

HETEROCYCLES, Vol. 95, No. 1, 2017, pp. 152-157. © 2017 The Japan Institute of Heterocyclic Chemistry
 Received, 24th August, 2016, Accepted, 30th September, 2016, Published online, 16th December, 2016
 DOI: 10.3987/COM-16-S(S)39

RHODIUM(I)-CATALYZED SILYLATION OF ARYL IODIDES WITH DI(2-FURYL)METHYLSILANE

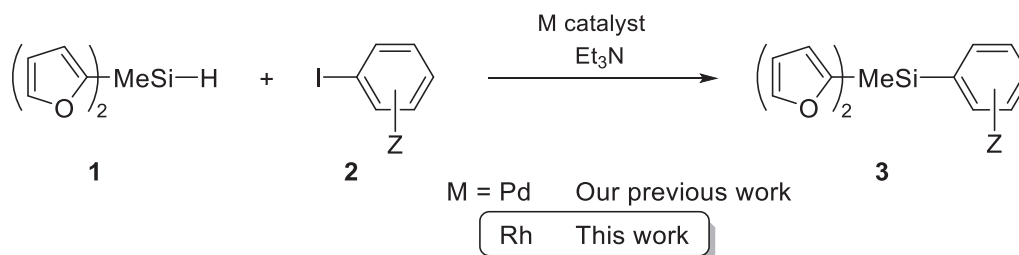
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Abstract – The efficient silylation of aryl iodides with di(2-furyl)methylsilane has been developed utilizing a rhodium catalyst. The substrate scope is broad and includes electron-rich and -deficient aryl iodides.

Arylsilanes are an important class of organometallics, which can be widely used as versatile building blocks in modern organic synthesis.¹ In many cases, aryl(halo)silanes and aryl(alkoxy)silanes, which are somewhat sensitive to moisture, were employed successfully for transition metal-catalyzed carbon–carbon bond-forming reactions.² On the other hand, all-carbon-substituted tetraorganosilicon reagents are desirable in view of their easy handling, but they are less reactive. One of the promising strategies for effective reaction systems employing tetraorganosilanes is the installation of heteroaryl groups on the silicon atom.³ From this point of view, our group previously developed the synthesis of (aryl)di(2-furyl)(methyl)silanes **3** by the palladium-catalyzed silylation of aryl halides **2** with di(2-furyl)(methyl)silane **1** (Scheme 1).⁴ Also, we have demonstrated that **3** participated in the palladium-catalyzed Hiyama cross-coupling as well as the rhodium-catalyzed 1,4-addition to α,β -unsaturated carbonyl compounds.

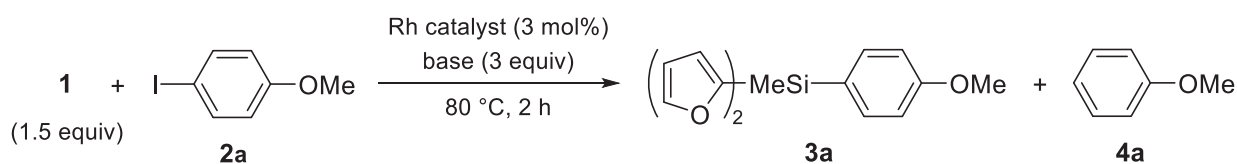


Scheme 1. Silylation of Aryl Iodides **2** with Di(2-furyl)(methyl)silane **1**

Unfortunately, however, the electronic and steric characteristics of aryl halides have a significant impact on the palladium-catalyzed silylation shown in Scheme 1; i.e., the substrates were restricted to aryl halides **2** having electron-donating groups at *para*-position. In the past decade, our group and other groups have disclosed that the rhodium-catalyzed silylation with hydrosilanes offers a much broader substrate scope.⁵⁻⁷ Additionally, the recent success of Gevorgyan in the rhodium-catalyzed silylation with di(alkyl)(heteroaryl)silane inspired us to expand the scope of the silylation using **1** to include electron-deficient and sterically hindered aryl iodides.⁸ Herein, we wish to report an rhodium-catalyzed silylation of aryl iodides **2** with di(2-furyl)(methyl)silane **1**.

In order to optimize reaction parameters, we investigated the reaction of 4-iodoanisole (**2a**) with **1**. The results are summarized in Table 1. The treatment of **2a** with **1** (1.5 equiv), Et₃N (3 equiv), and Rh(acac)(CO)₂ (3 mol%) in NMP at 80 °C afforded the corresponding silylated product **3a** in 77% yield; however, the reaction suffered from a trace amount of dehalogenated byproduct **4a** as a result of reduction of the C–I bond (entry 1). When cationic [Rh(cod)(MeCN)₂]BF₄ was used as catalyst, the yield and selectivity were slightly decreased (entry 2). Furthermore, employing K₃PO₄, which gave the best result in the previous report,^{7,8} provided poor yields of **2a** (entries 3 and 4). NMP was the solvent of choice, and other reaction media, such as DMF and THF, were less effective (entries 5 and 6). Thus, the optimized reaction conditions for this silylation using **1** are the Rh(acac)(CO)₂ catalyst and the Et₃N base in NMP.

Table 1. Silylation of 4-Iodoanisole (**2a**) with **1**^a

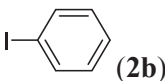
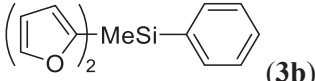
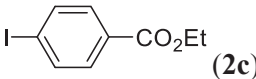
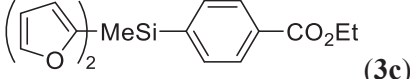
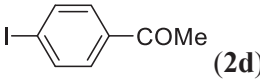
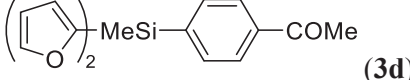
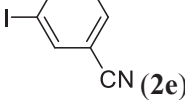
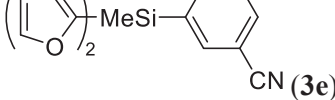
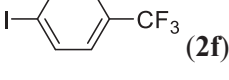
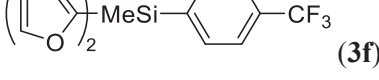
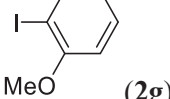
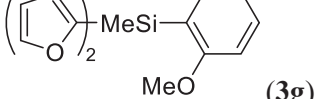
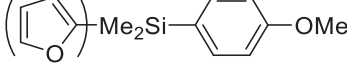
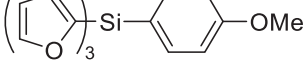


entry	catalyst	base	solvent	yield (%) ^b	
				3a	4a
1	Rh(acac)(CO) ₂	Et ₃ N	NMP	77	2
2	[Rh(cod)(MeCN) ₂]BF ₄	Et ₃ N	NMP	61	6
3	Rh(acac)(CO) ₂	K ₃ PO ₄	NMP	37	5
4	[Rh(cod)(MeCN) ₂]BF ₄	K ₃ PO ₄	NMP	48	18
5	Rh(acac)(CO) ₂	Et ₃ N	DMF	58	4
6	Rh(acac)(CO) ₂	Et ₃ N	THF	34	2

^a Reaction conditions: **2a** (0.250 mmol), **1** (0.375 mmol), base (0.75 mmol), catalyst (3 mol%) and solvent (1 mL) at 80 °C for 2 h. ^b GC yields are based on **2a**.

Having identified the best reaction conditions, we next investigated the substrate scope of the silylation of aryl iodides **2** using **1** (Table 2). The present conditions have improved the functional group tolerance of the catalytic silylation with **1**. The presence of functional groups, such as ester (entry 1), ketone carbonyl (entry 2), and cyano groups (entry 3), in the starting aryl iodides **2** did not interfere with the outcome of the silylation. In contrast to the previous palladium-catalyzed silylation with **1**, both the yield and the selectivity in the present silylation were almost independent of the electronic and steric requirement.⁴ Indeed, the differences in the yields and on the selectivity among **2** having electron-donating (Table 1) or -withdrawing groups (Table 2, entry 5) were not particularly large. The reaction of sterically hindered **2g** also took place without any difficulty (entry 6). Furthermore, (2-furyl)di(methyl)silane and tri(2-furyl)silane acted as a silicon source for the rhodium-catalyzed silylation (entries 7 and 8).

Table 2. Silylation of Representative Aryl Halides **2** with **1**^a

entry	aryl halide 2	product 3	yield (%) ^b
1	 (2b)	 (3b)	90
2	 (2c)	 (3c)	95
3	 (2d)	 (3d)	98
4	 (2e)	 (3e)	78
5	 (2f)	 (3f)	72
6	 (2g)	 (3g)	96
7 ^c	2a	 (3h)	87
8 ^d	2a	 (3i)	88

^a Reaction conditions: **2** (0.250 mmol), **1** (0.375 mmol), Et₃N (0.75 mmol), Rh(acac)(CO)₂ (3 mol%), in NMP (1 mL) at 80 °C for 2 h. ^b Isolated yields are based on **2**. ^c (2-Furyl)di(methyl)silane was used instead of **1**. ^d Tri(2-furyl)silane was used instead of **1**.

Our focus then turned to the mechanism of this rhodium-catalyzed silylation. The proposed catalytic cycle was computationally addressed by DFT calculations. We have adopted the reaction of $\text{RhI}(\text{CO})_2$, with PhI and HSiMe_3 , as a model reaction, and Et_3N was replaced by Me_3N in the computed structures. The calculated energy profile of a proposed catalytic cycle is depicted in Figure 1. As shown by the solid line, the first step of the silylation is oxidative addition of HSiMe_3 to $\text{RhI}(\text{CO})_2$ to form a silyl hydrido species **6**.⁹ Through reductive elimination of HI with the aid of Me_3N , a silyl rhodium(I) **7** is formed.¹⁰ The next step is oxidative addition of PhI to the silyl rhodium(I) **8**. Subsequent reductive elimination of Ph-Si bond would lead to a rhodium(I) complex **10**. After the ligand exchange between the product and the silane, **5** would be regenerated. As shown in Figure 1, the transition state for the oxidative addition TS_{8-9} is the highest point on the free energy profile of the catalytic cycle.

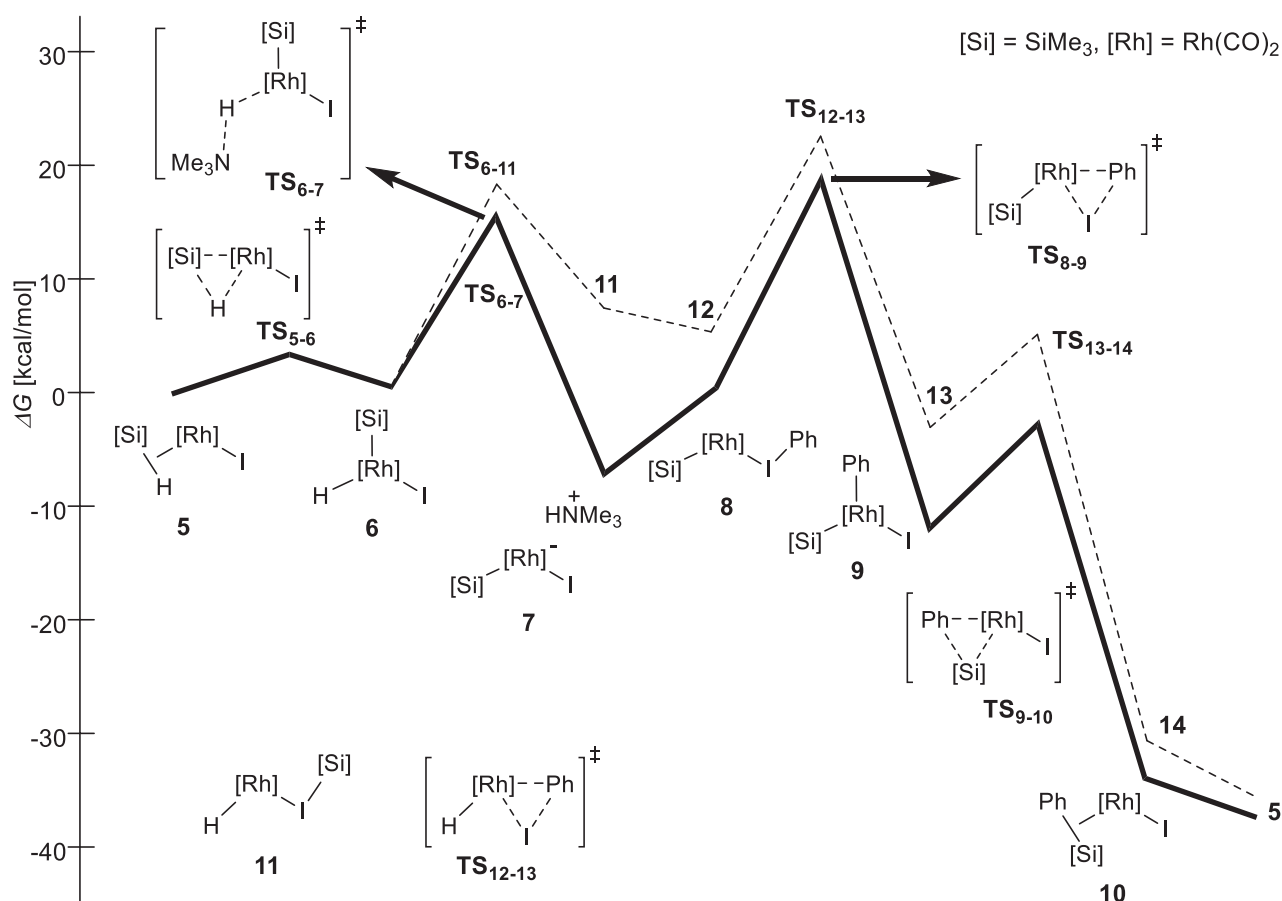


Figure 1. Free Energy Profile of Proposed Reaction Pathways

The catalytic cycle initially proposed by Yamanoi et al. has involved a $\text{Rh}(\text{V})$ intermediate via sequential oxidative addition both of HSiR_3 and ArI to the silyl rhodium(I).⁷ As all attempts to locate the $\text{Rh}(\text{H})(\text{I})(\text{Ar})(\text{SiR}_3)_2$ intermediate as not only a stationary point but a saddle point were unsuccessful probably because of the energetically unfavorable high oxidation state, we regard that the above

mechanism would be preferable to the Rh(V) pathway.

It is possible that Me₃SiI also eliminate from **6** to yield a hydrido rhodium(I) **11** (the dot line in Figure 1).¹¹ Subsequently, oxidative addition-reductive elimination results in the formation of byproduct (for structures, except for **11** and **TS**₁₂₋₁₃, see Supporting Information). The transition state for the oxidative addition of PhI, **TS**₁₂₋₁₃, is the highest point in the catalytic pathway of the side reaction. Comparing the energetics of these reactions, the solid versus the dot lines, we estimate that the silylation is more favorable than the reduction, which is in good agreement with the experimental results presented here.

In conclusion, we have developed a general and efficient method for the silylation of aryl iodides with di(2-furyl)methylsilane using Rh(acac)(CO)₂ as the catalyst. The substrate scope was broad and included electron-deficient and sterically hindered aryl iodides. Further investigations into expanding the substrate scope and understanding the detailed mechanism are currently ongoing in our laboratory.

ACKNOWLEDGEMENTS

We thank Mr. Kazutoshi Abe and Mr. Reiji Yamada for their help in preparing the manuscript.

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