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Hydrosilylation of Alkynes with a Cationic Rhodium Species Formed in an Anionic Micellar System

Akinori Sato,[†] Hidenori Kinoshita,[†] Hiroshi Shinokubo,*[,‡,§] and Koichiro Oshima*[,†]

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, and Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

hshino@kuchem.kyoto-u.ac.jp; oshima@fm1.kuic.kyoto-u.ac.jp

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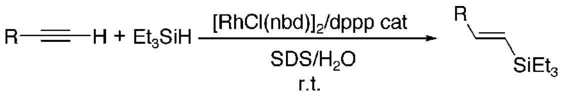
ABSTRACT

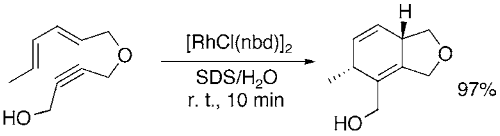


Rhodium-catalyzed hydrosilylation of alkynes in an aqueous micellar system has been developed. A combination of $[RhCl(nbd)]_2$ and bis(diphenylphosphino)propane (dppp) effects (*E*)-selective hydrosilylation in the presence of sodium dodecyl sulfate (SDS) in water. The (*E*)-selectivity strongly indicates the formation of a cationic rhodium species via dissociation of the Rh–Cl bond by the action of anionic micelles. The addition of sodium iodide provided (*Z*)-alkenylsilanes predominantly.

Water is a strongly coordinating solvent for ionic solutes. Due to its large dielectric constant (ϵ), it weakens coulombic interaction between anions and cations. In water, consequently, ionic compounds usually dissociate to their component ions in hydrated forms.

We have recently found that mixing $[RhCl(nbd)]_2$ and an anionic surfactant, sodium dodecyl sulfate (SDS), in water afforded a clear yellow homogeneous solution, although the rhodium chloride dimer itself is insoluble in water.[1] The combination of $[RhCl(nbd)]_2$−SDS in water provides a highly reactive catalyst for intramolecular [4 + 2] annulation of 2,4-dienyl propargyl ethers without the use of any phosphine ligands (Scheme 1). We have proposed formation of a cationic rhodium species in this aqueous reaction system on the basis of the detection of chloride ion by the electrode analysis (eq 1). Because cationic rhodium catalysts are frequently employed as a homogeneous catalyst in a number of transformations in organic synthesis,[2] we explored further the utility of the $[RhCl(nbd)]_2$−SDS combination in aqueous reactions.[3−5]

Scheme 1



$$[RhCl(nbd)]_2 + H_2O \xrightarrow{SDS} [Rh(nbd)(H_2O)_n]^+ + [Cl(H_2O)_m]^- \quad (1)$$

Transition metal-catalyzed hydrosilylation of alkenes and alkynes has been extensively investigated and has found

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[†] Graduate School of Engineering.

[‡] Graduate School of Science.

[§] PRESTO, Japan Science Technology Agency (JST).

(1) Motoda, D.; Kinoshita, H.; Shinokubo, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1860.

(2) (a) Suginome, M.; Ito, Y. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L., Ed.; Wiley: Chichester, 1995; p 426. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3090.

(3) For the use of surfactants in organic synthesis, see: Kobayashi, S.; Manabe, K. *Acc. Chem. Res.* **2002**, *35*, 209.

(4) For transition metal-catalyzed reactions in aqueous media, see: (a) Sinou, D. In *Modern Solvent in Organic Synthesis*; Knochel, P., Ed.; Springer-Verlag: Berlin, 1999; p 41. (b) Cornils, B.; Herrmann, W. A. *Aqueous-Phase Organometallic Chemistry*; Wiley-VCH: Weinheim, 1998. (c) Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; John Wiley: New York, 1997.

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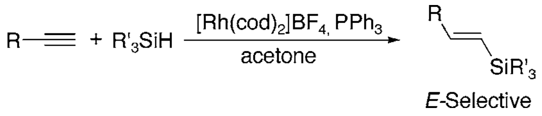
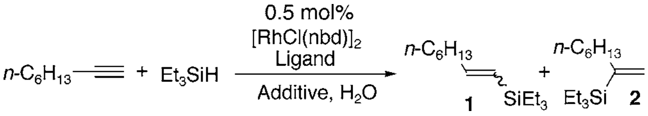
widespread application from asymmetric synthesis to material science.[6,7] A variety of transition metal complexes catalyze this process, and platinum and rhodium catalysts are most frequently employed. Among them, cationic rhodium complexes have achieved high regio- and stereoselectivity in hydrosilylation of terminal alkynes (Scheme 2).[8] This process exhibits high (*E*)-selectivity, whereas neutral rhodium complex-catalyzed hydrosilylation usually provides (*Z*)-alkenylsilanes predominantly.[9] We anticipated that a cationic rhodium species formed from the $[RhCl(nbd)]_2$−SDS combination in aqueous media would also exhibit (*E*)-stereoselectivity in hydrosilylation of alkynes.

Scheme 2



The aqueous rhodium catalyst was prepared by just mixing $[RhCl(nbd)]_2$ (0.005 mmol) and SDS (0.5 mmol) in degassed water (2.5 mL) at room temperature. After stirring for 10 min, the rhodium complex was cleanly dissolved to afford a clear light yellow solution. Then, 1-octyne (1.0 mmol) and triethylsilane (1.1 mmol) were sequentially introduced. The reaction mixture was stirred for 3 h, and then extracted with ethyl acetate. The reaction provided only polymeric material, and none of alkenylsilanes could be isolated (Table 1, entry 1). We then examined the addition of phosphine ligands, because the desired alkenylsilane **1** was obtained by the use of triphenylphosphine (entry 2). Bis(diphenylphosphino)propane (dppp) worked nicely to provide alkenylsilane **1** with high stereoselectivity, although a minor amount of the regioisomer **2** was obtained (entry 4). A water-soluble phosphine, the trisodium salt of tris(*m*-sulfonatophenyl)phosphine (tppts), which is employed in a number of aqueous rhodium-catalyzed reactions, was not effective (entry 7). Interestingly, the use of a neutral surfactant, Triton X-100, resulted in nonstereoselective hydrosilylation (entry 8). A cationic surfactant, methyltrioctylammonium chloride, provided none of the hydrosilylation products (entry 9). Furthermore, sodium methyl sulfate instead of SDS yielded a trace of the desired products (entry 10). The use of anionic surfactant is essential for the high stereoselectivity. It is also noteworthy that the reaction in acetone did not show any significant stereoselectivity (entries 11 and 12).

Table 1. Rhodium-Catalyzed Hydrosilylation of 1-Octyne in Water[a]



entry	ligand	additive	yield (%) (*E*)-1	(*Z*)-1	2
1	none	SDS			
2[b]	PPh_3	SDS	46	11	
3	dppe	SDS	59	0	2
4	dppp	SDS	77	0	3
5	dppb	SDS	76	7	3
6	dppf	SDS	56		
7[b]	tppts	SDS			
8	dppp	Triton-X100	53	23	
9	dppp	Oct_3NMeCl			
10	dppp	$MeOSO_3Na$	0.6	0.3	
11[c]	dppp	SDS	39	38	1
12[c]	dppp	none	36	33	2

[a] Reaction conditions: $[RhCl(nbd)]_2$ (0.005 mmol), 1-octyne (1.0 mmol), triethylsilane (1.1 mmol), additive (0.5 mmol), diphosphine (0.013 mmol), water (2.5 mL), room temperature, 3 h. [b] Monodentate phosphine (0.02 mmol) was employed. [c] Reaction was carried out in acetone instead of water.

Table 2 summarizes the results of hydrosilylation with a variety of alkynes in water under catalysis of the $[RhCl(ndb)]_2$−SDS combination. Alkynes with bulky substituents also yielded the products with high stereoselectivity, although a prolonged reaction time was required (entries 2 and 3). The use of aromatic alkynes afforded low yields due to the concomitant polymerization of the alkynes (entries 4 and 5). The reaction was compatible with functionalities such as alcohol, ether, ester, and carboxylic acid. Internal alkynes also provided the desired products with high stereoselectivity (entries 14 and 15). The solubility of alkynes in water seems to be related with the reaction efficiency. The use of very water-soluble alkynols resulted in lower yields (entries 6−9). We believe that the reaction proceeds in a micelle formed from SDS in water (vide infra), and a water-soluble substrate

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(5) For recent examples of rhodium-catalyzed reactions in aqueous media, see: (a) Dwars, T.; Oehme, G. *Adv. Synth. Catal.* **2002**, *344*, 239. (b) Dwars, T.; Schmidt, U.; Fischer, C.; Grassert, I.; Kempe, R.; Fröhlich, R.; Drauz, K.; Oehme, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 2851. (c) Selke, R.; Holz, J.; Riepe, A.; Börner, A. *Chem. Eur. J.* **1998**, *4*, 769. (d) Ludwig, M.; Kadyrov, R.; Fiedler, H.; Haage, K.; Selke, R. *Chem. Eur. J.* **2001**, *7*, 3298. (e) Fuji, K.; Morimoto, T.; Tsutsumi, K.; Kakiuchi, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2409. (f) Kinoshita, H.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2003**, *125*, 7784. (g) Lautens, M.; Roy, A.; Fukuoka, K.; Fagnou, K.; Martín-Matute, B. *J. Am. Chem. Soc.* **2001**, *123*, 5358. (h) Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2409. (i) Itooka, R.; Iguchi, Y.; Miyaura, N. *Chem. Lett.* **2001**, 722. (j) Yonehara, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 9381. (k) Huang, T.; Meng, Y.; Venkatraman, S.; Wang, D.; Li, C.-J. *J. Am. Chem. Soc.* **2001**, *123*, 7451. (l) Amengual, R.; Michelet, V.; Genêt, J.-P. *Tetrahedron Lett.* **2002**, *43*, 5905. (m) Amengual, R.; Michelet, V.; Genêt, J.-P. *Synlett* **2002**, 1791. (n) Pucheault, M.; Darses, S.; Genêt, J.-P. *Eur. J. Org. Chem.* **2002**, 3552.

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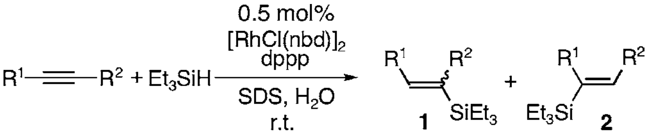
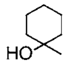
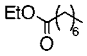
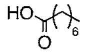
(7) Hydrosilylation in aqueous media has been reported recently. (a) Wu, W.; Li, C. J. *Chem. Commun.* **2003**, 1668. (b) Motoda, D.; Shinokubo, H.; Oshima, K. *Synlett* **2002**, 1529.

(8) (a) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Chem. Commun.* **1993**, 1319. (b) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2909. (c) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045.

(9) (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (b) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1974**, *66*, C14. (c) Doyle, M. P.; High, K. G.; Nesloney, C. L.; Clayton, T. W., Jr.; Lin, J. *Organometallics* **1991**, *10*, 1225.

Table 2. $[RhCl(nbd)]_2$–SDS-Catalyzed Hydrosilylation of Alkynes in Water[a]



entry	R^1	R^2	yield (%)		
			(*E*)-1	**(*Z*)-1**	**2**
1	*n*-$C_{10}H_{21}$	H	71	2	3
2	*t*-Bu	H	55	–	–
3[b]	Me_3Si	H	70	–	–
4	Ph	H	35	–	–
5	$CF_3(C_6H_4)$	H	59	–	1
6	$HOCH_2$	H	58	–	–
7	$HO(CH_2)_2$	H	67	1	5
8	$HO(CH_2)_3$	H	85	–	5
9		H	85	–	–
10	*t*-$BuMe_2SiO(CH_2)_3$	H	81	2	4
11	$BnO(CH_2)_3$	H	87	–	4
12		H	79	–	4
13		H	72	–	3
14	Ph	Ph	66	–	–
15	Et	Et	53	–	–

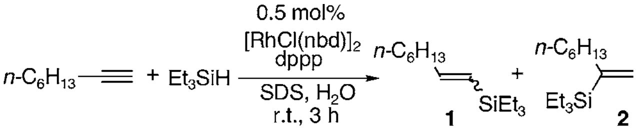
[a] Reaction conditions: $[RhCl(nbd)]_2$ (0.005 mmol), alkyne (1.0 mmol), triethylsilane (1.1 mmol), SDS (0.5 mmol), dppp (0.013 mmol), water (2.5 mL), room temperature, 3 h. [b] Reaction time was 16 h.

is predominantly present in the exterior phase of the micelle to lower the reaction rate.

From these experimental results, it is obvious that SDS plays a key role in this hydrosilylation reaction. We then investigated the effect of the concentration and amount of SDS on the yield and selectivity (Scheme 3). The yield and selectivity stay virtually constant with variations in the amount of SDS from 100 to 2.5 mol %. The efficiency and the stereoselectivity of the reaction decreased dramatically at 1.25 mol %. Meanwhile, in the presence of the same amount of SDS and $[RhCl(nbd)]_2$, a change in the concentration of SDS also has a significant effect.[10] Both the concentration and amount of SDS is essential. On the basis of these findings as well as the fact that sodium methyl sulfate does not work (Table 1, entry 10), we concluded that the formation of anionic micelle in water is critical for the generation of a cationic rhodium species that catalyzes (*E*)-selective hydrosilylation.

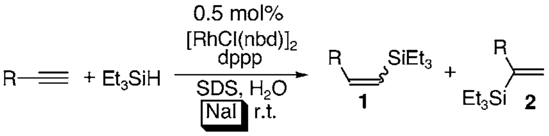
In the presence of halide ions, dissociation of the rhodium–chloride bond (eq 1) would be unfavorable, and the observed selectivity of alkenylsilanes would be affected. In fact, the addition of excess sodium chloride (2.0 equiv) reduced the stereoselectivity (*E*/*Z* = 90/10). We then examined the salt effect on the selectivity and found that sodium iodide (1.0 equiv) inverted the sense of stereoselectivity to provide (*Z*)-isomers predominantly (Table 3). Mori and Hiyama have already reported that the addition of sodium iodide to $RhCl(PPh_3)_3$ resulted in (*Z*)-selective hydrosilylation.[11] Imperfect selectivity might indicate that a cationic rhodium species that provides the (*E*)-isomer is still present in the reaction system even in the presence of sodium iodide.

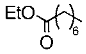
Scheme 3



amount of SDS	H_2O	[SDS]	1-(*E*)	1-(*Z*)	2
100 mol%	2.5 mL	400×10^{-3} M	77%	1%	3%
50 mol%	2.5 mL	200×10^{-3} M	75%	–	3%
10 mol%	2.5 mL	40×10^{-3} M	70%	–	3%
2.5 mol%	2.5 mL	10×10^{-3} M	69%	–	4%
2.5 mol%	3.5 mL	7×10^{-3} M	69%	3%	4%
2.5 mol%	5 mL	5×10^{-3} M	49%	7%	4%
1.25 mol%	2.5 mL	5×10^{-3} M	29%	13%	3%

Table 3. $[RhCl(nbd)]_2$–SDS–NaI-Catalyzed Hydrosilylation of Alkynes in Water[a]



entry	R	time (h)	yield (%)		
			(*E*)-1	**(*Z*)-1**	**2**
1	*n*-C_6H_{13}	3	5	70	–
2	*n*-$C_{10}H_{21}$	20	11	65	2
3		27	11	55	–
4	*t*-$BuMe_2SiO(CH_2)_3$	63	20	50	1
5	$BnO(CH_2)_3$	22	21	51	2

[a] Reaction conditions: $[RhCl(nbd)]_2$ (0.005 mmol), alkyne (1.0 mmol), triethylsilane (1.1 mmol), SDS (0.5 mmol), dppp (0.01 mmol), NaI (1.0 mmol), water (2.5 mL), room temperature.

In conclusion, we have developed a stereoselective rhodium-catalyzed hydrosilylation of alkynes in aqueous media. A combination of $[RhCl(nbd)]_2$ and bis(diphenylphosphino)-propane (dppp) effects (*E*)-selective hydrosilylation in the presence of SDS in water. The observed (*E*)-selectivity indicates the formation of cationic rhodium species. Finally,

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[10] Critical micelle concentration (cmc) of SDS without organic substrates is 8.1×10^{-3} M.

[11] Mori, A.; Takahashi, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443.

the selectivity can be switched from *E* to *Z* in the presence of sodium iodide.

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Supporting Information Available: Experimental procedures and compound data. This material is available free of charge via the Internet at http://pubs.acs.org.

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