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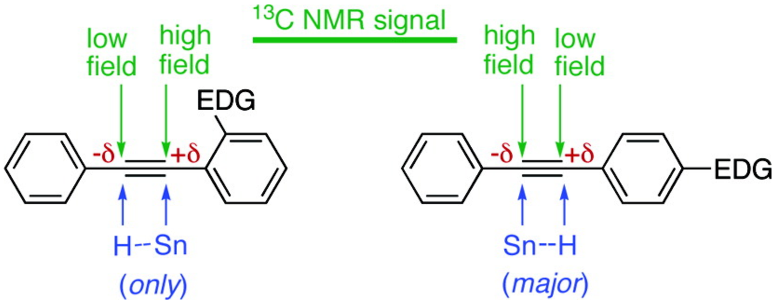

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Can Polarization of Triple Bond in Tolanes Be Deduced from ^{13}C NMR Shifts? Re-evaluation of Factors Affecting Regiochemistry of the Palladium-Catalyzed Hydrostannation of Alkynes

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Abstract: Polarization of the triple bond in a series of differently substituted *ortho*- and *para*-tolanes has been studied by NMR and computational methods in order to examine if ^{13}C NMR data can be effectively used for the assessment of electronic polarization of a triple bond in diarylacetylenes. DFT calculations of both natural charges and NMR properties revealed that chemical shifts concur with effective charges on *sp*-carbon atoms in *para*-tolanes, whereas in *ortho*-analogues magnetic anisotropy complicates the analysis making ^{13}C NMR data inapplicable for ascribing triple bond polarization. The obtained information was used to reevaluate factors affecting the regiochemistry of the Pd-catalyzed hydrostannation of the triple bond in tolanes. Computational study on the polarization of triple bonds taken together with the experimental data on hydrostannation of various mono- and disubstituted tolanes bearing *para*- and *ortho*-substituents demonstrated that the regioselectivity of hydrostannation is governed by a combination of electronic and steric factors. In *para*-tolanes, the electronic effect prevails and α- and β-vinylstannanes are obtained predominantly for substrates with electron-withdrawing and electron-donating groups, respectively. In the *ortho*-series, steric factors dominate over electronics and α-isomers are produced with high selectivity regardless of the substituents' nature. However, it was found that in disubstituted "push−pull" tolanes steric control of an *ortho*-group can be overruled by the very strong electronic effect of an electron-withdrawing substituent in *para*-position.

Introduction

Diarylacetylenes are convenient mechanistic probes for testing various addition and cycloaddition reactions involving a triple bond.[1,2] *para*-Substituted tolanes are particularly suitable for examining electronic effects,[1] which are expected to comply with Hammett−Taft plots,[3] since steric factors in these systems are negligible. *ortho*-Substituted tolanes potentially can be more attractive models, since they are set for simultaneous analysis of electronic and steric factors.[2] However, employment of the latter models can create a problem in distinguishing between these two factors. For estimation of the electronic effects, analysis of NMR chemical shifts was routinely used for various conjugated systems including tolanes.[4,5] This approach is based on the commonly held assumption that substituent-induced chemical shifts in NMR spectra primarily depend on the electronic density surrounding the corresponding probe nucleus (i.e., *sp*-^{13}C in acetylenes).[4] However, it can adequately represent shielding properties only in systems with an unperturbed spherical distribution of electron density.[6] In more complex systems, other factors affecting shielding, such as magnetic anisotropy, should be taken into account.[7] In other words, the chemical shift of any given nuclei in the molecule may depend not only on electronic density perturbation induced by an anisotropic group but also on its relative position and orientation in space. The effect of a distant anisotropic group can be rather insignificant, as in the case of *para*-tolanes; however it can be pronounced for proximate *ortho*-groups. Shielding analysis of *sp*-carbon atoms of alkynes is particularly difficult, since their easily polarizable π-density is extended along one of the axes. In-depth investigation of NMR shielding in acetylenes is in its early stage and has been performed on rather simple models only.[8] Thus, existing data do not allow for accurate assessment of factors affecting shielding in *ortho*-substituted aryl alkynes.

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(1) For example, see: (a) Xue, J.; Zhang, Y.; Wang, X.-I.; Fun, H. K.; Xu, J.-H. *Org. Lett.* **2000**, *2*, 2583. (b) Pfeffer, M.; Rotteveel, M. A.; Le Borgne, G.; Fischer, J. *J. Org. Chem.* **1992**, *57*, 2147. (c) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550.

(2) For example, see: (a) Tian, Q.; Pletnev, A. A.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 339. (b) Yamanoi, S.; Seki, K.; Matsumoto, T.; Suzuki, K. *J. Organomet. Chem.* **2001**, *624*, 143. (c) Bookham, J. L.; Smithies, D. M.; Wright, A.; Thornton-Pett, M.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1998**, 811.

(3) For review, see: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(4) (a) Sardella, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 3809. (b) Happ, B.; Bartik, T.; Zucchi, C.; Rossi, M. C.; Ghelfi, F.; Palyi, G.; Varadi, G.; Szalontai, G.; Horvath, I. T.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1995**, *14*, 809. (c) Itami, K.; Mitsudo, K.; Fujita, K.; Ohashi, Y.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 11058.

(5) Mueller, T. J. J.; Ansorge, M.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 1433.

(6) For example, see: Herzfeld, J.; Olbris, D. J.; Furman, E.; Benderskiy, V. *J. Chem. Phys.* **2000**, *113*, 5162.

(7) (a) Haigh, C. W.; Mallion, R. B. *J. Chem. Phys.* **1982**, *76*, 4063. (b) Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Res. Spectrosc.* **1979**, *13*, 303.

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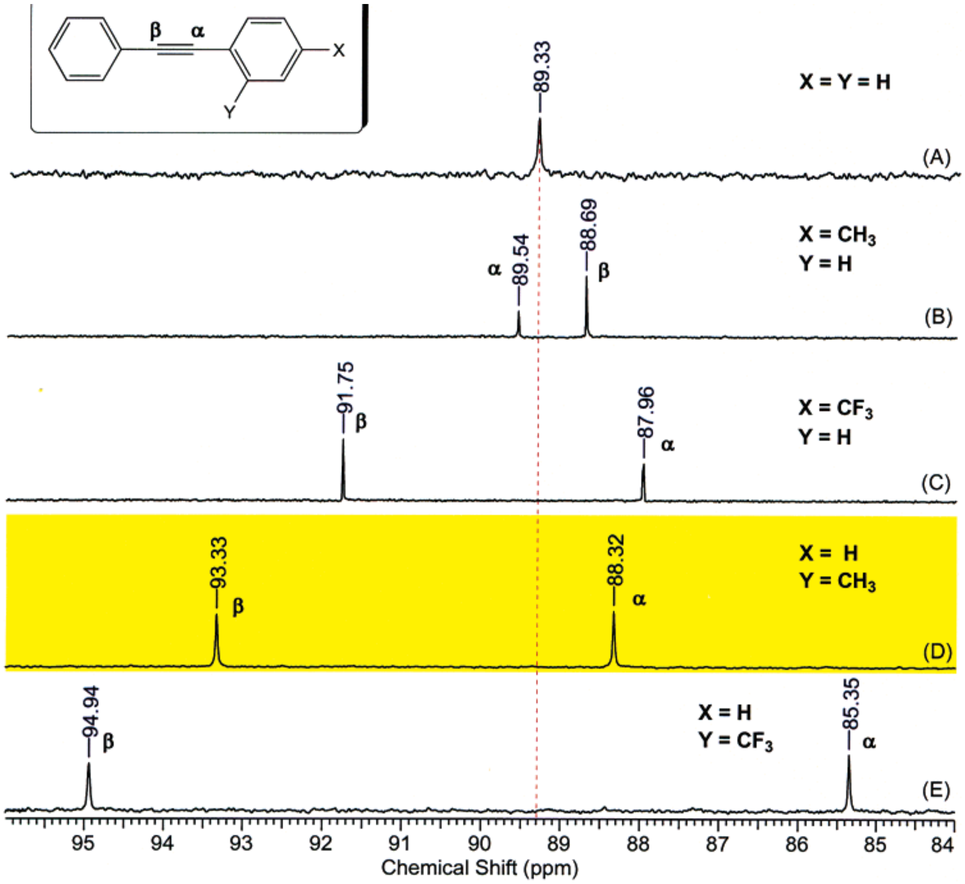

Figure 1. Experimental ^{13}C NMR spectra of tolanes **1r**, **1b**, **1i**, **1f**.

Recently, Alami proposed the use of ^{13}C NMR chemical shifts for the evaluation of triple bond polarization in the *ortho*-tolane series in his studies on the Pd-catalyzed hydrostannation reaction.[9] It was observed that, regardless of the substituent's nature, the signal of the α-*sp*-carbon appears in higher field relative to the *β*-carbon for all *ortho*-substituted tolanes tested. Based on these observations, it was proposed that any substituent in the *ortho*-position, including Me, MeO, CHO, and CO_2Et groups, polarizes the triple bond in the same way, making the α-*sp*-carbon more electron-rich and the *β*-carbon more electron-deficient. Furthermore, the Pd-catalyzed hydrostannation of all *ortho*-tolanes was found to proceed with exclusive formation of α-stannylated products, i.e., tin added to the "more electron-rich" carbon. This rationale led the authors to the conclusion that this reaction is governed exclusively by electronic factors, which is in sharp contradiction with the generally accepted belief that both steric and electronic factors affect regioselectivity in the Pd-catalyzed hydrostannation reaction.[10] Intrigued by these unusual findings, we performed a detailed investigation in order to (1) test if, indeed, any substituent in the *ortho*-position of tolane, regardless of its nature, causes similar polarization of the triple bond; (2) verify whether the ^{13}C NMR chemical shifts of *sp*-carbons in the *ortho*-tolane series can be used for the estimation of electronic polarization of a triple bond; and (3) to corroborate the factors affecting regiochemistry of the Pd-catalyzed hydrostannation of tolanes.

Results and Discussion

Theoretical and Experimental Investigation of NMR Properties and Polarization of Triple Bond in Tolanes. The influence of *para*-substituents on the ^{13}C NMR chemical shifts of *sp*-carbon in tolane is well documented.[5] Thus, the presence of electron-donating substituents moves the α-carbon signal slightly downfield, whereas the signal of the *β*-carbon is shifted upfield (Figure 1, spectrum B)[11] with respect to the signal of the parent diphenylacetylene (spectrum A). Alternatively, for a tolane possessing an electron-withdrawing substituent at the *para*-position, signals of α- and *β*-carbons appear at higher and lower field, respectively (spectrum C). This tendency can be adequately explained by substituent-induced electronic polarization of the triple bond.[4] In striking contrast, in the *ortho*-substituted tolane series, the ^{13}C NMR signals of α-carbons are always shifted upfield, while the corresponding signals of *β*-carbons appear at lower field for both electron-donating (spectrum D) and electron-withdrawing substituents (spectrum E). Naturally, in this case, Hammett−Taft coefficients simply do not correlate with NMR shifts.

Having first observed this, Alami speculated on the possibility of inverse polarization of the triple bond, induced by *ortho*-substituents of formal electron-donating nature.[9] We found this

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(8) (a) Wiberg, K. B.; Hammer, J. D.; Zilm, K. W.; Keith, T. A.; Cheeseman, J. R.; Duchamp, J. C. *J. Org. Chem.* **2004**, *69*, 1086. (b) Gryff-Keller, A. *THEOCHEM* **2002**, *587*, 171. (c) Bernard, G. M.; Wasylishen, R. E. *Solid State Nucl. Magn. Reson.* **2002**, *21*, 86. (d) Bohmann, J.; Farrar, T. C. *J. Phys. Chem.* **1996**, *100*, 2646. (e) Klaus, E.; Sebald, A. *Magn. Reson. Chem.* **1994**, *32*, 679.

(9) Alami, M.; Liron, F.; Gervais, M.; Peyrat, J.-F.; Brion, J.-D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1578.

(10) Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257.

(11) Assignments of the signals were performed based on ^{1}H−^{13}C HMQC and HMBC NMR spectroscopy for each of these compounds. See Supporting Information for details.

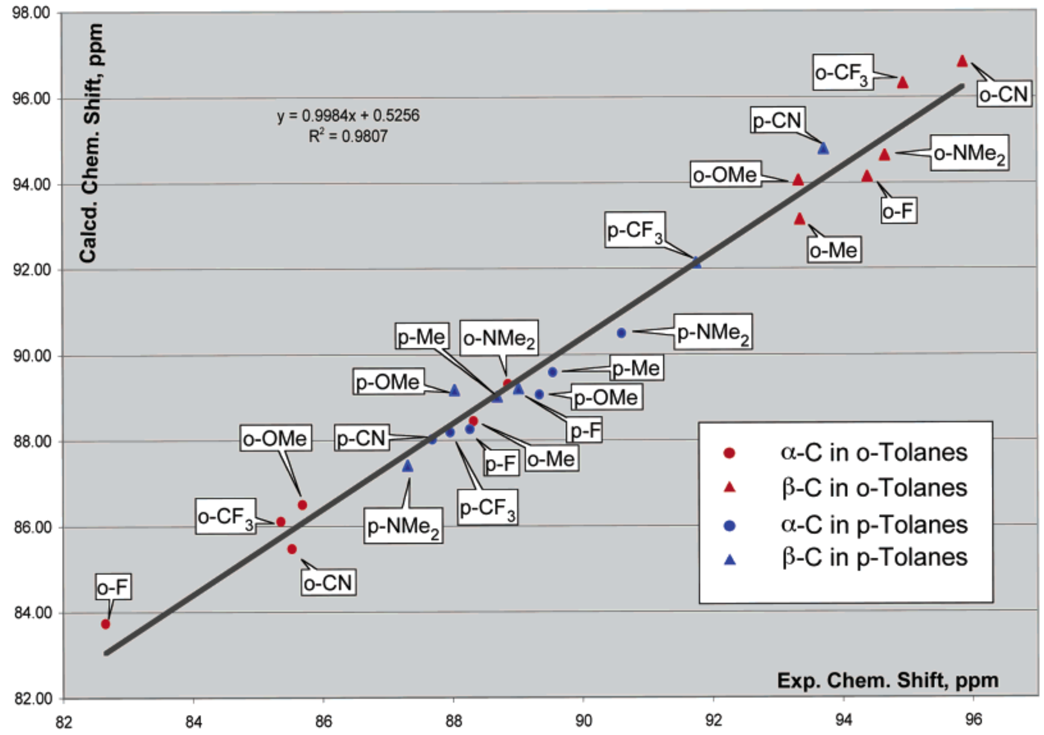
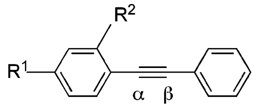


Figure 2. Correlation of GIAO-calculated substituent-induced ^{13}C chemical shifts vs experimental chemical shifts in tolane series.

explanation very peculiar and independently evaluated the polarization of a triple bond in tolane series by computational methods. DFT calculations (B3LYP/6-31+G*)[12] were performed to estimate natural charges[13] in the *para*- and *ortho*-tolane series. These calculations indicated that the natural charge located on the α-carbon is greater than that located on the β-carbon ($NC_\alpha > NC_\beta$) for all electron-donating *para*-substituents, including *p*-Me, *p*-MeO, *p*-NMe_2 groups (Table 1, entries 1−3). As expected, opposite relationships ($NC_\alpha < NC_\beta$) were obtained for *para*-tolanes with electron-withdrawing groups, such as *p*-F, *p*-CF_3, *p*-CN (Table 1, entries 4−6). Similar calculations performed for *ortho*-substituted analogues revealed the same trend: $NC_\alpha > NC_\beta$ was obtained for *o*-Me, *o*-MeO, *o*-NMe_2 groups (Table 1, entries 7−9), while *o*-F, *o*-CF_3, *o*-CN substituents showed $NC_\alpha < NC_\beta$ (Table 1, entries 10−12). These results unambiguously support that *electron-donating groups in ortho-position do not induce reverse electronic polarization of the triple bond*. In other words, electron-donating substituents polarize the triple bond in the same way regardless of the location. Thus, we sought for an alternative rationale to account for the unusual NMR properties of *ortho*-substituted tolanes.

Table 1. Experimental and Calculated ^{13}C NMR Chemical Shifts and Calculated Natural Charges of Acetylenic Carbons in Tolanes



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		tolane		carbon	GIAO shielding, ppm	GIAO shift, ppm	expmt shift, ppm	error, ppm	natural charge (NC)
		R^1	R^2						
1	**1r**	Me	H	α	102.52	89.58	89.54	−0.04	0.008
				β	103.10	89.01	88.69	−0.32	0.002
2	**1d**	OMe	H	α	103.04	89.06	89.34	0.28	0.006
				β	102.94	89.16	88.03	−1.13	0.004
3	**1t**	NMe_2	H	α	101.60	90.50	90.60	0.10	0.014
				β	104.69	87.41	87.31	−0.10	−0.015
4	**1s**	F	H	α	103.84	88.26	88.26	0.00	0.002
				β	102.90	89.20	89.01	−0.19	0.009
5	**1b**	CF_3	H	α	103.91	88.19	87.96	−0.23	−0.004
				β	99.96	92.14	91.75	−0.39	0.024
6	**1a**	CN	H	α	104.08	88.02	87.68	−0.34	−0.009
				β	97.33	94.78	93.72	−1.06	0.033
7	**1i**	H	Me	α	103.66	88.44	88.32	−0.12	0.004
				β	98.05	94.05	93.33	−0.72	0.003
8	**1h**	H	OMe	α	105.60	86.50	85.68	0.82	0.014
				β	98.96	93.14	93.35	−0.21	0.006
9	**1j**	H	NMe_2	α	102.79	89.31	88.85	−0.46	0.004
				β	97.47	94.63	94.66	0.03	−0.002
10	**1k**	H	F	α	108.36	83.74	82.65	−1.09	−0.001
				β	97.98	94.13	94.39	0.26	0.022
11	**1f**	H	CF_3	α	105.99	86.11	85.35	−0.76	−0.015
				β	95.78	96.32	94.94	−1.38	0.039
12	**1e**	H	CN	α	106.63	85.48	85.52	0.04	−0.020
				β	95.29	96.81	95.86	−0.95	0.051
13		H	H		102.76	89.34	89.34		0.006

To model the magnetic properties of tolanes in their complexity, we performed DFT calculations (B3LYP/6-31G(d)) of isotropic NMR shielding using the Gauge Independent Atomic Orbital method (GIAO).[14,15] Substituent-induced chemical shifts were calculated using unsubstituted tolane as a standard (δ 89.34 ppm) (Table 1). Remarkably, GIAO calculations accurately reproduced experimentally observed ^{13}C NMR chemical shifts.[16] It can be easily seen from the plot (Figure 2) that calculated values of ^{13}C chemical shifts are in good linear correlation with experimental data for all the tolanes studied, regardless of the nature of substituents and their position.

Polarization of the triple bond in tolanes can be better described in terms of $\Delta NC = NC_\alpha - NC_\beta$. Factor ΔNC has a

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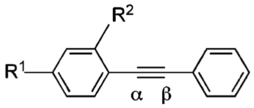
(12) Spartan 02; Wavefunction, Inc.; Irvine, CA, 2002.

(13) For reviews on natural population analysis, see: (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Pulay, P.; Bofill, J. M. *Chem. Phys. Lett.* **1989**, *156*, 501 and references cited therein.

(14) (a) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (b) Dodds, J. L.; McWeeny, R.; Sadlej, A. J. *Mol. Phys.* **1980**, *41*, 1419. (c) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (d) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028.

(15) Gaussian 03, revision B.05, Gaussian, Inc., Pittsburgh, PA, 2003.

Table 2. Polarization of Triple Bond in Tolanes and Their NMR Properties



1

	substituent		ΔNC	$\Delta\delta_{\text{expt}}$	$\Delta\delta_{\text{calcd}}$
	R^1	R^2	$NC_\alpha - NC_\beta$	$\delta_\alpha - \delta_\beta$	$\delta_\alpha - \delta_\beta$
1r	Me	H	0.006	0.85	0.58
1s	F	H	−0.007	−0.75	−0.94
1d	MeO	H	0.002	1.31	−0.10
1t	NMe_2	H	0.029	3.29	3.09
1b	CF_3	H	−0.028	−3.79	−3.95
1a	CN	H	−0.042	−6.04	−6.76
1i	H	Me	0.001	−5.01	−5.60
1k	H	F	−0.022	−11.74	−10.39
1h	H	MeO	0.008	−7.66	−6.64
1j	H	NMe_2	0.006	−5.81	−5.32
1f	H	CF_3	−0.054	−9.59	−10.21
1e	H	CN	−0.071	−10.34	−11.33

positive sign for tolanes with electron-donating groups and negative for ones bearing electron-withdrawing substituents (Table 2) regardless of their positions. Analogously, the difference in chemical shifts of the *sp*-carbons, $\Delta\delta$, is defined as $\delta_\alpha - \delta_\beta$, and its value depends on both the nature and position of a substituent. Thus, in *para*-substituted tolanes $\Delta\delta$ is positive for electron-donating and negative for electron-withdrawing groups, whereas in the *ortho*-series $\Delta\delta$ is always negative. Graphical representation of these data (Figure 3) reveals a linear correlation between $\Delta\delta$exp and ΔNC in the *para*-tolane series, while no trend for *ortho*-tolanes is obvious (Figure 3).

Having demonstrated that the values of ^{13}C chemical shifts of acetylenic carbons in *ortho*-substituted tolanes do not correlate with the distribution of electron density on the triple bond, we decided to investigate the influence of anisotropic properties of *ortho*-substituents on chemical shifts. To this end, we analyzed shielding density maps for *ortho*-methyl (**1i**) and *ortho*-trifluoromethyl (**1f**) tolanes as seen from α- or β-carbon, respectively (Figure 4).[17] For each probe nucleus,[18] blue and red colors stand for shielding and deshielding effects, respectively, induced by magnetic currents in the corresponding areas (Figure 4). The intensity of color is proportional to the value of shielding density; i.e., areas mapped with faded colors have negligible effect on the probe. This analysis demonstrated that, as expected, both *sp*-carbon atoms receive a major shielding contribution from their own magnetic current surrounding the triple bond. The detailed examination of this component, however, is complicated as it would require analysis of minor shielding density fluctuations on the background of its very high absolute value. In contrast, the background values of shielding density for peripheral groups are much smaller, and therefore their input can be more easily assessed. Remarkably, deshielding effects on β-*sp*-carbon atoms caused by *ortho*-substituents (Figure 4, charts B, D) were greater than those on α-*sp*-carbons (charts A, C) for both electron-donating (*ortho*-methyl) and electron-withdrawing (*ortho*-trifluoromethyl) groups. On the corresponding maps (Figure 4), this difference is indicated by a more intense red spot reflecting the deshielding effect cast on the β-carbon from both *o*-Me and *o*-CF_3 groups (B and D). At the same time the analogous red site on the shielding density maps projected on the α-carbon is relatively faint (A and C).

Shielding effects of *ortho*-substituents on *sp*-carbons in tolanes can be even better illustrated by analysis of corresponding anisotropy cones,[19] depicted in Scheme 1. As discussed above, electron-withdrawing and electron-donating substituents in the *ortho*-position of tolanes induce different polarization of the triple bond, as indicated by opposite directions of dipole moment vectors in cartoons **I** and **II**. If this were the major factor, the pattern of substituent-induced ^{13}C chemical shifts of *sp*-carbons in *ortho*-tolanes would be similar to that observed in the *para*-tolane series.[5] Yet, the anisotropic properties of a substituent placed in close proximity to a triple bond also contribute to the shielding. Although the value of anisotropy factor $\Delta\chi$ may vary, orientation of anisotropy cones and their effects are virtually the same for different groups, in accordance with the density map analysis provided above (Figure 4). As a result, the signal of the β-carbon atom, located closer to the center of the deshielding lobe of the cone, is being shifted to lower field regardless of the electronic nature of the anisotropic group. Undoubtedly, the observed strong equalizing anisotropic effect of *ortho*-substituents dominates over the differentiating electronic polarization effect. Consequently, while ^{13}C chemical shifts of *sp*-carbons can serve well as indices of natural charges on a triple bond in the *para*-tolane series, by no means can they be used for deducing electronic polarization of a triple bond in *ortho*-tolanes.

Investigation of Factors Affecting Pd-Catalyzed Hydrostannation of Tolanes. Having addressed the issue of adequate interpretation of *sp*-carbon chemical shifts and polarization of triple bond in diarylacetylenes, we turned our attention to the analysis of factors responsible for exclusive α-regioselectivity of Pd-catalyzed hydrostannation of *ortho*-tolanes.[9] To verify the assignment of regiochemistry and evaluate both electronic and steric effects, we performed analogous independent investigation,[20] in which monosubstituted tolanes **1** were subjected to the standard conditions for palladium-catalyzed hydrostannation.[9] It was found that, in the *para*-substituted series where steric effects are negligible, the regiochemistry of hydrostannation is entirely governed by polarization of the triple bond. All *para*-substituted tolanes afforded mixtures of regioisomeric vinylstannanes; the substrates bearing electron-withdrawing groups yielded α-vinylstannanes **2a**−**c** as major products (Table 3, entries 1−3), whereas those with electron-donating groups favored predominant formation of β-vinylstannanes (Table 3, entry 4).

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(16) Experimental ^{13}C NMR chemical shifts were measured for $CDCl_3$ solutions (6−10%) of corresponding tolanes at room temperature and were unambiguously assigned based on 2D correlation spectroscopy.[11]

(17) Shielding density maps were obtained from DFT B3LYP/6-31G(d) computations using GIAO method to generate three cubes for anisotropic magnetic current densities with magnetization vectors along *x*, *y*, and *z* axes. Surfaces were built using a cube for isotropic magnetic current density, which was obtained as $(\mathbf{j}_x + \mathbf{j}_y + \mathbf{j}_z)/3$. Analogously, shielding density cubes were obtained for shielding tensor components ρ_{xx}, ρ_{yy}, and ρ_{zz} at both α- and β-carbon atoms, after which isotropic shielding density cubes were generated as a trace of the shielding tensor $(\rho_{xx} + \rho_{yy} + \rho_{zz})/3$. Finally, current density surfaces were mapped with shielding densities, using GaussView 3.09W, Gaussian Inc, Pittsburgh, PA.

(18) Magnetic shielding phenomena may be viewed as a result of interaction between an induced magnetic field and the permanent magnetic moment of a given nucleus with a nonzero magnetic moment. Such a nucleus is referred here and below as a *probe nucleus*. For discussion, see: Wolinsky, K. *J. Chem. Phys.* **1997**, *106*, 6061.

(19) For example, see: Gunther, H. *NMR Spectroscopy: Basic Principles, Concepts, and Applications in* Chemistry, 2nd ed.; Wiley: 1994.

(20) Tolanes **1d**, **h**, **i** have been previously employed in the Pd-catalyzed hydrostannation.[9]

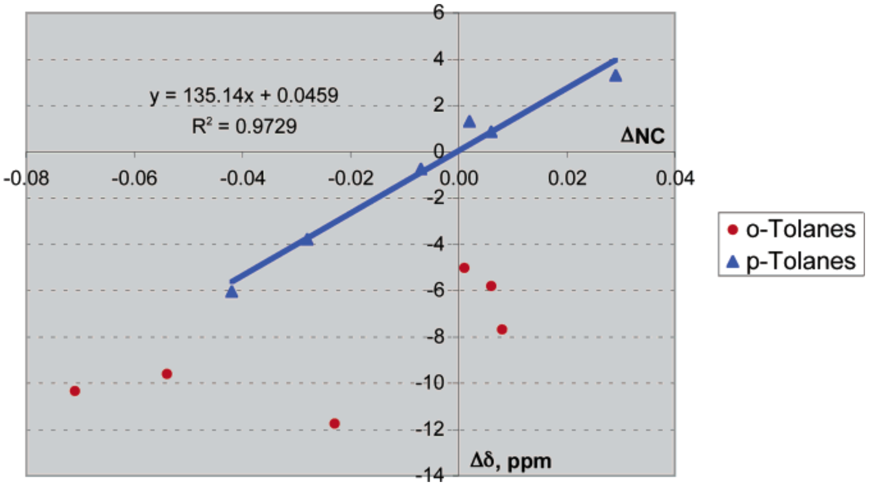


Figure 3. $\Delta\delta_{exp}$ plotted vs ΔNC.

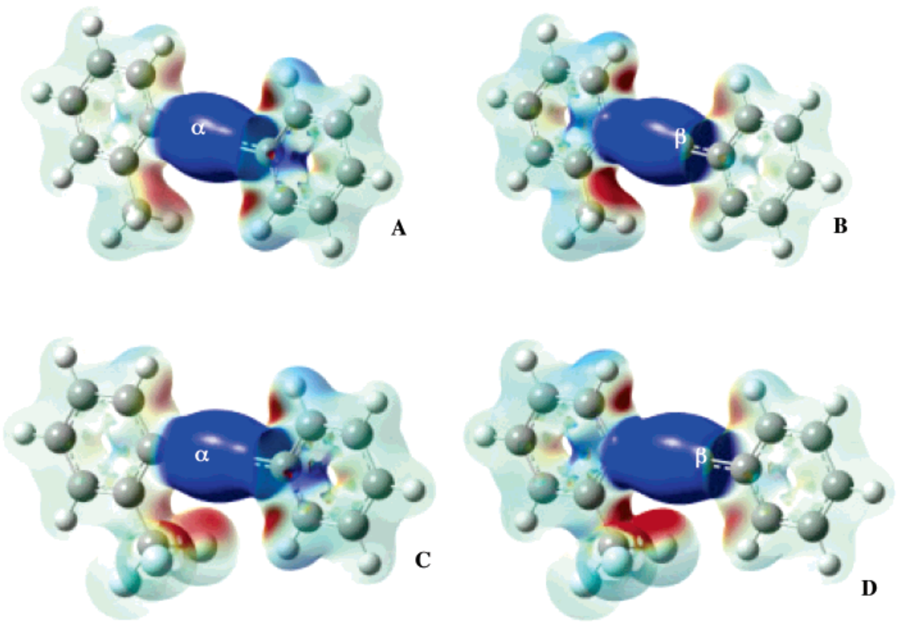
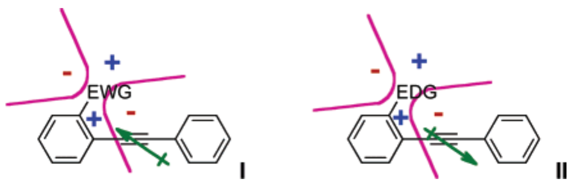


Figure 4. Surfaces of isotropic magnetic current density mapped with isotropic shielding density for *o*-Me-tolane and *o*-CF$_3$-tolane spawned on α and *β* alkyne carbon atoms, respectively.

Scheme 1



In contrast, hydrostannation of *ortho*-substituted tolanes displayed much higher regioselectivity; most substrates tested (**1e**−**g**, **i**−**k**) provided the corresponding α-vinylstannanes exclusively (Table 3, entries 5−7, 9−11), except for 2-methoxytolane **1h**, which afforded a mixture of α- and *β*-isomers in a ratio of 89:11 (Table 3, entry 8). Overall, the results obtained for hydrostannation of *para*- and *ortho*-tolanes, as well as structural assignment of products independently confirmed using ^{1}H−^{13}C HMQC and HMBC NMR spectroscopy, were in excellent agreement with data reported by Alami.[9]

The same regiochemistry of addition observed in the hydrostannation of differently polarized *ortho*-tolanes strongly suggests that this reaction is entirely controlled by steric factors.[21] Naturally, it was very intriguing to test if electronic effects can compete with the overwhelming α-selectivity governed by sterics. To check this possibility we prepared a series of disubstituted tolanes, possessing both *ortho*- and *para*-groups of different electronic nature, and subjected them to the Pd-catalyzed hydrostannation reaction (Table 4). It was found that hydrostannation of tolane **1m**, in which both steric and electronic effects cooperate, afforded α-substituted vinylstannane **2m** exclusively (Table 4, entry 1). For substrates **1n** and **1l**, the ratio of products was very similar to that obtained in the hydrostannation of monosubstituted tolanes **1e** and **1h**, respectively (Table 3, entries 5,8). The regiochemistry in this case is

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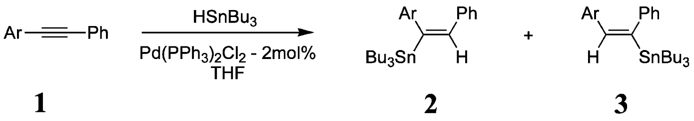
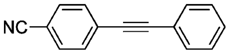
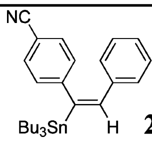
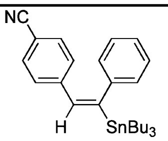
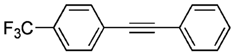
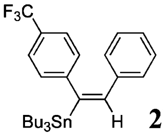
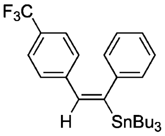
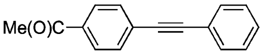
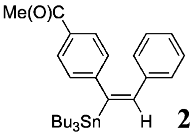
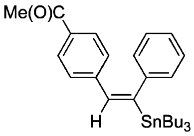
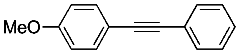
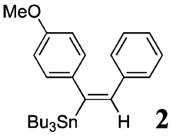
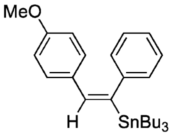
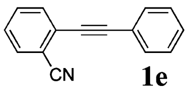
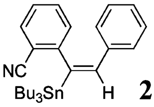
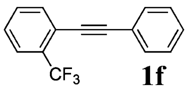
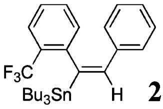
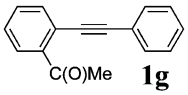
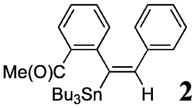
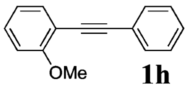
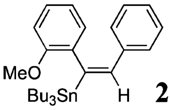
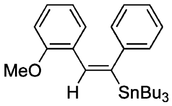
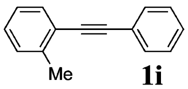
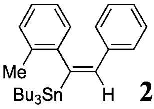
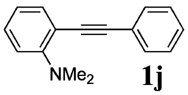
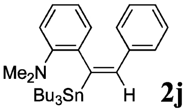
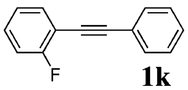
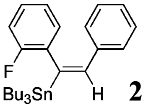
(21) Although the exact mechanism of the Pd-catalyzed hydrostannation is still unknown, it is generally believed that it proceeds via an initial hydropalladation rather than a palladastannation step (see ref 10). We propose that, in this case, nonconcerted migratory insertion results in hydride approaching and adding to a triple bond faster than palladium. Consequently, palladium adds last and to a more hindered site, overall affording α-stannylated stilbenes. For a similar steric effect governing regiochemistry of carbopalladation in the Heck reaction, see: Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

Table 3. Palladium-Catalyzed Hydrostannation of Monosubstituted Tolanes[a]



Entry	Substrate	Products		Yield,[b] %	Ratio[c] 2:3
1	 **1a**	 **2a**	 **3a**	75	84:16
2	 **1b**	 **2b**	 **3b**	67	78:22
3	 **1c**	 **2c**	 **3c**	53	77:23
4	 **1d**	 **2d**	 **3d**	54	39:61
5	 **1e**	 **2e**		40	100:0
6	 **1f**	 **2f**		43	100:0
7	 **1g**	 **2g**		76	100:0
8	 **1h**	 **2h**	 **3h**	75	89:11
9	 **1i**	 **2i**		88	100:0
10	 **1j**	 **2j**		35	100:0
11	 **1k**	 **2k**		90	100:0

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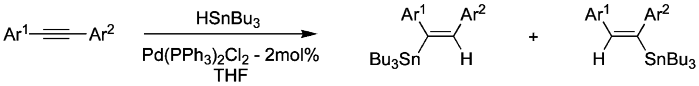
[a] See Supporting Information for general procedure. [b] Isolated yields. [c] Determined by ^{1}H NMR analysis of crude reaction mixtures.

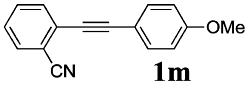
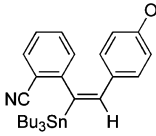
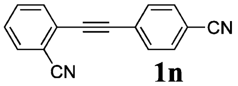
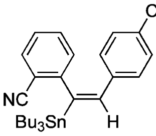
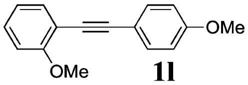
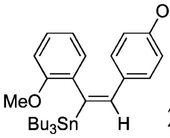
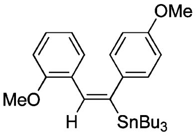
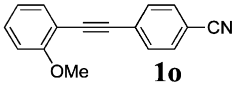
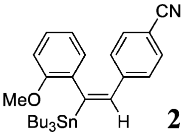
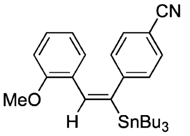
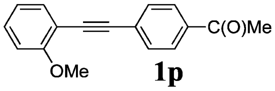
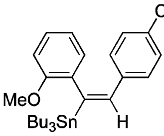
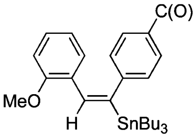
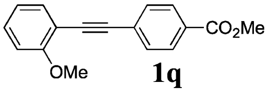
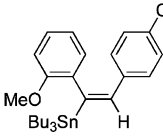
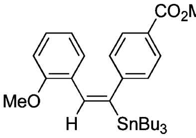
entirely governed by steric factors due to the rather insignificant polarization of the triple bond (Table 4, entries 2,3). In contrast, in "push−pull" tolanes **1o**−**q** where steric effect is opposed by very strong electronic factors, the regioselectivity of hydrostannation was reversed and β-vinylstannanes were obtained predominantly (Table 4, entries 4−6).

In conclusion, we disproved the previously reported statement on anomalous electronic polarization of triple bond in *ortho*-substituted tolane series. Analysis of ^{13}C NMR chemical shifts of *sp*-carbon atoms can provide a good approximation for electronic polarization of *para*-tolanes; however, such assessment is not applicable for the *ortho*-tolane series. Experimental and

Table 4. Palladium-Catalyzed Hydrostannation of Disubstituted Tolanes



1 **2** **3**

Entry	Substrate	Yield, %	Products	Ratio
1	 **1m**	73	 **2m**	100:0
2	 **1n**	83	 **2n**	100:0
3	 **1l**	98	 **2l**  **3l**	87:13
4	 **1o**	96	 **2o**  **3o**	40:60
5	 **1p**	88	 **2p**  **3p**	36:64
6	 **1q**	100	 **2q**  **3q**	36:64

computation data strongly support that the regiochemistry of palladium-catalyzed hydrostannation in tolane series is governed by a combination of steric and electronic effects. In *para*-substituted tolanes, where steric effects are minimal, electronic factors entirely control the regiochemistry of addition; however, in the *ortho*-substituted series, steric factors are predominant. In disubstituted "push−pull" tolanes steric control of regiochemistry can be overruled by a very strong electronic effect.

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Supporting Information Available: Full experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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