>3</sub>. Rh(ttp)Cl (4a; 10.0 mg, 0.012 mmol), K<sub>2</sub>CO<sub>3</sub> (3.4 mg, 0.024 mmol), and  $\beta$ -bromostyrene (2; 3.3  $\mu$ L, 0.024 mmol) were added to benzene (1.0 mL). The mixture was heated to 150 °C for 14 h. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) solvent mixture as eluent. The red solid product Rh(ttp)(styryl) (5; 7.8 mg, 0.009 mmol, 74%) was collected.

Reaction of Rh(ttp)Cl with  $\beta$ -Bromostyrene and 5 Equiv of K<sub>2</sub>CO<sub>3</sub>. Rh(ttp)Cl (4a; 10.0 mg, 0.012 mmol), K<sub>2</sub>CO<sub>3</sub> (8.6 mg, 0.060 mmol), and  $\beta$ -bromostyrene (2; 3.3  $\mu$ L, 0.024 mmol) were added to benzene (1.0 mL). The mixture was heated to 150 °C for 3 h. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) solvent mixture as eluent. The red solid product Rh(ttp)(styryl) (5; 7.9 mg, 0.009 mmol, 75%) was collected.

Reaction of Rh(ttp)Cl with  $\beta$ -Bromostyrene and 10 Equiv of  $K_2CO_3$ . Rh(ttp)Cl (4a; 10.0 mg, 0.012 mmol),  $K_2CO_3$  (17.1 mg, 0.124 mmol) and  $\beta$ -bromostyrene (2; 3.3  $\mu$ L, 0.024 mmol) were added to benzene (1.0 mL). The mixture was heated to 150 °C for 2 h. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) solvent mixture as eluent. The red solid product Rh(ttp)(styryl) (5; 7.6 mg, 0.009 mmol, 72%) was collected.

Reaction of Rh(ttp)Cl with  $\beta$ -Bromostyrene under N<sub>2</sub>. Rh(ttp)Cl (4a; 10.0 mg, 0.012 mmol), K<sub>2</sub>CO<sub>3</sub> (17.1 mg, 0.124 mmol) and  $\beta$ bromostyrene (2; 3.3  $\mu$ L, 0.024 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N<sub>2</sub>, and heated to 150 °C for 4 h. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) solvent mixture as eluent. The red solid product Rh(ttp)(styryl) (5; 7.1 mg, 0.008 mmol, 68%) was collected.

**Optimization of Vinyl C–Br Cleavage by Co(ttp).** Reaction of Co(ttp) with β-Bromostyrene without KOH. Co(ttp) (6; 10.0 mg, 0.014 mmol), 'BuOH (65.5  $\mu$ L, 0.687 mmol), and β-bromostyrene (2; 17.5  $\mu$ L, 0.137 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 120 °C for 20 h. The reaction was incomplete. Benzene solvent was removed by vacuum distillation. Co(ttp) (6; 9.4 mg, 0.013 mmol, 94%) was recovered.

Reaction of Co(ttp) with  $\beta$ -Bromostyrene and 10 Equiv of KOH. Co(ttp) (6; 10.0 mg, 0.014 mmol), KOH (7.7 mg, 0.137 mmol), <sup>t</sup>BuOH (65.5  $\mu$ L, 0.687 mmol), and  $\beta$ -bromostyrene (2; 17.5  $\mu$ L, 0.137 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N2, and heated to 120 °C for 20 h. The reaction was incomplete. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on alumina with the addition of  $H_2O$  (v/v 10/1) with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (4:1) solvent mixture as eluent. The red solid product Co(ttp)(styryl) (7; 3.9 mg, 0.005 mmol, 34%) was collected. Co(ttp)(styryl):  $R_f = 0.48$  (hexane/CH<sub>2</sub>Cl<sub>2</sub> 3/1); <sup>1</sup>H NMR (CDC1<sub>3</sub>, 400 MHz)  $\delta$  –0.35 (d, J = 11.8 Hz, 1 H), 0.20 (d, J = 11.8 Hz, 1 H), 2.67 (s, 12 H), 5.16 (d, J = 3.0 Hz, 2 H), 6.38 (t, J = 3.2 Hz, 3 H), 7.52 (d, J = 7.8 Hz, 8 H), 8.00 (d, J = 6.9 Hz, 8H), 8.85 (s, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 176 MHz) δ 21.7, 121.7, 123.8, 124.6, 127.1, 127.7, 131.2, 131.4, 132.8, 133.6, 137.4, 138.8, 145.4; HRMS (ESIMS) calcd for  $(C_{56}H_{43}CoN_4)^+ m/z$  830.2814, found m/z830.2817

Reaction of Co(ttp) with  $\beta$ -Bromostyrene and 10 Equiv of KOH in Air. Co(ttp) (6; 10.0 mg, 0.014 mmol), KOH (7.7 mg, 0.137 mmol), <sup>t</sup>BuOH (65.5  $\mu$ L, 0.687 mmol), and  $\beta$ -bromostyrene (2; 17.5  $\mu$ L, 0.137 mmol) were added to benzene (1.0 mL). The mixture was heated to 120 °C for 20 h. The reaction was incomplete. Benzene solvent was removed by vacuum distillation. Co(ttp)(styryl) (7) was estimated in 30% yield from <sup>1</sup>H NMR of the crude mixture. Reaction of Co(ttp) with  $\beta$ -Bromostyrene without <sup>t</sup>BuOH. Co(ttp) (6; 10.0 mg, 0.014 mmol), KOH (7.7 mg, 0.137 mmol), and  $\beta$ -bromostyrene (2; 17.5  $\mu$ L, 0.137 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 120 °C for 20 h. The reaction was incomplete. Benzene solvent was removed by vacuum distillation. Co(ttp)(styryl) (7) was estimated in 28% yield from <sup>1</sup>H NMR of the crude mixture.

Reaction of Co(ttp) with  $\beta$ -Bromostyrene at 90 °C. Co(ttp) (6; 10.0 mg, 0.014 mmol), KOH (7.7 mg, 0.137 mmol), 'BuOH (65.5  $\mu$ L, 0.687 mmol), and  $\beta$ -bromostyrene (2; 17.5  $\mu$ L, 0.137 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 90 °C for 20 h. The reaction was incomplete. Benzene solvent was removed by vacuum distillation. Co(ttp)(styryl) (7) was estimated in 5% yield from <sup>1</sup>H NMR of the crude mixture.

*Reaction of Co(ttp) with* β-Bromostyrene at 150 °C. Co(ttp) (6; 10.0 mg, 0.014 mmol), KOH (7.7 mg, 0.137 mmol), <sup>t</sup>BuOH (65.5 µL, 0.687 mmol), and β-bromostyrene (2; 17.5 µL, 0.137 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 150 °C for 20 h. The reaction was incomplete. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on alumina with the addition of H<sub>2</sub>O (v/v 10/1) with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (4:1) solvent mixture as eluent. The red solid product Co(ttp)(styryl) (7; 2.8 mg, 0.003 mmol, 25%) was collected.

*Reaction of Co(ttp) with* β-Bromostyrene at 180 °C. Co(ttp) (6; 10.0 mg, 0.014 mmol), KOH (7.7 mg, 0.137 mmol), <sup>t</sup>BuOH (65.5 µL, 0.687 mmol), and β-bromostyrene (2; 17.5 µL, 0.137 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 180 °C for 20 h. The reaction was incomplete. Benzene solvent was removed by vacuum distillation. Co(ttp)(styryl) (7) was estimated in 20% yield from <sup>1</sup>H NMR of the crude mixture. The organic fraction obtained after column chromatography on alumina with the addition of H<sub>2</sub>O (v/v 10/1) with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (4/1) solvent mixture as eluent was analyzed by GC-MS, and stilbene was detected.

**Reactivity of [M^{II}(ttp)]\_2 with \beta-Bromostyrene.** Reaction of  $[Ir^{II}(ttp)]_2$  with  $\beta$ -Bromostyrene.  $[Ir^{II}(ttp)]_2$  (2.0 mg, 0.001 mmol) and  $\beta$ -bromostyrene (2; 0.3  $\mu$ L, 0.002 mmol) were added to  $C_6D_6$  (0.5 mL). The mixture was allowed to react at room temperature. After 25 min,  $Ir^{III}(ttp)Br$  (1c) in 39% NMR yield and  $Ir^{III}(ttp)(styryl)$  (3) in 59% NMR yield were obtained.

Reaction of  $[Rh^{II}(ttp)]_2$  with  $\beta$ -Bromostyrene.  $[Rh^{II}(ttp)]_2$  (0.4 mg, 0.001 mmol) and  $\beta$ -bromostyrene (2; 0.1  $\mu$ L, 0.001 mmol) were added to  $C_6D_6$  (0.5 mL). The mixture was allowed to react at room temperature. After 25 min,  $Rh^{III}(ttp)Br$  (4b) in 47% NMR yield and  $Rh^{III}(ttp)(styryl)$  (5) in 53% NMR yield were obtained.

**Reaction of Ir(ttp)(CO)Cl with**  $\beta$ -Bromostyrene and Bromobenzene. Ir(ttp)(CO)Cl (1a; 10.0 mg, 0.011 mmol), K<sub>2</sub>CO<sub>3</sub> (29.9 mg, 0.216 mmol), bromobenzene (8; 11.5  $\mu$ L, 0.110 mmol), and  $\beta$ -bromostyrene (2; 14.0  $\mu$ L, 0.110 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze–pump–thaw cycles, purged with N<sub>2</sub>, and heated to 180 °C for 39 h. Benzene solvent was removed by vacuum distillation. The reaction mixture was worked up by extraction with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The combined organic extract was dried with MgSO<sub>4</sub>, filtered, and rotary evaporated. Excess  $\beta$ -bromostyrene and bromobenzene were removed by washing the reaction mixture with hexane, and the dark red solid Ir(ttp)(styryl) (3; 9.4 mg, 0.010 mmol, 89%) was obtained.

Reaction of Rh(ttp)Cl with with  $\beta$ -Bromostyrene and Bromobenzene. Rh(ttp)Cl (4a; 10.0 mg, 0.012 mmol), K<sub>2</sub>CO<sub>3</sub> (17.1 mg, 0.124 mmol), bromobenzene (8; 13.0  $\mu$ L, 0.124 mmol), and  $\beta$ -bromostyrene (2; 16  $\mu$ L, 0.124 mmol) were added to benzene (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N<sub>2</sub>, and heated to 120 °C for 18 h. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) solvent mixture as eluent. The red solid product Rh(ttp)(styryl) (5; 7.8 mg, 0.008 mmol, 73%) was collected.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00228.

Crystallographic data for Rh(ttp)(styryl) and <sup>1</sup>H and <sup>13</sup>C NMR spectra (PDF)

Crystallographic data for Rh(ttp)(styryl) (CIF)

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#### Notes

The authors declare no competing financial interest.

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