Palladium-Catalyzed Three-Component Assembling of Allenes, Organic Halides, and Arylboronic Acids

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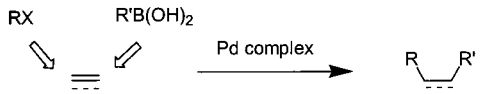
An efficient method for the construction of two carbon−carbon bonds in a regio- and stereoselective fashion via palladium-catalyzed assembling of allenes, organic halides, and arylboronic acids is described. Organic halides (RI = C_6H_5I, *o*-, *m*-, and *p*-$CH_3OC_6H_4I$, *p*-$C_2H_5OCOC_6H_4I$, *p*-$CH_3COC_6H_4I$, *p*-$CH_3C_6H_4I$, *p*-$CH_3C_6H_4Br$, *p*-$CH_3C_6H_4Cl$, *p*-$NO_2C_6H_4I$, *p*-$NO_2C_6H_4Br$, *p*-$NO_2C_6H_4Cl$, *p*-IC_6H_4Cl, 1-iodonaphthalene, 2-iodothiophene, 3-iodo-2-cyclopenten-1-one, 3-iodo-5,5-dimethyl-2-cyclohexen-1-one, $C_6H_5(Br)C{=}CH_2$ and $ICH_2CO_2C_2H_5$), and arylboronic acids ($ArB(OH)_2$, Ar = C_6H_5, *p*-$CH_3OC_6H_4$, *m*-$NO_2C_6H_4$, *p*-FC_6H_4, 1-$C_{10}H_7$, and *o*-, *m*-, and *p*-$CHOC_6H_4$) undergo Suzuki-type three-component assembling with 1,1-dimethylallene to give the corresponding allylic derivatives, $(CH_3)_2{=}CRCH_2Ar$, in DMF at 70 °C in the presence of CsF using $Pd(dba)_2$ as the catalyst. Higher yields of products were obtained for aryl iodides than for the corresponding aryl bromides and chlorides. This three-component assembling is highly regioselective, with the organic group on halides adding to the middle carbon and the aryl group on arylboronic acids to the unsubstituted terminal carbon of allenes. Monosubstituted allenes **1b**−**e** (cyclopentylallene, cyclohexylallene, *tert*-butylallene, and *n*-butylallene) also undergo similar assembling reaction with organic halides and arylboronic acids to afford the corresponding products **7a**−**i** with high regio- and stereoselectivity. Based on the known palladium chemistry, a mechanism is proposed to account for the catalytic reaction and the stereochemistry.

Introduction

Organoboronic acids are widely used in the palladium-catalyzed Suzuki cross-coupling with aryl or vinylic halides providing a very efficient route for carbon−carbon bond formation.[1] A practical advantage of the Suzuki reaction relative to many other cross-coupling processes is the mild nature of boronic acids that are readily prepared, nontoxic and thermally, air-, and moisture-stable, as well as compatibility with diverse functional groups.[2] While the cross coupling of organoboronic acids with aryl or vinylic halides has been well studied,[1,3] the application of these mild reagents in other reactions is much less documented.[4] Scattered reports on the arylation or alkenylation by organoboronic acids of palladium[1a,5] and nickel[6] π-allyl complexes are known. An extension of Suzuki cross coupling is the Suzuki-type three-component assembling reaction (Scheme 1).[7] The development of an efficient and general method for this three-component assembling reaction is highly attractive in view of the power to form two carbon−carbon bonds in a single reaction.[8]

Scheme 1



Recently, much attention has been drawn to the chemistry of allenes,[9] a class of unsaturated organic

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substrates with unique reactivity in the three-component assembling reaction.[10] An allene can insert rapidly into a metal−carbon bond from oxidative addition of an organic halide to the metal catalyst to give a π-allyl species that is reasonably stable to β-hydride elimination.[11] Attack of the π-allyl species by a nucleophile led to the three-component assembling product.[12] Several types of electrophile including acyl, aryl, and vinylic halides and nucleophiles such as amines, alkoxides, and stable carbon anions are known[13] in this palladium-catalyzed addition to allenes,[9] but low stereo- and regioselectivity were encountered in most cases.[14] Our interest in the palladium-catalyzed allene reactions has led us to successfully develop several regio- and stereoselective three-component assembling reactions of allenes.[10,12] In view of the ability of arylboronic acids as nucleophiles to attack palladium π-allyl species, we investigated the three-component assembling of organic halides, allenes, and arylboronic acids catalyzed by palladium complexes. The key to the success of the reaction lies on the choice of a proper base and solvent that can activate organoboronic acids[15] but without deprotonating the palladium π-allyl species to give the diene products.[12a] In this paper, we wish to report that by using $Pd(dba)_2$ as catalyst in the presence of CsF in DMF, the Suzuki-type three-component assembling proceeds smoothly. The reaction is compatible with various functional groups and provides an efficient method for preparing several types of organic compounds such as dienes, dienenones, and various substituted allylic species. Moreover, the reaction constructs two carbon−carbon bonds chemo-, regio-, and stereoselectively under mild conditions.

Results and Discussion

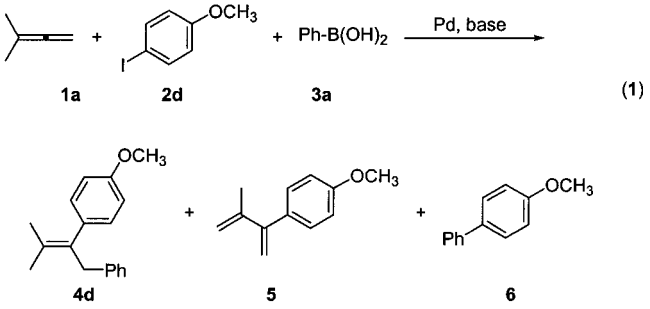
Reaction Conditions for Three-Component Assembling. Treatment of 1,1-dimethylallene (**1a**) with *p*-iodoanisole (**2d**) and phenylboronic acid (**3a**) in the presence of CsF catalyzed by $Pd(dba)_2$ in DMF at 70 °C for 7 h gave three-component assembling product **4d** in 88% isolated yield. No other product was observed, indicating that the reaction is highly chemo- and regioselective. Spectral data of this product showed that the *p*-$MeOC_6H_4$ and C_6H_5 groups were added to the middle and unsubstituted terminal carbons, respectively, of the allene moiety.

Table 1. Effect of Reaction Conditions on the Yields of the Three-Component Assembling of 1,1-Dimethylallene, *p*-Iodoanisole, and Phenylboronic Acid[a]

entry	Pd catalyst	base, solvent	temp (°C) time (h)	yield (%)[b] 4d	5	6
1	$Pd(OAc)_2$	CsF/DMF	70/7	67	--	10
2	$PdCl_2(PPh_3)_2$	CsF/DMF	70/7	17	--	53
3	$Pd(dba)_2$	CsF/DMF	70/7	88	--	--
4	$Pd(dba)_2/1PPh_3$	CsF/DMF	70/7	57	--	--
5	$Pd(dba)_2/2PPh_3$	CsF/DMF	70/7	40	--	--
6	$Pd(dba)_2/4PPh_3$	CsF/DMF	70/7	--	--	--
7	$Pd(dba)_2$	--/DMF	70/48	--	--	--
8	$Pd(dba)_2$	K_2CO_3/DMF	70/12	51	14	10
9	$Pd(dba)_2$	NaOH/DMF	70/7	--	12	63
10	$Pd(dba)_2$	Cs_2CO_3/DMF	70/12	46	9	--
11	$Pd(dba)_2$	Na_2CO_3/DMF	70/12	37	10	8
12	$Pd(dba)_2$	Li_2CO_3/DMF	70/12	--	9	--
13	$Pd(dba)_2$	CsF/DMF	rt/24	--	--	--
14	$Pd(dba)_2$	CsF/DMF	50/17	51	--	10
15	$Pd(dba)_2$	CsF/DMF	90/7	80	8	--
16	$Pd(dba)_2$	CsF/CH_3CN	70/24	12	--	23
17	$Pd(dba)_2$	CsF/THF	reflux/24	20	--	32
18	$Pd(dba)_2$	CsF/Toluene	70/48	26	--	10
19	$Pd(dba)_2$	CsF/CH_2Cl_2	reflux/24	--	--	--
20	$Pd(dba)_2$	CsF/Et_3N	70/48	--	15	44

[a] All reactions were carried out under the following conditions: 1,1-dimethylallene (**1a**, 1.00 mmol), *p*-iodoanisole (**2d**, 0.50 mmol), phenylboronic acid (**3a**, 0.750 mmol), Pd complex (0.0250 mmol), base (1.50 mmol), and solvent (2.5 mL). [b] Isolated yields are based on *p*-iodoanisole.

The yield of product **4d** depends greatly on the palladium catalyst, ligand, base, solvent, and temperature employed. Table 1 summarizes the results of these studies. Of the several solvents tested, DMF gave the highest yield of **4d**. The other solvents including CH_3CN, THF, toluene, CH_2Cl_2, and Et_3N showed either low chemoselectivity or low yield of product **4d**. Two side products **5**[12a] and **6** from the reaction were detected depending on the solvent used (eq 1). The three-



component assembling reaction requires the presence of a base (entries 3 and 7) to promote the reactivity of boronic acid **3a**.[15] However, a strong base such as NaOH greatly increases the direct coupling product **6** and diene **5**[12a] (entry 9). The use of weaker base such as K_2CO_3, Cs_2CO_3, or Na_2CO_3, improves the yield of **4d**, but side products **5** and **6** are still produced in substantial amount. Of the bases tested, CsF appears to be the best giving product **4d** with essentially no side products **5** and **6** detected. The effect of palladium complex and ligand on the catalytic activity was also investigated (entries 1−6). Phosphine-free palladium complexes $Pd(OAc)_2$ and $Pd(dba)_2$ catalyze this reaction smoothly, but the latter appears superior over the former in view of the selectivity of product **4d** (entry 3). The presence of PPh_3 inhibits the catalytic reaction; the yield of product **4d** decreases with increasing PPh_3/Pd ratio.

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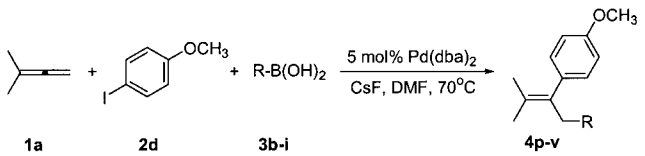
Table 2. Results of Three-Component Assembling of 1,1-Dimethylallene, Organic Halides, and Phenylboronic Acid[a]

entry	Organic halides **2**		Product **4**		Yield (%)[b]
1		**2a**		**4a**	89
2		**2b**		**4b**	48
3		**2c**		**4c**	63
4		**2d**		**4d**	88
5		**2e**		**4e**	70
6		**2f**		**4f**	68
7		**2g, X=I**			83
8		**2h, X=Br**		**4g**	70
9[c]		**2i, X=Cl**			21
10		**2j, X=I**			81
11		**2k, X=Br**		**4h**	80
12[c]		**2l, X=Cl**			36
13		**2m**		**4i**	82
14		**2n**		**4j**	51
15		**2o**		**4k**	91
16		**2p**		**4l**	42
17		**2q**		**4** **m**	68
18		**2r**		**4n**	62
19		**2s**		**4o**	68

[a] All reactions were carried out under the following conditions: **1a** (1.00 mmol), organic halide **2** (0.500 mmol), **3a** (0.750 mmol), 5 mol % $Pd(dba)_2$ (0.0250 mmol), CsF (1.50 mmol), and DMF (2.5 mL), and reaction time, 7 h. [b] Isolated yields are based on organic halide. [c] Reaction time is 12 h.

Three-Component Assembling of 1,1-Dimethylallene, Organic Halides, and Arylboronic Acids. The three-component assembling can be successfully extended to a variety of organic halides by carrying out the reactions in DMF at 70 °C in the presence of CsF. Thus, aryl iodides including C_6H_5I, *o*-, *m*-, and *p*-$CH_3OC_6H_4I$, *p*-$C_2H_5OCOC_6H_4I$, *p*-$CH_3COC_6H_4I$, *p*-$CH_3C_6H_4I$, *p*-$CH_3C_6H_4$-Br, *p*-$CH_3C_6H_4Cl$, *p*-$NO_2C_6H_4I$, *p*-$NO_2C_6H_4Br$, *p*-$NO_2C_6H_4$-Cl, *p*-IC_6H_4Cl, and 1-iodonaphthalene react smoothly with 1,1-dimethylallene (**1a**) and phenylboronic acid (**3a**) to yield the corresponding three-component assembling products in good to excellent yields (Table 2, entries 1−14). It is noteworthy that an electron-withdrawing or electron-donating substituent on aryl iodides does not significantly affect the product yield. However, aryl iodides with an ortho-substitutent such as *o*-iodoanisole and 1-iodonaphthalene clearly give lower yields of the assembling products. Aryl bromides also react with **1a** and **3a** efficiently to provide the expected products, but the yields are slightly lower than those of the corresponding aryl iodides (entries 8 and 11). The reaction of most aryl chlorides with **1a** and **3a** was very slow, and low yields of the desired products were obtained (entries 9 and 12). For aryl chlorides, the presence of an electron-withdrawing substituent (entry 12) improves the yields of assembling products significantly. These results may be understood based on the fact that an electron-withdrawing group on aryl halide generally enhances the rate of oxidative addition to the palladium center.[16] As expected, the reaction of 1-chloro-4-iodobenzene (**2m**) with **1a** and **3a** gave product **4i** with the 4-chlorophenyl instead of 4-iodophenyl group attached to the middle carbon of the 1,1-dimethylallene moiety, a result of the fact that cleavage of C−I bond is much faster than that of the C−Cl bond. Heterocyclic compound, 2-iodothiophene, also undergoes assembling reaction with **1a** and **3a** to give product **4k** in 91% yield (entry 15). A number of alkenyl iodides including 3-iodo-2-cyclopenten-1-one, 3-iodo-5,5-dimethyl-2-cyclohexen-1-one, and α-bromostyrene were also tested for the assembling reactions with **1a** and **3a** (entries 17−19). All these reactions proceed smoothly to give in 62−68% yield the corresponding dienones or dienes that are known to be very useful in organic synthesis. An example of alkyl iodide, ethyl 2-iodoacetate (**2p**), was used in the three-component assembling with **1a** and **3a** (entry 16). The reaction went on readily to give the expected product albeit in only 42% yield.

Scheme 2



3b: *p*-$MeOC_6H_4B(OH)_2$ **4p**: 78%
3c: *m*-$NO_2C_6H_4B(OH)_2$ **4q**: 64%
3d: *p*-$FC_6H_4B(OH)_2$ **4r**: 75%
3e: 1-$C_{10}H_7B(OH)_2$ **4s**: 72%
3f: *o*-$CHOC_6H_4B(OH)_2$ **4t**: 52%
3g: *m*-$CHOC_6H_4B(OH)_2$ **4u**: 72%
3h: *p*-$CHOC_6H_4B(OH)_2$ **4v**: 74%
3i: *n*-$C_4H_9B(OH)_2$, -- --

Under similar reaction conditions, arylboronic acids **3b**−**h** ($ArB(OH)_2$, Ar = C_6H_5, *p*-$CH_3OC_6H_4$, *m*-$NO_2C_6H_4$, *p*-FC_6H_4, 1-$C_{10}H_7$, and *o*-, *m*-, and *p*-$CHOC_6H_4$) also react efficiently with 1,1-dimethylallene (**1a**) and *p*-iodoanisole (**2d**) (Scheme 2) to give the corresponding three-component assembling products in moderate to excellent yields.

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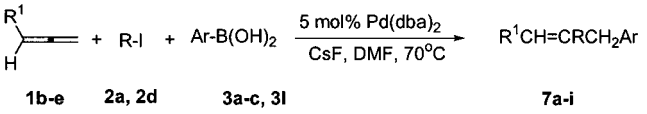
n-Butylboronic acid (**3i**), however, failed to give the desired products suggesting that alkylboronic reagents are difficult to react with π-allylpalladium(II) complexes.[1a]

Three-Component Assembling of Monosubstituted Allenes. Monosubstituted allenes including cyclopentyl- (**1b**), cyclohexyl- (**1c**), *tert*-butyl- (**1d**), and *n*-butylallene (**1e**) undergo this Suzuki-type three-component assembling with organic iodides (**2a** and **2d**) and arylboronic acids (**3a**−**c** and **3l**) efficiently, producing highly regioselective and stereoselective allylic derivatives **7a**−**i** in 69−85% yields (eq 2). The results of these



1b-e **2a, 2d** **3a-c, 3l** **7a-i** (2)

1b: R^1 = cyclopentyl **2a**: R = Ph

1c: R^1 = cyclohexyl **2d**: *R* = *p*-$MeOC_6H_4$

1d: R^1 = *t*-Bu

1e: R^1 = *n*-Bu

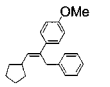
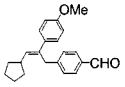
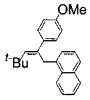
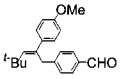
studies are listed in Table 3. The stereoselectivity of these products depends greatly on the substituent on the allene. A bulkier substituent on the allene gives products with higher *E*/*Z* ratios. In all cases, the *E* isomer was observed as the major product. For example, the reaction of *tert*-butylallene (**1d**), *p*-iodoanisole (**2d**), and *p*-fluorophenylboronic acid (**3c**) gave product **7f** with a *E*/*Z* ratio of 97/3 (entry 6). Other three-component assembling reactions of monosubstituted allenes, aryl iodides, and arylboronic acids afforded allylic derivatives with the *E*/*Z* ratios between 73/27 and 96/4.

The stereochemistry of these three-component assembling products was determined using the typical ^{1}H NMR NOE technique. For instance, there are two isomers (*E*)-**7c** and (*Z*)-**7c** isolated from the reaction of **1c**, **2a**, and **3a** (Scheme 3). The minor product (*Z*)-**7c** exhibits ^{1}H NMR signals at 3.59 and 5.32 ppm for the methylene (H_a) and olefin proton (H_b), respectively. Irradiation at H_a signal led to an increase of the H_b intensity by 5.97%. Similarly, irradiation at the H_b signal resulted in an increase of the H_a intensity by 5.96%. In contrast, irradiation at the methylene (H_c) and the olefin proton (H_d) signals of the major product, (*E*)-**7c**, showed essentially no change of the intensity of H_d and H_c signals, respectively. These NOE results unambiguously determine the stereochemistry of these two stereoisomers. Other pairs of *E*/*Z* isomers are also established by similar techniques.

The formation of *E* isomers from monosubstituted allenes is surprising in view of the fact that most carbopalladation reactions of monosubstituted allenes reported gave *E* and *Z* isomeric products with low selectivity.[11] To account for the present stereoselectivity, a mechanism based on face-selective coordination of allenes to the palladium center is proposed.[10d] The terminal double bond of allene is coordinated to the palladium moiety at the face opposite to the substituents R^1 favorably to avoid steric congestion (Scheme 4). Coordination of the terminal double bond at the other face or coordination of the internal double bond to the palladium center will lead to a great increase of steric repulsion and is less favorable. As shown in Scheme 4, the face-selective coordination results in a π-allylpalladium species with the R^1 group anti to the organic moiety R. Further reaction with arylboronic acid **3** affords product with *E* stereochemistry. It is necessary that the latter step is faster than the syn-anti rearrangement of π-allylpalladium species to obtain high *E* selectivity.

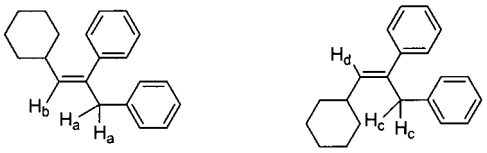
The presence of phosphorus ligand in the catalytic reaction immensely effects on the stereo- and regioselectivity of the three-component assembling product. Several phosphorus ligands, P(*o*-tol)$_3$, P(OPh)$_3$, PPh_2Me, and dppe

Table 3. Three-Component Assembling of Monosubstituted Allenes with Aryl Iodides and Arylboronic Acids[a]

entry	Allene 1	R-I 2	Ar-B(OH)$_2$ 3	Product		Yield (%)[b]	*E*/*Z*[c]
1	**1b**	**2d**	**3a**		**7a**	78	78/22
2	**1b**	**2d**	**3l**		**7b**	75	73/27
3	**1c**	**2a**	**3a**		**7c**	85	75/25
4	**1c**	**2d**	**3a**		**7d**	80	88/12
5	**1d**	**2d**	**3a**		**7e**	82	96/4
6	**1d**	**2d**	**3b**		**7f**	78	97/3
7	**1d**	**2d**	**3c**		**7g**	69	92/8
8	**1d**	**2d**	**3l**		**7h**	81	91/9
9	**1e**	**2a**	**3a**		**7i**	80	80/20

[a] All reactions were carried out using allene (**1**, 1.00 mmol), aryl iodide (**2**, 0.50 mmol), arylboronic acid (**3**, 0.750 mmol), Pd(dba)$_2$ (0.0250 mmol), CsF (1.500 mmol), and DMF (2.5 mL); reaction time is 7 h. [b] Isolated yields are based on aryl iodide. [c] The *E*/*Z* ratio was calculated from NMR peak intensities.

Scheme 3



minor, *Z*-**7c** major, *E*-**7c**

Scheme 4

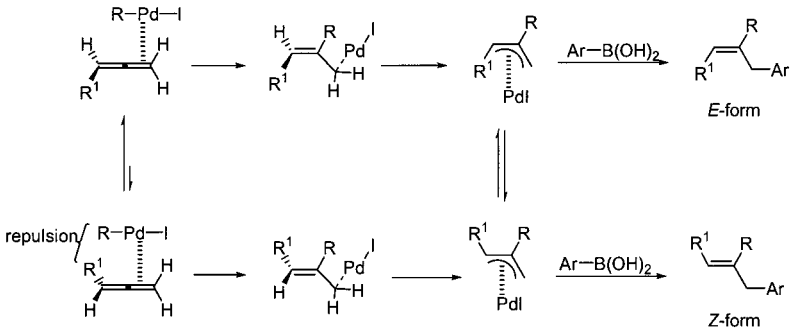
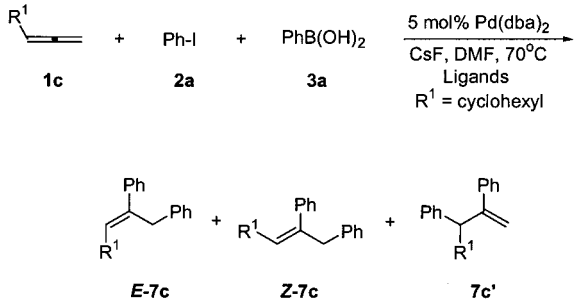


Table 4. Effect of Phosphorus Ligands on the Three-Component Assembling of Cyclohexylallene with Iodobenzene and Phenylboronic Acid[a]

entry	ligand	yield (%)[b]	product ratio (*E*-**7c**/*Z*-**7c**/**7′**)[c]
1	- -	85	75/25/- -
2	P(*o*-tol)$_3$	70	64/35/1
3	P(OPh)$_3$	68	60/39/1
4	2 PPh$_3$	40	50/18/32
5	PPh$_2$Me	50	84/12/4
6	dppe	30	70/20/10
7	2 dppe	- -	- -

[a] All reactions were carried out using cyclohexylallene (**1c**, 2.00 mmol), iodobenzene (**2a**, 1.00 mmol), phenylboronic acid (**3a**, 1.50 mmol), 5 mol % Pd(dba)$_2$ (0.0500−0.1000 mmol), ligand (0.0500−0.1000 mmol), CsF (4.50 mmol), and DMF (5.0 mL); reaction time is 7 h. [b] Isolated yields are based on iodobenzene. [c] The *E*/*Z* ratio was calculated from NMR spectra of the reaction mixture.

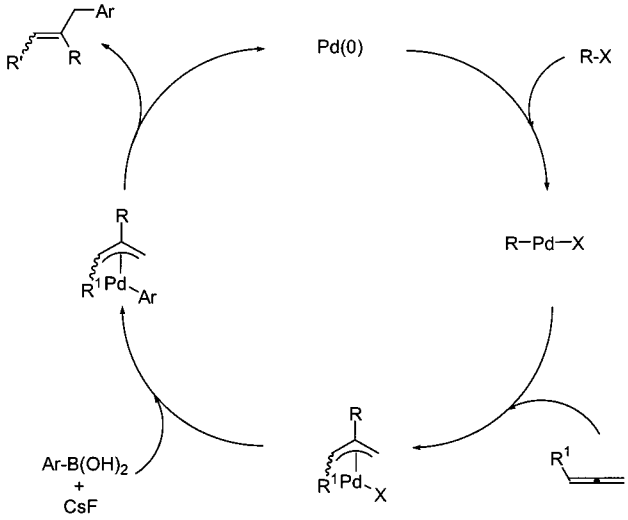
(1,2-bis(diphenylphosphino)ethane), were tested in the reaction of cyclohexylallene (**1c**) with **2a** and **3a** (eq 3)



(3)

catalyzed by Pd(dba)$_2$. The yields and *E*/*Z* ratios of these reactions are summarized in Table 4. It is clear that Pd(dba)$_2$ in the absence of a phosphorus ligand is most active and most regio- and stereoselective. The reaction required 7 h for completion at 70 °C using Pd(dba)$_2$ alone and gave product **7c** in 85% yield with a *E*/*Z* ratio of 75/25. Addition of phosphorus ligands to the reaction mixture greatly decreased the product yields and *E*/*Z* ratios of the products. In addition to the *E*/*Z* stereoisomers **7c**, regioisomer **7c′**, in which a phenyl group and the cyclohexyl group are both attached to the same carbon, was also observed. The decrease in *E*/*Z* ratio for monosubstituted allenes in the presence of a phosphorus ligand may be explained based on the fact that donor ligands readily promote anti-syn rearrangement of π-allylpalladium species via a σ-allylpalladium intermediate.[17] The anti and syn forms of π-allylpalladium complexes (Scheme 4) are responsible for the formation of *E* and *Z* isomers of allylic derivatives, respectively.

Scheme 5



Mechanism. On the basis of the known palladium chemistry,[15] we propose a catalytic cycle as illustrated in Scheme 5 to account for the present Suzuki-type three-component assembling. The catalytic reaction is initiated by oxidative addition of organic halide to palladium(0) to give Pd(II) intermediate. Allene insertion to the organopalladium complex produces a π-allylpalladium intermediate. Transmetalation with arylboronic reagent with the assistance of a base[18] followed by reductive elimination provides the observed product and regenerates the palladium(0) catalyst. The observation that phosphorus ligands diminish the yield of the three-component-coupling products may be understood in view of the fact that strong donor ligands are known to impede olefin coordination/insertion, which is central to the success of the present three-component assembling reaction.

Conclusion

We have successfully developed a palladium-catalyzed three-component assembling of allenes, organic halides, and arylboronic acids for the preparation of various types of organic compounds. A wide range of organic halides, arylboronic acids, and allenes may be used in this reaction. The catalysis assembles three different organic fragments together, constructing two carbon−carbon

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bonds in a regio- and stereoselective fashion. Further application of this powerful method in complicated organic compounds is in progress.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere unless otherwise mentioned and in oven-dried glassware. All solvents were dried according to known methods and distilled prior to use.[19] $PdCl_2(PPh_3)_2$,[20] $Pd(dba)_2$,[21] 1,1-dimethylallene,[22] cyclohexylallene,[23] cyclopentylallene,[23] *n*-butylallene,[23] *tert*-butylallene,[23] 3-iodo-2-cyclopenten-1-one,[24] and 3-iodo-5,5-dimethyl-2-cyclohexen-1-one[24] were prepared by procedures previously reported. Other reagents were commercially available and used as purchased.

General Procedure for the Three-Component Assembling of Allenes, Organic Halides, and Arylboronic Acids. A 25-mL round-bottom flask containing $Pd(dba)_2$ (0.0144 g, 0.0250 mmol), arylboronic acid (0.750 mmol), organic halide (0.500 mmol), and CsF (0.455 g, 1.50 mmol) was purged with nitrogen gas several times. To the flask were added DMF (2.50 mL) and allene (1.00 mmol). The reaction mixture was heated with stirring at 70 °C for 7 h. The solution changed color from purple red to black in 2 h and maintained at the same color during the reaction. As the reaction approached completion, a black precipitate of palladium metal surrounding the wall of the flask appeared gradually. At the end of the reaction, the solution was diluted with ether (30 mL) and extracted with ether and water. The organic layer was collected and dried over $MgSO_4$. After solvent removal by a rotary evaporator, the residue was separated on a silica gel column using hexane and ethyl acetate as eluent to give the desired product.

Compounds **4a**−**v** and **7a**−**i** were prepared according to this method. Product yields of these reactions are listed in Table 2 and Table 3, while important spectral data of these allylic compounds are shown below or listed in Supporting Information.

1-(1-Benzyl-2-methyl-1-propenyl)benzene (4a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3 H), 1.93 (s, 3 H), 3.73 (s, 2 H), 6.99−7.25 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.80 (q), 22.25 (q), 40.43 (t), 125.59 (d), 125.81 (d), 127.74 (d), 128.10 (d), 128.47 (d), 128.98 (d), 129.52 (s), 133.46 (s), 140.31 (s), 143.77 (s); IR (neat) 3059, 3025, 2916, 1600, 1492, 1447, 1072, 1029, 1013, 702, 582 cm^{-1}; GC-EIMS *m*/*z* (rel intensity) 222 (M^+, 100), 207 (38), 143 (20), 129 (25); HRMS calcd for $C_{17}H_{18}$ 222.1404, found 222.1413.

1-(1-Benzyl-2-methyl-1-propenyl)-2-methoxybenzene (4b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.92 (s, 3 H), 3.55 (d, J = 13.9 Hz, 1 H), 3.73 (s, 3 H), 3.84 (d, J = 13.9 Hz, 1 H), 6.73−6.84 (m, 3 H), 7.01−7.19 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.48 (q), 22.22 (q), 39.22 (t), 55.38 (q), 110.72 (d), 120.00 (d), 125.33 (d), 127.38 (d), 127.84 (d), 128.66 (d), 129.95 (s), 130.51 (s), 131.20 (d), 132.06 (s), 140.77 (s), 156.59 (s); IR (neat) 2906, 2830, 1600, 1575, 1488, 1459, 1243, 1117, 1056, 1034, 759, 709 cm^{-1}; HRMS calcd for $C_{18}H_{20}O$ 252.1514, found 252.1511.

1-(1-Benzyl-2-methyl-1-propenyl)-3-methoxybenzene (4c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 3 H), 1.91 (s, 3 H), 3.69 (s, 3 H), 3.70 (s, 2 H), 6.50−6.73 (m, 3H), 7.06−7.22 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.78 (q), 22.31 (q), 40.40 (t), 55.04 (q), 111.30 (d), 114.68 (d), 121.57 (d), 125.62 (d), 127.19 (s), 128.11 (d), 128.52 (d), 128.70 (d), 129.54 (s), 133.40 (s), 145.26 (s), 159.07 (s); HRMS calcd for $C_{18}H_{20}O$ 252.1514, found 252.1511.

1-(1-Benzyl-2-methyl-1-propenyl)-4-methoxybenzene (4d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (s, 3 H), 1.91 (s, 3 H), 3.71 (s, 2 H), 3.76 (s, 3 H), 6.76 (d, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 7.05−7.25 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.84 (q), 22.29 (q), 40.52 (t), 55.10 (q), 113.13 (d), 125.55 (d), 128.09 (d), 128.48 (d), 129.33 (s), 130.00 (d), 132.91 (s), 136.09 (s), 140.46 (s), 157.59 (s); IR (neat) 3062, 3048, 2983, 1605, 1505, 1417, 1251, 1177, 1034, 913, 915 cm^{-1}; HRMS calcd for $C_{18}H_{20}O$ 252.1514, found 252.1510.

2-(1-Benzyl-2-methyl-1-propenyl)thiophene (4k). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87 (s, 3 H), 1.95 (s, 3 H), 3.78 (s, 2 H), 6.65−7.28 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.40 (q), 22.82 (q), 41.04 (t), 123.68 (d), 125.82 (d), 126.26 (d), 126.37 (d), 128.19 (d), 128.35 (d), 133.35 (s), 140.01 (s), 145.25 (s); IR (neat) 3026, 2918, 1601, 1493, 1445, 1375, 1225, 1114, 1029, 849, 697, 526 cm^{-1}; HRMS calcd for $C_{15}H_{16}S$ 228.0972, found 228.0975.

Ethyl 3-Benzyl-4-methyl-3-pentenoate (4l). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, J = 7.2 Hz, 3 H), 1.81 (s, 3 H), 1.87 (s, 3 H), 2.99 (s, 2 H), 3.54 (s, 2 H), 4.06 (q, J = 7.2 Hz, 2 H), 7.13−7.29 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.13 (q), 20.91 (q), 37.26 (t), 38.35 (t), 60.32 (t), 124.28 (s), 125.92 (d), 128.29 (d), 128.61 (d), 130.84 (s), 140.05 (s), 172.14 (s); IR (neat) 3029, 2942, 1733, 1598, 1493, 1449, 1262, 1164, 1032, 703 cm^{-1}; GC-EIMS *m*/*z* (rel intensity) 232 (M^+, 100), 186 (25), 142 (24), 116 (10); HRMS calcd for $C_{15}H_{20}O_2$ 232.1458, found 232.1471.

3-(1-Benzyl-2-methyl-1-propenyl)-2-cyclopenten-1-one (4m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3 H), 1.83 (s, 3 H), 2.22−2.25 (m, 2 H), 2.45−2.49 (m, 2 H), 3.56 (s, 2 H), 5.83 (s, 1 H), 7.00−7.19 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.16 (q), 22.44 (q), 31.25 (t), 34.49 (t), 36.46 (t), 125.77 (d), 127.59 (d), 128.07 (d), 128.87 (s), 131.64 (d), 134.59 (s), 138.70 (s), 178.88 (s), 209.55 (s); IR (neat) 3026, 2921, 1697, 1593, 1493, 1444, 1277, 1177, 701 cm^{-1}; GC-EIMS *m*/*z* (rel intensity) 227 ($M^+ + 1$, 100), 208 (8), 141 (15), 91 (11); HRMS calcd for $C_{16}H_{18}O$ 226.1353, found 226.1352.

3-(1-Benzyl-2-methyl-1-propenyl)-5,5-dimethyl-2-cyclohexen-1-one (4n). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (s, 6 H), 1.73 (s, 3 H), 1.82 (s, 3 H), 2.07 (s, 2 H), 2.13 (s, 2 H), 3.52 (s, 2 H), 5.67 (s, 1 H), 7.05−7.26 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.66 (q), 22.04 (q), 28.21 (q), 33.65 (s), 37.11 (t), 43.72 (t), 50.98 (t), 126.12 (d), 127.32 (d), 128.35 (d), 128.38 (d), 129.98 (s), 132.96 (s), 139.30 (s), 163.08 (s), 184.58 (s); HRMS calcd for $C_{19}H_{24}O$ ($M^+ + 1$) 269.1905, found 269.1905.

1-[3-Methyl-2-(1-phenylvinyl)-2-butenyl]benzene (4o). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81 (s, 3 H), 1.98 (s, 3 H), 3.45 (s, 2 H), 4.76 (s, 1 H), 5.75 (s, 1 H), 7.08−7.38 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.44 (q), 22.23 (q), 37.81 (t), 114.77 (t), 125.55 (d), 126.50 (d), 127.34 (d), 128.00 (d), 128.27 (d), 128.71 (d), 130.27 (s), 133.37 (s), 140.00 (s), 140.56 (s), 148.61 (s); IR (neat) 3024, 2905, 1496, 1456, 1377, 1308, 1074, 1031, 908, 782, 728, 702 cm^{-1}; HRMS calcd for $C_{19}H_{20}$ 248.1565, found 248.1564.

1-[2-(4-Methoxyphenyl)-3-methyl-2-butenyl]-3-nitrobenzene (4q). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (s, 3 H), 1.92 (s, 3 H), 3.74 (s, 3 H), 3.79 (s, 2 H), 6.75 (dd, J_1 = 2.4 Hz, J_2 = 9.8 Hz, 2 H), 6.89 (dd, J_1 = 2.4 Hz, J_2 = 9.8 Hz, 2 H), 7.30−7.35 (m, 2 H), 7.92−8.01 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.83 (q), 22.28 (q), 40.12 (t), 55.13 (q), 113.46 (d), 120.90 (d), 123.30 (d), 128.87 (d), 129.98 (d), 130.72 (s), 131.81 (s), 134.76 (d), 135.06 (s), 142.65 (s), 148.30 (s), 157.93 (s); HRMS calcd for $C_{18}H_{19}NO_3$ 297.1365, found 297.1363.

4-[2-(4-Methoxyphenyl)-3-methyl-2-butenyl]benzaldehyde (4v). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 3 H), 1.90 (s, 3 H), 3.74 (s, 3 H), 3.76 (s, 2 H), 6.74 (d, J = 7.5 Hz, 2 H), 6.87 (d, J = 7.5 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.69 (d, J = 8.0 Hz, 2 H), 9.91 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.87 (q), 22.29 (q), 40.86 (t), 55.12 (q), 113.35 (d), 129.16 (d), 129.74 (d), 129.96 (d), 130.23 (s), 132.07 (s), 135.47 (s), 148.15 (s), 157.84 (s), 167.43 (s), 192.02 (d); IR (neat) 3013, 2970, 1698, 1604, 1509, 1244, 1016, 938, 857 cm^{-1}; HRMS calcd for $C_{19}H_{20}O_2$ 280.1463, found 280.1463.

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1-[(*Z*)-1-Benzyl-2-cyclopentyl-1-ethenyl]-4-methoxybenzene (*Z*-7a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19−1.76 (m, 8 H), 2.37−2.43 (m, 1 H), 3.58 (s, 2 H), 3.75 (s, 3 H), 5.38 (d, J = 10.0 Hz, 1 H), 6.75−7.59 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.50 (t), 34.15 (t), 39.68 (d), 45.73 (t), 55.10 (d), 113.21 (d), 114.19 (d), 125.76 (d), 126.72 (d), 128.13 (s), 128.94 (d), 129.60 (d), 133.57 (s), 137.73 (s), 140.15 (s), 158.02 (s); IR (neat) 2952, 2858, 1607, 1513, 1459, 1294, 1274, 1182, 1038, 839, 767, 701 cm^{-1}; HRMS calcd for $C_{21}H_{24}O$ 292.1841, found 292.1845.

1-[(*E*)-1-Benzyl-2-cyclopentyl-1-ethenyl]-4-methoxybenzene (*E*-7a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25−1.90 (m, 8 H), 2.72−2.83 (m, 1 H), 3.74 (s, 3 H), 3.86 (s, 2 H), 5.82 (d, J = 9.6 Hz, 1 H), 6.74 (d, J = 6.8 Hz, 2 H), 7.09−7.25 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.45 (t), 33.91 (t), 35.93 (t), 39.88 (d), 55.21 (q), 113.52 (d), 125.72 (d), 127.25 (d), 128.18 (d), 128.30 (d), 134.87 (s), 135.13 (d), 135.45 (s), 140.24 (s), 158.34; IR (neat) 2942, 1605, 1511, 1245, 1165, 1020, 668 cm^{-1}; HRMS calcd for $C_{21}H_{24}O$ 292.1841, found 292.1845.

1-[(*E*)-1-Benzyl-2-cyclohexyl-1-ethenyl]-4-methoxybenzene (*E*-7d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12−1.30 (m, 6 H), 1.62−1.71 (m, 4 H), 2.36−2.39 (m, 1 H), 3.74 (s, 3 H), 3.86 (s, 2 H), 5.74 (d, J = 9.4 Hz, 1 H), 6.75 (d, J = 6.7 Hz, 2 H), 7.10−7.27 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.91 (t), 26.04 (t), 33.36 (t), 35.76 (t), 37.89 (q), 55.18 (q), 113.49 (d), 125.70 (d), 127.30 (d), 128.19 (d), 128.29 (d), 134.48 (s), 135.33 (s), 135.55 (d), 140.19 (s), 158.35 (s); IR (neat) 2922, 2849, 1606, 1511, 1494, 1449, 1287, 1246, 1179, 1037, 969, 896, 832, 746, 700, 536 cm^{-1}; HRMS calcd for $C_{22}H_{26}O$ 306.1984, found 306.2001.

1-[(*E*)-1-(4-Fluorobenzyl)-3,3-dimethyl-1-butenyl]-4-methoxybenzene (*E*-7f). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 9 H), 3.73 (s, 3 H), 3.98 (s, 2 H), 5.88 (s, 1 H), 6.68−7.20 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.43 (q), 33.07 (s), 34.99 (t), 55.18 (q), 113.45 (d), 114.78 (d), 115.06 (d), 127.59 (d), 129.71 (d), 129.82 (d), 135.56 (s), 136.63 (s), 140.66 (d), 158.34 (s), 159.49 (s), 162.72 (s); IR (neat) 2945, 2846, 1605, 1509, 1465, 1291, 1242, 1179, 1156, 1035, 827, 505 cm^{-1}; HRMS calcd for $C_{20}H_{23}FO$ 298.1733, found 298.1734.

(*Z*)-1,2-Diphenyl-2-heptene (*Z*-7i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.0 Hz, 3 H), 1.22−1.33 (m, 4 H), 1.94−1.99 (m, 2 H), 3.63 (s, 2 H), 5.48 (t, J = 7.6 Hz, 1 H), 7.04−7.27 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.62 (q), 21.96 (t), 28.37 (t), 31.91 (t), 45.35 (t), 125.52 (d), 126.03 (d), 127.52 (d), 127.78 (d), 128.21 (d), 128.72 (d), 129.27 (d), 139.50 (s), 139.61 (s), 140.74 (s); IR (neat) 3026, 2957, 2862, 1729, 1600, 1493, 1452, 1276, 1072, 774, 699 cm^{-1}; GC-EIMS *m*/*z* (rel intensity) 250 (M^+, 100), 193 (43), 179 (18), 159 (22), 129 (27), 117 (62); HRMS calcd for $C_{19}H_{22}$ 250.1716, found 250.1727.

(*E*)-1,2-Diphenyl-2-heptene (*E*-7i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.35−1.47 (m, 4 H), 2.24 (q, J = 7.2 Hz, 2 H), 3.87 (s, 2 H), 5.98 (t, J = 6.8 Hz, 1 H), 7.12−7.33 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.66 (q), 22.15 (t), 28.34 (t), 31.54 (t), 35.37 (t), 125.41 (d), 125.88 (d), 126.17 (d), 127.81 (d), 127.99 (d), 130.98 (d), 136.77 (s), 139.61 (s), 142.67 (s); IR (neat) 3059, 3025, 2956, 2925, 2862, 1600, 1493, 1451, 1378, 1074, 1030, 753, 722, 696 cm^{-1}; GC-EIMS *m*/*z* (rel intensity) 250 (M^+, 23), 249 (M^+-1, 100), 192 (37), 172 (21), 158 (38), 129 (47), 105 (22); HRMS calcd for $C_{19}H_{22}$ 250.1716, found 250.1712.

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Supporting Information Available: Spectral data for compounds **4e**−**j**, **4p**, **4r**−**u** and **7b**−**c**, **7e**, **7g**−**h** and ^{1}H NMR spectra of products **4a**−**v** and **7a**−**i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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