Homogeneous Catalysis

DOI: 10.1002/ange.201108714

Platinum-Catalyzed Hydrosilylations of Internal Alkynes: Harnessing Substituent Effects to Achieve High Regioselectivity**

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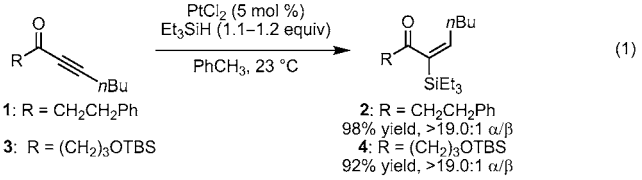
Dedicated to Professor Barry M. Trost on the occasion of his 70th birthday

The metal-catalyzed hydrosilylation of C–C multiple bonds is a well-studied and effective transformation.[1] Studies concerning catalyst activity, coordination environment, and mechanism have provided substantial insight into the nature of this reaction. Vinylsilanes, the product of the monohydrosilylation of alkynes, have proven to be highly useful synthetic compounds, and versatile reagents in both nucleophilic additions and cross-couplings.[2] Interestingly, the vast majority of research on alkyne hydrosilylation has focused on the anti-Markovnikov addition of a silane across a terminal alkyne. Hydrosilylations of internal alkynes, comparably, have received significantly less attention. A primary reason for this scarcity is that regioselectivity can be difficult to control when applying hydrosilylations to substrates featuring disubstituted alkynes.

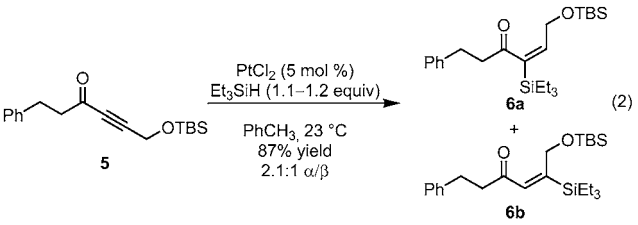
As a component of our efforts toward accessing geometrically complementary α silylenones, we recently described the platinum-catalyzed hydrosilylations of ynones.[3] Simply by using $PtCl_2$ in $PhCH_3$ at room temperature, the reactions proceeded in good yields with high stereoselectivity for the *E* silylenones [Eq. (1); TBS = *tert*-butyldimethylsilyl]. The regioselectivity was quite high in most of the cases initially evaluated. The selectivity was diminished, however, in the hydrosilylation of ynone **5**, where we observed a 2.1:1 α/β ratio of vinylsilane products [Eq. (2)].



1: R = CH_2CH_2Ph
3: R = $(CH_2)_3OTBS$

2: R = CH_2CH_2Ph
98% yield, >19.0:1 α/β
4: R = $(CH_2)_3OTBS$
92% yield, >19.0:1 α/β

(1)



(2)

Varyingly regioselective hydrosilylations of internal alkynes have been observed in multiple settings before. From Tsipis's seminal experimental analysis using [{(Cy_3P)-$(BzMe_2Si)(\mu\text{-}H)Pt\}_2$][4] he posited that an electronic effect dictated the regioselectivity of hydrosilylations. Both terminal and internal alkynes fit into this paradigm, but the only unsymmetrical internal alkynes evaluated were 2-pentyne and 2-hexyne. This electronic effect has been a recurrently observed trend in platinum-catalyzed internal alkyne hydrosilylations, but reports and applications have been somewhat sporadic, primarily emphasizing singular specific cases.[5,6] An exceptional example by Alami and co-workers evaluated arylacetylenes using either PtO_2 or H_2PtCl_6.[7] Marko and co-workers also investigated a number of internal alkynes as part of a study of hydrosilylations using NHC/Pt complexes.[8] Catalysis based on other metals has also been investigated, with organoyttrium complexes that provide steric-dictated regioselectivity, representing the most general example of non-platinum-catalyzed cis hydrosilylations.[9–11]

Intrigued by the chemo-, regio-, and stereoselectivity of our observed hydrosilylation with ynones, we sought to further expand upon these studies. Taking into account the advent of significant developments in the synthetic utility of vinylsilanes, most notably in cross-coupling, we believed an evaluation of the aspects that define the reactivity profile of hydrosilylations was in order. Herein, we describe a more detailed analysis of the platinum-catalyzed hydrosilylation of internal alkynes, thus illustrating the predominant and potentially quantifiable electronic influence on the regioselectivity of the process. We also highlight other factors, namely steric and functional group effects that attenuate this regioselection.

We initially attributed the ynone hydrosilylation regioselectivity to the electronic effect based on the differential inductive properties of a ketone and an aliphatic group. Consistent with Tsipis's rationale[4] and based on the Chalk–Harrod mechanism for platinum-catalyzed hydrosilylations,[12] we reasoned that the alkyne-coordinated Pt^{II} complex **9** was delivering hydride to the more electron-deficient alkyne carbon atom (Scheme 1). Reductive elimination from

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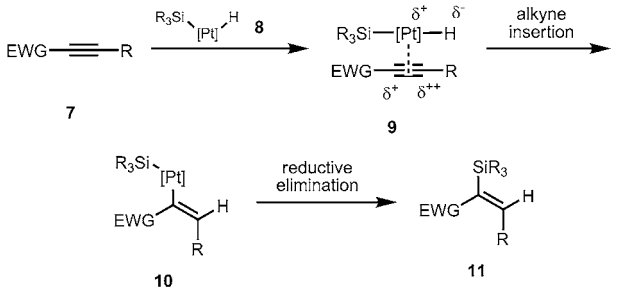
[**] Colorado State University is acknowledged for the support of our program. Eli Lilly is acknowledged for a graduate research fellowship to D. A. R.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108714.



Scheme 1. Electronic influence on platinum-catalyzed hydrosilylations.

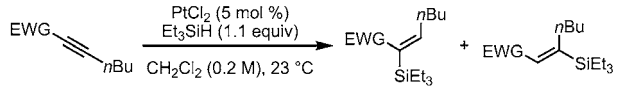
the vinylplatinum intermediate **10** resulted in the observed α selectivity.

Based on the high levels of regioselectivity in the hydrosilylations of ynones, we anticipated that other carbonyl-based groups could induce analogous selectivities. A number of electron-deficient alkynes were thus subjected to hydrosilylation conditions similar to what we had originally disclosed (5 mol% $PtCl_2$, Et_3SiH, CH_2Cl_2, 23 °C). In several cases, the hydrosilylation occurred with excellent regioselectivity, where the silicon was installed α to the electron-withdrawing group (Table 1, entries 1–5). Linear esters, phenyl and Weinreb amides, and carboxylic acids all provided effective differentiation to the *n*-butyl group, thus allowing exceptional α selectivity. Aldehydes displayed diminished and varying regioselectivity (3.1–5.8:1), with the yield compromised by competitive carbonyl hydrosilyation.[13] Branched esters were also less regioselective, thus providing 9.3:1 and 7.5:1 α selectivity for the isopropyl and *tert*-butyl esters, respectively.

We also conducted a detailed analysis of a series of methyl ynoates (Table 2). Compounds bearing aliphatic groups (i.e., *n*Bu, *t*Bu) were highly selective for the α silylenoates, although the reaction times were greatly influenced by the size of the group (3 h versus 6 d). Interestingly, a phenyl ring dramatically altered the regioselectivity, where the silyl group predominantly added β to the ester (entry 3). Oxygenation at the propargylic position also affected the regioselectivity (entries 4–5), much like in the aforementioned example of the ynone **5** [Eq. (2)]. The decreased selectivity likely arises as a result of inductive effects; more electron-withdrawing oxygen substituents induce a polarization more comparable to the electronic influence of the methyl ester. Homopropargylic oxygenation had a lesser effect on the regioselectivity, thus providing predominantly the corresponding α silylenoate, which is consistent with the decreased electronic induction.

Because of the pronounced effects of oxygenated groups on hydrosilylation regioselectivity, we probed whether these functionalities would be sufficiently different from aliphatic groups to allow discrimination by the catalytic system. In an isolated early example, Stork et. al had shown that the pivaloate ester of 2-butyn-1-ol was hydrosilylated with high α selectivity.[5a] Although a secondary silyl ether was not at all selective in our study (Table 3, entry 1), secondary esters afforded good to excellent levels of regioselectivity (entries 2–3). Primary propargylic esters also displayed effective levels of regioselectivity (entries 4–5). In both classes, the progression from acetate to trifluoroacetate increased the regioselection, which is aligned with the increasing electron-withdrawing nature of the oxygen substituent. This catalyst system distinguishes between the trifluoroacetate and the acetate with 3.8:1 selectivity (entry 6). Finally, inductive effects remained influential even with an additional methylene group; a 4.3:1 regioselectivity was observed with the electron-withdrawing trifluoroacetate in the homopropargylic position [Eq. (3)].

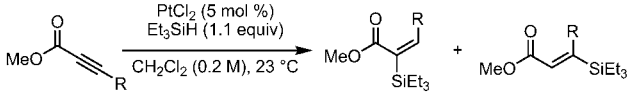
Table 1: Electron-withdrawing group analysis.



Entry	Substrate	EWG	*t* [h]	Product	Yield [%][a]	α/β[b]
1	**12**	CO_2Me	3	**13a/13b**	95	>19:1
2	**14**	CO_2Et	3	**15a/15b**	93	16:1
3	**16**	CONHPh	24	**17a/17b**	80	12:1
4	**18**	CON(OMe)Me	5	**19a/19b**	89	>19:1
5	**20**	CO_2H	5.5	**21a/21b**	95	13:1
6	**22**	CHO	3	**23a/23b**	58	3.1–5.8:1
7	**24**	CO_2iPr	3	**25a/25b**	93	9.3:1
8	**26**	CO_2tBu	7	**27a/27b**	95	7.5:1

[a] Yield of isolated product. [b] Determined by ^{1}H NMR spectroscopy. EWG = electron-withdrawing group.

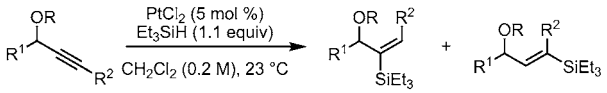
Table 2: Methyl ynoate analysis.



Entry	Substrate	R	*t* [h]	Product	Yield [%][a]	α/β[b]
1	**12**	*n*Bu	3	**13a/13b**	95	>19:1
2	**28**	*t*Bu	150	**29a/29b**	96	>19:1
3	**30**	Ph	11	**31a/31b**	90	1:3.5
4	**32**	CH_2OAc	7	**33a/33b**	97	1:1.1
5	**34**	CH_2OTHP	12	**35a/35b**	92	3.5:1
6	**36**	CH_2CH_2OAc	3	**37a/37b**	88	5.2:1

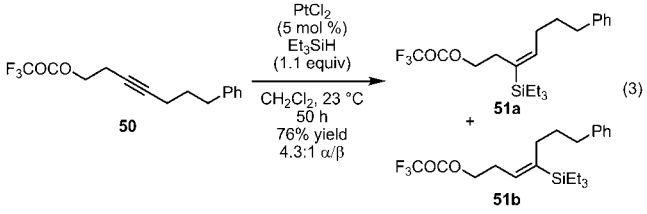
[a] Yield of isolated product. [b] Determined by ^{1}H NMR spectroscopy. THP = tetrahydropyran.

Table 3: Propargylic oxygenation analysis.



Entry	Substrate	R^1	R^2	R	*t* [h]	Product	Yield [%][a]	α/β[b]
1	**38**	CH_2CH_2Ph	*n*Bu	$SiEt_3$	16	**39a/39b**	98	1.0:1
2	**40**	CH_2CH_2Ph	*n*Bu	Ac	16	**41a/41b**	97	7.1:1
3	**42**	CH_2CH_2Ph	*n*Bu	$COCF_3$	12	**43a/43b**	95	>19:1
4	**44**	H	Me	Ac	10	**45a/45b**	90	3.7:1
5	**46**	H	Me	$COCF_3$	8	**47a/47b**	89	17:1
6	**48**	H	CH_2OAc	$COCF_3$	60	**49a/49b**	69	3.8:1

[a] Yield of isolated product. [b] Determined by ^{1}H NMR spectroscopy.



(3)

In order for the platinum-catalyzed hydrosilylation of internal alkynes to be considered a synthetically useful transformation, the process should be high yielding, with reasonably predictable regioselectivities based on the two alkyne substituents. The tabulated data as a whole implicates that the primary factor influencing the regioselectivity is the electronic nature of the substituents. In all cases, this reaction likely proceeds through the standard Chalk–Harrod mechanism (Scheme 1),[14] where the hydridic species prefers to add to the more electropositive carbon atom of the alkyne.

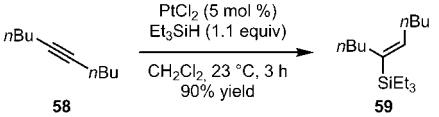
To define the electronic nature of different substituents and their respective influences on hydrosilylations, alkyne ^{13}C chemical shifts have been employed in the evaluation of terminal alkynes.[15] This same principle, however, has sparingly been applied with internal alkynes. Tsipis correlated ^{13}C NMR data for the aforementioned study of 2-pentyne and 2-hexyne.[4] In addition, Alami and co-workers described a ^{13}C NMR evaluation in palladium-catalyzed hydrostannylations of diarylacetylenes, the principle of which Gevorgyan and co-workers subsequently reexamined for validity both experimentally and computationally.[16] An example relevant to our studies is illustrated in Table 4. The hydrosilylations of select methyl ynoates afforded sequentially decreasing regioselectivities. The substituents on these four compounds are relatively similar in effective size. An evaluation of the chemical shifts of the alkyne carbon atoms in each compound shows that each of the four groups provides a noticeably different inductive effect. Importantly, the magnitude and direction of the difference between $\delta(C_\alpha)$ and $\delta(C_\beta)$ directly parallels the magnitude and direction of the regioselectivity of the transformation.[17]

To further illustrate this point, we synthesized a number of homopropargylic alcohol derivatives. Protecting these alcohols with moieties featuring different electronic properties should result in associated variations in the hydrosilylation regioselectivity. To that end, 7-phenylhept-3-yn-1-ol was substituted with four different protecting groups, and each substrate was subsequently analyzed by ^{13}C NMR spectroscopy and subjected to hydrosilylation (Table 5). As illustrated, both the chemical shifts and the hydrosilylation regioselectivity were consistent with the change in inductive effects of the substituents. This high level of correlation offers an excellent degree of predictability, which speaks well to synthetic planning incorporating this catalytic transformation.

Table 5: Manipulation of regioselectivity via alcohol protection.

Entry	Substrate	R	$\delta(C_\alpha)$ [ppm]	$\delta(C_\beta)$ [ppm]	$\delta_{diff.}$	Product	α/β
1	**52**	TBS	77.8	81.3	3.5	**53a/53b**	1.4:1
2	**54**	$COCH_3$	76.5	81.8	5.3	**55a/55b**	2.5:1
3	**56**	COPh	76.5	82.0	5.5	**57a/57b**	2.7:1
4	**50**	$COCF_3$	74.7	83.0	8.3	**51a/51b**	4.3:1

Other factors can also be influential on the overall process. To evaluate steric influences, we tested the hydrosilylations of alkynes **58** and **60** [Eqs. (4)–(5)]. The reaction time was substantially longer for the latter substrate, thus



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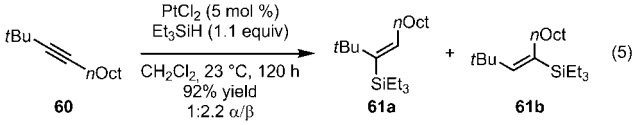

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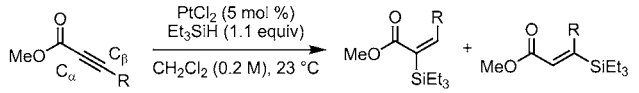
Table 4: Methyl ynoate hydrosilylation regioselectivity correlated to ^{13}C NMR data.



Entry	Substrate	R	α/β	$\delta(C_\alpha)$ [ppm]	$\delta(C_\beta)$ [ppm]	$\delta_{diff.}$
1	**12**	*n*Bu	>19:1	73.0	90.1	17.1
2	**36**	CH_2CH_2OAc	5.2:1	74.0	85.0	11.0
3	**34**	CH_2OTHP	3.5:1	77.4	84.2	6.8
4	**32**	CH_2OAc	0.9:1	81.6	78.0	−3.6

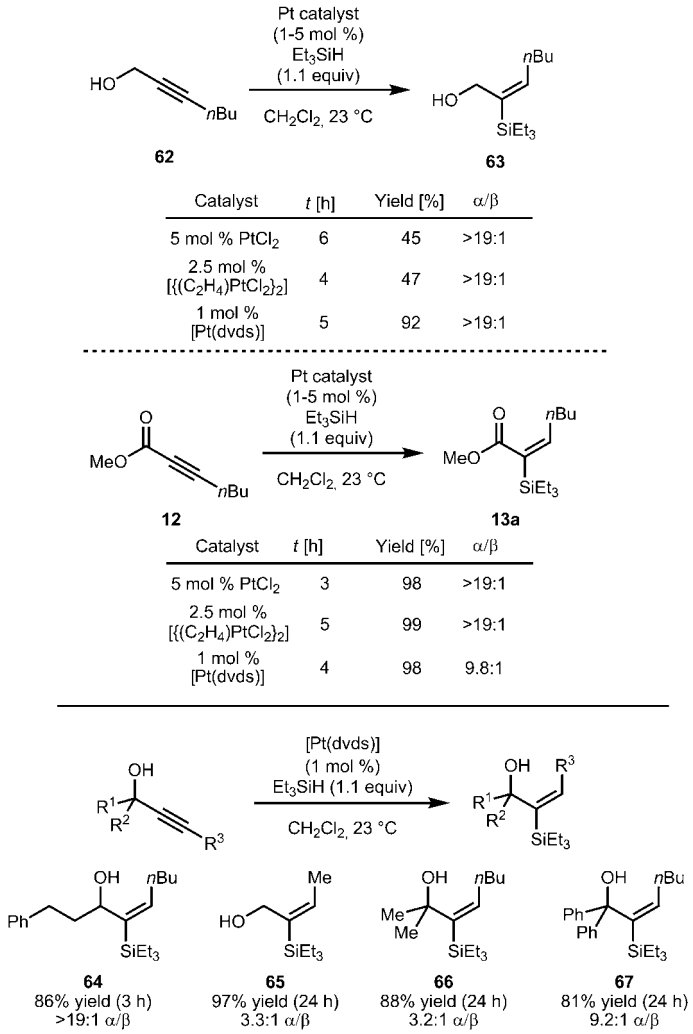
reflecting the difficulty of inserting a sterically hindered alkyne into a platinum hydride bond. Additionally, the presence of the *tert*-butyl group impacted the regioselectivity. Sterics likely play a role by developing a destabilizing interaction between the large group and the platinum metal center. Insertion of the alkyne consequently places the hydride on the same carbon atom as the large substituent and the larger platinum species away from this group. This premise is also aptly illustrated in the decreasing regioselectivities observed in the hydrosilylations of the ynoates in Table 1; the larger ester substituents (*i*Pr, *t*Bu) slightly, but measurably, impacted the regioselectivity.

The other significant effect on regioselection was the presence of a propargylic alcohol. In the hydrosilylation of alcohol **62**, the regioselectivity was high, but the yield was notably diminished (Scheme 2). We reasoned that HCl, presumably a by-product of catalyst initiation with the platinum chloride salts, was promoting decomposition of the product alcohols. Indeed, when Zeise's dimer—$[\{(C_2H_4)PtCl_2\}_2]$, also containing a chloride counterion—was used instead of $PtCl_2$, similarly low yields of allylic alcohols were observed. To circumvent HCl formation, Karstedt's catalyst ([Pt(dvds)]; dvds = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) was an ideal catalyst precursor, and the corresponding vinylsilanes could be obtained in excellent yields while maintaining the very high levels of regioselectivity. Both Zeise's dimer and [Pt(dvds)] were competent in the hydrosilylations of ynoates as well, although a small erosion in regioselectivity was observed with the latter. Using this catalyst, a number of propargylic alcohols, including ones particularly susceptible to ionization, could be hydrosilylated effectively with high yields.

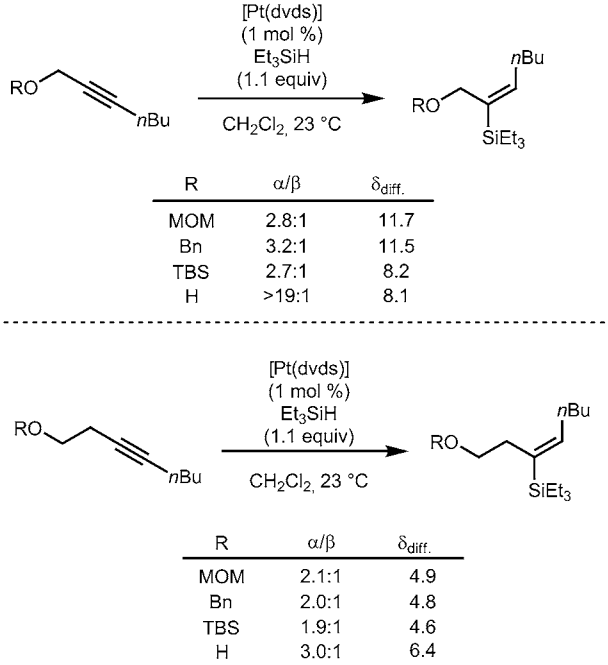
As these examples illustrate, the uniform α selectivity does not appear to be fully consistent with combined steric and electronic effects. For example, in comparing a secondary acetate (**41a**/**41b**, Table 3, 7.1:1 α/β) with the parent alcohol (**64**, >19:1 α/β), electronic effects predict that the acetate should give higher α selectivity. The tertiary alcohols (**66**, **67**) arise from notably α-selective hydrosilylations, wherein the functional group apparently overrides substantial steric effects. The presence of a propargylic alcohol could be engaging in a favorable hydrogen-bonding interaction to a platinum-based intermediate, thus steering the selectivity toward α.[18–20]

Finally, we sought to address the potential coordinative properties of substituents in directing the hydrosilylation regioselectivity. This issue is especially relevant considering the well-established method of intramolecular platinum-catalyzed hydrosilylation using a tethered silyl ether.[21] In altering the electronic nature of the alkyne substituents, in particular ones based on oxygenated species, the coordinative properties should also be changed. Alkynes based on both propargylic and homopropargylic alcohols were tested in the hydrosilylation, where the alcohols were substituted with protecting groups that have similar inductive but different coordinative properties. As illustrated in Scheme 3, the regioselectivities were similar for all protected alcohols, thus suggesting that possible coordination with these groups does not influence the regiochemistry.[6] The relevant ^{13}C NMR data reflects that the regioselectivity observed originates chiefly from inductive effects. The parent propargylic alcohol, as mentioned above, afforded very high regioselectivity; the homopropargylic alcohol, however, was more aligned with the substituted variants, thus reflecting the importance of alcohol proximity.

The hydrosilylation of internal alkynes can be performed with remarkably low catalyst loadings upon scale-up. For example, the hydrosilylation of alkyne **12** using 0.01 mol%



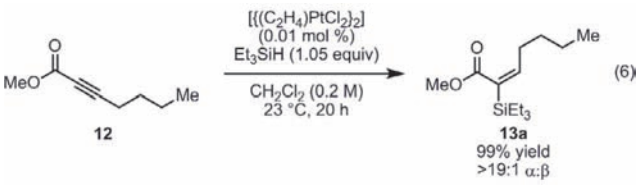
Scheme 2. Propargylic alcohol substrates: Catalyst evaluation.



Scheme 3. Coordinative effects. MOM = methoxymethyl.

$[\{(C_2H_4)PtCl_2\}_2]$ proceeds efficiently, thus affording vinylsilane **13a** with excellent yield and regioselectivity [Eq. 6].

The use of heptamethyldisiloxysilane as the reducing agent allows the formation of readily convertible vinylsilanes

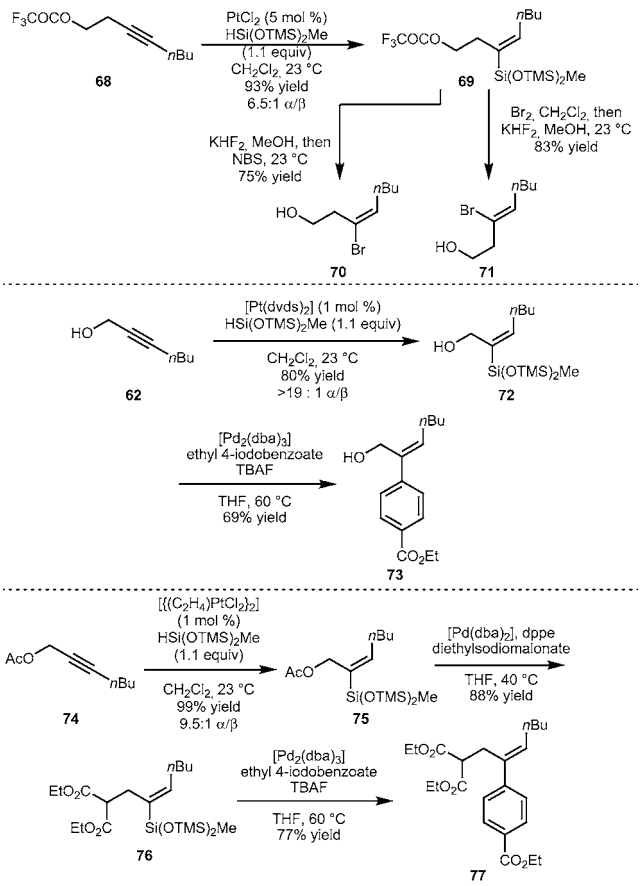


(Scheme 4).[22] Halodesilylation can be executed with either retention or inversion of olefin geometry to form alkenyl bromides **70** and **71**, respectively.[23] Hiyama couplings can also be performed with excellent conservation of the stereochemistry. The robust nature of the vinylsilane functionality allows other transformations to be executed prior to selective reaction, as highlighted by the palladium-catalyzed allylation using acetate **75**. Importantly, these example transformations are all highly specific in that the substitution patterns and geometrical integrities established in the hydrosilylation are transferred to the products.

In summary, we have illustrated the effective hydrosilylations of internal alkynes, where regioselectivity is predominantly governed by electronic effects. In particular, alkynes substituted with electron-withdrawing groups can afford very high levels of α selectivity. The transformations are high yielding, and appreciably low catalyst loadings can be employed. The electronic effect that dictates the regioselectivity is obtainable through ^{13}C NMR data, which we note can be correlated with computational predictions.[24] Vinylsilanes also represent useful synthetic handles that can be readily transformed while maintaining geometrical integrity. Given both the practicality and predictability of the process in combination with the overall utility of the product silanes, platinum-catalyzed hydrosilylations of internal alkynes should find widespread utility in synthetic applications.

Received: December 10, 2011
Published online: February 8, 2012

Keywords: alkynes · homogeneous catalysis · hydrosilylation · platinum · regioselectivity



Scheme 4. Select synthetic applications of internal vinylsilanes. dba = dibenzylideneacetone, dppe = 1,2-bis(diphenylphosphanyl)ethane, KHF_2 = potassium hydrogenfluoride, NBS = *N*-bromosuccinimide, TBAF = tetra-*n*-butylammonium fluoride, THF = tetrahydrofuran, TMS = trimethylsilyl.

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[17] The correlation is reasonably linear in nature, with slight deviations being attributable to steric variance in the substituents. See the Supporting Information for graphical depiction.
[18] a) An alternative hypothesis could involve the association of the alcohol to the platinum complex prior to insertion of the alkyne into the Pt–H bond. A four-membered platinacycle would be the subsequent intermediate, which makes this less likely of an explanation. The lack of a similar effect in homopropargylic alcohols also seems to refute this hypothesis; b) The higher regioselectivity observed in the formation of **67** relative to **66** is consistent with the diphenylalcohol functional group being a better hydrogen-bond donor. Inductive effects would also agree with this direction, but not likely to the extent observed. See the Supporting Information for discussion.
[19] McLaughlin and Cook recently described a $PtCl_2$/XPhos catalyst system in the hydrosilylations of propargylic alcohols, including a number of internal alkyne substrates. The regioselectivity observed appeared to be more driven by preferential addition away from the alcohol group, with steric factors also influential. See Ref. [5d].
[20] The difference in regioselectivities in products **63** and **65**, essentially evaluating *n*Bu versus Me, is intriguing. There is a larger alkyne chemical shift difference in the compounds featuring a butyl group relative to ones with a methyl group, implicating a well-established β-substituent effect by the β-carbon atom of the butyl chain on the alkyne carbon atom. This effect is nonexistent when the substituent is methyl. The difference may also involve a steric contribution.
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[22] a) The change in silane species has a small effect on hydrosilylation regioselectivity. Studies are currently underway to elucidate and understand the influence of different silane species; b) $HSi(OTMS)_2Me$ is an inexpensive and convenient silane to utilize that provides a readily transformable vinylsilane.
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