Synthesis of Substituted Indenes and *cis*-Stilbenoid Hydrocarbons via Palladium-Catalyzed Domino Reactions of Hindered Grignard Reagents with (*E*)-1,2-Dibromoethenes

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Abstract: Palladium-catalyzed domino reactions of (*E*)-1,2-dibromoethenes with hindered Grignard reagents based on carbopalladation, palladium-catalyzed cross-coupling, and C–H activation are described. These domino reactions could be influenced by the ligand, reaction temperature, nucleophilicity of Grignard reagents, and steric hindrance of the substrates. Our study provides an efficient access to some useful polysubstituted indenes and *cis*-substituted stilbenes, and may be useful for the development of other cross-coupling and C–H activation-based tandem/domino reactions.

Key words: palladium, Grignard reactions, domino reactions, cyclization, cross-coupling

Palladium-catalyzed cross-coupling reactions – for example, the Suzuki coupling, the Stille coupling, the Sonogashira coupling, and the amination of aryl halides with amines – have become powerful transformations in organic synthesis over past decades.[1,2] Such cross-coupling reactions have been established to occur through three key elementary steps:[1] oxidative addition of palladium(0) with an aryl halide to form a palladium(II) complex; transmetalation of the palladium(II) complex with an organometallic reagent to form a diorganopalladate complex; and reductive elimination of the diorganopalladate complex to form the cross-coupling product and regenerate the palladium(0) catalyst (Figure 1). Based on our understanding of the generalized mechanism depicted in Figure 1, we initialized a program to develop new reactions/processes by attempting to control the individual elementary steps in the cross-coupling catalytic cycle. We have documented palladium(0)/tri-*tert*-butylphosphine-catalyzed Suzuki cross-coupling reactions of dihaloarenes with arylboronic acids,[3] a process that relies on controlling the oxidative addition step, and palladium-catalyzed reaction of *o*-dihaloarenes and 2-haloaryl tosylates with hindered Grignard reagents to form substituted fluorenes,[4] cyclization processes that combines the control of the transmetalation step with sp^3 C–H activation. We have also reported type I palladacycle-catalyzed addition reactions of arylboronic acids with carbonyl-containing compounds, reaction processes that are believed to rely on controlling the reductive elimination step.[5]

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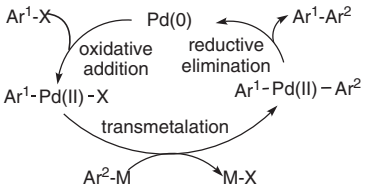
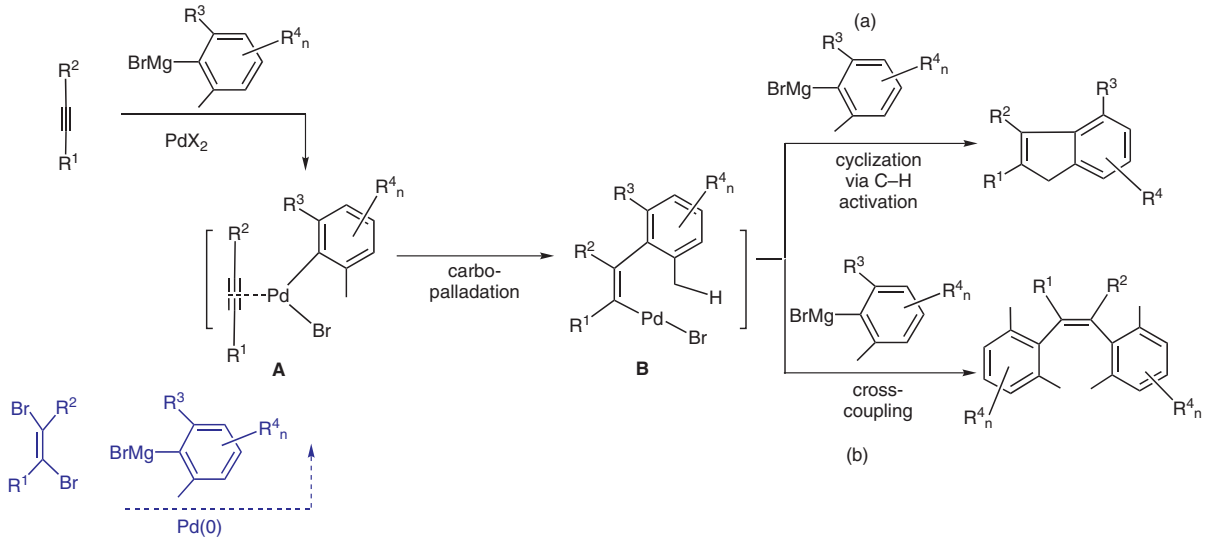


Figure 1 Generalized mechanism for palladium-catalyzed cross-coupling reactions

Based on our study on palladium-catalyzed tandem reaction of *o*-dihaloarenes and 2-haloaryl tosylates with hindered Grignard reagents to form substituted fluorenes, in which palladium-associated arynes were suggested to be most likely the intermediates,[4] we have further extended our study to involve internal alkynes as substrates.[6] We demonstrated that by controlling the reaction temperature and the use of ligands, two palladium-catalyzed domino reactions,[7–9] namely carbopalladation[10] followed by cyclization via C–H activation[11] to form substituted indenes and carbopalladation followed by cross-coupling to form *cis*-stilbenoid hydrocarbons could be realized from the same set of alkynes and hindered Grignard reagents. Substituted indenes are structural constituents of metallocene-based catalysts for olefin polymerizations, of biologically active compounds and of functional materials.[12,13] *cis*-Stilbenoid hydrocarbons are potentially useful in the fields of molecular sensors and molecular electronics.[14,15]

During our study of this type of domino reaction, we became interested in employing (*E*)-1,2-dibromoethenes, which are readily available from alkynes, as substrates. Our mechanistic analysis on palladium-catalyzed tandem reactions of internal alkynes with hindered Grignard reagents suggested that palladium-coordinated alkyne triple bond complexes **A** would be the initial intermediates (Scheme 1). A recent study of the Suzuki reaction of 1,2-dibromoethenes with arylboronic acids showed that the β-elimination of 2-bromoalkenyl–Pd(II)X complexes to form alkynes and palladium(II) complexes could readily occur,[16] suggesting complexes **A** could be generated from (*E*)-1,2-dibromoethenes. Therefore, (*E*)-1,2-dibromoethenes could be suitable substrates for the preparation of substituted indenes and *cis*-stilbenes. In addition, our preliminary study on the reaction of *trans*-dibromostilbene with hindered Grignard reagents was, to some extent, in conflict with the recently reported results,[15a] in which 1,2-dibromoethenes have been reported to react with hindered



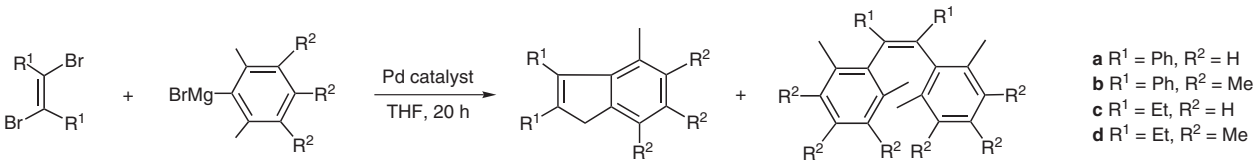
Scheme 1 Domino carbopalladation–cyclization via sp^3 C–H activation vs domino carbopalladation–cross-coupling reaction with (*E*)-1,2-dibromoethenes as substrates

Grignard reagents to form *cis*-tetrasubstituted stilbenes with dichlorobis(triphenylphosphine)palladium [$PdCl_2(PPh_3)_2$] as catalyst in excellent yields.[6] Furthermore, the use of (*E*)-1,2-dibromoethenes as substrates could eliminate the use of 1,2-dibromoethane as an additive for the reaction of internal alkynes with hindered Grignard reagents and expand the substrate scope. We have thus investigated the reactions of (*E*)-1,2-dibromoethenes with hindered Grignard reagents. Herein, our results are reported.

As depicted in Scheme 1, the key intermediates for the reaction with (*E*)-1,2-dibromoethenes as substrates would structurally resemble that with internal alkynes as substrates. We thus surmised that the reaction pathways (carbopalladation followed by cyclization vs carbopalladation followed by cross-coupling) would be influenced by the same factors demonstrated in the reaction with internal alkynes as substrates, e.g., reaction temperature, ligand effects. To understand the influence of these factors, we examined the reactions of *trans*-dibromostilbene and (*E*)-3,4-dibromohex-3-ene with 2,6-dimethylphenylmagnesium bromide and pentamethylphenylmagnesium bromide. Our results are listed in Table 1. We found with *trans*-dibromostilbene as substrate, the domino carbopalladation–cyclization product 4-methyl-2,3-diphenyl-1*H*-indene (**1a**) was the major product only with palladium(II) acetate as the catalyst, either at room temperature, 60 °C, or reflux (Table 1, entries 2–4, 11–13). Increasing the reaction temperature slightly led to more carbopalladation–cross-coupling product **2a** (Table 1, entries 2–4). The use of a phosphine ligand also slightly decreased the formation of the cyclization product **1a** (Table 1, entries 5–8). By using dichlorobis(triphenylphosphine)palladium or tetrakis(triphenylphosphine)palladium as catalyst and in refluxing tetrahydrofuran, pentamethylphenylmagnesium bromide reacted with *trans*-dibromostilbene to yield the domino carbopalladation–cross-coupling product **2b** as the major product (Table 1, entries 14, 15). Under the same conditions, the reaction *trans*-dibromostilbene with 2,6-dimethylphenylmagnesium bromide yielded carbopalladation–cyclization product 4-methyl-2,3-diphenyl-1*H*-indene (**1a**) as the major product (Table 1, entry 9), suggesting the nucleophilicity of the Grignard reagents played an important role in this reaction. We have also tested the reaction of (*E*)-3,4-dibromohex-3-ene with the same two Grignard reagents, 2,6-dimethylphenylmagnesium bromide and pentamethylphenylmagnesium bromide. Our results, which are also listed in Table 1 (entries 16–22), again show the effect of the reaction temperature, ligand, and nucleophilicity of Grignard reagents. In addition, we also observed that its reaction with 2,6-dimethylphenylmagnesium bromide catalyzed by dichlorobis(triphenylphosphine)palladium yielded carbopalladation–cross-coupling as the major product **2c** (Table 1, entry 21). This result was in contrast with that of *trans*-dibromostilbene as substrate, which gave **1a** as the major product (Table 1, entry 9), implying the reaction of (*E*)-dibromoalkene with hindered Grignard reagents was also influenced by the size of the groups attached to the double bond. Our results thus suggested that pathways for the reaction of (*E*)-1,2-dibromoethenes with hindered reagents depicted in Scheme 1 could be influenced by ligand, reaction temperature, nucleophilicity of the Grignard reagents, and structure of the substrate.

With 3 mol% palladium(II) acetate as the catalyst at room temperature, we examined several (*E*)-1,2-dibromoethenes and hindered Grignard reagents for the palladium-catalyzed domino reaction to form substituted indenes **3** and our results are listed in Table 2. We found that with mesitylmagnesium bromide and 2,6-dimethylphenylmagnesium bromide as reagents, 1,2-diaryl-, 1,2-dialkyl- and 1-alkyl-2-aryl-1,2-dibromoethenes were suitable substrates (Table 2, entries 1–7). With unsymmetrical (*E*)-1,2-dibromo-1-phenylpropene as the substrate, the domino reaction occurred mainly from the alkyl side of 1,2-dibromo-1-phenylpropene, as evidenced by the ratio of two

Table 1 Palladium-Catalyzed Domino Reaction of (*E*)-1,2-Dibromoethenes with 2,6-Dimethylmagnesium Bromide and Pentamethylmagnesium Bromide[a]



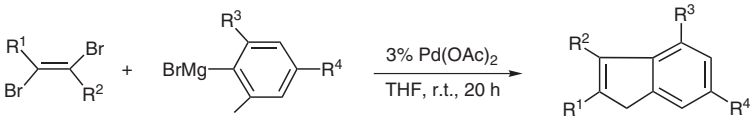
Entry	R^1	R^2	Pd catalyst	Temp (°C)	Ratio[b,c] **1/2**
1	Ph	H	none	r.t.	
2	Ph	H	3 mol% $Pd(OAc)_2$	r.t.	96:4
3	Ph	H	3 mol% $Pd(OAc)_2$	60	85:15
4	Ph	H	3 mol% $Pd(OAc)_2$	reflux	82:18
5	Ph	H	3 mol% $Pd(OAc)_2$, 6 mol% Ph_3P	r.t.	89:11
6	Ph	H	3 mol% $Pd(OAc)_2$, 6 mol% Ph_3P	r.t.	94:6
7	Ph	H	3 mol% $Pd(OAc)_2$, 6 mol% *t*-Bu_3P	r.t.	92:8
8	Ph	H	0.1 mol% $PdCl_2(PPh_3)_2$	r.t.	90:10
9	Ph	H	0.1 mol% $PdCl_2(PPh_3)_2$	reflux	79:21
10	Ph	H	1.5 mol% $Pd_2(dba)_3$	r.t.	95:5
11	Ph	Me	3 mol% $Pd(OAc)_2$	r.t.	97:3
12	Ph	Me	3 mol% $Pd(OAc)_2$	60	87:13
13	Ph	Me	3 mol% $Pd(OAc)_2$	reflux	88:12
14	Ph	Me	0.5 mol% $PdCl_2(PPh_3)_2$	reflux	<2:>98
15	Ph	Me	3 mol% $Pd(PPh_3)_4$	reflux	<2:>98
16	Et	H	3 mol% $Pd(OAc)_2$	r.t.	>98:<2
17	Et	H	3 mol% $Pd(OAc)_2$, 6 mol% Ph_3P	r.t.	98:2
18	Et	H	3 mol% $Pd(OAc)_2$, 6 mol% Ph_3P	reflux	16:84
19	Et	H	0.1 mol% $PdCl_2(PPh_3)_2$	r.t.	93:7
20	Et	H	3 mol% $PdCl_2(PPh_3)_2$, 6 mol% Cy_3P	r.t.	70:30
21	Et	H	3 mol% $PdCl_2(PPh_3)_2$	reflux	19:81
22	Et	Me	1 mol% $PdCl_2(PPh_3)_2$	reflux	<2:>98

[a] (*E*)-1,2-Dibromoethene (1.0 equiv), Grignard reagent (2.5 equiv), Pd catalyst, THF (2 mL), 20 h.
[b] No conversion was observed for entry 1, 99% conversion of (*E*)-dibromoethenes was observed for all other entries.
[c] Based on ^1H NMR.

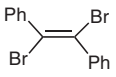
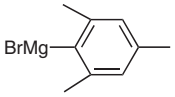
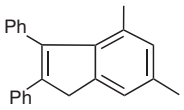
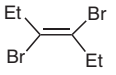
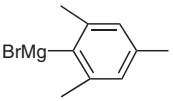
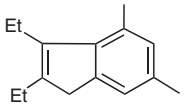
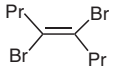
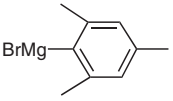
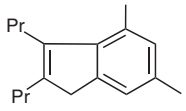
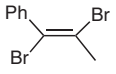
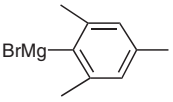
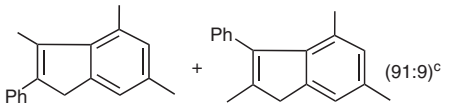
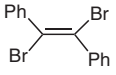
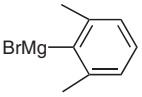
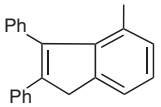
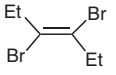
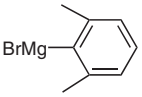
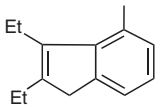
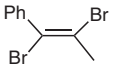
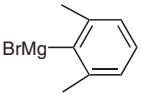
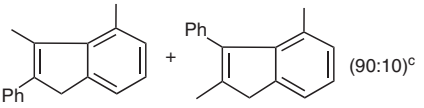
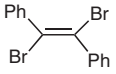
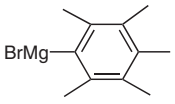
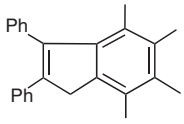
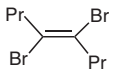
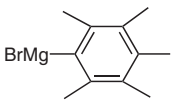
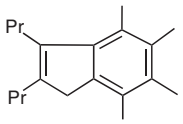
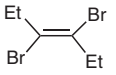
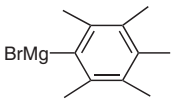
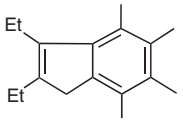
isomeric products (Table 2, entries 4, 7).[17] We also found that with pentamethylphenylmagnesium bromide as the reagent, low yields of substituted indenes were obtained (Table 2, entries 8–10), and the major products were alkynes and 1-bromo-2,3,4,5,6-pentamethylbenzene, the debrominated products of 1,2-dibromoethenes and the Grignard reagent.

We also examined the reaction of (*E*)-1,2-dibromoethenes with hindered Grignard reagents for the preparation of *cis*-substituted stilbenes containing substituted phenyl groups by using dichlorobis(triphenylphosphine)palladium as the catalyst in refluxing tetrahydrofuran. Our results are listed in Table 3. We found moderate to good yields of *cis*-substituted stilbenes **4** could be obtained for alkyl-containing (*E*)-1,2-dibromoethenes and hindered Grignard reagents (Table 3, entries 1–7). With *trans*-dibromostilbene as the substrate, we found the yields of *cis*-substituted stilbenes **4** were highly dependent on the Grignard reagents employed. A high yield was obtained for pentamethylphenyl-

Table 2 Palladium(II) Acetate Catalyzed Cyclizations of (*E*)-1,2-Dibromoethenes with Hindered Grignard Reagents[a]



3

Entry	Dibromoalkene	ArMgBr	Product		Yield[b] (%)
1				**3a**	81
2				**3b**	56
3				**3c**	81
4			 (91:9)[c]	**3d/3d′**	85
5				**3e**	80
6				**3f**	65
7			 (90:10)[c]	**3g/3g′**	89
8				**3h**	30
9				–	0
10				–	0

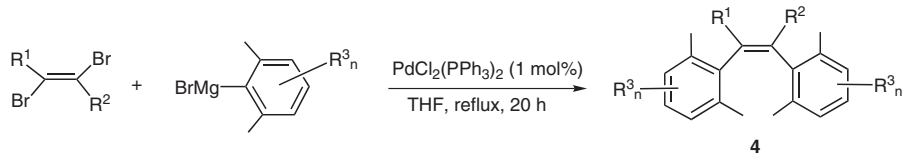
[a] (*E*)-1,2-Dibromoethene (1.0 equiv), Grignard reagent (2.5 equiv), $Pd(OAc)_2$ (3 mol%), THF (2 mL), r.t., 20 h.
[b] Isolated yields.
[c] Ratio based on ^1H NMR.

magnesium bromide (Table 3, entry 8). However, a low yield was observed with 2,6-dimethylphenylmagnesium bromide (Table 3, entry 9), with the major product being the cyclization product, 4-methyl-2,3-diphenyl-1*H*-indene. The different results observed for pentamethylmagnesium bromide and 2,6-dimethylphenylmagnesium bromide (Table 3, entries 8, 9) might be because 2,6-dimethylphenylmagnesium bromide was less nucleophilic

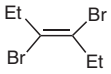
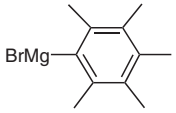
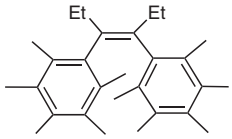
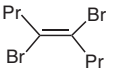
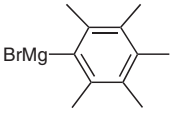
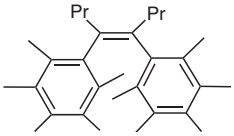
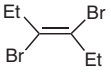
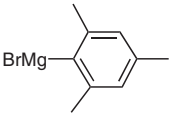
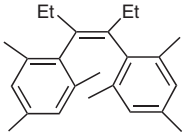
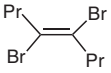
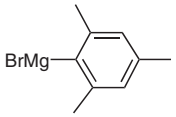
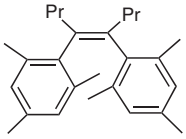
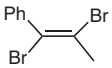
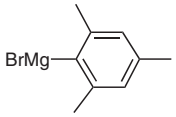
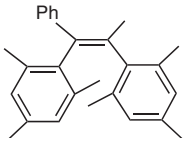
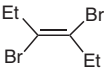
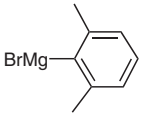
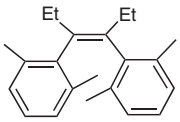
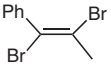
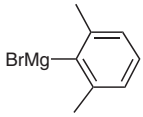
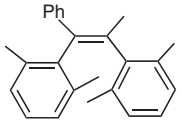
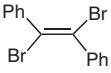
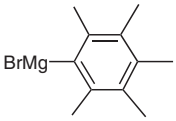
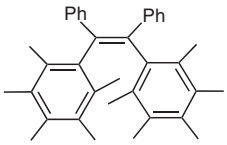
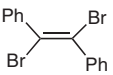
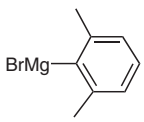
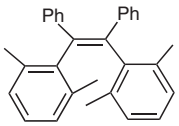
than pentamethylmagnesium bromide and C–H activation occurred faster than the transmetalation with 2,6-dimethylmagnesium bromide as reagent.

While our results supported the mechanism of carbopalladation of **A** followed by either cyclization or cross-coupling (Scheme 1), they did not provide much information about how **A** could be formed from (*E*)-1,2-dibromoeth-

Table 3 Palladium(II) Acetate Catalyzed Cyclizations of (*E*)-1,2-Dibromoethenes with Hindered Grignard Reagents[a]

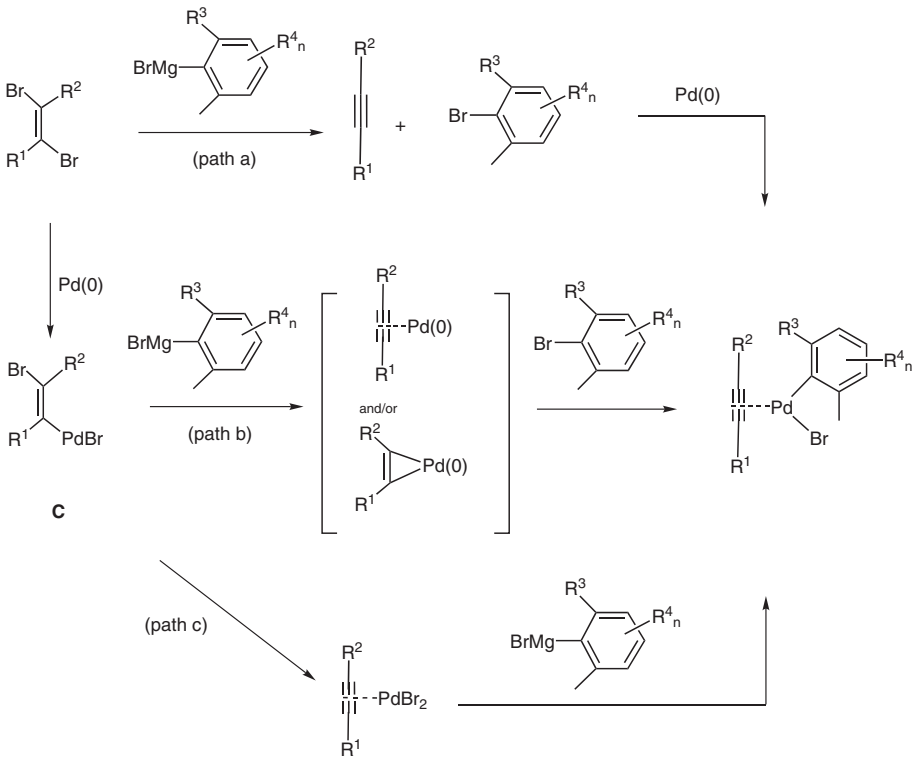


4

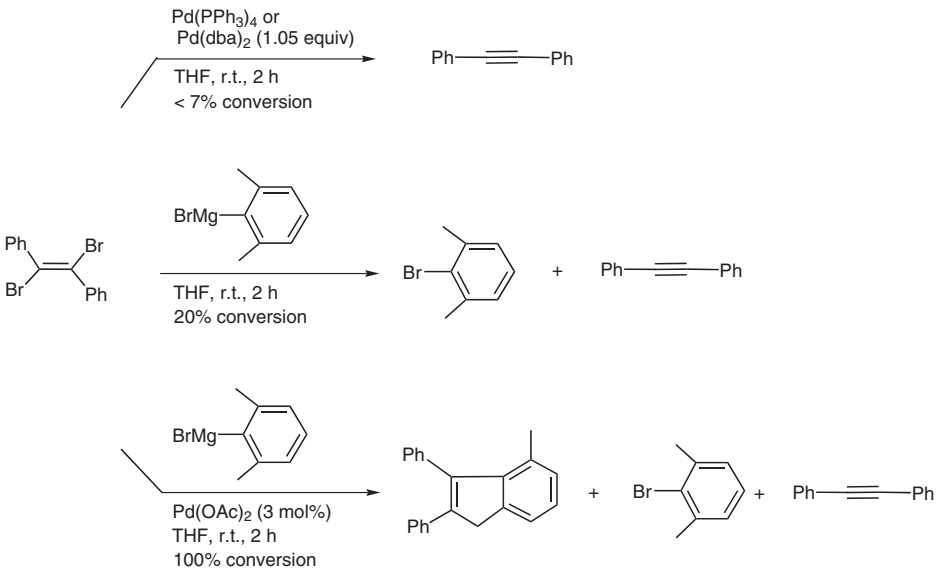
Entry	Dibromoalkene	ArMgBr	Product		Yield[b] (%)
1				**4a**	48
2				**4b**	61
3				**4c**	53
4				**4d**	51
5				**4e**	69
6				**4f**	70
7				**4g**	67
8				**4h**	82
9				**4i**	<20[c]

[a] (*E*)-1,2-Dibromoethene (1.0 equiv), Grignard reagent (2.5 equiv), $PdCl_2(PPh_3)_2$ (1 mol%), THF (2 mL), refluxing, 20 h.
[b] Isolated yields.
[c] Yield based on ^{1}H NMR, 4-methyl-2,3-diphenyl-1*H*-indene was isolated in 60% yield.

enes. Scheme 2 depicts three possible pathways for the formation of **A** from (*E*)-1,2-dibromoethenes. (*E*)-1,2-Dibromoethenes could react with Grignard reagents to form alkynes and bromobenzenes (path a). It could also undergo oxidative addition with palladium(0) catalyst to form oxidative addition product **C** that could then react with Grignard reagents to form alkynes along with bromobenzenes and palladium(0), which could be associated with the alkynes (path b).[18] Product **C** could also undergo β-elimination to form alkynes without the help of Grignard reagents (path c). Paths a and b require an oxidative addition of palladium(0), which could be ether associated or not associated with an alkyne, with bromoarenes to form A. Path c does not involve oxidative addition of palladium(0) with bromobenzenes after the formation of the alkynes, rather, it involves a transmetalation step for the formation of **A**. To differentiate these pathways, we have carried out the reaction of *trans*-dibromostilbene with a stoichiometric amount of tetrakis(triphenylphosphine)palladium or bis(dibenzylideneacetone)palladium (r.t., 2 h). We found less than 10% conversion with debrominated diphenylacetylene as the product (Scheme 3). We have also carried out the reactions of 2,6-dimethylphenylmagnesium bromide with *trans*-dibromostilbene in the presence or absence of palladium(II) acetate. We found in the absence of palladium(II) acetate, *trans*-dibromostilbene underwent debromination to give 2-bromo-1,3-dimethylbenzene and diphenylacetylene as the products in 20% conversion. In the presence of palladium(II) acetate, the reaction of *trans*-dibromostilbene with 2,6-dimethylphenylmagnesium bromide occurred much faster (100% conversion) to give substituted indene, 2-bromo-1,3-dimethylbenzene, and diphenylacetylene as the products (Scheme 3). The lower conversion observed for *trans*-dibromostilbene in the absence of palladium(II) acetate relative to the excellent conversion observed in the presence of palladium(II) acetate (20% vs 100%) suggested that the oxidative addition of palladium(0) to *trans*-dibromostilbene occurred much faster than the direct debromination of *trans*-dibromostilbene with 2,6-dimethylphenylmagnesium bromide The low conversion of *trans*-dibromostilbene with stoichiometric amount of tetrakis(triphenylphosphine)palladium or bis(dibenzylideneacetone)palladium suggested that the formation of alkynes should be facilitated with the help of Grignard reagent and it was unlikely that path c was the route for the formation of **A**. The observation of 2-bromo-1,3-dimethylbenzene in the palladium(II) acetate catalyzed reaction of *trans*-dibromostilbene with 2,6-dimethylphenylmagnesium bromide suggested that the oxidative addition of palladium(0), either associated or not associated with an alkyne, with 2-bromo-1,3-dimethylbenzene should be the rate-determining step for the reaction of *trans*-dibromostilbene with hindered Grignard reagents. The fact that pentamethylphenylmagnesium bromide was a poorer reagent than mesitylmagnesium bromide and 2,6-dimethylphenylmagnesium bromide supported this thinking as 1-bromo-2,3,4,5,6-pentamethylbenzene is more electron-rich and would be more reluctant to undergo oxidative addition with palladium(0) than 2-bromo-1,3-dimethylbenzene. Although our results cannot exclude path a for the formation of **A**, since it also involves the oxidative addition step, our study suggested that path b should be the major pathway, if not the only one, for the formation of **A** from 1,2-dibromoethenes.



Scheme 2 Possible pathways for the formation of **A**



Scheme 3 Reactions of *trans*-dibromostilbene with 2,6-dimethylphenylmagnesium bromide

In summary, we demonstrated that palladium-catalyzed domino reactions of (*E*)-1,2-dibromoethenes with hindered Grignard reagents could be influenced by ligand, reaction temperature, nucleophilicity of Grignard reagents, and steric hindrance of the substrates. By using palladium(II) acetate as the catalyst, substituted indenes could be obtained in good to high yields. With dichlorobis(triphenylphosphine)palladium as the catalyst in refluxing tetrahydrofuran, *cis*-stilbene products could be obtained in moderate to good yields with more nucleophilic Grignard reagents and less sterically hindered (*E*)-1,2-dibromoethenes. Our preliminary mechanistic study suggested that the reaction likely began with debromination of (*E*)-1,2-dibromoethenes to form alkynes and bromoarenes followed by oxidative addition of palladium(0) with bromoarenes. As (*E*)-1,2-dibromoethenes and hindered Grignard reagents are readily available, our study provided an efficient access to some useful polysubstituted indenes and *cis*-substituted stilbenes. The factors that could influence the domino reaction pathways identified in this study may also be useful for development of other cross-coupling and C–H activation-based tandem/domino reactions. Work toward this direction is underway.

NMR spectra were recorded on Varian 300 MHz or 600 MHz spectrometers. ^{1}H NMR data are reported using TMS as internal standard and ^{13}C NMR using $CHCl_3$. All yields reported refer to isolated yields (average of two runs) unless otherwise indicated, and the product purity was estimated to be greater than 95% as determined by ^{1}H NMR. THF and toluene were distilled from Na/benzophenone ketyl. Cy_3P, *t*-Bu_3P, *o*-Tol_3P, and $PdCl_2(PPh_3)_2$ were purchased from Strem Chemicals Inc. and used without further purification. Ph_3P was purchased from Acros Organics and grinded before use. $Pd(OAc)_2$ and $Pd(PPh_3)_4$ were gifts from Frontier Scientific. Other chemicals were purchased from Alfa Aesar and used directly.

Palladium(II) Acetate Catalyzed Cyclization Reactions of (*E*)-1,2-Dibromoethenes with Hindered Grignard Reagents; General Procedure

In a glove box with an N_2 atmosphere, $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (*E*)-1,2-dibromoethene (0.5 mmol), and THF (1 mL) were added to a Schlenk flask. The mixture was stirred for 2 min and then the Grignard reagent in THF soln (1.25 mmol) was added. The mixture was stirred at r.t. for 20 h. The reaction was quenched with H_2O and extracted with EtOAc (2 × 20 mL). The organic layer was washed with brine, dried (Na_2SO_4), and concentrated under vacuum. The crude mixtures were analyzed by ^{1}H NMR, from which the ratio of cyclization product to cross-coupling product were determined. Flash chromatography (silica gel, hexane–EtOAc, 100:0 to 90:10) gave the cyclization product.

4,6-Dimethyl-2,3-diphenyl-1*H*-indene (3a)[6]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.35 (m, 3 H), 7.31 (d, *J* = 7.2 Hz, 2 H), 7.21 (s, 1 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 7.14 (t, *J* = 7.2 Hz, 2 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 6.82 (s, 1 H), 3.86 (s, 2 H), 2.37 (s, 3 H), 1.81 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.1, 141.6, 141.4, 140.1, 139.3, 136.8, 134.8, 131.8, 130.4, 129.6, 128.6, 128.0, 127.9, 127.2, 126.5, 122.2, 40.6, 21.2, 19.8.

2,3-Diethyl-4,6-dimethyl-1*H*-indene (3b)[6]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.06 (s, 1 H), 6.83 (s, 1 H), 3.22 (s, 2 H), 2.64 (q, *J* = 7.6 Hz, 2 H), 2.54 (s, 3 H), 2.44 (q, *J* = 7.6 Hz, 2 H), 2.32 (s, 3 H), 1.13 (t, *J* = 7.6 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.9, 143.2, 141.3, 139.2, 132.9, 130.0, 129.1, 122.1, 39.4, 21.3, 20.9, 19.9, 19.6, 15.3, 14.6.

4,6-Dimethyl-2,3-dipropyl-1*H*-indene (3c)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.04 (s, 1 H), 6.82 (s, 1 H), 3.20 (s, 2 H), 2.57 (t, *J* = 7.8 Hz, 2 H), 2.52 (s, 3 H), 2.39 (t, *J* = 7.8 Hz, 2 H), 2.32 (s, 3 H), 1.53 (m, 4 H), 0.99 (t, *J* = 7.2 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.9, 142.2, 141.5, 138.3, 132.9, 130.0, 129.2, 122.1, 39.8, 30.6, 29.1, 23.9, 23.1, 20.9, 19.6, 14.2, 14.15.

3,4,6-Trimethyl-2-phenyl-1*H*-indene (3d)[6]

^{1}H NMR showed a 91:9 ratio. Analytic sample of 3,4,6-trimethyl-2-phenyl-1*H*-indene (**3d**) was obtained by recrystallization of the mixture of 3,4,6-trimethyl-2-phenyl-1*H*-indene (**3d**) and 2,4,6-trimethyl-3-phenyl-1*H*-indene (**3d′**) in hexanes.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (m, 4 H), 7.27 (m, 1 H), 7.13 (s, 1 H), 6.88 (s, 1 H), 3.64 (s, 2 H), 2.62 (s, 3 H), 2.42 (s, 3 H), 2.36 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.6, 142.1, 140.2, 138.0, 136.0, 134.3, 130.9, 130.2, 128.6, 128.2, 126.4, 122.2, 41.2, 21.1, 20.3, 15.6.

The structure of 3,4,6-trimethyl-2-phenyl-1*H*-indene (**3d**) was established by comparison with reported data.[6]

4-Methyl-2,3-diphenyl-1*H*-indene (3e)[6]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.37 (m, 4 H), 7.33 (m, 2 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 7.8 Hz, 2 H), 7.13 (t, *J* = 7.8 Hz, 2 H), 6.99 (d, *J* = 7.8 Hz, 1 H), 3.90 (s, 2 H), 1.85 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.1, 142.7, 141.5, 141.2, 139.2, 136.6, 131.9, 129.7, 129.6, 128.6, 128.0, 128.0, 127.2, 126.6, 124.9, 121.3, 40.9, 20.0.

2,3-Diethyl-4-methyl-1*H*-indene (3f)[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 1 H), 7.06 (m, 2 H), 3.31 (s, 2 H), 2.73 (q, *J* = 7.5 Hz, 2 H), 2.65 (s, 3 H), 2.52 (q, *J* = 7.5 Hz, 2 H), 1.21 (t, *J* = 7.5 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.7, 144.3, 143.8, 139.8, 129.9, 129.5, 123.8, 121.5, 39.9, 21.6, 20.3, 20.1, 15.6, 14.9.

3,4-Dimethyl-2-phenyl-1*H*-indene (3g)[6]

^{1}H NMR showed a 90:10 ratio. Analytic sample of 3,4-dimethyl-2-phenyl-1*H*-indene (**3g**) was obtained by recrystallization of the mixture of 3,4-dimethyl-2-phenyl-1*H*-indene (**3g**) and 2,4-dimethyl-3-phenyl-1*H*-indene (**3g′**) in hexanes. White solid; mp 75–77 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 (m, 4 H), 7.30 (m, 2 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 7.05 (d, *J* = 7.2 Hz, 1 H), 3.67 (s, 2 H), 2.66 (s, 3 H), 2.44 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.6, 143.3, 141.3, 137.9, 136.2, 131.3, 129.4, 128.6, 128.3, 126.6, 124.6, 121.4, 41.4, 20.4, 15.6.

The structure of 3,4-dimethyl-2-phenyl-1*H*-indene (**3g**) was established by comparison with reported data.[6]

4,5,6,7-Tetramethyl-2,3-diphenyl-1*H*-indene (3h)[6]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38 (t, *J* = 7.2 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.29 (d, *J* = 7.2 Hz, 2 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 7.13 (t, *J* = 7.8 Hz, 2 H), 7.09 (t, *J* = 7.8 Hz, 1 H), 3.79 (s, 2 H), 2.38 (s, 3 H), 2.30 (s, 3 H), 2.19 (s, 3 H), 1.80 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.16, 141.42, 140.5, 139.9, 139.1, 137.1, 134.6, 132.1, 129.7, 128.6, 128.2, 128.0, 127.9, 127.0, 126.3, 40.6, 16.4, 16.24, 16.21, 16.1.

Dichlorobis(triphenylphosphine)palladium-Catalyzed Cross-Coupling Reactions of (*E*)-1,2-Dibromoethenes with Hindered Grignard Reagents; General Procedure

In a glove box with an N_2 atmosphere, $PdCl_2(PPh_3)_2$ (0.015 mmol), (*E*)-1,2-dibromoethene (0.5 mmol), and THF (1 mL) were added to a Schlenk flask. The mixture was stirred for 2 min and then the Grignard reagent in THF soln (1.25 mmol) was added. The mixture was stirred under reflux for 20 h. The reaction was quenched with H_2O and extracted with EtOAc (2 × 20 mL). The organic layer was washed with brine, dried (Na_2SO_4), and concentrated under vacuum. The crude mixtures were analyzed by ^{1}H NMR, from which the ratio of cyclization product to cross-coupling product were determined. Flash chromatography (silica gel, hexane–EtOAc, 100:0 to 90:10) gave the cross-coupling product. The *Z* configuration of alkene products was established by comparison with reported data.[2,3]

(*Z*)-3,4-Bis(pentamethylphenyl)hex-3-ene (4a)[6,15a]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.50 (q, *J* = 7.8 Hz, 4 H), 2.10 (s, 6 H), 2.02 (s, 12 H), 2.00 (s, 12 H), 1.06 (t, *J* = 7.8 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.5, 139.3, 132.0, 131.6, 131.1, 29.3, 19.6, 16.5, 16.4, 13.3.

(*Z*)-3,5-Bis(pentamethylphenyl)oct-4-ene (4b)[15a]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.40 (m, 4 H), 2.11 (s, 6 H), 2.02 (s, 12 H), 2.00 (s, 12 H), 1.52 (m, 4 H), 0.93 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.6, 138.7, 131.9, 131.6, 131.1, 39.2, 22.2, 19.7, 16.6, 16.4, 15.0.

(*Z*)-3,4-Bis(2,4,6-trimethylphenyl)hex-3-ene (4c)[6,15a]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.63 (s, 4 H), 2.47 (q, *J* = 7.8 Hz, 4 H), 2.15 (s, 6 H), 2.06 (s, 12 H), 1.02 (t, *J* = 7.8 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.6, 138.5, 135.7, 134.9, 128.1, 28.2, 20.9, 20.8, 13.4.

(*Z*)-4,5-Bis(2,4,6-trimethylphenyl)oct-4-ene (4d)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.62 (s, 4 H), 2.37 (m, 4 H), 2.15 (s, 6 H), 2.05 (s, 12 H), 1.45 (m, 4 H), 0.93 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.7, 137.8, 135.6, 134.8, 128.1, 38.1, 22.4, 21.0, 20.8, 14.9.

(*Z*)-1-Phenyl-1,2-bis(2,4,6-trimethylphenyl)prop-1-ene (4e)[6]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27 (m, 4 H), 7.16 (m, 1 H), 6.68 (s, 2 H), 6.59 (s, 2 H), 2.173 (s, 3 H), 2.165 (s, 3 H), 2.16 (br s, 6 H), 2.13 (s, 3 H), 2.04 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.5, 139.3, 138.3, 137.9, 136.4, 135.7, 135.5, 135.3, 135.1, 130.1, 128.3, 127.3, 125.8, 23.0, 21.7, 21.0, 20.83, 20.81.

(*Z*)-3,4-Bis(2,6-dimethylphenyl)hex-3-ene (4f)[15a]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.90 (d, *J* = 7.2 Hz, 2 H), 6.80 (d, *J* = 7.2 Hz, 4 H), 2.52 (d, *J* = 7.2 Hz, 4 H), 2.11 (s, 12 H), 1.40 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.1, 138.7, 137.8, 136.9, 127.2, 125.8, 27.9, 21.0, 13.3.

(*Z*)-1,2-Bis(2,6-dimethylphenyl)-1-phenylprop-1-ene (4g)[6]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.29 (m, 4 H), 7.19 (m, 1 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 6.89 (t, *J* = 7.2 Hz, 1 H), 6.85 (d, *J* = 7.2 Hz, 2 H), 6.77 (d, *J* = 7.8 Hz, 2 H), 2.22 (s, 3 H), 2.20 (s, 6 H), 2.08 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.0, 140.9, 137.9, 136.6, 135.8, 135.3, 130.1, 127.4, 126.3, 126.1, 126.0, 22.8, 21.8, 21.1.

(*Z*)-1,2-Bis(pentamethylphenyl)-1,2-diphenylethene (4h)[6,15a]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.05–7.03 (m, 6 H), 7.00–6.98 (m, 4 H), 2.11 (s, 18 H), 2.01 (s, 12 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.3, 141.5, 139.0, 132.8, 131.8, 131.7, 130.9, 127.2, 125.6, 20.0, 16.6, 16.4.

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