Rhodium-catalyzed Addition of Organo[2-(hydroxymethyl)phenyl]dimethylsilanes to Arenesulfonylimines

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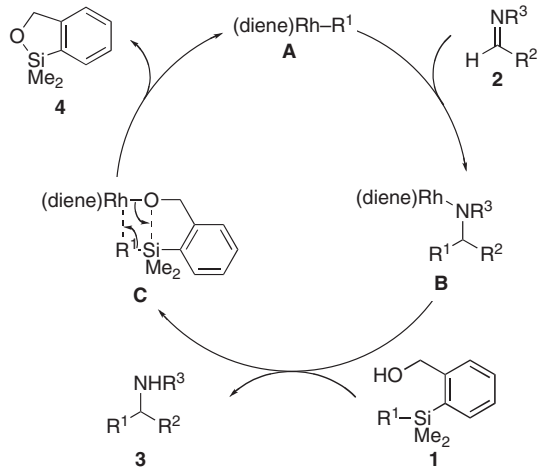
The title reaction is found to proceed in the presence of a rhodium/diene catalyst. Variously substituted diarylmethylamines and allylamines having an *N*-arenesulfonyl protection are obtained in good yields, which are important building blocks in organic synthesis.

Nucleophilic addition reactions of organometallic reagents to imines have been studied extensively as versatile protocols for synthesis of various *sec*-alkylamines, some of which exhibit remarkable biological activities.[1] Especially, recent studies on rhodium catalysis have allowed the use of mild nucleophiles such as organoboron reagents to participate in the transformation with high chemo- and enantioselectivities.[2] Whereas other organometallic reagents have also been employed in the rhodium-catalyzed reactions to compensate for the boron-based ones,[3] organosilicon reagents have remained unexplored except for labile aryl(difluoro)silanes which were employed in the presence of KF in excess.[4] In view of an increasing importance of the silicon-based protocol with respect to inherent stability, availability, and non-toxicity associated with organosilicon compounds, we report herein organo[2-(hydroxymethyl)phenyl]dimethylsilanes (**1**) as highly stable and reusable alternative organometallic reagents for the rhodium-catalyzed 1,2-addition reaction to imines.

We have recently disclosed that **1** undergoes transmetalation smoothly to rhodium(I) to give organorhodium species **A** possibly via rhodium alkoxide **C** to effect 1,4-addition reactions across electron-deficient olefins under mild conditions (Scheme 1).[5] Thus, it is reasonable to expect that **A** would react with imines to afford rhodium amide **B**, which then acts as a base to deprotonate **1** and generate **C**. Overall, the rhodium-catalyzed 1,2-addition reaction using **1** is anticipated to proceed under mild conditions without any activators.

To prove the viability of our working hypothesis, we first examined the reaction of [2-(hydroxymethyl)phenyl]phenyldimethylsilane (**1a**: 1.1 mmol) with *N*-phenylmethylidene-4-nitrobenzenesulfonamide (**2a**: 1.0 mmol). The *N*-sulfonyl protecting group was chosen simply because it is readily removal after the addition reaction.[6] The reaction proceeded smoothly in the presence of $[Rh(OH)(cod)]_2$ (1.0 mol % Rh) in THF at 70 °C to afford *N*-(diphenylmethyl)-4-nitrobenzenesulfonamide (**3aa**) in 86% yield (Table 1, Entry 1). Arylsilanes having a labile bromo group (**1b**) and sterically demanding 2-methyl group (**1c**) also underwent the reaction with **2a** in excellent yields (Entries 2 and 3). Silane reagent **1a** added to imines derived from electron-deficient and -rich benzaldehydes as well as alkanals to give the corresponding adducts in good yields (Entries 4–6). A wide range of allylic amines were obtained in high yields with excellent regio- and stereospecificities by the addition reactions of



R^1 =		R^2, R^3 =
Ph (**1a**)	(*E*)-HexCH=CH (**1f**)	Ph, Ns (**2a**)
4-Br–C_6H_4 (**1b**)	(*E*)-PhCH=CH (**1g**)	4-Cl–C_6H_4, Ns (**2b**)
2-Me–C_6H_4 (**1c**)	(*Z*)-MeCH=CH (**1h**)	4-MeO–C_6H_4, Ns (**2c**)
vinyl (**1d**)	(*E*)-PrCH=CPr (**1i**)	*c*-C_6H_{11}, Ts (**2d**)
H_2C=CMe (**1e**)	Me_2CH=CH (**1j**)	(Ns = 4-O_2N–C_6H_4–SO_2, Ts = 4-Me–C_6H_4–SO_2)

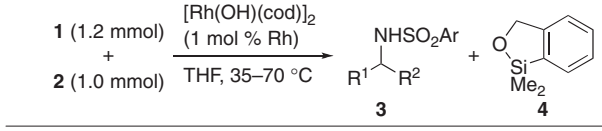
Scheme 1.

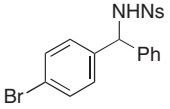
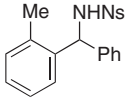
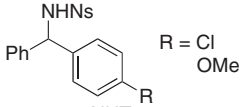
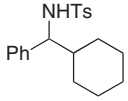
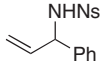
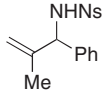
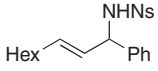
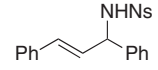
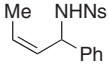
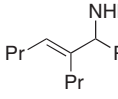
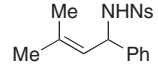
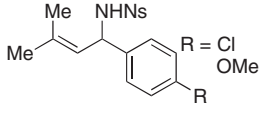
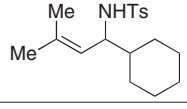
variously substituted alkenylsilanes carried out at 35–50 °C (Entries 7–16). Successful addition of vinylsilane **1d** and propen-2-ylsilane **1e** is worth noting, because the corresponding vinylboronic acids have rarely been employed in the rhodium-catalyzed transformations due mainly to thermal instability.[7] In all the addition reactions demonstrated herein, formation of silicon residue **4** in >80% yield, which is reusable for regeneration of the tetraorganosilicon reagents, were confirmed by ^{1}H NMR analyses of crude products.

In the presence of chiral diene ligand (*S*,*S*)-Ph-bnd*,[2e,2f] the reaction of **1e** with **2a** proceeded in an enantioselective manner to give substituted chiral allylamine (*R*)-**3ea** of 91% ee in 68% yield (eq 1).[8] This result represents, though preliminary, the first example of the enantioselective addition of an alkenyl nucleophile to imines by rhodium catalysis. Further efforts for the enantioselective 1,2-addition reaction of the silicon reagents to sulfonylimines are being made in our laboratories.

In summary, we have demonstrated that organo[2-(hydroxymethyl)phenyl]dimethylsilanes undergo the 1,2-addition reaction to arenesulfonylimines. Compared with the reported silicon-based reaction,[4] the present one allows use of readily accessible, highly stable, and reproducible tetraorganosilicon compounds in a stoichiometric amount in most cases under mild conditions without any activator. The present protocol provides us with

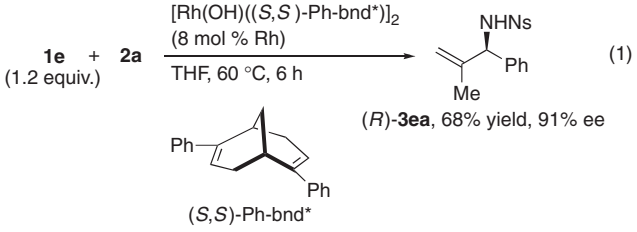
Table 1. Addition of organo[2-(hydroxymethyl)phenyl]dimethylsilanes (**1**) to arenesulfonylimines **2**



Entry	1	2	Temp/°C	Time/h	Product	Yield/%[a]
1	**1a**[b]	**2a**	70	1		86 (**3aa**)
2	**1b**[b]	**2a**	70	2		92 (**3ba**)
3	**1c**[b]	**2a**	70	2		98 (**3ca**)
4	**1a**[b]	**2b**	70	1	 R = Cl	90 (**3ab**)
5	**1a**[b]	**2c**	70	0.5	OMe	91 (**3ac**)
6	**1a**[b]	**2d**	70	1.5		94 (**3ad**)
7	**1d**[c]	**2a**	50	48		64 (**3da**)
8	**1e**	**2a**	35	3		96 (**3ea**)
9	**1f**[d]	**2a**	35	3		93 (**3fa**)
10	**1g**	**2a**	35	1		95 (**3ga**)
11	**1h**[e]	**2a**	35	3		89 (**3ha**)[f]
12	**1i**	**2a**	35	2		98 (**3ia**)
13	**1j**	**2a**	35	0.5		98 (**3ja**)
14	**1j**	**2b**	35	1	 R = Cl	93 (**3jb**)
15	**1j**	**2c**	35	0.5	OMe	96 (**3jc**)
16	**1j**	**2d**	35	4		95 (**3jd**)

[a]Isolated yields based on **2**. [b]Reaction run with 1.1 mmol of **1**. [c]Reaction run with 2.0 mmol of **1d**. [d]Reaction run with 1.0 mmol of **1f**. [e]E/Z = 12:88 (^{1}H NMR). [f]E/Z = 13:87 (^{1}H NMR).

an alternative to the boron-based one to synthesize variously substituted *sec*-alkylamines, especially in view that a wide variety of stable alkenyl(triorgano)silanes with various substitution patterns are available in a predictable manner by rich hydrosilylation chemistry.[9]



(1)

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10 Supporting Information is available electronically on the CSJ-Journal Web site; http://www.csj.jp/journals/chem-lett/.

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