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Hydrosilylation of alkynes catalyzed by platinum on carbon

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Abstract

Hydrosilylation of terminal and internal alkynes with chlorosilanes, alkylsilanes, and alkoxysilanes catalyzed by platinum on carbon are discussed. The yields of the isolated vinylsilanes are high and the selectivity of the product depends on the silane used. Hydrosilylation of alkynes with chlorosilanes produced the β-*trans* vinylsilanes, while alkyl and alkoxysilanes produced two or three vinylsilane isomers. The selectivity of the catalyst platinum on carbon is similar to Karstedt's catalyst in the reaction of phenylacetylene with triethylsilane or triethoxysilane. High resolution electron microscopy showed colloidal platinum to be present in these reactions. © 2002 Published by Elsevier Science B.V.

Keywords: Hydrosilylation; Catalyst; Colloids; Alkynes; Silanes

1. Introduction

The hydrosilylation reaction is second only to the direct process in producing compounds with silicon carbon bonds. Thus, it is not surprising that efforts to improve the efficiency and broaden the range of application of the process are ongoing [1]. The hydrosilylation of alkynes results in vinylsilanes that are versatile starting materials for natural products [2] and polymers [3]. Selectivity is a very important consideration in the hydrosilylation of alkynes because in addition to regioisomers and stereoisomers as legitimate products there is also the likelihood of the generation of diadducts [4].

Platinum on carbon (Pt/C) was first reported by Wagner to be an active hydrosilylation catalyst for alkenes and alkynes at 100–300 °C and 30–1000 psi [5]. Essentially, the stereochemistry of the addition of silanes to a variety of terminal alkynes using platinum on carbon or chloroplatinic acid [6] was the same. This supported the idea that similar mechanisms were operating and prompting the suggestion that finely divided platinum particles might be common intermediates in these reactions [4,7].

Evidence that platinum colloids play an essential role in hydrosilylation has been offered by Lewis and coworkers [8]. The belief that many ostensibly homogeneous platinum group metal catalyzed hydrosilylation reactions go through colloidal intermediates has broad implications regardless of which starting species is used as the catalyst [9]. The type of platinum compound that would generate the highest activity is one in which formation of a single Pt^0 atom and concomitant loss of ligands are facile [8f,8i]. Therefore, the most active catalysts are Pt^0L_x complexes where L is olefinic and least active catalysts are Pt^{II} or Pt^{IV} complexes with strongly bound ligands such as phosphines, amines and sulfides.

The hydrosilylation of alkynes offers a greater synthetic challenge than alkenes because of the higher reactivity of the triple bond and the potential for a broader product distribution. In this publication, we report the efficiency and selectivity of platinum on activated carbon in the formation of vinylsilanes. The yields and regioselectivities of the products from the addition of alkynes to silanes have been emphasized. A comparison of the reaction conditions was done to explore effects on selectivity. To assess the catalyst's efficiency against a common catalyst, a comparison of the selectivity was made with Karstedt's catalyst [8d]. In addition, the intermediacy of colloidal platinum in

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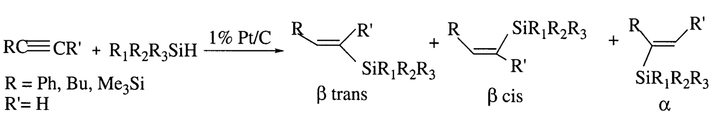
these reactions has been established by high resolution electron microscopy (HREM).

2. Results and discussion

All vinylsilanes were prepared by treating equimolar amounts of silane and alkyne with 0.8 g of 1% platinum on carbon (4.1 mmol of Pt, 0.00025 mol% Pt with respect to the alkyne). After 4–5 h of reflux (50–100 °C depending on the silane), the vinylsilanes were distilled under vacuum in 80–95% isolated yields. Most alkynes produced a mixture of regioisomers and stereoisomers, except for the symmetrical internal alkynes, which produced only the *cis* vinylsilane. The isomers were separated, where possible, by spinning band distillation or preparative GC. Structures were determined by ^{1}H-, and ^{13}C-NMR and mass spectral techniques.

2.1. Reactions with terminal alkynes (Reaction (1))



(1)

The reactions of phenylacetylene with silanes gave good yields, ranging from 81% ($MeHSiCl_2$) to 91%(Et_3SiH) (entries 1–5, Table 1). The distribution of adducts depends on the silane. Chlorosilanes are highly selective, forming virtually only β-*trans* products, while the alkyl and alkoxysilanes gave mixtures of α- and β-isomers. No Z-isomers were isolated in any of the reactions. The major by-product in these reactions was poly(phenylacetylene). It has been reported that the catalyst, $[\{Pt(SiCl_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$, used in the reaction of phenylacetylene with trichlorosilane gave 80% yield of β-*trans* isomer [10]. Similarly, 80% yield of a 76:24 mixture of β-*trans*:α triethoxysilylstyrene was obtained using $[\{Pt[Si(CH_2Ph)Me_2](\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ as the catalyst with triethoxysilane [10].

Reaction of 1-hexyne with chlorosilanes gave yields ranging from 88% ($MeSiHCl_2$) to 97% ($PhHSiCl_2$) (entries 6–11, Table 1). Chlorosilanes were more selective than triethylsilane, typically generating > 90% yields of the β-*trans* isomers. The reactions in entries 2, 3, 6 and 7 produced minor products in quantities too small to be isolated and characterized. Based on the identities of the minor products in the other entries, assigning α isomer structures seems reasonable. As with phenylacetylene, the alkyl and alkoxysilanes were less selective, producing all three isomers. However, Tsipis observed better selectivity with $[(Cy_3P)(PhMe_2Si)(\mu\text{-}H)Pt]_2$ as the catalyst [11]. He observed 95:5 mixture of β-*trans*:α for triethylsilane, trichlorosilane, and methyldichlorosilane in yields > 90%.

The activity and life of platinum on carbon from different lot numbers varied. When one sample of the catalyst was recycled by distilling off the products and adding more 1-hexyne and $MeSiHCl_2$, the yields were 95, 87 and 11%. Each time this procedure was repeated, similar results were obtained, i.e. a sharp drop in the

Table 1
Hydrosilylation of terminal alkynes [a]

Entry	R	Silane	Product distribution [b](%)			Isolated yield (%)
			β-*trans*	β-*cis*	α	
1	Ph	$HSiCl_3$	100	–	–	87
2	Ph	$MeSiHCl_2$	93	–	7	81
3	Ph	$PhSiHCl_2$	89	–	8	89
4	Ph	Et_3SiH	77	–	23	91
5	Ph	$(EtO)_3SiH$	70	–	30	89
6	Bu	$HSiCl_3$	92	–	8	95
7	Bu	$MeSiHCl_2$	91	–	9	88
8	Bu	$PhSiHCl_2$	100	–	–	97
9	Bu	$(EtO)_3SiH$	86	2	12	87
10	Bu	$(EtO)_3SiH$	75	12	13	86
11	Bu	Ph_2MeSiH	86	–	14	71
12	Me_3Si	$HSiCl_3$	100	–	–	92
13	Me_3Si	$MeHSiCl_2$	100	–	–	87
14	Me_3Si	Et_3SiH	74	26	–	88
15	Me_3Si	$(EtO)_2SiH$	88	12	–	97

[a] Alkyne (20 mmol)/20 mmol silane: 4.1 μmol Pt were used in all the above reactions.

[b] The product distribution is determined by the relative% areas in GC.

Table 2
Hydrosilylation of symmetrical alkynes [a]

Entry	R,R′	Silane	Product	Isolated yield (%) (purity) [b]
1	Et	$HSiCl_3$	*cis*-isomer	95 (100)
2	Et	$MeSiHCl_2$	*cis*-isomer	86 (97)
3	Et	Ph_2MeSiH	*cis*-isomer	85 (91)
4	Et	Et_3SiH	*cis*-isomer	95 (99)
5	Et	$(EtO)_3SiH$	*cis*-isomer	95 (99)
6	Ph	$HSiCl_3$	*cis*-isomer	63 (93)
7	Ph	$MeSiHCl_2$	*cis*-isomer	78 (98)
8	Ph	Et_3SiH	*cis*-isomer	90 (99)
9	Ph	$(EtO)_3SiH$	*cis*-isomer	94 (98)
10	Me_3Si	$MeHSiCl_2$	–	–
11 [c]	Me_3Si	Et_3SiH	–	–

[a] Alkyne (20 mmol)/20 mmol silane; 4.1 μmol Pt were used in all above reactions.

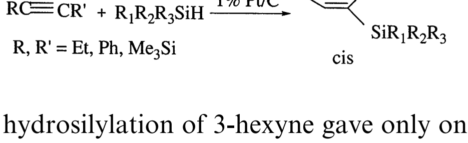
[b] The product distribution is determined by the relative % areas in GC.

[c] The reaction was heated for 96 h at 65 °C.

yield of the third cycle. However, recycling a sample of catalyst with a different lot number in the same manner resulted in yields of > 85% through five cycles. Thus, while we may normally ascribe the decrease in activity to poisoning or destruction of the catalytic species [12,13] it is clear that, at least for samples of platinum on carbon, the history of the sample can be vital.

The results from the hydrosilylation of trimethylsilylacetylene with trichlorosilane and methyldichlorosilane show excellent selectivities (entries 12–15, Table 1). There is exclusive formation of β-*trans* isomer in 87–92% yields. Triethylsilane and triethoxysilane gave yields of 88 and 97% of hydrosilylated products, respectively, as mixtures of the β-*trans* and β-*cis* isomers. There is no evidence for the formation of α-isomer from trimethylsilylacetylene. Thus, it appears that steric considerations dominate the regioselectivity. This rationale has been used to explain similar observations in the hydroboration of trimethylsilylacetylene [14].

2.2. Reactions with symmetrical internal alkyne (Reaction (2))

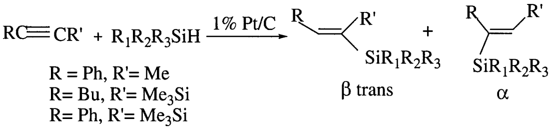


(2)

The hydrosilylation of 3-hexyne gave only one isomer in all cases (entries 1–5, Table 2). The stereochemistry of the products was not determined. However, in the examples studied previously, the *cis*-isomers were formed as a result of the expected *cis*-addition of Si–H [10,11]. All silanes were efficient in the hydrosilylation of 3-hexynes with yields ranging from 85% (Ph_2MeSiH) to 95% ($HSiCl_3$ and Et_3SiH). These results compare favorably to those obtained by Tamao et al. using $[Et_2(bpy)Ni]$(bpy = bipyridyl) as a catalyst [15]. With trichlorosilane and 3-hexyne, they observed 7% yield of the hydrosilylated product. The remaining product was the diadduct, $CH_3CH_2CH(SiCl_3)CH(SiCl_3)CH_2CH_3$.

Entries 6 and 7 in Table 2 reveal the sluggishness of the diphenylacetylene towards chlorosilanes. After 7 h of refluxing, only 63 and 78% yields of vinylsilanes resulted with trichlorosilane and methyldichlorosilane, respectively, similar to that observed by Green et al. [10]. The reaction with trichlorosilane required 8 h to reach 76% yield of the *cis*-isomer using $[\{Pt[Si(CH_2Ph)Me_2](\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ as the catalyst. The alkyl and alkoxysilanes gave higher yields (> 90%, entries 8 and 9). The hydrosilylation of 1,2-bis (trimethylsilyl)acetylene, did not occur under the usual reaction conditions (4–5 h, 50–100 °C) nor with heating for up to 96 h. The two trimethylsilyl groups, by means of steric and/or electronic means clearly deactivate the triple bond towards hydrosilylation.

2.3. Reactions with unsymmetrical internal alkynes (Reaction (3))



(3)

The results of hydrosilylation of phenylmethylacetylene are shown in entries 1–4 of Table 3. The reactions were complete in less than 4 h and with yields greater than 90%. The selectivity of the product depends on the particular silane; an observation similar to that made by Voronkov et al. [16]. Trichlorosilane and triethylsilane gave the α-isomer as the major product, while methyldichlorosilane and triethoxysilane gave the β-isomer in excess. Previous attempts to hydrosilylate this alkyne were less successful. Using a nickel(II) complex, Tamao et al. obtained a 52% yield of an unidentified mixture of isomers with methyldichlorosilane [15].

The results of the hydrosilylation of butyltrimethylsilylacetylene (entries 5–9) are similar to those with other alkynes. Yields remained high with the exception of $PhHSiCl_2$ (56%). For $MeHSiCl_2$ and Et_3SiH, a small quantity (< 2%) of a third isomer was detected but not identified. Hydrosilylation of phenyltrimethylsilylacetylene with $HSiCl_3$ (entry 10) was unsuccessful even after prolonged reaction times (up to 24 h) at temperatures as high as 62 °C. This observation appears inconsistent with other results, since $HSiCl_3$ is one of the more reactive silanes in the study. $MeSiHCl_2$ was inert at room temperature. However, when the reaction mixture was heated at 72 °C for 1 h, a 78% yield of a 94:6

mixture of isomers was isolated. Et_3SiH and $(EtO)_3SiH$, were sluggish, requiring 105 h and 21 h to reach 25 and 91% yields, respectively. The most efficient silane is $PhSiHCl_2$, requiring only 4 h to yield 92%. These results indicate that hydrosilylation of alkynes can be dominated by steric factors.

2.4. Comparison of the selectivity of Karstedt's catalyst with that of platinum on carbon

Lewis et al. showed that Karstedt's catalyst is an efficient catalyst for the hydrosilylation of alkynes [17]. Table 4 compares the selectivity of the platinum on carbon with that of Karstedt's catalyst $[Pt_2(Me_2(CH{=}CH_2)_2Si_2O)_3]$. In all cases, the selectivity of the two catalysts is similar. Hydrosilylation of phenylacetylene with triethylsilane using Karstedt's catalyst produced a 82:18 ratio of β-*trans* to α, while platinum on carbon gave a 77:23 mixture of the two isomers (entry 1, Table 4). The reaction of the triethoxysilane with phenylacetylene gave the same exact ratio of β-*trans* to α isomer (70:30) (entry 2, Table 4).

Similar isomeric product distribution ratios were obtained for hydrosilylation of pentyne and hexyne with triethylsilane and triethoxysilane (entries 3–6, Table 4). The reaction of triethylsilane to pentyne yields β-*trans* and α isomers in the ratio of 89:11 with the Karstedt's catalyst. This isomeric ratio is very similar to that of triethylsilane addition to hexyne in the presence of Pt/C to give a mixture of 86:12:2 of β-*trans*:α:β-*cis* isomers. Comparable results are obtained from the reaction of triethoxysilane to pentyne and hexyne. While the selectivity of the catalyst is similar, the difference in the reaction conditions is significant. Platinum on carbon

Table 3
Hydrosilylation of unsymmetrical internal alkynes [a]

Entry	R	R′	Silane	Product distribution (%) [b]			Isolated yield (%)
				α	*β*	Conditions	
1	Ph	Me	$HSiCl_3$	60 [c]	11	48 °C, 2.25 h	94
2	Ph	Me	$MeSiHCl_2$	11 [c]	88	82 °C, 1 h	92
3	Ph	Me	Et_3SiH	68 [c]	30	52 °C, 4 h	96
4	Ph	Me	$(EtO)_3SiH$	14	86	70 °C, 1.5 h	93
5	Bu	Me_3Si	$HSiCl_3$	84	9	62 °C, 18 h	93
6	Bu	Me_3Si	$MeSiHCl_2$	97	3	45 °C, 2.5 h	96
7	Bu	Me_3Si	$PhSiHCl_2$	87	3	45 °C 2.5 h	56
8	Bu	Me_3Si	Et_3SiH	56	26	65 °C 36 h	89
9	Bu	Me_3Si	$(EtO)_3SiH$	90	8	62 °C, 4 h	89
10	Ph	Me_3Si	Cl_3SiH	–	–	72 °C, 1 h	–
11	Ph	Me_3Si	$MeSiHCl_2$	94	6	72 °C, 1 h	78
12	Ph	Me_3Si	$PhSiHCl_2$	90	8 [c]	85 °C, 4 h	92
13	Ph	Me_3Si	Et_3SiH	70	–	80 °C, 105 h	25
14	Ph	Me_3Si	$(EtO)_3SiH$	49 [c]	43	110 °C, 21 h	91

[a] Alkyne (20 mmol)/20 mmol silane; 4.1 μmol Pt were used in all above reactions.
[b] The product distribution is determined by the relative % areas in GC.
[c] Identity of isomers is not known.

Table 4
Comparison of selectivity between Karstedt's catalyst [a] and platinum of carbon [b]

Entry	Substrate	Silane	Karstedt's (%) (Lewis)	Conditions	Pt/C (%)	Conditions	Karstedt's (%) (Hüls) [c]	Conditions
1	$PhC\equiv CH$	$HSiEt_3$	82 β-*trans*, 18 α	60 °C 1 h	77 β-*trans* 23 α	85°C 4.5 h	76 β-*trans* 24 α	65°C 2 h
2	$PhC\equiv Ch$	$(EtO)_3SiH$	70 β-*trans*, 30 α	25 °C, 1 h	70 β-*trans*, 30 α	85 °C, 4.5 h	80 β-*trans*, 20 α	58 °C, 1.5 h
3	$PrC\equiv CH$	$HSiEt_3$	89 β-*trans*, 11 α	25 °C, 1 h	–	–	–	–
4	$PrC\equiv CH$	$(EtO)_3SiH$	63 β-*trans*, 26 α, 11 β-*cis*	25 °C, 1 h	–	–	–	–
5	$BuC\equiv CH$	$HSiEt_3$	–	–	86 β-*trans*, 12 α, 2 β-*cis*	78 °C, 5 h	–	–
6	$BuC\equiv CH$	$(EtO)_3SiH$	–	–	75 β-*trans*, 13 α, 12 β-*cis*	70 °C, 7 h	–	–

[a] Alkyne (18.2 mmol), 18.2 mmol of silane and 0.8 μmol of Pt (0.004 mol% of Pt based on alkyne) were used.
[b] Alkyne (20 mmol), 20 mmol of silane and 4.1 μmol of Pt (0.02 mol% of Pt based on alkyne) were used.
[c] Karstedt's catalyst was prepared in our lab or obtained from Hüls.

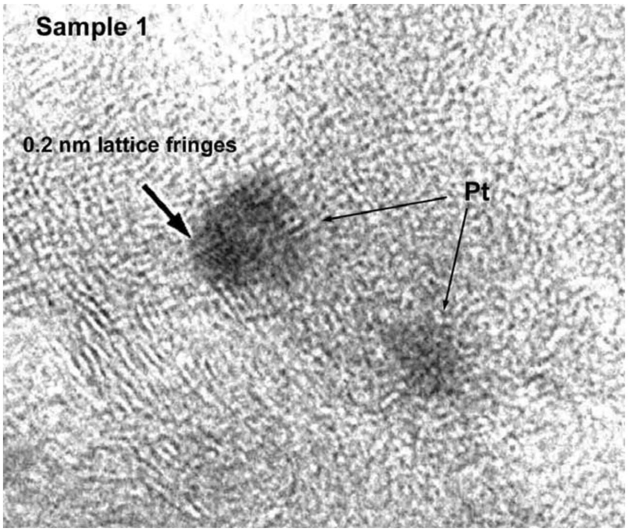


Fig. 1. Medium resolution image of the colloid formed in the reaction of triethylsilane with phenylacetylene in the presence of Pt/C. Pt nanoparticles are the small black spots indicated with arrows on the carbon.

required heating at 60–90 °C for approximately 4 h to reach yields of ~80%. The reactions (entries 2–4) catalyzed by Karstedt's catalyst occur at room temperature except for the reaction of phenylacetylene with triethylsilane (entry 1) [17].

These results prompted us to look for colloids as the possible catalytic species in the present reactions. HREM was used to analyze the reaction solution from the triethylsilane reaction with phenylacetylene in the presence of Pt/C. Fig. 1 is a medium resolution image showing the distribution of Pt nanoparticles on the carbon. Fig. 2 exhibits Pt grains of the size 2–5 nm in diameter and they exhibit lattice fringes that correspond to the spacing of the (111) and in some cases the (200) planes of Pt. These results confirm the formation of Pt colloids in the hydrosilylation of phenylacetylene with triethylsilane. It should be noted that there are a few examples of stable colloids of Pt in nonaqueous–nonalcoholic media [8h,8i,18]. The structure of the platinum observed from the reaction solution is consistent with the structure of platinum colloids already well established [8,9].

3. Conclusions

This work has shown that platinum on carbon is a cheap, efficient, and selective catalyst for the hydrosilylation of alkynes under relatively mild conditions. HREM analysis showed that colloidal platinum is formed. A similar observation was reported when Karstedt's catalyst was used for hydrosilylation of alkenes and alkynes [8]. The mechanism of the hydrosilylation reaction is probably similar to that proposed by Lewis et al. involving formation of ligand free Pt^0 species [8,9]. The selectivity of the products depends on the silane. Chlorosilanes usually produce one vinylsilane, while alkoxysilanes and alkylsilanes yield a mixture of two or more isomeric vinylsilanes. Thus, excellent yields of vinylsilanes (> 85%) can be achieved by using platinum on carbon providing a significant cost advantage over homogeneous platinum complexes.

4. Experimental

4.1. General methods

All manipulations were carried out under nitrogen. ^{1}H-NMR (270.16 MHz), (399.95 MHz) and ^{13}C-NMR (67.94 MHz), (100.57 MHz) spectra were obtained on JEOL GSX 270 and Varian INOVA 400 spectrometers at 25 °C and referenced to Me_4Si. Gas chromatography was performed on a Hewlett–Packard 5890II model equipped with a cross-linked methylsilicone capillary column. Some of the isomers were separated on a GOW-MAC series 580 gas chromatography unit. GC–MS data were obtained on a Hewlett–Packard 5988A with electron impact ionization (70 keV). Elemental analyses were performed by Desert Analytics of Tucson, Arizona. The HREM was performed on a JEOL 2010 instrument operated on 200 kV. Samples were prepared by evaporating the benzene solution of the reaction mixture on to a copper TEM grid covered with a thin amorphous carbon substrate. All reagents, including the 1% Pt on carbon, were purchased from Aldrich. The alkynes were used as received, while the silanes were distilled before use. Phenylmethylacetylene was prepared from lithium phenylacetylide and methyl iodide. Phenyltrimethylsilylacetylene and butyltrimethylsilylacetylene were prepared from the appropriate lithium salts and trimethylchlorosilane. Karstedt's catalyst was purchased from Hüls or prepared by the method of Lewis et al. [17].

4.2. General reaction procedure

A 25 ml three-necked flask equipped with a condenser/N_2 inlet and stir bar was charged with 0.08 g 1% Pt on carbon (4.1 μmol of Pt, 2.5×10^{-4} mol% Pt with respect to the alkyne). The flask was flushed with nitrogen for a few minutes and 20 mmol of alkyne and 20 mmol of silane were added by syringe. The solution was heated for few hours and monitored by gas chromatography. The products were distilled under vacuum and characterized by NMR and mass spectrometry.

4.2.1. Phenylacetylene + trichlorosilane (entry 1, Table 1)

Phenylacetylene (2.0 g, 2.2 ml, 20 mmol) and trichlorosilane (2.8 g, 2.1 ml, 20 mmol) were added to

0.08 g of 1% Pt on carbon (4.1 μmol of Pt). The solution was heated at 50–58 °C for 5 h and 4.0 g (17.4 mmol, 87%) of *E*-1-phenyl-2-trichlorosilylethene [10,19] was distilled under vacuum. Ph–C_a=C_b–$SiCl_3$ (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 6.36 (d, J(H,H) = 19 Hz, 1H, H_b), 7.30 (d, J(H,H) = 19.0 Hz, 1H, H_a); ^{13}C-NMR (C_6D_6): δ 118.39 (C_b), 128.15 (arom, C_o), 128.42 (arom, C_m), 130.10 (arom, C_p), 135.04 (arom, *ipso*-C_i), 151.58 (C_a); EIMS; m/z (relative intensity): 236 [M^+, 13], 201 (2), 165 (5), 103 (100).

4.2.2. Phenylacetylene + methyldichlorosilane (entry 2, Table 1)

Phenylacetylene (2.0 g, 2.2 ml, 20 mmol) and methyldichlorosilane (2.3 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). After heating at 56 °C for 3.5–4.5 h, vacuum distillation resulted in 3.2–4.4 g (15–19 mmol, 75–95%) of *E*-1-phenyl-2-methyldichlorosilylethene [10,20]. Ph–C_a=C_b–$SiCl_2C_c$ (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.96 (s, 1H, H_c), 6.46 (d, J(H,H) = 18.7 Hz, 1H, H_b), 7.27 (d, J(H,H) = 18.9 Hz, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 5.61 (C_c), 121.32 (C_b), 127.26 (arom, C_o), 128.77 (arom, C_m), 129.72 (arom, C_p), 136.25 (arom, *ipso*-C_i), 149.18 (C_a); EIMS; m/z (relative intensity): 216 [M^+, 43], 201 (35), 175 (9), 165 (100), 103 (5). Minor isomer: EIMS; m/z (relative intensity): 216 [M^+, 17], 201 (8), 165 (10), 103 (100).

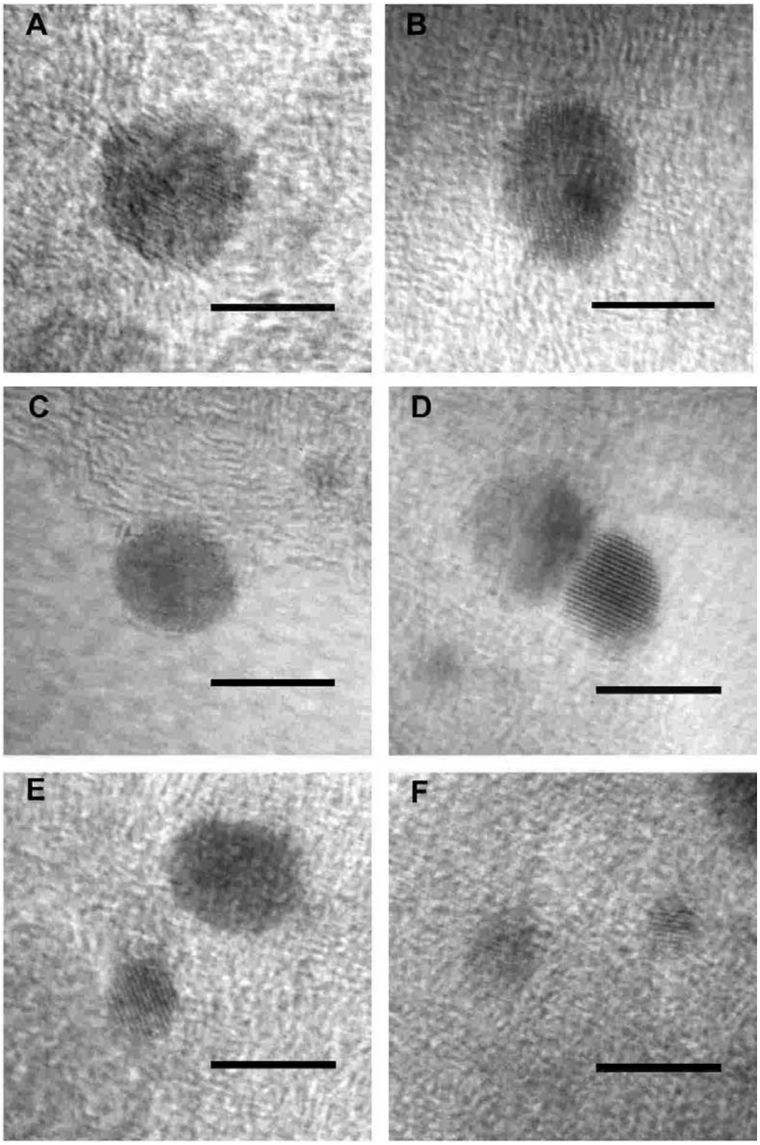


Fig. 2. HREM of the Pt colloid formed in the reaction of triethylsilane with phenylacetylene in the presence of Pt/C. 2–5 nm size particles are evident. Also evident are the diffraction fringes of the (111) planes and, in some cases, (200) planes. The scale bar in all the images is 5 nm. Fig. 2A shows polycrystalline Pt grains of size 2 nm.

4.2.3. Phenylacetylene + phenyldichlorosilane (entry 3, Table 1)

Phenyldichlorosilane (Hül's) (3.6 g, 3.0 ml, 20 mmol) and 0.08 g of 1% Pt on carbon (4.1 μmol of Pt) were placed in to a 25 ml flask. Phenylacetylene (2.0 g, 2.2 ml, 20 mmol) was added by addition funnel at 35 °C over 45 min. After an additional 30 min at 45 °C, vacuum distillation produced 5.2 g (17.8 mmol, 89%) of *E*-1-phenyl-2-phenyldichlorosilylethene.

Ph–C_a=C_b–$SiCl_2$Ph (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 6.61 (d, J(H,H) = 18.7 Hz, 1H, H_b), 7.34 (d, J(H,H) = 19.0 Hz, 1H, H_a); EIMS; m/z (relative intensity): 278 [M^+, 8], 243 (1), 202 (2), 180 (100), 165 (27).

4.2.4. Phenylacetylene + triethylsilane (entry 4, Table 1)

Phenylacetylene (2.0 g, 2.2 ml, 20 mmol) and triethylsilane (2.3 g, 3.2 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating at 70 °C for 4.5 h produced 3.9 g (18 mmol, 91%) of a mixture of *E*-1-phenyl-2-triethylsilylethene [10] and 1-phenyl-1-triethylsilylethene [10,17,21] after vacuum distillation.

Ph–C_a=C_b–Si–C_c–C_d (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.64 (q, J(H,H) = 8 Hz, 6H, H_c), 1.00 (t, J(H,H) = 8 Hz, 9 H, H_d), 6.45 (d, J(H,H) = 19 Hz, 1H, H_b), 6.91 (d, J(H,H) = 19.0 Hz, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 3.36 (C_d), 7.32 (C_c), 125.99 (C_a), 126.34 (arom, C_o), 128.11 (arom, C_m), 126.68 (arom, C_p), 128.80 (arom, *ipso*-C_i), 144.89 (C_b); EIMS; m/z (relative intensity): 218 [M^+, 12], 189 (99), 161 (98), 131 (100). (α-isomer) ^{1}H-NMR ($CDCl_3$): δ 0.66 (q, J(H,H) = 8 Hz, 6H, H_c), 0.95 (t, J(H,H) = 8 Hz, 9H, H_d), 5.60 (d, J(H,H) = 3.3 Hz, 1H, $H_{b'}$), 5.89 (d, J(H,H) = 3.3 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 3.59 (C_c), 7.43 (C_d), 126.10 (arom, C_o), 127.90 (arom, C_p), 128.53 (arom, C_m), 138.60 (C_b), 150.40(C_a); EIMS; m/z (relative intensity): 218 [M^+, 3], 189 (48), 161 (81), 133 (46), 103 (100).

4.2.5. Phenylacetylene + triethoxysilane (entry 5, Table 1)

Phenylacetylene (2.0 g, 2.2 ml, 20 mmol) and triethoxysilane (3.3 g, 3.7 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating the solution at 55 °C for 4.5 h, provided 4–4.9 g (15–18 mmol, 75–93%) of a mixture of *E*-1-phenyl-2-triethoxysilylethene [10,17] and 1-phenyl-1-triethoxysilylethene [10] after vacuum distillation.

Ph–C_a=C_b–Si–O–C_c–C_d (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 1.28 (t, J(H,H) = 7 Hz, 9H, H_d), 3.90 (q, J(H,H) = 7 Hz, 6H, H_c), 6.20 (d, J(H,H) = 19.4 Hz, 1H, H_b), 7.23 (d, J(H,H) = 19.4 Hz, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 18.19 (C_d), 58.52 (C_c), 117.7 (C_a), 126.70 (arom, C_o), 128.4 (arom, C_p), 128.65 (arom, C_m), 149.04 (C_b); EIMS; m/z (relative intensity): 266 [M^+, 9], 251 (45), 222 (100), 163(15), 135 (17). (α-isomer) ^{1}H-NMR ($CDCl_3$): δ 1.16 (t, J(H,H) = 7 Hz, 9H, H_d), 3.79 (q, J(H,H) = 7 Hz, 6H, H_c), 5.92 (d, J(H,H) = 2.93 Hz, 1H, $H_{b'}$), 6.10 (d, J(H,H) = 2.93 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 18.05 (C_d), 58.66 (C_c), 126.80 (C_o), 128.20 (arom, C_p), 131.49 (arom, C_m), 141.91 (C_b), 143.37 (C_a); EIMS; m/z (relative intensity): 266 [M^+, 7], 222 (84), 163 (39), 135 (100).

4.2.6. 1-Hexyne + trichlorosilane (entry 6 of Table 1)

1-Hexyne (1.6 g, 2.3 ml, 20 mmol) and trichlorosilane (2.8 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating the solution for 5 h at 50 °C produced, after vacuum distillation, 4.2 g (19 mmol, 95%) of *E*-1-trichlorosilylhex-1-ene [11].

Cl_3–Si–C_a=C_b–C_c–C_d–C_e–C_f (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.93 (t, J(H,H) = 7 Hz, 3H, H_f), 1.30–1.52 (m, 4H, H_d, H_e), 2.24–2.32 (m, 2H, H_c), 5.81 (d of t, J(H,H) = 18.3, 1.5 Hz, 1H, H_a), 6.71 (d of t, J(H,H) = 18.3, 6 Hz, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 13.84 (C_f), 22.19 (C_e), 29.81 (C_d), 35.54 (C_c), 121.71 (C_a), 157.36 (C_b); EIMS; m/z (relative intensity): 216 [M^+, 4], 187 (24), 174 (94), 151 (20), 133 (74), 83 (100).

4.2.7. 1-Hexyne + methyldichlorosilane (entry 7, Table 1)

1-Hexyne (1.6 g, 2.3 ml, 20 mmol) and methyldichlorosilane (2.3 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol Pt). Stirring the solution at room temperature for 1.5 h resulted in 3.8 g (17.6 mmol, 88%) of *E*-1-methyldichlorosilylhex-1-ene [11,22].

C_g–Si–C_a=C_b–C_c–C_d–C_e–C_f (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.84 (s, 3H, H_g), 0.92 (t, J(H,H) = 7 Hz, 3H, H_f), 1.27–1.48 (m, 4H, H_d, H_e), 2.19–2.26 (m, 2H, H_c), 5.75 (d of t, J(H,H) = 18.5, 1.5 Hz, 1H, H_a), 6.52 (d of t, J(H,H) = 18.5, 6.2 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 5.47 (C_g), 13.87 (C_f), 22.19 (C_e), 30.07 (C_d), 35.74 (C_c), 123.56 (C_a), 154.41 (C_b), EIMS; m/z (relative intensity): 196 [M^+, 1], 181 (1), 167 (10), 154 (32), 113 (100).

4.2.8. 1-Hexyne + phenyldichlorosilane (entry 8, Table 1)

Phenyldichlorosilane (Hül's) (3.6 g, 3.0 ml, 20 mmol) and 0.08 g of 1% Pt on carbon (4.1 μmol of Pt) were placed in to a 25 ml flask. 1-Hexyne (1.6 g, 2.2 ml, 20 mmol) was added by addition funnel over 30 min. After heating at 78 °C for 45 min, provided 5.0 g (19.4 mmol, 97%) of *E*-1-phenylldichlorosilylhex-1-ene after vacuum distillation.

Ph–Si–C_a=C_b–C_c–C_d–C_e–C_f (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.93 (t, J(H,H) = 7 Hz, 3H, H_f), 1.29–1.53 (m, 4H, H_d, H_e), 2.24–2.32 (m, 2H, H_c), 5.91 (d of t, J(H,H) = 18.3, 1.2 Hz, 1H, H_a), 6.60 (d of t, J(H,H) = 18.3, 6.2 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 13.87 (C_f), 22.20 (C_e), 30.02 (C_d), 35.88 (C_c), 121.88 (arom, C_o), 128.24 (arom, C_p), 131.52 (arom, C_m), 156.36 (C_b); EIMS; m/z (relative intensity): 258 [M^+, 1], 216 (26), 188 (8), 175 (100), 152 (12).

4.2.9. 1-Hexyne + triethylsilane (entry 9, Table 1)

1-Hexyne (1.6 g, 2.3 ml, 20 mmol) and triethylsilane (2.3 g, 3.2 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol Pt). Heating at 78 °C for 5 h produced 3.4 g (17 mmol, 87%) of a mixture of *E*-1-triethylhex-1-ene, *Z*-1-triethylsilylhex-1-ene and 2-triethylsilylhex-1-ene, after vacuum distillation [11,22].

$\mathrm{C_h{-}C_g{-}Si{-}C_a{=}C_b{-}C_c{-}C_d{-}C_e{-}C_f}$ (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.58 (q, J(H,H) = 7.8 Hz, 6H, H_g), 0.89 (t, J(H,H) = 7 Hz, 3H, H_f), 0.93 (t, J(H,H) = 7.8 Hz, 9H, H_h), 1.28–1.57 (m, 4H, H_d, H_e), 2.09–2.17 (m, 2H, H_c), 5.54 (d of t, J(H,H) = 18.7, 1.5 Hz, 1H, H_a), 6.04 (d of t, J(H,H) = 18.7, 6.6 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 3.58 (C_g), 7.36 (C_h), 13.95 (C_f), 22.18 (C_e), 31.03 (C_d), 36.74 (C_c), 125.50 (C_b), 148.78 (C_a); EIMS; *m*/*e* (relative intensity): 198 [M^+, 1], 169 (51), 141 (100), 113 (37).

(β-*cis*) EIMS; *m*/*z* (relative intensity): 198 [M^+, 1], 169 [$M^+ - Et$, 97], 141 (100), 113 (50).

(α-isomer) ^{1}H-NMR ($CDCl_3$): δ 0.53 (t, J(H,H) = 7.8 Hz, 6H, H_g), 0.91 (t, J(H,H) = 7.3 Hz, 3 H, H_f), 0.94 (q, J(H,H) = 7.8 Hz, 9H, H_h), 1.30–1.55 (m, 4H, H_d, H_e), 1.91–1.97 (m, 2H, H_c), 5.24–5.45 (m, 2H, H_a, H_b); ^{13}C-NMR ($CDCl_3$): δ 3.16 (C_g), 7.34 (C_h), 13.65 (C_f), 17.33 (C_e), 23.09 (C_d), 34.97 (C_c), 126.23 (C_b), 128.65 (C_a); EIMS; *m*/*z* (relative intensity): 198 [M^+, 2], 169 (1), 141 (2), 115 (50), 87 (100).

4.2.10. 1-Hexyne + triethoxysilane (entry 10, Table 1)

1-Hexyne (1.6 g, 2.2 ml, 20 mmol) and triethoxysilane (3.3 g, 3.7 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). After heating the solution at 65–70 °C for 7 h, vacuum distillation resulted in 4.3–4.8 g (17–19 mmol, 85–95%) of a mixture of *E*-1-triethoxysilylhex-1-ene [23] and 2-triethoxysilylhex-1-ene.

$\mathrm{C_h{-}C_g{-}O{-}Si{-}C_a{=}C_b{-}C_c{-}C_d{-}C_e{-}C_f}$ (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.89 (t, J(H,H) = 7 Hz, 3H, H_f), 1.23 (t, J(H,H) = 7 Hz, 9H, H_h), 1.35 (m, 4H, H_d, H_e), 2.14 (m, 2H, H_c), 3.83 (q, J(H,H) = 7 Hz, 6H, H_g), 5.42 (d of t, J(H,H) = 18.7, 1.5 Hz, 1H, H_a), 6.43 (d of t, J(H,H) = 18.7, 6.2 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 13.84 (C_f), 18.18 (C_h), 22.47 (C_e), 30.40 (C_d), 31.55 (C_c), 58.37 (C_g), 118.82 (C_b), 153.98 (C_a). EIMS; *m*/*z* (relative intensity): 246 [M^+, 1], 231 (3), 201 (12), 163 (100).

(α-isomer) ^{13}C-NMR ($CDCl_3$): δ 22.17 (C_h), 22.60 (C_e), 30.94 (C_d), 35.66 (C_c), 36.25 (C_g), 128.93 (C_a), 143.86 (C_b); EIMS; *m*/*z* (relative intensity): 246 [M^+, 1], 231 (1), 201 (5), 163 (100).

4.2.11. 1-Hexyne + diphenylmethylsilane (entry 11, Table 1)

Diphenylmethylsilane (Hül's) (4.0 g, 3.9 ml, 20 mmol) and 0.08 g of 1% Pt on carbon (4.1 μmol Pt) were placed in to a 25 ml flask. 1-Hexyne (1.6 g, 2.2 ml, 20 mmol) was added to it. After heating at 92 °C for 3 h, provided 4.0 g (14 mmol, 71%) of *E*-1-diphenylmethylsilylhex-1-ene after vacuum distillation [24].

$\mathrm{C_g{-}Si{-}C_a{=}C_b{-}C_c{-}C_d{-}C_e{-}C_f}$ (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.63 (s, 3H, H_g), 0.93 (t, J(H,H) = 7 Hz, 9H, H_h), 1.29–1.47 (m, 4H, $H_{d,e}$), 2.22 (q, J(H,H) = 7 Hz, 6H, H_c), 5.94 (d of t, J(H,H) = 18.7, 1.5 Hz, 1H, H_a), 6.19 (d of t, J(H,H) = 18.7, 6.2 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 3.30 (C_g), 13.95 (C_e), 22.27 (C_d), 30.75 (C_f), 36.60 (C_c), 125.02 (C_a), 127.73 (arom, C_o), 129.16 (arom, C_p), 134.81 (arom, C_m), 137.18 (arom, *ipso*-C_i), 151.63 (C_b); EIMS; *m*/*z* (relative intensity): 280 [M^+, 12], 265 (10), 237 (3), 223 (8), 197 (100). Minor isomer: ^{1}H-NMR ($CDCl_3$): δ 5.86 (m, 1H, H_b), 5.41 (m, 1H, H_a); EIMS; *m*/*z* (relative intensity): 280 [M^+, 4], 265 [$M^+ - Me$, 15], 183 (70), 121 (82), 105(100).

4.2.12. Trimethylsilylacetylene + trichlorosilane (entry 12, Table 1)

Trimethylsilylacetylene (2.0 g, 2.8 ml, 20 mmol) and trichlorosilane (2.8 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating the solution for 5 h at 40 °C produced, after vacuum distillation, 4.3 g (18 mmol, 92%) of *E*-1-trichlorosilyl-2-trimethylsilylethene [25].

$\mathrm{C_c{-}Si{-}C_a{=}C_b{-}Si}$ (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.16 (s, 1H, H_c), 6.52 (d, J(H,H) = 22 Hz, 1H, H_a), 7.24 (d, J(H,H) = 22 Hz, 1H, H_b). ^{13}C-NMR ($CDCl_3$): δ −2.07 (C_c), 138.20 (C_a), 161.50 (C_b); EIMS; *m*/*z* (relative intensity): 234 [M^+, 1], 219 (67), 135 (8), 99 (100).

4.2.13. Trimethylsilylacetylene + methyldichlorosilane (entry 13, Table 1)

Trimethylsilylacetylene (2.0 g, 2.8 ml, 20 mmol) and methyldichlorosilane (2.3 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). After heating the solution for 4.5 h at 45 °C, vacuum distillation gave, 3.7 g (17.4 mmol, 87%) of *E*-1-methyldichlorosilyl-2-trimethylsilylethene.

$\mathrm{C_c{-}Si{-}C_a{=}C_b{-}Si{-}C_d}$ (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.13 (s, 1H, H_c), 0.85 (s, 3H, H_d), 6.53 (d, J(H,H) = 22 Hz, 1H, H_a), 7.04(d, J(H,H) = 22 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ −1.97 (C_c), 4.91 (C_d), 141.38 (C_a), 158.26 (C_b); EIMS; *m*/*z* (relative intensity): 212 [M^+, 2], 197 (37), 113 (17), 103 (19), 99 (100).

4.2.14. Trimethylsilylacetylene + triethylsilane (entry 14, Table 1)

Trimethylsilylacetylene (2.0 g, 2.8 ml, 20 mmol) and triethylsilane (2.4 g, 3.2 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 μmol Pt). Heating the solution for 6 h at 75 °C, vacuum distillation gave, 3.8 g (18 mmol, 88%) of a mixture of *E*-1-triethylsilyl-2-trimethylsilylethene and *Z*-1-triethylsilyl-2-trimethylsilylethene.

C_c–Si–C_a=C_b–Si–C_d–C_e (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.07 (s, 1H, H_c), 0.58 (q, J(H,H) = 7.3 Hz, 6H, H_d), 0.94 (t, J(H,H) = 7.3 Hz, 9H, H_e), 6.53 (d, J(H,H) = 21 Hz, 1H, H_b), 6.64 (d, J(H,H) = 21 Hz, 1H, H_a); EIMS; m/z (relative intensity): 214 [M^+, 3], 199 (2), 185 (54), 157 (54), 87 (96), 73 (100). (β-*cis*): ^{1}H-NMR ($CDCl_3$): δ 0.10 (s, 1H, H_c), 0.62 (q, J(H,H) = 7.3 Hz, 6H, H_d), 0.92 (t, J(H,H) = 7.3 Hz, 9H, H_e), 6.28 (d, J(H,H) = 5.4 Hz, 1H, H_b), 6.39 (d, J(H,H) = 5.4 Hz, 1H, H_a); EIMS; m/z (relative intensity): 214 [M^+, 3], 199 (2), 185 (79), 157 (49), 87 (100), 73 (44).

4.2.15. Trimethylsilylacetylene + triethoxysilane (entry 15, Table 1)

Trimethylsilylacetylene (2.0 g, 2.8 ml, 20 mmol) and triethoxysilane (3.3 g, 3.7 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating the solution for 4.5 h at 83°C resulted in the isolation of 5.1 g (19.4 mmol, 97%) of a mixture of *E*-1-triethoxysilyl-2-trimethylsilylethene and *Z*-1-triethoxysilyl-2-trimethylsilylethene by vacuum distillation. C_c–Si–C_a=C_b–Si–O–C_d–C_e (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.086 (s, 3H, H_c), 1.24 (t, J(H,H) = 7 Hz, 9H, H_e), 3.82 (q, J(H,H) = 7 Hz, 6H, H_d), 6.31 (d, J(H,H) = 22 Hz, 1H, H_b), 6.99 (d, J(H,H) = 22 Hz, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ − 1.85 (C_c), 18.21 (C_e), 58.55 (C_d), 138.71 (C_b), 158.15 (C_a); EIMS; m/z (relative intensity): 261 [$M^+ - 1$, 1], 247 (100), 203 (88), 175 (64), 163 (98). (β-*cis*): ^{1}H-NMR ($CDCl_3$): δ 0.12 (s, 3H, H_c), 1.25 (t, J(H,H) = 7 Hz, 9H, H_e), 3.83 (q, J(H,H) = 7 Hz, 6H, H_d), 6.43 (d, J(H,H) = 5.5 Hz, 1H, H_b), 6.58 (d, J(H,H) = 5.5 Hz, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ − 1.06 (C_c), 18.43 (C_e), 58.35 (C_d), 145.20 (C_b), 158.15 (C_a); EIMS; m/z (relative intensity): 247 [$M^+ - Me$, 35], 203 (22), 175 (14), 163 (100). Anal. Found: C, 50.31; H, 9.83. Calc. for $C_{11}H_{26}O_3Si_2$: C, 50.32; H, 10.00%.

4.2.16. 3-Hexyne + trichlorosilane (entry 1, Table 2)

3-Hexyne (1.7 g, 2.3 ml, 20 mmol) and trichlorosilane (2.8 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol Pt). Heating the solution for 3.5 h at 43 °C produced, after vacuum distillation, 4.1 g (19 mmol, 95%) of 3-trichlorosilyl-*cis*-hex-3-ene [11].

C_a–C_b–($SiCl_3$)C_c=C_d–C_e–C_f: ^{1}H-NMR ($CDCl_3$): δ 1.07 (t, J(H,H) = 7 Hz, 3H, H_a), 1.10 (t, J(H,H) = 7Hz, 3H, H_f), 2.00–2.40 (m, 4H, $H_{b,e}$), 6.42 (t, J(H,H) = 7 Hz, 1H, H_d); ^{13}C-NMR ($CDCl_3$): δ 13.27 (C_b), 14.48 (C_a), 21.14 (C_f), 22.22 (C_e), 134.93 (C_c), 151.39 (C_d); EIMS; m/z (relative intensity): 216 [M^+, 3], 133 (21), 83 (100).

4.2.17. 3-Hexyne + methyldichlorosilane (entry 2, Table 2)

3-Hexyne (1.7 g, 2.3 ml, 20 mmol) and methyldichlorosilane (2.3 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). After heating the solution for 2.5–5 h at 52–65 °C produced after vacuum distillation 3.2 g (17 mmol, 86%) of 3-methyldichlorosilyl-*cis*-hex-3-ene.

C_a–C_b–(SiC_gCl_2)C_c=C_d–C_e–C_f (β-*trans*): ^{1}H-NMR ($CDCl_3$): δ 0.86 (s, 3H, H_g), 1.04 (t, J(H,H) = 7.6 Hz, 3H, H_a), 1.06 (t, J(H,H) = 7.6 Hz, 3H, H_f), 2.21 (q, J(H,H) = 7.6 Hz, 2H, H_b), 2.31 (q, J(H,H) = 7.6 Hz, 2H, H_e), 6.15 (t, J(H,H) = 7 Hz, 1H, H_d); ^{13}C-NMR ($CDCl_3$): δ 5.04 (C_g), 13.49 (C_a), 14.64 (C_f), 21.29 (C_b), 21.96 (C_e), 136.92 (C_c), 148.21 (C_d); EIMS; m/z (relative intensity): 196 [M^+, 14], 181 (2), 139 (11), 113 (86), 83 (100).

4.2.18. 3-Hexyne + diphenylmethylsilane (entry 3, Table 2)

3-Hexyne (1.6 g, 2.2 ml, 20 mmol) and diphenylmethylsilane (4 g, 3.9 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 μmol Pt). After heating at 96 °C for 1.5 h, provided 4.6 g (17 mmol, 85%) of 3-diphenylmethyl-silyl-*cis*-hex-3-ene after vacuum distillation.

C_a–C_b–(Si Ph_2 C_g)C_c=C_d–C_e–C_f ^{1}H-NMR ($CDCl_3$): δ 0.65 (s, 3H, H_g), 0.84 (t, J(H,H) = 7.5 Hz, 3H, H_f), 1.01 (t, J(H,H) = 7.5 Hz, 3H, H_a), 2.15–2.26 (m, 4H, H_b, H_e), 5.81 (t, J(H,H) = 7 Hz, 1H, H_d); ^{13}C-NMR ($CDCl_3$): δ − 3.61 (C_g), 14.07 (C_f), 14.84 (C_a), 21.90 (C_b), 22.92 (C_e), 127.63 (C_c), 128.99 (arom, C_o), 135.18 (arom, C_p), 136.99 (arom, C_m), 137.71 (arom, *ipso*-C_i), 146.71 (C_d); EIMS; m/z (relative intensity): 280 [M^+, 18], 265 (17), 251 (17), 197 (100).

4.2.19. 3-Hexyne + triethylsilane (entry 4, Table 2)

3-Hexyne (1.6 g, 2.2 ml, 20 mmol) and triethylsilane (2.3 g, 3.2 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). The solution was stirred and heated at 80 °C for 3–3.5 h and vacuum distilled to give 3.8 g (19 mmol, 95%) of 3-triethyl-silyl-*cis*-hex-3-ene [11].

C_a–C_b–(SiC_gC_h)C_c=C_d–C_e–C_f ^{1}H-NMR ($CDCl_3$): δ 0.58 (q, J(H,H) = 7.4 Hz, 6H, H_h), 0.92 (t, J(H,H) = 7.4 Hz, 9 H, H_g), 0.99 (t, J(H,H) = 7.4 Hz, 6 H, H_a, H_f), 2.06–2.18 (m, 4 H, H_b, H_e), 5.67 (t, J(H,H) = 5.9 Hz, 1H, H_d); ^{13}C-NMR ($CDCl_3$): δ 3.14 (C_h), 7.45 (C_g), 14.31 (C_f), 14.77 (C_a), 21.52 (C_e), 22.64 (C_b), 138.24 (C_c), 143.27 (C_d); EIMS; m/z (relative intensity): 198 [M^+, 4], 169 (63), 141 (100).

4.2.20. 3-Hexyne + triethoxysilane (entry 5, Table 2)

3-Hexyne (1.6 g, 2.2 ml, 20 mmol) and triethoxysilane (3.3 g, 3.7 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). After heating at 85 °C for 4.5 h, provided 4.7 g (19 mmol, 95%) of 3-triethoxysilyl-*cis*-hex-3-ene after vacuum distillation.

C_a–C_b–(Si–O–C_gC_h)C_c=C_d–C_e–C_f ^{1}H-NMR ($CDCl_3$): δ 0.98 (t, J(H,H) = 7 Hz, 3H, H_a), 1.00 (t, J(H,H) = 7

Hz, 3H, H_f), 1.22 (t, J(H,H) = 7 Hz, 9H, H_h), 2.10–2.20 (m, 4H, H_b, H_e), 3.83 (q, J(H,H) = 7 Hz, 6H, H_g), 6.07 (t, J(H,H) = 7 Hz, 1H, H_d); ^{13}C-NMR ($CDCl_3$): δ 13.84 (C_a), 14.36 (C_f), 18.15 (C_h), 21.38 (C_b), 21.97 (C_e), 58.29 (C_g), 133.60 (C_c), 147.07 (C_d); EIMS; m/z (relative intensity): 246 [M^+, 3], 200 (19), 163 (100).

4.2.21. *Diphenylacetylene + trichlorosilane (entry 6, Table 2)*

Diphenylacetylene (3.56 g, 20 mmol) and trichlorosilane (2.8 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating the solution for 4 h resulted in 1.6–2.3 g (10–14 mmol, 50–73%) of 1, 2-diphenyl-1-trichlorosilyl-*cis*-ethene [10] after filtration through a 0.2 μm filter and recrystallization from hexane.

$PhC_a(H)$=C_b–($SiCl_3$)Ph: ^{1}H-NMR ($CDCl_3$): δ 7.04–7.08 (m, 2H), 7.14–7.27 (m, 6H), 7.38–7.45 (m, 4H); ^{13}C-NMR ($CDCl_3$): δ 127.79 (arom, $C_{c'}$), 128.27 (arom, C_o), 128.98 (arom, $C_{p'}$), 129.16 (arom, C_p), 129.32 (arom, $C_{m'}$), 130.41 (arom, C_m), 135.98 (arom, *ipso*-C_i), 136.06 (C_b), 145.34 (C_a); EIMS; m/z (relative intensity): 312 [$M^+ - 1$, 18], 275 (2), 234 (1), 179 (100), 152 (13), 133 (11).

4.2.22. *Diphenylacetylene + methyldichlorosilane (entry 7, Table 2)*

Diphenylacetylene (3.56 g, 20 mmol) and methyldichlorosilane (2.4 g, 2.2 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol Pt). Heating the reaction at 50 °C for 1.5 h resulted in 4.6 g (15.6 mmol, 78%) of 1,2-diphenyl-1-tmethyldichlorosilyl-*cis*-ethene [10] by vacuum distillation.

$PhC_a(H)$=C_b–($SiCl_2C_c$)Ph: ^{1}H-NMR ($CDCl_3$): δ 0.85(s, 3H, H_c), 7.01–7.04 (m, 10H, Ph); ^{13}C-NMR ($CDCl_3$): δ 4.60(C_c), 127.18 (arom, $C_{c'}$), 128.13 (arom, C_o), 128.42 (arom, $C_{p'}$), 128.61 (arom, C_p), 129.03 (arom, $C_{m'}$), 130.09 (arom, C_m), 135.48 (arom, *ipso*-$C_{i'}$), 137.48 (arom, *ipso*-C_i), 138.49 (C_b), 143.04 (C_a); EIMS; m/z (relative intensity): 292 [M^+, 31], 241 (6), 198 (2), 179 (100).

4.2.23. *Diphenylacetylene + triethylsilane (entry 8, Table 2)*

Diphenylacetylene (3.56 g, 20 mmol) and triethylsilane (2.3 g, 3.2 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). After heating at 50 °C for 4 h, vacuum distillation resulted in 5.2–5.4 g (17.6–18.4 mmol, 89–92%) of 1, 2-diphenyl-1-triethylsilyl-*cis*-ethene [10].

$PhC_a(H)$=C_b–(SiC_cC_d)Ph: ^{1}H-NMR ($CDCl_3$): δ 0.68 (q, J(H,H) = 7.7 Hz, 3H, H_c), 0.99 (t, J(H,H) = 7.7 Hz, 9H, H_d), 6.80 (s, 1H, H_a) 7.01–7.04 (m, 10H, Ph); ^{13}C-NMR ($CDCl_3$): δ 2.75 (C_c), 7.29 (C_d), 125.49 (arom, $C_{o'}$), 126.92 (arom, C_o), 127.26 (arom, $C_{p'}$), 127.84 (arom, C_p), 128.58 (arom, $C_{m'}$), 129.48 (arom, C_m), 137.38 (arom, *ipso*-$C_{i'}$), 138.73 (arom, *ipso*-C_i), 143.14 (C_b), 144.07 (C_a); EIMS; m/z (relative intensity): 294 [M^+, 20], 265 (100), 237 (38), 207 (23).

4.2.24. *Diphenylacetylene + triethoxysilane (entry 9, Table 2)*

Diphenylacetylene (3.56 g, 20 mmol) and triethoxysilane (3.3 g, 3.8 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). After heating at 55 °C for 4 h, vacuum distillation resulted in 6.2–6.6 g (18.2–19 mmol, 91–95%) of 1, 2-diphenyl-1-triethoxylsilyl-*cis*-ethene [10].

$PhC_a(H)$=C_b–($SiOC_cC_d$)Ph: ^{1}H-NMR ($CDCl_3$): δ 1.22 (t, J(H,H) = 7.0 Hz, 9H, H_d), 3.85 (q, J(H,H) = 7.0 Hz, 6H, H_c), 7.20 (s, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 18.10 (C_d), 58.77 (C_c), 126.05 (arom, $C_{o'}$), 127.42 (arom, C_o), 127.82 (arom, $C_{p'}$), 128.21 (aroma, C_p), 128.42 (arom, $C_{m'}$), 129.80 (arom, C_m), 136.83 (arom, *ipso*-$C_{i'}$), 137.01 (arom, *ipso*-C_i), 140.66 (C_b), 142.35 (C_a); EIMS; m/z (relative intensity): 342 [M^+, 43], 298 (46), 252 (46), 178 (68), 119 (58), 79 (100).

4.2.25. *Phenylmethylacetylene + trichlorosilane (entry 1, Table 3)*

Phenylmethylacetylene (2.3 g, 2.5 ml, 20 mmol) and trichlorosilane (2.8 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating the solution for 2.25 h at 48 °C resulted in 4.7–4.8 g (18–19 mmol, 93–95%) of *E*-1-methyl-1-trichlorosilyl-2-phenylethene after vacuum distillation.

$PhC_a(H)$=C_b–($SiCl_3$)C_c: ^{1}H-NMR ($CDCl_3$): δ 2.03 (s, 3H, H_c), 7.13 (s, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 14.69 (C_c), 128.42 (arom, C_p), 128.53 (arom, C_o), 129.40 (arom, C_m), 135.64 (arom, *ipso*-C_i), 144.75 (arom, C_b), 146.37 (C_a). EIMS; m/z (relative intensity): 250 [M^+, 18], 235 (50), 215 (40), 199 (50), 175 (2), 133 (7), 117 (100).

4.2.26. *Phenylmethylacetylene + methyldichlorosilane (entry 2, Table 3)*

Phenylmethylacetylene (2.3 g, 2.5 ml, 20 mmol) and methyldichlorosilane (2.3 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 μmol of Pt). Heating the solution for 1 h at 82 °C gave 4.0–4.5g (17–19 mmol, 86–95%) of *E*-1-methyl-1-methyldichlorosilyl-2-phenylethene [15] and 1-phenyl-1-methyldichlorosilyl-2-methylethene by vacuum distillation.

$PhC_a(H)$=C_b–($SiCl_2C_d$)C_c: (β-isomer) ^{1}H-NMR ($CDCl_3$): δ 0.97 (s, 3H, H_d), 2.11 (s, 3H, H_c), 7.11 (s, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 4.09 (C_d), 14.87 (C_c), 127.90 (arom, C_p), 128.27 (arom, C_m), 129.22 (arom, C_o), 133.31 (C_b), 136.38 (arom, *ipso*-C_i), 142.09 (C_a); EIMS; m/z (relative intensity): 230 [M^+, 21], 215 [$M^+ -$ Me, 1], 195 [$M^+ -$ Cl, 1], 179 [$M^+ -$ Me, Cl, 7], 158 [$M^+ - 72$, 2], 117 [$M^+ - 113$, 100]. (α-isomer) ^{1}H-NMR ($CDCl_3$): δ 0.81 (s, 3H, H_d), 1.70 (d, J(H,H) =

6.9Hz, 3H, H_c), 6.66 (q, J(H,H) = 6.6 Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 4.70 (C_d), 16.12 (C_c), 126.84 (arom, C_p), 128.45 (arom, C_o), 128.66 (arom, C_m), 137.41 (C_a), 139.52 (arom, *ipso*-C_i), 143.22 (C_b); EIMS; m/z (relative intensity): 230 [M^+, 26], 215 (1), 194 (7), 179 (7), 158 (4), 117 (100).

4.2.27. Phenylmethylacetylene + triethylsilane (entry 3, Table 3)

Phenylmethylacetylene (2.3 g, 2.5ml, 20 mmol) and triethylsilane (2.3 g, 3.2 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). After heating the solution for 4 h at 52 °C gave 4.5 g (19.1 mmol, 96%) of a mixture of *E*-1-methyl-1-triethylsilyl-2-phenylethene and 1-phenyl-1-triethylsilyl-2-methylethene by vacuum distillation.

$PhC_a(H){=}C_b{-}(SiC_dC_e)C_c$: (β-isomer) ^{1}H-NMR ($CDCl_3$): δ 0.71 (q, J(H,H) = 7.8Hz, 6H, H_d), 1.00 (t, J(H,H) = 7.8 Hz, 9H, H_e), 1.96 (s, 3H, H_c), 6.73 (s, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 2.64 (C_d), 7.48 (C_e), 16.96 (C_c), 126.36 (arom, C_p), 128.00 (arom, C_o), 129.06 (C_m), 137.43 (C_b), 138.39 (arom, *ipso*-C_i), 138.54 (C_a); EIMS; m/z (relative intensity): 232 [M^+, 7], 203 (100), 175 (49), 163 (12), 147 (31), 135 (24). (α-isomer) ^{1}H-NMR ($CDCl_3$): δ 0.87 (q, J(H,H) = 7.9Hz, 6H, H_d), 1.23 (t, J(H,H) = 7.9Hz, 9H, H_e), 1.89 (d, J(H,H) = 6.6 Hz, 3H, H_c), 6.38 (q, J(H,H) = 6.6Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 2.88 (C_e), 7.29 (C_d), 15.91 (C_c), 125.12 (arom, C_p), 127.76 (arom, C_o), 127.95 (arom, C_m), 136.91 (C_b), 142.64 (arom, ipso-C_i), 142.85 (C_a); EIMS; m/e (relative intensity): 232 [M +, 31], 203 (100), 175 (81), 163 (23), 147 (41), 135 (47); Anal. Found: C, 77.86; H, 10.24. Calc. for $C_{15}H_{24}Si$: C, 77.49; H, 10.43%.

4.2.28. Phenylmethylacetylene + triethoxysilane (entry 4, Table 3)

Phenylmethylacetylene (2.3 g, 2.5 ml, 20 mmol) and triethoxysilane (3.3 g, 3.8 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). Heating for 1.5 h at 70 °C resulted in 5.1 g (18 mmol, 90%) of *E*-1-methyl-1-triethoxysilyl-2-phenylethene [26] and 1-phenyl-1-triethoxysilyl-2-methylethene [26] by vacuum distillation.

$PhC_a(H){=}C_b{-}(SiOC_dC_e)C_c$ (β-isomer): ^{1}H-NMR ($CDCl_3$): δ 1.29 (t, J(H,H) = 6.9 Hz, 9H, H_e), 2.01 (s, 3H, H_c), 3.90 (q, J(H,H) = 6.9 Hz, 6H, H_d) 7.08 (s, 1H, H_a); ^{13}C-NMR ($CDCl_3$): δ 16.12 (C_c), 18.20 (C_e), 58.56 (C_d), 126.92 (arom, C_p), 127.97 (arom, C_o), 129.14 (arom, C_m), 130.75 (arom, ipso-C_i), 137.73 (C_a), 142.03 (C_b); EIMS; m/z (relative intensity): 280 [M^+, 55], 265 (25), 251 (7), 236 (43), 221 (29), 192 (24), 163 (75), 147 (59), 135 (59), 119 (100). (α-isomer) ^{1}H-NMR ($CDCl_3$): δ 1.17 (t, J(H,H) = 6.9 Hz, 9H, H_e), 1.71 (d, J(H,H) = 6.6 Hz, 3H, H_c), 3.79 (q, J(H,H) = 6.9 Hz, 6H, H_d), 6.52 (q, J(H,H) = 6.6Hz, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 15.80 (C_c), 18.07 (C_e), 58.56 (C_d), 125.70 (arom, C_p), 127.90 (arom, C_o), 128.50 (arom, C_m), 136.54 (arom, *ipso*-C_i), 140.08 (C_a), 141.64 (C_b); EIMS; m/z (relative intensity): 280 [M^+, 25], 251 (2), 236 (100), 221 (34), 195 (7); Anal. Found: C, 64.20; H, 8.47. Calc. for $C_{15}H_{24}O_3Si$: C, 64.23; H, 8.64%.

4.2.29. Butyltrimethylsilylacetylene + trichlorosilane (entry 5, Table 3)

Butyltrimethylsilylacetylene (3.1 g, 4.0 ml, 20 mmol) and trichlorosilane (2.8 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 µmol Pt). Heating the solution for 18 h at 62 °C resulted in 5.6 g (18.7 mmol, 93%) of *E*/*Z*-1-trimethylsilyl-2-trichlorosilyl-hex-1-ene [27] after vacuum distillation.

$C_aSiC_b(H){=}C_c{-}(SiCl_3)C_d{-}C_e{-}C_f{-}C_g$ ^{1}H-NMR ($CDCl_3$): δ 0.21 (s, 9H, H_a), 0.94 (t, J(H,H) = 7.3Hz, 3H, H_g), 1.28–1.89 (m, 4H, $H_{e,f}$), 3.77 (t, J(H,H) = 6.4 Hz, 2H, H_d) 6.72 (s, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ −0.14 (C_a), 13.80 (C_g), 22.97 (C_f), 32.70 (C_e), 34.23 (C_d), 151.92 (C_b), 167.64 (C_c); EIMS; m/z (relative intensity): 275 [$M^+ - 15$, 13], 246 (2), 159 (4), 93(15), 73(100); (minor isomer) 275 [$M^+ - 15$, 13], 246 (2), 159 (21), 93 (14), 73 (100).

4.2.30. Butyltrimethylsilylacetylene + methyldichlorosilane (entry 6, Table 3)

Butyltrimethylsilylacetylene (3.1 g, 4.0 ml, 20 mmol) and methyldichlorosilane (2.3 g, 2.1 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). Heating the solution for 2.5 h at 45 °C gave 5.2 g (19.2 mmol, 96%) of *E*/*Z*-1-trimethylsilyl-2-methyldichlorohex-1-ene.

$C_aSiC_b(H){=}C_c{-}(SiCl_2C_h)C_d{-}C_e{-}C_f{-}C_g$ ^{1}H-NMR (C_6D_6): δ 0.08 (s, 9H, H_a), 0.59 (s, 3H, H_h), 0.87(t, J(H,H) = 7.3 Hz, 3H, H_g), 1.24–1.33 (m, 2H, H_f), 1.53–1.56 (m, 2H, H_e), 2.43–2.49 (m, 2H, H_d), 6.54(s, 1H, H_b). ^{13}C-NMR (C_6D_6): δ 0.02 (C_a), 5.36 (C_h), 14.03 (C_g), 23.33 (C_f), 33.21 (C_e), 35.09 (C_d), 148.45 (C_b), 157.81(C_c). EIMS; m/z (relative intensity) major isomer: 253 [$M^+ - 17$, 3], 226 (5), 159 (7), 125 (9), 73 (100); minor isomer 253 [$M^+ - 17$, 1], 159 (16), 118 (23), 73 (100). Anal. Found: C, 44.54; H, 8.30. Calc. for $C_{10}H_{22}Cl_2Si$: C, 44.58, H, 8.25%.

4.2.31. Butyltrimethylsilylacetylene + phenyldichlorosilane (entry 7, Table 3)

Butyltrimethylsilylacetylene (3.1 g, 4.0 ml, 20 mmol) and 0.08 g of 1% Pt on carbon (4.1 µmol of Pt) were placed in a 25 ml two-necked flask. Phenyldichlorosilane (3.5 g, 2.9 ml, 20 mmol) was added dropwise at 35 °C over 30 min. Heating the solution for 30 h at 85 °C gave 3.7 g (11 mmol, 56%) of *E*/*Z*-1-trimethylsilyl-2-phenyldichlorosilylhex-1-ene by vacuum distillation.

$C_aSiC_b(H){=}C_c{-}(SiCl_2Ph)C_d{-}C_e{-}C_f{-}C_g$ ^{1}H-NMR ($CDCl_3$): δ 0.18 (s, 9H, H_a), 0.87 (t, J(H,H) = 7.3 Hz, 3H, H_g), 1.28–1.47 (m, 4H, $H_{e,f}$), 2.43–2.49 (m, 2H, H_d), 6.51 (s, 1H, H_b); ^{13}C-NMR ($CDCl_3$): δ 0.08 (C_a), 13.82 (C_g), 23.04 (C_f), 32.09 (C_e), 34.83 (C_d), 128.19 (C_o, arom), 131.38 (C_p, arom), 133.31 (*ipso*-C_i, arom), 134.0 ($C_{m,}$ arom), 151.02 (C_b), 155.27 (C_c); EIMS; m/z (relative intensity): 315 [$M^+ - 17$, 3], 288 (8), 273 (2), 221 (2), 180 (32), 165 (8), 121 (11), 73 (100).

4.2.32. Butyltrimethylsilylacetylene + triethylsilane (entry 8, Table 3)

Butyltrimethylsilylacetylene (3.1 g, 4.0 ml, 20 mmol) and triethylsilane (2.3 g, 3.2 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). After heating the solution for 36 h at 65 °C gave 4.8 g (17.8 mmol, 89%) of a mixture of E/Z-1-trimethylsilyl-2-triethylsilylhex-2-ene and 1-triethylsilyl-1-trimethylsilylhex-1-ene by vacuum distillation.

$C_aSiC_b(H){=}C_c{-}(SiC_hC_i)C_d{-}C_e{-}C_f{-}C_g$ (β-isomer) ^{1}H-NMR (C_6D_6): δ 0.26 (s, 9H, H_a), 0.69 (q, J(H,H) = 8.1 Hz, 9H, H_i), 0.86 (t, J(H,H) = 7.0 Hz, 3H, H_g), 1.00 (t, J(H,H) = 7.7 Hz, 6H, H_h), 1.28–1.34 (m, 4H, $H_{e,f}$), 2.22 (d of t, J(H,H) = 7.3 Hz, 2H, H_d), 6.69 (t, J(H,H) = 6.9 Hz, H_c); ^{13}C-NMR (C_6D_6): δ 2.03 (C_a), 4.62 (C_i), 7.92 (C_h), 14.29 (C_g), 22.85 (C_f), 32.16 (C_e), 36.12 (C_d), 136.19 (C_b), 160.17 (C_c). EIMS; m/z (relative intensity): 270 [M^+, 6], 255 (8), 241 (100), 185 (4), 167 (24), 153 (82). (α-isomer) ^{1}H-NMR (C_6D_6): δ 0.21 (s, 3H, H_a), 0.63 (t, J(H,H) = 8.1 Hz, 3H, H_g), 0.66 (q, J(H,H) = 7.8 Hz, 6H, H_h), 0.85 (q, J(H,H) = 7.8 Hz, 6H, H_h), 1.00 (t, J(H,H) = 8.1 Hz, 9H, H_i), 1.31–1.41 (m, 2H, H_e), 2.35 (t, J(H,H) = 7.8 Hz, 2H, H_d), 6.19 (s, 1H, H_b); ^{13}C-NMR (C_6D_6): δ 0.74 (C_a), 3.85 (C_i), 7.77 (C_h), 14.24 (C_g), 23.67 (C_f), 33.67 (C_e), 37.39 (C_d), 143.33 (C_b), 162.80 (C_c). EIMS; m/z (relative intensity): 270 [M^+, 1], 241 (46), 228 (47), 200 (13), 185 (5), 167 (31), 153 (100).

4.2.33. Butyltrimethylsilylacetylene + triethoxysilane (entry 9, Table 3)

Butyltrimethylsilylacetylene (3.1 g, 4.0 ml, 20 mmol) and triethoxysilane (3.3 g, 3.8 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). After heating the solution for 4 h at 62 °C gave 5.2 g (17.8 mmol, 89%) of 1-trimethylsilyl-2-triethoxysilyl-hex-1-ene by vacuum distillation.

$C_aSiC_b(H){=}C_c{-}(SiOC_hC_i)C_d{-}C_e{-}C_f{-}C_g$ ^{1}H-NMR (C_6D_6): δ 0.18 (s, 9H, H_a), 0.96 (t, J(H,H) = 7.2 Hz, 3H, H_g), 1.19 (t, J(H,H) = 7.0 Hz, 9H, H_i), 1.40–1.43 (m, 2H, H_f), 1.66–1.69 (m, 2H, H_e), 2.47–2.53 (m, 2H, H_d), 3.85 (q, J(H,H) = 7.0 Hz, 6H, H_h), 6.66 (s, 1H, H_b); ^{13}C-NMR (C_6D_6): δ 0.47 (C_a), 14.27 (C_g), 18.47 (C_i), 23.57 (C_f), 33.05 (C_e), 36.81 (C_d), 58.66 (C_h), 146.26 (C_b), 157.54 (C_c); EIMS; m/z (relative intensity): 275 [$M^+ - 45$, 6], 228 (8), 206 (17), 162 (87), 134 (44), 118 (70), 72 (100).

4.2.34. Phenyltrimethylsilylacetylene + methyldichlorosilane (entry 11, Table 3)

Phenyltrimethylsilylacetylene (3.3 g, 3.0 ml, 20 mmol) and methyldichlorosilane (2.3 g, 2.1 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). Heating the solution for 1 h at 72 °C, provided 4.5 g (16 mmol, 78%) of E/Z-1-methyldichlorosilyl-1-phenyl-2-trimethylsilylethene after vacuum distillation.

$PhC_a(SiCl_2C_b){=}C_c(H)Si{-}C_d$ Major isomer: ^{1}H-NMR ($CDCl_3$): δ 0.28 (s, 9H, H_d), 1.23 (s, 3H, H_b), Minor isomer: 0.49 (s, 9H, H_d), 1.39 (s, 3H, H_b); ^{13}C-NMR ($CDCl_3$): $\delta -0.40$ (C_d), 4.46 (C_b), 127.17 (C_p, arom), 128.03 (C_o, arom), 128.19 (C_m, arom), 128.32 (*ipso*-C_i, arom), 151.55 (C_c), 156.84 (C_a); EIMS; m/z (relative intensity): 288 [M^+, 6], 273 (30), 237 (8), 180 (25), 165 (11), 145 (22), 135 (100).

4.2.35. Phenyltrimethylsilylacetylene + phenyldichlorosilane (entry 12, Table 3)

Phenyldichlorosilane (3.3 g, 3.0 ml, 20 mmol) and 0.08 g of 1% Pt on carbon (4.1 µmol of Pt) were placed in a 25 ml two-necked flask. Phenyltrimethylsilylacetylene (3.4 g, 3.7 ml, 20 mmol) was added dropwise at 50 °C over 30 min. Heating the solution for 4 h at 85 °C gave 6.8 g (18.4 mmol, 92%) of E/Z-1-phenyl-l-phenyldichlorosilyl-2-trimethylsilylethene by vacuum distillation.

$PhC_a(SiCl_2Ph){=}C_b(H)Si{-}C_c$. EIMS; m/z (relative intensity): 350 [M^+, 7], 335 (28), 242 (28), 175 (26), 145 (18), 135 (49), 73 (100).

4.2.36. Phenyltrimethylsilylacetylene + triethylsilane (entry 13, Table 3)

Phenyltrimethylsilylacetylene (3.5 g, 3.8 ml, 20 mmol) and triethylsilane (2.3 g, 3.2 ml, 20 mmol) were added to 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). Heating the solution for 105 h at 80 °C gave 1.8 g (5 mmol, 48%) of E/Z-1-phenyl-1-triethylsilyl-2-trimethylsilylethene by vacuum distillation.

$PhC_a(Si{-}C_b{-}C_c){=}C_d(H)SiC_e$ ^{1}H-NMR ($CDCl_3$): δ 0.13 (s, 9H, H_e), 0.89 (q, J(H,H) = 7.7 Hz, 6H, H_b), 1.23 (t, J(H,H) = 7.7 Hz, 9H, H_c), 6.62 (s, 1H, H_a); EIMS; m/z (relative intensity): major isomer 290 [M^+, 1], 275 (5), 261 (100), 233 (2), 163 (45), 159 (26). Minor isomer 290 [M^+, 1.4], 261 (72), 173 (43), 159 (37), 149 (71), 135 (41), 101 (68), 87 (100).

4.2.37. Phenyltrimethylsilylacetylene + triethoxysilane (entry 14, Table 3)

Phenyltrimethylsilylacetylene (3.5 g, 3.8 ml, 20 mmol) and triethoxysilane (3.3 g, 3.8 ml, 20 mmol) were combined with 0.08 g of 1% Pt on carbon (4.1 µmol of Pt). After heating the solution for 21 h at 110 °C, vacuum distillation resulted in 5.7 g (18.5 mmol, 91%) of *E*/*Z*-1-phenyl-1-triethoxylsilyl-2-trimethylsilyethene.

$PhC_a(Si–O–C_b–C_c)=C_d(H)SiC_e$. Major isomer ^{1}H-NMR ($CDCl_3$): δ 0.01 (s, 9H, H_e), 1.28 (t, $J(H,H) = 6.9$ Hz, 9H, H_c), 3.89 (q, $J(H,H) = 6.9$ Hz, 6H, H_b); Major isomer ^{13}C ($CDCl_3$): δ 1.16 (C_e), 18.20 (C_c), 58.44 (C_b), 159.91 (C_a); minor isomer δ: 0.23 (s, 9H, H_e), 1.11 (t, $J(H,H) = 6.9$ Hz, 9H, H_c), 3.68 (q, $J(H,H) = 6.9$ Hz, 6H, H_b). EIMS; *m*/*e* (relative intensity): major isomer 323 [$M^+ - 15$, 3], 265 (5), 221 (7), 163 (36), 135 (28), 119 (39), 73 (100). Minor isomer 323 [$M^+ - 15$, 100], 263 (12), 249 (8), 221 (16), 135 (31), 119 (38), 73 (57). Anal. Found: C, 60.62; H, 9.18. Calc. for $C_{17}H_{30}O_3Si_2$: C, 60.29; H, 8.95%.

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