Regio- and Stereochemical Aspects of the Palladium-Catalyzed Desilylation−Arylation of Substituted Vinylsilanes

Davide Alvisi,[†] Errol Blart,*[,‡] Bianca Flavia Bonini,[†] Germana Mazzanti,[†] Alfredo Ricci,*[,†] and Paolo Zani[†]

Dipartimento di Chimica Organica "A. Mangini", Facoltà di Chimica Industriale, viale Risorgimento 4, I-40136 Bologna, Italy, and Laboratoire de Synthèse Organique, Faculté des Sciences et Techniques, rue de la Houssinière 2, F-44072 Nantes Cedex 03, France

Received February 13, 1996[⊗]

The palladium-catalyzed desilylation−arylation of substituted vinylsilanes by *p*-iodoanisole in the presence of bidentate phosphine ligands is described. Apart from enhancing the rate of the reaction considerably, heteroatom-based functional groups in the vinylsilane moiety have a profound influence on the regiochemistry. A catalytic cycle for the chelation-controlled desilylation−arylation reaction involving five- and six-membered chelate rings is proposed.

Introduction

Vinylsilanes are readily available and fairly stable organometallics. Due to the weak polarization of the C−Si bond,[1] this functionality seldom exhibits substantial reactivity. In spite of this characteristic, these compounds have become increasingly important intermediates in synthesis.[1,2] Efficient replacement of the SiR_3 moiety in the Csp_2−Si bond by electrophiles requires enhancement of the electrophilicity of the latter *via* Lewis acid coordination[3] or an increase of the C−Si bond reactivity by attack of fluoride ions on silicon leading to the formation of a pentacoordinated species.[4]

To exploit further the synthetic potential of the carbon−silicon bond under mild conditions and to avoid the problems caused by Lewis acid or fluoride ion methodologies in vinylsilanes which contain reactive functional groups or highly acidic hydrogen atoms, we investigated a different method for the replacement of silicon with aryl groups based on the transition-metal-catalyzed coupling reaction between vinylsilanes and aryl iodides.

Herein we report our results for the Pd-catalyzed desilylation−arylation of a number of mono- and disubstituted vinylsilanes aimed at opening a novel selective synthetic route to polyfunctionalized olefins and at revaluating the reactivity of vinylsilanes.

Results and Discussion

The transition-metal-catalyzed coupling of aryl and vinyl halides and triflates with main group organometallics *via* oxidative addition−transmetalation−reductive elimination sequences has been broadly developed. In the reaction of an organometallic compound R−M with an organic compound R′−X, R−M can "transmetalate" to Pd (and also to Ni and Fe), and the transfer of the R′ groups to Pd in exchange for the leaving groups (halides or triflates) present in the R′−X reagent leads to a cross-coupling reaction with formation of R−R′. Many organometallic reagents of Li, B, Al, Zr, Zn, and Sn have been shown to undergo this kind of reaction, but a few of them (e.g. Sn, B, and Zn) are much more useful than the others.[5]

Within group 14 organometallics, transmetalation from tin to palladium is one of the most highly developed and extensively utilized processes in organopalladium chemistry,[6] whereas transmetalation from silicon to palladium is inherently difficult due to problems arising from activation of the silylated starting material and from stabilization of the silicon product in the transmetalation step, and thus to date has found little application in complex organic synthesis.

Palladium has been reported to be capable of cleaving the C−Si bond in alkyl-, vinyl-, and allylsilicon compounds in moderate yields, and in some selective palladium-catalyzed cross-coupling reactions the C−Si bond cleavage is an essential step. In 1982 Hallberg and Westerlund reported the synthesis of styrene derivatives[7] *via* palladium-catalyzed desilylation−vinylation of aromatic iodides using commercially available (trimethylvinyl)silane as an ethylene equivalent. Addition of silver salts in the same reaction completely suppressed the desilylation, leading[8] to (*E*)-(2-arylethenyl)silanes, in line with the expected outcome of an ordinary Heck reaction. The above mentioned reactions were normally performed under forcing conditions. However, an efficient activation of the organosilanes has been attempted by Hiyama and co-workers by using the combination TBAF (or TASF)−Pd catalysis for the activation and fluorosilanes as the starting materials.[9] This approach led to a remarkable

[†] Dipartimento di Chimica Organica "A. Mangini".

[‡] Laboratoire de Synthèse Organique.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981.

(2) (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (b) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4260.

(3) For leading references regarding the electrophilic substitution reactions of vinylsilanes, see: (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Magnus, P. *Aldrichimica Acta* **1980**, *13*, 41.

(4) (a) Fry, Y. L.; Mc Adam, M. A. *Tetrahedron Lett.* **1984**, *25*, 5859. (b) Furin, G. G.;Vyazankina, O. A.; Gostevsky, B. A.; Vyazankin, N. S. *Tetrahedron* **1988**, *44*, 2675 and references therein.

(5) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1987. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (c) Davies, S. G. *Organotransition Metal Chemistry. Application to Organic Synthesis*; Pergamon Press: Oxford, 1982. (d) Hegedus, L. S. *Organometallics in Synthesis*; John Wiley & Sons Ltd: Chichester, UK, 1994. (e) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918 and references therein.

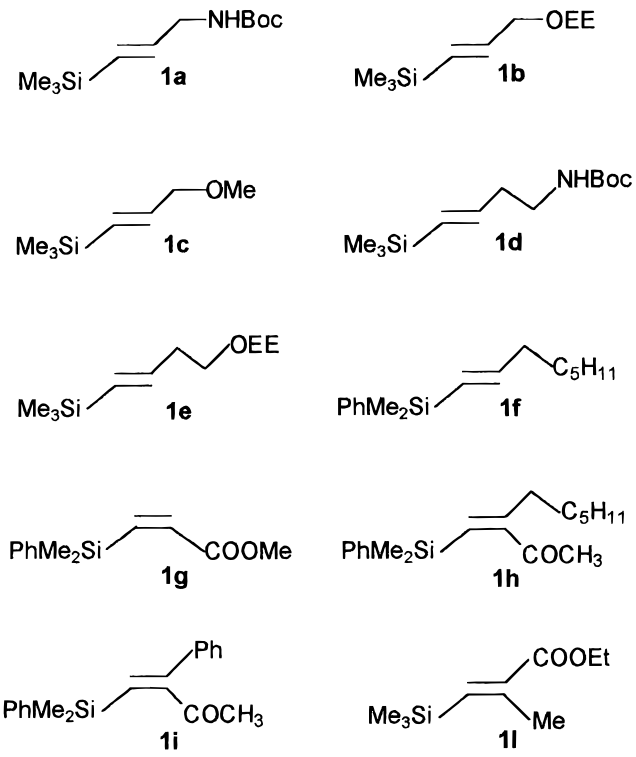
(6) For reviews, see: (a) Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508. (b) Mitchell, T. N. *Synthesis* **1992**, 803.

(7) Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993.

(8) (a) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896. (b) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.

S0022-3263(96)00301-5 CCC: $12.00

Chart 1



improvement of reactivity and selectivity in alkenyl cross-coupling. Nevertheless, in several cases, mixtures of *cine* and *ipso* substitution products were obtained.

In a series of previous papers[10] we devised, *via* silylcupration of propargylic amines, ynamines, and thioethers followed by hydrolytic quench or by quenching with electrophiles, a route to polyfunctionalized vinylsilanes bearing heteroatom-based or reactive functionalities. In all the cases we have investigated thus far, the reactions were found to be highly regio- and stereoselective. A number of vinylsilanes (**1a**−**l**) prepared by this method are now reported in Chart 1.

Experiments performed on vinylsilanes in Chart 1 under the conditions previously used by Hallberg[7,8] employing $Pd(OAc)_2$ and PPh_3 resulted in complete recovery of the starting material, with no coupling products observed. The Hiyama procedure,[9] based on the use of an allylpalladium chloride dimer catalyst and TASF, proved to be ineffective as well. The combined use of bidentate ligands such as DPPE [1,2-bis(diphenylphosphino)ethane] or DPPB [1,4-bis(diphenylphosphino)butane] with $Pd(OAc)_2$, Et_3N and *p*-iodoanisole led, on the other hand, to sizeable amounts of coupling products, as shown in Scheme 1.

The relevant results of the coupling reactions are reported in Table 1. When **1a** was allowed to react with *p*-iodoanisole, 1-arylethene **2a**, the *cine*-substitution product, was formed as the major product with minor amounts (10% ca.) of the *ipso*-substitution product **3a**, which had the opposite configuration (*Z*) with respect to that of the starting material (entries 1−3). Replacement of the Me_3-Si with the Me_2PhSi moiety did not lead to substantial variations in the coupling reactions.

The regiochemistry of this reaction was not affected by temperature or solvent, and only a decrease in the reaction rate was observed at lower temperatures. Moreover, bidentate ligands such as DPPE and DPPB proved to be equally effective.

Extension of the coupling reaction to the other monosubstituted vinylsilanes **1b**−**g**, under the optimized conditions employed for **1a**, suggested a sizeable variation of the reaction outcome in terms of both the efficiency of coupling and the regiochemical control when varying the side chain substituent. The beneficial role played by heteroatom-based functionalities on the coupling efficiency is also highlighted. Accordingly, a sizeable decrease in yields was observed for **1c** (entry 6) and for higher homologues such as **1d** (entry 7) and **1e** (entry 8). For compound **1f**, which bears no polar groups, the reaction failed. We observed that the nature of the heteroatom had a profound effect on the regioselectivity of the coupling reaction since, in contrast to the results for **1a**, equal amounts of the *ipso*- and the *cine*-substitution products were generated (entries 4 and 5) starting from (*E*)-3-(1-ethoxyethoxy)-1-(trimethylsilyl)propene **1b**. Complete control of the regioselectivity was finally achieved for (*Z*)-3-((dimethylphenyl)silyl)acrilic acid methyl ester **1g** and the disubstituted vinylsilanes **1h**−**l**, which bear carbonyl substituents. In these cases only the regioisomers resulting from an *ipso*-attack were formed (entries 10−13).

The mechanism which could account for the formation of type **2** and **3** products is depicted in Scheme 2. It is based on the standard hypothesis for the coordination−insertion process of unsaturated systems on Pd(II) complexes according to the Heck reaction mechanism.[11] We assume that palladium-catalyzed reactions of aryl iodides with vinylsilanes proceed *via* a 1,2-addition of "Ar−Pd−I" to the double bond of the vinylsilane followed by an ordinary Heck arylation at the terminal or the internal carbon leading to type **A** or type **B** σ-complexes. From **B**, "syn" Me_2RSi−Pd−I elimination leads directly to the *ipso*-substitution product with inversion of configuration at the double bond. From **A**, elimination−readdition of HPdI and subsequent irreversible desilylation could account for the formation of the *cine*-substitution product.

Experiments performed on substituted vinylsilanes $\mathbf{1a}_D$ and $\mathbf{1b}_D$ deuterated at C-2 (Scheme 3) led to the formation of products $\mathbf{2a}_D$ and $\mathbf{3a}_D$ or $\mathbf{2b}_D$ and $\mathbf{3b}_D$ respectively, indicating a 2,1-shift of deuterium for $\mathbf{2a}_D$ and $\mathbf{2b}_D$. This pathway previously suggested by Hallberg in his mechanistic rationale for the palladium-catalyzed desilylation−arylation of unsubstituted vinyltrimethylsilane[8b] now appears to be unambiguously demonstrated and provides strong support in favor of an elimination−readdition of hydridopalladium iodide (route *a* in Scheme 2).

The reaction pattern outlined in Table 1 is in apparent contrast with the observation that chelating diphosphines do not, in general, produce useful catalysts when aryl halides are used.[12] This pattern however can be accounted for by considering the pivotal role played by the heteroatoms in the reactions under study after oxidative addition has occurred. The failure of compound **1f**, which does not bear polar or heteroatom-based functionalities,

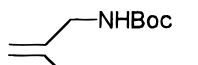
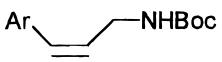
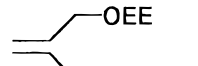
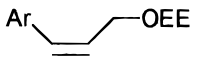
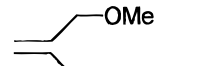
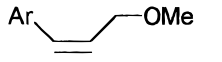
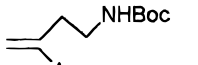
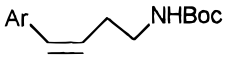
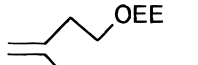
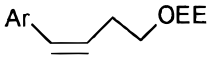
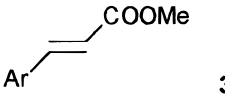
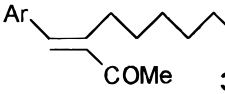
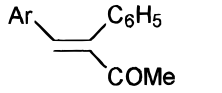
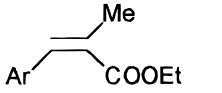
(9) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471 and references therein.

(10) (a) Capella, L.; Degl' Innocenti, A.; Reginato, G.; Ricci, A.; Taddei, M. *J. Org. Chem.* **1989**, *54*, 1473. (b) Casarini, A.; Jousseaume, B.; Lazzari, D.; Porciatti, E.; Reginato, G.; Ricci, A.; Seconi, G. *Synlett* **1992**, 981. (c) Capella, L.; Capperucci, A.; Curotto, G.; Lazzari, D.; Dembech, P.; Reginato, G.; Ricci, A. *Tetrahedron Lett.* **1993**, *34*, 3311.

(11) Heck, R. F.; Nolley, J. P., Jr. *J. Org. Chem.* **1972**, *37*, 2320.

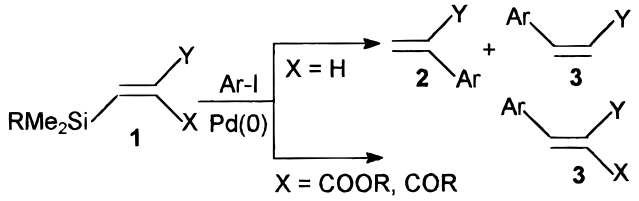
(12) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146 and references therein.

Table 1. Palladium-Catalyzed Reaction between Vinylsilanes 1a−l and *p*-Iodoanisole

		coupling products[a,b]					product yields[d]		
entry	olefin	2	3	cond[c]	T (°C)	time (h)	2 (%)	3 (%)	2/3
1	1a	 **2a**	 **3a**	A	25	48	22.5	2.5	10/1
2	1a			A,B	50	48	82	8	10/1
3	1a			A	80	16	65	6.5	10/1
4	1b	 **2b**	 **3b**	A	65	48	40	39	1/1
5	1b			C	80	48	35	35	1/1
6	1c	 **2c**	 **3c**	A	80	48	24	1	24/1
7	1d	 **2d**	 **3d**	D	80	16	18	≤1	20/1
8	1e	 **2e**	 **3e**	D	80	16	16	≤1	20/1
9	1f	--	--	A	80	48	--	--	--
10	1g	--	 **3g**	A	80	16	--	50[e]	
11	1h	--	 **3h**	A	80	48	--	93	
12	1i	--	 **3i**	A	80	48	--	62	
13	1l	--	 **3l**	A	80	16	--	64	

[a] Reactions were run under argon with 1 equiv of **1**, 2 equiv of *p*-iodoanisole, and 2.5 equiv of Et_3N. [b] Ar indicates *p*-MeO-C_6H_4; EE stands for 1-ethoxyethyl (CH(Me)OEt). [c] The following amounts of catalyst and ligands with the respect to **1** were used: condition A, 5% $Pd(OAc)_2$ and 10% DPPB; condition B, 5% $Pd(OAc)_2$ and 10% DPPE; condition C, 1% $Pd(OAc)_2$ and 2% DPPB; condition D, 10% $Pd(OAc)_2$ and 20% DPPB. [d] Yields of pure (>95% by GC−MS) products isolated (entries 1−8) as a mixture of **2** and **3** after chromatography over silica gel. The ratio has been determined by ^1H NMR (see the Experimental Section). [e] Only the *E* isomer was formed.

Scheme 1

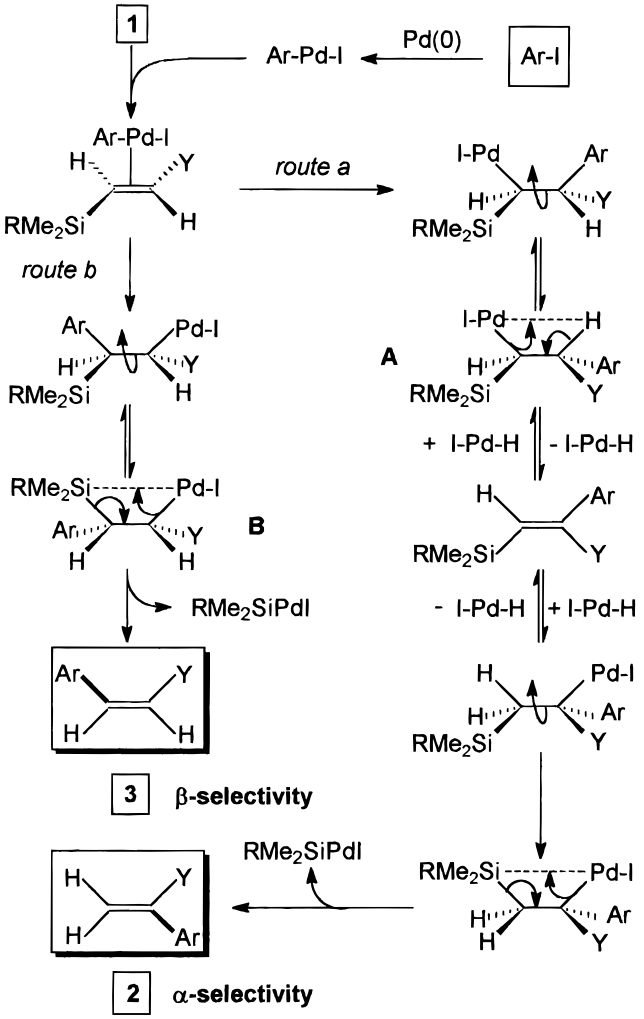


to form any coupling products is consistent with this hypothesis.

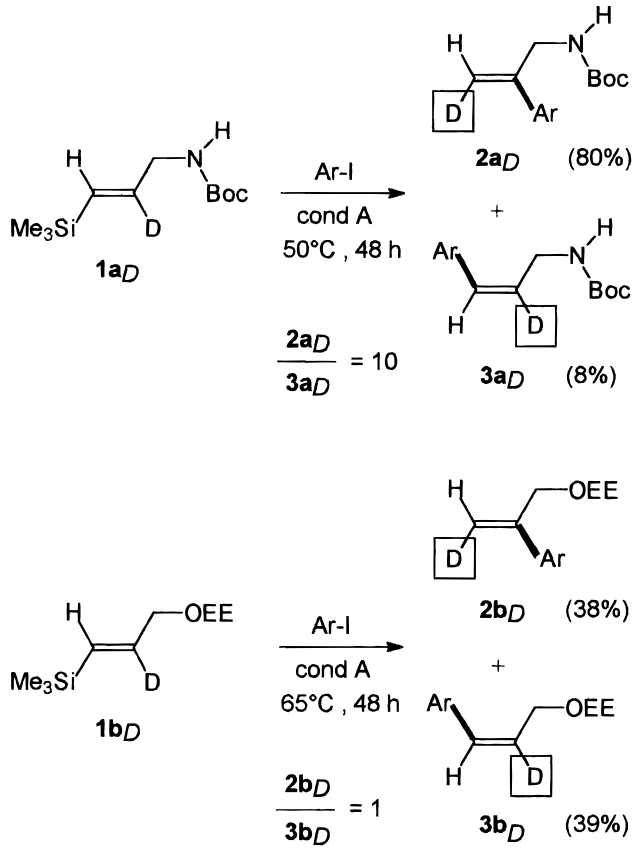
Anchoring the metal to the heteroatom-based substituent in the olefin might facilitate the otherwise difficult approach (due to steric crowding) of the Pd(II) complex to the vinylsilane, resulting in the formation of a π-complex. Even though stable palladium(II) complexes with bidentate amino-functionalized enol ethers have been reported,[13] in the case of the NHBoc or the OR moieties, the catalyst is not likely to be tied up in stable π- or σ-complexes, and thus the catalytic cycle can be initiated. The regioselectivity observed for the aromatic ring migration onto the coordinated olefin is generally thought to be due to a balance between electronic and steric factors.[14] With either DPPB or DPPE as the ligand and the iodide as the counterion strongly associated with Pd(II) in the oxidative-addition complex,[15] the coordination of the olefin is likely to take place by ligand dissociation[16] to afford neutral Pd(II) complexes. This would imply a reduced polarization of the double bond, and consequently, migration of the aryl moiety onto the α carbon is unfavored.[14] However, anchoring the metal to the heteroatom may cause the collapse of the π-complex as

(13) Mc Crindle, R.; Ferguson, G.; Khan, M. A.; Mc Alees, A. J.; Ruhl, B. L. *J. Chem. Soc. Dalton Trans.* **1981**, 986.
(14) Cabri, W.; Candiani, I.; Bedeschi, A. *J. Org. Chem.* **1992**, *57*, 3558.
(15) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Riedel: Dordrecht, Holland, 1980, pp 11−15.
(16) Cabri, W.; Candiani, I.; Bedeschi, A.; Penco, S. *J. Org. Chem.* **1992**, *57*, 1481.

Scheme 2



Scheme 3



a result of either direct steric constrains due to the steric bulk of the R_3Si group as well as of the favored formation of intermediate chelate rings. Furthermore, the so-called β-effect,[17] in which the build-up of the electrophilic character β to the C−Si bond is stabilized, would reinforce the tendency of the aryl group to migrate to the α position when going from the π- to the σ-complex.

Coordination of the catalyst with N or O in the NHBoc group in **1a** (Scheme 4) might drive the collapse of the π-complexes to five and six-membered σ-complexes **I** and **II**, respectively. From these σ-complexes, α and β selectivities could be achieved according to the routes depicted in Scheme 2. Route *a* is favored over route *b* by a factor of 10, probably due to the more efficient Pd−N coordination as well as to the directing effect of the $SiMe_3$ group.

The lack of selectivity observed for **1b** could be rationalized by the arguments above taking into account (Scheme 4) that both the internal and external O atoms of the EE protecting group are also likely to be engaged in the chelation step leading, through five- (**III**) and six- (**IV**) membered σ-complexes (both energetically favored), to the formation of the *cine* (α selectivity) and *ipso* (β selectivity) products, respectively, in nearly equal amounts.

The assumption that the regiochemistry and the efficiency of the transformation are controlled by the location and by the number of the Lewis basic coordination sites is substantiated by several of the results reported in Table 1. In the reaction performed on (*E*)-3-methoxy-1-(trimethylsilyl)propene **1c**, the collapse of the π-complex through type-**III** five-membered ring σ-complexes will be strongly favored as a result of the presence of one oxygen atom, thus accounting (entry 6) for the high ratio (24:1) of the *cine* (α-selectivity) and *ipso* (β-selectivity) isomers. The lower efficiency of this reaction with respect to **1b** could be tentatively explained by a diminished capability of a single heteroatom to stabilize the initially formed π-complex. The faster reactivity of the chelating *N*,*N*-dimethyl(ethyleneoxy)ethylamine with respect to that of the sterically similar (3-methyl-1-butoxy)ethene, which bears only a heteroatom-based functionality in the Pd-catalyzed arylation of vinyl ethers, recently reported in the literature,[18] appears consistent with this interpretation. Moreover, upon increasing the length of the ethylenic chain as in **1d** and **1e**, the role of the external heteroatomic moiety on the reaction efficiency and regioselectivity might become less effective as already observed[19] in the series of (ethenyloxy)-alkylamines representing different carbon tethers. Accordingly, the reaction efficiency in **1d** and **1e** is reduced and the collapse of the π-complex, apparently governed by steric constraints, would favor the six-membered σ-complex over the five-membered alternative (Scheme 5).

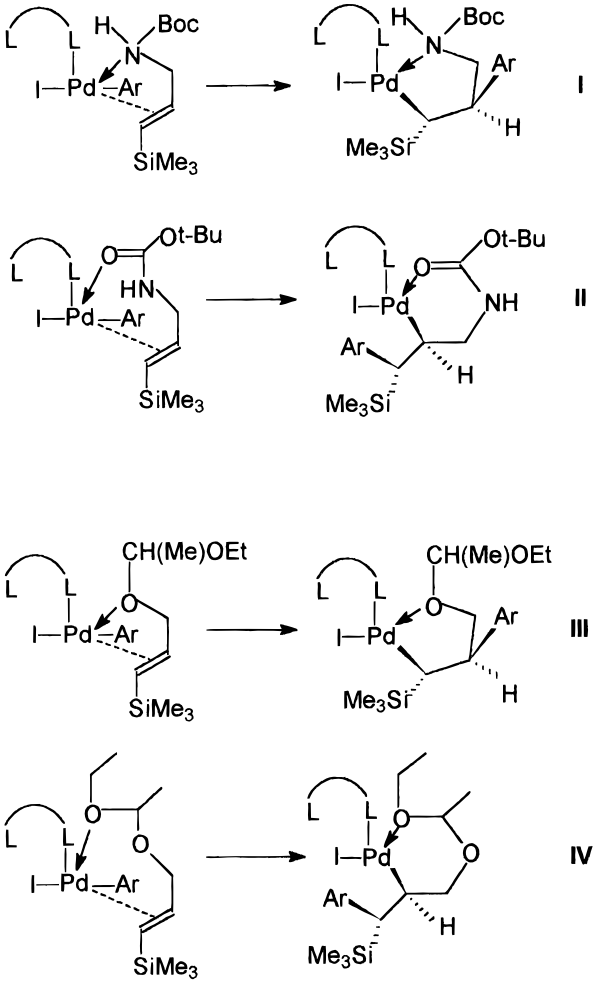
Finally, a reasonable explanation for the β-selectivity observed in the case of compounds **1g**−**l** (entries 10−13) relies on the well-established Michael-type 1,4-conjugate addition of cyclohexenone through a transient Pd−

(17) Jarvie, A. W. *Organomet. Chem. Rev.*, Sect. A **1970**, 6, 153.

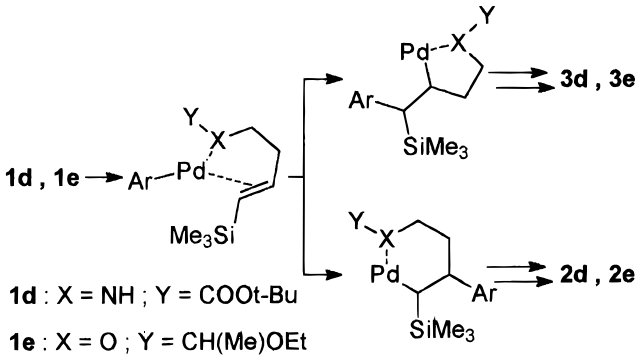
(18) Larhed, M.; Andersson, C.-M.; Hallberg, A. *Tetrahedron* **1994**, *50*, 285.

(19) Larhed, N.; Andersson, C.-M.; Hallberg, A. *Acta Chem. Scand.* **1993**, *47*, 212

Scheme 4



Scheme 5



enolate species.[20] The cross coupling−desilylation−arylation reaction must therefore occur exclusively *via* route b (Scheme 2), that is by Pd−desilylation from a σ-complex in which the Pd is bound to the α-carbon. This is the only reaction pathway through which arylation of disubstituted vinylsilanes **1h**−**l** can occur. No competition between vinylic substitution and conjugate addition[21] was observed in the reactions performed on these compounds.

In conclusion, the presence of heteroatom-based functional groups in substituted vinylsilanes facilitates the Pd-catalyzed desilylation−arylation and appears to greatly affect the regiochemistry, probably through chelation-controlled reaction pathways. Such a re-evaluation of the use of vinylsilanes in synthesis provides a novel entry to challenging compounds such as stereo- and regiochemically defined trisubstituted olefins to which many research efforts have been devoted[22] and the formation of which *via* Pd-catalyzed desilylation−arylation is unprecedented.

(20) Genet, J. P.; Blart, E.; Savignac, M. *Synlett* **1992**, 715.
(21) Cacchi, S.; Arcadi, A. *J. Org. Chem.* **1983**, *48*, 4236.

Experimental Section

Materials. $Pd(OAc)_2$, DPPB, DPPE, hexamethyldisilane, and dimethylphenyl chlorosilane were used as received from commercial sources. THF was rendered anhydrous by distillation over sodium wire after the characteristic blue color of *in situ* generated sodium diphenylketyl was found to persist. Diethyl ether was distilled over P_2O_5. Petroleum ether was distilled over CaH_2, and only the fraction with a bp of 40−70 °C was used for chromatography. Acetonitrile was stored over 4 Å molecular sieves. HMPA and DMF were distilled over CaH_2 and were stored under argon over 4 Å molecular sieves. CuCN was dried at 120 °C overnight under reduced pressure. (Trimethylsilyl)lithium[23] and (dimethylphenylsilyl)lithium[24] were prepared by literature methods.

General. All reactions were performed in oven-dried glassware under an atmosphere of dry argon. Arylation reactions were routinely performed in capped, heavy-walled Pyrex tubes. Ethereal extracts were dried over magnesium sulfate. TLC were performed on precoated silica gel plates and preparative layer chromatography (PLC) with silica gel 230−400 mesh. Purifications by chromatography were performed using glass columns (10−50 mm wide) with silica gel (70−230 mesh) as the stationary phase. ^{1}H-NMR spectra, unless otherwise stated, were recorded at rt in $CDCl_3$ at operating frequencies of 200 MHz and were referred to TMS. ^{13}C NMR spectra were recorded in $CDCl_3$ at 50.3 MHz. Capillary GC analysis was performed using a 25 m × 0.25 mm, cross-linked 5% methylphenylsilicone capillary column. High-resolution mass spectra (HRMS, EI/DP) were obtained at 70 eV. Elemental analyses are within ±0.3%.

(Trimethylsilyl)cupration. Procedure I. To a solution of (trimethylsilyl)lithium (6.4 mmol) in 16 mL of THF and 3.2 mL of HMPA was added 286 mg (3.2 mmol) of CuCN at −23 °C under argon. After stirring for 10 min, the alkyne (2.9 mmol) in dry THF (1 mL) was added with a syringe and the temperature held at −23 °C for the appropriate time. The reaction was followed by TLC and GC or GC−MS.

(Dimethylphenylsilyl)cupration. Procedure II. To a suspension of CuCN (286 mg, 3.2 mmol) in dry THF (5 mL) was added a solution of (dimethylphenylsilyl)lithium (6.4 mmol) in THF (16 mL) with a syringe at −78 °C under argon, and the mixture was stirred for 10 min. The alkyne (2.9 mmol) in 1 mL of dry THF was added with a syringe and the temperature held at −23 °C for the appropriate time. The reaction was followed by TLC and GC or GC−MS.

Representative Procedure. (*E*)-*N*-(*tert*-Butoxycarbonyl)-3-(trimethylsilyl)allylamine (1a). After 2 h the vinylcopper reagent, prepared from *N*-(*tert*-butoxycarbonyl)propargylamine (2.00 g, 12.9 mmol) following procedure I, was quenched with a saturated solution of NH_4Cl at −78 °C and stirred for 15 min. The reaction mixture was warmed to rt, filtered, and diluted with 20 mL of ether. The aqueous phase was separated and subjected to further extraction with ether (2 × 15 mL). The combined ethereal extracts were washed with water (20 mL) and dried over magnesium sulfate, and the solvent was evaporated. The crude mixture was purified by column chromatography with hexane/ethyl acetate (60:10) to give 2.68 g (90%) of **1a** as a colorless oil.

1a: ^{1}H NMR δ 0.06 (s, 9H), 1.46 (s, 9H), 3.60−3.80 (m, 2H), 4.68 (br s, 1H), 5.76 (dt, J = 18.7 Hz, 1.5 Hz, 1H), 5.99 (dt, J

(22) (a) Denmark, S. E.; Amburgey J. *J. Am. Chem. Soc.* **1993**, *115*, 10386. (b) Creton, I.; Marek, I.; Brasseur, D.; Jestin, J.-L.; Normant, J.-F. *Tetrahedron Lett.* **1994**, *35*, 6973.
(23) Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69.
(24) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc. Perkin Trans. 1* **1981**, 2527.

= 18.7 Hz, 4.6 Hz, 1H); ^{13}C NMR δ −1.40, 28.3, 45.0, 79.2, 130.2, 142.3, 155.1; MS *m*/*z* (relative intensity) 173 (6), 158 (54), 140 (32), 114 (30), 100 (53), 73 (100), 59 (70), 57 (60). Anal. Calcd for $C_{11}H_{23}NO_2Si$: C, 57.60; H, 10.12; N, 6.11, found: C, 57.62; H, 10.13; N, 6.13.

(*E*)-3-(1-Ethoxyethoxy)-1-(trimethylsilyl)propene (1b). The silylcupration was performed according to procedure I, starting from 666 mg (5.2 mmol) of 3-(1-ethoxyethoxy)propyne, and after 1 h was subjected to the usual workup. The crude mixture was purified by column chromatography with petroleum ether/ether (95:5) to give 735 mg (70%) of **1b** as a light yellow oil.

1b: ^{1}H NMR δ 0.30 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.29 (d, *J* = 5.3 Hz, 3H), 3.35−3.75 (m, 2H), 3.92−4.17 (m, 2H), 4.70 (q, *J* = 5.3 Hz, 1H), 5.87 (dt, *J* = 18.7 Hz, 1.3 Hz, 1H), 6.07 (dt, *J* = 18.7 Hz, 4.6 Hz, 1H); ^{13}C NMR δ −1.42, 15.2, 19.8, 60.6, 67.9, 99.1, 131.5, 142.3; MS *m*/*z* (relative intensity) 187 (5), 157 (5), 129 (23), 75 (45), 73 (100). Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96, found: C, 59.39; H, 10.95.

(*E*) 3-Methoxy-1-(trimethylsilyl)propene (1c). The silylcupration was performed according to procedure I, starting from 1.05 g (15.0 mmol) of 3-methoxypropyne, and after 2 h was subjected to the usual workup. The crude mixture was distilled at atmospheric pressure to give 890 mg (41%) of **1c** as a light yellow oil.

1c: ^{1}H NMR δ 0.05 (s, 9H), 3.35 (s, 3H), 3.90−3.98 (m, 2H), 5.90 (dt, *J* = 18.9 Hz, 1.2 Hz, 1H), 6.07 (dt, *J* = 18.9 Hz, 4.4 Hz, 1H); ^{13}C NMR δ −0.91, 58.6, 75.9, 132.6, 142.6; MS *m*/*z* (relative intensity) 129 (73), 99 (10), 89 (58), 75 (70), 73 (100), 59 (52), 45 (26). Anal. Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18, found: C, 58.29; H, 11.19.

(*E*)-*N*-(*tert*-Butoxycarbonyl)-4-(trimethylsilyl)but-3-enylamine (1d). The silylcupration was performed according to procedure I, starting from 330 mg (1.95 mmol) of *N*-(*tert*-butoxycarbonyl)butynylamine, and after 1 h was quenched and treated as usual. The crude mixture was purified by column chromatography with petroleum ether/ether (10:1) to give 370 mg (78%) of **1d** as a colorless oil.

1d: ^{1}H NMR δ 0.02 (s, 9H), 1.41 (s, 9H), 2.20−2.36 (m, 2H),3.10−3.26 (m, 2H), 4.57 (br s, 1H), 5.68 (dt, *J* = 18.7 Hz, 1 Hz, 1H), 5.92 (dt, *J* = 18.7 Hz, 6.1 Hz, 1H); ^{13}C NMR δ −0.81, 28.9, 37.5, 40.0, 79.5, 133.4, 142.5, 155.4; MS *m*/*z* (relative intensity) 187 (5), 172 (8), 99 (12), 73 (40), 59 (45), 57 (100). Anal. Calcd for $C_{12}H_{25}NO_2Si$: C, 59.21; H, 10.35; N, 5.75, found: C, 59.28; H, 10.37; N, 5.78.

(*E*)-4-(1-Ethoxyethoxy)-1-(trimethylsilyl)but-1-ene (1e). The silylcupration was performed according to procedure I, starting from 1.28 g (8.45 mmol) of 4-(1-ethoxyethoxy)but-1-yne, and after 2 h was subjected to the usual workup. The crude mixture was purified by column chromatography with petroleum ether/ethyl acetate (20:1) to give 1.08 g (59%) of **1e** as a light yellow oil.

1e: ^{1}H NMR δ 0.05 (s, 9H), 1.20 (t, *J* = 7.5 Hz, 3H), 1.30 (d, *J* = 5.0 Hz, 3H), 2.30−2.45 (m, 2H), 3.40−3.75 (m, 4H), 4.70 (q, *J* = 5.0 Hz, 1H), 5.70 (dt, *J* = 19.0 Hz, 2.0 Hz, 1H), 6.03 (dt, *J* = 19.0 Hz, 6.6 Hz, 1H); ^{13}C NMR δ −1.30, 15.3, 19.7, 37.0, 60.7, 64.1, 99.4, 132.2, 143.2; MS *m*/*z* (relative intensity) 170 (3), 155 (5), 103 (25), 89 (10), 73 (100). Anal. Calcd for $C_{11}H_{24}O_2Si$: C, 61.06; H, 11.18, found: C, 61.08; H, 11.18.

(*E*)-1-(Dimethylphenylsilyl)oct-1-ene (1f). The silylcupration was performed according to procedure II, starting from 0.620 mL (4.2 mmol) of oct-1-yne, and after 1 h was subjected to the usual workup. The crude reaction mixture was purified by column chromatography (petroleum ether) to give 1.04 g (100%) of **1f** as a colorless oil.

1f: ^{1}H NMR δ 0.35 (s, 6H), 0.80−1.00 (m, 3H), 1.25−1.60 (m, 8H), 2.10−2.24 (m, 2H), 5.77 (dt, *J* = 18.7 Hz, 1.4 Hz, 1H), 6.16 (dt, *J* = 18.6 Hz, 6.2 Hz, 1H), 7.30−7.60 (m, 5H); ^{13}C NMR δ −2.60, 13.9, 22.5, 28.5, 28.7, 31.6, 36.7, 127.4, 127.8, 128.9, 134.0, 139.5, 149.7; MS *m*/*z* (relative intensity) 246 (5%), 231 (10), 161 (25), 135 (100), 121 (40). Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63, found: C, 77.89; H, 10.60.

(*Z*)- and (*E*)-3-(Dimethylphenylsilyl)acrilic Acid Methyl Esters (1g). The silylcupration was carried out according to procedure II, starting from 0.374 mL (4.2 mmol) of methyl propiolate, and after 1 h was quenched and treated as usual. The crude mixture was purified by column chromatography with petroleum ether/diethyl ether (100/3) to give 300 mg (32%) of the (*Z*)-isomer **1g** and 280 mg (30%) of the (*E*)-isomer as light yellow oils.

1g, (*Z*)-isomer: ^{1}H NMR δ 0.45 (s, 6H), 3.75 (s, 3H), 6.58 (d, *J* = 14.7 Hz, 1H), 6.93 (d, *J* = 14.7 Hz, 1H), 7.30−7.60 (m, 5H); ^{13}C NMR δ −2.0, 51.4, 128.0, 129.2, 133.3, 135.5, 136.4, 150.3, 162.0; MS *m*/*z* (relative intensity) 220 (1), 205 (100), 175 (30), 143 (75), 135 (15). Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32, found: C, 66.51; H, 7.35.

1g, (*E*)-isomer: ^{1}H NMR δ 0.43 (s, 6H), 3.75 (s, 3H), 6.24 (d, *J* = 18.9 Hz, 1H), 7.26−7.56 (m, 6H); ^{13}C NMR δ −3.7, 51.3, 127.6, 127.9, 128.8, 129.5,133.7, 134.9, 166.0; MS *m*/*z* (relative intensity) 220 (20), 219 (65), 205 (60), 189 (25), 135 (50), 121 (65), 89 (100). Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32, found: C, 66.48; H, 7.34.

(*Z*)-4-(Dimethylphenylsilyl)-3-hexylbut-3-en-2-one (1h). The silylated vinyl-copper intermediate prepared according to procedure II, starting from 0.620 mL (4.2 mmol) of oct-1-yne, was treated, after 2 h, at −23 °C with 0.90 mL (12.6 mmol) of acetyl chloride. After stirring for 2 h at −23 °C, the resulting mixture was quenched and worked up as usual. The crude mixture was purified by column chromatography with petroleum ether/ether (90:5) to give 900 mg (75%) of **1h** as a colorless oil.

1h: IR (neat) 1692, 1420, 1245 cm^{-1}; ^{1}H NMR δ 0.38 (s, 6H), 0.90 (br s, 3H), 1.20−1.50 (m, 8H), 2.15 (s, 3H), 2.38 (m, 2H), 5.90 (br s, 1H), 7.25−7.60 (m, 5H); ^{13}C NMR δ −2.0, 13.8, 22.4, 27.9, 28.4, 28.7,31.4, 36.3, 127.7, 128.8, 133.8, 136.5, 140.2, 157.5, 203.1; MS *m*/*z* (relative intensity) 288 (1), 273 (100), 203 (63), 135 (33), 75 (15). Anal. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78, found: C, 75.01; H, 9.79.

(*Z*)-4-(Dimethylphenylsilyl)-3-phenylbut-3-en-2-one (1i). Following exactly the same procedure as for **1h**, but starting from 0.925 mL (8.4 mmol) of phenylacetylene, 2.15 g (91%) of **1i** were obtained as a colorless oil.

1i: IR (neat) 1700, 1688, 1427, 1246 cm^{-1}; ^{1}H NMR δ 0.35 (s, 6H), 1.90 (s, 3H), 6.15 (s, 1H), 7.05−7.55 (m, 10 H); ^{13}C NMR δ −2.0, 29.5, 127.1, 127.8, 128.4, 128.7, 129.0, 134.0, 136.0, 139.0, 139.2, 158.6, 204.0; MS *m*/*z* (relative intensity) 280 (5), 265 (100), 203 (54), 135 (32); HRMS (EI) calcd for $C_{18}H_{20}OSi$ 280.128 34, found 280.128 96.

(*E*)-2-Methyl-3-(trimethylsilyl)acrylic Acid Ethyl Ester (1l). The silylated vinylcopper intermediate prepared according to procedure I, starting from 1.21 mL (12.0 mmol) of ethyl propiolate, was treated, after 2 h, at −23 °C with 2.24 mL (36.0 mmol) of iodomethane. The reaction mixture was stirred under argon overnight at rt. After the usual quench and workup, the crude mixture was purified by column chromatography with petroleum ether/ether (95:5) to give 470 mg (21%) of **1l** as a colorless oil.

1l: ^{1}H NMR δ 0.13 (s, 9H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.95 (s, 3H), 4.15 (q, *J* = 7.5 Hz, 2H), 6.80 (s, 1H); ^{13}C NMR δ −0.73, 14.2, 17.4, 60.7, 140.7, 142.8, 167.4; MS *m*/*z* (relative intensity) 171 (42), 143 (66), 103 (17), 75 (100), 73 (60). Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74, found: C, 58.00; H, 9.74.

Deuteriated Vinylsilanes 1a$_D$ and 1b$_D$. 1a$_D$ was prepared by silylcupration of *N*,*N*′-bis(trimethylsilyl)propargylamine according to procedure I, followed by quench with deuteriated water. Subsequent deprotection of nitrogen and conversion to the NHBoc-protected derivative led to the target compound in 51% isolated yield.

1b$_D$ was obtained in 74% yield following the same procedure as for **1b** and quenching with deuteriated water.

General Procedure for the Generation of the Catalytic System. In a Pyrex tube with magnetic stirrer and rubber cap, THF (0.8 mL), $Pd(OAc)_2$ (10 mg, 0.045 mmol), and ligand (DPPE or DPPB) (0.090 mmol) were sequentially added and thoroughly degassed (argon) at rt. The stirred mixture became yellow-orange and was generally used immediately.

Palladium-Catalyzed Reactions. Typical Procedure. Preparation of *N*-(*tert*-Butoxycarbonyl)-2-(4-methoxyphenyl)allylamine (2a) and (*Z*)-*N*-(*tert*-Butoxycarbonyl)-3-(4-methoxyphenyl)allylamine (3a). In a Pyrex tube under an atmosphere of argon, vinylsilane **1a** (250 mg, 1.1 mmol), *p*-iodoanisole (515 mg, 2.2 mmol), triethylamine (0.38

mL, 2.75 mmol), and acetonitrile (2 mL) were sequentially added at rt. The mixture was degassed (argon) and transferred via syringe to the catalyst (5% with respect to **1a**, conditions A and B in Table 1) prepared by the general procedure. The capped tube was heated at 50 °C for 48 h. The precipitation of metallic palladium indicated the end of the catalytic cycle. The reaction mixture was cooled to rt, diluted with ether (25 mL), and washed with water (2 × 30 mL). The aqueous phase was separated and extracted again with ether (2 × 25 mL). The combined organic phases were dried over magnesium sulfate, filtered, and concentrated. The crude mixture was purified by column chromatography with petroleum ether/ether (90:10) to give 260 mg (90%) of a 10:1 mixture of **2a** and **3a** as a light yellow oil. ^{1}H NMR spectrum allowed determination of the isomeric ratio by examination of the vinylic protons [δ 5.34 (**2a**), 6.45 (**3a**)].

2a: ^{1}H NMR δ 1.43 (s, 9H), 3.8 (s, 3H), 4.15 (br s, 2H), 4.65 (br s, 1H), 5.14 (s, 1H), 5.34 (s, 1H), 6.8 (d, J = 9 Hz, 2H), 7.4 (d, J = 9 Hz, 2H); ^{13}C NMR δ 28.6, 44.6, 55.4, 79.3, 111.8, 113.8, 126.5, 127.3, 136.7, 158.0, 158.4; MS m/z (relative intensity) 263 (4), 207 (100), 133 (44), 57 (34); HRMS (EI) calcd for $C_{15}H_{21}NO_3$ 263.152 14, found 263.151 54.

3a: ^{1}H NMR δ 1.45 (s, 9H), 3.75 (s, 3H), 4.15 (br s, 2H), 4.55 (br s, 1H), 5.56 (dt, J = 12.5 Hz, 6.7 Hz, 1H), 6.45 (d, J = 12.5 Hz, 1H), 6.8 (d, J = 9 Hz, 2H), 7.4 (d, J = 9 Hz, 2H).

1-{1-[1-(1-Ethoxyethoxy)methyl]vinyl}-4-methoxybenzene (2b) and (*Z*)-1-[1-(1-Ethoxyethoxy)propenyl]-4-methoxybenzene (3b). These compounds were prepared from vinylsilane **1b** (250 mg, 1.24 mmol) by the general method under condition A by heating for 48 h at 65 °C. The crude mixture was subjected to column chromatography using silica gel and petroleum ether/ether (100:3) to give a mixture that was further purified by PLC with petroleum ether/ether (10:1) to give 230 mg (79%) of a 1:1 mixture of **2b** and **3b** as a light yellow oil. ^{1}H NMR allowed for the determination of the isomeric ratio by examination of the vinylic protons [δ 5.45 (**2b**), 5.60 (**3b**)].

2b: ^{1}H NMR δ 1.2 (t, J = 3 Hz, 3H), 1.35 (d, J = 5 Hz, 3H), 3.35−3.70 (m, 2H), 3.8 (s, 3H), 4.2−4.6 (m, 2H), 4.81 (q, J = 5 Hz, 1H), 5.25 (s, 1H), 5.45 (s, 1H), 6.87 (d, J = 9 Hz, 2H), 7.42 (d, J = 9 Hz, 2H); ^{13}C NMR δ 14.8, 19.5, 54.9, 60.5, 66.7, 98.9, 112.0, 113.6, 127.2, 128.0, 158.0, 158.2. The two isomers were indistinguishable by GLC−MS analysis. MS m/z (relative intensity) 190 (2), 148 (100), 133 (29), 108 (8); HRMS (EI) calcd for $C_{14}H_{20}O_3$ 236.141 24, found 236.141 67.

3b: ^{1}H NMR δ 1.25 (t, J = 3 Hz, 3H), 1.47 (d, J = 5 Hz, 3H), 3.30−3.65 (m, 2H), 3.8 (s, 3H), 4.2−4.6 (m, 2H), 5.05 (q, J = 5 Hz, 1H), 5.60 (dt, J = 11.5 Hz, 6.5 Hz, 1H), 6.75−6.85 (m, 3H), 7.25 (d, J = 9 Hz, 2H); ^{13}C NMR δ 15.0, 20.4, 55.0, 62.4, 66.7, 100.9, 113.6, 129.2, 130.1, 132.0, 138.5, 159.7.

1-Methoxy-4-(1-(methoxymethyl)vinyl)benzene (2c) and (*Z*)-1-Methoxy-4-(3-methoxypropenyl)benzene (3c). These compounds were prepared from vinylsilane **1c** (102 mg, 0.71 mmol) following the typical procedure under condition A by heating 48 h at 80 °C. The crude mixture was subjected to column chromatography using silica gel and petroleum ether/ether (90/10) to give a mixture that was further purified by PLC with petroleum ether/ether (95/5) to give 38 mg (25%) of a 24:1 mixture of **2c** and **3c** as a light yellow oil. ^{1}H NMR allowed for the determination of the isomeric ratio by examination of the vinylic protons [δ 5.46 (**2c**), 5.76 (**3c**)].

2c: ^{1}H NMR δ 3.37 (s, 3H), 3.82 (s, 3H), 4.31 (br s, 2H), 5.24 (br s, 1H), 5.46 (br s, 1H), 6.89 (d, J = 9.5 Hz, 2H), 7.43 (d, J = 9.5 Hz, 2H); ^{13}C NMR δ 55.3, 57.8, 74.8, 112.9, 113.7, 127.2, 131.2, 143.4, 159.3. The two isomers were indistinguishable by GLC−MS analysis. MS m/z (relative intensity) 178 (18), 148 (100), 133 (75), 77 (20); HRMS (EI) calcd for $C_{11}H_{14}O_2$ 178.099 38, found 178.099 26.

3c: ^{1}H NMR δ 4.17−4.23 (m, 2H), 5.76 (dt, J = 11.9 Hz, 6.8 Hz, 1H), 6.55 (br d, J = 11.9 Hz, 1H).

***N*-(*tert*-Butoxycarbonyl)-3-(4-methoxyphenyl)but-3-enylamine (2d) and (*Z*)-*N*-(*tert*-Butoxycarbonyl)-4-(4-methoxyphenyl)but-3-enylamine (3d).** These compounds were prepared from vinylsilane **1d** (150 mg, 0.62 mmol) by the typical procedure under condition D by heating for 16 h at 80 °C. Column chromatography of the crude mixture with petroleum ether/ether (90:10) gave a mixture that was further purified by PLC with petroleum ether/ether (50:10) to provide 33 mg (19%) of a 20:1 mixture of **2d** and **3d** as a light yellow oil. ^{1}H NMR allowed for the determination of the isomeric ratio by examination of the vinylic protons [δ 5.00−5.07 (**2d**), 6.42 (**3d**)].

2d: ^{1}H NMR δ 1.43 (s, 9H), 2.68 (br t, J = 7.5 Hz, 2H), 3.15−3.35 (m, 2H), 3.82 (s, 3H), 4.58 (br s, 1H), 5.00−5.07 (m, 1H), 5.26−5.34 (m, 1H), 6.87 (d, J = 9 Hz, 2H), 7.36 (d, J = 9 Hz, 2H); ^{13}C NMR δ 28.4, 35.6, 39.2, 55.3, 79.1, 112.5, 113.8, 127.2, 132.7, 144.6, 155.8, 159.2; MS m/z (relative intensity) 277 (6), 221 (25), 204 (10), 176 (40), 160 (34), 147 (15), 57 (100); HRMS (EI) calcd for $C_{16}H_{23}NO_3$ 277.167 79, found 277.168 57.

3d: ^{1}H NMR δ 5.48 (d, J = 12 Hz, 1H), 6.42 (d, J = 12 Hz, 1H).

1-{1-[2-(1-Ethoxyethoxy)ethyl]vinyl}-4-methoxybenzene (2e) and (*Z*)-1-[4-(1-Ethoxyethoxy)but-1-enyl]-4-methoxybenzene (3e). These compounds were prepared from vinylsilane **1e** (150 mg, 0.69 mmol) by the general method under condition D by heating for 16 h at 80 °C. Column chromatography of the crude mixture with petroleum ether/ether (50:10) gave 29 mg (17%) of a 20:1 mixture of **2e** and **3e** as a light yellow oil. ^{1}H NMR allowed determination of the isomeric ratio by examination of the vinylic protons [δ 5.03 (**2e**), 5.60 (**3e**)].

2e: ^{1}H NMR δ 1.13 (t, J = 3 Hz, 3H), 1.25 (d, J = 5 Hz, 3H), 2.75 (t, J = 5 Hz, 2H), 3.35−3.75 (m, 4H), 3.8 (s, 3H), 4.65 (q, J = 5 Hz, 1H), 5.03 (s, 1H), 5.28 (s, 1H), 6.85 (d, J = 9 Hz, 2H), 7.35 (d, J = 9 Hz, 2H); ^{13}C NMR δ 15.2, 19.8, 35.8, 55.2, 60.8, 63.9, 99.5, 112.2, 113.6, 127.1, 133.2, 141.1, 158.1; MS m/z (relative intensity) 250 (2), 205 (8), 177 (15),161 (32), 147 (29), 133 (17), 73 (100); HRMS (EI) calcd for $C_{15}H_{22}O_3$ 250.156 89, found 250.156 14.

3e: ^{1}H NMR δ 5.60 (dt, J = 11.4 Hz, 1H), 6.10 (m, 1H).

(*E*)-3-(4-Methoxyphenyl)acrylic Acid Methyl Ester (3g). This compound was prepared from vinylsilane **1g** (200 mg, 0.86 mmol) by the typical procedure under condition A by heating for 16 h at 80 °C. PLC with petroleum ether/ether (40:10) gave 83 mg (50%) of **3g** as a colorless oil.

3g: IR (neat) 1702, 1606 cm^{-1}; ^{1}H NMR δ 3.80 (s, 3H), 3.82 (s, 3H), 6.29 (d, J = 16 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 16 Hz, 1H); ^{13}C NMR δ 51.5, 55.3, 114.3, 115.2, 128.0, 129.8, 144.5, 161.3, 167.6; MS m/z (relative intensity) 192 (59), 177 (2), 161 (100), 133 (51), 91 (10); HRMS (EI) calcd for $C_{11}H_{12}O_3$ 192.078 64, found 192.078 54.

(*E*)-3-Hexyl-4-(4-methoxyphenyl)but-3-en-2-one (3h). According to the typical procedure this compound was obtained from vinylsilane **1h** (250 mg, 0.87 mmol) under condition A by heating for 48 h at 80 °C. Column chromatography of the crude product over silica gel with petroleum ether/ether (90:5) gave 210 mg (93%) of **3h** as a colorless oil.

3h: IR (neat) 1661, 1603 cm^{-1}; ^{1}H NMR δ 0.85 (br s, 3H), 1.2−1.5 (m, 8H), 2.38 (s, 3H), 2.45 (m, 2H), 3.80 (s, 3H), 6.9 (d, J = 9.5 Hz, 2H), 7.35 (s, 1H), 7.43 (d, J = 9.5 Hz, 2H); ^{13}C NMR δ 14.3, 22.8, 26.2, 26.5, 29.2, 29.8, 31.8, 55.6, 114.5, 128.7, 131.6, 139.8, 141.7, 160.5, 200.9; MS m/z (relative intensity) 260 (53), 245 (19), 229 (20), 121 (33), 108 (38), 43 (100); HRMS (EI) calcd for $C_{17}H_{24}O_2$ 260.177 60, found 260.179 05.

(*E*)-4-(4-Methoxyphenyl)-3-phenylbut-3-en-2-one (3i). This compound was prepared from vinylsilane **1i** (250 mg, 0.89 mmol) by the typical procedure under condition A by heating for 48 h at 80 °C. Column chromatography of the crude on silica gel with petroleum ether/ether (90:5) afforded 140 mg (62%) of **3i** as a colorless oil.

3i: ^{1}H NMR δ 2.50 (s, 3H), 3.80 (s, 3H), 6.7 (d, J = 8.9 Hz, 2H), 6.9−7.5 (m, 5H), 7.61 (s, 1H), 7.95 (d, J = 8.9 Hz, 2H); ^{13}C NMR δ 27.7, 55.3, 113.6, 127.7, 129.0, 129.5, 132.6, 137.4, 138.7, 160.3, 199.0; MS m/z (relative intensity) 252 (4), 150 (39), 135 (100), 107 (11); HRMS (EI) calcd for $C_{17}H_{16}O_2$ 252.115 02, found 252.116 08.

(*Z*)-3-(4-Methoxyphenyl)-2-methylacrilic Acid Ethyl Ester (3l). The typical procedure (condition A) was applied to the synthesis of this compound starting from vinylsilane **1l** (100 mg, 0.59 mmol). After heating for 16 h at 80 °C, a crude

mixture was obtained which was purified by column chromatography with silica gel and petroleum ether/ether (95:5) as eluent. The resulting mixture was further purified by PLC with ethyl acetate/cyclohexane (95:5), affording 84 mg (64%) of **3l** as a colorless oil.

3l: IR ($CDCl_3$) 1709, 1607 cm^{-1}; ^1H NMR δ 1.22 (t, J = 7.1 Hz, 3H), 2.12 (s, 3H), 3.85 (s, 3H), 4.2 (q, J = 7.1 Hz, 2H), 6.7 (br s, 1H), 6.9 (d, J = 9 Hz, 2H), 7.26 (d, J = 9 Hz, 2H); ^{13}C NMR δ 19.9, 21.6, 55.2, 60.5, 113.4, 128.0, 128.8, 129.7, 134.2, 159.2, 169.9; MS m/z (relative intensity) 220 (100), 175 (39), 146 (63), 77 (32); HRMS (EI) calcd for $C_{13}H_{16}O_2$ 220.109 84, found 220.109 90.

Acknowledgment. This work was financially supported by the "Human Capital and Mobility Program" of the European Community and by the "Ministero dell' Università e della Ricerca Scientifica e Tecnologica" (MURST, ex 60%). E.B. is the grateful recipient of an individual postgraduate fellowship (ERB4001GT930614) of the European Community. The authors would like to acknowledge the helpful comments of Prof. S. Cacchi (University of Rome).

JO960301K