

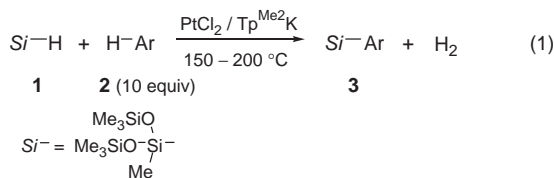
## Platinum-catalyzed Aromatic C–H Silylation of Arenes with 1,1,1,3,5,5,5-Heptamethyltrisiloxane

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The intermolecular dehydrogenative coupling of 1,1,1,3,5,5,5-heptamethyltrisiloxane with arenes proceeded in the presence of a catalytic amount of platinum complexes prepared in situ from  $\text{PtCl}_2$  and hydrotris(pyrazolyl)borate derivatives.

The versatility of arylsilanes in modern organic chemistry renders them attractive targets for synthesis. For example, the palladium-catalyzed Hiyama cross-coupling reaction of aryl-(alkoxy)silanes has become a powerful method for carbon–carbon bond formation.<sup>1</sup> Aryl(alkoxy)silanes can be easily prepared by the transition-metal-catalyzed silylation of aryl halides with hydrosilanes, such as triethoxysilane<sup>2</sup> and 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1**).<sup>3</sup> Clearly, from environmental and economical points of view, direct silylation of aromatic C–H bonds of arenes **2** is a more attractive goal. Therefore, much attention has been focused on the C–H silylation of aromatic hydrocarbons **2** using hydrosilanes as a silicon source, and numerous catalyst systems, such as  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ,<sup>4</sup>  $\text{Pt}(\text{dba})_2$ ,<sup>5</sup>  $\text{Tp}^{\text{Me}_2}\text{Pt}(\text{Me})_2(\text{H})$  ( $\text{Tp}^{\text{Me}_2}$  = hydrotris(3,5-dimethylpyrazolyl)-borate),<sup>6</sup>  $\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiEt}_3)_2$ ,<sup>7</sup> and  $\text{Ru}_3(\text{CO})_{12}$ ,<sup>8</sup> have been reported to affect this dehydrogenative coupling reaction. Above all, the platinum complexes are highly efficient catalysts for the hydrogen-acceptor-free processes; however, the silylating reagents were restricted to triorganosilanes.<sup>5,6</sup> Tetraorganosilicon reagents thus obtained are less reactive for the Hiyama cross-coupling reaction, mainly because electronegative groups, such as halogen and alkoxy group, on the silicon atom are required for the formation of penta-coordinated silicate intermediates.<sup>1</sup> Consequently, we have sought an alternative silylating reagent which provided reactive arylsilanes;<sup>9,10</sup> in this paper, wish to report a platinum-catalyzed C–H silylation of arenes **2** with 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1**; Eq 1).<sup>11</sup>



An initial screen was performed using platinum precursors and additional (pyrazolyl)borate ligands for the dehydrogenative coupling of benzene (**2a**) and **1**. These salts are commercially available and can be easily handled in air. The results are summarized in Table 1. This coupling work was achieved with the aid of the  $\text{Tp}$  ligand; i.e., treatment of **1** (1 equiv.) with **2a** (10 equiv.) in the presence of 3 mol % of a metal complex prepared in situ from  $\text{PtCl}_2$  and potassium hydrotris(pyrazolyl)borate ( $\text{TpK}$ ) at  $150^\circ\text{C}$  was found to lead to the corresponding phenyltrisiloxane **3a** in 80% yield (Entries 1 and 2). Under the conditions using an excess amount of **2a**, the formation of disilylated

**Table 1.** C–H silylation of benzene (**2a**) with hydrosilanes<sup>a</sup>

Entry	Hydrosilane	Ligand	Yield/% <sup>b</sup>
1	<b>1</b>	none	0
2	<b>1</b>	$\text{TpK}$	80
3	<b>1</b>	$\text{BpK}$	35
4	<b>1</b>	$\text{Tp}^{\text{Me}_2}\text{K}$	93
5 <sup>c</sup>	<b>1</b>	$\text{Tp}^{\text{Me}_2}\text{K}$	91
6	$(\text{Me}_3\text{SiO})\text{Me}_2\text{SiH}$	$\text{Tp}^{\text{Me}_2}\text{K}$	46 <sup>d</sup>
7	$\text{Et}_3\text{SiH}$	$\text{Tp}^{\text{Me}_2}\text{K}$	37 <sup>e</sup>

<sup>a</sup>Reaction conditions: **1** (0.5 mmol), **2a** (5 mmol),  $\text{PtCl}_2$  (0.015 mmol), ligand (0.015 mmol),  $150^\circ\text{C}$ , 24 h. <sup>b</sup>GC yields of **3a** are based on **1**. <sup>c</sup>The reaction was carried out at  $200^\circ\text{C}$  using  $\text{PtCl}_2$  (0.005 mmol) and  $\text{Tp}^{\text{Me}_2}\text{K}$  (0.005 mmol). <sup>d</sup>GC yield of  $(\text{Me}_3\text{SiO})\text{Me}_2\text{SiPh}$ . <sup>e</sup>GC yield of  $\text{Et}_3\text{SiPh}$ .

products was completely suppressed. Although dihydrido-bis(pyrazolyl)borate ( $\text{Bp}$ ) was less efficient than  $\text{Tp}$  as supporting ligands under the same conditions (Entry 3), the use of  $\text{Tp}^{\text{Me}_2}\text{K}$  showed improved reactivity, providing a 93% yield of **3a** (Entry 4). The present reaction system is similar to but more mild than the previously reported  $\text{Tp}^{\text{Me}_2}\text{Pt}(\text{Me})_2(\text{H})$ -catalyzed C–H silylation.<sup>6</sup> Additionally, it is noteworthy that this silylation was catalyzed by 1 mol % of the catalyst although the elevated temperature was required (Entry 5). Under our optimized conditions, the use of 1,1,1,3,3-pentamethyldisiloxane and triethylsilane induced a lowering of the reactivity (Entries 6 and 7). The present study demonstrates that **1** is an efficient silylating reagent for the aromatic C–H silylation.

The results obtained with representative arenes **2**, giving aryltrisiloxanes **3** similarly as above, are listed in Table 2.<sup>12</sup> The yields and product ratios were determined by GC analysis of crude reaction mixtures. The reaction of mono-substituted arenes, such as trifluoromethylbenzene (**2b**), toluene (**2c**), and chlorobenzene (**2d**), resulted in a mixture of meta and para regioisomers and electronic characteristics of the substituent on **2** hardly affected the meta/para ratios (Entries 1–3). Electron-deficient arene **2b** were more reactive than **2a**.<sup>13</sup> In these cases, the formation of ortho isomers was completely suppressed, whereas the reported platinum-catalyzed silylation of **2c** and **2d** generated ortho isomers.<sup>5,6</sup> In the reaction of anisole (**2e**), however, the product contained all regioisomers (Entry 4).<sup>5</sup> Being consistent with these results, disubstituted arenes **2f–2h** were silylated regioselectively for steric reasons (Entries 5–7).<sup>6,7</sup> In addition, the silylation of 1,4-difluorobenzene (**2i**) occurred exclusively at the 2-position (Entry 8). Unfortunately, all attempts at the C–H silylation of aniline and phenol were unsuccessful.

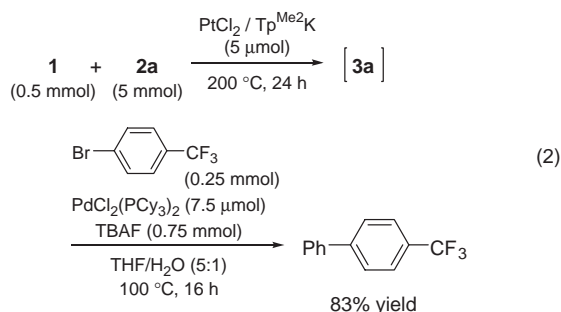
Finally, the potential versatility of the present silylation was demonstrated by the one-pot synthesis of unsymmetrical biaryls, as we have reported that isolated 3-aryl-1,1,1,3,5,5,5-hepta-

**Table 2.** Isomer distributions for C–H silylation<sup>a</sup>

Entry	Product <b>3</b>	Yield/% (o:m:p) <sup>b</sup>
1 <sup>c</sup>		72 (0:68:32)
2		62 (0:71:29)
3		45 <sup>d</sup> (0:75:25)
4		35 (14:57:28)
5		75
6		63
7		52
8		77

<sup>a</sup>Reaction conditions: **1** (0.5 mmol), **2** (5 mmol), catalyst (0.015 mmol), 200 °C, 24 h. <sup>b</sup>Yield and isomer ratio were determined by GC analysis. <sup>c</sup>At 150 °C. <sup>d</sup>A trace amount of **3a** (≈4%) was also obtained.

methyltrisiloxanes **3** participated in the palladium-catalyzed Hiyama cross-coupling.<sup>3</sup> Thus, the silylation of benzene (**2a**) (20 equiv.) with **1** (2.0 equiv.) followed by removal of the volatile materials gave the crude product **3a**, which coupled with 4-bromo- $\alpha,\alpha,\alpha$ -trifluorotoluene (1.0 equiv.) in the presence of  $\text{PdCl}_2(\text{PCy}_3)_2$  and TBAF to give the corresponding biaryl in 83% total yield (Eq 2).



In conclusion, 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1**) was found to promote the platinum-catalyzed intermolecular dehydrogenative coupling with arenes **2**. Since arylsiloxanes **3** thus obtained exhibited good reactivity for converting the silicon functionality, the present aromatic C–H silylation may be useful in the field of synthetic organic chemistry. Further investigations of this and related transition-metal-catalyzed C–H functionalizations are currently underway in our laboratory.

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- 1,1,1,3,5,5,5-Heptamethyltrisiloxane (**1**) is commercially available.
- General procedure for the aromatic C–H silylation:  $\text{PtCl}_2$  (15  $\mu\text{mol}$ ) and  $\text{Tp}^{\text{Me}_2\text{K}}$  (15  $\mu\text{mol}$ ) were placed in a resealable Schlenk tube. The tube was evacuated and backfilled with nitrogen and then charged with the arene **2** (5 mmol). After being stirred at room temperature for 1 h, 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1**; 0.50 mmol) was added. The reaction mixture was then stirred at 200 °C for 24 h. After the reaction, the mixture was analyzed by GC and GC-MS. The volatile material was removed in vacuo, and the residue was purified by Kugelrohr distillation to afford the desired 3-aryl-1,1,1,3,5,5,5-heptamethyltrisiloxane **3**.
- Relative product ratios from the reactions in equimolar mixtures of benzene (**2a**) and substituted arenes **2b**, **2c**, and **2e** were 1:1.33, 1:0.61, and 1:0.40, respectively.