Solvent-controlled Stereoselectivity in the Hydrosilylation of Alk-1-ynes Catalysed by Rhodium Complexes

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New methodology for complete control of stereoselectivity in the hydrosilylation of alk-1-ynes is described. Alk-1-ynes react with triethylsilane to produce both (E)- and (Z)-vinylsilane, depending upon the reaction conditions, with high selectivity (91–97%). A [{Rh(cod)Cl}₂]-catalysed reaction using ethanol as a solvent gave rise to Z-selective conditions whilst E-selective conditions were achieved in [{Rh(cod)Cl}₂]/PPh₃ or [RhCl(PPh₃)₃]-catalysed reactions using acetonitrile as a solvent. A cationic rhodium(I) phosphine complex generated *in situ* was found to be the active species in E-selective conditions.

Hydrosilylation, an important reaction for the preparation of organosilicon compounds,[1] is generally more difficult than hydroboration in the absence of catalyst; transition metal complexes, however, effectively catalyse the reaction.

Hydrosilylation of alkynes has special synthetic value, since the reaction gives vinylsilane, a versatile synthetic intermediate for organic synthesis.[2] The preparation of vinylsilanes have been extensively studied, the simplest and most straightforward method being the hydrosilylation of alkynes. The major drawback of this method for the preparation of vinylsilane is, however, its lack of selectivity, the control of which, although highly desirable, is difficult. For example, the hydrosilylation of alk-1-yne can produce three isomers including stereoisomers (Scheme 1).[3]

a R = (CH₂)₃CH₃
b R = (CH₂)₅CH₃
c R = (CH₂)₇CH₃
d R = (CH₂)₂CH₂Cl
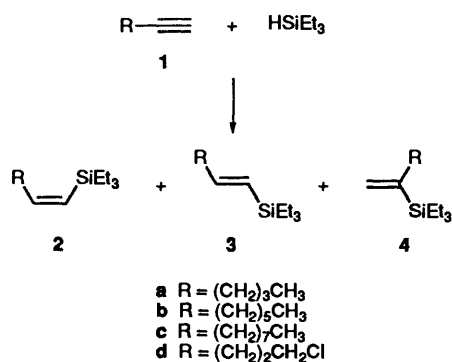
Scheme 1

The selectivity of the reaction depends on many factors, e.g., a substituent on the alkyne, the hydrosilane used, the catalytic metal species involved. The catalytic cycle of the hydrosilylation involves a variety of intermediates, the stabilization or destabilization of which by solvent has a great influence on the selectivity; thus, the effect of solvent on the reaction is likely to provide new methodology for the improvement of selectivity, although less attention has been paid to this. In the course of our organosilicon studies,[4] we have systematically investigated the rhodium complex-catalysed hydrosilylation of alk-1-ynes with triethylsilane in various solvents and found a means of controlling the stereoselectivity by choice of a suitable solvent and a ligand.[5]

Results

The hydrosilylation of hex-1-yne 1a with triethylsilane catalysed by several rhodium complexes and carried out in

Table 1 Rh-catalysed hydrosilylation of hex-1-yne 1a with Et₃SiH in benzene[a]

Entry	Catalyst	Yield (%)[b]	Product ratio[c]		
			2a	3a	4a
1	[RhCl(PPh₃)₃]	84	86	12	2
2[d]	[{Rh(cod)Cl}₂]	85	82	15	3
3	[RhH(CO)(PPh₃)₃]	69	84	10	6
4	[RhH(PPh₃)₄]	45	82	14	4

[a] A mixture of hex-1-yne (8 mmol), Et₃SiH (12 mmol), catalyst (0.008 mmol) and benzene (12 cm³) was stirred at room temperature for 41 h. [b] Isolated yield based on the amount of 1a employed. [c] Determined by ¹H NMR. [d] Catalyst (0.004 mmol).

benzene at room temperature for 41 h gave three isomeric products (see Scheme 1); the results are summarized in Table 1. All the reactions gave 2a as a major product, the degree of Z-selectivity being almost the same for each. The selectivity of the reaction appeared to be independent of the nature of the ligands coordinated to the rhodium.

Results for the hydrosilylation of hex-1-yne 1a with triethylsilane carried out in various solvents and with [{Rh(cod)Cl}₂] (cod = cycloocta-1,5-diene) and [RhCl(PPh₃)₃] as catalysts are summarized in Table 2. A high degree of Z-selectivity was attained by the use of EtOH or DMF (N,N-dimethylformamide) as a solvent in [{Rh(cod)Cl}₂]-catalysed reactions (entries 10 and 12), the selectivities being 94 and 97%, respectively. [RhCl(PPh₃)₃]-catalysed reactions using the same solvent were less Z-selective (vide infra) (entries 9 and 11). However, both catalysts gave similar results when used with benzene, acetone, THF (tetrahydrofuran) or dichloromethane (entries 1–8). The reaction in THF gave a somewhat lower yield of products, although Z-selectivity was higher than that of reactions in other solvents (entries 5 and 6). The reaction in triethylamine required heating. A [RhCl(PPh₃)₃]-catalysed reaction in triethylamine gave (Z)-vinylsilane 2a as a major product at 45 °C (entry 13), in contrast to the reaction with [{Rh(cod)Cl}₂] at 45 °C which gave no products (entry 14).

Use of a nitrile as solvent resulted in complete reversal of the stereoselectivity; the results are summarized in Table 3. A [RhCl(PPh₃)₃]-catalysed reaction in MeCN was highly E-selective to give 3a as a major product (entry 1) with 95% selectivity. A [{Rh(cod)Cl}₂]-catalysed reaction gave non-selective product formation and poor yields (entry 2). A [{Rh(cod)Cl}₂]/PPh₃-catalysed reaction gave a result comparable to that of the [RhCl(PPh₃)₃]-catalysed reaction

Table 2 The effect of solvent on Rh-catalysed hydrosilylation of hex-1-yne **1a** with Et₃SiH [a]

Entry	Catalyst	Solvent	Yield (%) [b]	Product ratio [c]		
				2a	**3a**	**4a**
1	[RhCl(PPh₃)₃]	Benzene	84	86	12	2
2 [d]	[{Rh(cod)Cl}₂]	Benzene	85	82	15	3
3	[RhCl(PPh₃)₃]	Acetone	86	66	33	1
4 [d]	[{Rh(cod)Cl}₂]	Acetone	89	68	29	3
5	[RhCl(PPh₃)₃]	THF	53	89	9	2
6 [d]	[{Rh(cod)Cl}₂]	THF	68	90	5	5
7	[RhCl(PPh₃)₃]	CH₂Cl₂	83	75	21	4
8 [d]	[{Rh(cod)Cl}₂]	CH₂Cl₂	91	77	13	10
9	[RhCl(PPh₃)₃]	EtOH	89	55	44	1
10 [d]	[{Rh(cod)Cl}₂]	EtOH	85	94	4	2
11	[RhCl(PPh₃)₃]	DMF	93	70	29	1
12 [d]	[{Rh(cod)Cl}₂]	DMF	80	97	1	2
13 [e]	[RhCl(PPh₃)₃]	Et₃N	88	75	25	0
14 [d,e]	[{Rh(cod)Cl}₂]	Et₃N	0	0	0	0

[a] A mixture of hex-1-yne (8 mmol), Et₃SiH (12 mmol), catalyst (0.008 mmol) and solvent (12 cm³) was stirred at room temperature for 41 h. [b] Isolated yield based on the amount of **1a** employed. [c] Determined by ¹H NMR. [d] Catalyst (0.004 mmol). [e] At 45 °C.

Table 3 Rh-catalysed hydrosilylation of hex-1-yne **1a** with Et₃SiH in nitrile solvent [a]

Entry	Catalyst	P/Rh	Solvent	Yield (%) [b]	Product ratio [c]		
					2a	**3a**	**4a**
1 [d]	[RhCl(PPh₃)₃]	3	MeCN	86	3	95	2
2	[{Rh(cod)Cl}₂]	0	MeCN	18	36	33	31
3 [e]	[{Rh(cod)Cl}₂] + PPh₃	2	MeCN	93	2	97	1
4 [d]	[RhCl(PPh₃)₃]	3	PrCN	86	3	96	1
5 [e]	[{Rh(cod)Cl}₂] + PPh₃	2	PrCN	85	2	96	2

[a] A mixture of hex-1-yne (8 mmol), Et₃SiH (12 mmol), catalyst (0.012 mmol) and solvent (12 cm³) was stirred at room temperature for 41 h. [b] Isolated yield based on the amount of **1a** employed. [c] Determined by ¹H NMR. [d] For 6 h, catalyst (0.024 mmol). [e] PPh₃ (0.048 mmol).
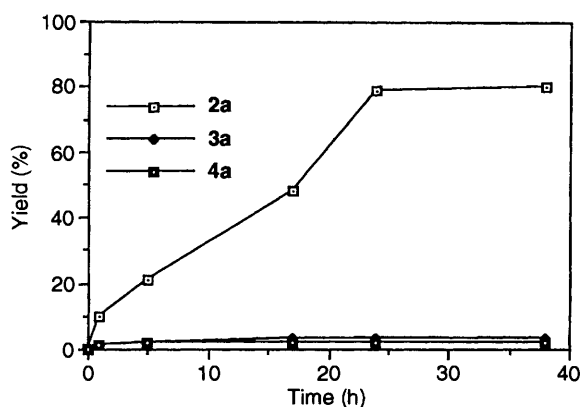

Fig. 1 The time course of the hydrosilylation of hex-1-yne in EtOH: 1-hexyne (8 mmol), HSiEt₃ (12 mmol), [{Rh(cod)Cl}₂] (0.004 mmol) and EtOH (12 cm³) at room temperature for 41 h
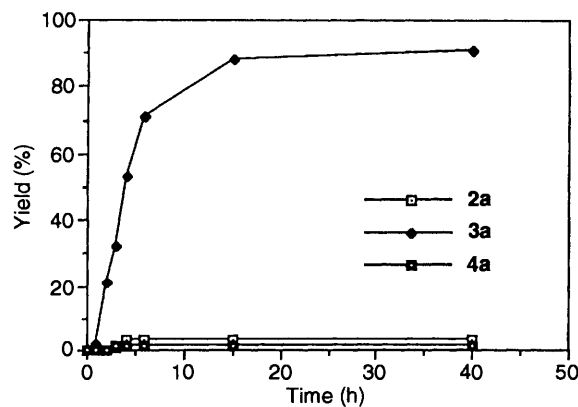

Fig. 2 The time course of the hydrosilylation of hex-1-yne in MeCN: 1-hexyne (8 mmol), HSiEt₃ (12 mmol), [{Rh(cod)Cl}₂] (0.012 mmol), PPh₃ (0.048 mmol) and MeCN (12 cm³) at room temperature for 41 h

(entry 3). The reactions in PrCN were also highly *E*-selective (entries 4 and 5). Although a rhodium catalyst has been known to show *Z*-selectivity,[6] to the best of our knowledge, our results which show that a rhodium-phosphine species in a nitrile solvent gives rise to *E*-selectivity represents the first example of highly *E*-selective hydrosilylation of alk-1-ynes with triethylsilane catalysed by a rhodium complex. Such results indicate that choice of an appropriate solvent and ligand is important.

To shed more light on the course of the reaction, we monitored both a [{Rh(cod)Cl}₂]-catalysed reaction in EtOH and a [{Rh(cod)Cl}₂]/PPh₃-catalysed one in MeCN, respectively; results were shown in Figs. 1 and 2. The reaction in EtOH gave (*Z*)-vinylsilane **2a** selectively and that in MeCN gave (*E*)-vinylsilane **3a**; there was no isomerization between (*Z*)-vinylsilane **2a** and (*E*)-vinylsilane **3a** under these reaction

conditions. Such results indicate that the reaction in EtOH proceeded by way of *trans* addition and that in MeCN by way of *cis* addition. Complete control of the mode of addition could, thus, be attained.

This solvent-assisted control of stereoselectivity was then applied to other alk-1-ynes; the results for such reactions are summarized in Table 4. *Z*-Selective conditions were [{Rh-(cod)Cl}₂]-catalysed reaction in EtOH and (*E*)-selective conditions were [{Rh(cod)Cl}₂]/PPh₃-catalysed reaction in MeCN; as seen from the results in Table 4, all the reactions were highly selective. The reactions of dec-1-yne **1c** gave a somewhat lower yield of products compared to that of hex-1-yne **1a** or oct-1-yne **1b** (entries 1–4). The hydrosilylation of 5-chloropent-1-yne **1d** under *E*-selective conditions gave a comparable yield of products to other cases (entry 6), while the reaction under

Table 4 Solvent-assisted hydrosilylation of alk-1-ynes 1b–d with triethylsilane[a]

Entry	Substrate	Catalyst	P/Rh	Solvent	Yield (%)[c]	Product ratio[d]		
						2	**3**	**4**
1	Oct-1-yne 1b	[{Rh(cod)Cl}$_2$]	0	EtOH	94	91	6	3
2[b]	Oct-1-yne 1b	[{Rh(cod)Cl}$_2$]/PPh$_3$	2	MeCN	86	3	95	2
3	Dec-1-yne 1c	[{Rh(cod)Cl}$_2$]	0	EtOH	77	91	5	4
4[b]	Dec-1-yne 1c	[{Rh(cod)Cl}$_2$]/PPh$_3$	2	MeCN	76	3	95	2
5	5-Chloropent-1-yne 1d	[{Rh(cod)Cl}$_2$]	0	EtOH	37	94	3	3
6[b]	5-Chloropent-1-yne 1d	[{Rh(cod)Cl}$_2$]/PPh$_3$	2	MeCN	84	6	91	3

[a] A mixture of alk-1-yne (8 mmol), triethylsilane (12 mmol), catalyst (0.004 mmol) and solvent (12 cm^3) was stirred at room temperature for 41 h. [b] Catalyst (0.012 mmol) and triphenylphosphine (0.048 mmol). [c] Isolated yield based on the amount of 1 employed. [d] Determined by ^{1}H NMR.

**Table 5** Cationic Rh^I complex-catalysed hydrosilylation of hex-1-yne 1a with Et$_3$SiH[a]

Entry	Solvent	Yield (%)[b]	Product ratio[c]		
			2a	**3a**	**4a**
1[d]	Acetone	97	1	99	0
2[e]	CH$_2$Cl$_2$	88	6	94	0
3[f]	MeCN	77	2	95	3
4[d]	EtOH	84	5	95	0

[a] A mixture of hex-1-yne (8 mmol), Et$_3$SiH (12 mmol), [Rh(cod)$_2$][BF$_4$] (0.016 mmol), PPh$_3$ (0.032 mmol) and solvent (12 cm^3) was stirred at room temperature. [b] Isolated yield based on the amount of 1a employed. [c] Determined by ^{1}H NMR. [d] For 30 min. [e] For 1 h. [f] For 41 h.

Z-selective conditions gave a decreased yield of products accompanied by formation of a considerable amount of insoluble solid (entry 5).
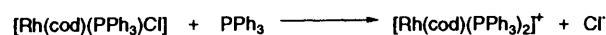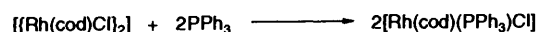
Discussion

It is proposed that the mechanism for Z-selective rhodium-catalysed hydrosilylation of an alk-1-yne involves isomerization of the β-silylalkenylrhodium complex 5, formed by the insertion of alkyne into silicon–rhodium bond, via the zwitterionic carbene complex 6.[3c] (Z)-Vinylsilane is produced by the reductive elimination of 7 (Scheme 2). The ease of the

Scheme 2
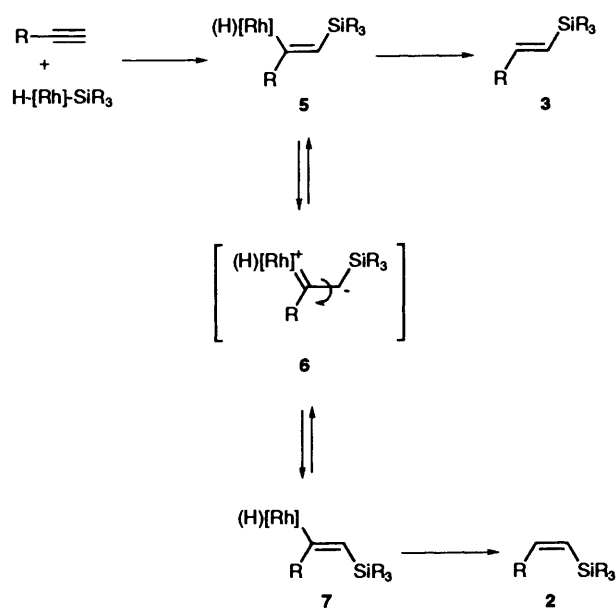
isomerization would depend on stabilization of the zwitterionic intermediate 6, polar solvents such as EtOH or DMF helping to achieve this and hence increasing the Z-selectivity.

The reaction in MeCN gave the reverse stereoselectivity, and its mechanism must, therefore, be different. Since triphenylphosphine is necessary for the highly selective formation of (E)-vinylsilane 3, clearly the rhodium-phosphine species plays a crucial role. [{Rh(cod)Cl}$_2$] is reported to react with PPh$_3$ to give a monomeric phosphine species,[7] whilst coordination of further molecule of PPh$_3$ to such a species in a polar medium (e.g. an alcohol) gives, by dissociation of a chloro ligand, a cationic species, isolable as a tetraphenylborate or percholate salt (Scheme 3).[8] Since it can be assumed that a cationic

$$[\{Rh(cod)Cl\}_2] + 2PPh_3 \longrightarrow 2[Rh(cod)(PPh_3)Cl]$$

$$[Rh(cod)(PPh_3)Cl] + PPh_3 \xrightarrow{\text{Polar solvent}} [Rh(cod)(PPh_3)_2]^+ + Cl^-$$

Scheme 3

rhodium(I) complex generated by the dissociation of a chloro ligand in MeCN would catalyse E-selective hydrosilylation, we examined cationic rhodium(I) complex-catalysed hydrosilylation of hex-1-yne with triethylsilane.

Results for the reaction of 1a with triethylsilane catalysed by [Rh(cod)$_2$][BF$_4$]/PPh$_3$ are summarized in Table 5. As expected, all the reactions examined were highly E-selective; this confirms that a cationic rhodium(I) complex was the active species under E-selective conditions.

Unlike [{Rh(cod)Cl}$_2$]-catalysed reactions of 1a in EtOH or DMF, the [RhCl(PPh$_3$)$_3$]-catalysed ones in EtOH or DMF were less Z-selective. This decrease in Z-selectivity is rationalized in terms of the co-existence of cationic Rh^I species and neutral Rh^I species. In such cases, a cationic Rh^I complex would be formed to some extent by the dissociation of a chloro ligand in such a polar solvent; thus, (E)-vinylsilane 3a was obtained as a minor product. In contrast, a chloro ligand in [{Rh(cod)Cl}$_2$] could not dissociate, PPh$_3$ being absent.

In conclusion, a high degree of the stereochemical control is attainable in the hydrosilylation of an alk-1-yne with triethylsilane. [{Rh(cod)Cl}$_2$]-catalysed reactions in EtOH or DMF give high Z-selectivity, whereas [{Rh(cod)Cl}$_2$]/PPh$_3$ or [RhCl(PPh$_3$)$_3$]-catalysed reactions in MeCN or PrCN are highly E-selective. The reactivity of the rhodium catalyst described here is useful for the preparation of vinylsilanes and the synthetic application[9] and mechanistic detail of cationic rhodium(I) complex-catalysed hydrosilylation of alk-1-ynes will be published separately.

Experimental

General Methods.—The ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX-270 spectrometers with Me_4Si as an internal standard. *J* Values are given in Hz. Gas chromatographic analysis was carried out on a Shimadzu GC-14A with a Shimadzu CR-6A integrator. Elemental analyses were performed at the Microanalytical Centre of Kyoto University.

Materials.—Reagents were purified by distillation under argon before use. Solvents were purified by the usual procedures. [$RhCl(PPh_3)_3$],[10] [{$Rh(cod)Cl$}$_2$],[11] [$RhH(CO)$-(PPh_3)$_3$],[12] [$RhH(PPh_3)_4$][13] and [$Rh(cod)_2$][BF_4][14] were prepared by literature methods. Chromatographic purification was performed with silica gel 60 (70–230 mesh, Merck).

General Procedure for the Hydrosilylation of Alk-1-ynes with Triethylsilane.—A two-necked flask equipped with a magnetic stirring bar was charged with catalyst (and PPh_3). The reactor was evacuated and filled with argon. Solvent (12 cm³) was added to the flask and the mixture was stirred in 5 min. Alk-1-yne (8 mmol) was then added *via* a syringe to the mixture, followed by similar addition of triethylsilane (1.395 g, 12 mmol). The mixture was stirred for the reaction times and at the temperatures shown in the Tables. After the reaction was completed, the solution was concentrated under reduced pressure. The residue was chromatographed to give vinylsilanes as colourless oils. Analytically pure samples for elemental analysis were purified by GLC.

(Z)-1-*Triethylsilylhex*-1-*ene* **2a**.[3c] δ_H(270 MHz; $CDCl_3$) 0.59 [6 H, q, *J* 7.9, $Si(CH_2CH_3)_3$], 0.86–0.99 (12 H, m, CH_3), 1.25–1.39 (4 H, m, $CH_3CH_2CH_2$), 2.03–2.12 (2 H, m, $CH_2CH=$), 5.37 [1 H, dt, *J* 14.2, 1.3, =CH(SiEt₃)] and 6.36 (1 H, dt, *J* 14.2, 7.3, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 4.8 ($SiCH_2CH_3$), 7.5 ($SiCH_2CH_3$), 14.0 (CH_3), 22.5 (CH_2), 32.0 (CH_2), 33.9 ($CH_2CH=$), 124.9 (vinyl) and 150.3 (vinyl).

(E)-1-*Triethylsilylhex*-1-*ene* **3a**.[3c] δ_H(270 MHz; $CDCl_3$) 0.54 [6 H, q, *J* 7.9, $Si(CH_2CH_3)_3$], 0.86–0.97 (12 H, m, CH_3), 1.24–1.43 (4 H, m, $CH_3CH_2CH_2$), 2.07–2.16 (2 H, m, $CH_2CH=$), 5.53 [1 H, dt, *J* 18.5, 1.3, =CH(SiEt₃)] and 6.02 (1 H, dt, *J* 18.5, 6.3, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 3.6 ($SiCH_2CH_3$), 7.4 ($SiCH_2CH_3$), 14.0 (CH_3), 22.2 (CH_2), 31.1 (CH_2), 36.8 ($CH_2CH=$), 125.5 (vinyl) and 148.8 (vinyl).

2-*Triethylsilylhex*-1-*ene* **4a**.[3c] Compound **4a** could not be isolated in pure form but was identified by comparison of its NMR spectra characteristics with those reported in the literature.[3c]

(Z)-1-*Triethylsilyloct*-1-*ene* **2b**.[6a] δ_H(270 MHz; $CDCl_3$) 0.61 [6 H, q, *J* 7.9, $Si(CH_2CH_3)_3$], 0.89 (3 H, t, *J* 6.9, CH_3), 0.95 [9 H, t, *J* 7.9, $Si(CH_2CH_3)_3$], 1.19–1.39 (8 H, m, CH_2), 2.09 (2 H, q, *J* 6.6, $CH_2CH=$), 5.38 [1 H, d, *J* 14.2, =CH(SiEt₃)] and 6.38 (1 H, dt, *J* 14.2, 6.6, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 4.8 ($SiCH_2CH_3$), 7.5 ($SiCH_2CH_3$), 14.1 (CH_3), 22.7 (CH_2), 29.1 (CH_2), 29.8 (CH_2), 31.8 (CH_2), 34.2 (CH_2), 124.9 (vinyl) and 150.4 (vinyl).

(E)-1-*Triethylsilyloct*-1-*ene* **3b**.[6a] δ_H(270 MHz; $CDCl_3$) 0.54 [6 H, q, *J* 7.9, $Si(CH_2CH_3)_3$], 0.88 (3 H, t, *J* 6.9, CH_3), 0.93 [9 H, t, *J* 7.9, $Si(CH_2CH_3)_3$], 1.16–1.52 (8 H, m, CH_2), 2.11 (2 H, q, *J* 6.3, $CH_2CH=$), 5.53 [1 H, dt, *J* 18.8, 1.3, =CH(SiEt₃)], 6.03 (1 H, dt, *J* 18.8, 6.3, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 3.6 ($SiCH_2CH_3$), 7.4 ($SiCH_2CH_3$), 14.1 (CH_3), 22.6 (CH_2), 28.8 (2CH_2), 31.7 (CH_2), 37.1 (CH_2), 125.5 (vinyl) and 148.8 (vinyl).

2-*Triethylsilyloct*-1-*ene* **4b**. Although compound **4b** could not be isolated pure, spectral characteristics for the impure sample were the same as for **2b**, except for the signals at δ_H(270 MHz; $CDCl_3$) 5.27–5.29 (m, 1 H, vinyl) and 5.61–5.64 (m, 1 H, vinyl).

(Z)-1-*Triethylsilyldec*-1-*ene* **2c**. (Found: C, 75.2; H, 13.4. $C_{16}H_{34}Si$ requires C, 75.50; H, 13.47; Si, 11.03%); δ_H(270 MHz; $CDCl_3$) 0.61 [6 H, q, *J* 7.9, $Si(CH_2CH_3)_3$], 0.88 (3 H, t, *J*

6.9, CH_3), 0.94 [9 H, t, *J* 7.9, $Si(CH_2CH_3)_3$], 1.27–1.36 (12 H, m, CH_2), 2.09 (2 H, q, *J* 7.3, $CH_2CH=$), 5.38 [1 H, dt, *J* 14.2, 1.3, =CH(SiEt₃)] and 6.37 (1 H, dt, *J* 14.2, 7.3, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 4.7 ($SiCH_2CH_3$), 7.5 ($SiCH_2CH_3$), 14.1 (CH_3), 22.7 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 31.9 (CH_2), 34.1 ($CH_2CH=$), 124.9 (vinyl) and 150.4 (vinyl).

(E)-1-*Triethylsilyldec*-1-*ene* **3c**. (Found: C, 75.4; H, 13.7. $C_{16}H_{34}Si$ requires C, 75.50; H, 13.47; Si, 11.03%); δ_H(270 MHz; $CDCl_3$) 0.54 [6 H, q, *J* 7.9, $Si(CH_2CH_3)_3$], 0.88 (3 H, t, *J* 6.9, CH_3), 0.93 [9 H, t, *J* 7.9, $Si(CH_2CH_3)_3$], 1.27–1.41 (12 H, m, CH_2), 2.11 (2 H, q, *J* 6.6, $CH_2CH=$), 5.53 [1 H, dt, *J* 18.8, 1.7, =CH(SiEt₃)] and 6.03 (1 H, dt, *J* 18.8, 6.3, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 3.6 ($SiCH_2CH_3$), 7.4 ($SiCH_2CH_3$), 14.1 (CH_3), 22.7 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 37.1 ($CH_2CH=$), 125.5 (vinyl) and 148.8 (vinyl).

2-*Triethylsilyldec*-1-*ene* **4c**. Although compound **4c** could not be isolated pure, spectral characteristics for the impure sample were the same as those for **2c**, except for signals at δ_H(270 MHz; $CDCl_3$) 5.27–5.29 (m, 1 H, vinyl) and 5.61–5.64 (m, 1 H, vinyl).

(Z)-5-*Chloro*-1-*triethylsilylpent*-1-*ene* **2d**. (Found: C, 60.1; H, 10.6; Cl, 16.1. $C_9H_{21}ClSi$ requires C, 60.37; H, 10.59; Cl, 16.20; Si, 12.84%); δ_H(270 MHz; $CDCl_3$) 0.63 [6 H, q, *J* 7.3, $Si(CH_2CH_3)_3$], 0.95 [9 H, t, *J* 7.3, $Si(CH_2CH_3)_3$], 1.86 (2 H, quintet, *J* 7.3, $CH_2CH_2CH_2$), 2.26 (2 H, q, *J* 7.3, $CH_2CH=$), 3.54 (2 H, t, *J* 7.3, $ClCH_2$), 5.48 [1 H, dt, *J* 14.2, 1.3, =CH(SiEt₃)] and 6.33 (1 H, dt, *J* 14.2, 7.3, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 4.6 ($SiCH_2CH_3$), 7.5 ($SiCH_2CH_3$), 31.2 (CH_2), 32.6 (CH_2), 44.5 (CH_2), 127.0 (vinyl) and 147.7 (vinyl).

(E)-5-*Chloro*-1-*triethylsilylpent*-1-*ene* **3d**. (Found: C, 60.4; H, 10.6; Cl. 16.3. $C_9H_{21}ClSi$ requires C, 60.37; H, 10.59; Cl, 16.20; Si, 12.84%); δ_H(270 MHz; $CDCl_3$) 0.54 [6 H, q, *J* 7.9, $Si(CH_2CH_3)_3$], 0.91 [9 H, t, *J* 7.9, $Si(CH_2CH_3)_3$], 1.86 (2 H, quintet, *J* 7.3, $CH_2CH_2CH_2$), 2.26 (2 H, q, *J* 7.3, $CH_2CH=$), 3.51 (2 H, t, *J* 6.3, $ClCH_2$), 5.61 [1 H, d, *J* 18.8, =CH(SiEt₃)] and 5.98 (1 H, dt, *J* 18.8, 6.3, $CH_2CH=$); δ_C(67.8 MHz; $CDCl_3$) 3.4 ($SiCH_2CH_3$), 7.3 ($SiCH_2CH_3$), 31.6 (CH_2), 34.0 (CH_2), 44.3 (CH_2), 127.6 (vinyl) and 146.1 (vinyl).

5-*Chloro*-2-*triethylsilylpent*-1-*ene* **4d**. Although compound **4d** could not be isolated pure, spectral characteristics of the impure sample were the same as those for **2d**, except for signals at δ_H(270 MHz; $CDCl_3$) 5.34–5.37 (m, 1 H, vinyl) and 5.65–5.68 (m, 1 H, vinyl).

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