

Palladium complex catalyzed Si–Si bond metathesis dimerization of 3,4-benzo-1,2-dimethyl-1,2-diethyl-1,2-disilacyclobut-3-ene and isomerization of the resulting and relevant dimers¹

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Abstract

Palladium–phosphine complex catalyzed Si–Si bond metathesis dimerization of 3,4-benzo-1,2-dimethyl-1,2-diethyl-1,2-disilacyclobut-3-ene (**1b**) took place at 80°C to give 3,4,7,8-dibenzo-1,2,5,6-tetramethyl-1,2,5,6-tetraethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2b**) and its isomer 4,5,7,8-dibenzo-1,2,3,6-tetramethyl-1,2,3,6-tetraethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3b**). Higher temperatures or longer reaction times enhanced the selectivity for **3b** relative to **2b**, indicative of concomitant isomerization of initially formed **2b** to **3b**. Isomerization of 3,4,7,8-dibenzo-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2a**), analogous to **2b**, also proceeded at 80°C in the presence of Pd(PPh₃)₄. Besides 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octamethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3a**), 4,5-benzo-1,1,2,3,3-pentamethyl-2-(*o*-trimethylsilylphenyl)-1,2,3-trisilacyclopentene (**4a**), 3,4,6,7-dibenzo-1,1,2,2,5,5-hexamethyl-1,2,5-trisilacycloheptadiene (**5a**) and 4,5-benzo-1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclopentene (**6a**) were also formed. Mechanisms of the dimerization of **1b** and isomerization of **2a** and **2b** are discussed.

Keywords: Silicon; Palladium; Disilane; Metathesis; Rearrangement; Catalysis

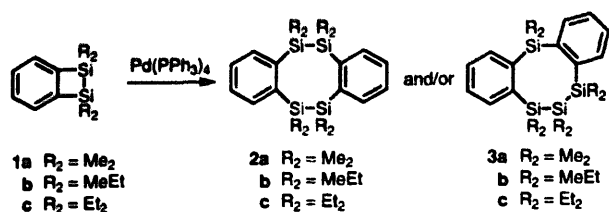
1. Introduction

Because of the unique chemical and physicochemical properties of organosilicon compounds and silicon-based polymers, much importance is attached to the development of new synthetic methodologies in silicon chemistry [1]. As Shiina [2] suggested, 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1a**) is a useful monomer. Upon treatment with low valent late transition metal complexes, it can be assumed to form five-membered bis(silyl)metal species by oxidative addition of the Si–Si bond. As Eaborn and coworkers reported and we confirmed [3], the same species are generated from *o*-bis(dimethylsilyl)benzene. Accordingly, we examined the metal complex catalyzed polymerization of *o*-bis(dimethylsilyl)benzene rather than that of **1a**, which appeared too unstable. However, the attempted polymerization of *o*-bis(dimethylsilyl)benzene was unsuccessful,

although reactions with various unsaturated compounds proceeded cleanly [4]. In contrast, our continued efforts to achieve metal complex catalyzed ring-opening polymerization have revealed dimerization and polymerization of 1,2-disilacyclopentane, silacyclobutanes and silicon- or germanium-bridged [1]ferrocenophanes [5]. During the course of the study, we encountered 3,4-benzo-1,2-dimethyl-1,2-diethyl-1,2-disilacyclobut-3-ene (**1b**), which is much more stable than **1a** and dimerizes to give an isomeric mixture comprising 3,4,7,8-dibenzo-1,2,5,6-tetramethyl-1,2,5,6-tetraethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2b**) and 4,5,7,8-dibenzo-1,2,3,6-tetramethyl-1,2,3,6-tetraethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3b**) (Scheme 1) [6]. Very recently, Ando's and Ishikawa's groups have also independently observed selective palladium catalyzed dimerizations of **1a** to 3,4,7,8-dibenzo-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2a**) [7a] and of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1c**) to 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octamethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3c**) [7b]. Our observation of the formation of an isomeric mixture

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¹ Dedicated to Professor Robert J.P. Corriu in honor of his tremendous contributions to organosilicon chemistry.



Scheme 1.

appeared to give much more information about the mechanism of the metathesis dimerization of benzodisilacyclobutenes. We report herein the detailed results of the study of the palladium catalyzed reaction of **1b** and the related isomerization of **2a**.

2. Results

2.1. Transition metal catalyzed reactions of **1b**

A toluene solution of a 1:1 diastereomeric mixture of **1b** (0.04 mmol) was heated in the presence of a catalytic amount of various transition metal complexes (10 mol%) at 80°C for 14 h in a sealed tube. The results are summarized in Table 1.

Analysis of the reaction mixture by GLC and GLC-MS revealed the formation of **2b**, **3b** and other species [8]. Palladium–triphenylphosphine complexes are known to be effective in the Si–Si bond metathesis reaction [7a,9]. Use of $Pd(dba)_2-2PPh_3$ did indeed give the

simple metathesis dimer **2b**, but the yield was only 15%. The main product was its isomer **3b** (48% yield, run 1). These products were not formed in the absence of a transition metal catalyst. When triethylphosphine, a stronger electron-donating ligand, was used instead of PPh_3 , the simple dimerization mainly predominated to afford **2b** in 44% yield (run 2). In contrast, the use of phosphites such as triphenylphosphite and trimethylphosphite again resulted in preferential formation of **3b** (runs 3 and 4). In both reactions with the phosphite ligands, however, low yields of various byproducts (vide infra), including those presumably arising from redistribution reactions of **1b**, **2b** and **3b**, were also detected by GLC and GLC-MS analyses, in addition to polymeric products. Reaction in the presence of $P(OMe)_3$ in particular gave a very complex mixture. The weakly chelating 1,4-bis(diphenylphosphino)butane was less effective for the reaction (run 5) than monodentate ligands, and its use gave mainly **3b**. Formation of polymers was also significant (approximately 10%; $M_w (M_w/M_n) = 6.5 \times 10^5$ (7.7) relative to polystyrene standards). However, the reaction was faster when the phosphine-free palladium(0) catalyst $Pd(dba)_2$ was used (run 6). Besides **2b** (30%) and **3b** (20%), an unidentified dimer (presumably **4b**, around 10%; MS m/z 440 (M^+)) and a fairly large quantity of polymers (approximately 15%; $M_w (M_w/M_n) = 3.4 \times 10^5$ (6.4)) were also formed. When $RuCl_2(PPh_3)_3$ was employed, **2b** was formed in 13% yield along with polymers (about 10%; $M_w (M_w/M_n) = 1.4 \times 10^5$ (4.4)), but other

Table 1
Effect of catalysts on the dimerization reaction of **1b**^a

Run	Catalyst	Recovery ^b (%)		Yield ^c (%)	
		1b		2b	3b
1	$Pd(dba)_2 + 2PPh_3$ ^d	27		15(21)	48(66)
2	$Pd(dba)_2 + 2PEt_3$	12		44(50)	7(8)
3	$Pd(dba)_2 + 2P(OPh)_3$	22		5(6)	32(45)
4	$Pd(dba)_2 + 2P(OMe)_3$	26		3(4)	7(9)
5	$Pd(dba)_2 + 1dppb$ ^e	73		1(4)	13(48)
6	$Pd(dba)_2$	0		30(30)	20(20)
7	$RuCl_2(PPh_3)_3$	69		13(42)	0
8	$RhCl(PPh_3)_3$	4		4(4)	0

^a Reaction conditions: **1b** (0.04 mmol), catalyst (0.004 mmol), toluene (0.2 ml), 80°C, 14 h, in a sealed tube. ^b Determined by GLC. ^c GLC yields based on the amount of **1b** charged. The figures in parentheses are GLC yields based on the amount of **1b** consumed. ^d dba = dibenzylideneacetone. ^e dppb = 1,4-bis(diphenylphosphino)butane.

Table 2
Dimerization reaction of **1b** in the presence of $Pd(PPh_3)_4$ ^a

Run	Temperature (°C)	Time (h)	Recovery ^b (%)		Yield ^c (%)	
			1b		2b	3b
1	80	14	70		12(40)	12(40)
2	80	40	58		4(10)	31(74)
3	120	14	24		0	51(67)

^a Reaction conditions: **1b** (0.04 mmol), $Pd(PPh_3)_4$ (0.004 mmol), toluene (0.2 ml) in a sealed tube. ^b Determined by GLC. ^c GLC yields based on the amount of **1b** charged. The figures in parentheses are GLC yields based on the amount of **1b** consumed.

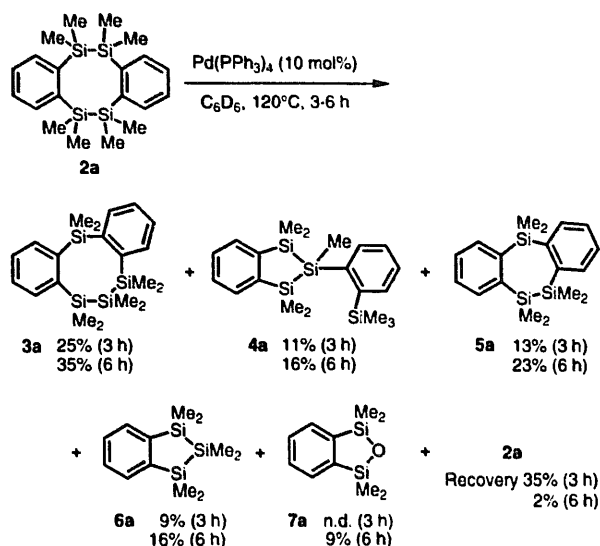
dimers were not detected (run 7). Phosphine free ruthenium complexes such as $\text{Ru}(\text{cod})(\text{cot})$ or $\text{Ru}_3(\text{CO})_{12}$ did not catalyze the dimerization. The reaction with $\text{RhCl}(\text{PPh}_3)_3$ gave a small amount of **2b**, but a considerable amount of oligomeric material ($M_w (M_w/M_n) = 1.2 \times 10^3 (1.2)$) was also formed (run 8) [10].

Experiments aimed at establishing the mode of production of **3b** indicated clearly that isomerization of **2b** to **3b** (and perhaps other reactions also [8,11]) takes place during the metathesis reaction (Table 2). First we examined the time dependence of the course of the $\text{Pd}(\text{PPh}_3)_4$ catalyzed reaction of **1b**. When the reaction time was prolonged from 14 to 40 h at 80°C , the yield of **3b** increased at the expense of **2b** (runs 1 and 2). Reaction at 120°C gave **3b** in a fairly high yield without formation of **2b** (run 3). As Ishikawa and coworkers [7b] reported, the dimerization of **1c** at 150°C gives exclusively **3c**. From our present results, it appears reasonable to consider that the exclusive formation is due at least in part to occurrence of a similar isomerization of the possible intermediate **2c**.

2.2. $\text{Pd}(\text{PPh}_3)_4$ catalyzed reaction of **2a**

To confirm the isomerization of the kinetically preferred **2b** to the thermodynamically more stable **3b** and to gain more mechanistic information, including the structural characterization of byproducts, it seemed necessary to simplify the reaction system. Accordingly, we decided to use **2a** in place of **2b** as the starting material for the possible isomerization in the presence of $\text{Pd}(\text{PPh}_3)_4$. When a mixture of **2a** (0.034 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.0034 mmol) and C_6D_6 (0.2 ml) was heated at 80°C for 12 h in an NMR tube, **2a** remained intact. However, heating at 120°C for 6 h led to nearly complete consumption of **2a** (2% recovery) and formation of several products was observed by NMR spectroscopy (Scheme 2). One of the major products was 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octamethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3a**, 35% yield) of the same cyclic framework as **3b**. The occurrence of the isomerization of **2a** to **3a** strongly supports the view that in the dimerization of **1b**, **3b** was formed via isomerization of the initially formed dimer **2b**. Besides **3a**, **4a** (16%), **5a** (23%), **6a** (16%) and **7a** (9%) were also detected [11]. The formation of **7a** clearly suggests the generation of species having five-membered 1-palladia-2,5-disilacyclopentene or related structures. However, **7a** was found not to have been present in the reaction mixture before opening of the sealed NMR tube, indicating that **7a** arises from reaction with traces of oxygen or moisture during the work-up.

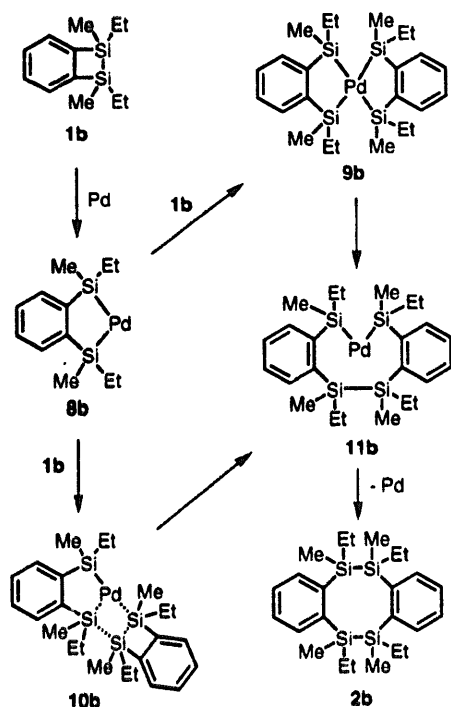
The time course of the reaction was quite informative about possible pathways leading to **4a**, **5a** and **6a**; in the reaction at 120°C , the yields of **3a**, **4a**, **5a** and **6a** were respectively 25, 11, 13 and 9% after 3 h. Comparison of



the yields of the various products after 6 h (vide supra) indicates that, as for **4a**, the ratio **4a/3a** remains nearly constant throughout the reaction; 0.44 at 3 h and 0.46 at 6 h. However, the ratios **5a/3a** and **6a/3a** increased as the isomerization of **2a** proceeded. These observations suggest that **4a** is also a primary product coming from elemental processes involved in the isomerization of **2a**, and that **5a** and **6a** are secondary products formed through further reactions of initially formed **3a** and/or **4a**.

3. Discussion

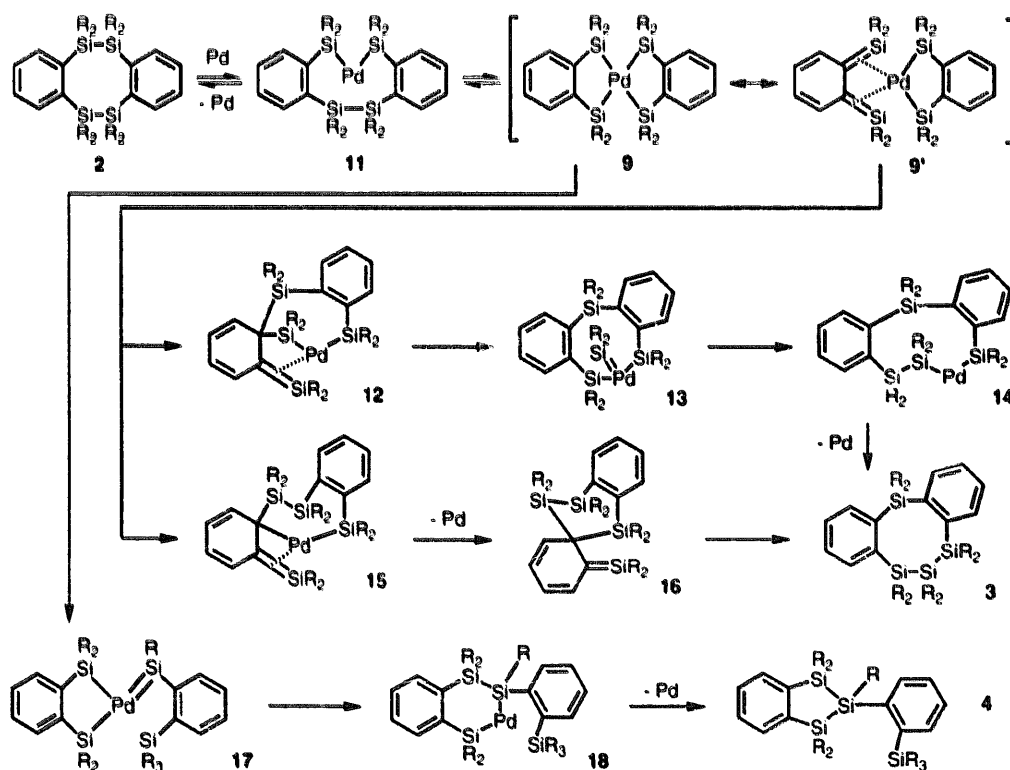
Possible mechanisms for the formation of **2b** from **1b** are illustrated in Scheme 3, involving oxidative addition of the Si–Si bond of **1b**, further reaction of the resulting complex **8b** with **1b** leading to **11b** via either **9b** or **10b**, and finally reductive elimination. Such elemental processes are well precedented. The oxidative addition of disilanes to palladium complexes [12] has been well documented. The transformation of **1b** to **11b** can be understood in terms of Ito and coworkers' [13] observation that a bis(disilanyl)methane derivative undergoes intramolecular bond transmutation with an isocyanide palladium complex to give a disilane and a 1-palladia-2,4-disilacyclobutane complex. The final reductive elimination of bis(silyl)palladium species has not been systematically studied, but can be assumed in the light of similar transformations of the corresponding platinum complexes [14]. The only rather uncertain event involved in Scheme 3 is the transient intermediacy of either **9b** or **10b** (or others) generated during the transformation of **8b** to **11b**. One of us recently isolated tetrakis(silyl)platinum(IV) and tetrakis(silyl)palladium(IV) complexes starting from an *o*-bis(silyl)ben-



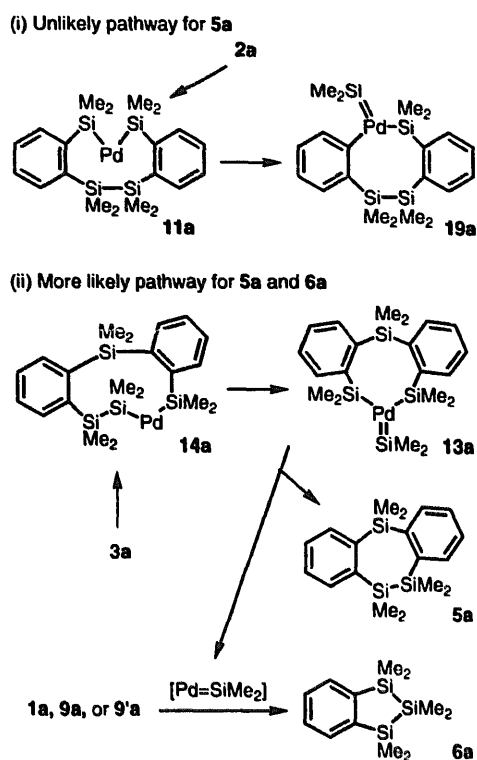
Scheme 3.

zene compound [15]. These findings clearly support the mechanism involving the rather rare Pd(IV) species **9b**. At present, however, we do not have evidence to argue against the σ -bond metathesis via a four-membered transition state like **10b**.

As described in the Results section, not only **2b** but also **3b** was formed in the dimerization of **1b**. This was ascribed to simultaneous isomerization of the initially formed **2b** to **3b**. A separate experiment using **2a** confirmed that such isomerization does indeed take place, but other products were also formed along with **3a**. On the basis of these observations, one can envisage the mechanism of isomerization of **2** to **3** (and also of **2a** to **4a**) as illustrated in Scheme 4. The formation of **7a** appears to substantiate the intermediacy of 1-palladia-2,5-disilacyclopentadiene species such as **9** (**9'**) during the isomerization of **2a**. Oxidative addition of the Si–Si bond in **2** leads, via **11**, to **9** (**9'**), which can display two modes of reaction. One involves reaction as an *o*-quinodisilane complex **9'** [16] to undergo intramolecular 1,2-addition of one of the Si–Pd bonds to afford either **12** or **15**. Aromatization of **12** may generate a silylene species **13**. 1,2-Migration of a Pd-bound silyl to the silylene ligand [17] yielding **14**, followed by reductive elimination, gives **3**. Alternatively, the formed **15** undergoes reductive elimination to generate **16**, which may isomerize to **3**. The other reaction that **9** can undergo is 1,3-migration of an alkyl group yielding **17**, which is likely to be transformed, via 1,2-migration [17] and subsequent reductive elimination, to **4**. 1,3-Migration is often postulated for metal catalyzed redistribution reactions [18]. However, migration of ethyl and higher alkyl groups is very rare, and is considered to be slower than methyl (and phenyl) migration. Accord-



Scheme 4.



Scheme 5.

ingly, the isomerization of 2b and 2c that takes place concomitantly as the dimerization of 1b and 1c proceeds would not be expected to afford 4a-type products in considerable yields, in agreement with observation.

Formation of 5a and 6a merits mechanistic consideration, although we do not have unequivocal information. From the time course of isomerization of 2a, these compounds were concluded to be formed via secondary reactions of 3a. Accordingly, the possibility that 5a is directly formed from 2a via 11a and 19a is ruled out (Scheme 5(i)). Most probable is the sequence of events depicted in Scheme 5(ii), involving oxidative addition of 3a, 1,2-shift of the β -silyl group [17,19] in 14a and reductive elimination of 5a from resulting 13a. The sequence is in full agreement with our previous observations; the stoichiometric reaction of 1,3-dichlorohexamethyltrisilane with $Pt(PEt_3)_3$ at 60°C yielded, besides (disilanyl)(silyl)platinum species, a bis(chlorodimethylsilyl)platinum complex, the oxidative addition product from the resulting 1,2-dichlorodisilane [17]. Furthermore, the results of a palladium catalyzed reaction of the trisilane with phenylacetylene [17] also strongly indicated a sequence such as 3a \rightarrow 14a \rightarrow 13a \rightarrow 5a + silylene species. Thus the reaction gave the by-products 1,2-bis(chlorodimethylsilyl)ethene and a silacyclopentadiene in considerable yields. The former came from acetylene insertion into the in situ generated dichloro-

disilane, and the latter by trapping of the extruded silylene species with acetylene molecules.

The formation of 6a can also be reasonably explained, given that 13a is generated from 3a. Thus, the reductive elimination yielding 5a, if it occurs, must extrude palladium silylene species from 13a. In the reaction mixture in which isomerization of 2a proceeds, there are various complexes (Scheme 4), including those containing coordinated *o*-phenylenedisila moieties such as 9a (9'a). The highly reactive 1a itself can also be expected to be generated in situ in low concentration from these complexes. The palladium silylene species extruded from 13a may either end up in polymer formation or be trapped by these *o*-phenylenedisila species or 1a to afford 6a, as suggested in our earlier paper [17].

4. Experimental section

4.1. General

All manipulations were carried out under nitrogen. 1H , ^{13}C and ^{29}Si NMR spectra were recorded in $CDCl_3$, unless otherwise noted, with tetramethylsilane or chloroform as standard on a Bruker ARX-300 (300 MHz for 1H , 75.5 MHz for ^{13}C and 59.6 MHz for ^{29}Si) instrument. Infrared spectra were recorded with neat samples on a JASCO FT/IR-5000 spectrometer. Mass spectra (EI, 70 eV) were recorded on Shimadzu QP-1000, Shimadzu QP-5000 and JEOL JMS-DX303 GC-MS spectrometers. All boiling points are uncorrected. Solvents were dried over sodium wire and distilled under nitrogen. Other liquids were also distilled before use. $RuCl_2(PPh_3)_4$ was used as purchased. $Pd(PPh_3)_4$ [20], $Pd(dba)_2$ [21], $RhCl(PPh_3)_3$ [22] and 2a [7a] were prepared by the published methods.

4.2. Preparation of 1b

Compound 1b was synthesized by the following three steps.

o-Bis(methylethylsilyl)benzene (1:1 diastereomeric mixture) was obtained (57% yield) from the reaction of *o*-dibromobenzene, chloromethylethylsilane and magnesium in diethyl ether as described for a similar compound [23]. B.p. 110°C/5 mmHg. IR: 2144, 1251, 1123 cm^{-1} . 1H NMR: δ 0.365 (d, $J = 3.7$ Hz, 3H, SiMe), 0.370 (d, $J = 3.7$ Hz, 3H, SiMe), 0.85–0.95 (m, 4H, Si- CH_2), 1.0–1.1 (m, 6H, CH_2-CH_3), 4.55–4.65 (m, 2H, SiH), 7.35–7.4 (m, 2H, aromatic), 7.55–7.60 (m, 2H, aromatic) ppm. ^{13}C NMR: δ -4.9 (SiMe), -4.8 (SiMe), 6.05 (Si- CH_2), 6.1 (Si- CH_2), 8.3 (2C, CH_2-CH_3), 128.3 (2C), 134.7 (2C), 143.7 (2C) ppm. ^{29}Si NMR: δ -13.90, -13.84 ppm. MS m/z (relative intensity): 222 (M^+ , 1), 221 ($M^+ - 1$, 3), 207 ($M^+ - Me$, 5), 193 ($M^+ - Et$, 100), 165 (39), 163 (29), 149

(12), 121 (15), 105 (11). Anal. Found: C, 64.76; H, 9.69. $C_{12}H_{22}Si_2$ Calc.: C, 64.78; H, 9.96%.

Chlorination of *o*-bis(methylethylsilyl)benzene with the $PdCl_2-CCl_4$ system [24] gave *o*-bis(chloromethylethylsilyl)benzene (1:1 diastereomeric mixture, 76% yield). B.p. 142°C/3 mmHg. IR: 1253, 1116 cm^{-1} . 1H NMR: δ 0.79 (s, 3H, SiMe), 0.80 (s, 3H, SiMe), 1.03–1.12 (m, 6H, CH_2-CH_3), 1.14–1.25 (m, 4H, Si- CH_2), 7.43–7.48 (m, 2H, aromatic), 7.85–7.91 (m, 2H, aromatic) ppm. ^{13}C NMR: δ 2.91 (SiMe), 3.06 (SiMe), 6.94 (CH_2-CH_3), 6.97 (CH_2-CH_3), 11.84 (Si- CH_2), 11.93 (Si- CH_2), 129.1 (2C), 135.87, 135.91, 140.97, 141.00 ppm. ^{29}Si NMR: δ 24.07, 24.12 ppm. MS m/z (relative intensity): 279 ($M^+ - Me$ for $2 \times ^{37}Cl$, 1), 277 ($M^+ - Me$ for ^{35}Cl and ^{37}Cl , 4), 279 ($M^+ - Me$ for $2 \times ^{35}Cl$, 6), 265 (17), 263 (70), 261 (100), 235 (16), 233 (24), 221 (3), 219 (6), 217 (6), 197 (18). Anal. Found: C, 49.56; H, 7.01. $C_{12}H_{20}Si_2Cl_2$ Calc.: C, 49.47; H, 6.92%.

3,4-Benzo-1,2-dimethyl-1,2-ethyl-1,2-disilacyclobut-3-ene **1b** (1:1 diastereomeric mixture) was prepared by the reductive coupling of *o*-bis(chloromethylethylsilyl)benzene with sodium in toluene as described for a similar compound [2]. After filtration of solid materials from the reaction mixture, the resulting colorless solution of **1b** was used for the catalytic reactions without further purification. The 1H NMR spectrum showed the purity to be higher than 85%. A major contaminant was 4,5-benzo-1,3-dimethyl-1,3-diethyl-1,3-disila-3-oxacyclopentene (**7b**) which displayed two singlets assignable to CH_3 at δ 0.42 and 0.46 ppm in $CDCl_3$; its concentration ranging from 5 to 10%. A trace of a polymer was also observed by GPC.

Compound **1b**. 1H NMR (C_7D_8): δ 0.37 (s, 3H, SiMe), 0.40 (s, 3H, SiMe), 0.7–1.1 (m, 10H, Si- CH_2-CH_3), 7.17–7.24 (m, 2H, aromatic), 7.37–7.42 (m, 2H, aromatic) ppm. ^{13}C NMR (C_7D_8): δ -0.95 (SiMe), -0.91 (SiMe), 6.88 (CH_2-CH_3), 6.94 (CH_2-CH_3), 7.86 (Si- CH_2), 7.90 (Si- CH_2), 129.6 (2C), 132.2, 132.3, 155.94, 156.00 ppm. ^{29}Si NMR (C_7D_8): δ 3.41, 3.46 ppm. MS m/z (relative intensity): 220 (M^+ , 22), 205 ($M^+ - Me$, 8), 191 ($M^+ - Et$, 96), 177 (15), 163 (100), 145 (29). HRMS Found: 220.1105. $C_{12}H_{20}Si_2$ Calc.: 220.1102.

4.3. General procedure for catalytic reactions of **1b**

A mixture of a transition metal complex (a palladium compound in most cases) (0.004 mmol), **1b** (0.04 mmol) and toluene (0.2 ml) was heated at 80°C for 14 h in a sealed glass tube. The mixture was analyzed by GLC, GLC-MS and GPC.

4.4. Compound **2b**

From the experiment represented by run 2 in Table 1, a mixture of compounds **2b** and **3b** (25:4) was isolated

by preparative TLC (silica gel, hexane) in 38% total yield. IR: 1250, 1114 cm^{-1} . 1H NMR: δ 0.35–0.52 (m, 12H, SiMe), 0.85–1.05 (m, 20H, SiEt), 7.17–7.22 (m, 4H, aromatic), 7.45–7.55 (m, 4H, aromatic) ppm. ^{29}Si NMR: δ -16.6–-15.7 (m) ppm. MS m/z (relative intensity): 440 (M^+ , 0.4), 425 (0.1), 411 (0.2), 325 (0.6), 309 (1), 295 (2), 281 (5), 267 (5), 163 (8), 144 (100), 116 (25), 73 (8), 59 (23). HRMS Found: 440.2178. $C_{24}H_{40}Si_4$ Calc.: 440.2205.

4.5. Compound **3b**

From the experiment represented by run 3 in Table 2, preparative TLC (silica gel, hexane) gave **3b** in 60% yield. IR: 1249, 1112 cm^{-1} . 1H NMR: δ -0.2–-0.1 (m, 3H, SiMe), -0.05–0.08 (m, 3H, SiMe), 0.11–0.20 (m, 3H, SiMe), 0.45–0.50 (m, 3H, SiMe), 0.60–0.90 (m, 20H, SiEt), 7.25–7.35 (m, 4H, aromatic), 7.45–7.55 (m, 2H, aromatic), 7.65–7.80 (m, 2H, aromatic) ppm. ^{13}C NMR: δ -4.5–-4.0 (m), 7.0–10.0 (m), 127.1, 127.3, 127.7, 127.8, 133.4, 134.7, 135.7, 136.7, 145.5–145.6 (m) ppm. ^{29}Si NMR: δ -40.6–-40.2 (m), -15.4–-15.0 (m), -4.8–-4.2 (m) ppm. MS m/z (relative intensity): 440 (M^+ , 1), 355 (1), 325 (1), 295 (3), 281 (11), 267 (8), 253 (4), 163 (4), 144 (100), 116 (29), 59 (14). HRMS Found: 440.2205. $C_{24}H_{40}Si_4$ Calc.: 440.2205.

4.6. Reaction of **2a** with $Pd(PPh_3)_4$

A mixture of **2a** (0.034 mmol), tetrakis(triphenylphosphine)palladium (0.0034 mmol) and benzene- d_6 (0.2 ml) was heated under nitrogen in a sealed NMR tube. The reaction was monitored by 1H , ^{13}C and ^{29}Si NMR spectroscopy. After heating at 120°C for 6 h, the NMR spectrum showed almost complete consumption of **2a** (δ_c 0.93 ppm for methyl carbons and $\delta_{Si} = 19.6$ ppm). In a separate reaction on a five-fold scale (120°C for 8 h), **3a** (26% yield), **6a** (20%) and a mixture of **4a** (11%) and **5a** (21%) were separated by preparative TLC (silica gel, hexane). Compound **4a** appeared to be rather unstable towards oxygen and/or moisture; when the mixture of **4a** and **5a** was exposed to the air, it gradually (over several months) deteriorated to give an intractable mixture. In contrast, compound **5a** remained unchanged under the same conditions. Therefore, we could isolate **5a** (18%) from the product mixture by preparative TLC (silica gel, hexane/benzene = 200/3).

Compound **3a**. IR: 1251, 1114 cm^{-1} . 1H NMR (C_6D_6): δ 0.00 (s, 6H, SiMe), 0.22 (s, 12H, SiMe), 0.54 (s, 6H, SiMe) ppm. 1H NMR: δ -0.08 (s, 6H, SiMe), 0.15 (s, 12H, SiMe), 0.54 (s, 6H, SiMe), 7.32–7.37 (m, 4H, aromatic), 7.50–7.56 (m, 2H, aromatic), 7.78–7.84 (m, 2H, aromatic) ppm. ^{13}C NMR: δ -7.8 (2C), -1.8 (4C), 3.7 (2C), 127.6 (2C), 127.8 (2C), 134.4 (2C), 135.3 (2C), 145.9 (2C), 146.8 (2C) ppm.

^{29}Si NMR: δ -45.7, -18.4, -6.3 ppm. MS m/z (relative intensity): 384 (M^+ , 2), 253 (15), 195 (4), 175 (5), 116 (100), 101 (6), 73 (35) ppm. HRMS Found: 384.1582. $\text{C}_{20}\text{H}_{32}\text{Si}_4$. Calc.: 384.1579.

Compound 4a. ^1H NMR (C_6D_6): δ 0.27 (s, 3H, SiMe), 0.39 (s, 21H, SiMe) ppm. ^{13}C NMR: δ -4.4, -1.0 (2C), -0.9 (2C), 1.5 (3C), 127.4, 127.5, 128.3 (2C), 133.2 (2C), 135.5, 137.7, 142.7, 147.2, 150.0 (2C), 145.7 (2C) ppm. ^{29}Si NMR: δ -42.9, -11.5, -3.3 ppm. MS m/z (relative intensity) 384 (M^+ , 10), 369 (M^+ - Me, 1), 325 (2), 311 (M^+ - SiMe₃, 41), 253 (65), 191 (17), 177 (15), 116 (36), 73 (SiMe₃⁺, 100). HRMS Found: 384.1573. $\text{C}_{20}\text{H}_{32}\text{Si}_4$. Calc.: 384.1579.

Compound 5a. IR: 1249, 1122 cm^{-1} . ^1H NMR (C_6D_6): δ 0.37 (s, 12H, SiMe), 0.60 (s, 6H, SiMe) ppm. ^1H NMR: δ 0.44 (s, 12H, SiMe), 0.71 (s, 6H, SiMe), 7.30–7.35 (m, 4H, aromatic), 7.62–7.67 (m, 4H, aromatic) ppm. ^{13}C NMR: δ 0.3 (4C), 1.9 (2C), 127.9 (2C), 128.4 (2C), 134.1 (2C), 134.3 (2C), 145.5 (2C), 145.7 (2C) ppm. ^{29}Si NMR: δ -21.3, -8.4 ppm. MS m/z (relative intensity): 326 (M^+ , 53), 311 (2), 295 (1), 253 (100), 195 (12), 175 (11), 73 (17). HRMS Found: 326.1344. $\text{C}_{18}\text{H}_{26}\text{Si}_3$. Calc.: 326.1341.

Compound 6a. B.p. 115°C/30 mmHg (Kugelrohr). IR: 1249, 1113 cm^{-1} . ^1H NMR (C_6D_6): δ 0.23 (s, 6H, SiMe), 0.34 (s, 12H, SiMe), 7.22–7.27 (m, 2H, aromatic), 7.54–7.58 (m, 2H, aromatic) ppm. ^1H NMR δ 0.26 (s, 6H, SiMe), 0.32 (s, 12H, SiMe), 7.32–7.37 (m, 2H, aromatic), 7.57–7.62 (m, 2H, aromatic) ppm. ^{13}C NMR: δ -8.4 (2C), 1.8 (4C), 128.2 (2C), 133.1 (2C), 150.5 (2C) ppm. ^{29}Si NMR: δ -53.6, -13.0 ppm. MS m/z (relative intensity): 250 (M^+ , 73), 235 (54), 219 (3), 191 (64), 177 (81), 161 (27), 147 (10), 145 (15), 105 (14), 93 (6), 73 (100). HRMS Found: 250.0998. $\text{C}_{12}\text{H}_{22}\text{Si}_3$. Calc.: 250.1027.

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