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Platinum-catalyzed reactions of 3,4-bis(dimethylsilyl)- and 2,3,4,5-tetrakis(dimethylsilyl)thiophene with alkynes and alkenes

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ABSTRACT

The reactions of 3,4-bis(dimethylsilyl)thiophene (**1**) and 2,3,4,5-tetrakis(dimethylsilyl)thiophene (**17**) with alkynes and alkenes have been reported. The reactions of **1** with alkynes such as diphenylacetylene, 3-hexyne, phenyltrimethylsilylacetylene, and trimethylsilylacetylene, in the presence of a catalytic amount of tetrakis(triphenylphosphine)platinum(0) at 80 °C gave the [1,4]disilino[2,3-*c*]thiophene derivatives. With alkenes under the same conditions, **1** afforded the five-membered ring products, in addition to hydrosilylation products. Treatment of 2,3,4,5-tetrakis(dimethylsilyl)thiophene (**17**) with diphenylacetylene and styrene gave the respective dehydrogenative double silylation products, arising from 2 equivalents of the alkyne and alkene, and compound **17**.

1. Introduction

The various synthetic methods of silyl-substituted thiophene derivatives have been reported so far [1]. These compounds are attractive as candidates for the optical and electronic materials such as organic thin film transistors, organic light-emitting diodes, and organic photovoltaics [2–7]. Many types of the transition-metal catalyzed reactions are used for the synthesis of compounds bearing the silyl-substituted π-electron systems [8–20]. We have reported that the platinum-catalyzed reactions of 2,3-bis(diethylsilyl)thiophene with alkynes such as diphenylacetylene, 3-hexyne, phenylacetylene, trimethylsilylacetylene, afforded the respective [1,4]disilino[2,3-*b*]thiophenes [21]. We also demonstrated that the reactions of 2,3-bis(diisopropylsilyl)thiophene with alkynes having the bulky substituents, such as trimethylsilylacetylene and mesitylacetylene gave the products arising from sp-hybridized C–H bond activation of the alkynes [22]. In these reactions, we proposed that the [1,2,5]platinadisilolo[3,4-*b*]thiophene derivatives would be formed as the reactive intermediates.

It is of considerable interest to us to investigate the chemical behavior of silyl-substituted thiophenes, and also their reactivity toward alkynes and alkenes in the presence of a platinum catalyst. In this paper we report the platinum–catalyzed reactions of 3,4-bis(dimethylsilyl)thiophene and 2,3,4,5-tetrakis(dimethlsilyl)thiophene with mono- and di-substituted alkynes, and with mono-substituted alkenes.

2. Results and discussion

The starting compounds, 3,4-bis(dimethylsilyl)thiophene (**1**), was prepared by the reaction of 3,4-dibromothiophene with magnesium and chlorodimethylsilane in the presence of a catalytic amount of copper(I) cyanide in THF (Scheme 1) [19].

We first examined the reaction of **1** with diphenylacetylene. Treatment of compound **1** with diphenylacetylene in the presence of a catalytic amount of $Pt(PPh_3)_4$ in refluxing benzene for 2 h gave 1,1,4,4-tetramethyl-2,3-diphenyl-1,4-dihydro-[1,4]disilino[2,3-*c*] thiophene (**2**) in quantitative yield (Scheme 2). The structure of **2** was verified by spectroscopic analysis. The mass spectrum for **2** shows parent ions at *m*/*z* 376, corresponding to the calculated molecular weight of $C_{22}H_{24}Si_2S$. The ^1H NMR spectrum for **2** shows a signal at 0.29 ppm due to the dimethylsilyl protons, and a signal at 7.67 ppm due to the thienylene protons, and signals attributed to the phenyl protons. The ^{29}Si NMR spectrum for **2** shows a signal at −19.2 ppm.

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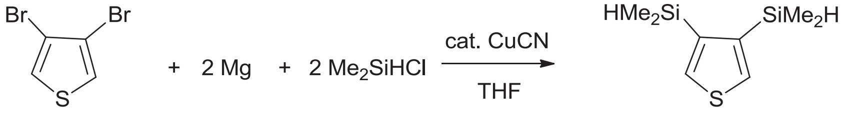

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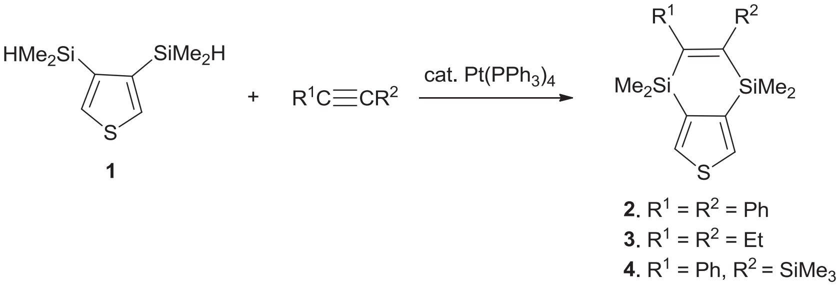
Scheme 1. Synthesis of compound **1**.



Scheme 2. Reactions of **1** with diphenylacetylene, 3-hexyne and phenyltrimethylsilylacetylene.

Similar reactions of **1** with 3-hexyne and phenyltrimethylsilylacetylene afforded 2,3-diethyl-1,1,4,4-tetramethyl-1,4-dihydro-[1,4]disilino[2,3-*c*]thiophene (**3**) and 1,1,4,4-tetramethyl-2-phenyl-3-(trimethylsilyl)-1,4-dihydro-[1,4]disilino [2,3-*c*]thiophene (**4**) in 62% and 98% yields, respectively.

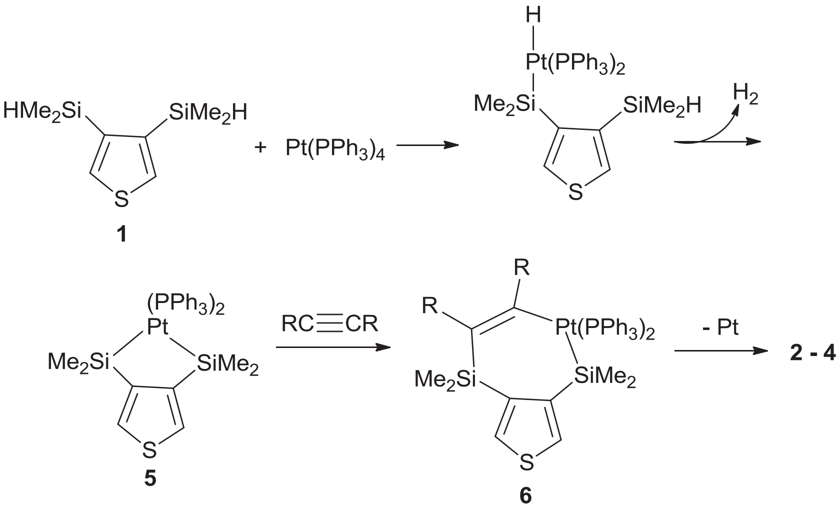
The platinum–catalyzed dehydrogenative double silylation reactions of various unsaturated compounds with bis(hydrosilane)s have been reported to date [8–11,20–22]. Scheme 3 illustrates a possible mechanistic interpretation of the reaction coure. The formation of the adducts **2**–**4** can be best explained by the reaction of bis(silyl)platinum complex (**5**) with disubstituted alkynes. The reaction of **5** with alkynes would produce platinum complex (**6**) as shown in Scheme 3, and then, the elimination of platinum species from **6** presumably affords compounds **2**–**4**.

Unfortunately, compound **1** did not react with bis(trimethylsilyl)acetylene. The starting compound **1** was recovered quantitatively.

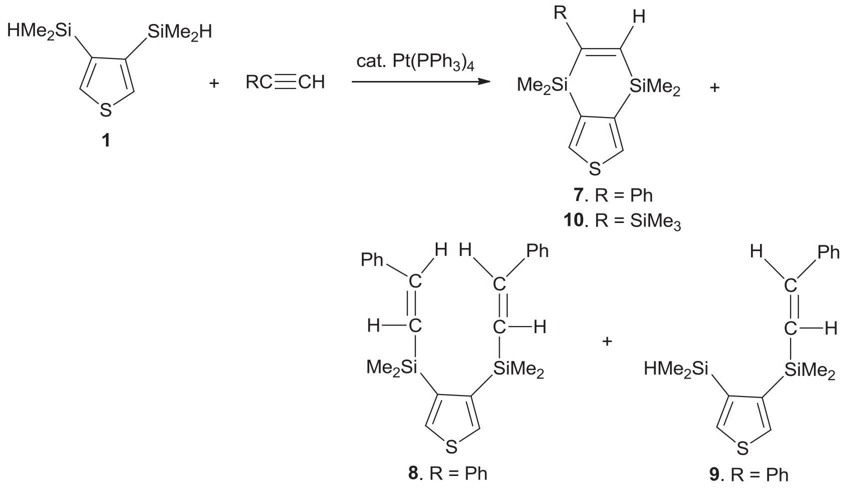
Next, we investigated the platinum-catalyzed reaction of **1** with mono-substituted alkynes under the same conditions as described above. Treatment of **1** with phenylacetylene at 80 °C gave a 1:1 cyclic product, 1,1,4,4-tetramethyl-2-phenyl-1,4-dihydro-[1,4]disilino[2,3-*c*]thiophene (**7**) in 72% yield, along with ring-opened products, 3,4-bis(dimethyl((*E*)-styryl)silyl)thiophene (**8**) and (*E*)-(4-(dimethylsilyl)thiophen-3-yl)dimethyl(styryl)silane (**9**), arising from hydrosilylation [23] of **1** with the alkynes (Scheme 4). The structures of the products **7**–**9** were verified by MS, and ^{1}H, ^{13}C, ^{29}Si NMR spectroscopic analysis.

When a mixture of **1** and trimethylsilylacetylene in the presence of a catalytic amount of Pt(PPh$_3$)$_4$ in benzene was heated to reflux for 1 h, 1,1,4,4-tetramethyl-2-trimethylsilyl-1,4-dihydro-[1,4]disilino[2,3-*c*]thiophene (**10**) was obtained in 90% yield. (Scheme 4). Compound **10** could readily be isolated by column chromatography.

The reaction of **1** with styrene in the presence of a platinum catalyst in refluxing benzene for 48 h gave 2-benzyl-1,1,3,3-tetramethyl-2,3-dihydro1*H*-[1,3]disilolo[4,5-*c*]thiophene (**13**) as a main product, together with a minor one, (4-(dimethylsilyl)thiophen-3-yl)dimethyl(phenethyl)silane (**14**) arising from hydrosilylation [23] of **1** with the alkene. The ratio of **13** and **14** was determined to be 5:1 by ^{1}H NMR spectroscopic analysis. Similar reaction of **1** with 1-hexene in refluxing benzene afforded 1,1,3,3-



Scheme 3. Proposed Mechanism for Production of Compound **2**–**4**.



Scheme 4. Reactions of **1** with phenylacetylene and trimethylsilylacetylene.

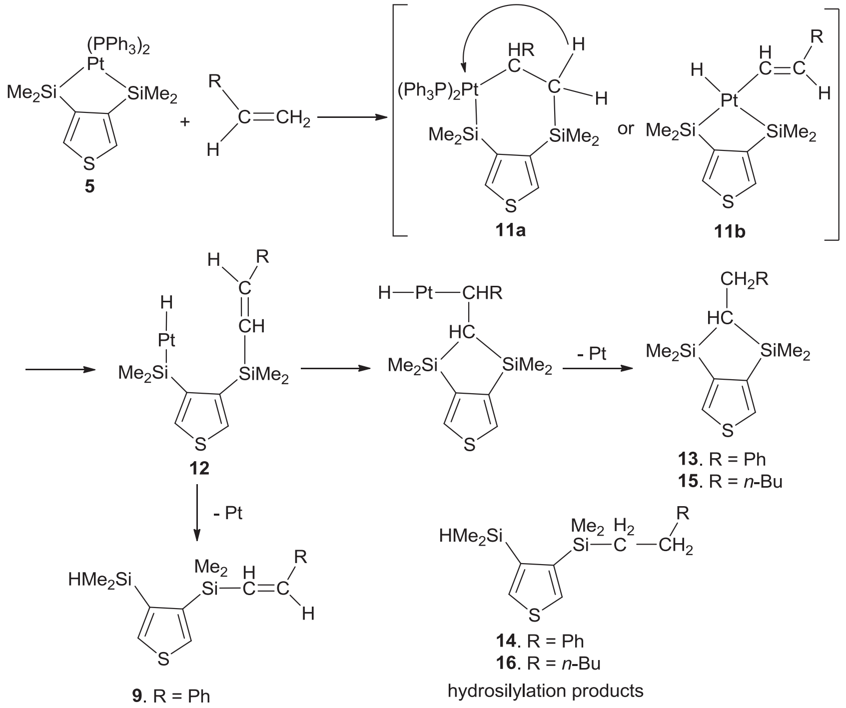
tetramethyl-2-pentyl-2,3-dihydro1*H*-[1,3]disilolo[4,5-*c*]thiophene (**15**) in 42% yield, together with (4-(dimethylsilyl)thiophen-3-yl)(hexyl)dimethylsilane (**16**) in 42% yield. No other products were detected in the reaction mixture by spectroscopic analysis.

Scheme 5 illustrates a possible mechanistic interpretation of the observed reaction course. The formation of **12** can be understood in terms of β-hydrogen elimination[10] from platinadisilacycloheptene **11a** formed from insertion of a carbon-carbon double bond of the alkenes into a platinum-silicon bond of **5**, or insertion of the Pt atom into the sp^2-hybridized C—H bond of the alkene leading to **11b**, followed by the reductive elimination of the C—Si bond. Finally, intramolecular hydrosilylation gives the products **13** and **15**.

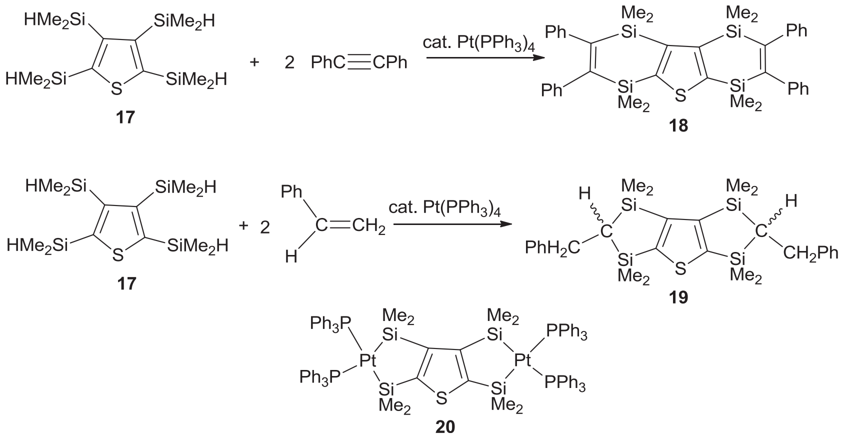
The elimination of platinum species from **12** gives compound **9**. In fact, the NMR spectroscopic analysis of the reaction mixture after 24 h reaction showed the existence of compound **9**.

Next, we carried out the reaction of 2,3,4,5-tetrakis(dimethylsilyl)thiophene (**17**) [19] with diphenylacetylene and styrene. Thus, when a mixture of compound **17** and diphenylacetylene was heated to reflux in the presence of a catalytic amount of tetrakis(triphenylphosphine)platinum(0) in benzene for 4 h, dehydrogenative double silylation product (**18**), arising from 2 equivalents of diphenylacetylene with compound **17** was obtained. Similar reaction of **17** with styrene for 90 h gave a mixture of the diastereomers, [1,3]disilolo[4,5-*b*]thiophene derivatives (**19**), formed from the reaction of two molecules of styrene and one molecule of **17**, in 95% combined yield, as shown in Scheme 6. All attempts to separate these products as a pure form were unsuccessful.

The ratio of the major units and minor ones was determined to be 1.5:1 by ^{1}H NMR spectrometric analysis. In this reaction, no



Scheme 5. Reactions of **1** with styrene and 1-hexene.



Scheme 6. Reactions of **17** with diphenylacetylene and styrene.

other volatile products such as [1,3]disilolo[4,5-*c*]thiophene derivatives were detected in the reaction mixture. We carried out the reaction of **17** with 2 equivalent of Pt(PPh$_3$)$_4$ in deuteriobenzene at room temperature, and analyzed the mixture of by NMR spectra [24]. On the basis of ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR data, we assigned this compound as bis(disilylplatina) complex **20**.

3. Conclusion

We describe here the preparation and platinum-catalyzed reactions of 3,4-bis(dimethylsilyl)thiophene. The reactions of 3,4-bis(dimethylsilyl)thiophene **1** with di-substituted alkynes in the presence of a catalytic amount of Pt(PPh$_3$)$_4$ proceeded to give cyclic products, [1,4]disilino[2,3-*c*]thiophene derivatives. Similar treatment of **1** with phenylacetylene afforded the six-membered ring products, together with ring opened products produced from the hydrosilylation reaction of **1** with phenylacetylene, while with trimethylsilylacetylene, **1** gives dehydrogenative double silylation products as a sole product. The reactions of **1** with mono-substituted alkenes such as styrene and 1-hexene proceeded to give the five-membered ring products, [1,3]disilolo[4,5-*c*]thiophene derivatives, in addition to the hydrosilylation products produced from the reaction of **1** with the alkenes. The platinum-catalyzed reactions of 2,3,4,5-tetrakis(dimethylsilyl)thiophene **17** with diphenylacetylene and styrene afforded dehydrogenative double silylation products formed from 2 equiv alkynes and alkenes with compound **17**.

4. Experimental section

4.1. General procedure

All reactions of 3,4-bis(dimethylsilyl)thiophene **1** and 2,3,4,5-tetrakis(dimethylsilyl)thiophene **17** with alkynes and alkenes were carried out under an atmosphere of dry nitrogen. Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard on the basis of the starting compound used. NMR spectra were recorded on a JMN–ECS400 spectrometer. Low– and high resolution mass spectra were measured on a JEOL Model JMS–700 instrument. Column chromatography was performed by using Wakogel C–300 (WAKO).

4.2. Preparation of 3,4-Bis(dimethylsilyl)thiophene **1**

In a 200 mL three-necked flask fitted with a stirrer, a reflux condenser and a dropping funnel was placed 2.23 g (91.8 mmol) of magnesium, 8.96 g (94.7 mmol) of chlorodimethylsilane and 0.570 g (6.36 mmol) of copper(I) cyanide in 10 mL of dry THF. To this mixture was added dropwise a solution of 6.49 g (26.8 mmol) of 3,4-dibromothiophene in 50 mL of dry THF. The mixture was heated to reflux for 66 h. The resulting magnesium salts were removed by filtration and washed with ether. The solvent was evaporated, and the residue was distilled under reduced pressure to give 2.82 g (52% yield) of 3,4-bis(dimethylsilyl)thiophene **1**: bp 43–45 °C/2 Torr; HR-MS: calcd for $C_8H_{16}Si_2S$ 200.0511, found: 200.0495. MS *m*/*z* 200 (M$^+$); ^{1}H NMR δ(CDCl$_3$) 0.37 (d, 12H, Me$_2$Si, *J* = 3.6 Hz), 4.58 (sep, 2H, HSi, *J* = 3.6 Hz), 7.60 (s, 2H, thienyl ring protons); ^{13}C NMR δ(CDCl$_3$) −2.68 (Me$_2$Si), 134.34, 143.02 (thienyl ring carbons); ^{29}Si NMR δ(CDCl$_3$) −23.7.

4.3. Platinum–catalyzed reaction of **1** with diphenylacetylene

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.310 g (1.55 mmol) of **1**, 0.533 g (3.10 mmol) of diphenylacetylene, and 0.0980 g (0.0788 mmol) of Pt(PPh$_3$)$_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 2 h. The mixture was analyzed by GLC as being **2** (quantitative yield). The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent: HR-MS: calcd for $C_{22}H_{24}Si_2S$ (M$^+$): 376.1137, found: 376.1167. MS *m*/*z* 376 (M$^+$); ^{1}H NMR δ(CDCl$_3$) 0.29 (s, 12H, Me$_2$Si), 6.79–6.81 (m, 4H, phenyl ring protons), 6.94–6.98 (m, 2H, phenyl ring protons), 7.05–7.09 (m, 4H, phenyl ring protons), 7.67 (s, 2H, thienyl ring protons); ^{13}C NMR δ(CDCl$_3$) −0.38 (Me$_2$Si), 124.00, 127.36, 128.02, 132.32, 142.76, 143.15, 157.41 (phenyl, thienyl ring and olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) −19.2.

4.4. Platinum–catalyzed reaction of **1** with 3-hexyne

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.272 g (1.36 mmol) of **1**, 0.254 g (3.09 mmol) of 3-hexyne, and 0.0890 g (0.0715 mmol) of Pt(PPh$_3$)$_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 1 h. The mixture was analyzed by GLC as being **3** (62% yield). The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent: HR-MS: calcd for $C_{14}H_{24}Si_2S$ (M$^+$): 280.1137, found: 280.1120. MS *m*/*z* 280 (M$^+$); ^{1}H NMR δ(CDCl$_3$) 0.32 (s, 12H, Me$_2$Si), 1.02 (t, 6H, CH$_3$, *J* = 7.6 Hz), 2.38 (q, 4H, CH$_2$, *J* = 7.6 Hz), 7.57 (s, 2H, thienyl ring protons); ^{13}C NMR δ(CDCl$_3$) 0.05 (Me$_2$Si), 15.10, 24.11 (Et), 131.43, 143.76, 153.63 (thienyl ring and olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) −19.7.

*4.5. Platinum–catalyzed reaction of **1** with phenyltrimethylsilylacetylene*

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.253 g (1.26 mmol) of **1**, 0.456 g (2.62 mmol) of phenyltrimethylsilylacetylene, and 0.0734 g (0.0590 mmol) of $Pt(PPh_3)_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 3 h. The mixture was analyzed by GLC as being **4** (98% yield). The solvent benzene was evapolated. Compound **4** was isolated by silica gel column chromatography. For **4**: HR-MS: calcd for $C_{19}H_{28}Si_3S$ (M^+): 372.1220, found: 372.1228. MS *m/z* 372 (M^+); ^1H NMR $\delta(CDCl_3)$ −0.17 (s, 9H, Me_3Si), 0.15 (s, 6H, Me_2Si), 0.48 (s, 6H, Me_2Si), 6.92–6.94 (m, 2H, phenyl ring protons), 7.17–7.22 (m, 1H, phenyl ring proton), 7.25–7.31 (m, 2H, phenyl ring protons), 7.57 (d, 1H, thienyl ring proton, $J = 2.4$ Hz), 7.62 (d, 1H, thienyl ring proton, $J = 2.4$ Hz); ^{13}C NMR $\delta(CDCl_3)$ −0.33, 1.95 (Me_2Si), 2.39 (Me_3Si), 125.83, 126.75, 127.87, 131.64, 131.83, 142.49, 144.74, 147.76, 158.71, 176.28 (phenyl, thienyl ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −22.4, −18.9, −6.6.

*4.6. Platinum–catalyzed reaction of **1** with phenylacetylene*

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.315 g (1.57 mmol) of **1**, 0.338 g (3.31 mmol) of phenylacetylene, and 0.0982 g (0.0789 mmol) of $Pt(PPh_3)_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 1 h. The mixture was analyzed by GLC as being **7** (72% yield), **8** (19% yield), and **9** (5% yield). The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent. Compounds **7**–**9** were isolated by silica gel column chromatography. For **7**: HR-MS: calcd for $C_{16}H_{20}Si_2S$: 300.0824, found: 300.0820. MS *m/z* 300 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.37 (s, 6H, Me_2Si), 0.38 (s, 6H, Me_2Si), 6.81 (s, 1H, olefinic proton), 7.22–7.27 (m, 3H, phenyl ring protons), 7.31–7.35 (m, 2H, phenyl ring protons), 7.635 (d, 1H, thienyl ring proton, $J = 2.4$ Hz), 7.644 (d, 1H, thienyl ring proton, $J = 2.4$ Hz); ^{13}C NMR $\delta(CDCl_3)$ −0.14, 0.46 (Me_2Si), 126.35, 126.47, 128.18, 131.00, 132.23, 142.67, 143.69, 146.10, 147.13, 162.32 (phenyl, thienyl ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −20.3, −19.0. For **8**: HR-MS: calcd for $C_{24}H_{28}Si_2S$: 404.1450, found 404.1459: MS *m/z* 404 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.46 (s, 12H, Me_2Si), 6.60 (d, 2H, olefinic protons, $J = 19.2$ Hz), 6.86 (d, 2H, olefinic protons, $J = 19.2$ Hz), 7.22–7.30 (m, 6H, phenyl ring protons), 7.35–7.38 (m, 4H, phenyl ring protons), 7.70 (s, 2H, thienyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ −0.33 (Me_2Si), 126.52, 128.08, 128.34, 128.50, 135.86, 138.08, 143.89, 145.01 (phenyl, thienyl ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −13.7. For **9**: HR-MS: calcd for $C_{16}H_{22}Si_2S$: 302.0981, found: 302.0980. MS *m/z* 302 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.32 (d, 6H, Me_2Si, $J = 3.6$ Hz), 0.49 (s, 6H, Me_2Si), 4.63 (sep, 1H, HSi, $J = 3.6$ Hz), 6.63 (d, 1H, olefinic protons, $J = 19.2$ Hz), 6.93 (d, 1H, olefinic protons, $J = 19.2$ Hz), 7.24–7.28 (m, 1H, phenyl ring proton), 7.32–7.35 (m, 2H, phenyl ring protons), 7.45 (dd, 2H, phenyl ring protons, $J = 7.2$ Hz, 1.6 Hz), 7.61 (d, 1H, thienyl ring proton, $J = 2.4$ Hz), 7.64 (d, 1H, thienyl ring proton, $J = 2.4$ Hz); ^{13}C NMR $\delta(CDCl_3)$ −2.31, −0.96 (Me_2Si), 126.48, 127.92, 128.12, 128.53, 134.64, 134.83, 138.20, 143.08, 144.33, 145.13 (phenyl, thienyl ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −23.9, −13.6.

*4.7. Platinum–catalyzed reaction of **1** with trimethylsilylacetylene*

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.333 g (1.66 mmol) of **1**, 0.365 g (3.72 mmol) of trimethylsilylacetylene, and 0.108 g (0.0868 mmol) of $Pt(PPh_3)_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 1 h. The mixture was analyzed by GLC as being **10** (90% yield). The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent. For **10**: HR-MS: calcd for $C_{13}H_{24}Si_3S$: 296.0907, found: 296.0876. MS *m/z* 296 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.15 (s, 9H, Me_3Si), 0.30 (s, 6H, Me_2Si), 0.36 (s, 6H, Me_2Si), 7.57 (s, 1H, olefinic proton), 7.59 (d, 1H, thienyl ring protons, $J = 2.4$ Hz), 7.60 (d, 1H, thienyl ring protons, $J = 2.4$ Hz); ^{13}C NMR $\delta(CDCl_3)$ −0.36, 1.33 (Me_2Si), −0.24 (Me_3Si), 131.64, 131.86, 142.49, 144.18, 161.61, 168.33 (thienyl ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −23.4, −19.5, −2.3.

*4.8. Platinum–catalyzed reaction of **1** with styrene*

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.302 g (1.51 mmol) of **1**, 0.338 g (3.25 mmol) of styrene, and 0.0950 g (0.0764 mmol) of $Pt(PPh_3)_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 48 h. The mixture was analyzed by GLC as being **13** and **14** (quantitative combined yield). The ratio of **13** and **14** was determined to be 5:1 by ^1H NMR spectroscopic analysis. The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent. For **13**: HR-MS: calcd for $C_{16}H_{22}Si_2S$: 302.0981, found: 302.0980. MS *m/z* 302 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.13 (s, 6H, Me_2Si), 0.23 (s, 6H, Me_2Si), 1.00 (t, 1H, CH, $J = 8.4$ Hz), 2.93 (d, 2H, CH_2, $J = 8.4$ Hz), 7.17–7.20 (m, 1H, phenyl ring proton), 7.23–7.31 (m, 4H, phenyl ring protons), 7.44 (s, 2H, thienyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ −1.56, −0.56 (Me_2Si), 125.71, 128.25, 128.27, 129.09, 144.28, 150.42 (thienyl ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −0.12. For **14**: HR-MS: calcd for $C_{16}H_{24}Si_2S$: 304.1137, found: 304.1127. MS *m/z* 304 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.345 (s, 6H, Me_2Si), 0.354 (d, 6H, Me_2Si, $J = 3.6$ Hz), 1.17–1.21 (m, 2H, CH_2), 2.59–2.63 (m, 2H, CH_2), 4.65 (sep, 1H, HSi, $J = 3.6$ Hz), 7.13–7.18 (m, 3H, phenyl ring protons), 7.24–7.28 (m, 2H, phenyl ring protons), 7.57 (d, 1H, thienyl ring proton, $J = 2.4$ Hz), 7.61 (d, 1H, thienyl ring proton, $J = 2.4$ Hz); ^{13}C NMR $\delta(CDCl_3)$ −2.19, −1.40 (Me_2Si), 18.46, 30.03 (CH_2), 125.49, 127.76, 128.27, 134.28, 134.59, 142.89, 144.55, 144.95 (phenyl and thienyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −24.1, −5.4.

*4.9. Platinum–catalyzed reaction of **1** with 1-hexene*

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.2881 g (1.45 mmol) of **1**, 0.279 g (3.32 mmol) of 1-hexene, and 0.0987 g (0.0793 mmol) of $Pt(PPh_3)_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 22 h. The mixture was analyzed by GLC as being **15** and **16** (84% combined yield). The ratio of **15** and **16** was determined to be 1:1 by ^1H NMR spectroscopic analysis. The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent. For **15**: HR-MS: calcd for $C_{14}H_{26}Si_2S$: 282.1294, found: 282.1292. MS *m/z* 282 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.18 (s, 6H, Me_2Si), 0.34 (s, 6H, Me_2Si), 0.55 (t, 1H, CH, $J = 8.0$ Hz), 0.91 (t, 3H, CH_3, $J = 6.8$ Hz), 1.28–1.44 (m, 6H, CH_2), 1.57–1.63 (m, 2H, CH_2), 7.44 (s, 2H, thienyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ −1.92, 0.14 (Me_2Si), 14.14 (CH_3), 18.00 (CH), 22.55, 25.48, 31.99, 33.55 (CH_2), 128.88, 150.99 (thienyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −0.2. For **16**: HR-MS: calcd for $C_{14}H_{28}Si_2S$: 284.1450, found: 284.1459. MS *m/z* 284 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.30 (s, 6H, Me_2Si), 0.34 (d, 6H, Me_2Si, $J = 3.6$ Hz), 0.78–0.82 (m, 2H, CH_2), 0.86 (t, 1H, CH, $J = 6.8$ Hz), 1.24–1.30 (m, 8H, CH_2), 4.62 (sep, 1H, HSi, $J = 3.6$ Hz), 7.53 (d, 1H, thienyl ring proton, $J = 2.4$ Hz), 7.59 (d, 1H, thienyl ring proton, $J = 2.4$ Hz); ^{13}C NMR $\delta(CDCl_3)$ −3.19, −1.37 (Me_2Si), 14.11 (CH_3), 16.61, 22.59, 23.88, 31.55, 33.22 (CH_2), 133.89, 134.43, 142.93, 145.30 (thienyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −24.1, −5.6.

*4.10. Platinum–catalyzed reaction of **17** with diphenylacetylene*

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.336 g (1.06 mmol) of **17**, 0.573 g (3.22 mmol) of diphenylacetylene, and 0.0690 g (0.0555 mmol) of $Pt(PPh_3)_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 4 h. The mixture was analyzed by GLC as being **18** (93% yield). The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent: HR-MS: calcd for $C_{40}H_{44}Si_4S$ (M^+): 668.2244, found: 668.2222. MS *m*/*z* 668 (M^+); ^1H NMR δ($CDCl_3$) 0.38 (s, 12H, Me_2Si), 0.39 (s, 12H, Me_2Si), 6.81–6.83 (m, 8H, phenyl ring protons), 6.93–6.99 (m, 4H, phenyl ring protons), 7.05–7.10 (m, 8H, phenyl ring protons); ^{13}C NMR δ($CDCl_3$) 0.47, 0.95 (Me_2Si), 125.05, 125.11, 127.31, 127.46, 127.99, 128.23, 142.62, 143.28, 151.81, 152.11, 155.35, 159.18 (phenyl, thienyl ring and olefinic carbons); ^{29}Si NMR δ($CDCl_3$) −19.5, −17.0.

4.11. Platinum–catalyzed reaction of 17 with styrene

In a 30 mL two–necked flask fitted with a reflex condenser were placed 0.290 g (0.916 mmol) of **17**, 0.313 g (3.00 mmol) of styrene, and 0.0590 g (0.0474 mmol) of $Pt(PPh_3)_4$ in 15 mL of dry benzene. The mixture was heated to reflux for 90 h. The mixture was analyzed by GLC as being a mixture of regioisomers **19** (95% combined yield). The ratio of major units and minor units was determined to be 1.5:1 by ^1H NMR spectrometric analysis. The solvent benzene was evapolated and the residue was chromatographed on silica gel column using hexane as the eluent. For **19**: HR-MS: calcd for $C_{28}H_{40}Si_4S$ (M^+): 520.1928, found: 520.1922. MS *m*/*z* 520 (M^+); For major units: ^1H NMR δ($CDCl_3$) 0.14 (s, 6H, Me_2Si), 0.20 (s, 6H, Me_2Si), 0.22 (s, 6H, Me_2Si), 0.24 (s, 6H, Me_2Si), 1.03 (br t, 2H, CH, $J = 8.4$ Hz), 2.86–2.99 (m, 4H, CH_2), 7.17–7.31 (m, 10H, phenyl ring protons); ^{13}C NMR δ($CDCl_3$) −1.21, −1.09, 0.25, 0.33 (Me_2Si), 19.57 (CH), 31.04 (CH_2), 125.75, 128.27, 128.29, 144.17, 158.48, 162.66 (phenyl and thienyl ring carbons); ^{29}Si NMR δ($CDCl_3$) 1.2, 2.5. For minor units: ^1H NMR δ($CDCl_3$) 0.16 (s, 6H, Me_2Si), 0.22 (s, 6H, Me_2Si) Other proton signals were overlapped with those of major units; ^{13}C NMR δ($CDCl_3$) −1.13 (2C), 0.74, 1.06 (Me_2Si), 18.09 (CH), 31.20 (CH_2), 125.73, 128.18, 128.27, 144.16, 158.41, 163.24 (phenyl and thienyl ring carbons); ^{29}Si NMR δ($CDCl_3$) 2.1, 3.0.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.10.013.

References

[1] I.F. Perepichka, D.F. Perepichka (Eds.), Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics, John Wiley & Sons, Ltd., Chichester, 2009.
[2] J. Ohshita, Y. Hatanaka, S. Matsui, T. Mizumo, Y. Kunugi, Y. Honsho, A. Saeki, S. Seki, J. Tibbelin, H. Ottosson, T. Takeuchi, Dalton Trans. 39 (2010) 9314–9320.
[3] J. Hou, H.-Y. Chen, S. Zhang, G. Li, Y. Yang, J. Am. Chem. Soc. 130 (2008) 16144–16145.
[4] O.V. Borshchev, S.A. Ponomarenko, N.M. Surin, M.M. Kaptyug, M.I. Buzin, A.P. Preshkova, N.V. Demchenko, V.D. Myakushev, A.M. Muzafarov, Organometallics 26 (2007) 5165–5173.
[5] H. Usta, G. Lu, A. Faccetti, T.J. Marks, J. Am. Chem. Soc. 128 (2006) 9034–9035.
[6] J. Ohshita, M. Nodono, H. Kai, T. Watanabe, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Okita, Y. Harima, K. Yamashita, M. Ishikawa, Organometallics 18 (1999) 1453–1459.
[7] J. Ohshita, M. Nodono, T. Watanabe, Y. Ueno, A. Kunai, Y. Harima, K. Yamashita, M. Ishikawa, J. Organomet. Chem. 428 (1992) 1–12.
[8] M. Tanaka, Y. Uchimaru, H.-J. Lautenschlager, Organometallics 10 (1991) 16–18.
[9] Y. Uchimaru, H.-J. Lautenschlager, A.J. Wynd, M. Tanaka, M. Goto, Organometallics 11 (1992) 2639–2643.
[10] M. Tanaka, Y. Uchimaru, H.-J. Lautenschlager, J. Organomet. Chem. 428 (1992) 1–12.
[11] Y. Uchimaru, A.M.M. El Sayed, M. Tanaka, Organometallics 12 (1993) 2065–2069.
[12] H. Tsutsumi, Y. Sunada, H. Nagashima, Organometallics 30 (2011) 68–76.
[13] C. Eaborn, T.N. Metham, A. Pidcock, J. Organomet. Chem. 63 (1973) 107–117.
[14] M. Ishikawa, A. Naka, J. Ohshita, Organometallics 12 (1993) 4987–4992.
[15] A. Naka, K. Yoshizawa, S.-Y. Kang, T. Yamabe, M. Ishikawa, Organometallics 17 (1998) 5830–5835.
[16] A. Naka, M. Ishikawa, Synlett 8 (1995) 794–802.
[17] A. Naka, T. Okada, A. Kunai, M. Ishikawa, J. Organomet. Chem. 547 (1997) 149–156.
[18] M. Ishikawa, A. Naka, K. Yoshizawa, Dalton Trans. 45 (2016) 3210–3235.
[19] S. Kyushin, T. Matsuura, H. Matsumoto, Organometallics 25 (2006) 2761–2765.
[20] A. Naka, S. Takase, A. Shimada, H. Kobayashi, M. Ishikawa, J. Organomet. Chem. 853 (2017) 13–17.
[21] A. Naka, T. Mihara, H. Kobayashi, M. Ishikawa, J. Organomet. Chem. 822 (2016) 221–227.
[22] A. Naka, T. Mihara, H. Kobayashi, M. Ishikawa, ACS Omega 2 (2017) 8517–8525.
[23] J.Y. Corey, Chem. Rev. 116 (2016) 11291–11435.
[24] In a 30 mL two-necked flask was placed 0.021 g (0.0066 mmol) of **17** and 0.164 g (0.013 mmol) of $Pt(PPh_3)_4$ in a 1 mL of benzene-d_6. The mixture was stirred at room temperature for 1 h, and washed by 150 mL of dry hexane to give **20**: ^1H NMR δ(C_6D_6) 0.58 (s with Pt satellite shoulders, 6H, Me_2Si), 0.71 (s with Pt satellite shoulders, 6H, Me_2Si), 6.77 (t, 12H, phenyl ring protons, $J = 7.2$ Hz), 6.87 (t, 6H, phenyl ring protons, $J = 7.2$ Hz), 7.44 (br t, 12H, phenyl ring protons, $J = 8.8$ Hz); ^{13}C NMR δ(C_6D_6) 8.23 (t, Me_2Si, $J_{C\text{-}P} = 4.8$ Hz), 8.58 (t, Me_2Si, $J_{C\text{-}P} = 4.8$ Hz), 129.31 (s), 132.40 (d, $J_{C\text{-}P} = 9.5$ Hz), 134.74 (br t, $J_{C\text{-}P} = 6.2$ Hz), 136.51 (d, $J_{C\text{-}P} = 39.1$ Hz) (phenyl ring carbons); ^{29}Si NMR δ(C_6D_6) 7.6 (t, $J_{Si\text{-}P} = 58$ Hz), 15.6 (t, $J_{Si\text{-}P} = 58$ Hz); ^{31}P NMR δ(C_6D_6) 35.0 ($J_{P\text{-}Pt} = 1715$ Hz).