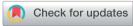
### Chemical Science



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# Intermolecular C-H silylations of arenes and heteroarenes with mono-, bis-, and tris(trimethylsiloxy)hydrosilanes: control of silane redistribution under operationally diverse approaches†

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Efficient catalytic protocols for C–H silylations of arenes and heteroarenes with sterically and electronically different hydrosiloxysilanes are disclosed. The silylations are catalyzed by a well-defined Rh-complex (1 mol%), derived from [Rh(1,5-hexadiene)Cl]<sub>2</sub> and a bulky BINAP type ligand. This catalyst not only promotes C–Si bond formation affording the desired products in up to 95% isolated yield, but also can suppress the silane redistribution side reactions of HSiMe<sub>2</sub>(OTMS). The protocol can also be applied for the C–H silylations of more reactive HSiMe(OTMS)<sub>2</sub> with a much lower catalyst loading (0.25 mol%) and even with sterically demanding HSi(OTMS)<sub>3</sub>. The steric bulk of the arene substituent and hydrosiloxysilane is a major factor in determining the regioselectivity and electronic effect as secondary. The current method can be performed under operationally diverse conditions: with/without a hydrogen scavenger or solvent.

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#### Introduction

The siloxysilane framework is widely used in the syntheses of polysiloxane-based silicone materials.¹ Due to their unique properties and versatility, polysiloxanes are used in many different applications, ranging from common consumer products (baby bottles, toys, shampoo, detergents) to high-tech products (electronics, automotives, aero- or spacecraft).² Their high biocompatibility and durability in the human body further expand the importance and utility of silicone materials in biomedical science and engineering.¹a,²b,e</sup> In order to prepare such polysiloxane materials, various functional groups are required in the polymer matrix; many functional alkyl groups can be readily incorporated by other organic transformations including hydrosilylations.³ For aryl substituents, however, only the phenyl group has been heavily employed due to the lack of a reliable synthetic method. Although there are some

C-H silylation is one of the most direct and atom-economical pathways to incorporate such functional aryl groups.<sup>6-9</sup> Though there are many reports on C-H silylation reactions, most of the catalytic systems either require a pre-engineered directing group in the arenes,<sup>6</sup> or involve a more reactive but less useful trialkyl- or phenylsilane reagent,<sup>7,8</sup> or have limited hydrosiloxysilane scope [only highly reactive HSiMe(OTMS)<sub>2</sub>].<sup>9</sup> Considering the dynamic structural framework of numerous silicone materials that contain simple and/or complex –(OSiMe<sub>2</sub>)<sub>n</sub>– units, structurally diverse hydrosiloxysilanes are needed for C-H silylations with various arenes and heteroarenes.

Here, we report operationally diverse synthetic methods to access functional aryl- and heteroaryl siloxysilanes by intermolecular C–H silylations of mono-, bis-, or tris(trimethylsiloxy) hydrosilanes with various arenes and heteroarenes. In the

traditional methods to form aryl–Si bonds including reactions between aryl Grignard or aryl lithium reagents and chlorosiloxysilanes, the arene scope is significantly limited due to their intrinsic incompatibility with electrophilic functional groups in the aryl groups. Furthermore, such methods are not welcome in industrial scale production because of the use of non-recyclable ethereal solvents and considerable amount of magnesium- or lithium salt waste at the end. Thus, to improve the physical and chemical properties of silicone materials, more reliable synthetic routes are needed to incorporate various aryl groups into the siloxane framework.

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presence of 0.25-1 mol% catalyst, C-H silylations can be performed under neat conditions with low/moderate concentration of arenes, or under solvent conditions. Development of a welldefined catalyst led us to successfully control redistribution of a hydrosiloxysilane, resulting in the desired products in up to 95% isolated yield. The efficiency of the silylation can be further improved by portion-wise addition of hydrosiloxysilanes. In addition, the current protocols can be applied for double C-H silylation or carried out without alkene as a hydrogen scavenger.

#### Results and discussion

We initiated our study by optimizing the C-H silvlation between benzene and the mono(siloxy)hydrosilane, HSiMe<sub>2</sub>(OTMS), as the initial arene and silane (Table 1). In the presence of [Rh(1,5hexadiene)Cl]2 and a bidentate phosphine ligand (L1), the desired product P1 was not observed. Instead, a significant amount of silane redistribution byproduct was obtained (54%). With L2, we started to obtain P1 (72% conv. and 55% isolated yield, entry 2) together with the undesired redistribution byproduct (28%). When BINAP ligand (L3) was employed, the silylation was less efficient (44% conv., entry 3). With a bulkier BINAP (L4), however, the conversion was significantly increased (74% conv. and 57% yield, entry 4) without improvement in the redistribution (26%). Although a few different Rh salts were tested for the silvlations, the similar silane redistribution (19-26%) and silvlation efficiencies were observed (74-81% conversions, entries 5-7).10 A cationic Rh salt, on the other hand, increased the redistribution (52%, entry 8).

To improve the efficiency of the C-H silvlations and to suppress the competing silane redistribution,11 several preformed complexes were prepared with L4. As shown in Table 2, C1 derived from [Rh(nbd)<sub>2</sub>Cl]<sub>2</sub> slightly decreased the conversion

Table 2 Preformed complexes in C-H silylations<sup>a</sup>

Entry [Rh]/L		Preformed catalyst	Si- Conv. redistribution	
1	[Rh(nbd)Cl] <sub>2</sub> /L4	C1	79% 21%	
2	$[Rh(coe)_2Cl]_2/L4$	C2	78% 22%	
3	[Rh(ethylene) <sub>2</sub> Cl] <sub>2</sub> /L4	C3	82% 18%	
4	[Rh(1,5-hexadiene)Cl] <sub>2</sub> /	C4	93% 7%	
	L4			

<sup>&</sup>lt;sup>a</sup> All reactions were performed under N<sub>2</sub>. Conversions were determined by <sup>1</sup>H NMR analysis.

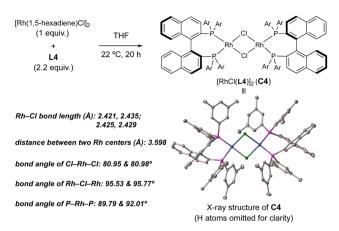
to the desired product (79% conv., entry 1). Compared to in situ reactions (entries 6 and 7, Table 1), the corresponding preformed complexes (C2 and C3) marginally improved the efficiency of the silylation (78% and 82% conversions, entries 2 and 3, Table 2). The complex C4, however, was much more efficient in delivering the desired silvlation product (93% conv., entry 4) with a significantly lower silane redistribution (7% vs. 26% in entry 4, Table 1). This increased conversion to the desired product P1 might be explained either by the improved efficiency of C4 toward the silvlation, or by suppressing the silane redistribution by C4.

Although hydrosiloxysilanes are generally known as a class of reactive hydrosilanes with stable Si-O-Si bonds,3 we have observed silane redistribution in our studies. In order to further understand the reactivity difference between in situ-formed

Table 1 Optimisation of C-H silylation<sup>a</sup>

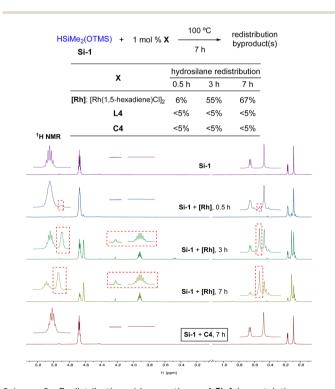
Entry	[Rh]	Ligar	nd [Rh] loading	Conv.; yield	Si-redistribution
1	[Rh(1,5-hexadiene)Cl] <sub>2</sub>	L1	1 mol%	<5%; -	54%
2	$[Rh(1,5-hexadiene)Cl]_2$	L2	1 mol%	72%; 55%	28%
3	[Rh(1,5-hexadiene)Cl] <sub>2</sub>	L3	1 mol%	44%; -	18%
4	[Rh(1,5-hexadiene)Cl] <sub>2</sub>	L4	1 mol%	74%; 57%	26%
5	[Rh(nbd)Cl] <sub>2</sub>	L4	1 mol%	81%; 53%	19%
6	$[Rh(coe)_2Cl]_2$	L4	1 mol%	74%; 55%	26%
7	[Rh(ethylene) <sub>2</sub> Cl] <sub>2</sub>	L4	1 mol%	77%; 64%	23%
8	$Rh(nbd)_2BF_4$	L4	2 mol%	48%; -	52%
		Et Et Et	\	PR <sub>2</sub> PR <sub>2</sub> yl-Ph (S)	

<sup>&</sup>lt;sup>a</sup> All reactions were performed under N<sub>2</sub>. Conversions were determined by <sup>1</sup>H NMR analysis.



Scheme 1 Synthesis of a well-defined Rh-complex C4 and its X-ray structure.

catalysts and preformed complexes (Tables 1 and 2), we decided to study the redistribution tendency of each component of the catalysts. First, like other preformed complexes used in Table 2 (C1–C3), we have synthesized C4 from [Rh(1,5-hexadiene)Cl]<sub>2</sub> and L4 in THF at 22 °C (Scheme 1). X-ray crystallography revealed that the complex was obtained in a dimeric form. Bond lengths of Rh and bridging Cl atoms are between 2.42 and 2.43 Å and the distance between two Rh centres is 3.60 Å. The bond angles of Cl–Rh–Cl and Rh–Cl–Rh are 81° and 96°, respectively.



Scheme 2 Redistribution side-reactions of Si-1 by catalytic components. The intensity of peaks between 3.2 and 5.2 ppm was manually increased for clarity (vs. peaks between 0 and 1.0 ppm). For unprocessed  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra, see the ESI.†

With C4, we investigated the redistribution tendencies of each catalytic component. As depicted in Scheme 2, the hydrosilane Si-1 alone does not undergo the redistribution at 100 °C for 7 h. When 1 mol% of [Rh(1,5-hexadiene)Cl]<sub>2</sub> was added to Si-1, however, the redistribution byproduct started to appear in <sup>1</sup>H NMR after 0.5 h (6%). A significant amount of the byproduct was observed in 3 h (55%), but during the next 4 hours the redistribution byproduct was slightly increased (67% after 7 h). On the other hand, the Lewis-basic phosphine L4 did not cause the side reaction. When the preformed complex C4 was subjected to Si-1, negligible amount of the redistribution byproduct was observed by <sup>1</sup>H NMR (<5%). The similar trend of the silane redistribution was also seen in <sup>29</sup>Si NMR spectroscopy analysis.10 This finding may partially explain the much lower redistribution with C4 (7%, entry 4 in Table 2), compared to 26% redistribution by the in situ protocol (entry 4, Table 1). Furthermore, this indicates that by using the well-defined catalyst (C4), the redistribution side reaction can be significantly suppressed. The different redistribution tendencies of [Rh(1,5-hexadiene)Cl]<sub>2</sub> and C4 may be explained by the steric and electronic effects; the less sterically hindered and more Lewis acidic [Rh(1,5-hexadiene)Cl]<sub>2</sub> can readily interact with Si-1, compared to C4 with the electron-rich and bulky ligand. The observed minimal redistribution (7%, entry 4 in Table 2) might result from the interaction of Si-1 with other active catalytic species in the C-H silylation process.

With the well-defined complex **C4**, we set out to investigate the C-H silylation of mono(siloxy)hydrosilane (**Si-1**). As shown in Scheme 3, benzene and naphthalene undergo the silylations

**Scheme 3** C-H silylations of arenes and heteroarenes with mono(siloxy)silane.

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to afford the desired products **P1** and **P2** in 71% and 41% of isolated yield, respectively. Electron-rich anisole and sterically hindered t-butylbenzene are effective substrates for the silylation (**P3**, 57% conv. and **P4**, 59% conv.). Halogen-containing arenes are also compatible with the catalytic system (**P5** and **P6**). For substituted arenes, o-silylation products are generally obtained as major products (**P3–P6**) except **P4** in which m-silylation is dominant due to the steric bulk of the t-butyl group. The silylations of heteroarenes are efficient to furnish desired products in up to 71% yield (**P7–P12**) where  $\alpha$ -silylation products are major regioisomers. Chelating thiofuran (**P10**) and benzothiophene<sup>10</sup> were relatively less effective (41% yield and 36% yield, respectively).

Next, the current protocol was tested for the silylation of bis(siloxy)silane **Si-2** (Scheme 4). It is noteworthy that **Si-2** is generally much more reactive in the C–H silylation than **Si-1** with no silane redistribution. Thus, 0.25 mol% of **C4** is sufficient to catalyse the C–H silylation to afford the desired product at an even lower reaction temperature (80 °C, Scheme 4 vs. 100 °C for **Si-1** in Scheme 3). The silylations of benzene, polyarene, anisole, and halogen-containing arenes proceeded efficiently to afford the desired products in up to 95% isolated yield (**P13–P18**). For the substituted arenes, *o*-silylation products were still the major products (**P15–P18**), but the ratio of *m*-silylation products were slightly increased, compared to **P3–P6** shown in Scheme 3. This difference may be attributed to the steric bulkiness of **Si-2** (vs. **Si-1**). Electronically activated heteroarenes are generally more effective in this C–H silylation,

Scheme 4 C-H silylation of arenes and heteroarenes with bis(siloxy) silane.

furnishing the silylation products in 80–92% conversions. The high reactivity of **Si-2** was also evidenced in the product distribution of heteroarene silylations; more and/or diverse double C-H silylation products are obtained (**P19–P21**). Fused heteroarenes were equally reactive toward the silylation, so that **P22** and **P23** were isolated in 66% and 88% yields, respectively. As aforementioned, sulfur-containing arenes are less reactive, delivering **P24** in moderate yields (44% yield, Scheme 4).

The present protocol was further expanded toward the silylation of a sterically demanding tris(siloxy)hydrosilane Si-3. As shown in Scheme 5, the silvlations of Si-3 require a relatively high catalyst loading (1 mol%) and an elevated reaction temperature (120 °C).10 With the sterically bulky Si-3, it is found that the in situ generated catalyst is slightly more efficient over the preformed C4 complex in general. This reaction condition was operable because any redistribution of Si-3 was not observed. For example, P25 is obtained in 92% yield in the presence of the *in situ* generated catalyst (vs. 80% yield with the preformed C4, Scheme 5). A polycyclic arene is an effective substrate to afford the desired silvlation product in 66% yield (P26). The silylation of electron-rich anisole is less efficient (53% conv., P27) with an increased amount of p-silylation product (45%). Fluorobenzene is effective enough to deliver the desired product P28 (71% yield) and the m-substituted product was obtained as the major product. This substitution pattern is in accordance with the observations in the reactions of Si-1 and Si-2, in which o-silvlation products are the major products with halogen substituents, but m-silvlation becomes favoured as the steric bulkiness of the silane increases (P5 vs. P17 vs. P28). This also implies that the current protocols are more sensitive to the steric effects of both arene substituents and silanes than the electronics of arene substituents: the steric bulk is a major determining factor of the regioselectivity in this C-H silylation. Heteroarenes are generally less efficient in the silylation with Si-3, furnishing the desired products in moderate yields (37-85%

**Scheme 5** C–H silylation of arenes and heteroarenes with tris(siloxy) silane.

## 0.25 mol % C4 2.5 equiv. Si-2 2.4 equiv. cyclohexene 100 °C, 7 h (TMSO)<sub>2</sub>MeSi X SiMe(OTMS)<sub>2</sub>

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Scheme 6 Double C-H silylation of heteroarenes.

**Scheme 7** Portion-wise C-H silylation of arenes and heteroarenes with various siloxysilanes.

[o:m:p = 47:36:17]

**Scheme 8** C-H silylation of arenes and heteroarenes without the hydrogen scavenger.

conversions, **P29–P33**). This observation is opposite to the reactions with **Si-1** and **Si-2** shown in Schemes 3 and 4.

Next, we briefly investigated the feasibility of double C–H silylations. With 2.5 equivalent of more reactive Si-2 and in the presence of 0.25 mol% C4, the double silylation of furan proceeded efficiently to afford P34 as a major product (>98% conv., 60% yield, Scheme 6). The double silylation products of *N*-methyl pyrrole were isolated in 86% yield with sizable amount of two different double silylation products (P36 and P37 in 67: 33 ratio). Though less efficient, the corresponding silylation of thiofuran resulted in appreciable amount of the product P38 along with the mono-silylation product P39 (27:73 ratio).

In order to further suppress the redistribution of silanes, thereby improving overall efficacy, the silylation reactions were performed by portion-wise addition of silanes. As illustrated in Scheme 7, the silylations involving Si-1, which is prone to redistribution became more efficient by the portion-wise addition protocol (P1-P7, 58-95% conversions). With relatively stable Si-2 and Si-3, similar efficiencies were observed in the silylation reactions (P13-P20 with Si-2 and P25-P29 with Si-3). Overall, the portion-wise protocol was especially useful for unactivated arenes rather than heteroarenes. Additionally, this portion-wise silylation protocol involving various hydrosiloxysilanes was further tested in the presence of a solvent (THF) and similar results were obtained.<sup>10</sup>

The current protocol was further tested for hydrogen scavenger-free C-H silylations. As shown in Scheme 8, the overall efficiency of the silylations of unactivated arenes was significantly decreased without alkenes as exemplified in P1 (32% conv. vs. 93% conv. in Scheme 3). For heteroarenes, however, similar (P8: 65% vs. 71% conv. in Scheme 3) or in some cases, much higher efficiencies are achievable (P12: 81% conv. vs. 51% conv. in Scheme 3).

#### Conclusions

In this report, Rh-based catalytic platforms for C–H silylations of arenes and heteroarenes were developed to prepare various arylsiloxysilanes from mono-, bis-, and tris(siloxy)hydrosilanes. The suppression of the redistribution by the well-defined catalyst C4 was an important finding, allowing us to utilize the labile Si-1 for C–Si bond formations and to improve overall catalytic efficiency. The same protocol can be further extended to the C–H silylations with much more reactive Si-2 and with the sterically demanding Si-3. The regioselectivity was mainly affected

[o:p = 57:43]

by the steric bulkiness of arene substituents or hydrosilanes and the electronic effects of the substituents were a secondary factor. The current protocols can be applied to introduce two siloxane moieties to a heteroarene and performed by a portionwise addition of silanes, or, although limited, without a hydrogen scavenger. Thus, this study can make a positive impact on innovating numerous silicone materials and products by introducing various functional aryl groups into polysiloxane systems.

#### Data availability

All the data supporting this article have been included in the main text and the ESI.† Crystallographic data have been deposited at the CCDC under 2351158.

#### Author contributions

N. S., K. T., J. N., J. L., S. S. and K. L. conceptualized the research and performed the investigation. M. D. studied HRMS. T. E. S. and S. A. K. analysed X-ray crystals. K. L. L. wrote the manuscript with contributions from all authors. K. L. L. supervised this study.

#### Conflicts of interest

There are no conflicts to declare.

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