Mercury in Organic Chemistry. 11.[1] Synthesis of Symmetrical 1,3-Dienes and Biaryls via Rhodium Catalyzed Dimerization of Vinyl- and Arylmercurials

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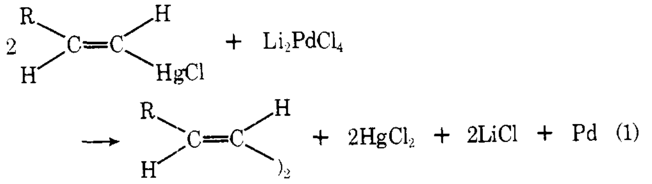
Vinyl- and arylmercuric chlorides readily react with rhodium(I) and -(III) catalysts in the presence of lithium chloride to give excellent yields of the corresponding symmetrical 1,3-dienes and biaryls, respectively. Organorhodium compounds are presumed to be intermediates in these reactions.

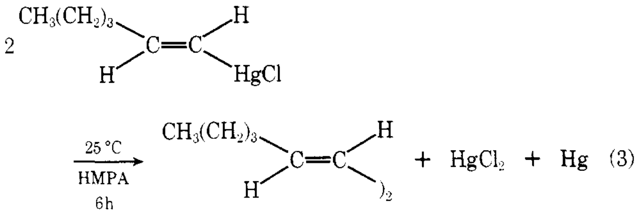
Conjugated 1,3-dienes are valuable intermediates in a number of synthetic organic processes, most notably the Diels–Alder reaction.[2] Considerable attention has been given of late to the synthesis of these compounds and a number of interesting methods employing vinylmetallic reagents have been reported in recent years. We recently reported a useful new method for the symmetrical dimerization of readily available vinylmercuric chlorides which employed stoichiometric amounts of palladium chloride and lithium chloride and provided 1,3-dienes in excellent yield (eq 1).[3] The reaction was carried out at 0 °C in hexamethylphosphoramide (HMPA) solvent. This procedure suffered three major disadvantages. First and foremost, it required stoichiometric amounts of expensive palladium chloride. Secondly, to achieve high stereospecificity the reaction had to be carried out at temperatures close to that at which HMPA begins to solidify. Finally, the solvent of choice, HMPA, has since been found to be carcinogenic. During the course of our work, Vedejs and Weeks reported a similar reaction employing *cis*- and *trans*-dipropenylmercury and catalytic amounts of tetrakis(triphenylphosphine)palladium(0) (eq 2).[4] Unfortunately, divinylmercurials are generally liquids and thus more difficult to handle and purify than the corresponding vinylmercuric chlorides. Furthermore, owing to their greater volatility, they are presumably much more toxic. This catalytic procedure also proceeds with approximately 4–8% loss of stereospecificity. At about the same time Elbe and Köbrich also reported a catalytic palladium chloride procedure which proceeded primarily with inversion of stereochemistry.[48] Recently, we discovered that both rhodium(I) and -(III) complexes very effectively catalyze the dimerization of vinylmercuric chlorides, and overcome all of the disadvantages of previous procedures. Under the appropriate conditions, excellent yields of isomerically pure 1,3-dienes are obtained. Arylmercuric chlorides are also dimerized in high yield and isomeric purity to the corresponding biaryls using these same catalysts.



$$(CH_3CH{=}CH)_2Hg \xrightarrow{\text{cat. Pd(PPh}_3)_4} (CH_3CH{=}CH)_2 + g \quad (2)$$

Results and Discussion

Synthesis of Dienes and Polyenes. During the course of our earlier studies on the synthesis of α,β-unsaturated ketones,[5] we studied the effect of a variety of transition metal catalysts on the reaction of acid chlorides and vinylmercurials. In most solvents rhodium catalysts were observed to give small amounts of 1,3-dienes as side products. In HMPA the diene was the only product observed. We subsequently studied the effect of 10% of a variety of commercially avaliable rhodium(I) and -(III) complexes on the room temperature dimerization of *trans*-1-hexenylmercuric chloride in HMPA (eq 3). The results are summarized in Table I.



All of the rhodium complexes studied proved to be catalytic. The rhodium(I) complexes generally appear to be more effective than rhodium trichloride. In all reactions the trans,trans diene was obtained in 98% or greater stereospecificity. Unlike our earlier palladium reactions, low temperatures are no longer necessary to achieve high stereospecificity. While the large majority of the diene product is formed in the first 6 h, we have subsequently observed that the yields can be slightly improved by letting the reactions proceed for 24 h, and all subsequent reactions have been run for 24 h. As in our earlier work with palladium chloride, we found that the addition of lithium chloride (2 equiv per vinylmercurial) can substantially improve the yield of diene. The combination of lithium chloride and $[ClRh(CO)_2]_2$ or $RhCl_3{\cdot}nH_2O$ appeared to be the most effective catalyst. A comparison of these two complexes at various catalyst concentrations demonstrated the superiority of the rhodium(I) complex (Table II). Even at concentrations as low as 0.01% and in the presence of air, this catalyst gives a 95% yield of *trans,trans*-5,7-dodecadiene from *trans*-1-hexenylmercuric chloride. For all subsequent work, however, it was more convenient to use 1% of the catalyst. We have also studied the effect of other solvents on this reaction and found that we need not use HMPA since diethyl ether or tetrahydrofuran (THF) work equally well (Table II).

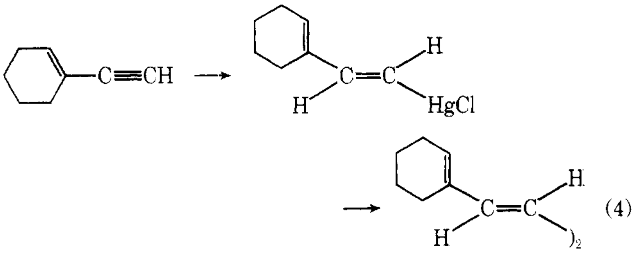
The full scope of this reaction has been investigated on a variety of vinylmercuric chlorides and the yields are indicated in Table III. Vinylmercurials derived from terminal alkynes[6,7] give excellent yields of the corresponding dienes. The more sterically hindered vinylmercurials derived from internal alkynes[6,7] react much more sluggishly and even after heating at 75 °C for 24 h still give only very poor yields of 1,3-dienes. Our earlier reported palladium procedure gives much higher yields with these compounds. Our new catalytic procedure also effectively dimerizes vinylmercurials derived from enynes providing a very mild, convenient route to polyenes (eq 4).

The ready availability of vinylmercurials from the corresponding alkynes,[6,7] the mild reaction conditions, the highly

Table I. Rhodium Catalyzed Dimerization of *trans*-1-Hexenylmercuric Chloride[a]

Rhodium complex	Diene yield, %[b]	Rhodium complex	Diene yield, %[b]
$ClRh(PPh_3)_3$	28	$[ClRh(CO)_2]_2$	87
$ClRh(CO)(PPh_3)_2$	74	$[ClRh(CO)_2]_2/LiCl$[d]	95
$[ClRh(CH_2{=}CH_2)_2]_2$	70	$RhCl_3{\cdot}nH_2O$[e]	61
$[ClRh(COD)]_2$[c]	81	$RhCl_3{\cdot}nH_2O$[e]$/LiCl$[d]	94

[a] All reactions were run with 10% "rhodium" per vinylmercurial (5% dimeric rhodium complex) for 6 h at room temperature in HMPA under a nitrogen atmosphere. [b] All yields were determined by GLC analysis using an internal standard. [c] COD = 1,5-cyclooctadiene. [d] Two equivalents of lithium chloride per vinylmercurial were employed. [e] n is approximately 2.3.

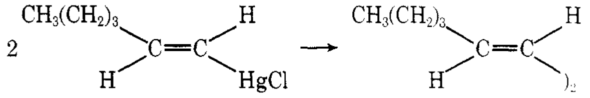

(4)

catalytic nature of the reaction, the high stereospecificity, and the ease of isolation of the products make this new catalytic rhodium procedure especially valuable for the synthesis of symmetrical 1,3-dienes and polyenes, particularly those containing functional groups.

Synthesis of Biaryls. Biaryls are usually prepared by the dimerization of aryl halides by copper (Ullmann reaction)[8-10] or zero-valent nickel reagents,[11-13] or through the reaction of aromatic Grignard[14-20] or lithium reagents[21,22] with any of a variety of inorganic salts. The Ullmann reaction suffers several disadvantages. It is best carried out with aryl iodides which are often difficult to obtain in high isomeric purity. It is incompatible with amine, amide, and hydroxyl functionality and it usually requires basic solvents and temperatures in excess of 200 °C for extended reaction times. The nickel(0) reagents are not readily available and are difficult to handle. The use of the highly reactive arylmagnesium and -lithium reagents is limited by the incompatibility of these organometallics with a variety of important organic functional groups.

Encouraged by our success in the dimerization of vinylmercurials, we chose to examine the corresponding reaction of arylmercuric chlorides as a possible new route to biaryls. Previous workers have reported the dimerization of diarylmercury compounds at high temperatures (>200 °C) in both the presence[23] and absence[24] of a variety of transition metals. Palladium salts are also reported to dimerize arylmercurials.[25-28] The yields in all of these reactions are, however, generally quite poor. During the course of our work Kretchmer and Glowinski reported an improved procedure for the synthesis of biaryls from arylmercuric salts using ~10% palladium chloride, a considerable excess of copper metal (~430%), and pyridine as a solvent, and heating to 115 °C for 5–24 h.[29] While this reaction tolerates a variety of functional groups, arylmercurials containing carboxylic acid and phenolic functionalities do not react. It also suffers the disadvantages of using a large amount of copper, a basic solvent, and high temperatures for a considerable length of time. We have found that 1% $[ClRh(CO)_2]_2$ effectively catalyzes the dimerization of arylmercurials to biaryls and overcomes some of the disadvantages of this earlier procedure. It, however, has its own limitations also.

Table II. Comparison of Rhodium Catalyst Activity



Rhodium catalyst	Solvent	Concn, %[a]	Yield, %[b]
$RhCl_3{\cdot}nH_2O$[c]$/LiCl$	HMPA	10	100
		1	85
$[ClRh(CO)_2]_2/LiCl$		10	98
		1	100
		0.01	90
			95[d]
	Et_2O	1	90
	THF		78[e]
			99

[a] Percent "rhodium" per vinylmercurial. [b] Analysis by GLC using an internal standard. [c] n is approximately 2.3. [d] Reaction run in the presence of air (all others are under nitrogen). [e] No lithium chloride used.

Using conditions similar to those worked out for the synthesis of dienes ($[ClRh(CO)_2]_2$ and lithium chloride), we have examined the effect of different catalyst concentrations, temperatures, and solvents on the dimerization of both phenylmercuric chloride and diphenylmercury (Table IV). Phenylmercuric chloride proved significantly less reactive than any of the vinylmercuric chlorides examined earlier and reaction temperatures greater than room temperature were required to obtain a reasonable rate of reaction. A reaction temperature of 80 °C was quite sufficient and all subsequent work was done at this temperature. Catalyst concentrations as low as 1% proved effective. Increasing or decreasing the amount of catalyst resulted in lower yields of biphenyl. Polar solvents proved most effective, with acetonitrile somewhat less effective than HMPA.

Using our optimum conditions, we have examined the generality of our approach to the synthesis of biaryls (eq 5)

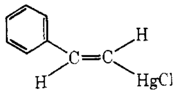
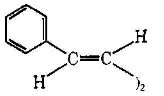
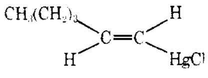
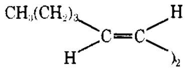
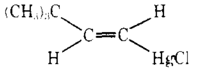
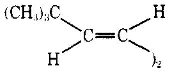
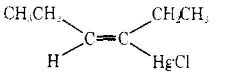
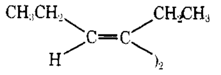
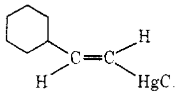
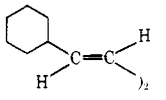
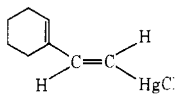
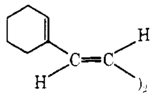
$$2ArHgCl \xrightarrow[\substack{4LiCl\\ HMPA\\ 24\ h\\ 80\ °C}]{0.5\%[ClRh(CO)_2]_2} ArAr + HgCl_2 + Hg^0 \qquad (5)$$

(Table V). In general the yields of biaryl are comparable to those obtained by other routes and the purity of the "crude" product often exceeds that of recrystallized literature samples. Moreover, the reaction proceeds at much lower temperatures than the Ullmann reaction and significantly lower than those of Kretchmer's procedure. In addition, basic solvents are not required. While the Ullmann reaction fails with aromatic amines, amides, phenols, and acids, Kretchmer's procedure overcomes the problems associated with amines and amides, but fails with phenols and acids. Our procedure works only poorly with amines, and amides were not examined. Better results were obtained with phenols, but acids were not studied owing to the reported reaction of acids with HMPA under reaction conditions similar to ours.[39] Neither of the procedures works well on sterically hindered arylmercurials such as mesitylmercuric acetate and chloride.

The ease with which arylmercurials are obtained through direct electrophilic aromatic mercuration of arenes and the high isomeric purity obtained by simple recrystallization of these stable organometallics recommends their use in organic synthesis. The mild conditions for dimerization and ease of isolation, plus the high isomeric purity of the products, make this a valuable new route to symmetrical biaryls.

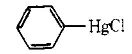
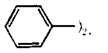
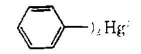
Attempted Dimerization of Alkylmercurials. In an attempt to extend the dimerization reaction to alkylmercurials,

Table III. Synthesis of Dienes and Polyenes

Vinylmercurial	Registry no.	Catalyst[a]	Solvent	Diene	Registry no.	Yield, %[b]
	36525-03-8	$RhCl_3 \cdot nH_2O$	HMPA		538-81-8	65
		$[ClRh(CO)_2]_2$				100
			THF			84
	50874-36-7	$RhCl_3 \cdot nH_2O$	HMPA		30651-68-4	85
		$[ClRh(CO)_2]_2$				100
			THF			99
	36525-02-7	$RhCl_3 \cdot nH_2O$	HMPA		22430-49-5	98
		$[ClRh(CO)_2]_2$				100 (88)
			THF			100
	36525-04-9	$RhCl_3 \cdot nH_2O$	HMPA		30651-70-8	24[c]
		$[ClRh(CO)_2]_2$				35[c]
	36525-01-6				55712-53-3	(90)
			THF			(97)
	56453-89-5		HMPA		61665-42-7	(92)

[a] 1% "rhodium" and 2 equiv of lithium chloride per vinylmercurial. [b] GLC analysis (isolated yield). [c] Reactions run at 75 °C.

Table IV. $[ClRh(CO)_2]_2$ Catalyzed Dimerization of Arylmercurials[a]

Arylmercuric chloride[b]	Biaryl	Solvent	Catalyst concn, %[c]	Temp, °C	Yield, %[d]
		THF	1	66	15[e]
					25
		MeOH		65	24
		CH_3CN		82	65
		HMPA	1	25	25
			0.5	80	61
			1		81
			2		67
			1	125	78
			1	25	36
			1	80	66

[a] All reactions were run for 24 h with 2 equiv of lithium chloride per arylmercurial under a nitrogen atmosphere. [b] One millimole of phenylmercuric chloride or 0.5 mmol of diphenylmercury. [c] Percent "rhodium" per vinylmercurial. [d] GLC analysis using an internal standard. [e] No lithium chloride present. [f] Registry no., 587-85-9.

n-hexylmercuric chloride was stirred with lithium chloride (2 equiv) and 0.5% $[ClRh(CO)_2]_2$ under a nitrogen atmosphere at room temperature for 1 day. No dodecane was observed by gas chromatography so the reaction mixture was heated to 180 °C for 1 day and analyzed again. Again no dodecane was observed. This is consistent with our earlier observations on the reactions of alkylmercuric chlorides with palladium chloride.[3] It appears unlikely that reaction conditions can be found which will allow the rhodium catalyzed coupling of simple alkylmercurials. We previously reported the palladium promoted coupling of alkylmercuric chlorides which do not contain β-hydrogen atoms bonded to sp^3 hybridized carbon atoms.[3]

Mechanism. While analogies to other transition metal coupling reactions, especially those of nickel, palladium, and rhodium, can be cited, we presently have little direct evidence on which to base a mechanism. We believe, however, that both the aryl- and vinylmercury dimerization reactions involve (1) a transfer of the organic moiety from mercury to rhodium producing mercuric chloride and an organorhodium(I) species, (2) an oxidative addition across the carbon–mercury bond of a second equivalent of organomercurial to produce a rhodium(III) species, and (3) a reductive elimination of the organic dimer which regenerates the rhodium(I) catalyst and metallic mercury (Scheme I). The many reported exchange reactions of organomercurials with palladium salts suggest that rhodium should also readily undergo such reactions. The large number of oxidative addition reactions of rhodium(I) species, including the reported rhodium(I) oxidative addition of organomercurials across the carbon–mercury bond,[40] lend credence to the second step of our proposed mechanism. In line with our previous work with palladium, one might then expect these compounds to reductively eliminate the dimeric product. Metallic mercury is in fact observed in these reactions.

Scheme I

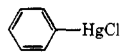
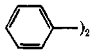
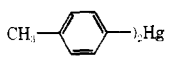
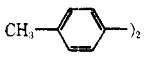
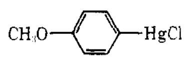
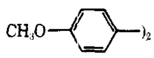
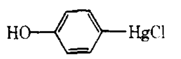
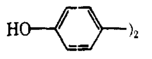
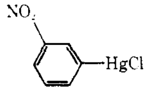
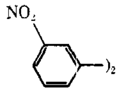
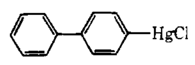
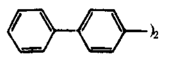
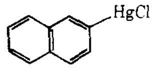
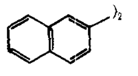
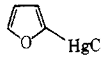
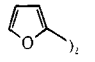
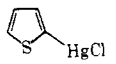
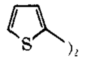
$$RHgCl + RhCl \rightarrow RhR + HgCl_2 \quad (1)$$

$$RhR + RHgCl \rightarrow R_2RhHgCl \quad (2)$$

$$R_2RhHgCl \rightarrow R\text{-}R + RhCl + Hg \quad (3)$$

Since a rhodium(III) species is presumably formed in our reactions, we reasoned that rhodium trichloride would also serve as a suitable catalyst and this indeed proved true. Pre-

Table V. Synthesis of Biaryls

Arylmercuric chloride	Registry no.	Biaryl	Registry no.	Isolated yield, %	Mp, °C (lit. mp, °C)	Ref
	100-56-1		92-52-4	84	62–65.5 (70.5)	*a*
	537-64-4		613-33-2	92	120–121.5 (121–122)	*b*
	3009-79-8		2132-80-1	88	177–178 (175)	*c*
	623-07-4		92-88-6	88	277–278.5 (272)	*d*
	2865-17-0		958-96-3	53	202-202.5 (200)	*e*
	20883-34-5		135-70-6	40	312–313 (320)	*f*
	39966-41-1		612-78-2	94	185–186 (187–188)	*g*
	5857-37-4		5905-00-0	70	Oil	*h*
	5857-39-6		492-97-7	96	32–33 (32.5)	*i*

[a] See ref 30. [b] See ref 31. [c] See ref 32. [d] See ref 33. [e] See ref 34. [f] See ref 35. [g] See ref 36. [h] See ref 37. [i] See ref 38.

sumably transmetalation occurs to directly produce the diorganorhodium(III) species which after reductive elimination generates a rhodium(I) species which goes on to react as indicated in Scheme I (Scheme II).

Scheme II

$$2RHgCl + RhCl_3 \rightarrow R_2RhCl + 2HgCl_2$$

$$R_2RhCl \rightarrow R\text{-}R + RhCl$$

Conclusion

Vinyl- and arylmercuric chlorides, readily available from acetylenes and arenes, are catalytically dimerized to symmetrical 1,3-dienes and biaryls by 1% $[ClRh(CO)_2]_2$ and lithium chloride in THF and HMPA, respectively. The products are obtained in excellent yield and high isomeric purity.

Experimental Section

Reagents. All chemicals were used directly as obtained commercially unless otherwise indicated. HMPA was distilled from lithium aluminum hydride under vacuum. Pentane was stirred over fuming sulfuric acid, washed with water, and stored over anhydrous sodium sulfate after distillation. Ether and THF were distilled from $LiAlH_4$.

Phenylmercuric chloride (Aldrich), diphenylmercury (Eastman), di-*p*-tolylmercury (Eastman), and 4-chloromercuriphenol (Eastman) were used directly as obtained. 4-Methoxyphenylmercuric chloride,[41] 4-aminophenylmercuric chloride,[42] 3-nitrophenylmercuric chloride,[43] 2-chloromercurinaphthalene,[44] mesitylenemercuric chloride,[45] 2-chloromercurifuran,[42] 2-chloromercurithiophene,[46] and 4-chloromercuribiphenyl[45] were all prepared using literature procedures.

The vinylmercurials used have all been described elsewhere and were prepared using a standard hydroboration–mercuration sequence.[6]

$[ClRh(CO)_2]_2$ (PCR), $[(CH_2{=}CH_2)_2RhCl]_2$ (Strem), (1,5-COD $RhCl)_2$ (ROC/RIC), $(Ph_3P)_2Rh(CO)Cl$ (Alfa Inorganics-Ventron), and $RhCl_3 \cdot nH_2O$ (Matthey Bishop) were used directly as obtained. Wilkinson's catalyst, $(Ph_3P)_3RhCl$, was prepared from $RhCl_3 \cdot nH_2O$ according to published procedures.[47]

All GLC yields are corrected by the use of appropriate hydrocarbon internal standards.

Rhodium Catalyzed Dimerization of *trans*-1-Hexenylmercuric Chloride. The catalytic activity of a variety of different rhodium catalysts was examined using the following standard procedure for the dimerization of *trans*-1-hexenylmercuric chloride. The catalyst (0.10 mmol of monomeric, and 0.05 mmol of dimeric rhodium catalysts), tetradecane (internal standard, ca. 0.5 mmol), and lithium chloride (2.0 mmol) where appropriate were dissolved in HMPA (5 mL) in a 25-mL round-bottom flask which has been previously flushed with nitrogen. The *trans*-1-hexenylmercuric chloride (1.00 mmol) was added and the reaction mixture stirred for 6 h at room temperature. Ether (5 mL) was then added and the mixture analyzed on a 10-ft 10% DC-550 GLC column. The results are included in Table I.

Comparison of Rhodium Catalyst Activity. The appropriate amount of $RhCl_3 \cdot nH_2O$ ($n \simeq 2.3$) (0.1 or 0.01 mmol) or $[ClRh(CO)_2]_2$ (0.05, 0.005, or 0.00005 mmol), lithium chloride (2 mmol), and tetradecane were dissolved in 5 mL of the appropriate solvent. *trans*-1-Hexenylmercuric chloride (1 mmol) was added and the reaction mixture stirred for 24 h at room temperature. The yields in HMPA were determined by GLC as described above. The ether and THF reactions were analyzed by GLC after adding water or saturated ammonium chloride solution, respectively. $[ClRh(CO)_2]_2$ (0.01%) was achieved by adding 0.025 mL of a solution containing 4.0 mg of catalyst in 5.0 mL of HMPA. The results are summarized in Table II.

Synthesis of Dienes and Polyenes. The following procedure for the synthesis of *trans,trans*-2,2,7,7-tetramethylocta-3,5-diene is representative. $[ClRh(CO)_2]_2$ (0.05 mmol) and lithium chloride (20 mmol) were placed in a 250-mL round-bottom flask equipped with a septum inlet and gas inlet tube which has been flushed with nitrogen. HMPA (50 mL) and then *trans*-3,3-dimethyl-1-butenylmercuric chloride (10.0 mmol) were added and the reaction mixture stirred for 24 h at room temperature. The reaction mixture was poured into water and pentane added. A gray suspension formed and was filtered off. The gray residue was washed with pentane. The pentane layer was separated and the water layer reextracted with pentane. The combined pentane extracts were washed with water and dried over anhydrous sodium sulfate, and the pentane removed under vacuum. A white solid [0.73 g, 88%, crude mp 74–77 °C, mp 77–78 °C (EtOH), lit.[3] mp 78–79 °C] was obtained: ^1H NMR (CCl_4) δ 1.00 (18 H, s, CH_3) and 5.6 (4 H, m, vinyl).

The following new compounds were prepared in a similar manner. *trans,trans*-1,4-Di(1-cyclohexenyl)buta-1,3-diene: yellowish solid, mp 100–104 °C (pentane); ^1H NMR (CCl_4) δ 1.60 (8 H, m, aliphatic), 2.10 (8 H, m, allyl), 5.56 (2 H, m, cyclohexenyl vinyl), 5.97 (4 H, s, vinyl); IR (max) (KBr) 3020, 2940, 2920, 1625, 1440, 1345, 1130, 1070, 980, 920, and 850 cm^{-1}; *m/e* 214.1723 (calcd for $C_{16}H_{22}$, 214.1722). *trans,trans*-1,4-Dicyclohexylbuta-1,3-diene: low-melting solid (~20–25 °C); ^1H NMR (CCl_4) δ 0.8–2.3 (22 H, m, cyclohexyl) and 5.1–6.1 (4 H, m, vinyl); IR (max) (Nujol) 3015, 1455, 1355, 990, 965, 895, and 845 cm^{-1}; *m/e* 218.2040 (calcd for $C_{16}H_{26}$, 218.2035).

The THF preparative reaction was worked up by adding saturated ammonium chloride, separating the layers, and washing the aqueous layer with hexane. The combined organic layers were then washed with saturated ammonium chloride, 3 M sodium thiosulfate, and saturated sodium chloride and dried over anhydrous sodium sulfate, and the solvent was removed.

All GLC yields were determined on reactions run on one-tenth the above scale following GLC analysis procedures identical with those outlined above. Internal standard correction factors were determined using authentic diene samples.[3] All isolated dienes were obtained in greater than 95% purity and required no additional purification, although simple recrystallization gave excellent recovery.

$[ClRh(CO)_2]_2$ Catalyzed Dimerization of Arylmercurials. The effect of catalytic amounts of $[ClRh(CO)_2]_2$ on the dimerization of phenylmercuric chloride and diphenylmercury was examined as follows. The appropriate quantity of $[ClRh(CO)_2]_2$ (0.01, 0.005, and 0.0025 mmol), lithium chloride (2.0 mmol), and octadecane were dissolved in the appropriate solvent (5 mL) in a 25-mL round-bottom flask equipped with a rubber septum. After adding phenylmercuric chloride (1.0 mmol) or diphenylmercury (0.50 mmol) the reaction mixture was stirred for 24 h at room temperature or in a preheated oil bath. The HMPA reaction was poured into water and ether added. The ether layer was analyzed by GLC on a 10-ft 10% DC-550 column. The THF reactions were analyzed as described previously and the methanol and acetonitrile reactions were analyzed directly.

Synthesis of Biaryls. The following procedure for the synthesis of 4,4′-bianisole is representative. $[ClRh(CO)_2]_2$ (0.05 mmol) and lithium chloride (20 mmol) were dissolved in HMPA (50 mL) in a 250-mL round-bottom flask equipped with a gas inlet tube and a side arm fitted with a rubber septum. After 4-methoxyphenylmercuric chloride (10 mmol) was added the reaction mixture was stirred in a preheated oil bath at 80 °C for 24 h. A puddle of metallic mercury was observed. The reaction mixture was then poured onto ice and benzene added. After the layers were separated, the water was reextracted with benzene. The combined organic layers were washed with water, 10% HCl, 3 M sodium thiosulfate, water, and saturated sodium chloride, and dried over anhydrous magnesium sulfate. Removal of the solvent under vacuum provided 0.94 g of white solid (88%): mp 174.5–175.5 °C before recrystallization, mp 177–178 °C (hexane) (lit.[32] mp 175 °C).

The following biaryls were prepared in a similar manner. As indicated, the purity of crude products often exceeded that of recrystallized literature samples. Biphenyl: 84% yield; crude mp 62–65.5 °C (lit.[30] mp 70.5 °C). 4,4′-Bitolyl (from di-*p*-tolylmercury): 92%, mp 118–120 °C, 120–121.5 °C (hexane) (lit.[31] mp 121–122 °C). Bifuran: 70% reddish oil;[37] ^1H NMR (CCl_4) δ 6.15 (2 H, dd, $J = 1$ and 3 Hz, 4 and 4′), 6.35 (2 H, d, $J = 3$ Hz, 3 and 3′), and 7.10 (2 H, d, $J = 1$ Hz, 5 and 5′) (NMR assignments based on those of ref 37). 3,3′-Dinitrobiphenyl: 53%, mp 200.5–201 °C, mp 202–202.5 °C (benzene) (lit.[34] mp 200 °C). 2,2′-Binaphthyl: 94%, mp 184.5–185 °C, mp 185–186 °C (benzene–hexane) (lit.[36] mp 187–188 °C). Bithiophene: 96%, greenish oil which solidifies on standing, mp 30–32 °C, mp 32–33 °C (hexane) (lit.[38] mp 32.5 °C). Quaterphenyl: 40%, mp 307–310 °C, mp 312–313 °C (benzene) (lit.[35] mp 320 °C). 4,4′-Dihydroxybiphenyl: 88%, mp 267–271 °C, mp 277–278.5 °C (ether–hexane) (lit.[33] mp 272 °C).

The following biaryls required the indicated modifications in their workup. 3,3′-Dinitrobiphenyl: a suspension occurred on adding benzene, so the resulting mixture was filtered and the solid washed with a large volume of benzene. The aqueous and organic layers were then worked up according to the standard procedure. Quaterphenyl: the reaction was carried out at 120 °C and worked up by pouring the reaction mixture onto ice, filtering and collecting the crude solid, washing with water, and then dissolving in a large volume of boiling benzene and filtering hot. The benzene was removed under vacuum and a white solid collected. 4,4′-Dihydroxybiphenyl: ether was used for the workup and sodium thiosulfate was omitted during the workup. Extra water washes were required to remove HMPA.

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