Inorg. Chem. **2009**, *48*, 1198−1206

Chelation-Assisted Carbon-Halogen Bond Activation by a Rhodium(I) Complex

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Received October 2, 2008

Chelation-assisted activation of C−X bonds (X = Cl, Br, and I) took place in the reaction of $[Rh(PPh_3)_2(acetone)_2]^+$ and 2-(2-halophenyl)pyridine or 10-halobenzo[*h*]quinoline. A series of 16-electron five-coordinate cationic rhodium(III) monohalide complexes was synthesized at room temperature. Neutral octahedral rhodium(III) dihalide complexes were obtained when the corresponding cationic monohalide complexes were further heated in acetone. Rhodium and iridium diiodides with these cyclometalation motifs could be alternatively synthesized from the reaction of the corresponding cyclometalated hydride complexes and I_2. X-ray crystal structures of representative monohalide and dihalide complexes are reported. Octahedral rhodium(III) dihalide complexes are active catalysts for the dimerization of terminal alkynes, while 16-electron cationic rhodium(III) monohalides are inactive.

Introduction

Haloarenes are ubiquitously used as organic substrates in catalysis. The interactions between aryl halides and low-valent transition metals often entail carbon−halide bond oxidative addition, which is a key step in transition-metal-catalyzed cross-coupling reactions involving haloarenes.[1] Oxidative addition reactions of aryl halides have been studied mostly for group 10 metals, particularly for Pd(0).[2,3] Catalytic functionalization of C_{aryl}−Cl bonds has also been achieved in cross-coupling reactions, although C_{aryl}−Cl bonds have relatively high dissociation energy.[4,5] As a contrast to the tremendously ample examples of carbon−halogen oxidative addition to Pd(0), C_{aryl}−halogen oxidative addition is less common for Co(I), Rh(I), and Ir(I) complexes.[6−16] The generation of such group

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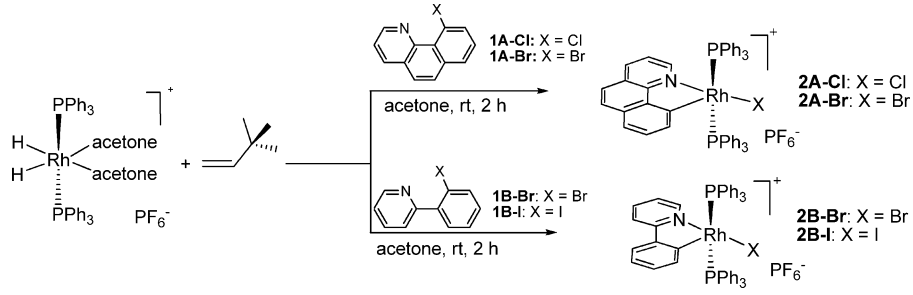
10.1021/ic801878e CCC: $40.75
Published on Web 12/23/2008

Scheme 1. Synthesis of Five-Coordinate Rh(III) Halide Complexes



9 metal aryl species followed by further functionalization entails synthetically important rhodium-catalyzed C−C coupling reactions,[17] which is typically achievable with Pd(0) complexes. Recent examples of C_{aryl}−Cl oxidative addition for rhodium and iridium are almost limited to (PNP)M,[7] $[Ir(CO)(PPh_3)_2]^+$,[8] (Phebox)$Rh(H_2O)Cl_2$,[9] $RhCl_3(py)_3$,[10] $Rh(PCy_3)_2(H)(Cl)_2$,[11] Rh(diiminate)(COD),[12] $Rh(PPh_3)_3F$,[13] $[Rh(coe)_2Cl]_2$,[14] (NNN)RhX,[15] cyclometalated phosphinimine rhodium(I) complexes,[16] and a low-coordinate Rh(I) phosphine system.[18]

Weller and co-workers[18] have recently reported intermolecular C_{aryl}−Cl activation that took place on $[Rh(P^tBu_3)_2L_2]BAr_4^F$ (L = weakly coordinating ligands or solvent molecules), which is generated in situ from the 14-electron $[Rh(H)_2(P^tBu_3)_2]BAr_4^F$ precursor. The high reactivity of this system likely results from the electron-rich character of the metal and the readily accessible coordination sites. It has been recently reported that $[Rh(PPh_3)_2(acetone)_2]^+$, $[Rh(H)_2(PPh_3)_2(acetone)_2]^+$, and $[Ir(H)_2(PPh_3)_2(acetone)_2]^+$ could mediate the intramolecular C−H activation of arenes, provided there is sufficient chelation assistance from chelating groups such as imines.[19,20] In this context, we are interested in the $[Rh(PPh_3)_2(acetone)_2]^+$ system for the activation of C_{aryl}−halogen bonds. We feel that this rhodium(I) system might also achieve this goal owing to the low valence of this rhodium complex and high lability of acetone ligands. It is also important to investigate the selectivity of C_{aryl}−H versus C_{aryl}−X activation when these bonds are both accessible. Selective C−H activation in the presence of C_{aryl}−Cl or C_{aryl}−Br bonds has been reported for Pd, Rh, Ir, and Au systems.[7,21]

We now report activation of C_{aryl}−X (X = Cl, Br, and I) bonds by $[Rh(PPh_3)_2(acetone)_2]^+$ under mild conditions by oxidative addition assisted by prior substrate coordination. Different rhodium(III) halide products were obtained under different reaction conditions.

Results and Discussion

The $[Rh(PPh_3)_2(acetone)_2]^+$ complex is the dehydrogenation product of $[Rh(H)_2(PPh_3)_2(acetone)_2]^+$, which could be synthesized by bubbling H_2 through a suspension of $[Rh(NBD)(PPh_3)_2]^+$ (NBD = norbornadiene) in acetone.[22] No attempt was made to isolate the dihydride product due to its poor stability. On the basis of related iridium dihydride chemistry,[7,23] the addition of a hydrogen acceptor such as *tert*-butylethylene (TBE) to this rhodium(III) dihydride should reversibly strip the hydride ligands and afford the proposed $[Rh(PPh_3)_2(acetone)_2]^+$ complex in situ, although an alternative access to this complex is also known.[19] Here, only $[Rh(PPh_3)_2(acetone)_2]^+$ generated in situ was utilized throughout this work.

Attempts to activate the C−X bonds in iodobenzene or 2-bromopyridine by reacting it with $[Rh(H)_2(PPh_3)_2(acetone)_2]PF_6$ and TBE in acetone resulted in a mixture of unidentifiable species. Thus, we focused on C−X activation with chelation assistance. Stirring a mixture of 10-chlorobenzo[*h*]quinoline (**1A-Cl**), TBE (20 equiv), and $[Rh(H)_2(PPh_3)_2(acetone)_2]PF_6$ in acetone slowly led to a yellow precipitate (**2A-Cl**) at ambient temperature (Scheme 1). The resulting complex **2A-Cl** was isolated in 89% yield and was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. In the ^1H NMR spectrum, neither hydride resonance signal nor any signal of ligated acetone could be detected. In the ^{13}C NMR spectrum, a characteristic quaternary carbon signal at δ 154.2 (dt, $^1J_{RhC}$ = 27.7 Hz, $^2J_{PC}$ = 9.5 Hz) was detected and was assigned to Rh−*C*, suggestive of the metalation of the ligand, likely at the C10 position facilitated by chelation assitance. In the ^{31}P NMR spectrum, a doublet signal (δ 13.87, $^1J_{RhP}$ = 95.0 Hz) was

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Table 1. Crystallographic Data for Complexes **2A-Br**, **2B-I**·0.5CH_2Cl_2, and **4A-Br$_2$**·0.5MeCN·Et_2O

	2A-Br	**2B-I**·0.5CH_2Cl_2	**4A-Br$_2$**·0.5MeCN·Et_2O
empirical formula	$C_{48}H_{38}BrF_6NP_3Rh$	$C_{47.5}$ $H_{39}ClF_6INP_3Rh$	$C_{54}H_{49.5}Br_2N_{1.5}OP_2Rh$
fw (g mol^{-1})	1030.54	1095.97	1060.12
radiation, λ	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
T (K)	173(2)	173(2)	173(2)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	P_{bca}	$P2_1/n$	$P2_1/c$
a (Å)	19.7286(5)	12.6321(3)	12.0657(3)
b (Å)	19.7688(6)	20.3275(4)	18.4792(4)
c (Å)	22.2111(7)	17.1309(4)	20.7142(5)
β (deg)	90	91.5330(10)	96.1040(10)°
V (Å^3)	8662.6(4)	4397.28(17)	4592.35(19)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.580	1.655	1.533
μ (mm^{-1})	1.490	1.321	2.223
cryst size (mm)	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.05	0.20 × 0.16 × 0.10
total, unique no. of rflns	473175, 13285	106611, 13627	60594, 14723
R_{int}	0.0864	0.0467	0.0720
data, restraints, params	13285, 0, 550	13627, 0, 550	14723, 0, 561
R, R_w (all data)	0.0361, 0.0900	0.0555, 0.1044	0.1106, 0.1568
GOF	1.128	**1.122**	1.052
min., max. resid dens (eÅ^{-3})	−1.283, 1.098	−1.264, 1.060	−1.377, 1.059

observed for two equivalent phosphines, indicating their *trans* orientation. The haloarene starting materials can be extended to the bromo analogue (**1A-Br)** and 2-(2-halophenyl)pyridines (**1B-Br** and **1B-I**), and the corresponding monohalide products were isolated in 86−92% yield. All of these rhodium monohalide complexes are soluble in CH_2Cl_2 and MeCN but are sparingly soluble in acetone. Complexes **2A-Br**, **2B-Br**, and **2B-I** are relatively stable in CH_3CN, but they decompose in CH_2Cl_2 solutions to give dihalide complexes among other products (vide infra).

Single crystals of **2A-Br** and **2B-I** suitable for X-ray crystallographic studies were obtained by the slow diffusion of diethyl ether to their dichloromethane solutions at −20 °C. X-ray crystallography unambiguously confirmed the identity of **2A-Br** and **2B-I** as rather rare five-coordinate rhodium(III) halide complexes (Table 1 and Figures 1 and 2). In the crystal structures of **2A-Br** and **2B-I**, the PPh_3 ligands are trans to each other and the coordination sphere involves five regular bonds, while the sixth coordination site is empty and is trans to the high trans-effect aryl ligand. This type of five-coordinate binding mode has been observed mostly for Rh, Ir, and Ru pincer complexes.[7,18,24] The Rh−N [2.047(2) Å] and Rh−C [1.991(3) Å] distances in the metalacycles of **2A-Br** are nearly identical to the corresponding ones in **2B-I**. The phenyl and the pyridyl rings in **2B-I** are essentially coplanar so that there is negligible difference between the N(1)−Rh(1)−C(19) angle of these two complexes [81.43(3)° for **2A-Br** and 79.49(9)° for **2B-I**]. The C(19)−Rh(1)−Br(1) angle in **2A-Br** [105.59(8)°] deviates significantly from 90°, and this is even more pronounced for **2B-I** [C(19)−Rh(1)−I(1) = 114.44(7)°], which is possibly due to the steric repulsion caused by the bulky iodide ligand.

We noted that both *ortho*-C−X and *ortho*-C−H bonds in **1B-Br** or **1B-I** can be potentially activated. However, only

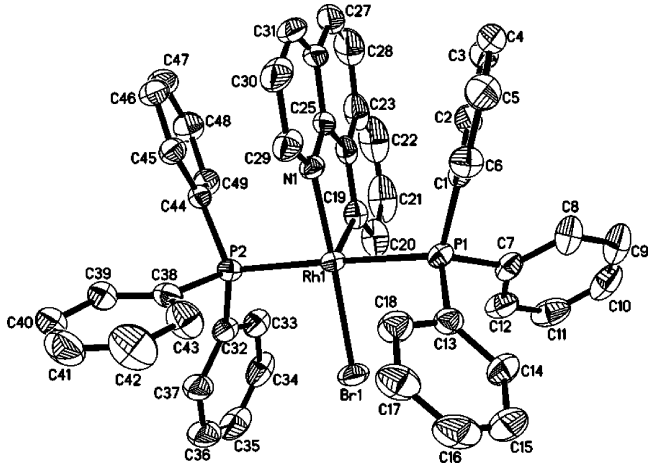


Figure 1. Molecular structure (ORTEP) of the cation of **2A-Br** with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Rh1−Br1, 2.4465(3); Rh1−C19, 1.991(3); Rh1−N1, 2.047(2); Rh1−P1,2.3675(7);Rh1−P2,2.3737(7);P1−Rh1−P2,177.01(3);N1−Rh1−C19, 81.43(3); C19−Rh1−Br1, 105.59(8).

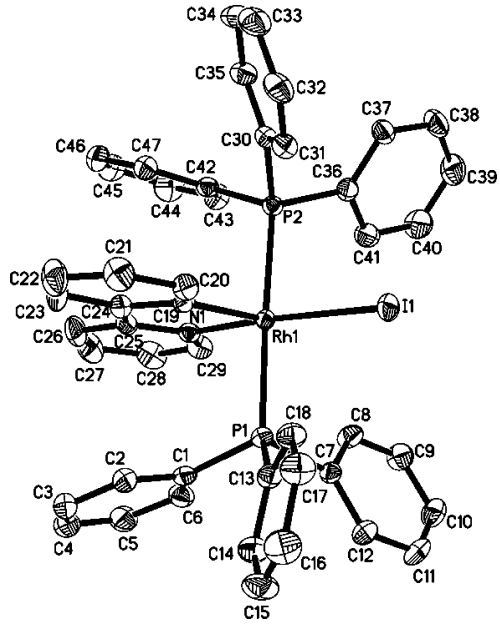
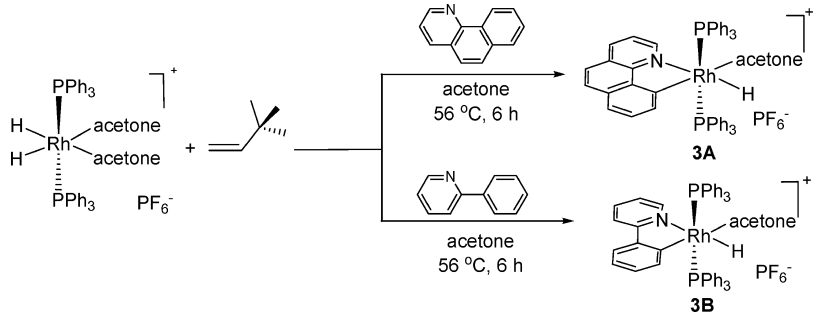


Figure 2. Molecular structure (ORTEP) of the cation of **2B-I**·0.5CH_2Cl_2 with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Rh1−I1, 2.6399(2); Rh1−C19, 1.990(2); Rh1−N1, 2.053(2); Rh1−P1, 2.3605(7); Rh1−P2, 2.3747(7); P1−Rh1−P2, 176.97(2); N1−Rh1−C19, 79.49(9); C19−Rh1−I1, 114.44(7).

Scheme 2. Synthesis of Rhodium Hydride Complexes

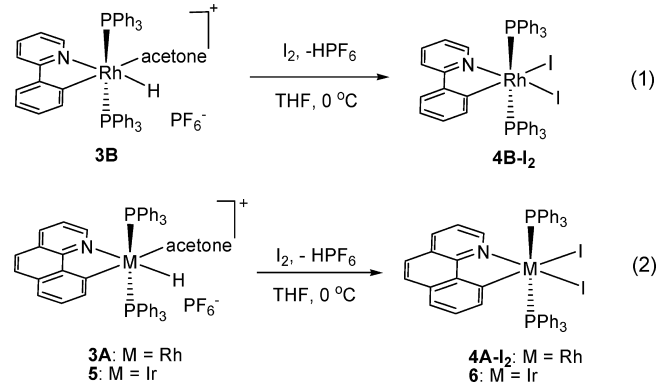


the C−X activation was observed. To explore the activation of C−H bonds, benzo[*h*]quinoline and 2-phenylpyridine were allowed to react with $[Rh(H)_2(PPh_3)_2(acetone)_2]^+$. The activation of C−H bonds in these arenes did proceed, but only at elevated temperatures (>50 °C), to afford isolable hydride complexes **3A** and **3B** in 86% and 87% yields, respectively (Scheme 2), which have been fully characterized. In the ^{1}H NMR spectrum of **3A**, the hydride resonates at δ −12.29 (dt, $^1J_{RhH}$ = 16.6 Hz, $^2J_{PH}$ = 11. 0 Hz), and the ligated acetone was also detected. These results indicate that the activation of the ortho C−H bonds in **1B-Br** and **1B-I** likely has a higher barrier. The differences between the coordination numbers of **2A-Cl** and **-Br** (or **2B-Br**, **I**) and **3A** (or **3B**) seem accountable to steric effects: since electronically one would predict that complexes **2A-Cl** and **-Br** (or **2B-Br**, **I**) should be more electrophilic than **3A** (or **3B**) and should have a stronger tendency of acetone binding.

Heating an acetone solution of **1A-Br** (1.2 equiv), $[Rh(H)_2(PPh_3)_2(acetone)_2]^+$, and TBE (20 equiv) under reflux, however, afforded a precipitate, and product **4A-Br$_2$** was isolated in analytically pure form in 40% yield (Scheme 3). Complex **4A-Br$_2$** could also be obtained in similar yield by heating an acetone suspension of **2A-Br**. These results indicate that **2A-Br** is an intermediate leading to the decomposition product **4A-Br$_2$**. ^{31}P NMR analysis of the acetone solution from which **4A-Br$_2$** precipitated shows a major peak at δ 25.2 (d, $^2J_{RhP}$ = 100 Hz), and the ESI-MS spectrum of this acetone solution gives a peak of *m*/*e* = 391.62. Both this *m*/*e* value and the isotopic pattern agree with a structure of $[(N^C)Rh(PPh_3)_2]^{2+}$ in mass spectrometry. The corresponding species in acetone solution is tentatively assigned to $[(N^C)Rh(PPh_3)_2(acetone)]^{2+}$. However, no such analytically pure product could be isolated. We propose that **2A-Br** reversibly dimerizes to a dicationic bridging bromide intermediate which undergoes an irreversible ligand redistribution process to give these two products as a major decomposition pathway (Scheme 4). Similar reactions of the shifting of two bridging halide ligands to one metal center have been reported for Rh, Ir, and Pd.[25]

Complex **4A-Br$_2$** has been unambiguously identified by NMR spectroscopy, X-ray crystallography, and elemental analysis. In the ^{31}P or ^{19}F NMR spectrum, no resonance signal of PF_6^- could be detected, indicating that **4A-Br$_2$** is a neutral complex. The ^{31}P NMR spectrum (CD_2Cl_2) shows that the PPh_3 ligands are equivalent (δ 14.6, d, $^1J_{RhP}$ = 91.6 Hz). Analogously, neutral rhodium(III) dihalides **4B-Br$_2$** and **4B-I$_2$** could be synthesized from **1B-Br** and **1B-I** with 38% and 42% yields, respectively (Scheme 4). These dihalide complexes have poor solubility in common organic solvents and are sparingly soluble in CH_2Cl_2.

Alternatively, rhodium(III) diiodide complexes (such as **4B-I$_2$**) could be synthesized from the reaction of the corresponding rhodium hydride (such as **3B**) and I_2 in THF (eq 1), and the products obtained via these two routes have identical spectroscopic data. The scope of this reaction could also be extended to its iridium analogue (complex **5**, eq 2). One possible mechanism to account for this transformation is that I_2 oxidatively adds to the metal center to give a rhodium(V) or iridium(V) hydride diiodide complex, followed by proton abstraction. Conversion of transition metal hydrides to metal halides has been reported using various halogenating reagents.[26]



Single crystals of complex **4A-Br$_2$** were obtained by the slow diffusion of diethyl ether into its acetonitrile solution.

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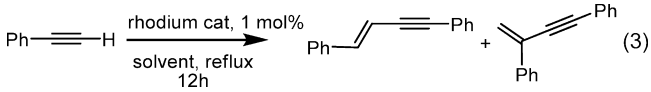
Table 2. Screening of Rhodium Catalysts for the Dimerization of Phenylacetylene[a]

entry	catalyst	solvent	temp (°C)	selectivity (trans:gem)	NMR yield of trans product (%)[b]
1	**4A-Br$_2$**	acetone	56	72:28	40
2	**4A-Br$_2$**	CH_2Cl_2	40	82:18	56
3	**4A-I$_2$**	CH_2Cl_2	40	90:10	69
4	**4B−Br$_2$**	CH_2Cl_2	40	77:23	49
5	**4B−I$_2$**	CH_2Cl_2	40	90:10	70
6	**4B−I$_2$**	acetone	56	70:30	48
7	**4B−I$_2$**	CH_2ClCH_2Cl	83	65:35	31
8	**2A-Br**	CH_2Cl_2	40		<5
9	**4A-Br$_2$**/$NaBArF_4$	CH_2Cl_2	40		<5
10	**2B-I**	CH_2Cl_2	40		<5
11	**4B−I$_2$**/PPh_3 (1:6)	CH_2Cl_2	40		<5

[a] Conditions: 0.8 mmol phenylacetylene, 0.008 mmol rhodium catalyst, 4 mL solvent, 12 h, reflux. [b] NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

One equivalent of ether and half an equivalent of acetonitrile cocrystallized with **4A-Br$_2$**. X-ray crystallography unambiguously confirmed the identity of this complex (Figure 3 and Table 1). The Rh(1)−C(1) distance [2.028(4) Å] here is slightly longer than the corresponding one in **2A-Br** [1.991(3) Å]. In complex **4A-Br$_2$**, the Rh(1)−Br(1) length is significantly longer (ca. 0.1 Å longer) than that of the Rh(1)−Br(2) bond, undoubtedly due to the significantly high trans influence of the aryl ligand compared with the quinoline N atom. Either of the Rh−Br bonds in **4A-Br$_2$** is at least 0.05 Å longer than the Rh−Br bond in **2A-Br**. In contrast to complex **2A-Br**, the C(1)−Rh(1)−Br(2) angle [90.13(12)°] in **4A-Br$_2$** is essentially 90°.

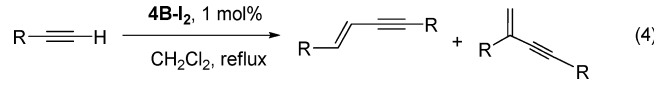
Rhodium complexes have been widely used in the dimerization of terminal alkynes, and the most common dimerization products are *trans*-enynes, although *cis*- or *gem*-enynes are also known.[27] Our investigations of the applications of these rhodium monohalide and dihalide complexes started from the catalytic dimerization of phenylacetylene (eq 3). Both rhodium monohalide and dihalide complexes have been screened with 1 mol % loading under refluxing conditions, and the results are given in Table 2.



(3)

The 18-electron neutral rhodium dihalide complexes are active to different extents in catalyzing the dimerization of phenylacetylene, and in all cases the *trans*-enyne is the major product and the *gem*-enyne is the only minor product based on ^{1}H NMR analysis. Catalyst screening in different solvents under refluxing conditions indicates that dichloromethane seems to be the optimal solvent (Table 2). Screening of rhodium catalysts with the same metallacycle entity but with different dihalides shows that diiodide complexes give higher activity and selectivity than dibromides (entry 2 vs entry 3; entry 4 vs entry 5). The activity and selectivity are essentially the same for rhodium catalysts with the same dihalides but with a different metallacyclic motif (entry 3 vs entry 5; entry 2 vs entry 4). The highest NMR yield obtained for the *anti*-enyne is 70%. To our surprise, 16-electron ionic monohalide complexes **2A-Br** and **2B-I** showed very poor NMR yields (entries 8 and 10). This is consistent with the result obtained when a combination of **4A-Br$_2$** and $NaBAr_4^F$ was used in a 1 to 1.2 ratio (entry 9). Here, the addition of $NaBAr_4^F$ inhibits this reaction, and this system is in fact equivalent to the cation of **2A-Br** generated in situ: the bromide trans to the aryl ligand should be readily removed under these conditions. We also noted that this dimerzation reaction is inhibited by the addition of PPh_3 (entry 11, Table 2).

Complex **4B−I$_2$** was then retained to further study the scope of this type of catalytic reaction (eq 4) in CH_2Cl_2, and NMR yields are given in Table 3. Terminal alkyne substrates with electron-rich or electron-poor aryl substituents all dimerize, with the lowest trans to gem selectivity (87:13) observed for *para*-$NO_2(C_6H_4)C{\equiv}CH$ (entry 5). Alkynes with electron-poor aryl groups tend to have low reactivity but still give yields comparable to that of phenylacetylene (entries 4−5). For $EtOC(O)C{\equiv}CH$, the dimerization is highly selective, although only 65% NMR yield was obtained (entry 6).



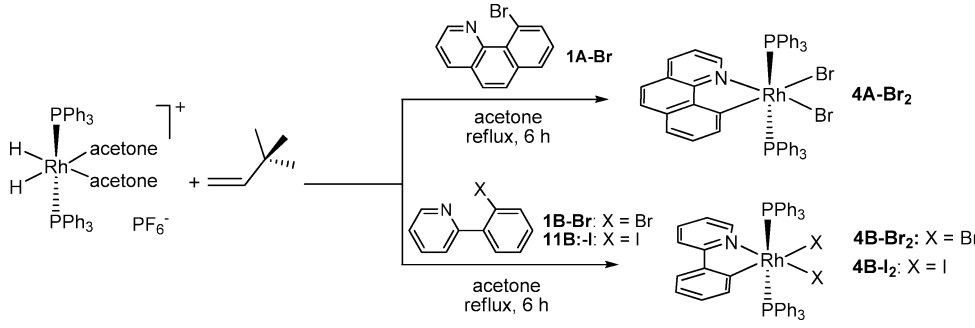
(4)

Compared with other representative systems of catalytic alkyne dimerization,[16] the rhodium dihalides show lower catalytic activity. This is likely due to the 18-electron structures of these complexes with active species. Instead, a vacant coordination site should be generated to accommodate an incoming alkyne substrate. This could be achieved by (i) the dissociation of a halide ligand, particularly the labile halide that is trans to the aryl ligand, (ii) dechelation of the nitrogen arm, or (iii) dissociation of one of the phosphine ligands. Dissociation of a labile halide ligand (such as in **4A-Br$_2$**) seems unlikely since the resulting 16-electron cationic species is in fact the cation part of the corresponding rhodium monohalide (such as **2A-Br**), which proved to be inactive in catalysis (entries 8−9, Table 2). The likelihood of the dissociation of the nitrogen arm of the chelating ligand can be evaluated by comparing the activity of rhodium complexes with different cyclometalated motifs. It is known that dissociation of the nitrogen arm in a flexible chelating system (such as in 2-phenylpyridyl) should have a lower barrier than that in a rigid one (such as in benzo-[*h*]quinolyl).[28] In fact, both activity and selectivity are essentially the same[29] for rhodium catalysts with different metalacyclic motifs (entries 3 and 5, Table 2), which indicates that nitrogen arm dissociation is unlikely.

To examine the likelihood of phosphine dissociation, we then compared complexes **2B-I** and **4B-I$_2$** for phosphine exchange reactions. In two separate reactions, **2B-I** or equimolar **4B-I$_2$** was allowed to react with 10 equiv of tris(*p*-fluorophenyl)phosphine in CH_2Cl_2 for 1 h (Scheme 5). The ratios of starting materials, monophosphine substitution

(27) (a) Weng, W.; Guo, C.; Celenligil-Cetin, R.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2006**, 197. (b) Lee, C.-C.; Lin, Y.-C.; Liu, Y.-H.; Wang, Y. *Organometallics* **2005**, *24*, 136. (c) Katagiri, T.; Tsurugi, H.; Satoh, T.; Miura, M. *Chem. Commun.* **2008**, 3405. (d) Nishimura, T.; Guo, X.-X.; Ohnishi, K.; Hayashi, T. *Adv. Syn. Catal.* **2007**, *349*, 2669. (e) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731.

Scheme 3. Synthesis of 18-Electron Rhodium Dihalide Complexes



Scheme 4. Formation of Complex **4A-Br$_2$**

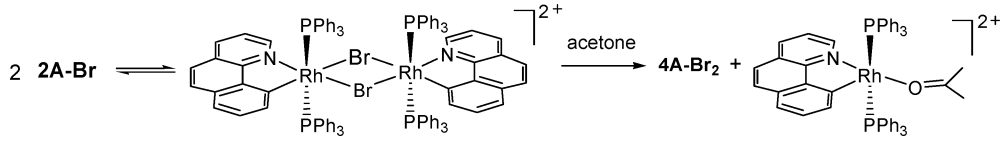


Table 3. Dimerization of Terminal Alkynes Catalyzed by Complex **4B-I$_2$**[a]

entry	R	time (h)	Selectivity (*trans*: *gem*)	NMR yield of *trans* product (%)[b]
1	Ph−	12	90:10	70
2	*p*-$CH_3(C_6H_4)$−	12	91:9	88
3	*p*-$CH_3O(C_6H_4)$−	12	94:6	94
4	*p*-$CF_3(C_6H_4)$−	24	98:2	71
5	*p*-$NO_2(C_6H_4)$−	24	87:13	70
6	EtO(O)C−	12	100:0	65

[a] Conditions: 0.8 mmol alkyne, 0.008 mmol rhodium catalyst, 4 mL solvent, 12 h, reflux.. [b] NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

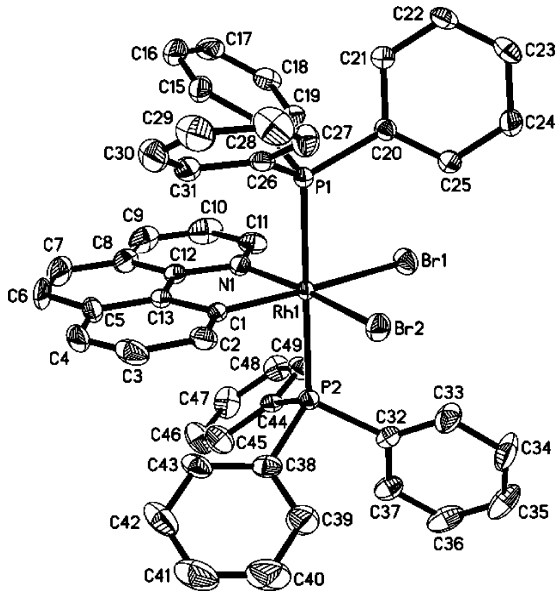


Figure 3. Molecular structure (ORTEP) of **4A-Br$_2$**·0.5MeCN·$C_4H_{10}O$ with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Rh1−Br1, 2.6022(5); Rh1−Br2, 2.5053(5); Rh1−C1, 2.028(4); Rh1−N1, 2.061(3); Rh1−P1, 2.3725(10); Rh1−P2, 2.3913(11); P1−Rh1−P2, 179.49(4); N1−Rh1−C1, 81.85(15); C1−Rh1−Br2, 90.13(12).

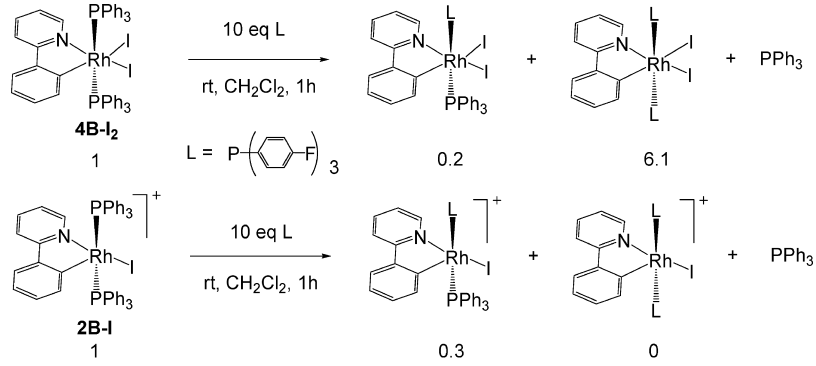
products, and diphosphine substitution products were analyzed by ^{31}P NMR spectroscopy and are given in Scheme 5. The phosphine substitution reaction of **4B-I$_2$** is significantly faster than that of **2B-I**. The correlation between rates of phosphine substitution and catalytic activity of complexes **2B-I** and **4B-I$_2$** agrees with the hypothesis that the five-coordinate species derived from the dissociation of a PPh_3 ligand is the most likely active catalyst. This hypothesis is also consistent with the fact that rhodium diiodides possess higher catalytic activity than rhodium dibromides (entries 4 and 5, Table 2): the dissociation of a PPh_3 ligand from a rhodium diiodide complex is favored for both electronic and steric reasons. Electronically, the metal center is relatively more electron-rich for diiodide complexes. Sterically, the large bulk of iodides provides steric repulsion to facilitate the departure of a phosphine ligand. Both of these factors will favor the dissociation of a phosphine ligand to generate an active 16-electron intermediate.

Conclusions

We have achieved nitrogen coordination-assisted activation of C−X bonds (X = Cl, Br, and I) in the reaction of 2-(2-halophenyl)pyridine or 10-halobenzo[*h*]quinoline and $[Rh(PPh_3)_2(acetone)_2]^+$. A series of rather rare five-coordinate 16-electron cationic rhodium(III) halides has been synthesized under mild conditions. However, reactions of these haloarenes and $[Rh(PPh_3)_2(acetone)_2]^+$ in acetone under reflux afforded neutral octahedral rhodium(III) dihalide complexes. Alternatively, rhodium and iridium diiodides with these cyclometalation motifs could be synthesized from the corresponding hydride complexes via hydride−iodide exchange. X-ray crystal structures of representative mono- and dihalide complexes have been reported. The aryl ligands are trans to vacant coordination sites in these five-coordinate monohalide complexes.

The catalytic activity of these rhodium(III) halide complexes has been assessed for the dimerization of terminal alkynes. The 18-electron rhodoium dihalides are much more active catalysts, while cationic rhodium monohalide complexes are essentially inactive. Screening of catalysts shows that such rhodium diiodide complexes possess higher catalytic activity than the dibromide complexes. A five-coordinate phosphine dissociation product of a dihalide complex has been proposed as the active species in the catalytic cycle.

Scheme 5



Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques. All chemicals were used as received without any further purification unless otherwise specified. All solvents were degassed and dried by standard techniques. NMR spectra were obtained on a Bruker DPX 300, AMX 400 or 500, or JEOL ECA 400 spectrometer. The chemical shift is given as dimensionless δ values and is referenced relative to $SiMe_4$ for ^1H and ^{13}C NMR spectroscopy. Elemental analyses were performed at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer.

Compounds **1A-Cl**, **1A-Br**, **1B-Br**, and **1B-I** were prepared on the basis of a recent report.[30] Some of the ^{13}C NMR spectra of dihalide complexes could not be obtained with acceptable signal-to-noise ratios due to their poor solubility in common solvents.

Compound 2A-Cl. To a suspension of $[Rh(NBD)(PPh_3)_2]PF_6$ (100 mg, 0.116 mmol) in acetone (5 mL) was bubbled H_2 for 15 min at 0 °C, during which time the color of the solution changed from red to yellow. *tert*-Butylethylene (0.5 mL) and 10-chlorobenzo[*h*]quinoline (30 mg, 0.139 mmol) were then added to the solution and were stirred at room temperature for 2 h. The resulting precipitate was then filtered and washed with 2 × 20 mL diethyl ether to give a yellow powder, **2A-Cl**. Yield: 102 mg (0.103 mmol, 89%). ^1H NMR (δ, 400 MHz, CD_3CN, 298 K): 6.85 (dd, ^3J = 8.0 Hz, ^3J = 5.6 Hz, 1H), 7.05−7.09 (m, 12H, P*Ph*$_3$), 7.12−7.21 [m, 13H, 12H (P*Ph*$_3$) + 1H ($C_{13}H_8N$)], 7.26 (m, 6H, P*Ph*$_3$), 7.33 (d, ^3J = 8.0 Hz, 1H), 7.58 (d, ^3J = 7.8 Hz, 1H), 7.71−7.74 (m, 2H), 7.80 (d, ^3J = 8.0 Hz, 1H), 8.15 (d, ^3J = 5.5 Hz, 1H). ^{31}P {^1H} NMR (δ, 162 MHz, CD_3CN, 298 K): −144.62 (m, $^1J_{F-P}$ = 706.5 Hz, *P*F_6), 13.87 (d, $^1J_{Rh-P}$ = 95.0 Hz, *P*Ph_3). ^{13}C {^1H} NMR (δ, 100 MHz, CD_3CN, 298 K): 122.08 (s), 122.38 (s), 123.64 (s), 127.02 (s), 127.90 (t, J_{P-C} = 4.8 Hz, P*Ph*$_3$), 128.70 (t, $^1J_{P-C}$ = 23.9 Hz, *ipso*-P*Ph*$_3$), 128.81 (s), 129.43 (s), 130.48 (s, *p*-P*Ph*$_3$), 133.29 (s), 133.74 (t, J_{P-C} = 4.8 Hz, P*Ph*$_3$), 136.25 (s), 137.55 (s), 139.27 (s), 150.03 (s), 152.56 (s), 154.18 (dt, $^1J_{Rh-C}$ = 27.7 Hz, $^2J_{P-C}$ = 9.5 Hz, *C*Rh). Anal. calcd for $C_{49}H_{38}ClF_6NP_3Rh$ (986.10): C, 59.68; H, 3.88; N, 1.42. Found: C, 59.66; H, 3.50; N, 1.73.

Compound 2A-Br. Complex **2A-Br** was synthesized by directly following the procedure for the preparation of **2A-Cl**. The reaction of $[Rh(NBD)(PPh_3)_2]PF_6$ (500 mg, 0.578 mmol) and 10-bromobenzo[*h*]quinoline (179 mg, 0.694 mmol) gave a yellow powder, **2A-Br**. Yield: 513 mg (0.497 mmol, 86%). ^1H NMR (δ, 400 MHz, CD_3CN, 298 K): 6.91 (dd, ^3J = 8.0 Hz, ^3J = 5.6 Hz, 1H), 7.05−7.12 (m, 24H, P*Ph*$_3$), 7.21 (t, ^3J = 7.8 Hz, 1H), 7.25−7.29 (m, 6H, P*Ph*$_3$), 7.36 (d, ^3J = 8.8 Hz, 1H), 7.63 (d, ^3J = 7.6 Hz, 1H), 7.78 (m, 2H), 7.85 (d, ^3J = 8.0 Hz, 1H), 8.19 (d, ^3J = 5.2 Hz, 1H). ^{31}P {^1H} NMR (δ, 162 MHz, CD_3CN, 298 K): −144.62 (m, $^1J_{F-P}$ = 706.7 Hz, *P*F_6), 14.62 (d, $^1J_{Rh-P}$ = 94.6 Hz, *P*Ph_3). ^{13}C {^1H} NMR (δ, 100 MHz, CD_3CN, 298 K): 122.09 (s), 122.98 (s), 123.63 (s), 127.17 (s), 127.75 (t, J_{P-C} = 4.88 Hz, P*Ph*$_3$), 128.77 (t, $^1J_{P-C}$ = 23.8 Hz, *ipso*-P*Ph*$_3$), 128.79 (s), 129.82 (s), 130.41 (s, *p*-P*Ph*$_3$), 133.31 (s), 133.93 (t, J_{P-C} = 5.0 Hz, P*Ph*$_3$), 136.29 (s), 138.96 (s), 138.44 (s), 139.31 (s), 149.82 (s), 152.48 (s), 154.38 (dt, $^1J_{Rh-C}$ = 27.8 Hz, $^2J_{P-C}$ = 10.5 Hz, *C*Rh). Anal. calcd for $C_{49}H_{38}BrF_6NP_3Rh$ (1030.55): C, 57.11; H, 3.72; N, 1.36. Found: C, 57.19; H, 3.27; N, 1.31.

Compound 2B-Br. Complex **2B-Br** was synthesized by directly following the procedure for the preparation of **2A-Cl**. The reaction of $[Rh(NBD)(PPh_3)_2]PF_6$ (100 mg, 0.116 mmol) and 2-(2-bromophenyl)pyridine (32 mg, 0.139 mmol) gave **2B-Br** as a yellow powder. Yield: 107 mg (0.107 mmol, 92%). ^1H NMR (δ, 400 MHz, CD_3CN, 298 K): 6.52 (t, ^3J = 6.6 Hz, 1H), 6.72 (t, ^3J = 7.6 Hz, 1H), 7.08 (t, ^3J = 7.6 Hz, 2H), 7.16−7.19 (m, 12H, P*Ph*$_3$), 7.23−7.25 [m, 13H, 12H (P*Ph*$_3$) + 1H ($C_{11}H_8N$)], 7.26 (m, 6H, P*Ph*$_3$), 7.30 (d, ^3J = 8.0 Hz, 1H), 7.35 (d, ^3J = 8.0 Hz, 1H), 7.88 (d, ^3J = 6.0 Hz, 1H). ^{31}P {^1H} NMR (δ, 162 MHz, CD_3CN, 298 K): −144.62 (m, $^1J_{F-P}$ = 705.8 Hz, *P*F_6), 14.95 (d, $^1J_{Rh-P}$ = 95.8 Hz, *P*Ph_3). ^{13}C {^1H} NMR (δ, 100 MHz, CD_3CN, 298 K): 119.92 (s), 123.64 (s), 123.82 (s), 124.12 (s), 128.00 (t, J_{P-C} = 4.8 Hz, P*Ph*$_3$), 129.06 (t, $^1J_{P-C}$ = 23.9 Hz, *ipso*-P*Ph*$_3$), 130.51 (s, *p*-P*Ph*$_3$), 130.85 (s), 131.54 (s), 134.28 (t, J_{P-C} = 4.8 Hz, P*Ph*$_3$), 137.96 (s), 140.92 (s), 143.73 (s), 150.56 (s), 157.93 (dt, $^1J_{Rh-C}$ = 26.7 Hz, $^2J_{P-C}$ = 9.5 Hz, *C*Rh). Anal. calcd for $C_{47}H_{38}BrF_6NP_3Rh$ (1006.53): C, 56.08; H, 3.81; N, 1.39. Found: C, 56.48; H, 4.22; N, 1.42.

Compound 2B-I. Complex **2B-I** was synthesized by directly following the procedure for the preparation of **2A-Cl**. The reaction of $[Rh(NBD)(PPh_3)_2]PF_6$ (500 mg, 0.578 mmol) and 2-(2-iodophenyl)pyridine (195 mg, 0.694 mmol) gave **2B-I** as an orange powder. Yield: 548 mg (0.520 mmol, 90%). ^1H NMR (δ, 300 MHz, CD_3CN, 298 K): 6.60 (t, ^3J = 6.4 Hz, 1H), 6.72 (t, ^3J = 8.5 Hz, 1H), 7.13−7.24 [m, 26H, 24H (P*Ph*$_3$) + 2H ($C_{11}H_8N$)], 7.31−7.40 [m, 7H, 6H (P*Ph*$_3$)+1H ($C_{11}H_8N$)], 7.45 (d, ^3J = 9.2 Hz, 1H), 7.74 (d, ^3J = 8.5 Hz, 1H), 7.94 (d, ^3J = 6.4 Hz, 1H). ^{31}P {^1H} NMR (δ, 162 MHz, CD_3CN, 298 K): −143.99 (m, $^1J_{F-P}$ = 703.5 Hz, *P*F_6), 16.15 (d, $^1J_{Rh-P}$ = 94.0 Hz, *P*Ph_3). ^{13}C {^1H} NMR (δ, 100 MHz, CD_3CN, 298 K): 120.19 (s), 123.76 (s), 123.95 (s), 124.05 (s), 127.85 (t, J_{P-C} = 4.8 Hz, P*Ph*$_3$), 129.56 (t, $^1J_{P-C}$ = 23.95 Hz, *ipso*-P*Ph*$_3$), 130.48 (s, *p*-P*Ph*$_3$), 131.39 (s), 134.59 (t, J_{P-C} = 5.8 Hz,

(28) Dick, A. R.; Kampf, J. W.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 12790.
(29) We have also confirmed that the yields and selectivity for **4A-Br$_2$** and **4B-Br$_2$** are essentially the same for the dimerization of phenylacetylene after 6 h.
(30) Kalyani, D.; Dick, A. R.; Anani, W. Q.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 11483.

P*Ph*$_3$), 138.06 (s), 143.77 (s), 144.11 (s), 150.10 (s), 158.06 (dt, $^1J_{Rh-C}$ = 26.8 Hz, $^2J_{P-C}$ = 10.5 Hz, *C*Rh), 163.61 (s). Anal. calcd for $C_{47}H_{38}IF_6NP_3Rh$ (1053.53): C, 53.58; H, 3.64; N, 1.33. Found: C, 53.17; H, 3.86; N, 1.44.

Complex 3A. To a suspension of [Rh(NBD)(PPh$_3$)$_2$]PF$_6$ (500 mg, 0.578 mmol) in acetone (8 mL) was bubbled H_2 for 15 min at 0 °C, during which time the color of the solution changed from red to light yellow. *tert*-Butylethylene (0.8 mL) and benzo[*h*]quinoline (124 mg, 0.694 mmol) were then added to the solution, and the mixture was refluxed for 5 h. The solution was concentrated to 0.5 mL under reduced pressure. The residue was washed with diethyl ether (2 × 20 mL) to give **3A** as a white powder. Yield: 502 mg (0.497 mmol, 86%). ^{1}H NMR (δ, 300 MHz, CD_3COCD_3, 295 K): −12.29 (dt, $^1J_{Rh-H}$ = 16.6 Hz, $^2J_{P-H}$ =11.0 Hz, 1H, Rh*H*), 2.06 (s, 6H, acetone), 6.96 (t, ^3J = 7.7 Hz, 1H), 7.05−7.38 [m, 32H, 2H ($C_{13}H_8N$) + 30H (P*Ph*$_3$)], 7.43 (d, ^3J = 7.7 Hz, 1H), 7.57 (d, ^3J = 8.8 Hz, 1H), 7.78 (dd, ^3J = 8.0 Hz, ^3J = 5.0 Hz, 1H), 8.16 (d, ^3J = 7.9 Hz, 1H), 9.79 (d, ^3J = 4.9 Hz, 1H). ^{31}P {^{1}H} NMR (δ, 121 MHz, CD_3COCD_3, 295 K): −143.56 (m, $^1J_{F-P}$ = 704.0 Hz, *P*F$_6$), 39.91 (d, $^1J_{Rh-P}$ = 114.3 Hz, *P*Ph$_3$). ^{13}C {^{1}H} NMR (δ, 100 MHz, CD_3COCD_3, 295 K): 120.52 (s), 122.44 (s), 122.83 (s), 126.83 (s), 127.31 (s), 128.08 (t, J_{P-C} = 4.7 Hz, P*Ph*$_3$), 128.60 (t, $^1J_{P-C}$ = 23.0 Hz, *ipso*-P*Ph*$_3$), 130.30 (s, *p*-P*Ph*$_3$), 133.36 (t, J_{P-C} = 5.6 Hz, P*Ph*$_3$), 134.73 (s), 135.73 (s), 138.44 (s), 139.65 (s), 148.19 (s), 150.71 (s), 153.08 (dt, $^1J_{Rh-C}$ = 31.0 Hz, $^2J_{P-C}$ = 11.2 Hz, *C*Rh), 205.26 (*C*O). Anal. calcd for $C_{54}H_{45}F_6NOP_3Rh$ (1009.74): C, 61.85; H, 4.49; N, 1.39. Found: C, 61.54; H, 4.95; N, 1.43.

Complex 3B. Complex **3B** was obtained as a white powder by directly following the synthesis of **3A**. Yield: 428 mg (0.44 mmol, 87%). ^{1}H NMR (δ, 300 MHz, CD_3COCD_3, 295 K): −12.26 (dt, 1H, $^1J_{Rh-H}$ = 15.6 Hz, $^2J_{P-H}$ =10.9 Hz, Rh−H), 2.06 (s, 6H, acetone), 6.50 (t, ^3J = 6.7 Hz, 1H), 6.87 (t, ^3J = 7.6 Hz, 1H), 7.03 (d, ^3J = 7.7 Hz, 1H), 7.12−7.42 [m, 33H, 3H ($C_{11}H_8N$) + 30H (P*Ph*$_3$)], 7.62 (t, ^3J = 6.8 Hz, 1H), 9.46 (d, ^3J = 5.5 Hz, 1H). ^{31}P {^{1}H} NMR (δ, 121 MHz, CD_3COCD_3, 295 K): −143.58 (m, $^1J_{F-P}$ = 705.1 Hz, *P*F$_6$), 39.91 (d, $^1J_{Rh-P}$ = 115.8 Hz, *P*Ph$_3$). ^{13}C {^{1}H} NMR (δ, 75 MHz, CD3CN, 295 K): 119.31 (s), 121.99 (s), 122.22 (s), 124.64 (s), 128.54 (s), 128.16 (t, J_{P-C} = 4.9 Hz, P*Ph*$_3$), 129.93 (t, $^1J_{P-C}$ = 23.4 Hz, *ipso*-P*Ph*$_3$), 130.30 (s, *p*-P*Ph*$_3$), 133.39 (t, J_{P-C} = 5.8 Hz, P*Ph*$_3$), 136.85 (s), 142.10 (s), 144.03 (s), 149.33 (s), 161.69 (s), 159.56 (dt, $^1J_{Rh-C}$ = 28.4 Hz, $^2J_{P-C}$ = 10.3 Hz, Rh−C), 206.45 (*C*O). Anal. calcd for $C_{50}H_{45}F_6NOP_3Rh$ (985.72): C, 60.92; H, 4.60; N, 1.42. Found: C, 60.52; H, 4.96; N, 1.51.

Compound 4A-Br$_2$. To a suspension of [Rh(NBD)(PPh$_3$)$_2$]PF$_6$ (100 mg, 0.116 mmol) in acetone (5 mL) was bubbled H_2 for 15 min at 0 °C, during which time the color of the solution changed from red to yellow. *tert*-Butylethylene (0.5 mL) and 10-bromobenzo[*h*]quinoline (60 mg, 0.231 mmol) were then added to the solution, which was refluxed for 10 h. The precipitate was then filtered and washed with acetone, cold CH_2Cl_2, and then diethyl ether to give **4A-Br$_2$** as a yellow powder. Yield: 45.6 mg (0.047 mmol, 41%). ^{1}H NMR (δ, 400 MHz, CD_2Cl_2, 298 K): 6.53 (dd, ^3J = 8.0 Hz, ^3J = 5.7 Hz, 1H), 6.87 (t, ^3J = 7.5 Hz, 1H), 6.94−6.97 (m, 12H, P*Ph*$_3$), 7.14 (t, ^3J = 7.4 Hz, 6H, P*Ph*$_3$), 7.19−7.24 (m, 12H, P*Ph*$_3$), 7.41 (d, ^3J = 8.4 Hz, 2H), 7.56 (d, ^3J = 7.7 Hz, 1H), 7.69 (d, ^3J = 8.0 Hz, 1H), 7.74 (d, ^3J = 8.7 Hz, 1H), 9.02 (d, ^3J = 5.4 Hz, 1H). ^{31}P {^{1}H} NMR (δ, 162 MHz, CD_3CN, 298 K): 13.25 (d, $^1J_{Rh-P}$ = 96.9 Hz, *P*Ph$_3$). No ^{13}C NMR spectra could be obtained with an acceptable signal-to-noise ratio due to the compound's poor solubility in common NMR solvents. Single crystals of **4A-Br$_2$** could be obtained by the diffusion of diethyl ether into a dilute solution of **4A-Br$_2$** in CH_2Cl_2 or MeCN. Anal. calcd for $C_{49}H_{38}Br_2NP_2Rh$ (965.49): C, 60.96; H, 3.97; N, 1.45. Found: C, 60.69; H, 4.01; N, 1.47.

Compound 4A-I$_2$. To a suspension of rhodium hydride **3A** (100 mg, 0.116 mmol) in THF was added I_2 (50 mg, 0.231 mmol), and the mixture was stirred at 0 °C for 4 h. The precipitate was then filtered and was washed with 2 × 20 mL diethyl ether to give **4A-I$_2$** as an orange powder. Analytically pure **4A-I$_2$** could be obtained after recrystallization from the diffusion of diethyl ether into a dilution of **4A-I$_2$** in CH_2Cl_2. Yield: 87 mg (0.084 mmol, 73%). ^{1}H NMR (δ, 400 MHz, CD_2Cl_2, 298 K): 6.55 (dd, ^3J = 7.6 Hz, ^3J = 5.8 Hz, 1H), 6.85 (t, ^3J = 7.6 Hz, 1H), 6.90−6.93 (m, 12H, P*Ph*$_3$), 7.10−7.16 (m, 18H, P*Ph*$_3$), 7.42 (d, ^3J = 8.7 Hz, 1H), 7.50 (d, ^3J = 7.9 Hz, 1H), 7.70 (d, ^3J = 7.7 Hz, 1H), 7.75 (d, ^3J = 7.9 Hz, 1H), 7.78 (d, ^3J = 8.8 Hz, 1H), 9.32 (d, ^3J = 5.5 Hz, 1H). ^{31}P {^{1}H} NMR (δ, 162 MHz, CD_2Cl_2, 298 K): 11.98 (d, $^1J_{Rh-P}$ = 94.9 Hz, *P*Ph$_3$). No ^{13}C NMR spectra could be obtained with an acceptable signal-to-noise ratio due to the compound's poor solubility in common NMR solvents. Anal. calcd for $C_{49}H_{38}I_2NP_2Rh$ (1035.47): C, 55.55; H, 3.62; N, 1.32. Found: C, 55.53; H, 3.86; N, 1.40.

Compound 4B-I$_2$. Complex **4B-I$_2$** was synthesized by following either the procedure for **4A-Br$_2$** or that for **4A-I$_2$**. The reaction of [Rh(NBD)(PPh$_3$)$_2$]PF$_6$ (100 mg, 0.116 mmol) and 2-(2-iodophenyl)pyridine (65 mg, 0.232 mmol) gave **4B-I$_2$** as an orange powder. Yield: 50 mg (0.049 mmol, 42%). ^{1}H NMR (δ, 300 MHz, CD_2Cl_2, 298 K): 6.17 (t, ^3J = 6.0 Hz, 1H), 6.38 (t, ^3J = 8.0 Hz, 1H), 6.92−7.04 (m, 12H, P*Ph*$_3$), 7.13−7.25 [m, 9H, 6H (P*Ph*$_3$) + 3H ($C_{11}H_8N$)], 7.35−7.44 [13H, 12H (P*Ph*$_3$) + 1H ($C_{11}H_8N$)], 7.53 (d, ^3J = 8.4 Hz, 1H), 9.16 (d, ^3J = 5.8 Hz, 1H). ^{31}P {^{1}H} NMR (δ, 162 MHz, CD_2Cl_2, 298 K): 12.23 (d, $^1J_{Rh-P}$ = 95.7 Hz, *P*Ph$_3$). No ^{13}C NMR spectra could be obtained with an acceptable signal-to-noise ratio due to the compound's poor solubility in common NMR solvents. Anal. calcd for $C_{47}H_{38}I_2NP_2Rh$ (1035.47): C, 54.52; H, 3.70; N, 1.35. Found: C, 54.09; H, 4.04; N, 1.37.

Compound 4B-Br$_2$. Complex **4B-Br$_2$** could be synthesized by directly following the procedure for the preparation of **4A-Br$_2$**. The reaction of [Rh(NBD)(PPh$_3$)$_2$]PF$_6$ (100 mg, 0.116 mmol) and 2-(2-bromophenyl)pyridine (54 mg, 0.232 mmol) gave **4B-Br$_2$** as a yellow powder. Yield: 41 mg (0.044 mmol, 38%). ^{1}H NMR (δ, 300 MHz, CD_2Cl_2, 298 K): 6.17 (t, ^3J = 7.6 Hz, 1H), 6.41 (t, ^3J = 7.3 Hz, 1H), 6.89 (t, ^3J = 7.2 Hz, 1H), 7.01−7.06 (m, 12H, P*Ph*$_3$), 7.16−7.21 [m, 7H, 6H (P*Ph*$_3$) + 1H ($C_{11}H_8N$)], 7.26−7.33 (m, 2H), 7.37−7.45 [13H, 12H (P*Ph*$_3$) + 1H ($C_{11}H_8N$)], 8.92 (d, ^3J = 5.9 Hz, 1H). ^{31}P {^{1}H} NMR (δ, 121 MHz, CD_2Cl_2, 298 K): 13.66 (d, $^1J_{Rh-P}$ = 96.2 Hz, *P*Ph$_3$). No ^{13}C NMR spectra could be obtained with an acceptable signal-to-noise ratio due to the compound's poor solubility in common NMR solvents. Anal. calcd for $C_{47}H_{38}Br_2NP_2Rh$ (941.47): C, 59.96; H, 4.07; N, 1.49. Found: C, 59.99; H, 4.06; N, 1.39.

Compound 6. Iridium hydride **5** was synthesized by following a literature report.[20a] To a suspension of **5** (100 mg, 0.091 mmol) in THF was added I_2 (46 mg, 0.182 mmol), and the mixture was stirred at 0 °C for 4 h. The precipitate was then filtered and was washed with diethyl ether (2 × 20 mL) to give **6** as a yellow powder. Yield: 88 mg (0.077 mmol, 85%). ^{1}H NMR (δ, 400 MHz, CD_2Cl_2, 298 K): 6.52 (dd, ^3J = 7.7 Hz, ^3J = 5.8 Hz, 1H), 6.89 (t, ^3J = 7.8 Hz, 1H), 6.93−6.97 (m, 12H, P*Ph*$_3$), 7.14−7.17 (m, 18H, P*Ph*$_3$), 7.41 (d, ^3J = 8.7 Hz, 1H), 7.49 (d, ^3J = 7.7 Hz, 1H), 7.62 (m, 2H), 7.80 (d, ^3J = 8.7 Hz, 1H), 9.26 (d, ^3J = 5.6 Hz, 1H). ^{31}P {^{1}H} NMR (δ, 162 MHz, CD_2Cl_2, 298 K): −26.54 (s, *P*Ph$_3$). ^{13}C {^{1}H} NMR (δ, 100 MHz, CD_2Cl_2, 298 K): 120.14 (s), 122.04 (s), 122.92 (s), 126.38 (s), 126.68 (t, J_{P-C} = 4.8 Hz, P*Ph*$_3$), 128.77 (s), 129.25 (s, *p*-P*Ph*$_3$), 130.63 (t, $^1J_{P-C}$ = 26.7 Hz, *ipso*-P*Ph*$_3$), 131.19

(s), 133.21 (s), 135.12 (t, J_{P-C} = 4.8 Hz, P*Ph*$_3$), 138.08 (s), 140.66 (t, $^2J_{P-C}$ = 8.4 Hz, Ir−C), 153.51 (s), 155.94 (s). One *C*H resonance signal is missing due to signal overlapping. Anal. calcd for $C_{49}H_{38}I_2IrNP_2$ (1148.81): C, 51.23; H, 3.33; N, 1.22. Found: C, 51.08; H, 3.76; N, 1.25.

General Method for Alkyne Dimerization. A rhodium catalyst (0.01 mmol, 1 mol %) was added to a dichloromethane solution (3 mL) of an alkyne (1 mmol) in a Schlenk flask, and the mixture was then heated under reflux for 12 h. The reaction mixture was cooled to room temperature, and all volatiles were removed under reduced pressure to give a residue, which was then chromatographed on silica gel to give the enyne product. The ratio of *trans*- to *gem*-enyne was analyzed by ^{1}H NMR spectroscopy for the crude product. The *trans*- to *gem*-enyne ratios and the NMR yields of the major products are listed in Table 3. The identities of the dimerization products of entries 1,[31] 2,[27b] 3,[31] 4,[31] and 5[31] were confirmed by comparisons with reported NMR data.

Dimerization Product of EtOC(O)C≡CH (entry 6, Table 3). ^{1}H NMR (δ, 400 MHz, $CDCl_3$, 298 K): 1.27 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.29 (t, ^3J = 7.2 Hz, 3H, CH_3), 4.20 (q, ^3J = 7.1 Hz, 2H, CH_2), 4.24 (q, ^3J = 7.1 Hz, 2H, CH_2), 6.42 (d, ^3J = 16 Hz, 1H), 6.74 (d, ^3J = 16 Hz, 1H). ^{13}C {^{1}H} NMR (δ, 100 MHz, $CDCl_3$, 298 K): 13.99 (s, *C*H$_3$), 14.13 (s, *C*H$_3$), 61.34 (s, *C*H$_2$), 62.49 (s, *C*H$_2$), 81.50 (s, *C*≡C), 87.02 (s, C≡*C*), 121.54 (s, *C*═C), 135.42 (s, *C*═*C*), 153.15 (s, *C*O), 164.72 (s, *C*O). Anal. calcd for $C_{10}H_{12}O_4$ (196.2): C, 61.21; H, 6.16. Found: C, 61.38; H, 6.31.

Crystallographic Analysis. X-ray-quality single crystals of complexes **2A-Br**, **2B-I**, and **4A-Br$_2$** were obtained by the slow diffusion of diethyl ether into their dichloromethane or MeCN solutions. Complex **2B-I** cocrystalized with half an equivalent of ether. Complex **4A-Br$_2$** cocrystalized with half an equivalent of MeCN and 1 equiv of Et_2O. Crystal data were collected on a Bruker X8 Kappa CCD diffractometer at 173 K using graphite monochromated Mo Kα radiation (λ = 0.71073Å). The APEX2 Software Suite (Bruker, 2005) was used for data acquisition, structure solution, and refinement. Absorption corrections were applied using SADABS. The structure was solved by direct method and refined by full-matrix least-squares method on F^2 using Xshell.

Acknowledgment. We thank the School of Physical and Mathematical Sciences, Nanyang Technological University for financial support and the Johnson Matthey Co. for a loan of iridium and rhodium chloride. Jing Zhao thanks Nanjing University for financial support. We also thank Prof. Robert Crabtree (Yale University) for helpful discussions.

Supporting Information Available: Crystal data of complexes **2A-Br**, **2B-I**, and **4A-Br$_2$** in PDF and CIF formats. This material is free of charge via the Internet at http://pubs.acs.org.

IC801878E

(31) Bassetti, M.; Pasquini, C.; Raneri, A.; Rosato, D. *J. Org. Chem.* **2007**, *72*, 4558.