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Boron Trihalide Mediated Alkyne-Aldehyde Coupling Reactions: A Mechanistic Investigation

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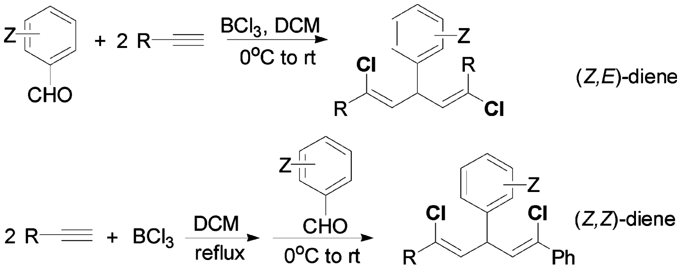
Received December 17, 2007



A boron trihalide mediated alkyne-aldehyde coupling reaction leading to stereodefined 1,3,5-triaryl-1,5-dihalo-1,4-pentadienes is described. The study led to the discovery of a direct substitution of hydroxyl groups by stereodefined alkenyl moieties using alkenylboron dihalides. During the investigation, it was also discovered that, at low temperatures, the reaction of BCl_3 with alkynes produces monovinylboron dichloride rather than the reported divinylboron chloride. A modified reaction mechanism for the boron trichloride mediated alkyne-aldehyde coupling reaction is now proposed. The reaction temperature and mode of addition have been found to have dramatic affects on the stereochemistry of the diene products.

Introduction

Efficient one-pot syntheses of complex molecules from readily available starting materials are always desirable. Especially attractive are reactions affording multifunctionalized molecules.[1] The alkyne-aldehyde coupling reaction is a prime example. A variety of molecules can be generated from this coupling reaction by varying the Lewis acids and transition metal complexes employed. Synthons afforded by this coupling reaction include propargylic alcohols,[2] α,β-unsaturated ketones,[3] allylic alcohols,[4] stereodefined enynols,[5] and naphthalene derivatives.[6] When carried out in an intramolecular fashion, the reaction provides an efficient route to α-alkylidenecycloalkanones,[7] and cycloalkenones.[8] Using transition metal complexes, additional products can be generated through either carbon−carbon triple bond cleavage in alkynes[9] or decarbonylation of aldehydes.[10]

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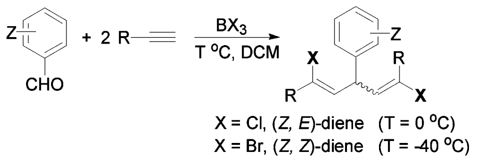
SCHEME 1. Boron Halide Mediated Coupling of Aryl Aldehydes and Alkynes

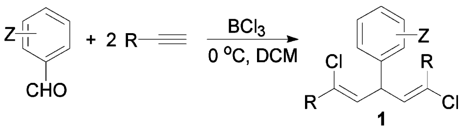


A new alkyne-aldehyde coupling reaction was recently discovered.[11] In the presence of a stoichiometric amount of boron trihalide, aryl aldehydes were found to couple with 2 equiv of aryl alkynes to provide stereodefined 1,3,5-triaryl-1,5-dihalo-1,4-pentadienes (Scheme 1). Interestingly, the stereochemistry of the diene products is dependent on the boron halide employed. If boron trichloride is used, the reactions afford (*Z*,*E*)-1,4-pentadienes as major products along with minor quantities of the (*Z*,*Z*)-1,4-pentadienes. However (*Z*,*Z*)-1,4-pentadienes are the products formed if boron tribromide is used. In view of the potential value of these dihalodiene products in organic synthesis, the study led to the use of other Lewis acids, including TiX$_4$,[12] FeCl$_3$[13] and GaX$_3$.[14] A tentative reaction mechanism for these coupling reactions was proposed.[11−13] In this paper, we describe an investigation initially designed to validate the originally proposed mechanism. A modified reaction mechanism was subsequently put forward and led to the discovery of the dramatic influence of temperature on the stereochemistry of the boron trichloride mediated alkyne-aldehyde coupling reaction. In addition, it was found that the mode of reagent addition greatly affects the stereochemistry of the products formed in these three-component reactions (allyloxide, boron trihalide and alkyne).

Results and Discussions

Boron Trihalide Mediated Alkyne-Aldehyde Coupling Reaction. We have been investigating the chemistry of boron halide derivatives for many years, and a number of novel reactions have been developed.[15] In a continuation of a study focused on the Grignard-like alkylation of aryl aldehydes using dialkylboron halides,[15e] we investigated the addition of alkenylboron dihalide reagents to aldehydes. Brown[16] and Soderquist[17] had earlier reported the successful 1,2-addition of *B*-alkenyl-9-BBN derivatives to aldehydes. The rigid nature of the 9-BBN ring prohibits reduction of the aldehyde via a β-hydride transfer.[18] The low reactivity of *B*-alkenyl-9-BBN derivatives and the limited availability of functionally substituted *B*-alkenyl-9-BBN derivatives restrict the scope of the 9-BBN reactions. Alkenylboron dihalides exhibit high reactivity and are not prone to β-hydride transfer; these chemical features led us to investigate the reaction of aldehydes with (*Z*)-2-halo-1-alkenylboron dihalides.

TABLE 1. Boron Trichloride Mediated Coupling of Aryl Aldehydes and Alkynes[a]



entry	Z	R	product	yield (%)[b]
1	H	Ph	**1a**	65
2	4-F	Ph	**1b**	73
3	4-Br	Ph	**1c**	68
4	4-Me	Ph	**1d**	65
5	4-CN	Ph	**1e**	27[c,d]
6	H	4-Me-Ph	**1f**	67
7	4-F	4-Me-Ph	**1g**	63
8	4-Me	4-Me-Ph	**1h**	62
9	4-F	4-F-Ph	**1i**	76
10	4-Me	4-F-Ph	**1j**	62

[a] Reaction carried out at 0 °C for 2 h and then maintained at room temperature (see Experimental Section for details). [b] Isolated yields based on the starting aldehyde. [c] (*Z*,*Z*)-Isomer (41%) was isolated as the major product. [d] (*Z*,*E*)-Isomer was obtained in 66% isolated yield when the reaction was kept at 0 °C for 5 h while using excess alkyne (3.0 equiv).

The reaction of benzaldehyde with preformed (*Z*)-2-chloro-2-phenylvinylboron dichloride was first examined in dichloromethane at room temperature. Surprisingly, the reaction afforded (*Z*,*Z*)-1,5-dichloro-1,3,5-triphenyl-1,4-pentadiene along with the expected allylic alcohol (*Z*)-3-chloro-1,3-diphenylprop-2-en-1-ol. It has been reported that boron trihalides add to terminal alkynes readily at −78 °C.[19] Therefore, we examined the possibility of a one-pot reaction by mixing boron trichloride, phenylacetylene and benzaldehyde at 0 °C. The diene product formed. However, the (*Z*,*E*)-1,4-pentadiene was isolated as the major product along with minor amounts of the expected (*Z*,*Z*)-1,4-pentadiene. None of the (*E*,*E*)-1,4-pentadiene isomer was detected. A series of aldehydes and alkynes were then subjected to the new reaction. The results are presented in Table 1. Generally, reactions involving aryl aldehydes bearing electron-withdrawing groups tend to proceed more slowly. The ^{1}H and ^{13}C NMR spectra of each 1,5-dichloro-1,4-diene derivative displayed two sets of vinyl hydrogen resonances, indicating that all were (*Z*,*E*)-1,4-pentadienes.[20]

(*Z*,*Z*)-1,5-Dibromo-1,4-pentadienes (rather than (*Z*,*E*)-1,5-dibromo-1,4-pentadienes) were obtained as the major products from the one-pot BBr$_3$-mediated alkyne-aldehyde coupling reaction. Since the bromination of aryl aldehydes by boron

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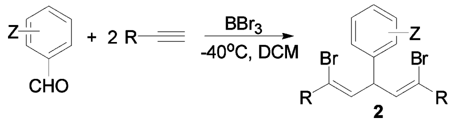
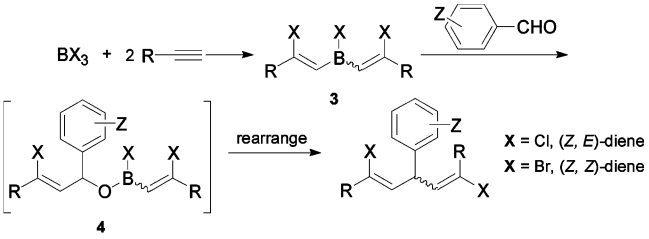
TABLE 2. Boron Tribromide Mediated Coupling of Aryl Aldehydes and Alkynes[a]



entry	Z	R	product	yield (%)[b]
1	4-F	Ph	**2a**	91
2	4-Cl	Ph	**2b**	95
3	4-Me	Ph	**2c**	80
4	2-Me	Ph	**2d**	83
5	4-NO_2	Ph	**2e**	80
6	4-F	4-Me-Ph	**2f**	80
7	4-Br	4-Me-Ph	**2g**	70
8	4-F	4-Cl-Ph	**2h**	83
9	4-Br	4-Cl-Ph	**2i**	74
10	2-Me	4-Cl-Ph	**2j**	89

[a] Reaction carried out at −40 °C (see experimental section for detail). [b] Isolated yields based on the starting aldehydes.

SCHEME 2. Tentative Reaction Mechanism for Boron Halides Mediated Coupling Reaction

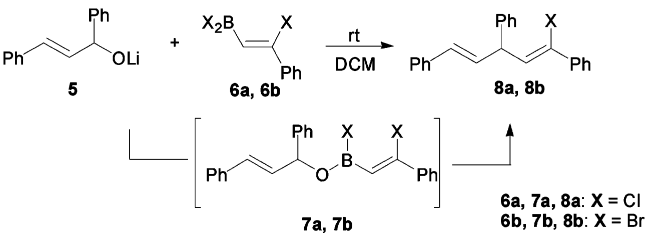


tribromide has been reported to be quite facile,[15c] the boron tribromide mediated reactions were carried out at −40 °C. Consistent with the fact that the haloboration of alkynes is faster with boron tribromide than boron trichloride, coupling reactions involving boron tribromide are also faster than those using boron trichloride. The results are summarized in Table 2. As anticipated, the ^1H and ^{13}C NMR spectra of the symmetrical (*Z*,*Z*)-1,5-dibromide-1,4-pentadiene derivatives exhibited only one set of vinyl resonances.

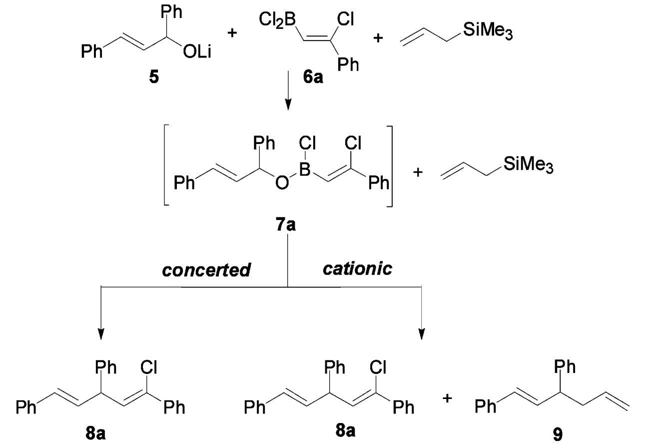
Tentative Reaction Mechanism. Due to the facile nature of the haloboration reaction, the boron trihalide mediated alkyne-aldehyde coupling reactions were initially postulated to occur as outlined in Scheme 2. Haloboration of the alkyne first generates di(halovinyl)boron halide **3**, which then adds to the aldehyde in a Grignard-like fashion to form **4**. The migration of the second halovinyl group from boron to carbon center then affords the final product. The retention of the vinyl group configuration during migration leads to high stereoselectivity. (The *E*,*Z* stereochemistry of the vinyl groups was believed to have been established during the formation of the divinylboron halide intermediate; a postulation that was later shown to be incorrect.) This tentative mechanism was based on the following two factors: isolation of the anticipated 1,4-pentadiene from the reaction of preformed dialkenylboron bromides with aldehydes and isolation of (*Z*)-3-halo-1,3-diarylprop-2-en-1-ol, the expected product from intermediate **4**, when the reactions were quenched with water prior to completion.

To examine the feasibility of a halovinyl group migration from boron to carbon, the reaction shown in Scheme **3** was carried out. The reaction of allyloxide **5** and alkenylboron dihalide **6** would be expected to generate intermediate **7**, which is similar to the proposed reaction intermediate **4**. If the migration outlined in Scheme **2** occurred, intermediate **7** would be expected to rearrange to the desired product **8**. Indeed, reactions of allyloxides with alkenylboron dihalides proceed efficiently at room temperature and generate **8** in good yields. Thus, the proposed migration appeared reasonable since the stereochemistry of the vinyl group was also retained. These preliminary results were communicated.[21] From the viewpoint of organic synthesis, the reaction shown in Scheme 3 provides a formal, transition-metal-free Suzuki reaction.[22]

SCHEME 3. Direct Evidence Supporting Alkenyl Group Migration



SCHEME 4. Competitive Reaction Designed To Distinguish Concerted and Cationic Mechanisms



Upon confirmation of vinyl group migration, we attempted to ascertain whether the vinyl group migration proceeded via a cationic or concerted pathway. It is known that allyltrimethylsilane readily captures cationic intermediates.[23] Therefore, a competition reaction involving vinylboron dihalide, allylsilane and an allyloxide was designed to probe the vinyl group migration (Scheme 4). To a mixture of preformed alkenylboron dichloride **6a** and allyltrimethylsilane, 1 equiv of allyloxide **5** was added to generate intermediate **7a**. If the vinyl group migration proceeds in a concerted fashion, only product **8a** should form. In contrast, if the vinyl group migration proceeds via a cationic route, allyltrimethylsilane should capture a percentage of the cation intermediate, generating **9** in addition to the desired product **8a**. When the reaction was carried out, a mixture of allylated product **9** and **8a** formed in a ratio of 5:2

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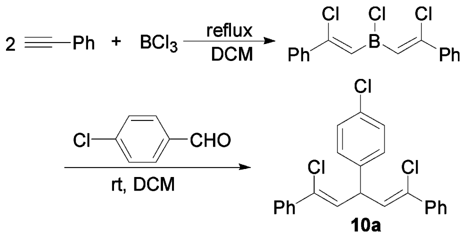
SCHEME 5. Reaction of (*Z*,*Z*)-Dialkenylboron Chloride with 4-Chlorobenzylaldehyde



(isolated yields of **9** and **8a** are 62% and 25%, respectively, based on **5**).

The identification of a cationic intermediate[24] raises questions relating to the stereochemistry of products isolated from the boron trichloride mediated alkyne-aldehyde coupling reaction. The intermediacy of the (*Z*,*E*)-di(chlorovinyl)boron chloride, postulated earlier to explain the predominant formation of (*Z*,*E*)-diene products, is probably not correct. Therefore, we reinvestigated the boron trichloride mediated alkyne-aldehyde coupling reaction.

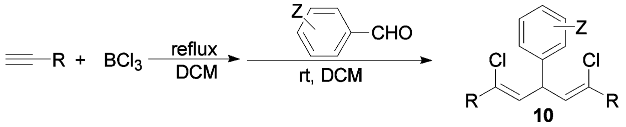
Reinvestigation of the Boron Trichloride Mediated Alkyne-Aldehyde Coupling Reaction. The intermediacy of a (*Z*,*E*)-di(chlorovinyl)boron chloride was initially postulated to explain the *Z*,*E*-stereochemistry of the product dienes. However, the reaction of boron halides with 2 equiv of alkyne has been reported to afford only (*Z*,*Z*)-di(halovinyl)boron halides.[19] Upon reexamining the initial report, we noted that the (*Z*,*Z*)-di(2-chloro-2-phenylvinyl)boron chloride used for product characterization was obtained by distillation and in relatively low yield (the reaction of alkynes with BBr_3 gives quantitative yields). Therefore, it is reasonable to postulate that, at low temperatures, the reaction of 2 equiv of phenylacetylene with 1 equiv of boron trichloride might produce the monovinylboron dichloride product and that the divinylboron chloride product would be formed only during distillation.

To support the postulation that (*Z*,*Z*)-di(vinylchlorophenyl)-boron chloride formed only during distillation, phenylacetylene and boron trichloride (2:1) were refluxed in dichloromethane for 3 h and the reaction mixture then allowed to cool to 0 °C. Addition of *p*-chlorobenzaldehyde to the mixture produced (*Z*,*Z*)-diene **10a** in 78% isolated yield (Scheme 5). This strongly supports the postulation that the observed (Z,Z)-diene products arise from divinylboron halide intermediates (the reaction of aldehyde with preformed dialkenylboron bromide also produces (*Z*,*Z*)-dienes).

Reactions of preformed (*Z*,*Z*)-di(chlorovinyl)boron chlorides with various aryl aldehydes were then carried out. The results are summarized in Table 3. The ^1H and ^{13}C NMR spectra of each product revealed only one set of vinyl group resonances due to a single vinyl group, supporting the formation of (*Z*,*Z*)-1,5-dichloro-1,4-pentadienes. In addition, a single crystal of compound **10b** was analyzed by X-ray crystallography.[25] The X-ray molecular structure confirmed the NMR assignment.

Thus, by changing the reaction sequence, and the temperature at which the reaction is conducted, either (*Z*,*E*)-dichloro-1,4-pentadienes **1** or (*Z*,*Z*)-dichloro-1,4-pentadienes **10** can be prepared from the same starting materials (alkynes, aldehydes and boron trichloride).

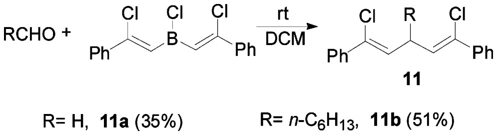
TABLE 3. Reaction of Preformed (*Z*,*Z*)-Dialkenylboron Chloride with Aryl Aldehydes[a]



entry	Z	R	product	yield (%)[b]
1	4-Cl	Ph	**10a**	78
2	4-Br	Ph	**10b**	83
3	4-CN	Ph	**10c**	82
4	2-Me	Ph	**10d**	76
5	H	Ph	**10e**	60
6	4-Cl	4-MePh	**10f**	81
7	4-NO_2	4-MePh	**10g**	82
8	3,4-*di*-OMe	4-MePh	**10h**	34
9	4-Cl	4-BrPh	**10i**	75
10	4-CF_3	3-OMePh	**10j**	48
11	4-Cl	3-FPh	**10k**	76

[a] Reaction carried out at 0 °C and then maintained at room temperature (see Experimental Section for details). [b] Isolated yields based on the starting aldehyde.

SCHEME 6. Dialkenylation of Aliphatic Aldehydes Using Preformed Divinylboron Halides



We also investigated the reactions of preformed divinylboron halides with aliphatic aldehydes. The reactions afforded the desired dialkenylation products **11** in moderate yields (Scheme 6). The use of preformed divinylboron halide reagents minimizes enolization reactions leading to aldol products.

To summarize, the formation of (*Z*,*Z*)-1,5-dihalo-1,4-pentadienes from mixtures of alkynes with boron tribromide at −40 °C and from mixtures of alkynes refluxed with boron trichloride, *both* involve the (*Z*,*Z*)-di(halovinyl)boron halide intermediates. Grignard-like addition of the divinylboron halide intermediate to the aryl aldehyde, followed by migration of the second vinyl group proceeds with retention of olefin configuration, leads to high stereoselectivity in the alkyne-aldehyde coupling.

A Modified Reaction Mechanism for the Boron Trichloride Mediated Alkyne-Aldehyde Coupling Reaction at 0 °C. Since the reaction of boron trichloride with alkynes at 0 °C generates only the (*Z*)-chlorovinylboron dichloride species, a modified reaction mechanism is now proposed for the boron trichloride mediated reaction at 0 °C (Scheme 7). The Grignard-like addition of (*Z*)-halovinylboron dichloride to the aldehyde forms intermediate **12**. The subsequent cleavage of the carbon-oxygen bond affords carbocation intermediate **13**. Addition of cation **13** to the second alkyne then generates the more thermodynamically stable (*Z*,*E*)-diene product **1** with high stereoselectivity.[26] The isolation of pure (*Z*)-3-chloro-1,3-diarylprop-2-en-1-ol from experiments in which incomplete reactions were quenched with water is thus readily explained.

The modified mechanism (Scheme 7) involves an unusual carbon-oxygen bond cleavage to generate a cation intermediate

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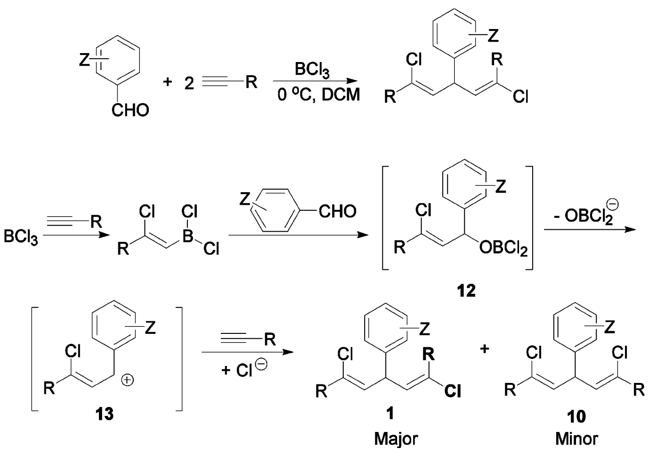
[24] Other evidence supporting a cationic mechanism includes the ring opening of a cyclopropyl group and the racemization of a chiral center in benzyloxide derivatives in the coupling reaction of benzyloxides and vinylboron dihalides. See: Kabalka, G. W.; Yao, M.-L.; Borella, S.; Wu, Z. *Org. Lett.* **2005**, *7*, 2865.

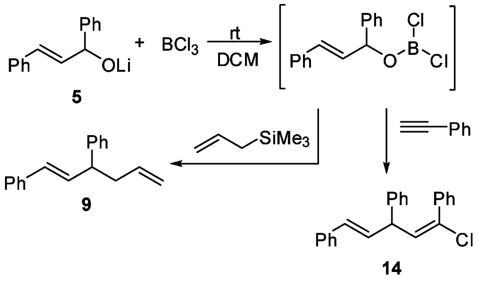
[25] See Supporting Information.

[26] It is reported that the addition of benzylic carbocation to terminal alkynes stereoselectively gives (*Z*)-alkenyl halides. See: Marcuzzi, F.; Melloni, G.; Modena, G. *J. Org. Chem.* **1979**, *44*, 3022.

SCHEME 7. Modified Mechanism for BCl_3-Mediated Coupling of Aryl Aldehydes and Alkynes at 0 °C



SCHEME 8. Evidence Supporting the Cleavage of the C−O Bond via BCl_3



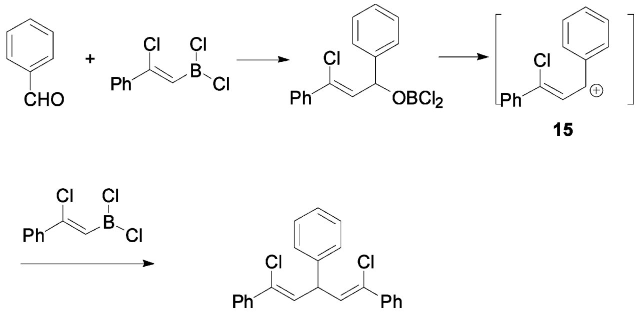
13.[27] To validate the formation of **13**, the reaction of allyloxide **5** with phenylacetylene in the presence of boron trichloride was examined at room temperature (Scheme 8). The (*E*,*E*)-1-chloro-1,3,5-triphenyl-1,4-pentadiene (**14**) was isolated in 78% yield, only 4% of (*Z*,*E*)-1-chloro-1,3,5-triphenyl-1,4-pentadiene was formed. The isolation of diene **9** when allyltrimethylsilane is present in the reaction mixture provides further support for the intermediacy of a carbocation. The generation of cations from alkoxides with the assistance of a Lewis acid is unprecedented. This unusual carbon-oxygen cleavage reaction led to the discovery of straightforward allylation of propargyl alcohols.[28]

Significantly, the stereochemistry of the 1,4-diene product obtained (Scheme 8) is opposite to that of the products from the reaction shown in Scheme 3. Thus, by changing the mode of addition of the reactants, both (*Z*,*E*)-1-halo-1,3,5-triphenyl-1,4-pentadienes **8** and (*E*,*E*)-1-halo-1,3,5-triphenyl-1,4-pentadienes **14** can be prepared from the same starting materials (alkynes, boron trihalide and allyloxides)!

Since the *syn*-additions of TiX_4[29] and $FeCl_3$[13,30] to terminal alkynes are known, the TiX_4- and $FeCl_3$-mediated alkyne-aldehyde coupling reactions to form (*Z*,*E*)-dienes most likely proceed through the pathway similar to that in Scheme 7.

The intermediacy of a carbocation intermediate such as **13** could also explain the formation of (*Z*,*Z*)-1,5-dichloro-1,3,5-triaryl-1,4-pentadiene products from preformed (*Z*)-2-chloro-2-phenylvinylboron dichloride (vide supra). It is well-known that electrophiles can add to vinylboron reagents stereoselectively with retention of configuration of the vinyl group.[31] Thus an intermediate cation would add to a second equivalent of the monovinylboron dihalide to generate the observed *Z*,*Z*-diene product as illustrated for the formation of (*Z*,*Z*)-1,5-dichloro-1,3,5-triphenyl-1,4-pentadiene (Scheme 9).

SCHEME 9. Reaction of *Z*-Chlorovinylboron Dichloride with Aldehyde



Conclusion

The effects of reactant addition and temperature on the boron trihalide mediated alkyne-aldehyde coupling reaction is described. It is now possible, by controlling the sequence of reactant addition and the reaction temperature, to generate either (*Z*,*Z*)-1,5-dichloro-1,4-pentadienes or the corresponding (*Z*,*E*)-isomers. The (Z,Z)-1,5-dibromo-1,4-pentadienes are the primary products under all reaction conditions. It was discovered that, at room temperature, the reaction of boron trichloride with 2 equiv of alkynes actually generates only the monovinylboron dichloride products and not the originally reported divinylboron chloride! Several novel carbon−carbon bond-forming reactions were developed, including a direct substitution of a hydroxyl group with a stereodefined alkenyl moiety.

Experimental Section

All glassware was dried in an oven heated to 100 °C for at least 12 h and then cooled prior to use. Dichloromethane was distilled from appropriate drying agents prior to use. Reactions were magnetically stirred and monitored by TLC. Products were purified by flash chromatography, using silica gel (230−400 mesh, 60 Å). Boron trichloride (1.0 M methylene chloride solution) and boron tribromide were used as received. All aldehydes and alkynes were used as received.

Synthesis of (*Z*,*E*)-1,5-dichloro-1,3,5-triphenyl-1,4-pentadiene (1a). Representative Procedure for the Synthesis of (*Z*,*E*)-1,5-Dichloro-1,4-pentadienes (1a−j). Benzaldehyde (0.42 g, 4.0 mmol) and phenylacetylene (0.82 g, 8.0 mmol) were placed in a dry argon-flushed, 50 mL round-bottomed flask equipped with a stirring bar and containing 20 mL of dry CH_2Cl_2. The solution was cooled to 0 °C in an ice bath, and boron trichloride (4.4 mmol, 4.4 mL of a 1.0 *M* CH_2Cl_2 solution) was added via syringe. The solution was allowed to stir for 2 h at 0 °C and then for 4 h at room temperature. The reaction solution gradually turned dark purple. The resulting mixture was hydrolyzed with water (20 mL) and

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[27] A similar cleavage has been proposed recently in the $TiCl_4/R_3N$-mediated conversion of propargyl alcohols to chloroallenes; see: Karunakar, G. V.; Periasamy, M. *J. Org. Chem.* **2006**, *71*, 7463.

[28] (a) Kabalka, G. W.; Yao, M.-L.; Borella, S. *J. Am. Chem. Soc.* **2006**, *128*, 11320. (b) Kabalka, G. W.; Yao, M.-L.; Borella, S.; Goins, L. K. *Organometallics*, **2007**, *26*, 4112.

[29] Lemarchand, D.; M'Baye, N.; Braun, J. *J. Organomet. Chem.* **1972**, *39*, C69.

[30] Cassagne, D.; Gillet, M.; Braun, J. *Bull. Soc. Chim. Fr.* **1979**, 140.

[31] (a) Hara, S.; Dojo, H.; Takinami, S.; Suzuki, A. *Tetrahedron Lett.* **1983**, *24*, 731. (b) Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1995**, *36*, 3925. (c) Lightfoot, A. P.; Maw, G.; Thirsk, C.; Twiddle, S. J. R.; Whiting, A. *Tetrahedron Lett.* **2003**, *44*, 7645. (d) Kabalka, G. W.; Mereddy, A. R. *Organometallics* **2004**, *23*, 4519. (e) Batsanov, A. S.; Knowles, J. P.; Whiting, A. *J. Org. Chem.* **2007**, *72*, 2525.

extracted with hexanes (3 × 30 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. Product **1a** (0.95 g, 65% yield) was isolated by flash column chromatography. ^{1}H NMR (250 MHz): δ 7.57−7.21 (m, 15H), 6.26 (d, J = 9.2 Hz, 1H), 6.19 (d, J = 10.6 Hz, 1H), 4.88 (dd, J = 10.6 and 9.2 Hz, 1H). ^{13}C NMR: δ 141.5, 137.6, 136.7, 133.7, 129.0, 128.9, 128.8, 128.3, 127.6, 127.2, 126.9, 126.5, 45.6. Anal. Calcd for $C_{23}H_{18}Cl_2$: C, 75.62; H, 4.97. Found: C, 75.48; H, 4.88.

Synthesis of (*Z*,*Z*)-1,5-dibromo-3-(4-fluorophenyl)-1,5-diphenyl-1,4-pentadiene (2a). Representative Procedure for the Synthesis of (*Z*,*Z*)-1,5-Dibromo-1,4-pentadienes (2a−j). 4-Fluorobenzaldehyde (0.52 g, 4.2 mmol) and phenylacetylene (0.86 g, 8.4 mmol) were placed in a dry argon-flushed, 50 mL round-bottomed flask equipped with a stirring bar and containing 20 mL of dry CH_2Cl_2. The solution was cooled to −40 °C, and boron tribromide (4.5 mmol, 4.5 mL of a 1.0 M CH_2Cl_2 solution) was added via syringe. The reaction solution turned purple immediately. The solution was allowed to stir at −40 °C for 4 h. The resulting mixture was hydrolyzed with water (20 mL) and extracted with hexanes (3 × 25 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. Product **2a** (1.8 g, 91% yield) was isolated by flash column chromatography. ^{1}H NMR (250 MHz): δ 7.58−7.00 (m, 14H), 6.40 (d, J = 8.9 Hz, 2H), 5.31 (t, J = 8.9 Hz, 1H). ^{13}C NMR: δ 163.8, 159.8, 139.4, 136.5, 130.7, 129.0, 128.9, 128.3, 127.7, 127.3, 115.8, 115.5, 50.7. Anal. Calcd for $C_{23}H_{17}Br_2F$: C, 58.50; H, 3.63. Found: C, 58.41; H, 3.73.

Coupling of Alkoxides with Vinylboron Dihalides To Afford Dienes 8. (Evidence supporting the migration of the halovinyl group from boron to the carbon center.) Boron trihalide (1.5 mmol, 1.5 mL of a 1.0 M CH_2Cl_2 solution), phenylacetylene (153 mg, 1.5 mmol) and dry dichloromethane (8 mL) were combined in a 50 mL flask and stirred for 1 h under a nitrogen atmosphere. Alkoxide **5** (generated in situ by treating 315 mg, 1.5 mmol of (*Z*)-1,3-diphenylprop-2-en-1-ol with 1 mL of 1.6 M *n*-BuLi) was added at 0 °C and allowed to stir at room temperature overnight. Water (20 mL) was added, the reaction mixture extracted with ethyl acetate (3 × 20 mL), and then dried over anhydrous $MgSO_4$. Product **8a** (412 mg, 83% yield) was isolated by flash column chromatography using hexane as an eluent. Spectra for diene **8a**. ^{1}H NMR (250 MHz): δ 7.60−7.57 (m, 2H), 7.37−7.15 (m, 13H), 6.58−6.34 (m, 3H), 4.94 (dd, J = 9.0 and 8.9 Hz, 1H). ^{13}C NMR: δ 142.1, 137.9, 137.1, 133.4, 130.9, 130.3, 128.7, 128.5, 128.3, 127.8, 127.4, 126.9, 126.6, 126.3, 48.5. Anal. Calcd for $C_{23}H_{19}Cl$: C, 83.50; H, 5.79. Found: C, 83.57; H, 5.65.

Competition Reaction between Vinylboron Dihalides and Allyltrimethylsilane. (Evidence supporting a cationic mechanism.) Boron trihalide (1.5 mmol, 1.5 mL of a 1.0 M CH_2Cl_2 solution), phenylacetylene (153 mg, 1.5 mmol) and dry dichloromethane (8 mL) were combined in a 50 mL flask and stirred for 1 h under a nitrogen atmosphere. The reaction mixture was cooled to 0 °C, allyltrimethylsilane (171 mg, 1.5 mmol) and alkoxide **5** (generated in situ by treating 315 mg, 1.5 mmol of (*Z*)-1,3-diphenylprop-2-en-1-ol with 1 mL of 1.6 M *n*-BuLi) were then added. The resulted reaction mixture was stirred at room temperature overnight. Water (20 mL) was added, the reaction mixture extracted with ethyl acetate (3 × 20 mL) and dried over anhydrous $MgSO_4$. The products **8a** (125 mg, 25% yield) and **9** (218 mg, 62% yield) were isolated by flash column chromatography using hexane as an eluent.

Synthesis of (*Z*,*Z*)-1,5-dichloro-3-(4-chlorophenyl)-1,5-diphenyl-1,4-pentadiene (10a). Representative Procedure for the Synthesis of (*Z*,*Z*)-1,5-Dichloro-1,4-pentadienes (10a−k and 11a,b). Phenylacetylene (306 mg, 3.0 mmol) and boron trichloride (1.5 mmol, 1.5 mL of a 1.0 M CH_2Cl_2 solution) were placed in a dry argon-flushed, 50 mL round-bottomed flask equipped with a stirring bar and containing 20 mL of dry CH_2Cl_2. The solution was refluxed for 3 h and then cooled down to 0 °C using an ice-bath. To this solution, 4-chlorobenzaldehyde (210 mg, 1.5 mmol) was added. The solution was allowed to stir for 2 h at 0 °C and then 6 h at room temperature. The resulting mixture was hydrolyzed with water (20 mL) and extracted with hexanes (3 × 20 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. Product **10a** (471 mg, 78% yield) was isolated by flash column chromatography. ^{1}H NMR (300 MHz): δ 7.62−7.58 (m, 4H), 7.37−7.29 (m, 10H), 6.29 (dd, J = 9.0 and 0.9 Hz, 2H), 5.42 (t, J = 9.0 Hz, 1H). ^{13}C NMR: δ 139.8, 137.5, 134.8, 132.6, 128.9, 128.8, 128.4, 126.8, 126.6, 45.2. IR (Neat, ν_{max}/cm^{-1}): 3032, 1596, 1491, 1445, 1093, 827, 759, 693. Anal. Calcd for $C_{23}H_{17}Cl_3$: C, 69.11; H, 4.29. Found: C, 69.27; H, 4.31.

BCl_3-Mediated Coupling Reaction of Allyloxide 5 with Phenylacetylene. (Evidence supporting the C−O bond cleavage in alkoxide.) Alkoxide **5** (generated in situ by treating 315 mg, 1.5 mmol of (*Z*)-1,3-diphenylprop-2-en-1-ol with 1 mL of 1.6 M *n*-BuLi), phenylacetylene (153 mg, 1.5 mmol) and dry dichloromethane (8 mL) were combined in a 50 mL round-bottomed flask under a nitrogen atmosphere at 0 °C. Boron trihalide (1.5 mmol, 1.5 mL of a 1.0 M CH_2Cl_2 solution) was added and the mixture stirred at room temperature overnight. Water (20 mL) was added, the reaction mixture extracted with ethyl acetate (3 × 20 mL) and dried over anhydrous $MgSO_4$. Product **14** (275 mg, 78% yield) was isolated by flash column chromatography using hexane as an eluent. Spectra for diene **14**. ^{1}H NMR (250 MHz): δ 7.44−7.12 (m, 15H), 6.47−6.20 (m, 3H), 4.32 (dd, J = 10.6 and 10.5 Hz, 1H). ^{13}C NMR: δ 142.2, 136.9, 131.6, 131.2, 130.7, 130.3, 128.8, 128.7, 128.5, 128.3, 127.6, 127.5, 126.8, 126.3, 48.4. Anal. Calcd for $C_{23}H_{19}Cl$: C, 83.50; H, 5.79. Found: C, 83.44; H, 5.82.

Acknowledgment. Acknowledgment is made to the Donors of the Petroleum Research Fund for support of this research. We also wish to thank the U.S. Department of Energy and the Robert H. Cole Foundation for partial support of this research.

Supporting Information Available: ^{1}H and ^{13}C NMR data for all compounds reported, IR data for **10a** and **10i**, elemental analysis for all new compounds, and X-ray file in CIF format for Compound **10b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO702493J