Rhodium-Catalyzed Hydroarylation and Hydroalkenylation of Alkynes Using Organo[2-(hydroxymethyl)phenyl]dimethylsilanes

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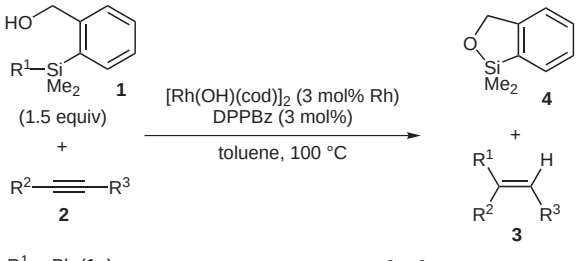
Received 30 November 2007

Abstract: The title reaction was found to proceed in the presence of a rhodium/1,2-bis(diphenylphosphino)benzene catalyst. Variously substituted arylethenes and 1,3-dienes were obtained in good yields.

Key words: silicon, alkyne, rhodium, addition reaction

Construction of multisubstituted ethenes with a defined stereochemistry is of significant importance in organic synthesis. Of many protocols, rhodium-catalyzed addition of organometallic reagents across alkynes provides a chemo- and stereoselective access to trisubstituted ethenes.[1,2] Arylboronic acids have been extensively employed in this transformation in view of ready availability, stability, and chemoselectivity, little attention being paid to other organometallic reagents.[3] Despite an increasing importance of the silicon-based protocol with respect to inherent stability, availability, and nontoxicity associated with organosilicon compounds, the use of labile organosilanediols by Mori and co-workers has been a single example ever reported on the rhodium-catalyzed reaction of alkynes.[4] We report herein organo[2-(hydroxymethyl)phenyl]dimethylsilanes (**1**) as highly stable and reusable alternative organometallic reagents for the rhodium-catalyzed addition reaction across alkynes (Equation 1).[5]



R^1 = Ph (**1a**)
4-MeOC$_6$H$_4$ (**1b**)
4-FC$_6$H$_4$ (**1c**)
2-MeC$_6$H$_4$ (**1d**)
(*E*)-HexCH=CH (**1e**)
(*E*)-Cl(CH$_2$)$_3$CH=CH (**1f**)
(*E*)-TBSO(CH$_2$)$_3$CH=CH (**1g**)
(*E*)-NC(CH$_2$)$_3$CH=CH (**1h**)
(*E*)-(MeO$_2$C)$_2$CHCH$_2$CH=CH (**1i**)
(*Z*)-MeCH=CH (**1j**)
(*E*)-PhCH=CH (**1k**)
H$_2$C=CPh (**1l**)

R^2, R^3 = Pr, Pr (**2a**)
Ph, Ph (**2b**)
Me, *t*-Bu (**2c**)
Me, Ph (**2d**)

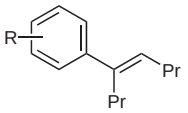
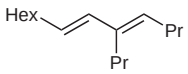
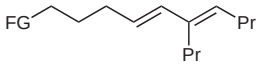
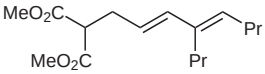
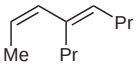
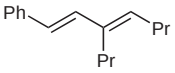
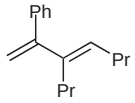
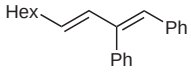
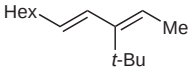
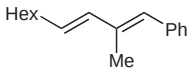
Equation 1

We first examined the reaction of [2-(hydroxymethyl)phenyl]phenyldimethylsilane (**1a**: 1.5 mmol) with 4-octyne (**2a**: 1.0 mmol) in the presence of [Rh(OH)(cod)]$_2$ (3.0 mol% Rh) in toluene at 100 °C using various bisphosphine ligands[1a] and found that 1,2-bis(diphenylphosphino)benzene (DPPBz) was effective to afford (*E*)-4-phenyl-4-octene (**3aa**) in 59% yield (Table 1, entry 1).[6] Other rhodium complexes such as [RhCl(cod)]$_2$ and [RhCl(ethylene)$_2$]$_2$ were completely ineffective. Absence of a phosphine ligand resulted in a slightly decreased yield, and the effect of a small amount of water was negligible,[4] because the hydroxy group of **1** acts as an efficient proton donor in our system. Whereas arylsilanes having an electron-donating 4-methoxy (**1b**) and 2-methyl (**1d**) groups, though the latter being sterically demanding, enhanced the reaction rates and yields of the reaction with **2a** (entries 2 and 4), the addition of less nucleophilic (4-fluorophenyl)silane **1c** was sluggish (entry 3). We then turned our attention to the reaction of alkenylsilanes. (*E*)-Octenylsilane (**1e**) added across **2a** smoothly in an exclusive *cis* fashion to give highly substituted 1,3-diene **3ea** in an excellent yield (entry 5). Silyl-protected hydroxy, cyano, and ester functionalities with an acidic hydrogen were tolerated (entries 7–9), whereas the yield of chloro-substituted 1,3-diene **3fa** was modest due to low conversions of substrates (entry 6). (*Z*)-Propenylsilane **1j** and isomeric styrylsilanes, **1k** and **1l**, underwent the addition reaction in stereo- and regiospecific manners (entries 10–12). Since a wide variety of alkenylsilanes with various substitution patterns are readily available in a predictable manner by rich hydrosilylation chemistry,[7] the present protocol is apparently a promising alternative to that using alkenylboronic acids, some of which are known to be thermally unstable.[8] The scope of alkynes was also briefly investigated using **1e** as a coupling partner. The addition across diphenylacetylene (**2b**) was sluggish to give the corresponding adduct in a modest yield due to incomplete conversion of the alkyne (entry 13). Unsymmetrical alkynes **2c** and **2d** underwent the reaction in good yields but to give a mixture of regioisomers (entries 14 and 15). Formation of recoverable and reusable silicon residue **4**[5] in good yields was confirmed by ^{1}H NMR and/or GC analyses of crude products of the respective reaction run.

The catalytic cycle should involve organorhodium species **A**, which then carbometalate alkynes to give alkenylrhodium intermediate **B** (Scheme 1). Protonolysis of the C–Rh bond of **B** and/or **C**, which is derived from 1,4-shift of

SYNLETT 2008, No. 5, pp 0774–0776
Advanced online publication: 26.02.2008
DOI: 10.1055/s-2008-1042812; Art ID: Y0207ST

Table 1 Addition of Organo[2-(hydroxymethyl)phenyl]dimethylsilanes **1** across Alkynes **2**

Entry	1	2	Time (h)	Product	Yield (%)[a]
					
1	**1a**	**2a**	3	R = H: **3aa**	59
2	**1b**	**2a**	1	4-MeO: **3ba**	85
3	**1c**	**2a**	6	4-F: **3ca**	26
4	**1d**	**2a**	0.5	2-Me: **3da**	78
5	**1e**	**2a**	0.5	 **3ea**	97
					
6	**1f**	**2a**	20	FG = Cl: **3fa**	58[b]
7	**1g**	**2a**	1	OTBS: **3ga**	74
8	**1h**	**2a**	1	CN: **3ha**	89
9	**1i**	**2a**	0.5	 **3ia**	91
10	**1j**[c]	**2a**	2	 **3ja**	79[d]
11	**1k**	**2a**	3	 **3ka**	63
12	**1l**	**2a**	0.5	 **3la**	69
13	**1e**	**2b**	102	 **3eb**	54[e]
14	**1e**	**2c**	2	 **3ec**	84[f]
15	**1e**	**2d**	17	 **3ed**	64[g]

[a] Isolated yields based on **2**.
[b] Conversions of **1f** and **2a** were about 60% based on GC and ^{1}H NMR analyses of a crude mixture.
[c] *E*/*Z* = 12:88.
[d] 2*E*/2*Z* = 9:91.
[e] Conversion of **2b** was 89% based on recovered **2b**.
[f] Regioselectivity was 69:31.
[g] Regioselectivity was 76:24.

rhodium,[1a] by the hydroxy group of **1** gives adduct **3** and rhodium alkoxide **D**. Intramolecular transmetalation in **D** would be responsible for regeneration of **A**, giving reusable silicon residue **4**.[5a] A similar sequence involving the reaction of **1** with Rh–OH to form **D** followed by the intramolecular transmetalation to generate **A** would be responsible for the initiation of the catalytic cycle.

The C–Rh bond in alkenylrhodium intermediate **B** participates in another C–C bond-forming event, as is the case with the reactions of arylboronic acids.[2] Thus, the reaction of diyne **5** with **1a** gave substituted 1,3-diene **6** (Equation 2).[2t] In this particular transformation, the use of a phosphine-free rhodium catalyst showed higher reactivity due presumably to the ability of diynes to chelate to a rhodium catalyst as a bidentate ligand and, thus, show a greater reactivity than simple alkynes.

In summary, we have demonstrated that organo[2-(hydroxymethyl)phenyl]dimethylsilanes undergo 1,2-addition reaction across alkynes to give a wide range of substituted ethenes in highly chemo- and stereoselective manners. This protocol provides us with an attractive alternative to the boron-based one in view of the diversity of available alkenylsilanes and the reusability of a silicon residue.

Acknowledgment

We thank Mr. Hidekazu Imanaka for experimental elaboration at the initial stage. This work has been supported financially by a Grant-in-Aid for Creative Scientific Research and that for Priority Areas ‘Synergy of Elements’ from MEXT.

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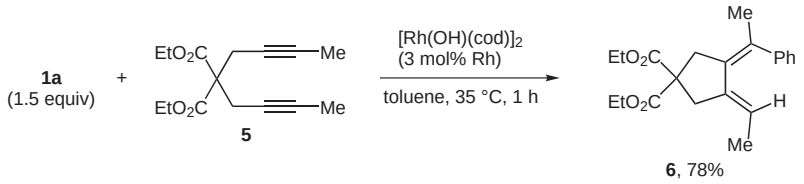
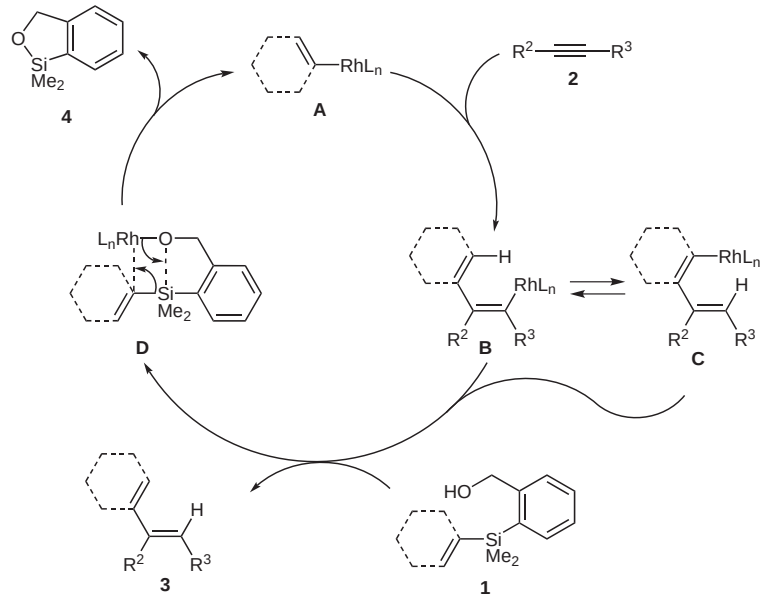


Equation 2



Scheme 1 Plausible mechanism

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(6) **General Experimental Procedure**
A solution of $[Rh(OH)(cod)]_2$ (6.8 mg, 30 μmol Rh) and DPPBz (13.4 mg, 30 μmol) in toluene (1.0 mL) were added **1** (1.50 mmol), **2** (1.00 mmol), and tridecane (an internal standard, 92 mg, 0.50 mmol) sequentially, and the resulting mixture was stirred at 100 °C. After the time specified in Table 1, the mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the corresponding adducts in yields listed in Table 1.

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