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Rhodium-Catalyzed Hydroarylation and -alkenylation of Alkynes with Silanediols. A Crucial Role of the Hydroxy Group for the Catalytic Reaction

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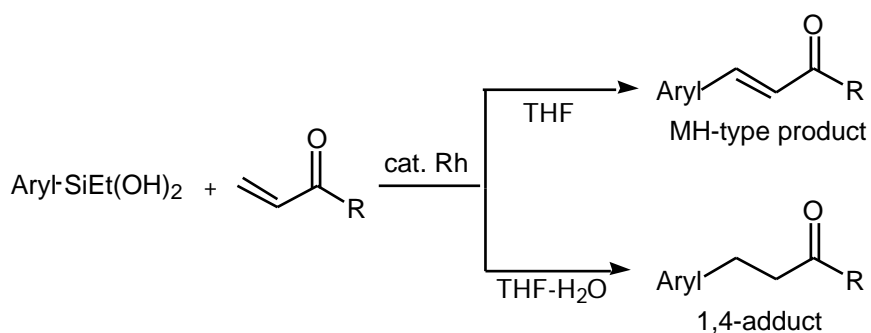
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Abstract : Aryl- and alkenylsilanediols, which possess two hydroxy groups on the silicon atom, undergo the rhodium-catalyzed addition of an organic group on silicon to internal alkynes. Treatment of several internal alkynes with aryl- or alkenylsilanediols in the presence of 3 mol % of $[\text{Rh}(\text{OH})(\text{cod})]_2$ affords the hydroarylated or hydroalkenylated products in good yields. A crucial role of the hydroxy group of silanediol for the catalytic reaction is also discussed with the related aryltin reagent.

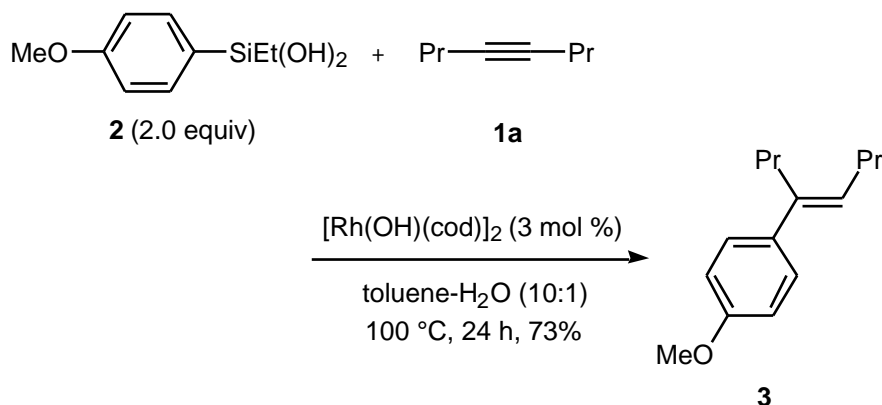
Key words: silanediol, rhodium complex, hydroarylation, hydroalkenylation, internal alkyne

We have recently described rhodium-catalyzed C-C bond-forming reactions with silanediols to α,β -unsaturated carbonyl compounds affording both conjugate addition and Mizoroki-Heck (MH)-type products in a controllable manner as shown in Scheme 1.¹⁻² Further studies on the rhodium-catalyzed reactions with organosilicon compounds have been partly focused on a substrate that is unable to undergo β -hydride elimination leading to the MH-type product. Internal alkyne is a choice since it does not possess an appropriate hydrogen atom to facilitate β -hydride elimination of the arylmetallated product.³ A recent communication by Hayashi and co-workers on the rhodium-catalyzed addition of arylboronic acids to alkynes⁴ prompted us to report our findings on the reaction with silanediols. We discuss also that the hydroxy group on the silicon atom plays a crucial role for the rhodium-catalyzed reaction.



Scheme 1

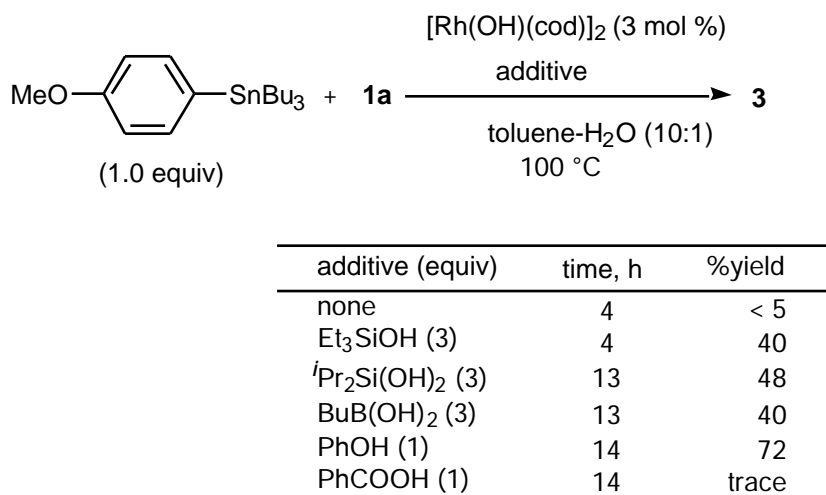
When 4-octyne (**1a**) was treated with 4-methoxyphenyl(ethyl)silanediol (**2**) in the presence of $[\text{Rh(OH)(cod)}]_2$ (3 mol %) in toluene- H_2O at 100 °C for 24 h, **3** was obtained in 73% yield (eq 1). Table 1 shows the results on various alkynes (**1a-1c**) with aryl- and alkenylsilanediols (**2** and **4-6**). A cationic rhodium complex, $[\text{Rh(cod)}_2]\text{BF}_4$, also catalyzed the arylation (64 %, for 18 h), whereas no reaction occurred with a neutral rhodium complex, $[\text{RhCl(cod)}]_2$. The reaction took place in toluene- H_2O system efficiently, while the yield was found to be much inferior in the absence of water. Symmetrical internal alkynes **1a** and **1b** with alkyl or aryl substituents proceeded smoothly.⁵ On the other hand, phenylacetylene, a terminal alkyne, resulted in polymerization, and disubstituted alkynes bearing electron-withdrawing groups such as methyl phenylpropiolate ($\text{PhC}\equiv\text{CCOOMe}$) and dimethyl acetylenedicarboxylate ($\text{MeOCOC}\equiv\text{CCOOMe}$) afforded a complex mixture of unidentified products. In addition to arylsilanediols, alkenylsilanediol **6** also affected the hydroalkenylation to afford the corresponding dienes **9** and **10**⁶ in good yields. Although the reaction with an unsymmetrical alkyne **1c** proceeded, the regiochemistry was not controlled effectively to result in giving a mixture of isomers **11** and **12**.⁷



Equation 1

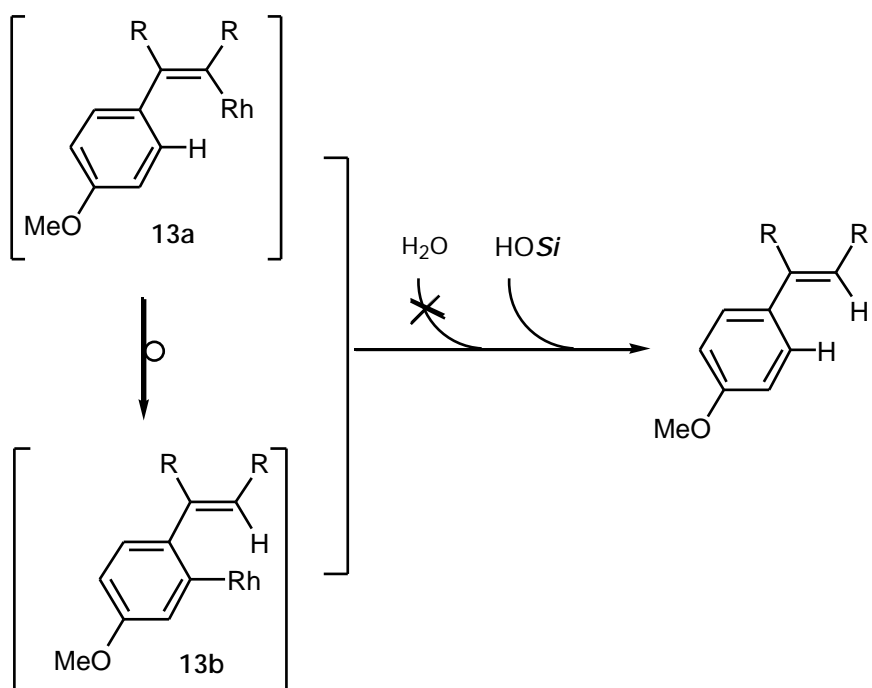
insert Table

We consider that the key intermediate of the catalytic reaction is an alkenylrhodium species, which would be subjected to protonolysis leading to the product. On the other hand, the similar reaction with tributyl(4-methoxyphenyl)tin that did not possess any hydroxy groups resulted to afford the hydroarylated product in <5 % yield with recovery of a considerable amount of the tin reagent both in the presence and the absence of water.⁸ The results suggest that the hydroxy group of silanediol plays a significant role for protonolysis. Indeed, addition of triethylsilanol or diisopropylsilanediol that did not possess a transferable organic group on silicon to the reaction with the tin reagent could affect the hydroarylation as shown in Scheme 2. Butylboronic acid and phenol were also found to be effective additives whereas benzoic acid resulted in no reaction.



Scheme 2

The rhodium-catalyzed reaction would occur via transmetalation-insertion sequence to give alkenylrhodium species **13a** in a similar manner to other rhodium-catalyzed reactions of silanediols^{1a} and boron reagents.² The intermediate **13a** would partly rearrange into **13b** via intramolecular 1,4-hydrogen shift.^{4,9} The result that hydroarylation with the aryltin reagent has not proceeded even in the presence of water suggests following: Subsequent protonolysis of **13a** or **13b** does not proceed with water but occurs via the reaction of **13** with SiO-H to result in giving the hydroarylated product as illustrated in Scheme 3.



Scheme 3

In conclusion, aryl and alkenylsilanediols were found to promote the rhodium-catalyzed addition of an organic group on silicon to internal alkynes. Although the similar reaction with aryltributyltin that possess no hydroxy group on tin did not proceed, several additives bearing hydroxy groups to the reaction could affect the reaction of the tin reagent. The results suggest that the hydroxy group of silanediol was found to play a crucial role for the arylation and alkenylation of organosilicon reagents.

Typical experimental procedure for the rhodium-catalyzed hydroarylation and hydroalkenylation with silandiols is as follows: **(E)-4-(4-Methoxyphenyl)-4-octene (3)**: To a mixture of **2** (595 mg, 3 mmol) and [Rh(OH)(cod)]₂ (20 mg, 0.045 mmol) in 15 mL of toluene and 1.5 mL of H₂O was added **1a** (0.22 mL, 1.5 mmol) and the resulting light yellow solution was stirred at 100 °C for 24 h. After cooling to room temperature the mixture was poured into the mixture of 1 M HCl and diethyl ether and the two phases were separated. The organic layer was washed with saturated aqueous NaHCO₃ solution and brine and dried over anhydrous magnesium sulfate. Concentration of the solvent left a crude oil, which was subjected to chromatography on silica gel (hexane) to afford 216 mg of **3** (66%).

Acknowledgment


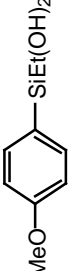
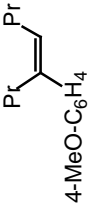
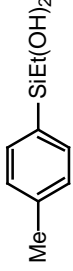
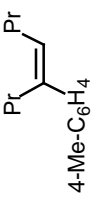
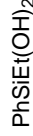
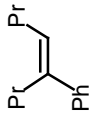
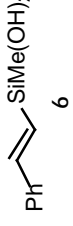
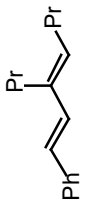

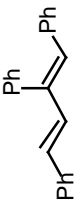


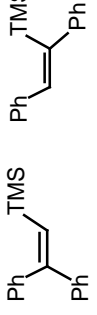

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Table Rhodium-catalyzed hydroarylation and -alkenylation of alkynes with silanediols ^a

alkyne	silanediol	solvent	time, h	product, (%yield ^b)
 1a	 2	toluene-H ₂ O (10:1)	24	 3 (73)
		toluene-H ₂ O (10:1)	18	3 (60)
		toluene-H ₂ O (1:1)		3 (58)
		toluene		3 (28)
		dioxane-H ₂ O (10:1)		3 (39)
		dioxane		3 (27)
		MeOH-H ₂ O (10:1)		3 (25)
	 4	toluene-H ₂ O (10:1)	24	 7 (67)
	 5			 8 (65)
	 6			 9 (66)
 1b				 10 (49)
 1c	 5			 11 (39)
				 12 (22)

^a The reaction was carried out using 0.3 mmol of **1**, 0.6 mmol of **2** and **4-6**, and 0.009 mmol of [Rh(OH)(cod)]₂ at 100 °C in 3.3 mL of solvent.

^b Isolated yield after silica gel chromatography.

Graphical abstract

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