

Journal of Organometallic Chemistry 521 (1996) 335-341

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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Received 10 January 1996

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-tetrasilacycloocta-3,7-diene (2b) and its isomer 4,5,7,8-dibenzo-1,2,3,6-tetramethyl-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), 4,5benzo-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 fivemembered 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 3,4benzo-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-1,2,3,6tetramethyl-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-1,1,2,2,5,5,6,6octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (2a) [7a] and of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-4-ene (1c) to 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-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.



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 diastereometric 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

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

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 PPh₃, 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%; $M_{\rm w} (M_{\rm w}/M_{\rm n}) = 6.5 \times 10^5$ (7.7) relative to polystyrene standards). However, the reaction was faster when the phosphine-free palladium(0) catalyst Pd(dba), 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 RuCl₂(PPh₃)₃ was employed, 2b was formed in 13% yield along with polymers (about 10%; M_w (M_w/M_n) = 1.4 × 10⁵ (4.4)), but other

Run	Catalyst	Recovery ^b (%)	Yield (%)		A.C. MARKAN MARKEN STATE
		tin and the second s	2b	3b	
1	$Pd(dba)_2 + 2PPh_3^{d}$		15(21)	48(66)	
2	$Pd(dba)_2 + 2PEt_1$	12	44(50)	7(8)	
3	$Pd(dba)_{3} + 2P(OPh)_{1}$	22	5(6)	32(45)	
4	$Pd(dba)_{2} + 2P(OMe)_{1}$	26	3(4)	7(9)	
5	Pd(dba), + ldppb °	73	1(4)	13(48)	
6	Pd(dba),	0	30(30)	20(20)	
7	RuCl, (PPh,),	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** consumed. ^d dba = dibenzylideneacetone. ^e dppb = 1,4-bis(diphenylphosphino)butane.

Table 2 Dimerization reaction of 1b in the presence of $Pd(PPh_1)_a$ *

Run	Temperature	Time	Recovery ^b (%)	Yield ' (%)	
		(h)	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(PPh₃)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 Ru(cod)(cot) or Ru₃(CO)₁₂ did not catalyze the dimerization. The reaction with RhCl(PPh₃)₃ gave a small amount of **2b**, but a considerable amount of oligomeric material $(M_w (M_w/M_n) =$ 1.2×10^3 (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 Pd(PPh₃)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. $Pd(PPh_3)_4$ 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 $Pd(PPh_3)_a$. When a mixture of **2a** (0.034 mmol), $Pd(PPh_3)_4$ (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 3h. 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-



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-disilasyclopentadiene 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 silvlene species 13. 1,2-Migration of a Pd-bound silvl to the silvlene 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-



(i) Unlikely pathway for 5a



(ii) More likely pathway for Sa and 6a



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 $3a \rightarrow 14a \rightarrow 13a \rightarrow 5a +$ silvlene 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 dichlorodisilane, 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, ¹³C and ²⁹Si NMR spectra were recorded in CDCl₃, unless otherwise noted, with tetramethylsilane or chloroform as standard on a Bruker ARX-300 (300 MHz for ¹H, 75.5 MHz for ¹³C and 59.6 MHz for ²⁹Si) 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. RuCl₂(PPh₃)₃ was used as purchased. Pd(PPh₃)₄ [20], Pd(dba)₂ [21], RhCl(PPh₃)₃ [22] and **2a** [7a] were prepared by the pablished 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–CH₂), 1.0–1.1 (m, 6H, CH₂–CH₃), 4.55–4.65 (m, 2H, SiH), 7.35–7.4 (m, 2H, aromatic), 7.55–7.60 (m, 2H, aromatic) ppm. ¹³C NMR: δ –4.9 (SiMe), –4.8 (SiMe), 6.05 (Si–CH₂), 6.1 (Si–CH₂), 8.3 (2C, CH₂–CH₃), 128.3 (2C), 134.7 (2C), 143.7 (2C) ppm. ²⁹Si 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 PdCl₂-CCl₄ 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, CH₂-CH₃), 1.14-1.25 (m, 4H, Si-CH₂), 7.43-7.48 (m, 2H, aromatic), 7.85-7.91 (m, 2H, aromatic) ppm. ¹³C NMR: δ 2.91 (SiMe), 3.06 (SiMe), 6.94 (CH₂-CH₃), 6.97 (CH₂-CH₃), 11.84 (Si-CH₂), 11.93 (Si-CH₂), 129.1 (2C), 135.87, 135.91, 140.97, 141.00 ppm. ²⁹Si NMR: δ 24.07, 24.12 ppm. MS *m/z* (relative intensity): 279 (*M*⁺ – Me for 2 ×³⁷Cl, 1), 277 (*M*⁺ – Me for ³⁵Cl and ³⁷Cl, 4), 279 (*M*⁺ – Me for 2 × ³⁵Cl, 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. C₁₂H₂₀Si₂Cl₂ 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-3oxacyclopentene (**7b**) which displayed two singlets assignable to CH₃ at δ 0.42 and 0.46 ppm in CDCl₃; 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=CH₂= CH₃), 7.17=7.24 (m, 2H, aromatic), 7.37=7.42 (m, 2H, aromatic) ppm. ¹³C NMR (C_7D_8): δ =0.95 (SiMe), =0.91 (SiMe), 6.88 (CH₂=CH₃), 6.94 (CH₂=CH₃), 7.86 (Si=CH₂), 7.90 (Si=CH₂), 129.6 (2C), 132.2, 132.3, 155.94, 156.00 ppm. ²⁹Si 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 (13), 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. ²⁹Si 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. C₂₄H₄₀Si₄ 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: $\delta - 0.2 - 0.1$ (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. ¹³C NMR: $\delta - 4.5 - 4.0$ (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. ²⁹Si NMR: $\delta - 40.6 - 40.2$ (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. C₂₄H₄₀Si₄ Calc.: 440.2205.

4.6. Reaction of 2a with $Pd(PPh_3)_3$

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, ¹³C and ²⁹Si 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 δ_{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 (C₆D₆): 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. ¹³C 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.

²⁹Si 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. C₂₀H₃₂Si₄ Calc.: 384.1579.

Compound 4a. ¹H NMR ($C_6 D_6$): δ 0.27 (s, 3H, SiMe), 0.39 (s, 21H, SiMe) ppm. ¹³C 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. ²⁹Si 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. $C_{20} H_{32} Si_4$ Calc.: 384.1579.

Compound **5a**. IR: 1249, 1122 cm⁻¹. ¹H NMR (C₆D₆): 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. ¹³C 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. ²⁹Si 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. C₁₈H₂₆Si₃ 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. ¹³C NMR: δ – 8.4 (2C), 1.8 (4C), 128.2 (2C), 133.1 (2C), 150.5 (2C) ppm. ²⁹Si 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: $C_{12}H_{22}Si_3$ Calc.: 250.1027.

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