An Improved Synthesis of 2-Aryl-1,1-bis(trimethylsilyl)ethenes

Piotr Pawluć,* Grzegorz Hreczycho, Martyna Madalska, Justyna Szudkowska, Maciej Kubicki, Bogdan Marciniec*
Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland
Fax +48(61)8291508; E-mail: marcinb@amu.edu.pl; E-mail: piotrpaw@amu.edu.pl

Received 23 March 2009; revised 20 July 2009

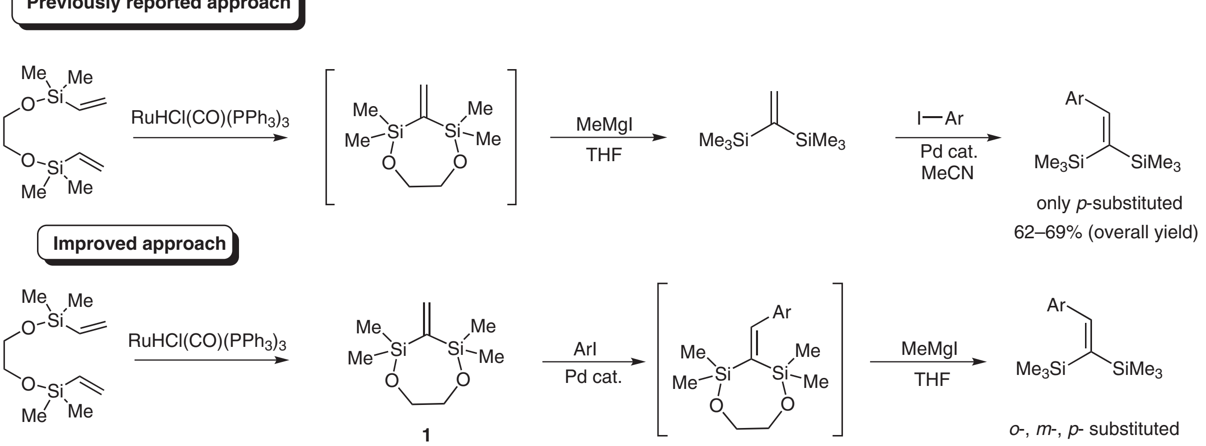
Abstract: A series of new 2-aryl-1,1-bis(trimethylsilyl)ethenes containing *ortho*-, *meta*-, and *para*-substituted aryl or heteroaryl groups has been efficiently synthesized using an improved two-step approach based on a silylative coupling cyclization–Heck coupling/Grignard reaction sequence. The crystal structure of the first 1,1-bis(trimethylsilyl)alk-1-ene containing a heteroaryl group is reported.

Key words: bis(silyl)alkene, Heck reaction, Grignard reaction, cross coupling, organometallic reagent

1,1-Bis(silyl)alk-1-enes are a class of compounds that has attracted significant attention in recent years as important intermediates in organic and organometallic synthesis.[1] In particular, geminal silyl-substituted alkenes can serve as precursors for the preparation of ketones[2] as well as a variety of important organosilicon intermediates such as acylsilanes,[3] epoxysilanes,[3b] silyl enol ethers,[4] (*E*)-alkenylsilanes,[5] α-silyl-α,β-unsaturated enones,[6] etc. Recently, we have successfully explored the synthetic utility of acyclic 2-aryl-1,1-bis(silyl)ethenes for the selective synthesis of 2-aryl-1,1-dibromoethenes[7] and (*Z*)-2-aryl-1-iodo-1-silylethenes.[8] Moreover, a cyclic 1,1-bis(silyl)ethene has been found to be a versatile building block for the synthesis of (*E*)-stilbenes and (*E*)-arylenevinylene polymers.[9]

Conventional approaches to 1,1-bis(silyl)alk-1-enes involve multistep reactions of carbonyl compounds with commercially unavailable dihalobis(silyl)methanes.[3b,4] Hodgson and co-workers have developed chromium(II)-mediated reaction of aldehydes with dibromobis(silyl)methanes.[3b] The reaction of dibromobis(silyl)methanes with lithium trialkylmagnesate or (trialkylsilyl)methylmagnesium chloride followed by dehydrobromination of the resulting 1-bromo-1,1-bis(silyl)alkanes provides an alternative route to 1,1-bis(silyl)alk-1-enes.[10] Several independent methods such as Peterson olefination of carbonyl compounds using lithium tris(trimethylsilyl)methanide[6,11] or regioselective hydrosilylation of alkynylsilanes[12] have also been investigated. However, the application of most of these methods is limited by complicated synthetic procedures involving the use of harmful starting materials and highly reactive organolithium compounds.

Recently, we have developed a new protocol for the synthesis of 2-aryl-1,1-bis(silyl)ethenes from easily available starting materials using a sequential procedure: ethylene glycol silylation–one-pot silylative coupling cyclization/Grignard reagent treatment–Heck coupling (Scheme 1).[1] Starting from 1,2-bis[dimethyl(vinyl)siloxy]ethane we synthesized various *para*-substituted 2-aryl-1,1-bis(silyl)ethenes in two steps with 62–69% overall yield. The first step, however, of this transformation, i.e. the one-pot



Scheme 1 Synthesis of 2-aryl-1,1-bis(silyl)ethenes

SYNTHESIS 2009, No. 22, pp 3843–3847
Advanced online publication: 07.10.2009
DOI: 10.1055/s-0029-1218155; Art ID: T06609SS

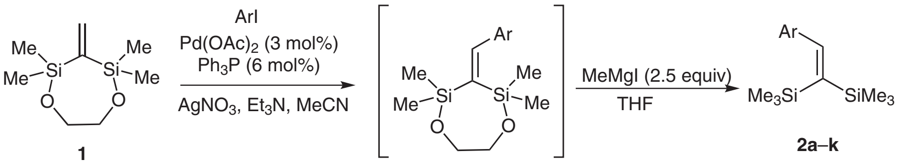
silylative coupling cyclization/Grignard substitution occurred with a moderate 72% yield. This limitation resulted in the search for a more efficient methodology for the synthesis of 2-aryl-1,1-bis(silyl)ethenes by changing the reaction sequence. As the initial step of this sequential transformation proceeds with higher yield under optimized conditions, we decided to isolate the cyclic derivative **1** and then perform the Heck coupling and Grignard reagent substitution as a one-pot procedure, without isolation of the cyclic Heck coupling product (Scheme 1).

We report here on the improved synthesis of new *ortho*-, *meta*-, and *para*-substituted 2-aryl-1,1-bis(silyl)ethenes **2** based on a modification of our previously reported method, using a sequential silylative coupling cyclization–Heck coupling and Grignard reaction.

As we reported earlier, the $RuHCl(CO)(PPh_3)_3$-catalyzed silylative coupling cyclization of 1,2-bis[dimethyl(vinyl)siloxy]ethane [prepared via O-silylation of ethylene glycol by chlorodimethyl(vinyl)silane][13] gives exclusively 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane (**1**) in 85% yield. During the course of our recent studies, we observed that this reaction occurred even more efficiently when conducted in toluene (1 M solution) with lower catalyst loading (0.5 mol%), however, it required a longer time (24 h). Application of these optimized conditions for silylative coupling cyclization of 1,2-bis[dimethyl(vinyl)siloxy]ethane led to compound **1** in almost quantitative yield (~95%).

Since we have recently reported an efficient procedure for the selective Heck coupling of acyclic 1,1-bis(silyl)ethenes with aryl and alkenyl iodides,[1] the coupling of **1** with aryl iodides was performed in the presence of palladium(II) acetate/triphenylphosphine as catalyst, using triethylamine and silver nitrate as iodine abstractor.[14] The reaction of compound **1** (1 equiv) with aryl iodide (1 equiv), silver nitrate (1 equiv), and triethylamine (1.5 equiv), in the presence of palladium(II) acetate (3 mol%) and triphenylphosphine (6 mol%), conducted in acetonitrile at 60 °C for one hour, afforded exclusively the corresponding 3-benzylidene-2,2,4,4-tetramethyl-1,5-dioxa-2,4-disilacycloheptane derivatives in quantitative yield (GCMS analysis of the reaction mixture confirmed the absence of the starting compounds and formation of a single product). However, when heteroaryl iodides or 1-chloro-2-iodobenzene were used, the coupling reaction required a longer time (24 h) and in the case of 1-chloro-2-iodobenzene and 2-iodothiophene reaction proceeded with 80% conversion of the iodide. The noteworthy features of these processes are that the formation of styrene and stilbene derivatives (via desilylation) was completely suppressed, and the formation of biaryls (by homocoupling of the aryl iodides) was not observed. The intermediate b-aryl-substituted cyclic 1,1-bis(silyl)ethenes (Heck coupling products) were not isolated, but were concentrated under reduced pressure to remove acetonitrile and then extracted with a small amount of hexane to remove the palladium catalyst. The hexane solution of crude cyclic compounds was directly subjected to reaction with excess methylmagnesium iodide (1 M in THF; molar ratio **1**/MeMgI 1:2.5) and the reaction mixture was heated in tetrahydrofuran under a flow of argon at 65 °C for 24 hours to form the desired 2-aryl-1,1-bis(trimethylsilyl)ethenes **2**. The crude products obtained was purified by column chromatography (silica gel/hexane) to give corresponding 2-aryl-1,1-bis(silyl)ethenes **2** in 62–90% overall yield (Table 1)..

Table 1 2-Aryl-1,1-bis(trimethylsilyl)ethenes via Sequential Heck Coupling–Grignard Substitution[a]



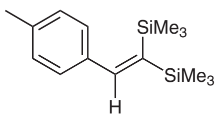
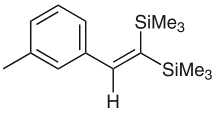
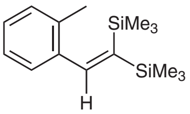
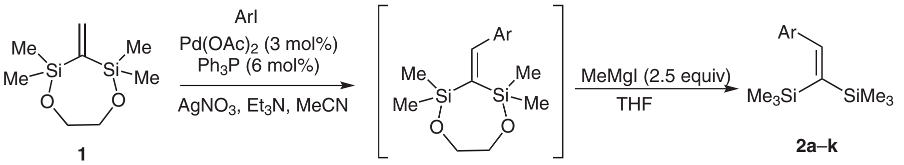
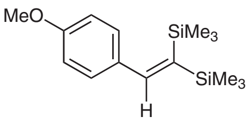
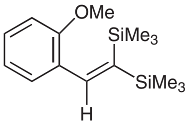
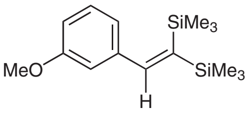
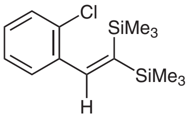
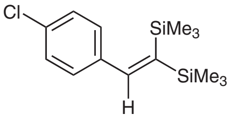
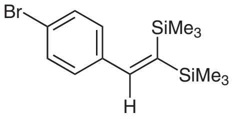
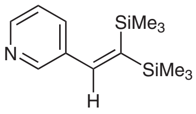
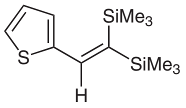
Entry	Ar	Product	Yield[b] (%)
1	4-MeC_6H_4	 **2a**	90
2	3-MeC_6H_4	 **2b**	76
3	2-MeC_6H_4	 **2c**	74

Table 1 2-Aryl-1,1-bis(trimethylsilyl)ethenes via Sequential Heck Coupling–Grignard Substitution[a] (continued)



Entry	Ar	Product	Yield[b] (%)
4	4-$MeOC_6H_4$	 **2d**	88
5	2-$MeOC_6H_4$	 **2e**	74
6	3-$MeOC_6H_4$	 **2f**	80
7	2-ClC_6H_4	 **2g**	62[c,d]
8	4-ClC_6H_4	 **2h**	82
9	4-BrC_6H_4	 **2i**	85
10	3-pyridyl	 **2j**	74[c]
11	2-thienyl	 **2k**	68[c,d]

[a] Reaction conditions: Heck coupling: $Pd(OAc)_2/Ph_3P/AgNO_3/Et_3N/ArI/\mathbf{1}$ = 0.03:0.06:1:1.5:1:1, 60 °C, 1 h; Grignard substitution: MeMgI (2.5 equiv), 65 °C, 24 h.

[b] Isolated yields of chromatographically pure products.

[c] Heck coupling performed at 60 °C for 24 h.

[d] The conversion of iodide was 80% after 24 h.

2-(3-Pyridyl)-1,1-bis(trimethylsilyl)ethene (**2j**) proved to be a solid and yielded a crystal amenable to X-ray crystal structure determination. To the best of our knowledge, this is the first structural characterization of a geminal silyl-substituted alkene containing a heteroaryl group. The thermal-ellipsoid representation of molecule **2j** is shown in Figure 1. The crystal structure of **2j** contains two symmetry-independent molecules that have different conformation along the C3–C7 bond. In one of the molecules the C7=C8 bond is turned towards the nitrogen atom [C2–

C3–C7–C8 torsion angle is 63.6(3)°], while in the second one it is turned in opposite direction [–122.4(3)°]. In this structure only van der Waals forces determine the crystal packing.

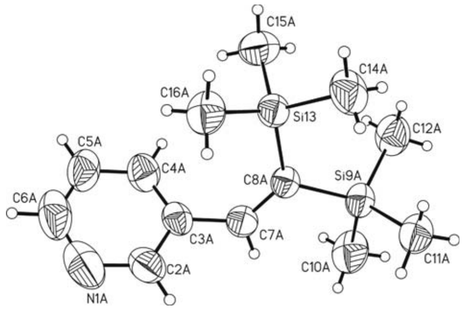


Figure 1 Perspective view of one of the symmetry-independent molecules of **2j(A)**.[16] The anisotropic displacement ellipsoids were drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii. Only the atoms with larger occupancy are shown.

In conclusion, a new high-yielding reaction sequence based on ruthenium-catalyzed silylative coupling cyclization and palladium-catalyzed Heck coupling/Grignard substitution has been applied to the preparation of synthetically useful 2-aryl-1,1-bis(silyl)ethenes. Further results on the application of these compounds to the reactions with electrophiles will be reported in due course.

Et_3N and *n*-hexane were dried over CaH_2, distilled under argon, and stored over 4 Å molecular sieves. THF was dried over Na/benzophenone and freshly distilled prior to use. 1,2-Bis[dimethyl(vinyl)siloxy]ethane was synthesized using ethylene glycol silylation procedure described in the literature.[13] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ as a solvent. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. Mass spectra of the products were determined by GCMS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and a Finigan Mat 800 ion trap detector.

2,2,4,4-Tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane (1)

$RuHCl(CO)(PPh_3)_3$ (0.20 g, 0.215 mmol), 1,2-bis[dimethyl(vinyl)siloxy]ethane (10.0 g, 43 mmol), and toluene (35 mL) were placed in a two-necked, 100-mL flask equipped with a magnetic stirring bar and a reflux condenser. The mixture was heated at 110 °C for 24 h with stirring. The cyclic product was isolated by evaporation of toluene and bulb-to-bulb distillation of the crude compound to give **1** (8.34 g, 95%).

2-Aryl-1,1-bis(trimethylsilyl)ethenes 2; General Procedure

A mixture consisting of $Pd(OAc)_2$ (33.5 mg, 0.15 mmol), Ph_3P (78.6 mg, 0.3 mmol), $AgNO_3$ (0.85 g, 5 mmol), ArI (5 mmol), 1,1-bis(silyl)ethene **1** (1.00 g, 5 mmol), Et_3N (1.05 mL, 0.762 g, 7.5 mmol), and MeCN (10 mL) was placed in a two-necked, 50-mL, round-bottomed flask equipped with a magnetic stirring bar and reflux condenser. The suspension was heated in an oil bath at 60 °C for 1 h. After cooling to r.t., the solvent was evaporated and the mixture was extracted with hexane (2 × 10 mL) to remove inorganic salts and catalyst. The combined organic layers were dissolved in anhyd THF (100 mL) and 1 M MeMgI in THF (2.5 equiv) was added dropwise. The mixture was heated under a flow of argon at 65 °C for 24 h with stirring. The crude products obtained were then purified by column chromatography (silica gel, hexane) to give the corresponding compounds **2a**–**k**. The structures of known 2-aryl-1,1-bis(trimethylsilyl)ethenes, i.e., compounds **2a** and **2d**, were confirmed by GC-MS and NMR spectroscopy matching data reported in the literature.[1]

2-(3-Methylphenyl)-1,1-bis(trimethylsilyl)ethene (2b)

Colorless oil; yield: 0.99 g (76%).

^1H NMR ($CDCl_3$): δ = –0.04 (s, 9 H, $SiCH_3$), 0.20 (s, 9 H, $SiCH_3$), 2.35 (s, 3 H, CH_3), 6.97–7.07 (m, 2 H, Ar), 7.16–7.21 (t, 2 H, Ar), 7.74 (s, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ = 0.7 ($SiCH_3$), 2.2 ($SiCH_3$), 21.4 (CH_3), 124.7, 127.7, 128.3, 136.5, 139.7, 142.5 (Ar), 145.4 (CH=), 154.8 (C=).

MS (EI): *m/z* (%) = 262 ($[M]^+$, 20), 247 (100), 189 (55), 173 (30), 159 (20), 159 (20), 149 (70), 73 (95), 59 (15).

HRMS: *m/z* $[M]^+$ calcd for $C_{15}H_{26}Si_2$: 262.1573; found: 262.1578.

2-(2-Methylphenyl)-1,1-bis(trimethylsilyl)ethene (2c)

Colorless oil; yield: 0.97 g (74%).

^1H NMR ($CDCl_3$): δ = –0.13 (s, 9 H, $SiCH_3$), 0.20 (s, 9 H, $SiCH_3$), 2.20 (s, 3 H, CH_3), 7.09–7.15 (m, 4 H, Ar), 7.69 (CH=).

^{13}C NMR ($CDCl_3$): δ = 0.6 ($SiCH_3$), 1.7 ($SiCH_3$), 19.7 (CH_3), 125.1, 127.1, 128.1, 129.2, 134.8, 142.4 (Ar), 145.7 (CH=), 154.6 (C=).

MS (EI): *m/z* (%) = 262 ($[M]^+$, 10), 247 (100), 231 (5), 189 (25), 173 (20), 159 (10), 159 (20), 149 (30), 131 (10), 119 (10), 73 (50).

HRMS: *m/z* $[M]^+$ calcd for $C_{15}H_{26}Si_2$: 262.1573; found: 262.1575.

2-(2-Methoxyphenyl)-1,1-bis(trimethylsilyl)ethene (2e)

Colorless oil; yield: 1.03 g (74%).

^1H NMR ($CDCl_3$): δ = –0.04 (s, 9 H, $SiCH_3$), 0.21 (s, 9 H, $SiCH_3$), 3.81 (s, 3 H, CH_3), 7.14–7.21 (m, 4 H, Ar), 7.69 (s, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ = –4.9 ($SiCH_3$), –2.1 ($SiCH_3$), 52.7 (CH_3O), 111.5, 126.8, 129.6, 138.3 (Ar), 149.2 (CH=), 154.5 (C=).

MS (EI): *m/z* (%) = 278 ($[M]^+$, 15), 263 (100), 184 (60), 175 (15), 153 (10), 73 (55).

HRMS: *m/z* $[M]^+$ calcd for $C_{15}H_{26}OSi_2$: 278.1522; found: 278.1603.

2-(3-Methoxyphenyl)-1,1-bis(trimethylsilyl)ethene (2f)

Colorless oil; yield: 1.11 g (80%).

^1H NMR ($CDCl_3$): δ = –0.03 (s, 9 H, $SiCH_3$), 0.19 (s, 9 H, $SiCH_3$), 3.82 (s, 3 H, CH_3), 6.72–6.80 (m, 3 H, Ar), 7.17–7.22 (m, 1 H, Ar), 7.67 (s, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ = –6.6 ($SiCH_3$), –4.1 ($SiCH_3$), 49.9 (CH_3O), 107.8, 108.4, 115.0, 123.7, 124.3, 137.3 (Ar), 149.2 (CH=), 154.5 (C=).

MS (EI): *m/z* (%) = 278 ($[M]^+$, 10), 263 (100), 205 (30), 189 (20), 175 (15), 165 (30), 73 (55).

HRMS: *m/z* $[M]^+$ calcd for $C_{15}H_{26}OSi_2$: 278.1522; found: 278.1537.

2-(2-Chlorophenyl)-1,1-bis(trimethylsilyl)ethene (2g)

Colorless oil; yield: 0.88 g (62%).

^1H NMR ($CDCl_3$): δ = –0.07 (s, 9 H, $SiCH_3$), 0.20 (s, 9 H, $SiCH_3$), 7.15–7.29 (m, 4 H, Ar), 7.59 (s, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ = 0.4 ($SiCH_3$), 1.5 ($SiCH_3$), 127.1, 128.5, 129.8, 135.8 (Ar), 147.6 (CH=), 151.7 (C=).

MS (EI): *m/z* (%) = 282 ($[M]^+$, 5), 241 (10), 214 (80), 159 (20), 133 (100), 83 (25).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{23}ClSi_2$: 282.1027; found: 282.1003.

2-(4-Chlorophenyl)-1,1-bis(trimethylsilyl)ethene (2h)

Colorless oil; yield: 1.16 g (82%).

^{1}H NMR ($CDCl_3$): δ = –0.03 (s, 9 H, $SiCH_3$), 0.19 (s, 9 H, $SiCH_3$), 7.12 (d, *J* = 8.1 Hz, 2 H, Ph), 7.27 (d, *J* = 8.4 Hz, 2 H, Ph), 7.66 (s, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ = 0.6 ($SiCH_3$), 2.1 ($SiCH_3$), 127.8, 129.1, 132.7, 141.0 (Ar), 147.6 (CH=), 153.2 (C=).

MS (EI): *m/z* (%) = 282 ($[M]^+$, 5), 193 (30), 169 (60), 159 (55), 73 (100).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{23}ClSi_2$: 282.1027; found: 282.1035.

2-(4-Bromophenyl)-1,1-bis(trimethylsilyl)ethene (2i)

Colorless oil; yield: 1.39 g (85%).

^{1}H NMR ($CDCl_3$): δ = –0.08 (s, 9 H, $SiCH_3$), 0.78 (s, 9 H, $SiCH_3$), 7.03–7.06 (m, 2 H, Ar), 7.42 (dd, 2 H, Ar), 7.60 (s, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ = 0.6 ($SiCH_3$), 2.1 ($SiCH_3$), 120.8, 129.4, 135.4, 141.5 (Ar), 130.7 (CH=), 153.1 (C=).

MS (EI): *m/z* (%) = 326 ($[M]^+$, 5), 311 (40), 237 (100), 213 (30), 159 (50), 73 (100).

HRMS: *m/z* $[M]^+$ calcd for $C_{14}H_{23}BrSi_2$: 326.0522; found: 326.0520.

2-(3-Pyridyl)-1,1-bis(trimethylsilyl)ethene (2j)

White crystals; yield: 0.92 g (74%).

^{1}H NMR ($CDCl_3$): δ = –0.05 (s, 9 H, $SiCH_3$), 0.20 (s, 9 H, $SiCH_3$), 7.20–7.24 (m, 1 H, Ar), 7.45–7.49 (m, 1 H, Ar), 7.65 (s, 1 H, =CH), 8.44–8.49 (m, 2 H, Ar).

^{13}C NMR ($CDCl_3$): δ = 0.5 ($SiCH_3$), 2.1 ($SiCH_3$), 122.5, 148.0, 148.6, 150.2 (Ar), 134.8 (CH=), 138.1 (C=).

MS (EI): *m/z* (%) = 248 ($[M-1]^+$, 60), 234 (75), 176 (22), 160 (25), 136 (16), 73(100).

HRMS: *m/z* $[M]^+$ calcd for $C_{13}H_{23}NSi_2$: 249.1291; found: 249.1301.

2-(2-Thienyl)-1,1-bis(trimethylsilyl)ethene (2k)

Colorless oil; yield: 0.86 g (68%).

^{1}H NMR ($CDCl_3$): δ = –0.20 (s, 9 H, $SiCH_3$), –0.06 (s, 9 H, SiCH $_3$), 7.00–7.18 (m, 3 H, Ar), 7.21 (s, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ = –0.3 ($SiCH_3$), 0.7 ($SiCH_3$), 123.7, 124.3, 127.8 (Ar), 144.4 (CH=), 147.9 (C=).

MS (EI): *m/z* (%) = 254 ($[M]^+$, 25), 239 (100), 181 (25), 165 (10), 151 (10), 141 (50), 73 (50).

HRMS: *m/z* $[M]^+$ calcd for $C_{12}H_{22}Si_2S$: 254.0980; found: 254.0992.

X-ray Crystal Structure Analysis

Compound **2j**: CCDC 640132; formula $C_{13}H_{23}NSi_2$, M_r = 249.50, crystal 0.1 × 0.1 × 0.3 mm from hexane soln, triclinic, space group $P\bar{1}$, $a = 9.1811(7)$ Å, $b = 11.8067(14)$ Å, $c = 15.1746(9)$ Å, $\alpha = 85.300(7)°$, $\beta = 78.733(6)°$, $\gamma = 79.160(8)°$, $V = 1582.7(2)$ Å^3, $\rho_{calcd} = 1.05$ g cm^{-3}, $\mu = 0.20$ mm^{-1}, $Z = 4$, r.t., λ(MoKα) = 0.71073 Å, 19419 reflections collected ($\Theta_{max} = 27.95°$), 6885 unique ($R_{int} = 0.024$), $R(F)$ $[I > 2\sigma(I)] = 0.042$, $wR(F^2) = 0.147$, $S = 1.1$–, max/min residual electron density 0.23/–0.23 e·Å^{-3}. Oxford Diffraction four-circle diffractometer equipped with CCD detector.[15] The structures were solved by direct methods with SHELXS97[16] and refined by full-matrix least squares with SHELXL97.[16] Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located from the ideal geometry[16] and refined as 'riding model'. The isotropic displacement parameters of hydrogen atoms were set at 1.2 (1.3 for methyl groups) times the equivalent displacement parameters of appropriate carrier atoms. In both symmetry-independent molecules the pyridine ring was found to be disordered; the disorder is connected with the rotation by 180° around C3–C6 axis and results in two alternative positions of nitrogen atom. The site occupation factors refined at 0.66(2)/0.34(2) in molecule A and 0.70(2)/0.30(2) in molecule B. Weak restraints for the anisotropic displacement parameters of disordered atoms were applied.

Acknowledgment

Financial support from the Ministry of Science and Higher Education (Poland); Grant NN 204 238734 is gratefully acknowledged.

References

(1) Pawluć, P.; Hreczycho, G.; Marciniec, B. *J. Org. Chem.* **2006**, *71*, 8676; and references cited therein.

(2) (a) Gröbel, B. T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 83. (b) Seebach, D.; Bürstinghaus, R.; Gröbel, B. T.; Kolb, M. *Justus Liebigs Ann. Chem.* **1977**, 830. (c) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *Chem. Commun.* **2002**, 114.

(3) (a) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 11109. (b) Hodgson, D. M.; Comina, P. J.; Drew, M. G. B. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2279.

(4) Cuadrado, P.; Gonzales-Nogal, A. M.; Sarmentero, M. A. *Chem. Eur. J.* **2004**, *10*, 4491.

(5) Hudrlik, P. F.; Agwaramgbo, E. L. O.; Hudrlik, A. M. *J. Org. Chem.* **1989**, *54*, 5613.

(6) Safa, K. D.; Samani, S. P.; Tofangdarzedeh, S.; Hassanpour, A. *J. Organomet. Chem.* **2008**, *693*, 2004.

(7) Pawluć, P.; Hreczycho, G.; Walkowiak, J.; Marciniec, B. *Synlett* **2007**, 2061.

(8) Pawluć, P.; Madalska, M.; Hreczycho, G.; Marciniec, B. *Synthesis* **2008**, 3687.

(9) Prukała, W.; Pawluć, P.; Posała, K.; Marciniec, B. *Synlett* **2008**, 41.

(10) (a) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *Chem. Lett.* **2001**, 956. (b) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 3488. (c) Kondo, J.; Inoue, A.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **2002**, *43*, 2399.

(11) (a) Gröbel, B. T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852. (b) Fleming, I.; Floyd, C. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 969. (c) Jones, A. C.; Sanders, A. W.; Sikorski, W. H.; Jansen, K. L.; Reich, H. J. *J. Am. Chem. Soc.* **2008**, *130*, 6060. (d) Safa, K. D.; Namvari, M. P.; Hassanpour, A.; Tofangdarzedeh, S. *J. Organomet. Chem.* **2009**, *694*, 2448.

(12) (a) Molander, G. A.; Romero, J. A. C.; Corrette, C. P. *J. Organomet. Chem.* **2002**, *647*, 225. (b) Sanada, T.; Kato, T.; Mitani, M.; Mori, A. *Adv. Synth. Catal.* **2006**, *348*, 51.

(13) Pawluć, P.; Marciniec, B.; Hreczycho, G.; Gaczewska, B.; Itami, Y. *J. Org. Chem.* **2005**, *70*, 370.

(14) For application of $AgNO_3$ to palladium-catalyzed arylation of vinylsilanes, see: (a) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286. (b) Karabelas, K.; Hallberg, A. *Tetrahedron Lett.* **1985**, *26*, 3131. (c) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4909.

(15) Oxford Diffraction(2007). CrysAlis CCD (Version 1.171.32.5) and CrysAlis RED (Version 1.171.32.5). Oxford Diffraction Ltd.

(16) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.