

Rhodium-Catalyzed Activation and Functionalization of the C–C Bond of Biphenylene

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Biphenylene reacts with the rhodium(I) dimer [(dtbpm)RhCl]₂ (**1**) (dtbpm = bis(di-*tert*-butylphosphino)methane) to yield (dtbpm)Rh(2,2'-biphenyl)Cl (**2**). Lewis bases react with compound **2** at room temperature, displacing the chelating phosphine. A new five-coordinate complex, (PPh₃)₂Rh(2,2'-biphenyl)Cl (**3**), is formed when the base is triphenylphosphine. Fluorenone and fluorenimine are formed when the base used is carbon monoxide and isonitrile, respectively. The dimer **1** and compound **2** are catalysts for coupling reactions of biphenylene with unsaturated organic substrates. Substituted phenanthrenes and benzenes are formed using alkynes with simple alkyl or aryl substituents. Substituted phenanthrenes and fluorenes are produced using alkynes with trimethylsilyl substituents. Olefinic substrates yield vinylbiphenyls. The production of vinylbiphenyls is hindered by steric substitution on the olefin. α -Olefins with substituents that block double-bond migration yield the cleanest product ratios.

Introduction

The activation of C–C bonds is a current topic of interest in the chemical literature. C–C bond cleavage has been achieved with a variety of organic substrates using many different transition metal complexes. Most of the organic substrates chosen for these studies use ring strain, carbonyl-induced enhanced reactivity, aromatization, or forced proximity of the bond to a metal center to effect bond activation.¹ The ultimate goal of these projects is to understand factors that govern this transformation and use this knowledge to selectively and efficiently activate and functionalize C–C bonds. To date, most reported examples of this type of cleavage have been stoichiometric, although catalytic reactions are known.² Rhodium complexes in particular have been successful in C–C bond activation processes; carbonyl complexes,³ "Cp*Rh(PMe₃)",⁴ [(olefin)₂RhCl]₂,⁵ (PCP)Rh pincer complexes,⁶ and L₃RhCl⁷ have all shown activity

toward breaking C–C bonds in the types of organic substrates described above.

We recently began exploring the reactivity of the bisphosphine rhodium(I) dimer [(dtbpm)RhCl]₂ (dtbpm = bis(di-*tert*-butylphosphino)methane) with organic substrates in the hopes of extending the scope of known reactivity in this field.⁸ Originally reported by Hofmann,⁹ this complex offers several properties that are conducive to its use; it is related to L₃RhCl complexes that are known to deactivate C–C bonds, it is thermally stable toward decomposition even though the dimer dissociates into the monomeric unit at high temperatures, and the bisphosphine ligand has a small chelation angle, thus providing a wider open site for coordination to the metal center. We report here that [(dtbpm)RhCl]₂ (**1**) is successful in breaking C–C bonds and acts as a catalyst for the functionalization of biphenylene.

Results and Discussion

1 reacts with excess biphenylene in CH₂Cl₂ or THF solvent in a closed vessel at 85 °C to generate a new

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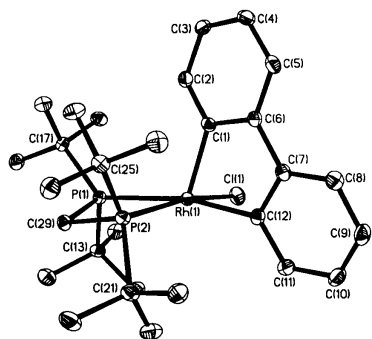
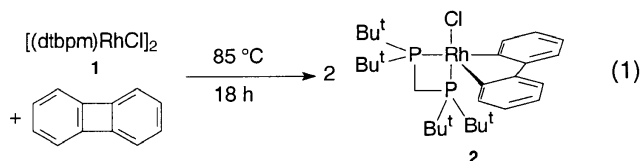


Figure 1. Molecular structure of (dtbpm)Rh(2,2'-biphenyl)Cl (**2**). Hydrogen atoms are omitted for clarity, and ellipsoids are shown at the 30% probability level.

complex, **2**. Isolated in 65% yield, the ^1H NMR spectrum has four new resonances for the biphenylene ligand, including one further downfield than the others that is coupled to rhodium (δ 7.85, $^3J_{\text{Rh-H}} = 3$ Hz). A doublet of doublets and two doublets are observed for the methylene and *t*-Bu groups of the bisphosphine, respectively. Integration of the peaks indicates that one biphenylene has been incorporated per bisphosphine ligand. The ^{31}P NMR spectrum has two resonances at δ 20.7 and -10.9 , each a doublet of doublets due to coupling to each other as well as the rhodium metal center. The signal at δ 20.7 has $^1J_{\text{Rh-P}} = 137$ Hz, and the signal at δ -10.9 has $^1J_{\text{Rh-P}} = 55$ Hz, with $J_{\text{P-P}} = 12$ Hz. The values for $^1J_{\text{Rh-P}}$ are consistent with the two phosphorus atoms occupying positions *trans* to chlorine and aryl groups, respectively.¹⁰ Considering the NMR characteristics and the penchant for biphenylene to ring open along the bridging C–C bonds, the product is formulated as the Rh(III) complex (dtbpm)Rh(2,2'-biphenyl)Cl (eq 1).

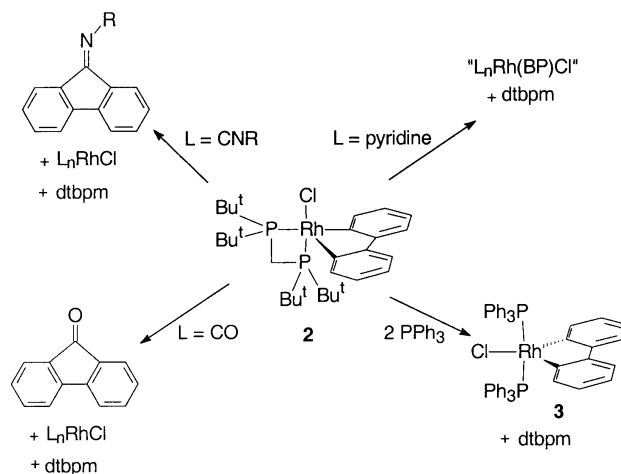


Compound **2** was characterized by X-ray crystallography (Figure 1). The complex adopts a distorted square pyramidal geometry in the solid state, a common structural motif for five-coordinate Rh(III) complexes with chelating ligands. C(1) occupies the apex of the pyramid, while the basal plane is composed of the chloride ligand, the two phosphorus atoms, and C(12). The rhodium metal center lies 0.205 Å above the mean plane of the pyramidal base. The P–C–P angle of 74.1° is typical for complexes containing dtbpm.^{8,9,11} The P(1)–Rh–C(12) angle of 166.7° and P(2)–Rh–Cl angle of 168.0° leave a considerably large open coordination site opposite C(1). The solid state structure clearly contradicts that observed in solution by ^1H and ^{31}P NMR spectroscopy at room temperature. Presumably com-

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Scheme 1



pound **2** undergoes rapid interconversion between the trigonal bipyramidal and square pyramidal geometries via a pseudorotation that involves “rocking” of the biphenyl ligand into the vacant site opposite C(1). This process equilibrates halves of the biphenyl ligand while keeping the phosphines distinct. Although we were unable to observe the slow limit structure suggested by X-ray crystallography, moderate broadening of the resonances in the ^1H NMR spectrum is observed upon cooling a CD_2Cl_2 solution of compound **2** to -80 °C. The coupling constant, $^2J_{\text{P-P}}$, also disappears at this temperature.

Scheme 1 shows the effect of reacting **2** with a variety of Lewis bases (L = pyridine, PPh_3 , CO, and *t*-BuNC) at room temperature. The products formed by reaction with excess pyridine and 2 equiv of PPh_3 are the result of simple substitution of the chelating phosphine with incoming Lewis base. In both cases, free dtbpm is observed by ^1H and ^{31}P NMR spectroscopy. Although the metal-containing product formed in the pyridine reaction proved to be intractable, we were able to characterize the PPh_3 -substituted product **3**. The ^1H NMR spectrum revealed four new resonances for the biphenylene ligand, denoting a symmetric environment, and the integration of PPh_3 to biphenylene aromatic resonances indicated a 2 to 1 ligand ratio, respectively. Unlike **2**, a simple doublet was observed for **3** in the ^{31}P NMR spectrum at δ 31.2 with $^1J_{\text{Rh-P}} = 119$ Hz, implying the phosphine ligands are located in axial positions. Suitable crystals for X-ray crystallographic analysis were obtained from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -25 °C. Compound **3** (Figure 2) has a trigonal bipyramidal structure with *trans* PPh_3 groups, consistent with the NMR data.

In contrast to pyridine and triphenylphosphine, carbon monoxide and *tert*-butylisocyanide react with the biphenyl portion of the complex. The organic compounds 9-fluorenone and 9-(*tert*-butylimino)fluorene, respectively, are produced via formal insertion into the C–C bond of biphenylene.^{12a} Attempts to catalytically produce the functionalized fluorenes from biphenylene were unsuccessful, as the bisphosphine ligand in **1** was easily displaced again in the presence of excess CO or *t*-BuN≡C. The fluorenone can also be formed from the

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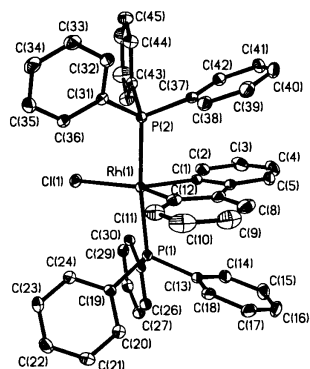
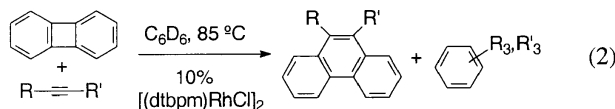


Figure 2. Molecular structure of $(\text{PPh}_3)_2\text{Rh}(2,2'\text{-biphenyl})\text{-Cl}$ (**3**). Hydrogen atoms are omitted for clarity, and ellipsoids are shown at the 30% probability level.

reaction of $(\text{dtbpm})\text{Rh}(\text{CO})\text{Cl}$,⁹ the Lewis acid/base adduct of the monomer, with an excess of biphenylene. Although production of fluorenone is essentially quantitative by ^1H NMR spectroscopy, complex **2** is not the only rhodium-containing species observed in solution at the end of the reaction.

We have previously reported on the catalytic insertion of alkynes into the C–C bond of biphenylene, leading to the formation of substituted phenanthrenes.¹² The catalytically active species in these reactions is a bisphosphine nickel(0) chelate complex. We reasoned that the rhodium dimer might behave in a similar fashion; therefore, we examined the addition of a variety of alkynes to biphenylene in the presence of the rhodium dimer. In a typical experiment, equimolar amounts of biphenylene and alkyne were dissolved in 600 μL of C_6D_6 , along with 10 mol % of **1** (20 mol % " L_2RhCl "). The solution was then heated at 85 $^\circ\text{C}$ and monitored by ^1H and ^{31}P NMR spectroscopy. The results are summarized in Table 1. Compound **2** was the major rhodium-containing product formed; however, some uncharacterized rhodium species were observed during the course of each reaction. Decomposition of the metal-containing species is also apparent, as free phosphine is observed in both the ^1H and ^{31}P NMR spectra. Rates are qualitatively the same in either C_6D_6 or $\text{THF-}d_8$ solutions but significantly hindered when performed in CD_2Cl_2 . In the case of aryl- or alkyl-based alkynes (eq 2), the primary organic products observed by ^1H NMR spectroscopy and GC/MS are substituted phenanthrenes and benzenes (via cyclotrimerization of alkyne).¹³ Con-



trol experiments indicate that cyclotrimerization does not necessarily proceed through the rhodium dimer. Thermolysis of C_6D_6 solutions of either 2-butyne or diphenylacetylene in the presence of complex **1** results in no observable amounts of hexamethylbenzene or hexaphenylbenzene, respectively. In contrast, dimethylacetylene-dicarboxylate undergoes facile cyclotrimerization with **1** under moderate reaction conditions.

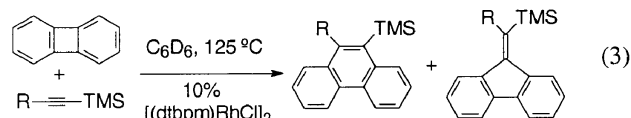
(13) With phenylacetylene, trace amounts (approximately 3%) of **2** + **1** (2 alkyne + biphenylene) products were observed by GC/MS analysis ($m/z = 356$ for parent ion).

Table 1. Product Distributions and Yields for the Addition of Alkynes to Biphenylene^a

Alkyne	Products (%)	Time (h)
$\text{Me-C}\equiv\text{C-Me}$	(96) (4)	18
$\text{Ph-C}\equiv\text{C-Ph}$	(78) (22)	51
$\text{H-C}\equiv\text{C-Ph}$	(82) (15)	18
$\text{MeO}_2\text{C-C}\equiv\text{C-CO}_2\text{Me}$	(23) (77)	12
$\text{TMS-C}\equiv\text{C-TMS}$	(95)	37
$\text{TMS-C}\equiv\text{C-Ph}$	(50) (33)	41
$\text{H-C}\equiv\text{C-TMS}$	(20) (70)	16
$\text{Me-C}\equiv\text{C-TMS}$	(31) (39) (29)	38
$\text{Bu}^t\text{-C}\equiv\text{C-TMS}$	No product	48

^a All reactions were performed at 85 $^\circ\text{C}$ with 10 mol % **1** in 600 μL of C_6D_6 . Yields based on ^1H NMR.

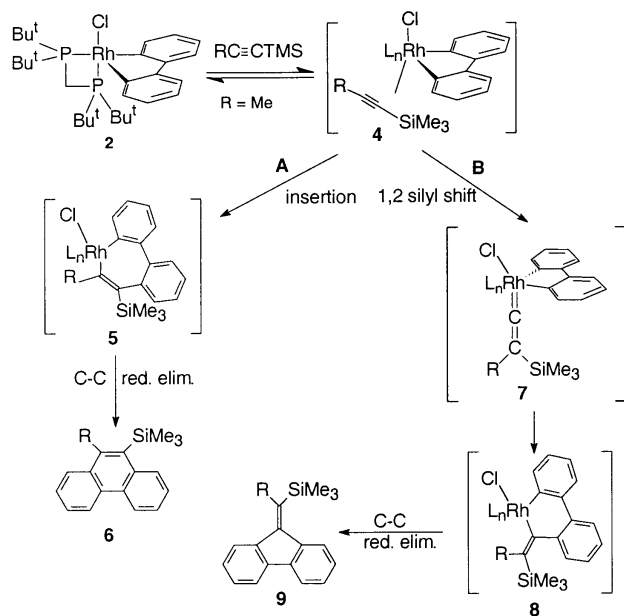
As alkynes with trimethylsilyl substituents offer the potential for functionalizing the product phenanthrenes through silane substitution chemistry, we therefore examined the use of disilyl- and monosilylalkynes in this system (eq 3, Table 1). The reaction of bis(trimethylsi-



lyl)acetylene with biphenylene in the presence of **1** proceeds cleanly at 85 $^\circ\text{C}$ to yield 9-(bis(trimethylsilyl)methylidene)fluorene as the primary product instead of the anticipated phenanthrene. Although indistinguishable by ^1H NMR spectroscopy, the two compounds can be differentiated by ^{13}C NMR spectroscopy; nine resonances are observed, as would be expected for the fluorene, as opposed to eight for the phenanthrene. 1-Phenyl-2-(trimethylsilyl)acetylene and (trimethylsilyl)acetylene produce mixtures of phenanthrene and fluorene products, whereas 1-*tert*-butyl-2-(trimethylsilyl)acetylene does not yield any product.

When 1-trimethylsilyl-1-propyne was used in the reaction, however, three major organic products are observed. GC/MS analysis of the reaction mixture revealed that all three of the major products have a parent ion peak at $m/z = 264$. The three products were characterized as 9-methyl-10-trimethylsilylphenan-

Scheme 2



threne (**6**) (31%), 9-(1-trimethylsilylethylidene)fluorene (**9**) (39%), and 9-(1-trimethylsilylethenyl)fluorene (**10**) (29%).¹⁴

Scheme 2 displays a possible mechanism for the formation of the phenanthrene and fluorene products. Initial formation of $(\text{dtbpm})\text{Rh}(2,2'\text{-biphenyl})\text{Cl}$ precedes coordination of the alkyne substrate. Insertion of the alkyne into the Rh–C bond to form intermediate **5** is shown in path A. Subsequent C–C reductive elimination from **5** results in formation of the phenanthrene product. Path B shows 1,2-silyl migration to produce intermediate **7**, a vinylidenerhodium complex, from which fluorene **9** is derived following insertion and reductive elimination steps. Werner has previously reported the formation of (silyl)vinylidenes from alkyne-silanes in a number of rhodium and iridium systems and proposed a 1,2-silyl migration.¹⁵

No evidence for cyclotrimerization of the trimethylsilyl-substituted alkynes was observed by either ^1H NMR spectroscopy or GC/MS possibly due to the steric bulk of the trimethylsilyl substituents. It is also interesting to note that only insertion chemistry is observed, in contrast to the $\text{L}_2\text{Ni}(0)$ system, where multiple pathways occur for alkynes with trimethylsilyl substituents.^{12b} Also, although compounds **9** and **10** are apparent tautomers, control experiments attempting to interconvert the two compounds were not successful.¹⁶

Catalytic functionalization of biphenylene by the rhodium dimer is not limited to insertion of alkynes. When norbornene is used in place of an alkyne, a very

(14) The structures of compounds **9** and **10** were verified by NMR and chemical methods. In particular, separate hydrogenolysis of **9** and **10** over Pd/C yielded the identical product, 9-(1-trimethylsilylethyl)fluorene. See Supporting Information for details of these reactions.

(15) Werner, H.; Lass, R. W.; Gevert, O.; Wolf, J. *Organometallics* **1997**, *16*, 4077. Werner, H.; Baum, M.; Schneider, D.; Windmueller, B. *Organometallics* **1994**, *13*, 1089. Rappert, T.; Nuernberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359.

(16) Compounds **9** and **10** do not interconvert by either acid or base catalysis. We also considered that a metal-containing product formed during the course of the reaction promoted an isomerization. However, when a solution of either **9** or **10** was added to the reaction mixture upon completion of a catalytic run and heated at 125 °C, no discernible change in the ratio of the compounds was observed.

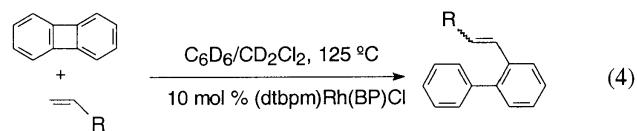
Table 2. Product Distributions and Yields for the Addition of Olefins to Biphenylene^a

Olefin	% Conversion (E:Z ratio)	Time (h)
	61% (5.5:1)	13
	95% (18:1)	10
	92% (1.7:1)	72
	92% (1:1.1)	151
	 50%	58
	 95%	25
	No product	20
	No product	20
	No product	13

^a All reactions were performed at 125 °C with 10 mol % **2** in 600 μL of $\text{C}_6\text{D}_6/\text{CD}_2\text{Cl}_2$ (1:1 by volume) except where noted. Yields based on ^1H NMR. ^b 10 mol % **1** in C_6D_6 at 85 °C.

clean reaction ensues in which the C=C bond of norbornene inserts into the C–C bond of biphenylene, producing a dihydrophenanthrene.¹⁷ The facility with which the olefin undergoes insertion may be due in part to relief of ring strain encountered in norbornene. Hydrogenolysis of biphenylene to biphenyl under an atmosphere of H_2 also occurs cleanly and quantitatively in the presence of compound **1**, as judged by NMR spectroscopy.

Interestingly, substituted vinylbiphenyls are the major products formed instead of phenanthrenes when other olefins are used in the reaction (eq 4, Table 2).¹⁸ For example, 4-methylstyrene reacts with biphenylene



to form a mixture of cis and trans 2-(1-(4-methylstyrenyl)biphenyl) in the presence of 10 mol % **2**.¹⁹ The reactions tend to be cleaner when α -olefins are used as opposed to cyclic or internal olefins. Double-bond migra-

(17) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1985**, *286*, C13.

(18) This transformation has been reported before in our labs via base-assisted palladium catalysis. See: Satoh, T.; Jones, W. D. *Organometallics* **2001**, *20*, 2916.

(19) The true cis/trans product ratio in these reactions is unknown, as isomerization occurs under the reaction conditions, presumably via a rhodium-promoted pathway. The *E* isomer is always formed in a higher amount initially, however, and is slowly converted to the *Z* isomer.

tion occurs with substrates that have $-(CH_2)_nR$ substitution on the olefin, leading to the formation of other vinylbiphenyl products. The use of substrates containing vinyl substituents that block the migration of the double bond, such as butyl vinyl ethers and 4-methylstyrene, yield clean product mixtures derived from the parent α -olefin, whereas 1-pentene forms numerous vinylbiphenyl products and does not go to completion. Substrates that are sterically hindered also appear to inhibit product formation. For instance, tetramethylethylene, *tert*-butylethylene, and *trans*-stilbene each yielded no product when reacted with biphenylene in the presence of **2**.

Conclusions

In summary, we have prepared a new C–C bond activated complex of biphenylene with $[(dtbpm)RhCl]_2$. The rhodium dimer and $(dtbpm)Rh(2,2'$ -biphenyl)Cl both act as catalysts for the functionalization of biphenylene. Insertion of unsaturated carbon–carbon bonds leads to substituted phenanthrenes, fluorenes, and biphenyls. Ongoing studies in this lab will focus on extending the scope of unsaturated substrates used in the addition to biphenylene in this system and examining the mechanistic details of these reactions.

Experimental Section

General Considerations. All manipulations were performed using glovebox, Schlenk, or vacuum-line techniques. Diethyl ether and hexanes were predried over sodium and distilled from sodium/benzophenone ketyl. CH_2Cl_2 was dried over CaH_2 and distilled prior to use. C_6D_6 and THF- d_8 were purchased from Cambridge Isotope Laboratories and dried and distilled from sodium/benzophenone ketyl. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and dried over 3 Å sieves. CD_2Cl_2 was dried over P_2O_5 and vacuum distilled prior to use. $[(dtbpm)RhCl]_2^9$ and biphenylene²⁰ were prepared according to literature methods.

¹H spectra were recorded on Bruker AMX400 or AVANCE400 spectrometers and referenced to residual proton solvent signals. ¹³C and ³¹P spectra were recorded on Bruker AMX400 or AVANCE400 spectrometers. Carbon chemical shifts were referenced to residual solvent resonances. Phosphorus chemical shifts were referenced to an 85% phosphoric acid external standard. GC/MS was conducted on a 5890 Series II gas chromatograph fitted with an HP 5970 series mass selective detector. Elemental analyses were performed by Desert Analytics. A Siemens SMART system with a CCD area detector was used for X-ray structure determinations.

(dtbpm)Rh(2,2'-biphenyl)Cl. $[(dtbpm)RhCl]_2$ (150 mg, 0.017 mmol) and biphenylene (152.2 mg, 0.085 mmol) were dissolved in 15 mL of CH_2Cl_2 and heated at 85 °C for 18 h in an air-free flask. The solvent was removed in vacuo, and the orange residue was washed with 4 × 3 mL of Et_2O . The remaining solids were redissolved in CH_2Cl_2 , layered with Et_2O , and allowed to stand at –25 °C. Orange crystals (131 mg, 65% yield) precipitated after 3 days. ¹H NMR ($CDCl_3$): δ 7.54 (dd, 2 H, $H_{ortho-Rh}$, ³ $J_{Rh-H} = 3$ Hz, ³ $J_{H-H} = 8$ Hz), 7.27 (d, 2 H, $J = 8$ Hz), 6.91 (t, 2 H, $J = 7.0$ Hz), 6.82 (t, 2 H, $J = 7.2$ Hz), 3.52 (dd, 2 H, PCH_2P , ² $J_{P-H} = 9$ Hz, ³ $J_{Rh-H} = 5$ Hz), 1.56 (d, 18 H, $(CH_3)_3P$, ³ $J_{P-H} = 12$ Hz), 1.06 (d, 18 H, $(CH_3)_3P$, ³ $J_{P-H} = 12$ Hz). ³¹P NMR ($CDCl_3$): δ 20.7 (d, ¹ $J_{Rh-P} = 137$ Hz, ² $J_{P-P} = 12$ Hz), –10.9 (dd, ¹ $J_{Rh-P} = 55$ Hz, ² $J_{P-P} = 12$ Hz). Anal.

Calcd (found) for $(dtbpm)Rh(2,2'$ -biphenyl)Cl· Et_2O : C 59.24 (59.03); H 8.44 (8.27).

(PPh₃)₂Rh(2,2'-biphenyl)Cl. A solution of PPh_3 (44 mg, 0.17 mmol) in 1 mL of CH_2Cl_2 was added dropwise via pipet to a solution of $(dtbpm)Rh(2,2'$ -biphenyl)Cl (48 mg, 0.081 mmol) dissolved in 6 mL of CH_2Cl_2 . The color of the solution immediately changed from orange to yellow. The solution was stirred for 30 min and then reduced in volume to 3 mL. The solution was filtered, layered with 3 mL of Et_2O , and cooled to –25 °C. Yellow crystals (33 mg, 50%) deposited after several days. ¹H NMR (CD_2Cl_2): δ 7.42 (d, 2 H, $H_{ortho-Rh}$, ³ $J_{H-H} = 7.8$ Hz), 7.32 (br m, 18 H), 7.17 (br t, 12 H, $J = 7.2$ Hz), 6.57 (t, 2 H, $J = 7.2$ Hz), 6.45 (t, 2 H, $J = 7.5$ Hz), 6.33 (dd, 2 H, $J = 7.4$ Hz, 1.4 Hz). ³¹P NMR (CD_2Cl_2): δ 30.2 (d, ¹ $J_{Rh-P} = 119$ Hz). Anal. Calcd (found) for $(PPh_3)_2Rh(2,2'$ -biphenyl)Cl· $(CH_2Cl_2)_{0.25}$: C 69.25 (68.98), H 4.65 (4.78).

Alkyne/Biphenylene Coupling Experiments. A general procedure for the coupling of alkynes to biphenylene with **1** is as follows: $[(dtbpm)RhCl]_2$ (9.0 mg, 0.010 mmol) and biphenylene (15.5 mg, 0.10 mmol) were placed in a resealable NMR tube and dissolved in 600 μ L of C_6D_6 . The alkyne (0.10 mmol) was then added via microliter syringe (except for diphenylacetylene, which was added as a solid prior to dissolution in C_6D_6). The mixture was heated at 85 °C and monitored by ¹H and ³¹P NMR spectroscopy. Yields were determined by integration of the aromatic region of the spectrum and comparing areas of selected resonances to the area of the entire region. The products of the reactions with 2-butyne, phenylacetylene, and diphenylacetylene were compared to those of authentic samples or literature. Other data are presented below.

9,10-Di(methylcarboxylate)phenanthrene. ¹H NMR (C_6D_6): δ 8.31 (m, 2 H), 8.27 (m, 2 H), 7.32 (m, 4 H), 3.59 (s, 6 H). MS: m/z 294 (M^+).

Benzenhexacarboxylic Acid Hexamethyl Ester. ¹H NMR (C_6D_6): δ 3.41 (s). MS: m/z 395 (M^+).

9-(Bis(trimethylsilyl)methylene)fluorene. ¹H NMR (C_6D_6): δ 7.83 (d, ³ $J_{H-H} = 7.6$ Hz, 2 H), 7.41 (d, ³ $J_{H-H} = 7.2$ Hz, 2 H), 7.10 (td, ³ $J_{H-H} = 7.2$ Hz, ⁴ $J_{H-H} = 1.2$ Hz, 2 H), 7.04 (td, ³ $J_{H-H} = 7.6$ Hz, ⁴ $J_{H-H} = 1.2$ Hz, 2 H), 0.41 (s, 18 H, $(CH_3)_3Si$). ¹³C NMR (C_6D_6): δ 164.1, 151.9, 142.2, 139.9, 129.1, 126.8, 126.5, 119.7, 3.2. MS: m/z 322 (M^+).

9-(Trimethylsilyl)-10-phenylphenanthrene. ¹H NMR ($CDCl_3$): δ 8.77 (d, ³ $J_{H-H} = 8$ Hz, 1 H), 8.72 (d, ³ $J_{H-H} = 7.6$ Hz, 1 H), 8.31 (d, ³ $J_{H-H} = 7.6$ Hz, 1 H), 7.56–67 (m, 2 H), 7.27–7.48 (m, 8 H), 0.09 (s, 9 H, $(CH_3)_3Si$). MS: m/z 326 (M^+).

9-(trimethylsilylphenylmethylene)fluorene. ¹H NMR ($CDCl_3$): δ 7.97 (d, ³ $J_{H-H} = 8$ Hz, 1 H), 7.70 (d, ³ $J_{H-H} = 7.2$ Hz, 1 H), 7.56–7.67 (m, 2 H), 7.27–7.48 (m, 4 H), 7.16 (t, ³ $J_{H-H} = 7.4$ Hz, 1 H), 7.07 (d, ³ $J_{H-H} = 7.6$ Hz, 2 H), 6.79 (t, ³ $J_{H-H} = 7.6$ Hz, 1 H), 5.94 (d, ³ $J_{H-H} = 8$ Hz, 1 H), 0.27 (s, 9 H, $(CH_3)_3Si$). MS: m/z 326 (M^+).

9-(Trimethylsilyl)phenanthrene. ¹H NMR ($CDCl_3$): δ 8.74 (d, ³ $J_{H-H} = 8.0$ Hz, 1 H), 8.67 (d, ³ $J_{H-H} = 8.0$ Hz, 1 H), 8.15 (d, ³ $J_{H-H} = 7.6$ Hz, 1 H), 7.95 (s, 1 H), 7.88 (d, ³ $J_{H-H} = 7.6$ Hz, 1 H), 7.71–7.64 (m, 2 H), 7.40–7.25 (m, 2 H), 0.52 (s, 9 H, $(CH_3)_3Si$). MS: m/z 250 (M^+).

9-(Trimethylsilylmethylene)fluorene. ¹H NMR ($CDCl_3$): δ 7.81 (d, ³ $J_{H-H} = 7.6$ Hz, 1 H), 7.71–7.64 (m, 3 H), 7.40–7.25 (m, 4 H), 6.84 (s, 1 H, $CH(SiMe_3)=C$), 0.40 (s, 9 H, $(CH_3)_3Si$). MS: m/z 250 (M^+).

9-(Trimethylsilyl)-10-methylphenanthrene. ¹H NMR (C_6D_6): δ 8.52 (m, 2H), 8.24 (m, 1 H), 7.93 (m, 1 H), 7.44 (m, 2 H), 7.39 (m, 2 H), 2.61 (s, 3 H, CH_3), 0.48 (s, 9 H, $(CH_3)_3Si$). MS: m/z 264 (M^+).

9-(1-Trimethylsilylethylidene)fluorene. ¹H NMR (C_6D_6): δ 7.87 (m, 2 H), 7.58 (m, 1H), 7.54 (m, 1H), 7.10–7.25 (m, 4 H), 2.34 (s, 3 H, CH_3), 0.32 (s, 9 H, $(CH_3)_3Si$). MS: m/z 264 (M^+).

9-(1-Trimethylsilylethenyl)fluorene. ¹H NMR ($CDCl_3$): δ 7.75 (d, 2 H, $J = 7.5$ Hz), 7.38 (m, 4 H), 7.28 (td, 2 H, $J = 7.4$ Hz, $J = 1.1$ Hz), 6.08 (d, 1 H, ¹ $J_{H-H} = 2.9$ Hz, $H_2C=C(SiMe_3)-$

(20) Yates, P. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 5, p 772.

CH-), 5.69 (d, 1 H, $^1J_{\text{H-H}} = 2.9$ Hz, $\text{H}_2\text{C}=\text{C}(\text{SiMe}_3)\text{CH-}$), 4.61 (s, 1 H, $\text{H}_2\text{C}=\text{C}(\text{SiMe}_3)\text{CH-}$), -0.47 (s, 9 H, SiMe₃). ^{13}C NMR (CDCl₃): δ 151.6, 146.8, 141.2, 129.4, 127.3, 126.8, 125.6, 119.7, 58.7, -0.0. MS: m/z 264 (M⁺).

9-(1-Trimethylsilylethenyl)fluorene. ^1H NMR (C₆D₆): δ 7.59 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2 H), 7.34 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2 H), 7.22 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 2 H), 7.14 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 2 H), 5.90 (d, $^2J_{\text{H-H}} = 2.8$ Hz, 1 H, $\text{CH}_2=\text{C}(\text{SiMe}_3)\text{CH}$), 5.63 (d, $^2J_{\text{H-H}} = 2.8$ Hz, 1 H, $\text{CH}_2=\text{C}(\text{SiMe}_3)\text{CH}$), 4.50 (s, 1 H, $\text{CH}_2=\text{C}(\text{SiMe}_3)\text{CH}$), -0.38 (s, 9 H, (CH₃)₃Si).

Addition of Norbornene to Biphenylene with 1. [(dtbpm)RhCl]₂ (9 mg, 0.010 mmol), biphenylene (15.5 mg, 0.10 mmol), and norbornene (9.6 mg, 0.10 mmol) were placed in a resealable NMR tube and dissolved in 600 μL of C₆D₆. The mixture was heated at 85 °C and monitored by ^1H and ^{31}P NMR spectroscopy. The coupling of norbornene with biphenylene to form the dihydrophenanthrene (*cis,exo-1,2,3,4,4a,12b*-hexahydro-1,4-methanotriphenylene) was approximately 95% complete after 25 h. Heating for an additional 11 h drives the reaction to completion. ^1H NMR (C₆D₆): δ 7.73 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 2 H), 7.06 (m, 6 H), 2.96 (s, 2 H), 2.23 (s, 2 H), 1.45 (m, 4 H), 1.36 (m, 1 H), 0.81 (d, 1 H, $J_{\text{H-H}} = 7.0$ Hz). MS: m/z 246 (M⁺).

Hydrogenation of Biphenylene with 1. [(dtbpm)RhCl]₂ (9 mg, 0.010 mmol) and biphenylene (15.5 mg, 0.10 mmol) were placed in a resealable NMR tube and dissolved in 600 μL of C₆D₆. The mixture was frozen in N₂(l) and the headspace evacuated twice prior to filling the headspace of the tube with an atmosphere of H₂. The mixture was heated at 85 °C and monitored by ^1H and ^{31}P NMR spectroscopy. The conversion of biphenylene to biphenyl was complete within 20 h. ^1H NMR (C₆D₆): δ 7.45 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 4 H), 7.20 (t, $J_{\text{H-H}} = 7.2$ Hz, 4 H), 7.12 (t, $J_{\text{H-H}} = 7.2$ Hz, 2 H).

α -Olefin/Biphenylene Coupling Experiments. A general procedure for the coupling of olefins to biphenylene with **2** is as follows: (dtbpm)Rh(2,2'-biphenyl)Cl (5.5 mg, 0.0092 mmol) and biphenylene (14 mg, 0.092 mmol) were placed in a resealable NMR tube and dissolved in 600 μL of a C₆D₆/CD₂Cl₂ solution (1:1 by volume). The olefin (0.092 mmol) was then added via microliter syringe. The mixture was heated at 125 °C and monitored by ^1H and ^{31}P NMR spectroscopy.

2-(2-(4-Methylphenyl)ethenyl)-1,1'-biphenyl (95% conversion, *E:Z* = 18:1). ^1H NMR (*E* isomer, CDCl₃): δ 7.75 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1 H), 7.32–7.44 (m, 8 H), 7.26 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 2 H), 7.10 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 2 H), 7.07 (d, $^3J_{\text{H-H}} = 16$ Hz, 1 H, C=CH), 7.01 (d, $^3J_{\text{H-H}} = 16$ Hz, 1 H, C=CH), 2.32 (s, 3 H, CH₃); (*Z* isomer, CDCl₃): δ aromatic resonances are

obscured due to *E* isomer, 6.47 (d, $^3J_{\text{H-H}} = 12$ Hz, 1 H, C=CH), 6.34 (d, $^3J_{\text{H-H}} = 12$ Hz, 1 H, C=CH), 2.30 (s, 3 H, CH₃). MS: m/z 270 (M⁺).

2-(2-*tert*-Butoxyethenyl)-1,1'-biphenyl (92% conversion, *E:Z* = 1:1.1). ^1H NMR (*E* isomer, C₆D₆): δ 7.32–6.95 (m, 9 H, Ph), 6.77 (d, $^3J_{\text{H-H}} = 12$ Hz, 1 H, C=CH), 5.92 (d, $^3J_{\text{H-H}} = 12$ Hz, 1 H, C=CH), 1.12 (s, 9 H, ^tBu); (*Z* isomer, C₆D₆): δ 7.32–6.95 (m, 9 H, Ph), 6.13 (d, $^3J_{\text{H-H}} = 7.4$ Hz, 1 H, C=CH), 5.14 (d, $^3J_{\text{H-H}} = 7.4$ Hz, 1 H, C=CH), 1.06 (s, 9 H, ^tBu). MS: m/z 252 (M⁺).

2-(2-*n*-Butoxyethenyl)-1,1'-biphenyl (92% conversion, *E:Z* = 1.7:1). ^1H NMR (*E* isomer, C₆D₆): δ 7.0–7.26 (m, 9 H, Ph), 6.75 (d, $^3J_{\text{H-H}} = 13$ Hz, 1 H, C=CH), 5.75 (d, $^3J_{\text{H-H}} = 13$ Hz, 1 H, C=CH), 3.42 (t, $^3J_{\text{H-H}} = 6.5$ Hz, 2 H, OCH₂), 1.12–1.45 (m, 4 H, CH₂CH₂CH₃), 0.74 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 3 H, CH₃); (*Z* isomer, C₆D₆): δ 7.0–7.26 (m, 9 H, Ph), 5.86 (d, $^3J_{\text{H-H}} = 7.3$ Hz, 1 H, C=CH), 5.10 (d, $^3J_{\text{H-H}} = 7.3$ Hz, 1 H, C=CH), 3.56 (t, $^3J_{\text{H-H}} = 6.5$ Hz, 2 H, OCH₂), 1.12–1.45 (m, 4 H, CH₂CH₂CH₃), 0.78 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 3 H, CH₃). MS: m/z 252 (M⁺).

2,3-Dihydro-4-(2-(1,1'-biphenyl))furan (50% conversion). ^1H NMR (C₆D₆): δ 7.21–7.04 (m, 9 H, Ph), 5.85 (t, $^4J_{\text{H-H}} = 2.0$ Hz, 1 H, OCH=C), 3.97 (t, $^3J_{\text{H-H}} = 9.4$ Hz, 2 H, OCH₂CH₂), 2.34 (td, $^3J_{\text{H-H}} = 9.4$ Hz, $^4J_{\text{H-H}} = 2.0$ Hz, OCH₂CH₂). MS: m/z 222 (M⁺).

2-(1-Pentenyl)-1,1'-biphenyl (61% conversion, *E:Z* = 5.5:1). ^1H NMR (*E* isomer, CDCl₃): δ 6.34 (d, $^3J_{\text{H-H}} = 16$ Hz, 1 H, C=CH), 6.13 (dt, $^3J_{\text{H-H}} = 16$ Hz, $^4J_{\text{H-H}} = 6.9$ Hz, 1 H, C=CH), 2.08 (q, $J_{\text{H-H}} = 7.3$ Hz, 2 H, C=CHCH₂), 1.42 (sextet, $J_{\text{H-H}} = 7.4$ Hz, 2 H, CH₂CH₂CH₃), 0.89 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 3 H, CH₃); (*Z* isomer, CDCl₃): δ 6.23 (d, $^3J_{\text{H-H}} = 12$ Hz, 1 H, C=CH), 5.58 (dt, $^3J_{\text{H-H}} = 12$ Hz, $^4J_{\text{H-H}} = 7.2$ Hz, 1 H, C=CH), 2.22 (q, $J_{\text{H-H}} = 7.4$ Hz, 2 H, C=CHCH₂), 1.44 (sextet, $J_{\text{H-H}} = 7.4$ Hz, 2 H, CH₂CH₂CH₃), 0.90 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 3 H, CH₃). MS: m/z 222 (M⁺).

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Supporting Material Available includes experimental details for the identification of compounds **6**, **9**, and **10**, experimental details for the X-ray structure determinations of **2** and **3**, and tables of crystallographic data including atomic coordinates, thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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