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Hydroxorhodium Complex-Catalyzed Carbon−Carbon Bond-Forming Reactions of Silanediols with α,*β*-Unsaturated Carbonyl Compounds. Mizoroki-Heck-Type Reaction vs Conjugate Addition

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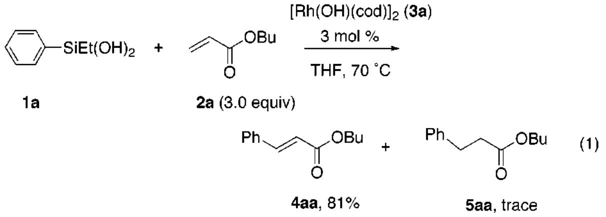
The development of novel carbon−carbon bond forming reactions is a continuing goal in organic synthesis. Organometalloids of boron, silicon, and tin are among the most powerful reagents employed in C−C bond forming reactions. The propensity of these reagents to undergo transition metal-catalyzed cross-coupling reactions with a variety of organic electrophiles is what makes them so valuable in organic synthesis.[1] The transmetalation step, in which an organic group on the organometalloid becomes bound to the transition metal catalyst, is often the key to the success of the entire process. Of the many organometalloids known to undergo coupling reactions, *organosilicon* reagents are the most intriguing since they are inexpensive, readily prepared, and environmentally benign.

Organosilicon reagents bearing hydroxy groups on the silicon atom such as silanols, silanediols, and silanetriols are particularly useful.[2] These compounds are readily available by hydrolysis of the corresponding chlorosilanes. They are also unexpectedly stable and easy to handle, and at the same time undergo smooth transmetalation to palladium, which enables cross-coupling reactions with organohalogen compounds and olefinic compounds.[3,4]

We have recently found that rhodium[5] is also a suitable catalyst for the transmetalation of silanediols **1**, and can catalyze the addition of such species to α,*β*-unsaturated carbonyl compounds **2**. Interestingly, the most effective rhodium complex is hydroxorhodium **3a**,[6] which has rarely been applied in organic synthesis. The reaction furnishes either Mizoroki−Heck (MH)[7,8]-type or 1,4-conjugate addition[5c,d] product with high specificity depending on the reaction conditions.

The reaction of phenyl(ethyl)silanediol (**1a**) with *n*-butyl acrylate (**2a**) catalyzed by 3 mol % of $[Rh(OH)(cod)]_2$ (**3**) afforded *n*-butyl 3-phenylacrylate (**4aa**) in 81% yield along with only a trace amount of conjugate adduct **5aa** (eq 1).



Silanols and organostannanes both undergo Mizoroki−Heck-type reactions with Pd complexes, but under the conditions examined to date the reaction did not necessarily proceed in a reasonable yield.[9] A stoichiometric amount of $Pd(OAc)_2$ or the combined use of catalytic $Pd(OAc)_2$ with excess $Cu(OAc)_2$−LiOAc as an oxidant is usually required.[3c−e] In contrast, rhodium complex **3** affected the desired reaction at 3 mol % loading with no further additives. Among several solvents examined, ethereal solvents such as THF and 1,4-dioxane were the best.

As shown in Table 1,[10] the use of a silanediol as the substrate appears to be important. Silanols, although reactive, were inferior to silanediol **1**, and afforded product **4** in only moderate yield. Other organosilicon reagents such as $PhSi(OMe)_3$ were completely unreactive. The reactions of several acrylates and acryl amides occurred in good yields, but *β*-substitued substrates were so far unsuccessful under similar conditions. Silanediols such as (4-methylphenyl)(ethyl)silanediol (**1b**) and (4-methoxyphenyl)(ethyl)silanediol (**1c**) also underwent MH-type reaction smoothly.

Table 1. Rh-Catalyzed Mizoroki−Heck-Type Reaction of α,*β*-Unsaturated Carbonyl Compounds[a]

substrate	α,*β*-unsaturated carbonyl compound	% yield of **4**[b]
$PhSiEt(OH)_2$ (**1a**)	$H_2C{=}CHCO_2Bu$ (**2a**)	81
$(4\text{-}Me\text{-}C_6H_4)SiEt(OH)_2$ (**1b**)	**2a**	99
1b	**2a**	79[c]
$(4\text{-}Me\text{-}C_6H_4)SiMe_2OH$	**2a**	34
$PhSi(OMe)_3$	**2a**	0
1b	$H_2C{=}CHCO_2Et$ (**2b**)	83[c]
1b	$H_2C{=}CHCO_2Me$ (**2c**)	61
1b	$H_2C{=}CHCO_2CH_2CF_3$ (**2d**)	48[d]
1b	$H_2C{=}CHCO_2{}^t\text{Bu}$ (**2e**)	78
1b	$H_2C{=}CHCONMe_2$ (**2f**)	70[c]
1b	$H_2C{=}CHCONH{}^t\text{Bu}$ (**2g**)	68
$(4\text{-}MeO\text{-}C_6H_4)SiEt(OH)_2$ (**1c**)	**2b**	76

[a] Unless noted all reactions were carried out in THF with 3 mol % of **3** and 2.5−3.0 equiv of unsaturated carbonyl compound (relative to the substrate, respectively) at 70 °C for 24 h. [b] Isolated yield. [c] The reaction was carried out in 1,4-dioxane at 100 °C. [d] Conjugate adduct **5bd** was obtained in 7% yield.

As noted in eq 1, trace amounts of the product of conjugate addition **5** were observed under the standard conditions. However, simply changing the solvent from THF to THF/H_2O, gave the 1,4-conjugate addition product **5** as the major product. As shown in Table 2,[10] the amount of the 1,4-adduct increased as more water was added to the reaction solvent. Optimum conditions for the production of **5** were found to be THF−H_2O (2:1) as a solvent system (eq 2). Under these conditions, ethyl 3-(4-methylphenyl)-propanoate (**5bb**) was obtained in 53% yield along with only 5%

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(9) Although we also examined the Pd-mediated MH-type reactions of silanediols, a remarkable difference from those of silanols was not observed; unpublished results.

(10) Additional examples are shown in the Supporting Information.

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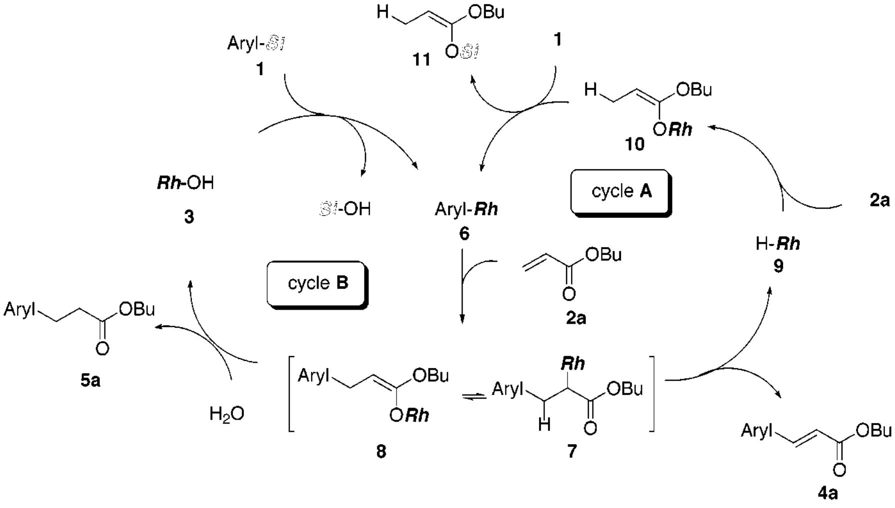
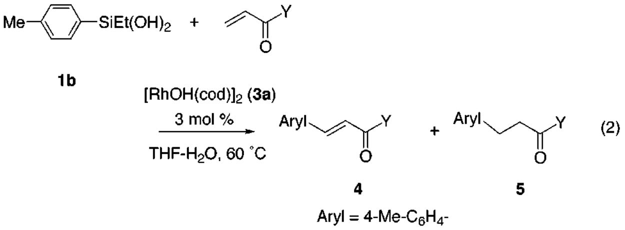
Scheme 1. A Plausible Mechanism for the Rh-Catalyzed MH-Type Reaction and Conjugate Addition



of **4bb** in the reaction of **1b** with **2b**. Thus, the course of the reaction (MH-type reaction vs conjugate addition) can be controlled by the use of water as a cosolvent.[10] Preference of the conjugate addition appears to improve when the substrate has a more electron-deficient carbonyl group. Accordingly, the reaction of the electron-donationg unsaturated amide **2f** and **2g** resulted in a mixture of **4** and **5**. In contrast, an unsaturated ketone such as methyl vinyl ketone with less electron density on the carbonyl oxygen atom gave only the 1,4-adduct even under nonaqueous conditions.[11]



A plausible mechanism for the reactions described herein is given in Scheme 1; transmetalation of the aryl group of the silanediol to the hydroxorhodium complex **3** gives arylrhodium species **6**. Insertion of butyl acrylate (**2a**) forms **7**, which would be in equilibrium with the rhodium enolate **8**. When water is absent from the reaction system, **7** undergoes β-hydride elimination to afford MH-type product **4a** along with hydridorhodium species **9**. The rhodium complex **9** reacts with **2a** to form enolate **10**, which is transmetalated with silanediol **1** to generate enolsilane **11** and complete the catalytic **cycle A**. In support of this proposed mechanism, $EtCO_2Bu$, the protonated version of **11**, is obtained in 53% under anhydrous reaction conditions. In the presence of water, the intermediate rhodium enolate **8** is readily protonated to form the conjugate adduct **5a** and at the same time regenerate hydroxorhodium **3** (**cycle B**).[12]

The rhodium-catalyzed reaction of silanediols with α,β-unsaturated esters can be directed toward the Mizoroki-Heck-type reaction and/or conjugate addition depending on the solvent system and the electronic nature of the carbonyl substrate. Among various organosilicon reagents, this interesting reactivity seems to be specific to silanediols. By contrast, other silyl species were unreactive or considerably less reactive. The present reactions expand the synthetic versatility of silanediols and provide a new method for the catalytic formation of carbon−carbon bonds with innocuous organosilicon reagents.

Table 2. Rhodium Complex **3a**-Catalyzed Reaction of **1b** with α,β-Unsaturated Carbonyl Compounds[a]

Y	solvent	% yield of MH product	% yield of 1,4-adduct
OEt (**2b**)	THF[b]	74	trace
	THF−H_2O (180:1)[b]	55	8
	THF−H_2O (5:1)[b]	26	40
	THF−H_2O (2:1)	**5**	**53**
OBu (**2a**)		5	83
OMe (**2c**)		4	61
O^{t}Bu (**2e**)		9	73
NMe_2 (**2f**)		13	11
NH^{t}Bu (**2g**)		26	46[c]
Me	THF	0	56

[a] Unless noted, the reaction was carried out with 3 mol % of **3** and 1.0 equiv of unsaturated carbonyl compound (to silanediol, respectively) at 70 °C for 24 h. After chromatography, yields of MH product and 1,4-adduct were estimated by ^1H NMR. [b] The ratio of **1b**/**2b** was 1:3. [c] An additional 0.5 mL of Et_3N was used in the solvent system.

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Note Added in Proof. After submission of this manuscript the following papers concerning refs 5 and 6 appeared: Lautens, M.; Roy, A.; Fukuoka, K.; Fagnou, K.; Martin-Matute, B. *J. Am. Chem. Soc.* **2001**, *123*, 5358 (ref 5) and Itooka, R.; Iguchi, Y.; Miyaura, N. *Chem. Lett.* **2001**, *722* (ref 6).

Supporting Information Available: Experimental procedures for rhodium-catalyzed reactions and additional results for Tables 1 and 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The reaction with methyl methacrylate in 1,4-dioxane at 100 °C (nonaqueous conditions) also gave 1,4-adduct in 56% yield along with 11% of the MH product.

(12) In the presence of a certain amount of water, immediate protonation of enolate **8** would be preferred to the β-elimination as cycle A. An alternative possibility to afford the conjugate adduct **5** via sequential β-elimination and conjugate reduction with the formed H−Rh (**9**) species was found to be unlikely by the following experiment: the reaction of **1b** to *tert*-butyl acrylate (**2e**) in the presence of ethyl cinnamate (**4ab**) afforded **5be** in 64% yield along with 97% recovery of **4ab**. (No scrambling to give **5ab** occurred.)