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Selective Arylation of a Si–H Bond in *o*-Bis(dimethylsilyl)benzene via C–H Bond Activation of Arenes

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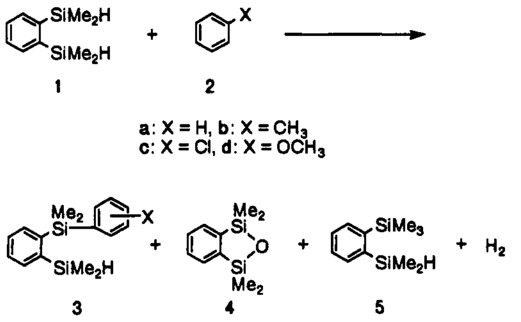
Tris(dibenzylideneacetone)diplatinum catalyzed arylation of a Si–H bond in *o*-bis(dimethylsilyl)benzene at 110 °C via C–H bond activation of arenes to give *o*-(aryldimethylsilyl)(dimethylsilyl)benzene in 81–87% yields. Chlorobenzene and anisole mainly gave the ortho isomers, while the meta isomer was the major product in the reaction of toluene. The relative reactivity trends among arenes, as examined in competitive experiments, were toluene < benzene < chlorobenzene < anisole. In the reaction of *o*-bis(deuteriodimethylsilyl)benzene with benzene, extensive H–D exchange took place between these two components, while the deuterium label was not found in the phenylation product. H–D exchange between the phenylation product and benzene-d_6 did not occur either. A mechanism involving $\overline{\mathrm{PtSiMe_2(\mathit{o}\text{-}C_6H_4)Si}}\mathrm{Me_2}$ species via dihydrogen elimination followed by the reaction of the species with an arene molecule was proposed.

In view of the renewed interest in organosilicon chemistry,[1] development of new synthetic methods of organosilicon compounds becomes more important. Among the conventional syntheses, transition-metal-complex-catalyzed hydrosilylation has been extensively studied and widely used to functionalize the Si–H bond. On the other hand, functionalization via dehydrogenation between C–H and Si–H bonds, despite the great potential, has not been equally explored. To the best of our knowledge, such reactions catalyzed by homogeneous catalysts have been reported only in two cases. Curtis et al. found during the study of iridium-catalyzed redistribution reactions that hydrodisiloxanes underwent phenylation with benzene used as the solvent.[2] We also reported that a Vaska-type rhodium complex promoted similar reactions with triethylsilane under photolytic conditions.[3] In both cases, however, the yields of the arylation products were very low. We previously reported that dehydrogenative double silylation of various unsaturated compounds with *o*-bis(dimethylsilyl)benzene (1) readily proceeded in the presence of platinum complex catalysts.[4] In the course of the study, we found that 1 underwent selective arylation with arenes, via C–H bond activation, to give *o*-(aryldimethylsilyl)(dimethylsilyl)benzenes in high yields. Herein are reported the details of the new arylation reaction.[5]

Results and Discussion

$Pt_2(dba)_3$-Catalyzed Reaction of *o*-Bis(dimethylsilyl)benzene with Arenes. When *o*-bis(dimethylsilyl)benzene (**1**) dissolved in benzene (**2a**) was heated in a sealed tube at 110 °C in the presence of $Pt_2(dba)_3$ (dba = dibenzylideneacetone),[6] one of the two Si–H bonds of **1** selectively reacted with benzene in a dehydrogenative manner to give 87% yield of phenylsilane **3a** in 84 h (eq 1; Table I, entry 1). GC and GC–MS analyses revealed that the cyclic disiloxane **4** and *o*-(trimethylsilyl)(dimethylsilyl)benzene (**5**) were also formed in 3 and 1% yields, respectively. However, *o*-bis(phenyldimethylsilyl)benzene was not found at all even after prolonged reaction.



(1)

Substituted benzenes also reacted similarly to give all possible isomeric arylsilanes (**3b–d**) and small amounts (1–10% combined yields) of **4**, **5**, and phenyldimethylsilane

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[1] Zeigler, J. M., Fearon, F. W. G., Eds. *Silicon-Based Polymer Science*; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. Corey, J. Y.; Corey, E. R.; Gaspar, P. P., Eds. *Silicon Chemistry*; Ellis Horwood: Chichester, U.K., 1988. Sakurai, H., Ed. *Organosilicon and Bio-organosilicon Chemistry*; Ellis Horwood: Chichester, U.K., 1985. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, Germany, 1983.

[2] Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *Organometallics* **1982,** *1,* 884.

[3] Sakakura, T.; Tokunaga, Y.; Sodeyama, T.; Tanaka, M. *Chem. Lett.* **1987,** 2375.

[4] (a) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991,** *10,* 16. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992,** *428,* 1. (c) Reddy, N. P.; Uchimaru, Y.; Lautenschlager, H.-J.; Tanaka, M. *Chem. Lett.* **1992,** 45. (d) Uchimaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992,** *11,* 2639.

[5] Very recently, nickel-catalyzed metathesis of a Si–Si bond of a benzodisilacyclobutene and C–H bonds of arenes was reported. See: Ishikawa, M.; Sakamoto, H.; Okazaki, S.; Naka, A. *J. Organomet. Chem.* **1992,** *439,* 19. Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992,** *11,* 4135.

[6] The platinum complex was synthesized according to Maitlis's method for $Pt(dba)_2$. However, the analytical data for the obtained complex showed that its composition was close to the formula $Pt_2(dba)_3$ rather than $Pt(dba)_2$. Anal. Calcd for $C_{51}H_{42}O_3Pt_2$ ($Pt_2(dba)_3$): C, 56.04; H, 3.87. Found: C, 56.65; H, 3.99. In addition, Maitlis et al. themselves also reported synthesis of $Pt_2(p\text{-}i\text{-}PrC_6H_4CH{=}CHCOCH{=}CHC_6H_4\text{-}p\text{-}i\text{-}Pr)_3$ by a similar method in their later publication. See: Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974,** 169. Keasey, A.; Mann, B. E.; Yates, A.; Maitlis, P. M. *J. Organomet. Chem.* **1978,** *152,* 117.

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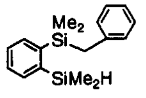
Table I. Platinum-Catalyzed Reactions of Arenes 2 with *o*-Bis(dimethylsilyl)benzene (1)

entry no.	arene **2**	temp, °C	time, h	yield of **3**, %	*o*:*m*:*p* selectivity, %
1	Ph-H (**2a**)	110[a]	84	87	
2	Ph-CH$_3$ (**2b**)	110	24[b]	53	17:55:28
			48	84	18:54:28
3	Ph-Cl (**2c**)	110	24	81	59:30:11
4	Ph-OCH$_3$ (**2d**)	110	8	84	87:10:3

[a] In a sealed tube. [b] Conversion of **1** was 70%.

Chart I



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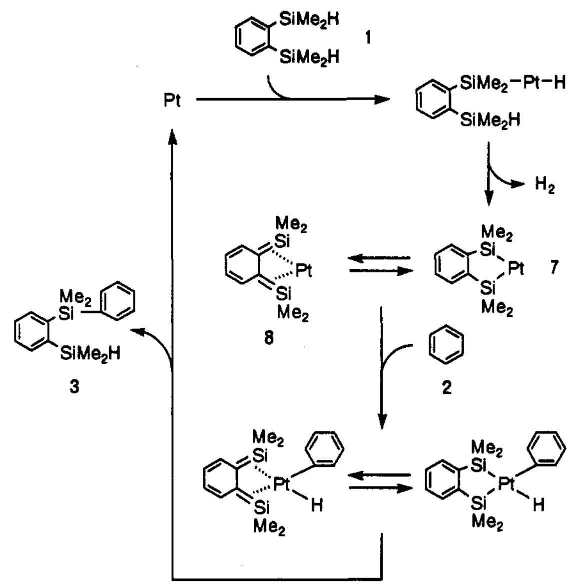
(entries 2–4). The structures of the isomeric arylsilanes were confirmed by comparison of their spectral data and GC retention times with those of authentic samples prepared through different routes. The reaction of toluene (**2b**) gave the meta isomer of **3b** as the major product. The benzylsilane derivative **6**, which could have been formed via C–H bond activation at the methyl group, was not found at all. On the other hand, *o*-**3c** was mainly formed in the reaction of chlorobenzene (**2c**). Preferential reaction at the ortho position was more distinct for anisole (**2d**). It is interesting to note that the RhCl(CO)(PMe$_3$)$_2$-catalyzed reaction of toluene **2b** with triethylsilane under photolytic conditions also gave the meta isomer of tolyltriethylsilane as the major product (*o*:*m*:*p* = 4:58:38).[3] Furthermore, the regioselectivity among isomeric **3**'s is similar to that observed in the C–H bond carbonylation of arenes by the RhCl(CO)(PMe$_3$)$_2$–*hν* system[7] as well as other C–H bond activation processes involving low-valent transition-metal complexes.[8] Accordingly, we believe that a similar C–H bond activation process is involved in the catalytic cycle (vide infra).

Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$ was generally the best catalyst for the dehydrogenative double silylation of acetylenes with **1**.[4a] It proved to be much less active than Pt$_2$(dba)$_3$ in the present reaction of toluene to give only traces of isomeric tolylsilanes **3b**'s in nearly the same selectivity. This may suggest that the precoordination of toluene prior to the C–H bond cleavage (vide infra) is hindered by the coordination of phosphines.

Relative reactivity of arenes was examined in a competitive reaction using a mixture of benzene and a substituted benzene (1:1 mol/mol) with **1** under reflux conditions. The trends were toluene (0.67) < benzene (1.00) < chlorobenzene (1.88) < anisole (2.69), as estimated by the relative ratio of the yields of **3b–d** to that of **3a** (in parentheses).

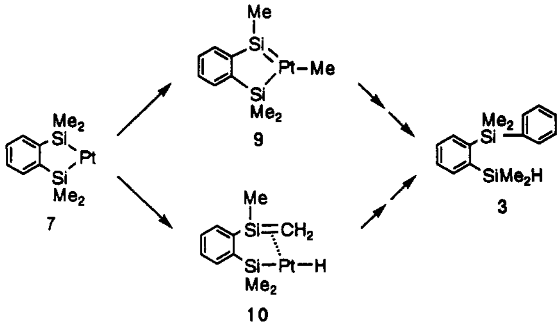
An attempted reaction of phenyldimethylsilane with toluene **2b** at 110 °C for 24 h consumed 72% of the hydrosilane (Pt$_2$(dba)$_3$ catalyst, 2.4% with respect to the platinum atom). However, neither the expected phenyltolyldimethylsilanes nor benzylphenyldimethylsilane was formed. GC and GC–MS analyses showed the formation of diphenylmethylsilane (4%), diphenyldimethylsilane (4%), phenyldimethylsilanol (2%), 1-phenyl-1,1,3,3-tetramethyldisiloxane (1%), and benzene (10%). Unsatisfactory material balance may be due at least partly to the formation of gaseous methylsilanes that were not quantified. What other products were formed is ambiguous at the moment.

Scheme I[a]



[a] Only actively reacting ligands are illustrated in the scheme, with disregard of other incidental ligands that may be bound to platinum.

Scheme II



Reaction Mechanism. The foregoing results can be best explained by the reaction pathways outlined in Scheme I, although some variations are possible (vide infra). On the basis of previous studies on the reactivities of **1**, it appears reasonable to assume the generation of the bis(silyl)platinum species **7**. This species may interact with an arene molecule to somehow end up with the oxidative addition of a C–H bond. Metathetical reaction of the resulting species forms the arylation product and regenerates the active species.

At the moment, the detailed reaction sequence that follows the formation of **7** to cleave the arene C–H bond is ambiguous. One of the possibilities is the direct reaction between an arene and species **7** as such. Another mechanism that involves silylene–platinum species (**9**) formed via α-migration[9] of a methyl group (Scheme II, top) or silene–platinum species (**10**) formed via β-hydride mi-

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(7) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221.

(8) (a) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (c) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73. (d) Lehmkuhl, H.; Bellenbaum, M.; Grundke, J. *J. Organomet. Chem.* **1987**, *330*, C23. (e) Fryzuk, M. D.; MacNeil, P. A.; McManus, N. T. *Organometallics* **1987**, *6*, 882.

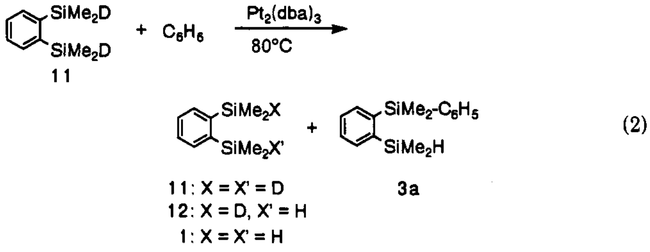
(9) α-Migration has been postulated as a key process behind the catalysis like metal-complex-catalyzed redistribution reactions. See: Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

gration[10] (Scheme II, bottom) also merits consideration. As is widely accepted, Pt(II) and analogous Pd(II) species are capable of C–H bond activation of aromatics.[11] The reaction shows characteristic regioselectivity (so-called *o,p*- or *m*-orientation), depending on the nature of the substituent attached to the aromatic ring. Accordingly, the reaction is believed to be triggered by electrophilic attack of the metal species. However, the regioselectivity of the present reaction does not seem to fit with the electrophilic aromatic substitution. At the moment, however, we cannot totally neglect the mechanism in which platinum(II) species such as **7**, **9**, and **10** attack an arene molecule. On the other hand, an alternative mechanism involving low-valent platinum species such as an (*o*-quinodisilane)platinum(0) complex (**8**) appears more consistent with the observed regioselectivity (vide infra). Species **7** is likely to be in equilibrium with the quinodisilane complex that can be the real species reacting with an arene molecule. Although convincing evidence for the quinodisilane complex is not available, generation of an analogous nickel species has very recently been suggested by Ishikawa and co-workers.[5]

As to the regioselectivity of C–H bond activation, toluene usually exhibits a *m,p*-orientation ($m:p \approx 2:1$) in the reaction with low-valent transition metals, the ortho isomer being formed in a trace quantity.[7,8] According to Jones, the meta isomer is both kinetically and thermodynamically most favorable.[8b] On the other hand, arenes having coordinative substituents such as cyanide and fluorine undergo preferential C–H bond cleavage at the ortho position.[8a] As described in the previous section, this was also the case for the carbonylation reactions of chlorobenzene and anisole promoted by the $RhCl(CO)(PMe_3)_2$–$h\nu$ system.[7] The ortho orientation in these reactions is due to the initial interaction of the metal center with an arene taking place at the substituent. Thence, the C–H bond activation proceeds preferentially at the neighboring ortho position (so-called ortho metalation). The regioselectivity found in the present reaction is in good agreement with the general trends of the C–H bond activation processes by low-valent transition-metal complexes.

The reactivity trends in the competitive reactions of the substituted arenes are also associated with the initial interaction of the arene molecule with the metal complex. The trends indicate that an arene which undergoes preferential reaction at the ortho position reacts faster. η^2-Arene complex formation is suggested to precede the C–H bond activation of arenes such as benzene, toluene, *p*-xylene, and *p*-di-*tert*-butylbenzene.[8b] The present results seem to indicate that the coordination through the lone-pair electrons of chlorobenzene and, to a greater extent, anisole is stronger than the η^2-complexation. Although a detailed kinetic study has not been undertaken, it is likely that the initial interaction through η^2-complexation or coordination through the lone-pair electrons may be the rate-determining step, as is suggested in C–H bond activation reactions of arenes.[8b]

Deuterium Labeling Experiment. To look into the provenance of the Si–H hydrogen of **3**, *o*-bis(deuteriodimethylsilyl)benzene (**11**) was heated in benzene at 80 °C for 24 h (eq 2). The deuterium label was not found in the resulting **3a**. On the other hand, MS analysis of the GC peak corresponding to the unreacted silane revealed that extensive H–D exchange had taken place between the Si–D bond and benzene. When the mixture was further heated for an additional 96 h to lead to completion of the phenylation reaction, **3a** was isolated in 56% yield. ^1H NMR and MS analyses of the isolated sample further confirmed the absence of the deuterium label.



The results described above suggest that the hydrogen of the Si–H bond of **3a** has come from benzene. This is totally consistent with the proposed mechanism. An alternative mechanism that involves prior partial (or total) H–D exchange followed by phenylation at the Si–D (or Si–H) bond can be ruled out in view of **3a** not being contaminated by deuterium throughout the reaction. Another possibility leading to the same results may be phenylation of one of the Si–D bonds of **11** to give HD and **3a**-d_1, followed by H–D exchange between **3a**-d_1 and benzene. However, this reaction sequence appears less likely because of the same reason, and because phenylation of the Si–H bond of phenyldimethylsilane did not work. To gain more convincing evidence against this possibility, we heated **3a** in benzene-d_6 in the presence of $Pt_2(dba)_3$ (2.4% with respect to the platinum atom) at 80 °C for 24 h. GC–MS analysis confirmed no deuterium incorporation in the recovered **3a**, indicative of the lack of H–D exchange.[12]

Reactions in the Presence of Radical Initiators or Inhibitors. Rather high ortho selectivities observed in the arylation of **1** seem to suggest the intervention of silyl radical species. For example, the selectivity of the reaction of the trimethylsilyl radical with toluene was reported to be $\alpha:o:m:p = 0:14:61:25$ (at 145 °C),[13] the ratio being rather similar to the present result. The effects of radical initiators or inhibitors found in the reaction of toluene with **1** are summarized in Table II.

α,α'-Azobis(isobutyronitrile) and di-*tert*-butyl peroxide are capable of generating silyl radicals upon reactions with hydrosilanes.[14] However, the reaction of **1** in the presence of the former (1 equiv with respect to **1**) in place of the platinum complex catalyst did not work at all, and the starting material **1** was recovered quantitatively after heating at 110 °C for 24 h. On the other hand, the reaction with di-*tert*-butyl peroxide at 110 °C for 120 h did give **3b**'s and the isomeric ratio among them was similar to that in the platinum-catalyzed reaction. Although this

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[10] β-Hydride migration to generate silene species has been suggested by several groups. See, for instance: Berry, D. H.; Procopio, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 4099. Procopio, L.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 4039. Zlota, A. A.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1826. Yamashita, H.; Kawamoto, A. M.; Tanaka, M.; Goto, M. *Chem. Lett.* **1990**, 2107.

[11] Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel: Dordrecht, The Netherlands, 1984. Moritani, I.; Fujiwara, Y. *Synthesis* **1973**, 524. Fuchita, Y.; Kawakami, M.; Shimoke, K. *Polyhedron* **1991**, *17*, 2037 and references cited therein.

[12] Compound **3a** (54%), diphenyldimethylsilane (10%), and C_6H_5–CH_3 (33%) were detected by GC and GC–MS analyses.

[13] Bennett, S. W.; Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Organomet. Chem.* **1971**, *28*, 59.

[14] Jackson, R. A. *Adv. Free-Radical Chem.* **1969**, *3*, 231. Sakurai, H.; Hosomi, A. *J. Am. Chem. Soc.* **1971**, *93*, 1709.

Table II. Effect of Radical Initiators or Inhibitors on the Reaction of Toluene (2b) with *o*-Bis(dimethylsilyl)benzene (1)[a]

entry no.	Pt catalyst	additive	amt of additive, mmol	conversn of **1**, %	**3b** yield, % (*o*:*m*:*p*)
1	yes	none		70	53 (17:55:28)
2	no	α,α'-azobis(isobutyronitrile)	0.25	0	0
3	no	di-*tert*-butyl peroxide[b]	0.25	32	0.9 (19:59:22)
4	yes	2,6-di-*tert*-butyl-*p*-cresol	0.025	76	56 (16:55:29)
5	yes	galvinoxyl	0.025	85	51 (18:53:29)

[a] Conditions: **1** (0.25 mmol), toluene (**2b**; 4 mL), $Pt_2(dba)_3$ (0.003 mmol), 110 °C, 24 h. [b] 120 h.

result may support silyl radical species involved in the platinum-catalyzed reaction, the total yield was only 0.9%.[15] Evidence against the radical mechanism, however, came from the platinum-catalyzed reactions in the presence of radical inhibitors such as 2,6-di-*tert*-butyl-*p*-cresol and galvinoxyl (4.1 equiv with respect to the platinum atom); despite the addition of these inhibitors, dramatic changes in the yield and the selectivity were not found.

Trimethylsilyl,[16] triethylsilyl,[17] and triphenylsilyl[18] radicals are known to react with chlorobenzene to give the corresponding chlorosilanes, and the corresponding (chlorophenyl)silanes, simple arylation products, are not formed. The reaction of trimethylsilyl radical with anisole is reported to give phenoxytrimethylsilane.[13] However, the platinum-catalyzed reactions of chlorobenzene and anisole selectively gave simple arylation products. Neither chlorosilane nor phenoxysilane was detected at all. This also serves as evidence against the radical mechanism. Combining all these observations together, we conclude the mechanism involving the reaction of the cyclic bis(silyl)platinum intermediate with an arene C–H bond is most reasonable.

Experimental Section

General Comments. All manipulations were carried out under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a tetramethylsilane standard on a Bruker AC-200 instrument. Infrared spectra were measured neat on a JASCO FT/IR-5000 spectrometer. Mass spectra (EI, 70 eV) were recorded on Shimadzu GC-MS QP-1000 and JEOL JMS-DX303 spectrometers. Distillation of the products and authentic samples was carried out using a Büchi Kugelrohr apparatus fitted with a diagram for correlation between the "setup" temperatures and real temperatures. Solvents were dried by standard techniques and distilled under nitrogen. Other liquid materials were also distilled before use. *o*-Bis(dimethylsilyl)benzene (1),[19] *o*-bis(deuteriodimethylsilyl)benzene (11),[4b] $Pt_2(dba)_3$,[6] and $Pt(CH_2{=}CH_2)(PPh_3)_2$[20] were prepared by literature methods.

Typical Procedure for Catalytic Reactions: Reaction of Benzene (2a) with *o*-Bis(dimethylsilyl)benzene (1). A mixture of 1 (0.25 mmol), $Pt_2(dba)_3$ (0.003 mmol), tetradecane (an internal standard for GLC analysis, 40 μL), and benzene (**2a**; 4 mL) was heated at 110 °C for 120 h. *o*-(Phenyldimethylsilyl)(dimethylsilyl)benzene (**3a**) was isolated by Kugelrohr distillation (130 °C/1.5 Torr) in 86% yield: IR (cm^{-1}) 2166 (Si–H), 1251 (Si–Me); ^{1}H NMR δ 7.6–7.3 (m, 9H, aromatic), 4.51 (septet, J = 3.6 Hz, 1H, SiMe$_2$*H*), 0.61 (s, 6H, SiMe), 0.09 (d, J = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 145.2 (aromatic Si–C), 144.3 (aromatic Si–C), 139.9 (aromatic Si–C), 135.3, 134.5, 134.3 (2C), 128.8, 128.4, 128.0, 127.7 (2C), –0.1 (2C, Si–Me), –2.8 (2C, Si–Me); MS *m/z* 270 (M$^+$, 3), 255 (M$^+$ – Me, 22), 192 (42), 177 (100), 135 (25). Anal. Calcd for $C_{16}H_{22}Si_2$: C, 71.04; H, 8.20. Found: C, 71.02; H, 8.03.

Reaction of Toluene (2b). Using the typical procedure, a regioisomeric mixture of *o*-(tolyldimethylsilyl)(dimethylsilyl)benzenes (**3b**'s) was obtained from the Table I (entry 2) experiment by Kugelrohr distillation (100 °C/0.7 Torr) in 62% combined yield (*o*:*m*:*p* = 18:54:28). Anal. Calcd for $C_{17}H_{24}Si_2$: C, 71.76; H, 8.50. Found: C, 71.75; H, 8.34. The structures of the products were confirmed by the comparison of the ^{1}H and ^{13}C NMR, IR, and GC mass spectra of the mixture with those of authentic samples of all isomers prepared separately.

Authentic Sample of *o*-(*o*-Tolyldimethylsilyl)(dimethylsilyl)benzene (*o*-3b). The CuI-catalyzed reaction of 1 with 2 equiv of $CuCl_2$ in a diethyl ether solution was carried out according to Ishikawa's method.[21] After removal of copper salt by filtration, a crude mixture of ether, 1, *o*-(chlorodimethylsilyl)(dimethylsilyl)benzene (13), *o*-bis(chlorodimethylsilyl)benzene (14), and the cyclic disiloxane 4 (1:13:14:4 = 23:46:15:16, containing 0.19 mmol of 13 in 1 mL) was obtained (solution A) and was used in the next step without further purification. Compound **13**: MS *m/z* 230 (M$^+$ for ^{37}Cl, 2), 229 (6), 228 (M$^+$ for ^{35}Cl, 5), 227 (15), 215 (M$^+$ – Me for ^{37}Cl, 38), 213 (M$^+$ – Me for ^{35}Cl, 100), 197 (10), 177 (23), 175 (10), 161 (6), 135 (25); HRMS calcd for $C_{10}H_{17}Si_2Cl$ (M$^+$) 228.0557, found 228.0523; calcd for $C_9H_{14}Si_2Cl$ (M$^+$ – Me) 213.0323, found 213.0308.

An ether solution of *o*-tolyllithium (6.6 mmol/5 mL) was added to solution A (containing 1.5 mmol of 13 in 8.1 mL of ether) at 0 °C, and the mixture was stirred at room temperature. After 5 h, the GC and GC–MS analyses showed the complete consumption of **13** and the formation of *o*-**3b**. The usual workup of the reaction mixture followed by Kugelrohr distillation (160 °C/1.5 Torr) gave *o*-**3b** in 30% isolated yield based on the amount of **13** charged: IR (cm^{-1}) 2166 (Si–H), 1249 (Si–Me); ^{1}H NMR δ 7.70–7.0 (m, 8H, aromatic), 4.46 (septet, J = 3.6 Hz, 1H, SiMe$_2$*H*), 2.15 (s, 3H, C_6H_4–*Me*), 0.63 (s, 6H, SiMe), 0.02 (d, J = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 145.4 (aromatic Si–C), 144.8 (aromatic Si–C), 143.8 and 137.9 (aromatic Si–C and aromatic *C*–Me), 135.5, 134.7, 134.5, 129.7, 129.3, 128.2, 128.1, 124.9, 23.0 (C_6H_4–*Me*), 0.3 (2C, Si–Me), –2.9 (2C, Si–Me); MS *m/z* 284 (M$^+$, 3), 269 (M$^+$ – Me, 13), 253 (3), 209 (10), 192 (41), 177 (100), 149 (9); HRMS calcd for $C_{17}H_{24}Si_2$ (M$^+$) 284.1417, found 284.1390.

Authentic Sample of *o*-(*m*-Tolyldimethylsilyl)(dimethylsilyl)benzene (*m*-3b). The same procedure as for *o*-**3b** gave 60% yield based on the amount of **13** charged (Kugelrohr distillation, 120 °C/0.5 Torr): IR (cm^{-1}) 2166 (Si–H), 1249 (Si–Me); ^{1}H NMR δ 7.65–7.1 (m, 8H, aromatic), 4.51 (septet, J = 3.6 Hz, 1H, SiMe$_2$*H*), 2.31 (s, 3H, C_6H_4–*Me*), 0.60 (s, 6H, SiMe), 0.10 (d, J = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 145.2 (aromatic Si–C), 144.4 (aromatic Si–C), 139.7 (aromatic Si–C), 136.9 (aromatic *C*–Me), 135.4, 135.0, 134.5, 131.4, 129.6, 128.3, 128.0, 127.6, 21.5 (C_6H_4–*Me*), 0.06 (2C, Si–Me), –2.8 (2C, Si–Me); MS *m/z* 284 (M$^+$, 5), 269 (M$^+$ – Me, 27), 253 (5), 209 (14), 192 (45), 177 (100), 149 (17); HRMS calcd for $C_{17}H_{24}Si_2$ (M$^+$) 284.1417, found 284.1409.

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(15) The benzylsilane derivative 6 and dibenzyl (13 and 190% yields based on the charged di-*tert*-butyl peroxide, respectively), coming from benzyl radical species formed by the reaction of toluene with the initiator, were also detected.

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Authentic Sample of *o*-(*p*-Tolyldimethylsilyl)(dimethylsilyl)benzene (*p*-3b). The same procedure as for *o*-**3b** gave 24% yield based on the amount of **13** charged (Kugelrohr distillation, 145 °C/1.0 Torr): IR (cm^{-1}) 2166 (Si–H), 1249 (Si–Me); ^{1}H NMR δ 7.65–7.1 (m, 8H, aromatic), 4.52 (septet, *J* = 3.6 Hz, 1H, SiMe$_2$*H*), 2.34 (s, 3H, C$_6$H$_4$–*Me*), 0.59 (s, 6H, SiMe), 0.11 (d, *J* = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 145.2 (aromatic Si–C), 144.6 (aromatic Si–C), 138.6 (aromatic Si–C), 136.2 (aromatic *C*–Me), 135.4, 134.5, 134.4 (2C), 128.5 (2C), 128.3 (2C), 128.0, 21.5 (C$_6$H$_4$–*Me*), 0.00 (2C, Si–Me), –2.7 (2C, Si–Me); MS *m/z* 284 (M$^+$, 4), 269 (M$^+$ – Me, 23), 253 (4), 209 (15), 192 (44), 177 (100), 149 (17); HRMS calcd for $C_{17}H_{24}Si_2$ (M$^+$) 284.1417, found 284.1404.

Reaction of Chlorobenzene (2c). Using the typical procedure, a regioisomeric mixture of *o*-[(chlorophenyl)dimethylsilyl]-(dimethylsilyl)benzenes (**3c's**) was obtained from the Table I (entry 3) experiment by Kugelrohr distillation (120 °C/0.4 Torr) in 69% combined yield (*o:m:p* = 60:29:11). Anal. Calcd for $C_{16}H_{21}ClSi_2$: C, 63.02; H, 6.94. Found: C, 63.16; H, 6.89. The structures of the products were confirmed by the comparison of the ^{1}H and ^{13}C NMR, IR, and GC mass spectra of the mixture with those of authentic samples of meta and para isomers prepared separately. *o*-[(*o*-Chlorophenyl)dimethylsilyl](dimethylsilyl)-benzene (*o*-**3c**): ^{1}H NMR δ 7.7–7.15 (m, 8H, aromatic), 4.45 (septet, *J* = 3.6 Hz, 1H, SiMe$_2$*H*), 0.70 (s, 6H, SiMe), 0.10 (d, *J* = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 144.7 (aromatic Si–C), 144.2 (aromatic Si–C), 141.0 (aromatic Si–C), 138.5 (C–Cl), 137.0, 135.0, 134.4, 130.7, 129.2, 128.3, 127.9, 125.8, 0.1 (2C, Si–Me), –2.8 (2C, Si–Me); MS *m/z* 306 (M$^+$ for ^{37}Cl, 1), 304 (M$^+$ for ^{35}Cl, 3), 291 (M$^+$ – Me for ^{37}Cl, 9), 289 (M$^+$ – Me for ^{35}Cl, 22), 269 (M$^+$ – Cl, 16), 195 (47), 192 (48), 177 (100), 135 (11); HRMS calcd for $C_{16}H_{21}ClSi_2$ (M$^+$ for ^{35}Cl) 304.0870, found 304.0868.

Authentic Sample of *o*-[(*m*-Chlorophenyl)dimethylsilyl]-(dimethylsilyl)benzene (*m*-3c). The same procedure as for *o*-**3b** gave 52% yield based on the amount of **13** charged (Kugelrohr distillation, 160 °C/1.1 Torr): IR (cm^{-1}) 2166 (Si–H), 1251 (Si–Me); ^{1}H NMR δ 7.6–7.2 (m, 8H, aromatic), 4.46 (septet, *J* = 3.6 Hz, 1H, SiMe$_2$*H*), 0.60 (s, 6H, SiMe), 0.11 (d, *J* = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 145.2 (aromatic Si–C), 143.2 (aromatic Si–C), 142.9 (aromatic Si–C), 135.3, 134.7, 134.0 (C–Cl), 133.9, 132.2, 129.1, 128.8, 128.6, 128.1, –0.2 (2C, Si–Me), –2.9 (2C, Si–Me); MS *m/z* 306 (M$^+$ for ^{37}Cl, 2), 304 (M$^+$ for ^{37}Cl, 5), 291 (M$^+$ – Me for ^{37}Cl, 6), 289 (M$^+$ – Me for ^{35}Cl, 15), 269 (M$^+$ – Cl, 16), 195 (36), 192 (33), 177 (100), 135 (13); HRMS calcd for $C_{16}H_{21}ClSi_2$ (M$^+$ for ^{35}Cl) 304.0870, found 304.0864.

Authentic Sample of *o*-[(*p*-Chlorophenyl)dimethylsilyl]-(dimethylsilyl)benzene (*p*-3c). The same procedure as for *o*-**3b** gave 75% yield based on the amount of **13** charged (Kugelrohr distillation, 130 °C/0.8 Torr): IR (cm^{-1}) 2166 (Si–H), 1251 (Si–Me); ^{1}H NMR δ 7.6–7.2 (m, 8H, aromatic), 4.47 (septet, *J* = 3.6 Hz, 1H, SiMe$_2$*H*), 0.59 (s, 6H, SiMe), 0.11 (d, *J* = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 145.2 (aromatic Si–C), 143.6 (aromatic Si–C), 138.4 (aromatic Si–C), 135.7 (2C), 135.3, 135.1 (C–Cl), 134.3, 128.5, 128.1, 127.9 (2C), –0.1 (2C, Si–Me), –2.8 (2C, Si–Me); MS *m/z* 306 (M$^+$ for ^{37}Cl, 1), 304 (M$^+$ for ^{35}Cl, 2), 291 (M$^+$ – Me for ^{37}Cl, 5), 289 (M$^+$ – Me for ^{35}Cl, 12), 269 (M$^+$ – Cl, 10), 195 (29), 192 (41), 177 (100), 135 (9); HRMS calcd for $C_{16}H_{21}ClSi_2$ (M$^+$ for ^{35}Cl) 304.0870, found 304.0871.

Reaction of Anisole (2d). Using the typical procedure, a regioisomeric mixture of *o*-[(methoxyphenyl)dimethylsilyl]-(dimethylsilyl)benzenes (**3d's**) was obtained from the Table I (entry 4) experiment by Kugelrohr distillation (110 °C/0.3 Torr) in 72% combined yield (*o:m:p* = 82:13:5). Anal. Calcd for $C_{17}H_{24}OSi_2$: C, 67.93; H, 8.05. Found: C, 68.02; H, 8.06. The structures of the products were confirmed by the comparison of the ^{1}H and ^{13}C NMR, IR, and GC mass spectra of the mixture with those of authentic samples of all isomers prepared separately.

Authentic Sample of *o*-[(*o*-Methoxyphenyl)dimethylsilyl](dimethylsilyl)benzene (*o*-3d). The same procedure as for *o*-**3b** gave 56% yield based on the amount of **13** charged (Kugelrohr distillation, 120 °C/0.7 Torr): IR (cm^{-1}) 2166 (Si–H), 1238 (Si–Me); ^{1}H NMR δ 7.65–7.55 (m, 2H, aromatic), 7.40–7.25 (m, 4H, aromatic), 6.95–6.8 (m, 2H, aromatic), 4.54 (septet, *J* = 3.6 Hz, 1H, SiMe$_2$*H*), 3.65 (s, 3H, OMe), 0.60 (s, 6H, SiMe), 0.14 (d, *J* = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 164.2 (C–O), 145.4 (aromatic Si–C), 144.6 (aromatic Si–C), 136.4, 135.0, 134.2, 130.8, 127.9, 127.8, 127.4 (aromatic Si–C), 120.4, 109.9, 55.0 (OMe), –0.0 (2C, Si–Me), –2.7 (2C, Si–Me); MS *m/z* 300 (M$^+$, 4), 285 (M$^+$ – Me, 25), 255 (8), 253 (12), 192 (50), 177 (100), 165 (10), 135 (34); HRMS calcd for $C_{17}H_{24}OSi_2$ (M$^+$) 300.1366, found 300.1361.

Authentic Sample of *o*-[(*m*-Methoxyphenyl)dimethylsilyl](dimethylsilyl)benzene (*m*-3d). The same procedure as for *o*-**3b** gave 45% yield based on the amount of **13** charged (Kugelrohr distillation, 130 °C/0.5 Torr): IR (cm^{-1}) 2166 (Si–H), 1284 (C–O–C), 1247, 1232 (Si–Me); ^{1}H NMR δ 7.65–7.45 (m, 2H, aromatic), 7.40–7.25 (m, 3H, aromatic), 7.15–7.0 (m, 2H, aromatic), 6.95–6.8 (m, 1H, aromatic), 4.52 (septet, *J* = 3.6 Hz, 1H, SiMe$_2$*H*), 3.78 (s, 3H, OMe), 0.60 (s, 6H, SiMe), 0.12 (d, *J* = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 158.8 (C–O), 145.2 (aromatic Si–C), 144.1 (aromatic Si–C), 141.6 (aromatic Si–C), 135.4, 134.5, 128.8, 128.3, 128.0, 126.7, 119.9, 113.8, 55.0 (OMe), –0.1 (2C, Si–Me), –2.7 (2C, Si–Me); MS *m/z* 300 (M$^+$, 18), 285 (M$^+$ – Me, 21), 255 (8), 253 (13), 192 (36), 177 (100), 165 (19), 135 (13); HRMS calcd for $C_{17}H_{24}OSi_2$ (M$^+$) 300.1366, found 300.1367.

Authentic Sample of *o*-[(*p*-Methoxyphenyl)dimethylsilyl](dimethylsilyl)benzene (*p*-3d). The same procedure as for *o*-**3b** gave 90% yield based on the amount of **13** charged (Kugelrohr distillation, 130 °C/0.4 Torr): IR (cm^{-1}) 2166 (Si–H), 1280 (C–O–C), 1249 (Si–Me); ^{1}H NMR δ 7.65–7.55 (m, 2H, aromatic), 7.45–7.35 (m, 4H, aromatic), 6.95–6.82 (m, 2H, aromatic), 4.53 (septet, *J* = 3.6 Hz, 1H, SiMe$_2$*H*), 3.81 (s, 3H, OMe), 0.60 (s, 6H, SiMe), 0.12 (d, *J* = 3.6 Hz, 6H, Si*Me*$_2$H); ^{13}C NMR δ 160.2 (C–O), 145.1 (aromatic Si–C), 144.7 (aromatic Si–C), 135.8 (2C), 135.6 (aromatic Si–C), 135.3, 134.5, 128.2, 128.0, 113.4 (2C), 55.0 (OMe), 0.1 (2C, Si–Me), –2.7 (2C, Si–Me); MS *m/z* 300 (M$^+$, 3), 285 (M$^+$ – Me, 13), 255 (5), 253 (9), 192 (39), 177 (100), 165 (19), 135 (8); HRMS calcd for $C_{17}H_{24}OSi_2$ (M$^+$) 300.1366, found 300.1364.

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