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A Study of Polarization and Directing Effects of Unsymmetrical Alkynes Using Regioselective Pd-catalyzed Bromoallylation

Nikola Topolovčan,[a] Shuto Hara,[a,b] Ivana Císařová,[c] Zdeněk Tošner[d] and Martin Kotora*[a]

[a] Dr. N. Topolovčan, S. Hara, Prof. M. Kotora
Department of Organic Chemistry, Faculty of Science
Charles University
Hlavova 8, 128 43 Praha 2, Czech Republic
E-mail: kotora@natur.cuni.cz
Homepage: http://orgchem.natur.cuni.cz/_kotora

[b] S. Hara
Visiting student from: Okayama University,
3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan. Current address: NOF Corporation, Yebisu garden place tower, 20-3, Ebisu 4-chome, Shibuya-ku, Tokyo, 150-6019, Japan

[b] Dr. I. Císařová
Department of Inorganic Chemistry, Faculty of Science
Charles University
Hlavova 8, 128 43 Praha 2, Czech Republic

[d] Dr. Z. Tošner
NMR Laboratory, Faculty of Science
Charles University
Hlavova 8, 128 43 Praha 2, Czech Republic

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Abstract: Herein is disclosed the first comprehensive study of factors that affect the regioselectivity of $PdBr_2(PhCN)_2$—catalyzed bromoallylation of unsymmetrically substituted internal alkynes. The study was performed on a wide array of electronically and structurally diverse alkynes with aryl-aryl, aryl-ferrocenyl, and aryl-alkyl substitutions. The regioselective formation of bromoallylation products was mostly driven by the polarization of the triple bond in aryl-aryl and aryl-ferrocenyl substituted ethynes. On the other hand, directing effect, which arises from the presence of a directing group in the side-chain of aryl-alkyl substituted alkynes, was the dominating factor that determined the regioselectivity of these reactions.

Introduction

Regioselective functionalization of multiple bonds such as C-C double and triple bonds is influenced by several different factors, including steric, electronic, and directing effects caused by adjacent substituents. Unfortunately, in many cases it is challenging, if not impossible to determine their respective contributions. The polarization of the triple bond has been proposed to be the main factor affecting preferential formation of one regioisomer in many cases of triple bond functionalizations (vide infra);[1] however, the majority of these reports lack any detailed discussion. On the other hand, *para*-substituted diarylethynes constitute a class of compounds where steric factors are negligible (or similar) allowing electronic effects to be investigated. In 2005, an elegant study by Gevorgyan *et al*. on the deduction of electronic polarization of a triple bond using ^{13}C NMR [2,3] showed that regioselectivity of Pd-catalyzed hydrostannation of variously substituted diarylethynes is driven by the polarization of the triple bond. The effect of the polarization of the triple bond on regioselective functionalization of internal alkynes was also studied by Helaja *et al*. in a Pauson-Khand reaction[4] and by Alami *et al*. in Pd-catalyzed hydrostannation of *Z*-enynols.[5] A slightly different approach was taken by Bennett *et al*. who used electronic factors based on frontier orbitals to rationalize the observed regioselectivities in the insertion of unsymmetrical alkynes into Ni-C bonds.[6] Electronic control of regioselectivity was proposed for Rh- and Pd-catalyzed hydroarylations of propargyl amines.[7] In general, these precedents indicate that the polarization of the triple bond drives the observed regioselectivity. On the other hand, primary control of regioselective functionalization of the triple bond by steric effects was proposed as well. Representative examples include the work of Larock and Cacchi *et al.* on carbopalladations of unsymmetrically substituted diynes.[8]

$PdCl_2$-Catalyzed haloallylation of internal alkynes is a reaction of significant synthetic interest and importance and represents a facile approach towards functionalized haloalkenes. In

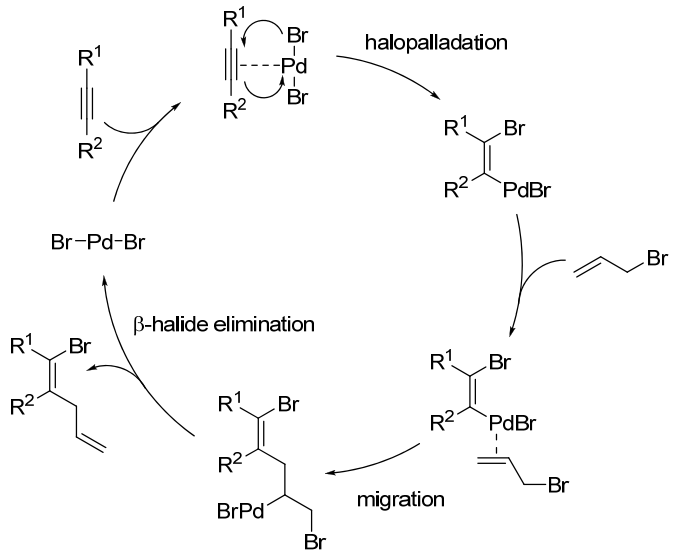
a series of publications, Kaneda *et al.* demonstrated that a catalytic amount of PdX_2 is effective in bringing about a stereoselective haloallylation of a variety of terminal and internal alkynes with allyl halides, resulting in the exclusive formation of *cis*-1-halo-1,4-dienes.[9] The presence of the carbon-halogen bond in the formed products allows for further transformations as it was well exemplified in the Stille[10] and Suzuki[11] cross-couplings, Wacker-Tsuji oxidation, Sonogashira reaction,[12] and in the Ni-promoted formation of cyclopentenones.[13]

These findings encouraged further expansion of the methodology, which was successfully applied in the haloallylation of aromatic ynol ethers, ynamides, alkynyl ketones, and sulfones, resulting in the synthesis of the corresponding α-haloenol ethers,[14] polysubstituted enamides,[15] β-halo alkenyl ketones, and sulfones,[16] respectively. Haloallylation was also one of the key steps in syntheses of natural compounds such as (–)-haterumalide and (–)-oocydin A.[17]

Recently, we have reported a three-step procedure for the synthesis of a variety of 1,2-disubstituted cyclopentadienes based on Pd-catalyzed haloallylation of internal alkynes.[18] During the course of this study, it was observed that $PdBr_2(PhCN)_2$—catalyzed bromoallylation of various unsymmetrically substituted internal alkynes proceeded in the *syn* manner giving the *cis* regioisomers (with respect to the relative position of the bromine atom and allyl group) with good to modest regioselectivity. Nevertheless, the formation of the opposite *cis* regioisomer was also observed in several cases. These findings sparked our interest on factors dictating the observed regioselectivity. A generally accepted mechanism, proposed by Kaneda,[9a,d] suggests the following: *syn* halopalladation, that is, the addition of halogen and palladium atoms as components of the catalyst across the triple bond of the alkyne, is the first step,[19,20] which is followed by migration of the allyl halide into the C—Pd bond of the formed vinylpalladium intermediate (Scheme 1). In the last step of the catalytic cycle, β-halide elimination occurs, which results in the formation of the *cis* halodiene, with simultaneous regeneration of the catalytically active Pd species.

It should be mentioned that other haloallylation reactions have been reported as well. For example, PdX_2-catalyzed haloallylation of alkynes in the presence of allyl alcohols and CuX_2 salts in aqueous media or ionic liquids may give either *cis* or *trans* halodienes.[21] Even though the halopalladation of the triple bond is considered the first step of the proposed reaction mechanism, the subsequent steps differ from the one depicted in Scheme 1.

10.1002/ejoc.201901476



Scheme 1. Proposed mechanism for the bromoallylation of internal alkynes.

Taking into the account the proposed catalytic cycle that leads to the predominant formation of *cis* 1-halo-1,4-dienes, it is reasonable to assume that the regioselectivity of the reaction is defined in the first step. In this respect, we hypothesized that a preferential formation of one of the two possible *cis* regioisomers is affected by the polarization of the triple bond of the unsymmetrically substituted alkynes. By allocating the charges on the triple bond carbon atoms of unsymmetrical internal alkynes, it is easy to see that the halide (the bromide) would attack the carbon atom possessing a lower electron density (an electrophilic carbon atom) whereas the palladium center should form a bond with the carbon atom with a higher electron density (a nucleophilic carbon atom) (Figure 1).

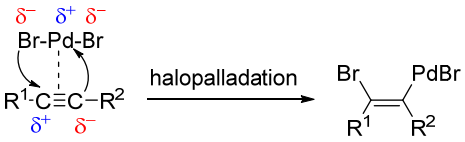


Figure 1. Influence of the triple bond polarization on the regioselectivity of the halopalladation step.

Results and Discussion

Easy access to electronically unsymmetrical diarylethynes makes them attractive model substrates to test the proposed hypothesis. Moreover, the electron density around sp-carbon atoms in phenylethynes is largely affected by the nature and position of the substituent on the aromatic ring,[22] meaning that alteration of substituents would allow smooth control over the

direction of polarization of the triple bond. On top of that, a comparison of the relative position of signals in ^{13}C NMR spectra constitutes a simple method for identification of nucleophilic and electrophilic character of the corresponding alkyne carbon atoms.[2] In this respect, herein, we focus primarily on the *para*-functionalized diarylethynes in order to avoid steric influence of *ortho*- and *para*-positioned substituents on the regioselectivity. Initially, a series of *para*-substituted diarylethynes **1** was prepared to determine the polarization of the carbon atoms of the triple bonds. Moreover, the chemical shift difference of the respective signals of the sp-carbon atoms were calculated assuming that higher Δ ppm would translate into higher regioselectivity (Table 1).

Bromoallylation of unsymetrical diarylethynes. To test these proposals, Pd-catalyzed bromoallylation of the above mentioned diarylethynes was carried out under previously used reaction conditions (Table 1).[18] At first, bromoallylation of 1-(4-cyanophenyl)-2-phenylethyne **1a** afforded a mixture of two regioisomers, **2a** and **3a,** in a 2:1 ratio with a combined isolated yield of 48% (Entry 1). On the other hand, a single regioisomer **2b** was obtained upon bromoallylation of 1-(4-methoxyphenyl)-2-(4-trifluoromethylphenyl)ethyne **1b**, which possess a "push-pull" system consisting of the trifluoromethyl and methoxy groups (Entry 2). Reaction with 1-(4-trifluoromethylphenyl)-2-phenylethyne **1c** gave two products: **2c** and **3c** in a 1:1 ratio (Entry 3). Again, two regioisomers, **2d** and **3d,** were obtained by bromoallylation of 1-(4-bromophenyl)-2-phenylethyne **1d** in a 2.5:1 ratio and 79% isolated yield (Entry 4). On the other hand, high regioselectivity was observed for 1-(4-methoxyphenyl)-2-phenylethyne **1e** and 1-(4-methylphenyl)-2-phenylethyne **1f** bearing the electron-donating methoxy or methyl groups. Their bromoallylation yielded regioisomers **3e** and **3f** in 77% and 82% isolated yields, respectively (Entries 5 and 6). Finally, regioisomers **2g** and **3g** were obtained by bromoallylation of 1-(biphen-4-yl)-2-phenylethyne **1g** in a 2.5:1 ratio (Entry 7). In general, higher regioselectivity and yields were observed with diarylethynes possessing electron-donating groups (perhaps by a combination of resonance and inductive effects). In the cases where the mixtures of two regioisomers were obtained in unequal ratios (Entries 1, 4, and 7), the major regioisomer was always the one whose formation is directed by polarization of the triple bond. Intriguingly, bromoallylation of 1-(pentadeuterophenyl)-2-phenylethyne **1h** with the Δδ of 0.06 ppm provided exclusively regioisomer **2h** (Entry 8). Although it could be assumed that the larger chemical shift difference should reflect higher regioselectivity that trend was not observed. The obtained data summarized in Table 1 clearly indicates correlation between the direction of polarization and regioselectivity of bromoallylation reactions, while

the strength of polarization of the triple bond expressed as the "polarization effect" ($\Delta\delta$)[2] does not parallel observed regioselectivity ratios.

The case of 1-(4-methoxyphenyl)-2-(4-trifluoromethylphenyl)-ethyne **1b**, which has a large $\Delta\delta$ value (5.09 ppm), deserves a closer look. Since this compound has been used as a substrate in various carbometallations under different reaction conditions, we decided to compare our results with the published ones. The polarization product was obtained predominantly or solely in the following cases: a) Rh-catalyzed C-C and C-O coupling of quinoline *N*-oxides with alkynes (two regioisomers in a 1.5:1 ratio);[23] b) Rh-catalyzed C-H activations of 3-aryl-dihydrooxazoles (a single regioisomer was formed),[24] of sultams (two regioisomers in a 2:1 ratio),[25] of 2-phenylimidazolino[1,2-a]pyridines (two regioisomers in a 2:1 ratio),[26] of 2-aminopyridines (two regioisomers in a 2.2:1 ratio),[27] and of α,β-unsaturated ketoximes (two regioisomers in a 7:3 ratio);[28] c) Co-catalyzed C-H activation of α,β-unsaturated imines proceeding via hydrometallation (two regioisomers in a 8.1:1 ratio);[29] d) Pd-catalyzed oxidative dearomatization of naphthols with alkynes (three regioisomers in a 4:3:1 ratio),[30] e) Ni-catalyzed C-C bond cleavage (two regioisomers in a 55:45 ratio),[31] and f) Ni-catalyzed C-S bond cleavage (two regioisomers in a 2:1 ratio). It should be noted that additional examples of reactions with other unsymmetrically substituted diarylethynes were previously reported and proceeded according to the polarization of the triple bond.[32]

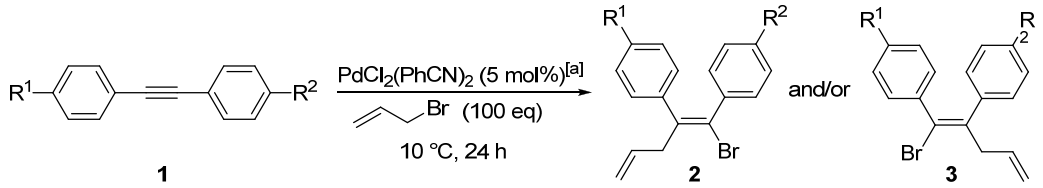
It should be also noted that there have been reports of reactions where the major products were not those expected to be formed according to the polarization of the triple bond. As typical examples may serve the Pd-catalyzed C-H activation of *ortho*-aminoanilines (two regioisomers in a 1:2.4 ratio),[33] catalytic boracupration,[34] Pd-catalyzed spirocyclization of aryl halides,[35] Rh-catalyzed C—H activation of benzamides[36] and alkenyl sulfonamides,[37] Ir-catalyzed C—H activation of ketimines,[38] and in Ni-catalyzed C—S bond activation of thiocarbamates.[39]

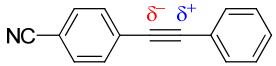
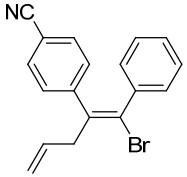
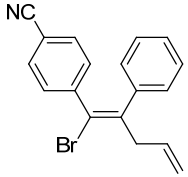
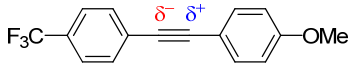
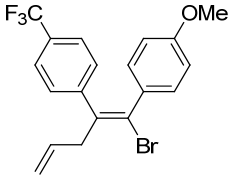
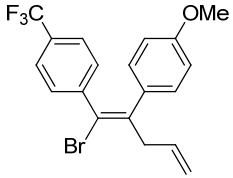
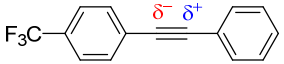
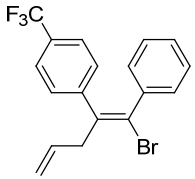
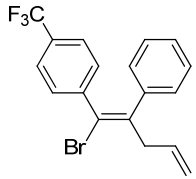
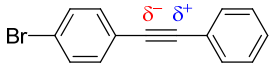
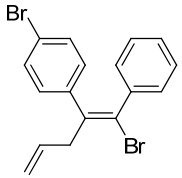
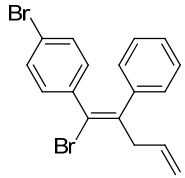
The above mentioned data as well as our results indicate that there is a general trend suggesting that the regioselective addition across the polarized triple bond could be predominantly controlled by the electron distribution, resulting in the formation of polarization products. On the other hand, taking into account the differences in reaction conditions, type of catalyst, and mechanism between the provided examples, the observed results suggest that the regioselectivity cannot be attributed only to the polarization in a common substrate, but rather should be treated as a combination of distinct factors such, as the electron distribution around the metal center, steric effects of the respective ligand environments, and the nature of the

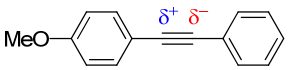
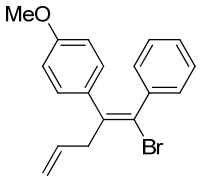
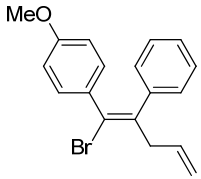
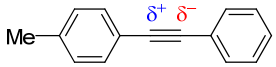
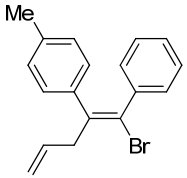
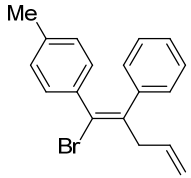
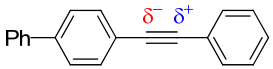
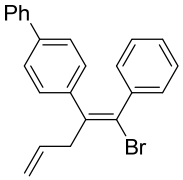
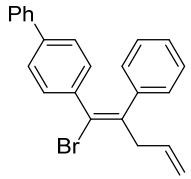
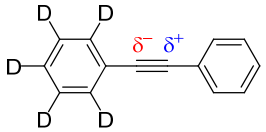
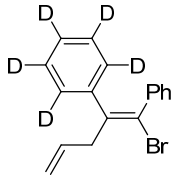
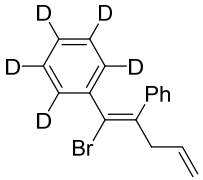
10.1002/ejoc.201901476

migrating group. Nevertheless, the recognized close correlation, in most of the cases, between the regioselectivity and polarization of a triple bond may serve as a springboard for further exploratory studies of this interesting and important topic.

Table 1. Bromoallylation of alkynes **1**.



Entry	Alkyne **1**		Δδ/ppm	Products	**2**		**3**	**2**:**3** ratio[b]	Yield (%)[c]
1		**1a**	6.07		**2a**		**3a**	2:1	48
2[d]		**1b**	8.09		**2b**		**3b**	>20:1[e]	82
3		**1c**	3.79		**2c**		**3c**	1:1	36
4		**1d**	2.20		**2d**		**3d**	2.5:1	79

5		**1e**	1.30		**2e**		**3e**	>20:1[e]	77
6		**1f**	0.84		**2f**		**3f**	>20:1[e]	82
7		**1g**	0.77		**2g**		**3g**	2.5:1	54
8		**1h**	0.06		**2h**		**3h**	>20:1[e]	79

[a] A mixture of $PdCl_2(PhCN)_2$ and allyl bromide was initially stirred for 10 min. at 0 °C. During that period, halogen exchange between catalyst and allyl bromide took place, which resulted in the formation of $PdBr_2(PhCN)_2$. [b] ^1H NMR ratio determined by analysis of the crude mixture. [c] Isolated yields of analytically pure compounds. [d] This result was reported in ref. 18. [e] The other regioisomer was not detected (according to ^1H NMR).

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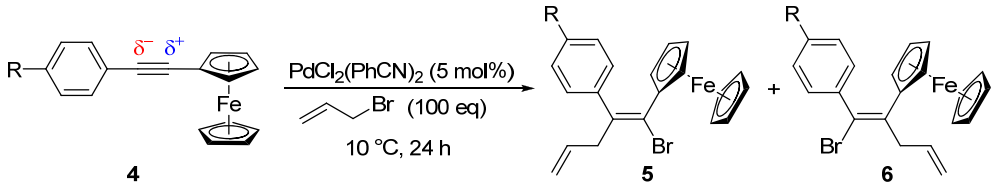
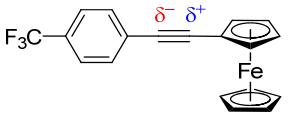
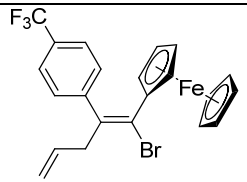
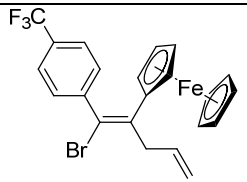
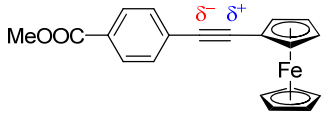
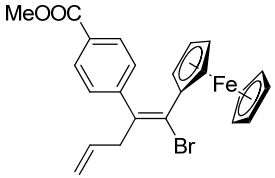
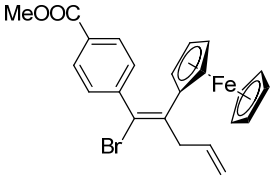
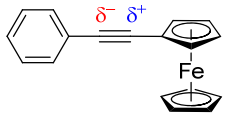
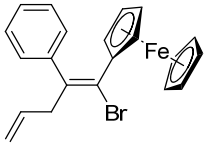
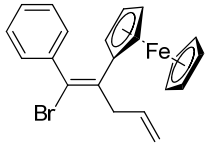
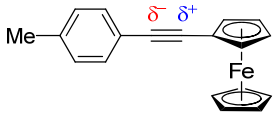
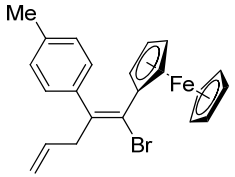
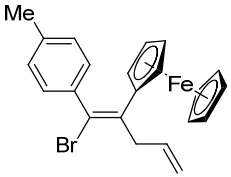
Bromoallylation of ferrocenylarylethynes. Then our attention turned to the internal alkynes possessing the ferrocenyl group. It was assumed that the ferrocenyl component of an internal alkyne would have substantial influence on the direction of polarization of the triple bond, since the ferrocenyl group possesses electron-donating ability in comparison with the phenyl group.[40] To test this assumption, four differently substituted alkynes **4** were prepared for the study of the bromoallylation. The presence of the ferrocenyl group steers polarization in one direction regardless of the other substituent (Table 2). As a consequence, a higher electron density is located around the sp-carbon atom at the β-position to the ferrocenyl group, while a partially positive charge is assigned to the carbon atom bonded to the ferrocenyl moiety. Even though the electron-withdrawing or electron-donating properties of the substituents on the aromatic ring do not affect the direction of polarization, large differences in sp-carbon Δδ values in ^{13}C NMR were observed. The presence of the electron-withdrawing trifluoromethyl and methoxycarbonyl groups is exhibited by higher values of Δδ: 6.85 and 6.29 ppm, respectively. On the other hand, the presence of the phenyl and *para*-tolyl groups significantly reduces these values to 2.54 ppm and 1.51 ppm, respectively. With respect to the observed polarization, it can be expected that products of bromoallylation of these alkynes would have the bromine atom positioned at the α-position to the ferrocenyl group, while the allyl moiety would be placed at the β-position. Bromoallylation reactions, indeed, provided bromodienes **5** with the proposed regioselectivity (Table 2). Specifically, only one regioisomer **5** was formed upon bromoallylation of **4b** and **4d**, while bromoallylation of **4a** and **4c** yielded a mixture of regioisomers **5a** and **6a**, and **5c** and **6c** in 2:1 ratios. The structures of **5b** and **5c** were confirmed by a single crystal X-ray diffraction analysis (Figures SI-35 and SI-36). Regioisomers **5** were obtained as major products, despite the polarization. The observed regioselectvity was rationalized by the steric effect as a main contributing factor. It is reasonable to assume that a larger steric hindrance resulting from an interaction between the ferrocenyl group and the large Pd atom compared to the bromine atom might influence the direction of the halopalladation step. A single crystal X-ray diffraction analysis of **5d** unambiguously confirmed its structure (Figure 2).

Table 2. Bromoallylation of ferrocenylalkynes **4**.



Entry	Alkyne **1**		Δδ/ppm	Products	**2**		**3**	**2**:**3** ratio[a]	Yield (%)[b]
1		**4a**	6.85		**5a**		**6a**	2:1	48
2		**4b**	6.29		**5b**		**6b**	>20:1[c]	82
3		**4c**	2.54		**5c**		**6c**	2:1	36
4		**4d**	1.51		**5d**		**6d**	>20:1[c]	79

[a] ^{1}H NMR ratio determined by analysis of the crude mixture. [b] Isolated yields of analytically pure compounds. [c] The other regioisomer was not detected (according to ^{1}H NMR).

10.1002/ejoc.201901476

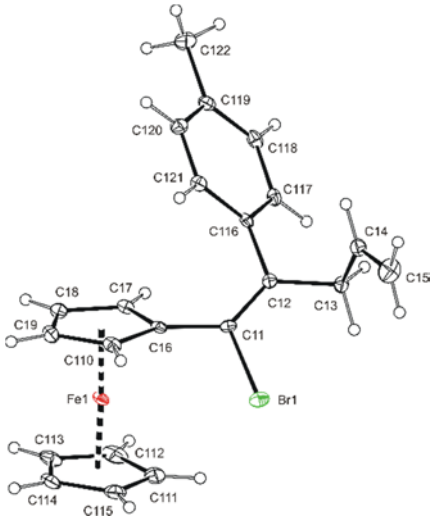
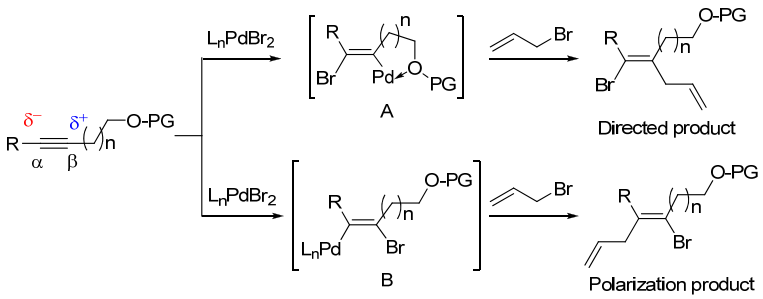


Figure 2. PLATON drawing of **5d**. Displacement ellipsoid are drawn on 30% probability level.

Bromoallylation of arylalkylethynes with a pendant chelating group. Controlling the regioselectivity of the bromoallylation of internal alkynes independently of polarization of the triple bond would allow a design of a synthetically useful approach towards regio- and stereodefined halodienes. Undoubtedly, it would represent a valuable tool for accessing appropriate building blocks suitable for specific transformations. In this respect, we turned our attention to the factors that could either overcome or attenuate the effect of polarization on the regioselectivity of bromoallylation reactions. Again, we assumed that the control over the halopalladation step would be reflected in the overall regioselectivity of the process. One way to direct approach of a Pd-catalyst to the triple bond is to introduce a chelating group in the side chain of the substrate. In this respect, the influence of chelation to direct the regioselectivity of transition-metal-catalyzed transformations has been observed before, e.g. in the regioselective Rh- and Pd-catalyzed carbometallation of alkynyl pyridines and other heterocycles,[41] Pd-catalyzed carbometallation of alkynes possessing various amide directing groups,[42] Pd-catalyzed *anti* hydrochlorination of alkynes bearing pendant directing groups such as amides and amines,[43] and Pd-catalyzed carbonylation.[44] Halopalladations of alkynes with pendant heteroatom groups are also worth mentioning. [45]

The presence of a heteroatom possessing electron lone pairs could result in coordination to the palladium atom, which would consequentially lead, after the halopalladation step, to the vinylpalladium intermediate **A** (Scheme 2). Then, insertion of allyl bromide into the Pd-C bond followed by β-halide elimination should give the directed bromoallyltion product. On the other

hand, if the direction of polarization would be the main factor controlling the course of the halopalladation step, then it should provide the vinylpalladium intermediate **B**.



Scheme 2. Directing vs polarization effects on bromoallylation.

As far as polarization of the triple bonds in **7** is concerned, partially negative charges based on ^{13}C NMR spectral data were assigned to α-carbon atoms and partially positive charges to β-carbons. To verify our hypothesis regarding the directing effect, bromoallylation of several aryl-alkyl substituted internal alkynes was explored. Depending on the prevailing factor, two types of products can be expected: a) directed bromoallylation through chelation products **8** with the allyl group attached to β-carbon atom and b) polarization products **9** where the bromine atom is positioned at the β-carbon (Table 3). First, bromoallylation of the TBS-protected alkyne **7a** under the standard conditions gave a mixture of regioisomers **8a** and **9a** in 66% isolated combined yield and in a 2:1 ratio (Entry 1). In a similar fashion, but with higher regioselectivity, the Bn-protected alkyne **7b** provided regioisomers **8b** and **9b** in 53% isolated yield and in a 6:1 ratio (Entry 2). Next, bromoallylation of alkyne **7c** gave rise exclusively to product **8c** with the allyl group connected to the β-carbon atom. Although **8c** was isolated in a rather modest yield of 33%, which could be attributed to isolation problems of the product from the reaction mixture, the other possible regioisomer **9c** was not detected (Entry 3). The same result, with respect to regioselectivity, was obtained in the reaction of alkyne **7d**. The reaction provided regioisomer **8d** in 66% isolated yield (Entry 4). The bromoallylation of alkyne **7e** gave again a mixture of regioisomers **8e** and **9e** in combined isolated yield of in 40% and in a 3:1 ratio (Entry 5).

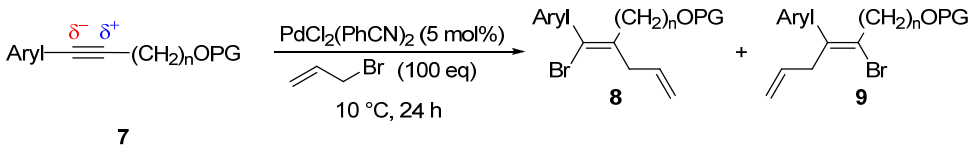
In general, in all these examples, the bromodienes in which the allyl group is positioned to the β-carbon atom (more electrophilic carbon atom) were formed as the sole products or as the major regioisomers. These results imply the dominating directing effect via chelation over the polarization of the triple bond on the regioselectivity of bromoallylation of this type of unsymmetrical alkynes. Interestingly enough, the higher regioselectivity was observed in the

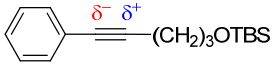
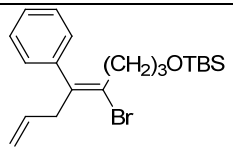
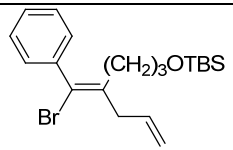
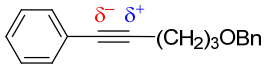
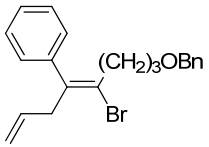
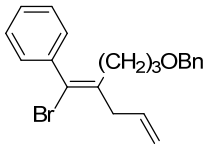
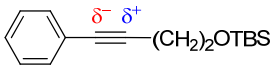
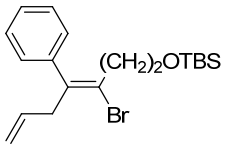
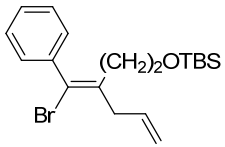
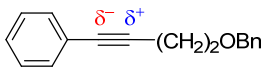
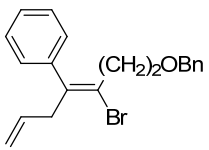
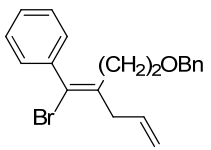
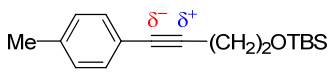
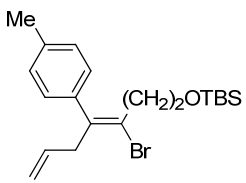
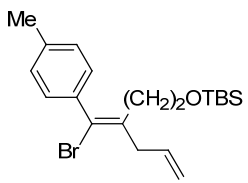
10.1002/ejoc.201901476

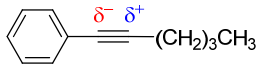
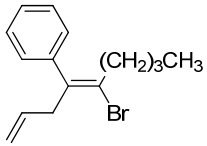
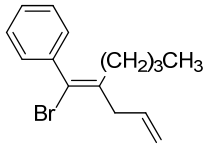
bromoallylation of **7c** and **7d** compared with **7a** and **7b**. In the former case, the halopalladation as the first step of the catalytic cycle would proceed via a five-membered chelating ring, while a six-membered ring would be formed in halopalladation of **7a** and **7b**. The effect of the chelating ring size in the formation of the intermediate is not clear at the moment.

Finally, to assess the influence of the directing effect via chelation, alkyne **7f** bearing the *n*-butyl side chain was prepared. It was expected that the direction of the polarization, which is the same as in **7a-7e**, in combination with the absence of the chelating group, should result in the predominant formation of the polarization product. Indeed, the bromoallylation reaction afforded two regioisomers **8f** and **9f** in a 1:2 ratio. These results confirm our hypothesis about directing effect via chelation to a Lewis basic group as the key factor controlling the regioselectivity of these reactions.

Table 3. Bromoallylation of alkynes **7**.



Entry	Alkyne **7**		Δδ/ppm	Products	**8**		**9**	**2**:**3** ratio[b]	Yield (%)[c]
1		**7a**	9.20		**8a**		**9a**	2:1	66
2		**7b**	8.71		**8b**		**9b**	6:1	53
3		**7c**	5.64		**8c**		**9c**	>20:1[c]	33
4		**7d**	5.24		**8d**		**9d**	>20:1[c]	66
5		**7e**	4.74		**8e**		**9e**	3:1	40

6		**7f**	9.90		**8f**		**9f**	1:2	47

[a] ^{1}H NMR ratio determined by analysis of the crude mixture. [b] Isolated yields of analytically pure compounds. [c] The other regioisomer was not detected (according to ^{1}H NMR).

Conclusions

In conclusion, we have shown that the unequal electron distribution around the sp-carbon atoms of unsymmetrically substituted alkynes dictates the regioselectivity of several reactions. First, regioselective Pd-catalyzed bromoallylation of non-equivalent internal alkynes was controlled by the polarization of the triple bond and proceeded in primarily to give the polarization products (with one exception). Second, we have demonstrated that the presence of a directing group, such as oxygen containing groups, in the pendant side-chain of unsymmetrically substituted alkynes can alter the regioselectivity, overriding the polarization of the alkyne. Third, the regioselectivity of several previously reported catalytic reactions involving alkyne **1b** was compared with our system. It was concluded that, in most cases, the major products were the expected polarization products. On the other hand, our results as well as those obtained by others , indicate that the level of regioselectivity does not correlate with the values of the chemical shift difference of the respective sp-carbon atoms, indicating that other previously unraveled effects might be involved in the control of regioselectivity. Nonetheless, it may be concluded that the polarization of the triple bond has, in many cases, a strong effect and may help to predict the predominat regioisomer.

Experimental Section

Electronic Supplementary Information (ESI) available: Experimental details and spectral data. CCDC 1858621, 1858622, 1858623, 1858624, 1858625 contain the supplementary crystallographic data for this paper.

Acknowledgments

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Keywords: bromoallylation • catalysis • directing effect • polarization • regioselectivity

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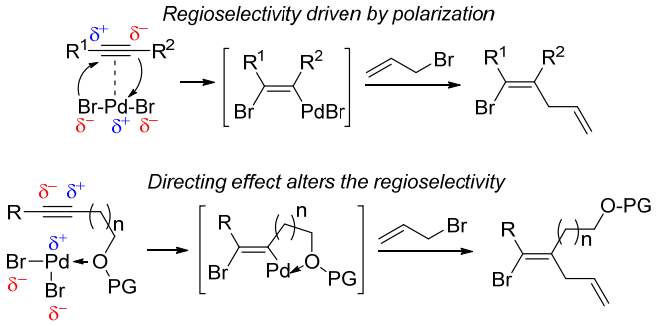
Abstract

Key topic: Regioselective functionalization

Nikola Topolovčan, Shuto Hara, Ivana Císařová, Zdeněk Tošner and Martin Kotora*

Page No. – Page No.

A Study of Polarization and Directing Effects of Unsymmetrical Alkynes using Regioselective Pd-catalyzed Bromoallylation



Pd-catalyzed bromoallylation of unsymmetrical alkynes represents a simple approach towards functionalized olefins. The regioselectivity of this process is influenced by the direction of the polarization of the triple bond as well as by directing effects of a coordinating group in the pendant chain.