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Unexpected regioselectivity in the palladium-catalyzed reaction of silacyclobutanes with aryl iodides

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The reaction of aryl iodides with 1,1-diphenylsilacyclobutane in the presence of a catalytic amount of $Pd(PPh_3)_4$ affords unexpected ring-opening adducts, 1- and 2-propenyl(triaryl)silanes, in good yields. On the other hand, the $PdCl_2(PhCN)_2$-catalyzed reaction of 1,1-diphenylsilacyclobutanes with aryl halides gives unexpected products, triarylsilanols, after hydrolysis in moderate yields. The catalysis involves the reaction of aryl–palladium intermediates with silacyclobutanes along with regioselective aryl–silicon bond formation.

Keywords: iodobenzenes; palladium complexes; silacyclobutanes; aryl–silicon bond formation; propenylsilanes; triarylsilanols

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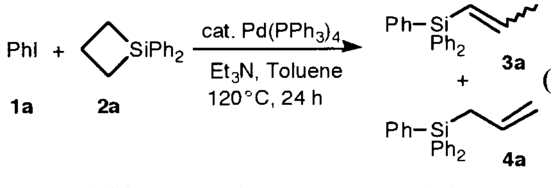
Aryl halides such as iodobenzenes (**1**) are well-known that can react with transition-metal complexes on their carbon–halogen bond to form aryl(halo)metal complexes.[1] We previously reported the palladium-catalyzed reaction of **1** with silacyclobutanes (**2**) under CO atmosphere in the presence of an excess amount of triethylamine to give cyclic silyl enol ethers *via* 3-(iodosilylpropyl)ketone as an intermediate.[2] This reaction was supposed to proceed *via* an acyl(iodo)palladium complex obtained from the CO insertion reaction to the aryl(iodo)palladium complex.[3] Then, acylpalladium complex reacted with **2** to form cyclic silyl enol ethers along with CO–carbon bond formation. We expected that the reaction of aryl(iodo)palladium derived from **1** with silacyclobutane would afford 3-(iodosilyl)propylbenzene derivatives along with aryl–carbon bond formation. However, the reaction gives unexpected products with regioselective aryl–silicon bond formation. In this paper, we wish to report the reaction of **1** with **2** affording two types of product, 1- and 2-propenyl(aryl)silanes (**3** and **4**) and arylsilanols (**5**) depending on the palladium complexes.

A mixture of $Pd(PPh_3)_4$ (0.01 mmol), iodobenzene (**1a**, 0.25 mmol), triethylamine (1 mmol), 1, 1-diphenyl-1-silacyclobutane (**2a**, 0.25 mmol), and dry toluene (0.5 ml) was heated in a sealed glass tube under nitrogen at 120 °C for 24 h. The usual workup followed by gas chromatography (GC) and GC–mass spectrometry (MS) analyses showed that 1- and 2-propenyltriphenylsilane (**3a** and **4a**) were formed in 63% total yield (**3a**/**4a** = 77/23) (Eqn [1]).[4,5] Concentration of the reaction mixture followed by silica gel column chromatography (eluent: hexane/dichloromethane = 4/1 (v/v)) gave a mixture of **3a** and **4a** in 52% total isolated yield.



(1)

In addition to $Pd(PPh_3)_4$, the $PdCl_2(PhCN)_2$–$4PPh_3$ and the $Pd_2(dba)_3$–$8PPh_3$ (dba = dibenzylideneacetone) system also catalyzed the foregoing reaction to give **3a** and **4a** in 31% and 51% total yields respectively. On the other hand, in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ the

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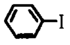
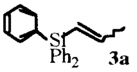
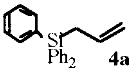
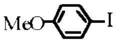
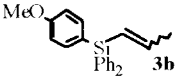
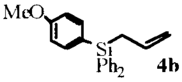
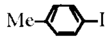
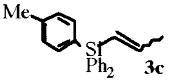
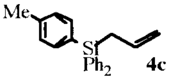
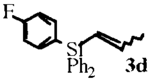
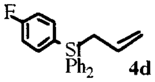
Table 1 Reactions of **1** with **2a** catalyzed by $Pd(PPh_3)_4$[a]

Run	**1**	Product		Yield (%)[b]
1	 **1a**	 **3a**	 **4a**	63 (77:23)
2	 **1b**	 **3b**	 **4b**	53 (22:78)
3	 **1c**	 **3c**	 **4c**	83 (47:53)
4	 **1d**	 **3d**	 **4d**	95 (4:96)

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), Et_3N (1.0 mmol), $Pd(PPh_3)_4$ (0.01 mmol), toluene (0.5 ml), 120 °C, 24 h.
[b] Determined by GC. Figures in parentheses are ratios of **3**:**4** (estimated by ^1H NMR).

reaction gave a complex mixture. Thus, the reaction proceeds smoothly in the presence of four equivalents of triphenylphosphine towards the palladium complex in order to afford compounds **3a** and **4a**.

The effects of amines were examined using $Pd(PPh_3)_4$. In both the absence and presence of a catalytic amount of the amines, **1a** did not react with **2** at all, and the formation of a black precipitate was observed.

Selected results are summarized in Table 1. In the presence of triethylamine and $Pd(PPh_3)_4$, aryl iodides **1a–d** reacted with **2a** to give 1- and 2-propenyl(aryl)silanes (**3a–d** and **4a–d**)[6] in good yields. In contrast, bromobenzenes and alkyl iodides such as *n*-hexyl and cyclohexyl iodide did not react with **2** owing to their low reactivity with the palladium complex.

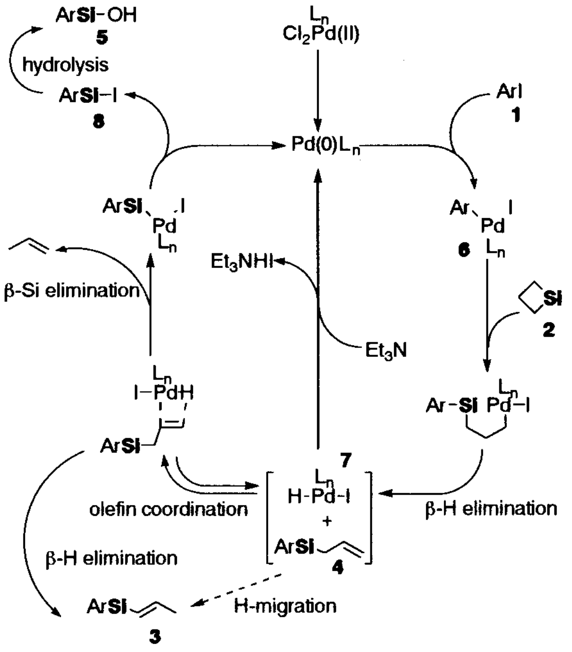
1,1-Dimethyl-1-silacyclobutane (**2b**) also reacted with **2a** under identical conditions to give 1- and 2-propenyldimethylphenylsilanes **3a′** and **4a′** in 16% total yield (**3a′**/**4a′** = 50/50). However, 1,1-dimethyl-1-silacyclopentane and 1,1-dimethyl-1-silacyclohexane did not react with **1a**, presumably because of their nearly strain-free ring system.[7]

On the other hand, a similar reaction of **1a** with **2a** in the presence of $PdCl_2(PhCN)_2$ gave another unexpected product, triphenylsilanol (**5a**),[8] in 78% GC yield after hydrolysis (Eqn [2]). In addition, free-phosphine palladium complexes, $Pd_2(dba)_3$ and $PdCl_2$, also catalyze the reaction to afford **5a** in 10% and 23% yields respectively. Using $PdCl_2(PEt_3)_2$ and $PdCl_2(dppb)$ also gave **5a** in 4% and 8% yields respectively, owing to their low reactivity for the reaction derived from their strong coordinate ligands.

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\substack{\text{Et}_3\text{N, Toluene} \\ 120\,^\circ\text{C, 24 h}}]{\text{cat. PdCl}_2\text{(PhCN)}_2} \xrightarrow{\text{H}_2\text{O}} \underset{\mathbf{5a}}{\text{Ph}_3\text{Si–OH}} \quad (2)$$

In contrast, bromobenzene did not react with **2a** owing to its low reactivity to the palladium complex, but *p*-bromobenzonitrile, which involves an electron-withdrawing group, showed a slight response to this reaction, although the yield was very low.

To consider the reaction mechanism, a mixture of **1c** (0.125 mmol), **2a** (0.125 mmol), and C_6D_6 (0.25 ml) were added to a stoichiometric amount of $Pd(PPh_3)_4$ (0.125 mmol) in a sealed NMR tube. Monitoring of the reaction by ^1H NMR revealed that most of the **1c** was consumed at 120 °C for 24 h, whereas **2a** remained intact. With regard to the formation mechanism of **3** and **4**, therefore, an



Scheme 1

aryl(iodo)palladium species (**6**) should be formed as an intermediate in the present reaction.

A possible mechanism for this reaction is shown in Scheme 1. First, an iodo(aryl)palladium species **6**[1] is formed in the reaction of **1** with *in situ* generated palladium(0) complex, then intermediate **6** would react with **2** followed by β-elimination to provide compound **4** and a hydride(iodo)palladium complex (**7**). Furthermore, a reaction of **4** with **7** followed by β-silyl group elimination[9] gives arylsilyl iodide (**8**) and propene. Finally, silanol **5** is formed by hydrolysis of silyl iodide **8**. In practice, using methanol instead of water for the treatment of the reaction gave aryl(methoxy)silane (**9**)[10] in a 50% isolated yield (Eqn [3]). To confirm this hypothesis, the propene generated was trapped by bromine to give 1,2-dibromopropane.[11]

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\substack{\mathrm{Et_3N,\ Toluene} \\ 120\,^\circ\mathrm{C,\ 24\ h}}]{\mathrm{cat.\ PdCl_2(PhCN)_2}} \xrightarrow{\mathrm{MeOH}} \underset{\mathbf{9}}{\mathrm{Ph_3Si{-}OMe}} \qquad (3)$$

In conclusion, the reaction of aryl iodides with silacyclobutanes affords two classes of compounds, 1- and 2-propenyl(aryl)silanes and arylsilanols, depending on the palladium catalysts, with unexpected aryl–silicon bond formation. In this catalysis, the presence of triphenylphosphine determines the kind of product.

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3. Collman JP, Hegedus LS, Norton JR, Fink RG. *Principles and Applications of Organotransition Metal Chemistry*, 2nd edn. University Science Books, Mill Valley, CA, 1987; 720.
4. These ratios of **3a**/**4a** were determined based on integration of the CH_3 ^1H NMR signals of **3a** and CH_2 ^1H NMR signals of **4a**.
5. Compounds **3a** and **4a** showed satisfactory ^1H and ^{13}C NMR and MS data. **3a**: ^1H NMR ($CDCl_3$) δ 1.93 (d, $J = 4.3$ Hz, 3H, $SiCH{=}CHCH_3$), 6.04–6.85 (several peaks for vinyl group could not be assigned), 7.33–7.57 (m, 15H, Ar); ^{13}C NMR ($CDCl_3$) δ 22.95, 125.10, 127.77, 129.38, 134.96, 135.92, 148.33; GC–MS *m/z* (relative intensity) 300 (25, *M*), 285 (42), 259 (25), 222 (62), 207 (49), 181 (100), 105 (82), 79 (20), 43 (66). **4a**: ^1H NMR δ 1.92 (d, $J = 4.3$ Hz, 3H, $SiCH{=}CHCH_3$), 2.36 (s, 3H, $CH_3C_6H_5Si$), 6.16–6.83 (several peaks for vinyl group could not be assigned), 7.17–7.61 (m, 14H, Ar); ^{13}C NMR ($CDCl_3$) δ 21.54, 22.95, 125.28, 127.73, 127.76, 127.80, 128.64, 129.29, 129.38, 135.89, 135.96, 148.11; GC–MS *m/z* (relative intensity) 314 (64, *M*), 299 (80), 273 (45), 236 (53), 221 (59), 197 (100), 181 (76), 165 (30), 119 (22), 105 (73), 53 (29).
6. Compounds **3b–d** and **4b–d** showed satisfactory ^1H and ^{13}C NMR and MS data.
7. The strain energies of silacyclobutane, silacyclopentane, and silacyclohexane are 102.5 kJ mol^{-1}, 20.1 kJ mol^{-1}, and 13.0 kJ mol^{-1} respectively. See: Gordon MS, Boatz JA, Walsh R. *J. Phys. Chem.* 1989; **93**: 1584.
8. A mixture of $PdCl_2(PhCN)_2$ (0.01 mmol), iodobenzene (**1a**, 0.25 mmol), triethylamine (1 mmol), 1,1-diphenyl-1-silacyclobutane (**2a**, 0.25 mmol), and dry toluene (0.5 ml) was heated in a sealed glass tube under nitrogen at 120 °C for 24 h. Usual workup followed by GC and GC–MS analyses showed that triphenylsilanol (**5a**) was formed in 78% yield. Recrystallization from diethyl ether gave nearly pure **5a** in 65% isolated yield. Compound **5a** showed satisfactory ^1H and ^{13}C NMR and MS data. **5a**: ^1H NMR ($CDCl_3$) δ 1.83 (s, 1H, SiOH), 7.22–8.01 (m, 15H, Ar); ^{13}C NMR ($CDCl_3$) δ 127.67, 127.91, 129.77, 130.11, 134.96, 135.16; GC–MS *m/z* (relative intensity) 276 (43, *M*), 199 (100), 122 (28), 77 (33), 45 (37).
9. (a) Marciniec B, Gulinski J. *J. Organomet. Chem.* 1984; **266**: C19; (b) Seki Y, Takeshita K, Kawamoto K. *J. Organomet. Chem.* 1989; **369**: 117; (c) Wakatsuki Y, Yamazaki H, Nakano M, Yamamoto Y. *J. Chem. Soc.*

Chem. Commun. 1991; 703; (d) Kakuuchi F, Yamada A, Chatani N, Murai S. *Organometallics* 1999; **18**: 2033 and references cited therein.

10. Compound **9** showed satisfactory ^{1}H and ^{13}C NMR and MS data. **9**: ^{1}H NMR ($CDCl_3$) δ 3.69 (s, 3H, $SiOCH_3$), 7.42–7.76 (m, 15H, Ar); ^{13}C NMR ($CDCl_3$) δ 51.85, 127.95, 129.65, 130.04, 135.36; GC–MS *m/z* (relative intensity) 290 (39, *M*), 243 (100), 183 (70), 136 (61), 105 (30), 59 (37).
11. During the catalytic reaction, nitrogen gas was passed slowly into the reaction mixture and the gases introduced into a solution of Br_2 in CCl_4. ^{1}H NMR and GC–MS analysis showed the formation of 1,2-dibromopropane.