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Platinum complex-catalyzed dehydrogenative double silylation of olefins and dienes with *o*-bis(dimethylsilyl)benzene *

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Abstract

Olefins underwent dehydrogenative 1,2- and/or 1,1-double silylation with *o*-bis(dimethylsilyl)benzene (1) in the presence of a catalytic amount of $Pt(CH_2{=}CH_2)(PPh_3)_2$ to afford benzo-1,4-disilacyclohexene (3) and/or benzo-1,3-disilacyclopentene (4) derivatives, respectively. In reactions of aliphatic olefins, single hydrosilylation with one of the Si–H bonds took place as a side reaction to give $HMe_2Si(o\text{-}C_6H_4)SiMe_2R$ compounds. Depending on the conditions of the latter reactions, $HMeRSi(o\text{-}C_6H_4)SiMe_3$ compounds arising from 1,4-rearrangement of a methyl group were also formed. The cyclic bis(silyl)platinum complex $Me_2\overline{Si(o\text{-}C_6H_4)SiMe_2Pt}(PPh_3)_2$ (11) formed upon treatment of 1 with the platinum-ethylene complex readily reacted with olefins in the presence of 1 to afford 3 and/or 4. Compound 4 coming from the catalytic reaction of styrene with *o*-bis(deuteriodimethylsilyl)benzene did not have the deuterium label incorporated. Based on these results, the dehydrogenative double silylation is proposed to take place via 11 as a key intermediate.

Introduction

The double silylation of acetylenes and dienes with disilanes has been well known for two decades. The reaction provides a unique way to introduce two silicon functionalities to the unsaturated compounds in one step. Increasing interest in organosilicon-mediated selective organic synthesis and functional silicon-containing polymers has led to the development of new variations in which isocyanides [1] and olefins [2] also undergo the reaction. In addition, our recent finding of the highly efficient $Pd\text{–}P(OCH_2)_3CEt$ catalyst system has demonstrated the opportunities in the reconstruction of the polymer backbone of polycarbosilanes and polysilanes [3].

One of the modified procedures to be investigated to upgrade the value of the double silylation reaction is to utilize hydrosilanes under dehydrogenative condi-

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* Dedicated to Professor Akio Yamamoto upon his retirement from the Tokyo Institute of Technology and in honor of his contributions to organometallic chemistry.

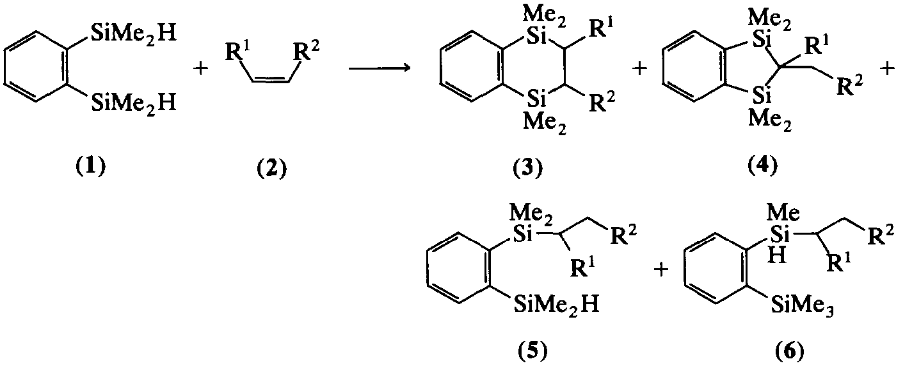
tions. Note that hydrosilanes are, in general, more readily available than disilanes with the exception of some chloromethyldisilanes. A survey of the literature revealed that the dehydrogenative double silylation with hydrosilanes has been encountered in only two cases; i.e. the nickel-catalyzed reaction of internal acetylenes with chlorohydrosilanes [4] and the rhodium-catalyzed reaction of nitriles with bis(hydrosilane) compounds [5]. We have recently reported that dehydrogenative double silylation of various unsaturated carbon compounds with bis(hydrosilane) species proceeds smoothly in the presence of platinum complex catalysts [6]. The details of the reaction of olefins and dienes with *o*-bis(dimethylsilyl)benzene are reported here.

Results and discussion

Catalytic reactions of olefins with o-*bis(dimethylsilyl)benzene*

The results are summarized in Table 1.

Ethylene (**2a**) at atmospheric pressure (balloon) was allowed to react with *o*-bis(dimethylsilyl)benzene (**1**) in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$. At 30°C, 1,2- and 1,1-double silylation took place to form **3a** and **4a** (eq. 1), but the major reaction was simple hydrosilylation of one of the two Si–H moieties to give **5a**. Another byproduct that appeared to be **6a** was also formed, indicative of 1,4-migration of a methyl group having taken place. Addition of extra phosphine to the reaction system retarded the formation of **5a** and **6a** to a significant extent while the double silylation was rather accelerated. The structure of **6a** was determined based on the spectral data and was further confirmed by comparison with an authentic sample prepared by a different route. Similar 1,4-migration of a methyl group has also been noted to proceed during the $RhCl(PPh_3)_3$-catalyzed single hydrosilylation of **1** with ketones [7].



(1)

(**a**: $R^1 = R^2 = H$, **b**: $R^1 = H$, $R^2 = {}^nHex$, **c**: $R^1 = H$, $R^2 = Ph$, **d**: $R^1 = H$, $R^2 = p\text{-}C_6H_4\text{-}Cl$, **e**: $R^1 = H$, $R^2 = p\text{-}C_6H_4\text{-}Me$, **f**: $R^1 = H$, $R^2 = p\text{-}C_6H_4\text{-}OMe$, **g**: $R^1 = H$, $R^2 = CO_2Me$, **h**: $R^1 = R^2 = CO_2Me$)

When the reaction was carried out at 80°C, higher selectivities for **3a** and **4a** could be obtained while the formation of **5a** decreased. Occurrence of the 1,4-migration was negligible at this temperature.

Table 1

Reaction of *o*-bis(dimethylsilyl)benzene **1** and olefins **2** in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ [a]

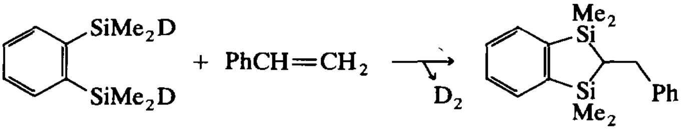
Entry	Olefin	Temperature (°C)	Time (h)	Recovery (%) (1)	Yield (%) [b]			
					3	**4**	**5**	**6**
1	Ethylene [c]	30	19	0	13	11	57	16
2	Ethylene [c,d]	30	19	25	23	21	13	2
3	Ethylene [c]	80	2	0	30	24	42	0
4	Oct-1-ene	30	19	68	0	11	19	0
5	Oct-1-ene [e]	30	19	0	0	41	42	9
6	Oct-1-ene	80	14	0	0	82	14	0
7	Styrene	30	2	59	0	33	0	0
		30	19	0	0	82 (67)	0	0
8	Styrene [f]	110	2	0	0	94	0	0
9	Styrene [f,g]	110	2	0	0	(76)	0	0
10	*p*-Chlorostyrene	30	2	21	0	76	0	0
11	*p*-Methylstyrene	30	2	60	0	29	0	0
12	*p*-Methoxystyrene	30	2	67	0	27	0	0
13	Methyl acrylate	30	2	50	0	40	0	0
		30	19	4	0	86 (48)	0	0
14	Dimethyl maleate	30	40	69	23	1	0	0
15	Dimethyl maleate	80	1	0	77	22	0	0

[a] Conditions: $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.005 mmol), *o*-bis(dimethylsilyl)benzene (**1**) (0.25 mmol), olefin (**2**) (0.25 mmol), benzene (4 ml). [b] GLC yields. The figures in parentheses are isolated yields. [c] Ethylene 1 atm. [d] $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.005 mmol), PPh_3 (0.01 mmol). [e] **2b** (1.56 mmol). [f] Effected in toluene (4 ml). [g] *o*-Bis(deuteriodimethylsilyl)benzene (0.25 mmol) was used.

Oct-1-ene (**2b**), when treated with **1** at 30°C, underwent 1,1-double silylation and simple hydrosilylation to give **4b** and **5b**, respectively. Unlike the reaction of ethylene, the 1,2-double silylation product was not obtained at all. 1,4-Migration of a methyl group did not proceed either. However, it did proceed when the reaction was effected in the presence of excess of oct-1-ene. As was observed in the reaction of ethylene, the selectivity for 1,1-double silylation significantly increased when the reaction temperature was elevated to 80°C.

Styrene (**2c**) reacted with **1** faster and more selectively than oct-1-ene. Thus, **4c** arising from 1,1-double silylation was obtained as nearly a sole product, irrespective of the reaction temperature. The high reactivity of styrene in the present reaction as compared with the aliphatic olefins is presumably associated with the phenyl group being electronegative. In agreement with this was the reactivity trend among *p*-substituted styrenes that was found to be *p*-Cl (76%) > *p*-H (33%) > *p*-Me (29%) > *p*-MeO (27%), as estimated based on the yield (in parentheses) of 1,1-double silylation at 30°C for 2 h.

To gain mechanistic information, we repeated the styrene reaction using *o*-bis(deuteriodimethylsilyl)benzene (eq. 2). The product was identical in all respects with **4c** obtained from the non-deuterated starting material **1**.



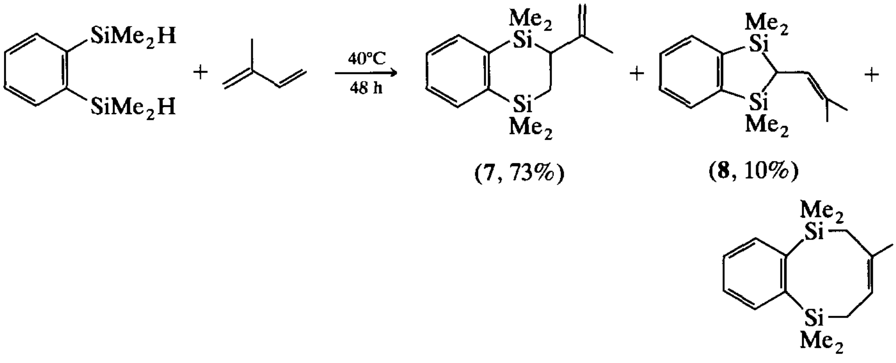
(2)

(**4c**)

The reaction of methyl acrylate (**2g**) was also very selective and fast, and **4g** was obtained in high yield. 1,4-Double silylation across the α,β-unsaturated carbonyl linkage was not observed at all although 1,4-double silylation was the major pathway in the reaction of methyl vinyl ketone with **1** [8].

On the other hand, internal olefins like *cis*-but-2-ene and *cis*-stilbene did not react with **1** at 80°C. This is presumably due to the increased steric hindrance. An exception is dimethyl maleate (**2h**), the double bond of which is activated by the electronegative ethoxycarbonyl groups. In practice, it underwent both 1,1- and 1,2-double silylation, the latter being the major reaction.

Isoprene also reacted with **1** under mild conditions. Unlike the double silylation with disilanes [9], the major pathway was not 1,4- but 1,2-addition across the less substituted double bond (eq. 3). Likewise, penta-1,2-diene underwent 1,2-double silylation at the terminal double bond (eq. 4).

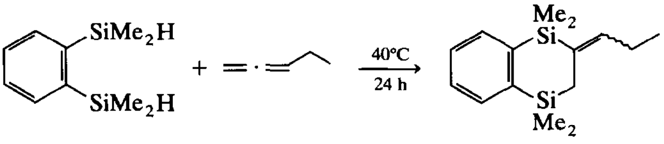


(**7**, 73%)

(**8**, 10%)

(**9**, 9%)

(3)

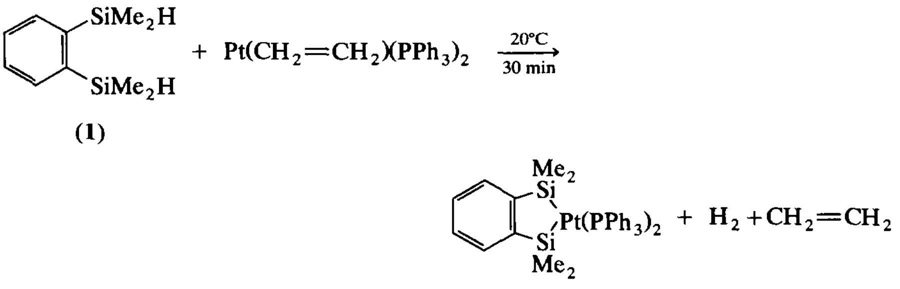


(**10**, 75%)

(4)

Reactions of $\overline{Me_2Si(o\text{-}C_6H_4)SiMe_2Pt}(PPh_3)_2$ *with olefins*

Eaborn and co-workers have reported that treatment of **1** with $Pt(CH_2{=}CH_2)(PPh_3)_2$ forms the cyclic bis(silyl)platinum complex $\overline{Me_2Si(o\text{-}C_6H_4)SiMe_2Pt}(PPh_3)_2$ (**11**, eq. 5) [10]. Our previous paper has revealed that **11** readily reacts with

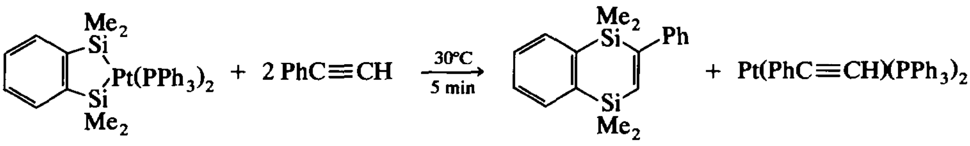


(**1**)

(**11**, 95%)

(5)

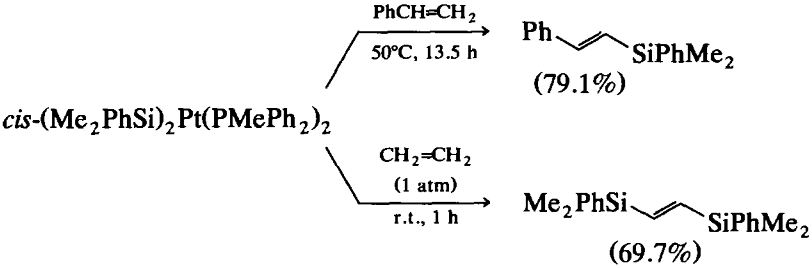
phenylacetylene to undergo stoichiometric 1,2-double silylation (eq. 6) [6]. We



(11) (100%)

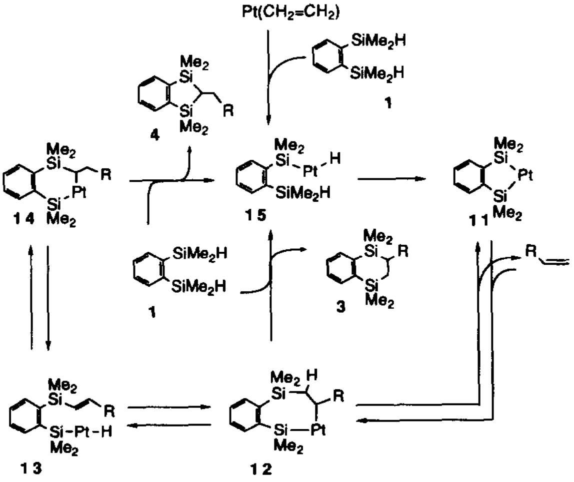
(6)

have also reported that olefins react with a non-cyclic bis(silyl)platinum complex. The reaction gave either 1,2-double or dehydrogenative single silylation product, depending on the nature of the olefins (eq. 7) [11].



(7)

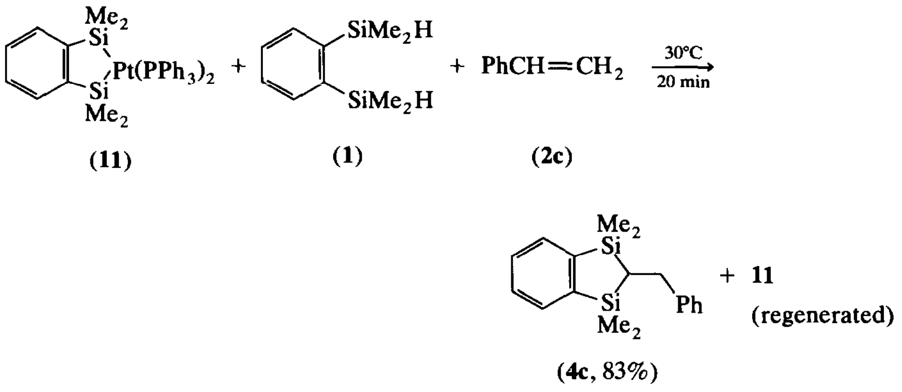
Different from these precedents, complex **11** did not react with styrene (18 equivalent) at 30°C (3.5 h) or at 120°C (25 h). However, when the reaction with styrene (1.2 equivalent) was carried out in the presence of **1** (1.1 equivalent), **4c** was formed in 83% yield based on complex **11** (35°C, 20 min) (eq. 8). Ethylene, dimethyl maleate, and isoprene also showed similar reactivities in the reaction with **11**; thus, in the absence of **1**, double silylation products were not formed while they reacted smoothly when **1** was added to the reaction system. The selectivity among the double silylation products was basically the same as observed in the catalytic reactions. Different from these unsaturated compounds, maleate did undergo



(Pt =Pt(PPh$_3$)$_2$)

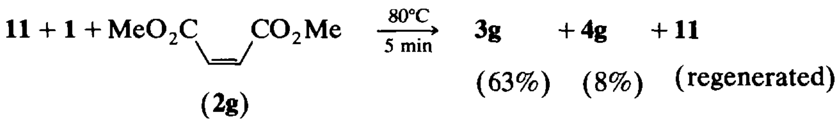
Scheme 1.

unknown reactions slowly with **11** in the absence of **1**. However, **3h**, **4h**, **12h**, and **14h** did not seem to be formed.

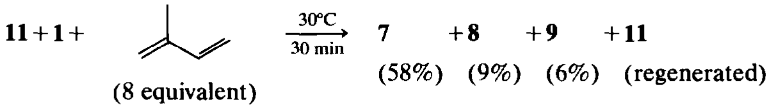


(8)

$$\mathbf{11} + \mathbf{1} + \underset{\substack{(1\ \text{atm})\\ (\mathbf{2a})}}{CH_2{=}CH_2} \xrightarrow[30\ \text{min}]{25°C} \underset{(10\%)}{\mathbf{3a}} + \underset{(8\%)}{\mathbf{4a}} + \underset{(50\%)}{\mathbf{5a}} + \underset{(31\%)}{\mathbf{6a}} + \underset{(\text{regenerated})}{\mathbf{11}} \qquad (9)$$



(10)



(11)

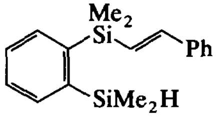
Mechanism of the olefin reactions

We propose the reaction mechanism of the dehydrogenative double silylation as illustrated in Scheme 1. The formation of **11** has been reported and confirmed by us. We presume that an olefin then inserts into one of the Si–Pt bonds to generate the seven-membered intermediate (**12**). This reacts in two pathways. One is straightforward reductive elimination leading to **3**. In the other, the intermediate undergoes β-hydrogen elimination which is followed by insertion of the resulting olefinic bond into the Pt–H bond to give **14**. Finally, reductive elimination takes place to afford **4**. Mechanistic features described in the previous sections appear to be all in agreement with this mechanism. In addition, the proposed mechanisms of the double silylation of olefins with disilanes [2] and of the dehydrogenative single silylation of olefins with disilanes [12] are also consistent with the present mechanism.

Somewhat puzzling, however, is the lack of the reaction of the cyclic bis(silyl) complex **11** with olefins in the absence of the bis(hydrosilane) species **1**. This may be associated with the stability of the five-membered complex **11** as compared with the seven-membered intermediate **12**, which we suggest is in equilibrium with **11**. The reverse reaction, i.e. **12** → **11**, takes place through β-silyl group transfer. This elemental process appears rather unusual, but has been verified unequivocally for ruthenium and iron complexes [13] and is believed to participate in some catalytic reactions [14]. We speculate that reductive elimination of **12** and **14**, which are present in the catalytic reaction system in very low concentrations, is somehow promoted by their interaction with **1**. Such a possibility has been suggested for unusually fast and selective single hydrosilylation with bis(hydrosilane) compounds catalyzed by $RhCl(PPh_3)_3$ [15], although unsubstantiated by independent experimental data.

One can consider an alternative mechanism which involves dehydrogenative silylation with one of the Si–H moieties followed by hydrosilylation of the resulting alkenylsilane intermediate (eq. 12).

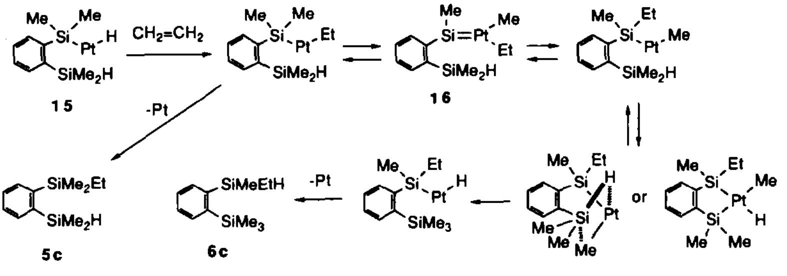
$1 + PhCH{=}CH_2 \xrightarrow[H_2]{}$



$\longrightarrow$ **13** $\longrightarrow$ **3** and/or **4** (12)

Some platinum complexes have been reported to promote dehydrogenative silylation of olefins with hydrosilanes [16]. However, this possibility is safely excluded since we did not find the deuterium label in **4c** coming from styrene and the bis(deuteriosilane). In addition, styrene, when treated with phenyldimethylsilane in place of **1** in the presence of the ethylene-platinum complex (30°C, 19 h, in benzene), did not undergo dehydrogenative silylation or hydrosilylation.

The formation of **5** is presumably due to the interception of the intermediate **15** by an olefin prior to the formation of **11**; see Scheme 2 written for ethylene. To compare the reactivity of olefins in hydrosilylation, we treated a 1 : 1 (mol/mol) mixture of styrene and oct-1-ene with phenyldimethylsilane at 50°C using the same catalyst. Styrene remained intact even after 90 h while the corresponding octylsilane was formed in 20% yield. Accordingly, it is reasonable to assume that the intermediate **15**, which leads to **11**, is more easily intercepted by ethylene or oct-1-ene than by styrene. The difference among olefins in their ability to intercept is presumably the origin of the extensive occurrence of single hydrosilylation for ethylene and oct-1-ene and of more selective double silylation for styrene as well as the other olefins examined.



(Pt = $Pt(PPh_3)_n$, n = 2 or 1)

Scheme 2.

The 1,4-rearrangement of a methyl group may be envisioned to have come from the initially formed normal single hydrosilylation product **5** via a subsequent redistribution reaction. However, the ratio of **6b** to **5b** remained nearly constant when the reaction of Entry 5 (19 h reaction time; **6b**, 9%; **5b**, 42%) was continued up to 30 h (10 and 41%, respectively). Accordingly, such a redistribution reaction may not be the major pathway for the rearrangement. Tentatively, we propose a mechanism depicted in Scheme 2. Besides this, various alternative mechanisms may rationalize the rearrangement. However, we believe that the rearrangement proceeds via α-elimination of a methyl group to generate a silylene-platinum species [17] such as **16** as a key intermediate. In our previous paper, we suggested that a similar α-elimination process took place during thermolysis of bis(silyl) platinum complexes, and that the rearrangement via this process was suppressed by the addition of an extra phosphine to the reaction system [18]. Accordingly, we examined the effect of extra phosphine added to the present reaction of ethylene. Although the effect was not very dramatic, the ratio of **6a** to **5a** indeed decreased (0.28 (Entry 1) versus 0.15 (Entry 2)).

Experimental

All manipulations were carried out under nitrogen. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane or chloroform standard on Hitachi R-40 (90 MHz) and/or Bruker AC-200 (200 MHz) instruments. Infrared spectra were measured on a JASCO A-302 spectrometer. Mass spectra (EI) were recorded on Shimadzu QP-1000 and JEOL JMS-DX303 GC-MS spectrometers. Solvents were dried over sodium wire, and distilled under nitrogen. Other liquid materials were also distilled before use. *o*-Bis(dimethylsilyl)benzene (**1**) [19], $Pt(CH_2{=}CH_2)(PPh_3)_2$ [20], $Me_2\overline{Si(o\text{-}C_6H_4)SiMe_2Pt}(PPh_3)_2$ (**11**) [10] and $RhCl(PPh_3)_3$ [21] were prepared by the literature methods.

Preparation of o-bis(deuteriodimethylsilyl)benzene

Chlorination of **1** with the $PdCl_2$–CCl_4 system (71% yield) [22] followed by reduction with $LiAlD_4$ gave *o*-bis(deuteriodimethylsilyl)benzene (76%), b.p. 125°C/22 mmHg. IR: 1244, 824, 792, 742 cm^{-1}. ^1H NMR: δ 0.35 (s, 12H, SiMe), 7.3–7.4 (m, 2H, aromatic), 7.5–7.6 (m, 2H, aromatic). ^{13}C NMR: δ −2.7 (4C, SiMe), 128.4 (2C), 134.3 (2C), 144.3 (2C, aromatic Si–C). MS *m/z* (relative intensity): 196 (M^+, 16), 194 (M^+-2, 7), 192 (M^+-4, 5), 136 (100).

General procedure for catalytic reactions

(Ethylene)bis(triphenylphosphine)platinum (0.005 mmol) and a mixture of **1** (0.25 mmol), an internal standard and benzene (2 ml) were placed in a 20 ml flask. A benzene solution (2 ml) of an olefin or a diene (0.25 mmol) was added to the system kept at an appropriate temperature, dropwise using a syringe. The reaction was monitored by periodic GLC analysis. Reaction products were isolated by distillation of the reaction mixture unless otherwise stated.

Compounds 3a, 4a and 5a

A mixture of **3a, 4a, 5a** and **6a** (13 : 11 : 57 : 16) was obtained from the Entry 1 experiment by Kugelrohr distillation (b.p. 100°C/25 Torr) in 87% combined yield.

After the $PdCl_2$-catalyzed transformation of the hydrosilanes **5a** and **6a** into the benzyloxysilane derivatives, a mixture of **3a** and **4a** was obtained (13% (1:1) combined yield based on **1**) by preparative TLC (silica gel/hexane). ^{1}H NMR assignment of **4a** was confirmed by ^{1}H-^{1}H COSY. All spectral data obtained for **6a** were identical with those of an authentic sample.

3a. ^{1}H NMR: δ 0.23 (s, 12H, SiMe), 1.01 (s, 4H, Si–CH_2), 7.2–7.7 (m, 4H, aromatic). ^{13}C NMR: δ −1.5 (4C, SiMe), 7.5 (2C, Si–CH_2), 128.0 (2C), 133.4 (2C), 145.8 (2C, aromatic Si–C). MS m/z (relative intensity): 220 (M^+, 12), 205 (M^+ − Me, 100). HRMS Found: 220.1103. $C_{12}H_{20}Si_2$ calc.: 220.1104.

4a. ^{1}H NMR: δ 0.20 (s, 6H, SiMe), 0.23 (q, $J = 7.6$ Hz, 1H, Si–CH–Si), 0.28 (s, 6H, SiMe), 1.15 (d, 3H, CH–CH_3), 7.30–7.37 (m, 2H, aromatic), 7.53–7.60 (m, 2H, aromatic). ^{13}C NMR: δ −2.8 (2C, SiMe), −0.7 (2C, SiMe), 3.5, 8.3, 128.6 (2C), 132.0 (2C), 149.8 (2C, aromatic Si–C). MS m/z (relative intensity): 220 (M^+, 6), 205 (M^+ − Me, 100). HRMS Found: 220.1088. $C_{12}H_{20}Si_2$ calc.: 220.1104.

5a. IR: 2152 (SiH), 1246 cm^{-1}. ^{1}H NMR: δ 0.319 (d, $J = 3.7$ Hz, 6H, SiMe_2H), 0.322 (s, 6H, SiMe), 0.80–1.0 (m, 5H, Si–Et), 4.74 (septet, 1H, $SiMe_2H$), 7.30–7.37 (m, 2H, aromatic), 7.53–7.60 (m, 2H, aromatic). ^{13}C NMR: δ −2.3 (2C, SiMe), −1.2 (2C, SiMe), 7.6, 8.7, 127.91, 127.98, 134.4, 134.6, 144.6 (aromatic Si–C), 145.7 (aromatic Si–C). MS m/z (relative intensity): 222 (M^+, 2), 207 (M^+ − Me, 39), 193 (100). HRMS Found: 222.1254. $C_{12}H_{22}Si_2$ calc.: 222.1260.

*Preparation of an authentic sample of **6a***

The compound **6a** was prepared by the Diels–Alder reaction of $Me_3SiC{\equiv}CSiMeEtH$ (1 mmol) with α-pyrone (1 mmol) in the presence of NEt_3 (0.3 mmol) in benzene (0.2 ml) at 160°C for 3 days (30% yield) [23], b.p. 95–105°C/25 Torr (Kugelrohr). IR: 2158, 1248, 1246 cm^{-1}; ^{1}H NMR: δ 0.29 (d, $J = 3.6$ Hz, 3H, Si*Me*H), 0.33 (s, 9H, SiMe), 0.70–0.82 (m, 2H, Si–CH_2), 0.98 (t, $J = 7.5$ Hz, 3H, Me), 4.63 (sextet, $J = 3.6$ Hz, 1H, SiMeEt*H*), 7.30–7.35 (m, 2H, aromatic), 7.52–7.60 (m, 2H, aromatic). ^{13}C NMR: δ −4.6 (SiMe), 1.2 (3C, SiMe), 6.2, 8.2, 127.8, 128.0, 134.2, 134.6, 143.5 (aromatic Si–C), 147.0 (aromatic Si–C). MS m/z (relative intensity): 222 (M^+, 10), 207 (M^+ − Me, 100). HRMS Found: 222.1264. $C_{12}H_{22}Si_2$ calc.: 222.1260.

*Compound **4b***

Separation between **4b** and **5b** was carried out by preparative GLC. ^{1}H NMR assignment of **4b** was confirmed by ^{1}H-^{1}H COSY, and ^{13}C NMR spectra of **4b** were analyzed using the GASPE technique. All spectral data obtained for **5b** were identical to those of an authentic sample.

4b. B.p. 100°C/0.25 Torr (Kugelrohr). IR: 1246, 822, 781 cm^{-1}. ^{1}H NMR: δ 0.15 (s, 6H, SiMe), 0.25 (t, $J = 7.8$ Hz, 1H, Si–CH–Si), 0.32 (s, 6H, SiMe), 0.88 (t, $J = 6.5$ Hz, 3H, Me), 1.2–1.4 (m, 10H), 1.5–1.6 (m, 2H), 7.3–7.4 (m, 2H, aromatic), 7.45–7.6 (m, 2H, aromatic). ^{13}C NMR: δ −2.0 (2C, SiMe), −0.2 (2C, SiMe), 12.9 (Si–CH–Si), 14.1 (Me), 22.7, 25.2, 29.3, 29.8, 31.9, 34.2, 128.5 (2C), 131.9 (2C), 149.9 (2C, aromatic Si–C). MS m/z (relative intensity): 304 (M^+, 10), 289 (M^+ − Me, 63), 191 (100). Anal. Found: C, 70.72; H, 10.56. $C_{18}H_{32}Si_2$ calc.: C, 70.97; H, 10.59%.

Preparation of an authentic sample of ***5b***

Compound **5b** was prepared by $RhCl(PPh_3)_3$-catalyzed hydrosilylation [15] of **2b** with **1** in 97% GLC yield and isolated by preparative GLC. IR: 2132 cm^{-1}. ^1H NMR: δ 0.30 (d, $J = 3.6$ Hz, 6H, Si*Me*$_2$H), 0.31 (s, 6H, SiMe), 0.8 (m, 5H, Me, Si–CH_2), 1.0–1.2 (br s, 12H), 4.73 (septet, 1H, SiMe$_2$*H*), 7.3–7.4 (m, 2H, aromatic), 7.5–7.6 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$): δ -2.2 (2C, SiMe), -0.5 (2C, SiMe), 14.1 (Me), 17.1, 22.7, 24.1, 29.3 (2C), 31.9, 33.7, 127.9, 128.0, 134.4 (2C), 144.1 (aromatic Si–C), 145.6 (aromatic Si–C). MS (EI, 20 eV) *m/z* (relative intensity): 306 (M^+, 0.3), 291 ($M^+ -$ Me, 3), 193 (100). Anal. Found: C, 70.57; H, 11.22. $C_{18}H_{34}Si_2$ calc.: C, 70.51; H, 11.18%.

Compound ***6b***

^1H NMR δ 4.64 (sextet, $J = 3.6$ Hz, 1H, SiMeOct*H*). ^{13}C NMR: δ -4.0 (SiMe), 1.2 (3C, SiMe), 14.3 (Me), 24.6, 33.2, 134.2, 134.5 (2C), 134.6, 143.7 (aromatic Si–C), 146.9 (aromatic Si–C). MS *m/z* (relative intensity): 306 (M^+, 7), 291 ($M^+ -$ Me, 5), 193 (100).

Compound ***4c***

^{13}C NMR assignment of **4c** was confirmed by integration, b.p. 110°C/0.3 Torr (Kugelrohr). IR: 1600, 1250, 830, 780, 740 cm^{-1}. ^1H NMR: δ 0.15 (s, 6H, SiMe), 0.21 (s, 6H, SiMe), 0.74 (t, $J = 8.5$ Hz, 1H, Si–CH–Si), 2.93 (d, 2H, CH_2), 7.2–7.6 (m, 9H, aromatic). ^{13}C NMR: δ -1.7 (2C, SiMe), -0.9 (2C, SiMe), 15.0 (Si–CH–Si), 30.8 (*C*H_2–Ph), 125.7, 128.3 (4C), 128.7 (2C), 131.9 (2C), 144.5 (aromatic *C*–CH_2), 149.5 (2C, aromatic Si–C). MS *m/z* (relative intensity): 296 (M^+, 2), 281 ($M^+ -$ Me, 100). HRMS Found: 296.1402. $C_{18}H_{24}Si_2$ calc.: 296.1417.

Compound ***4d***

Compound **4d** was isolated in 80% yield from the reaction at 30°C for 19 h, b.p. 125–130°C/0.5 Torr (Kugelrohr). IR: 1245 cm^{-1}. ^1H NMR: δ 0.16 (s, 6H, SiMe), 0.18 (s, 6H, SiMe), 0.69 (t, $J = 8.6$ Hz, 1H, Si–CH–Si), 2.89 (d, 2H, CH_2), 7.18 and 7.26 (AB, $J = 8.5$ Hz, 4H, *p*-C_6H_4), 7.3–7.4 (m, 2H), 7.45–7.55 (m, 2H). ^{13}C NMR: δ -1.8 (2C, SiMe), -0.8 (2C, SiMe), 14.8 (Si–CH–Si), 30.3 (CH_2), 128.3 (2C), 128.7 (2C), 129.6 (2C), 131.4 (C–Cl), 131.9 (2C), 143.0 (aromatic *C*–CH_2), 149.3 (2C, aromatic Si–C). MS *m/z* (relative intensity): 332 ($M^+ + 2$, 3), 330 (M^+, 7), 315 ($M^+ -$ Me, 100). Anal. Found: C, 64.82; H, 6.90. $C_{18}H_{23}Si_2Cl$ calc.: C, 65.32; H, 6.94%.

Compound ***4e***

Compound **4e** was isolated in 54% yield from the reaction at 30°C for 19 h, b.p. 150–155°C/0.7 Torr (Kugelrohr). IR: 1245 cm^{-1}. ^1H NMR: δ 0.16 (s, 6H, SiMe), 0.20 (s, 6H, SiMe), 0.72 (t, $J = 8.6$ Hz, 1H, Si–CH–Si), 2.33 (s, 3H, *p*-C_6H_4–*Me*), 2.89 (d, 2H, CH_2), 7.10 and 7.14 (AB, $J = 8.2$ Hz, 4H, *p*-C_6H_4), 7.30–7.40 (m, 2H, aromatic), 7.45–7.55 (m, 2H, aromatic). ^{13}C NMR: δ -1.8 (2C, SiMe), -0.8 (2C, SiMe), 14.9 (Si–CH–Si), 21.0 (Me), 30.3 (CH_2), 128.1 (2C), 128.6 (2C), 128.9 (2C), 131.9 (2C), 135.0, 141.4, 149.6 (2C, aromatic Si–C). MS *m/z* (relative intensity): 310 (M^+, 8), 295 ($M^+ -$ Me, 100). Anal. Found: C, 72.71; H, 8.41. $C_{19}H_{26}Si_2$ calc.: C, 73.48; H, 8.44%.

Compound ***4f***

Compound **4f** was isolated in 63% yield from the reaction at 30°C for 19 h, b.p. 140–145°C/0.25 Torr (Kugelrohr). IR 1245 cm^{-1}. ^1H NMR: δ 0.16 (s, 6H, SiMe), 0.19 (s, 6H, SiMe), 0.71 (t, $J = 8.6$ Hz, 1H, Si–CH–Si), 2.86 (d, 2H, CH_2), 3.78 (s, 3H, OMe), 7.03 and 7.36 (AB, $J = 8.6$ Hz, 4H, p-C_6H_4), 7.31–7.37 (m, 2H), 7.47–7.59 (m, 2H). ^{13}C NMR: δ −1.7 (2C, SiMe), −0.8 (2C, SiMe), 15.1 (Si–CH–Si), 29.8 (CH_2), 55.2 (OMe), 113.6 (2C), 128.6 (2C), 129.1 (2C), 131.9 (2C), 136.6, 149.6 (2C, aromatic Si–C), 157.6 (C–OMe). MS m/z (relative intensity): 326 (M^+, 91), 311 ($M^+ -$ Me, 100). HRMS Found: 326.1527. $C_{19}H_{26}OSi_2$ calc.: 326.1522.

*Compound **4g***

B.p. 92°C/0.6 Torr (Kugelrohr). IR: 1737 (C=O), 1243 cm^{-1}. ^1H NMR: δ 0.18 (s, 6H, SiMe), 0.36 (s, 6H, SiMe), 0.61 (t, $J = 8.5$ Hz, 1H, Si–CH–Si), 2.56 (d, CH_2), 3.70 (s, 3H, CO_2Me), 7.34–7.38 (m, 2H, aromatic), 7.52–7.56 (m, 2H, aromatic). ^{13}C NMR: δ −2.4 (2C, SiMe), −0.8 (2C, SiMe), 7.2 (Si–CH–Si), 30.0 (CH_2), 51.6 (CO_2CH_3), 128.8 (2C), 131.9 (2C), 149.1 (2C, aromatic Si–C), 175.7 (CO_2). MS m/z (relative intensity): 278 (M^+, 3), 263 ($M^+ -$ Me, 20), 143 (100). Anal. Found: C, 60.62; H, 7.90. $C_{14}H_{22}Si_2O_2$ calc.: C, 60.38; H, 7.96%.

*Compounds **3h** and **4h***

A mixture of **3h** and **4h** (9 : 1), b.p. 160°C/0.6 Torr (Kugelrohr). Anal. Found: C, 57.09; H, 7.18. $C_{16}H_{22}Si_2O_4$ calc.: C, 57.10; H, 7.19%. These compounds were purified by preparative GLC. ^{13}C NMR assignment of **3h** and **4h** was confirmed using the GASPE technique.

3h. IR: 1721 (C=O), 1245 cm^{-1}. ^1H NMR: δ 0.32 (s, 6H, SiMe), 0.44 (s, 6H, SiMe), 2.72 (s, 2H, Si–CH), 3.63 (s, 6H, CO_2Me), 7.30–7.36 (m, 2H, aromatic), 7.45–7.51 (m, 2H, aromatic). ^{13}C NMR: δ −3.3 (2C, SiMe), −0.1 (SiMe), 1.1 (SiMe), 33.4 (2C, Si–CH), 51.4 (2C, CO_2Me), 128.5 (2C), 133.1 (2C), 147.6 (2C, aromatic Si–C), 175.0 (2C, CO_2Me). MS m/z (relative intensity): 336 (M^+, 1), 321 ($M^+ -$ Me, 100).

4h. IR: 1750 (C=O), 1721 (C=O), 1254 cm^{-1}. ^1H NMR: δ 0.21 (s, 6H, SiMe), 0.41 (s, 6H, SiMe), 2.72 (s, 2H, Si–CH_2), 3.46 (s, 3H, CO_2Me), 3.74 (s, 3H, CO_2Me), 7.35–7.41 (m, 2H, aromatic), 7.48–7.55 (m, 2H, aromatic). ^{13}C NMR: δ −0.1 (2C, SiMe), 1.0 (2C, SiMe), 30.2, 33.5 (CH_2), 50.9 (CO_2Me), 51.8 (CO_2Me), 128.9 (2C), 131.5 (2C), 147.6 (2C, aromatic Si–C), 174.6 (CO_2Me), 176.1 (CO_2Me). MS m/z (relative intensity): 336 (M^+, 51), 321 ($M^+ -$ Me, 25), 89 (100).

*Compounds **7**, **8**, and **9***

The 1,2-, 1,1-, 1,4-adducts (**7**, **8**, and **9**) were separated from each other by preparative GLC. ^1H NMR spectra of **9** were assigned by ^1H-^1H COSY.

7. IR: 1630 (C=C), 1260, 1250, 870, 830 cm^{-1}. ^1H NMR: δ 0.12 (s, 3H, SiMe), 0.22 (s, 3H, SiMe), 0.28 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 1.04 (dd, $J = 14$, 3 Hz, 1H), 1.22 (dd, $J = 14$, 14 Hz, 1H), 1.81 (s, 3H, Me–C=C), 1.98 (dd, $J = 14$, 3 Hz, 1H), 4.63 (s, 1H, C=CH), 4.76 (s, 1H, C=CH), 7.19–7.55 (m, 4H, aromatic). ^{13}C NMR: δ 2.0 (2C, SiMe), 2.5 (2C, SiMe), 19.1 (Me), 27.9, 34.4, 111.3 (CH_2=C), 128.1, 128.2, 133.4, 133.6, 145.1 (aromatic Si–C), 145.5 (aromatic Si–C), 150.1, (C=CH_2). MS m/z (relative intensity): 260 (M^+, 19), 245 ($M^+ -$ Me, 19), 218 ($M^+ - C_3H_6$, 60), 177 (100). HRMS Found: 260.1404. $C_{15}H_{24}Si_2$ calc.: 260.1417.

8. ^1H NMR: δ 0.15 (s, 6H, SiMe), 0.26 (s, 6H, SiMe), 1.49 (d, $J = 11$ Hz, 1H, CH), 1.56 (d, $J = 1$ Hz, 3H, CH_3), 1.68 (d, $J = 1$ Hz, 3H, CH_3), 5.09 (ddd, $J = 11$, 1, 1 Hz, vinyl–H), 7.27–7.52 (m, 4H, aromatic). ^{13}C NMR: δ −1.9 (2C, SiMe),

-0.5 (2C, SiMe), 17.2 (Si–CH), 17.7 (Me), 25.9 (Me), 120.3 (C=*C*H), 127.1 (*C*=CH), 129.7 (2C), 132.0 (2C), 149.6 (2C, aromatic Si–C). MS m/z: 260 (M^+, 100), 245 (M^+- Me, 49), 217 ($M^+-C_3H_6$, 14), 203 ($M^+-C_4H_9$, 21). HRMS Found: 260.1436. $C_{15}H_{24}Si_2$ calc.: 260.1417.

9. IR: 1260, 1250 cm^{-1}. ^{1}H NMR: δ 0.00 (s, 6H, SiMe), 0.40 (s, 6H, SiMe), 1.57 (d, $J = 8$ Hz, 2H, CH_2–CH=), 1.60 (s, 3H, CH_3), 1.76 (s 2H, CH_2), 5.17 (t, 1H, CH), 7.29–7.62 (m, 4H, aromatic). MS m/z: 260 (M^+, 25), 245 (M^+- Me, 19), 218 ($M^+-C_3H_6$, 49), 177 (100). HRMS Found: 260.1436. $C_{15}H_{24}Si_2$ calc.: 260.1417.

Compound 10

IR: 1604 (C=C), 1255, 1245, 830, 740 cm^{-1}. ^{1}H NMR: δ 0.22 (s, 6H, SiMe), 0.29 (s, 6H, SiMe), 1.01 (t, $J = 8$ Hz, 3H, Me), 2.02 (s, 2H, Si–CH_2–C=), 2.08–2.22 (m, 2H, C=C–CH_2), 5.73 (t, $J = 7$ Hz, 1H, C=CH), 7.25–7.55 (m, 4H, aromatic). ^{13}C NMR: δ -2.2 (2C, SiMe), -1.7 (2C, SiMe), 14.0 (Me), 20.0, 21.3, 127.9, 128.2, 133.3, 133.5, 133.9, 138.4, 146.0 (aromatic Si–C), 147.0 (aromatic Si–C). MS m/z: 260 (M^+, 41), 245 (M^+- Me, 29), 191 (100). HRMS Found: 260.1445. $C_{15}H_{24}Si_2$ calc.: 260.1417.

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