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Electrochemical Synthesis of 1,2-Disilylethanes from α-Silylacetic Acids

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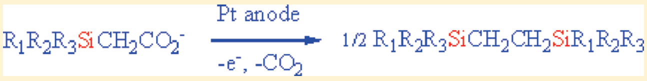
Supporting Information

ABSTRACT: The synthesis of 1,2-disilylethanes [$R_1R_2R_3Si(CH_2)_2SiR_1R_2R_3$] is usually conducted by using noble metal reagents or catalysts. This work describes a new electrochemical synthetic method for their preparation in good yields by oxidation of α-silylacetic acids at Pt anodes (Kolbe electrolysis). Most of the reported synthesized 1,2-disilylethanes in this work are unknown.



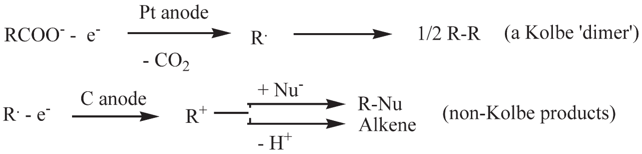
The well-known Kolbe electrolysis has been utilized as a useful method for the synthesis of 1,2-disilylethanes of the type $R_1R_2R_3Si(CH_2)_2SiR_1R_2R_3$ that have been prepared so far by using noble metal reagents or catalysts. The anodic oxidation of various α-silylacetic acids [$(R_1R_2R_3)SiCH_2COOH$] under basic conditions at Pt anodes provided the corresponding homocoupling products, after decarboxylation, in moderate to good yields.

Organic electrosynthesis has been established for selective and efficient chemical transformations.[1] The first and best known anodic electrosynthesis reaction is the Kolbe electrolysis, and it is still under active investigation.[2] It has been a simple and effective way of preparing a variety of organic compounds, also in industry, in large quantities.[3] In principle, Kolbe electrolysis leads to oxidative decarboxylation of carboxylate anions to generate radical intermediates that undergo C−C coupling to provide Kolbe "dimers".

However, under certain conditions, the radical intermediate could be further oxidized to the corresponding carbenium ion to afford the so-called "non-Kolbe" products, as illustrated in Scheme 1.

The selectivity of the Kolbe reaction depends on the structural parameters of the carboxylic acid and electrochemical conditions. For instance, the Kolbe dimers are favored when a platinum anode is used and the radical intermediate is either primary or substituted by electron-withdrawing group(s).[4] From this point of view, it is interesting to investigate the Kolbe oxidation of carboxylic acids with silyl substituents at the α-position because of two contradictive effects. Previously, Wilt and co-workers[5] demonstrated that α-silyl groups stabilize alkyl radicals to some extent. A similar trend was also shown by gas phase kinetic experiments.[6] Therefore, it is reasonable to assume that this property (known as the "α-effect") may also contribute to the stabilization of radicals generated in the Kolbe oxidation of α-silylcarboxylic acids and promote the formation of "dimeric" products. However, there is a contradictive effect that stems from the polarity of the Si−C bond, causing the silyl group at the α-position to be the electron-donating group in nature. This property causes the carboxylic group to be less acidic and, therefore, more reluctant to form a carboxylate anion, which is necessary for the Kolbe reaction to take place.

Scheme 1



Organosilicon chemicals and materials are attracting an increasing amount of attention because of their versatile chemical and physical properties. Over the past three decades, organosilicon chemistry has grown rapidly, and today organosilicon compounds are widely utilized as various functional materials and reagents.[7] For example, symmetric 1,2-disilylethanes of the type $R_3Si(CH_2)_2SiR_3$ (R = alkyl, Ph, or mixed) have been used as precursors for a wide range of organosilicon derivatives, including molecular,[8] polymeric,[9] dendritic,[10] and drug design[11] entities. They are also used for the preparation of novel complexes[12] and as new ligands for bioorganic[13] and catalytic purposes.[14]

1,2-Disilylethanes are usually prepared by the use of expensive noble metal reagents or catalysts. The most useful catalysts for their preparation are based on platinum and have been developed by Speier[15] and Karstedt.[16] Additional noble metal systems predominantly contain Rh, Ru, Ir, and Pt centers and have been used efficiently in specific reactions.[17] Dunoges et al. synthesized phenyl-substituted 1,2-disilylethanes by reductive silylation of alkenes using magnesium and the carcinogenic solvent hexamethylphosphoric triamide (HMPT).[18] Fry et al. obtained 1,2-bis(trimethylsilyl)-1,2-diphenylethanes among other products by electrochemical reduction of α-trimethylsilylbenzyl bromide.[19]

This work demonstrates a new synthetic method for the preparation of functional 1,2-disilylethanes in good yields by Kolbe anodic oxidation of α-silylacetic acids prepared previously.[20]

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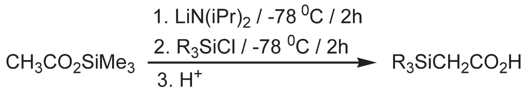
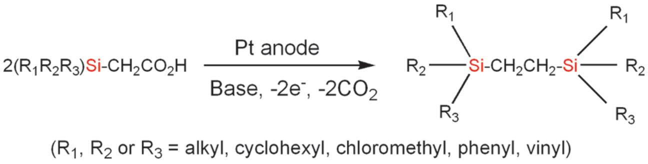
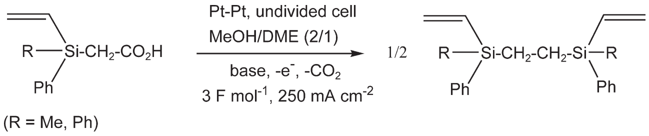
Scheme 2



Scheme 3



Scheme 4



Scheme 2 outlines the favorable experimental conditions for synthesizing different types of α-silylacetic acids.

Previously, we investigated the preferred conditions for the electrochemical decarboxylation of $Ph_2MeSiCH_2CO_2H$ (**1**) as a model for α-silylacetic acids, by examining various parameters (e.g., solvent, nature of base, concentration of base, current density, etc.).[21] It turned out that such investigations were necessary and unavoidable because the commonly used conditions for Kolbe electrolysis of carboxylic acids were not useful for α-silylcarboxylic acids. For example, when initially $Ph_2MeSiCH_2CO_2H$ was dissolved in methanol containing sodium methoxide or potassium hydroxide to neutralize a small portion (~2−5%) of the acid and then electrolyze the solution between two platinum electrodes at a high current density,[22] the reaction did not take place at all. Apparently, the weak nature of the α-silylacetic acid did not allow the formation of the corresponding carboxylate anion in a meaningful amount. Indeed, this assumption is supported by the claim that α-silylacetic acids are weak acids with pK_a values of >5.22 (for comparison, the pK_a of acetic acid is 4.75).[23] Obviously, the inductive effect exerted by the silicon group decreases the strength of the acid.

In this respect, we have also examined Kolbe electrolysis by using solid-supported bases (e.g., silica gel-supported piperidine), following recent work by Fuchigami and co-workers.[2a] Again, the basic power of the organic base was too weak to allow formation of carboxylate anions and therefore caused a high cell voltage that prevented a high current density, necessary to obtain Kolbe-type products. Consequently, under these conditions, the electrochemical decarboxylation of $Ph_2MeSiCH_2CO_2H$ provided the desired Kolbe dimer in low yields.

Finally, by adopting the "optimal" conditions reported previously[21] for the Kolbe electrolysis of $Ph_2MeSiCH_2CO_2H$ to other α-silylacetic acids, and especially when a high concentration of a strong base was used (3 N KOH, 25%), the decarboxylation process afforded dimeric products in moderate to good yields. A summary of the optimized reaction conditions is illustrated in Scheme 3, and the results of the Kolbe reaction are described in Table 1. It appears that α-silylacetic acids with less hindered silyl substituents [Me_3Si, $Me_2(CH_2Cl)Si$, Me_2PhSi, and $MePh_2Si$] undergo a smooth Kolbe anodic oxidation to give dimeric products in good isolated yields (entries 1−4). In these cases, it is likely that the α-silyl group favors stabilization of a carbon radical rather than a carbenium ion and, consequently, increases the yield of Kolbe dimers. However, when more sterically hindered silyl substituents were employed (entries 5−7), the yields of the dimeric products decreased in the following order: $Me_3Si \sim Me_2(CH_2Cl)Si \sim Me_2(Ph)Si \sim Me(Ph)_2Si > Ph_3Si >$ *n*-$Pr_3Si > Me_2(cyclohexyl)Si$.

Interestingly, these results are in good correlation with the data reported in the literature. The relative steric bulk of trialkylsilyl groups was described by Cheng and co-workers,[24] and the same order of bulkiness for trialkylsilyl groups was observed. Apparently, it seems that steric effects play an important role in the Kolbe decarboxylation of α-silylacetic acids.

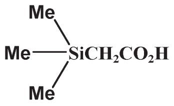
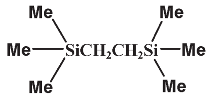
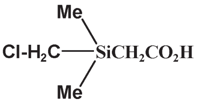
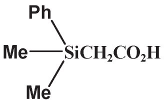
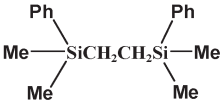
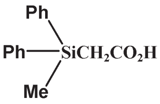
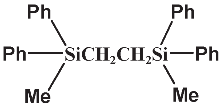
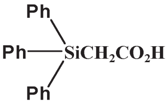
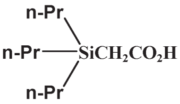
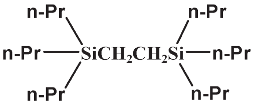
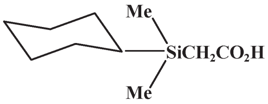
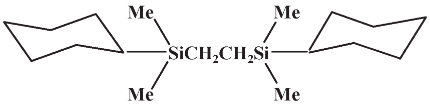
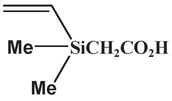
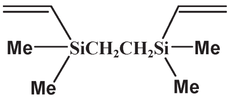
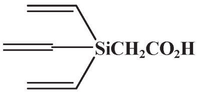
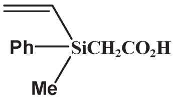
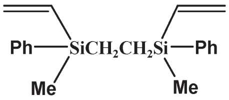
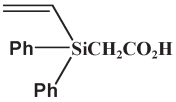
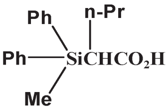
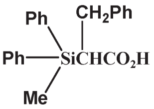
To investigate the usefulness of the Kolbe electrolysis for other types of silyl groups bearing unsaturated alkene(s), we used α-silylacetic acids with silylvinyl moieties, as shown in Table 1 (entries 8−11). The results indicate that the Kolbe oxidation of Me_2(vinyl)silylacetic and $(vinyl)_3$silylacetic acids (entries 8 and 9, respectively) affords Kolbe dimers in moderate yields (~50%) with only partial polymerization of the substrate (15−20%). The isolated polymers (white powders) can be easily separated at the end of the electrolysis by filtration because of their insolubility in the CH_3CN/MeOH reaction medium. The formation of polymers is not surprising, because the Kolbe reaction includes radical intermediates that could encourage polymerization of the substrate via its vinyl moieties.

It is noteworthy that the Kolbe electrolysis of α-silylacetic acids with silyl(vinyl)(phenyl) substituents (entries 10 and 11) afforded mostly polymerization at the surface of the platinum anode under similar experimental conditions. In attempts to prevent the polymerization, we changed the electrolysis medium by employing 1,2-dimethoxyethane (DME) (instead of CH_3CN) as a cosolvent with methanol. Indeed, the polymerization at the substrate was prevented, and the desired Kolbe dimers were formed in moderate yields. Possibly, DME acts as a sacrificial solvent, being electrolyzed by itself at the electrode surface, and competes favorably with the polymerization reaction, or it is preferably adsorbed at the electrode surface compared to the substrate.

A mixture of MeOH/DME in a 2/1 ratio (v/v) was found to be the best choice for the Kolbe oxidation of such acids. Interestingly, a larger volume of DME in the MeOH/DME mixture decreases both the current density and yield of the dimeric product but encourages the non-Kolbe process. On the other hand, a larger volume of MeOH in the mixture causes the polymerization process to become predominant. The overall experimental conditions for the preparation of 1,2-disilylethanes **10** and **11** are illustrated in Scheme 4.

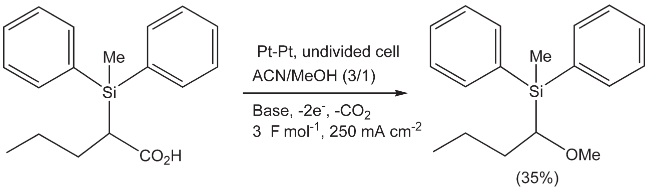
It was claimed that the yields of Kolbe dimers are very low when the α-position of the acid bears an electron-donating substituent capable of stabilizing carbenium ions.[4] In this respect, the anodic oxidation of α-silylcarboxylic acids with alkyl subsituents at the α-position in addition to the silyl group at the same position has been investigated as well. Although it has been known that α-silyl groups stabilize alkyl radicals, as also demonstrated above, an addition of an alkyl substituent should favor carbenium ion stabilization and, at the same time, a reduction in acid strength. Therefore, it is not surprising that no Kolbe dimers were detected from electrolysis of such acids (entries 12 and 13).

Table 1. Synthesis of 1,2-Disilylethanes by Kolbe Anodic Oxidation of α-Silylacetic Acids

Entry	Substrate	Electricity consumption (Faradays)	Product	Product assignment	Yield[a]
1[b]		4		**1**	77
2[b]		4		**2**	70
3[b]		3		**3**	76
4[b]		3		**4**	71
5[b]		3		**5**	62
6[b]		3		**6**	53
7[b]		5		**7**	45
8[b]		3		**8**	50
9[b]		4		**9**	47
10[c]		3		**10**	62
11[c]		3		**11**	52
12[b]		4	-	-	0[d]
13[b]		4	-	-	0[d]

[a] Isolated yields. No attempts were made to optimize yields. [b] Conducted in a MeCN/MeOH mixture (3/1). [c] Conducted in a MeOH/DME mixture (2/1). Unreacted starting material was left and minor non-Kolbe products were formed. [d] No dimer was found (see the text for more details).

Scheme 5



In fact, electrolysis of $Ph_2MeSiCH(n\text{-}Pr)CO_2H$ afforded 50% of the recovered starting material and non-Kolbe products, with no evidence of a dimeric product, as shown in Scheme 5, where only the major non-Kolbe product is described. On the other hand, electrolysis of $Ph_2MeSiCH(benzyl)CO_2H$ led to a complete desilylation under the same experimental conditions.

In summary, an electrochemical method has been utilized for the synthesis of symmetric 1,2-disilylethanes of the type $R_3Si(CH_2)_2SiR_3$ in good isolated yields, based on Kolbe anodic oxidation of various α-silylacetic acids. Most of the dimeric products are new, and three of them (**9**−**11**) could be potentially useful as precursors for preparing novel polymers and dendrones.

EXPERIMENTAL SECTION

General. α-Silylacetic acids were prepared according to our previously published report (see ref 20). All other reagents and solvents were purchased from commercial suppliers and used without further purification.

^1H NMR spectra were recorded for all samples in $CDCl_3$. Chemical shifts for ^1H NMR spectra are reported as δ in parts per million relative to the signal of chloroform-*d* (δ, 7.26, singlet). The number of protons (*n*) for a given resonance is indicated by n_H. Coupling constants are reported as *J* values in hertz. ^{13}C NMR spectra are reported as δ in parts per million relative to the signal of chloroform-*d* (δ, 77.03, triplet). ^{29}Si NMR spectra are reported as δ in parts per million. Mass spectral data are reported in units of mass to charge (*m*/*z*). Kolbe electrolyses were performed in an undivided cell, using a Potentiostat/Galvanostat.

Procedures and Spectral Data of Products. *General Procedure for the Synthesis of Dimer **4** as a Representative for 1,2-Disilylethanes **1**−**9**.* A mixture of $Ph_2MeSiCH_2CO_2H$ (2.5 mmol) and 3 N KOH (0.63 mmol) was electrolyzed in a wall-jacketed (to allow a steady flow of tab water during electrolysis) undivided cell, equipped with two platinum plates electrode (2 cm × 1.2 cm), in 20 mL of a MeOH/MeCN solvent mixture (1/3, v/v). In a typical experiment, after the desired electricity was consumed, a few drops of concentrated acetic acid were added to acidify the mixture, and the solvents were removed by evaporation. The crude product was dissolved in diethyl ether and washed with a 5% sodium bicarbonate solution and finally with brine. After phase separation, the ethereal solution was dried over magnesium sulfate and filtered. Evaporation of the ether gave a crude dimeric nonpolar product that was simply purified with a silica gel column via elution with a hexane/acetone mixture (95/5, v/v, %). Evaporation of the solvents afforded a pure dimeric product **4**, after separation from unreacted starting material.

Electrolysis of substrates **10** and **11** was conducted in 20 mL of a MeOH/DME solvent mixture (2/1, v/v) (DME = 1,2-dimethoxyethane). Constant-current electrolysis was conducted with magnetic stirring. The conversion of the substrate to the Kolbe dimer was monitored by ^1H NMR and TLC, using hexane as the eluent.

*1,2-Bis(trimethylsilyl)ethane (**1**)*:[25] colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ −0.04 (s, 18H), 0.36 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −2.2, 8.7; ^{29}Si NMR (100 MHz, $CDCl_3$) δ 3.4; GC−MS (*m*/*z*) (%) $M^{+\bullet}$ 174 (16), 159 (25), 86 (33), 73 (100), 58 (5), 45 (5).

*1,2-Bis[dimethyl(chloromethyl)silyl]ethane (**2**)*: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.11 (s, 12H), 0.55 (s, 4H), 2.80 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.2, 5.4, 29.8; ^{29}Si NMR (100 MHz, $CDCl_3$) δ 4.6; MS (MALDI-TOF) *m*/*z* calcd for $C_8H_{20}Cl_2Si_2$ $[M + H]^+$ 243.056, found 243.120.

*1,2-Bis[dimethyl(phenyl)silyl]ethane (**3**)*:[26] mp 57−59 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 0.28 (s, 12H), 0.70 (s, 4H), 7.34−7.58 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −3.6, 7.8, 127.7, 128.8, 133.6, 139.3; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −1.2; GC−MS (*m*/*z*) (%) $M^{+\bullet}$ 298 (8), 283 (12), 135 (100), 120 (5), 105 (5).

*1,2-Bis[diphenyl(methyl)silyl]ethane (**4**)*: mp 85−87 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 0.62 (s, 6H), 1.10 (s, 4H), 7.35−7.56 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.2, 6.3, 127.8, 129.1, 134.5, 139.0; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −5.4; GC−MS (*m*/*z*) (%) $M^{+\bullet}$ 422 (1), 394 (6), 197 (100), 165 (5), 105 (11). Anal. Calcd for $C_{28}H_{30}Si_2$: C, 79.56; H, 7.15. Found: C, 79.27; H, 7.32.

*1,2-Bis(triphenylsilyl)ethane (**5**)*: mp 207−209 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.46 (s, 4H), 7.31−7.57 (m, 30H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.6, 127.8, 129.4, 134.8, 135.7; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −10.7; MS (MALDI-TOF) *m*/*z* calcd for $C_{38}H_{34}Si_2$ $[M + Ag]^+$ 653.125, found 653.137. Anal. Calcd for $C_{38}H_{34}Si_2$: C, 83.46; H, 6.27. Found: C, 83.28; H, 6.32.

*1,2-Bis(tri-n-propylsilyl)ethane (**6**)*: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.37 (s, 4H), 0.48−0.52 (m, 12H), 0.94−0.98 (t, *J* = 7.0, 18H), 1.28−1.34 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.4, 14.9, 17.5, 18.7; ^{29}Si NMR (100 MHz, $CDCl_3$) δ 5.5; MS (MALDI-TOF) *m*/*z* calcd for $C_{20}H_{46}Si_2$ $[M + Ag]^+$ 449.219, found 449.461. Anal. Calcd for $C_{20}H_{46}Si_2$: C, 70.08; H, 13.52. Found: C, 70.15; H, 13.31.

*1,2-Bis[dimethyl(cyclohexyl)silyl]ethane (**7**)*: mp 52−53 °C; ^1H NMR (500 MHz, $CDCl_3$) δ −0.10 (s, 12H), 0.35 (s, 4H), 0.59−0.65 (m, 2H), 1.05−1.27 (m, 10H), 1.62−1.75 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.9, 5.4, 25.0, 27.1, 27.6, 28.2; ^{29}Si NMR (100 MHz, $CDCl_3$) δ 4.9; MS (MALDI-TOF) *m*/*z* calcd for $C_{18}H_{38}Si_2$ $[M + Na]^+$ 333.241, found 333.576. Anal. Calcd for $C_{18}H_{38}Si_2$: C, 69.59; H, 12.33. Found: C, 69.72; H, 12.62.

*1,2-Bis[dimethyl(vinyl)silyl]ethane (**8**)*:[27] colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 0.07 (s, 12H), 0.48 (s, 4H), 5.68 (d × d, 2H, ^2J = 4.8, ^3J = 19.6), 5.91−6.25 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −4.0, 7.4, 131.5, 139.0; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −5.1; GC−MS (*m*/*z*) (%) $M^{+\bullet}$ 199 (1), 171 (71), 133 (85), 97 (31), 85 (100).

*1,2-Bis(trivinylsilyl)ethane (**9**)*: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.71 (s, 4H), 5.77 (d × d, 6H, ^2J = 5.5, ^3J = 19.0), 6.06−6.18 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.3, 127.9, 129.4, 134.2, 135.0, 135.3, 136.0; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −12.2; MS (MALDI-TOF) *m*/*z* calcd for $C_{14}H_{22}Si_2$ $[M + Ag]^+$ 353.031, found 353.303. Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.21; H, 9.00. Found: C, 68.54; H, 8.90.

*1,2-Bis[methyl(vinyl)phenylsilyl]ethane (**10**)*: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.43 (s, 6H), 0.80 (s, 4H), 5.77 (d × d, 2H, ^2J = 3.5, ^3J = 20), 6.11 (d × d, ^2J = 3.5, ^3J = 14.5, 1H), 6.27 (d × d, ^3J = 14.5, ^3J = 20.0, 1H), 7.33−7.50 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.6, 6.2, 127.8, 129.0, 133.6, 134.2, 136.5, 137.3; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −6.6; MS (MALDI-TOF) *m*/*z* calcd for $C_{20}H_{26}Si_2$ $[M + Ag]^+$ 429.062, found 429.315. Anal. Calcd for $C_{20}H_{26}Si_2$: C, 74.46; H, 8.12. Found: C, 74.66; H, 7.96.

*1,2-Bis[diphenyl(vinyl)silyl]ethane (**11**)*: mp 95−97 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.24 (s, 4H), 5.80 (d × d, ^2J = 3.0, ^3J = 20.5, 2H), 6.28 (d × d, ^2J = 3.5, ^3J = 14.5, 2H), 6.54 (d × d, ^3J = 20.5, ^3J = 14.5, 2H), 7.37−7.54 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.28, 127.9, 129.4, 134.2, 135.0, 135.3, 136.0; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −12.2; MS (MALDI-TOF) *m*/*z* calcd for $C_{30}H_{30}Si_2$ $[M + Ag]^+$ 553.094, found 553.078. Anal. Calcd for $C_{30}H_{30}Si_2$: C, 80.66; H, 6.77. Found: C, 80.35; H, 6.80.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Copies of ^{1}H, ^{13}C, and ^{29}Si NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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