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Tandem Hydrosilylation/*o*-C−H Silylation of Arylalkynes Catalyzed by Ruthenium Bis(silyl) Aminophosphine Complexes

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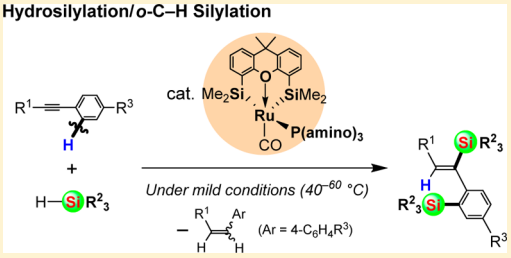
Supporting Information

ABSTRACT: An unprecedented reaction via consecutive trans-selective hydrosilylation and *o*-C−H silylation of arylalkynes with hydrosilanes was developed by use of ruthenium complex catalysts Ru{κ^3(*Si*,*O*,*Si*)-xantsil}(CO)(PR_3) (R = NC_4H_8 (**1-Pyrr**), NC_5H_{10} (**1-Pip**); xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)). This reaction proceeded with gentle heating at 40−60 °C and afforded novel 2,α-bis-silylated (*Z*)-stilbene or (*Z*)-styrene derivatives **2** together with an equimolar amount of (*E*)-/(*Z*)-arylalkenes as byproducts. The selectivity of the formation of **2** reached a maximum by employing catalyst **1-Pyrr** ligated by the less bulky triaminophosphine $P(NC_4H_8)_3$ and hydrosilane $HSiMe(OSiMe_3)_2$ having moderately bulky and electron withdrawing substituents.

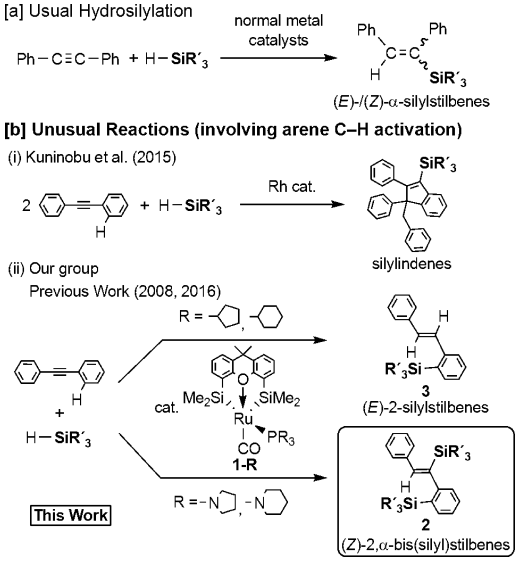


Metal-catalyzed Si−C(sp^2) bond-forming reactions for simple hydrocarbons with easily available hydrosilanes[1,2] have attracted enormous attention as a straightforward method to synthesize silyl-functionalized organic molecules such as silylalkenes and silylarenes. This is mainly because these silyl compounds are useful as organometallic reagents[3] as well as functional materials.[4] Among these reactions, hydrosilylation of alkynes can be regarded as the most extensively studied process for the synthesis of silylalkenes.[1a] For the synthesis of silylarenes, dehydrogenative C−H silylation of arenes with hydrosilanes has made a major advance in recent decades.[2] In this paper, we will present a new catalytic reaction involving both of these two types of silylation processes in one cycle to produce 2,α-bis-silylated stilbene or styrene derivatives.[5]

Transition-metal-catalyzed reactions of diarylalkynes such as diphenylacetylene with hydrosilanes usually afford hydrosilylated (*E*)-/(*Z*)-stilbene derivatives (Scheme 1a),[1a,6] but two unusual reactions using the same substrates have recently been discovered. Kuninobu and Sueki have developed a rhodium-catalyzed reaction of diphenylacetylene with tertiary silanes in a 2:1 molar ratio to produce silylindene derivatives (Scheme 1b(i)).[7] This catalytic reaction involves activation of an arene C−H bond as a key step. We have previously developed a ruthenium-catalyzed *o*-C−H silylation/hydrogenation reaction of diphenylacetylene with tertiary silanes to give (*E*)-2-silylstilbenes **3** (Scheme 1b(ii)).[8] This reaction involving arene C−H bond activation is promoted by 16-electron ruthenium complexes bearing a strongly electron donating bis(silyl) ligand, i.e. Ru{κ^3(*Si*,*O*,*Si*)-xantsil}(CO)(PR_3) (xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl); R = Cyp (**1-Cyp**), Cy (**1-Cy**))[8b,9] and proceeds under mild conditions (room temperature to 40 °C).[10] The reaction rates and yields of **3** were found to be highly dependent on the bulkiness of trialkylphosphine ligands.

During the course of elucidating the electronic and steric effects of the phosphine ligands of **1-R** on their catalytic performance, we employed slightly less electron donating[11] and less bulky[11b,12] triaminophosphines ($P(NC_4H_8)_3$ and $P(NC_5H_{10})_3$) having five- and six-membered-ring substituents instead of trialkylphosphines ($PCyp_3$ and PCy_3). By this approach, we unexpectedly found a new reaction pathway of diphenylacetylene with tertiary silanes catalyzed by the aminophosphine complexes **1-R** (R = NC_4H_8, NC_5H_{10}) to give (*Z*)-2,α-bis(silyl)stilbenes **2** under mild conditions (40 °C) (Scheme 1b(ii)). Novel organosilicon compounds **2** are considered to

Scheme 1. Reaction Patterns of Diphenylacetylene with Hydrosilanes Catalyzed by Transition-Metal Complexes



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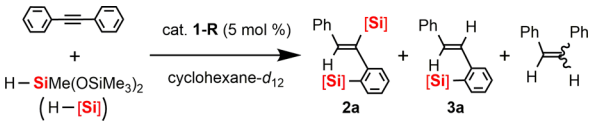
form via consecutive trans-selective hydrosilylation of the C≡C triple bond and *o*-C−H silylation. Herein we report the details of the research on this hydrosilylation/*o*-C−H silylation reaction.

Bis(silyl) aminophosphine complexes Ru{κ^3(*Si*,*O*,*Si*)-xantsil}(CO)(PR_3) (R = NC_4H_8 (**1-Pyrr**), NC_5H_{10} (**1-Pip**)) were synthesized by a ligand substitution reaction of the η^6-toluene complex Ru{κ^2(*Si*,*Si*)-xantsil}(CO)(η^6-toluene) with the corresponding phosphines PR_3 in a manner similar to that for the $PCyp_3$ analogue **1-Cyp**[8b] in 69% (**1-Pyrr**) and 60% (**1-Pip**) yields (eqs S1 and S2 in the Supporting Information. Complexes **1-Pyrr** and **1-Pip** were characterized by NMR, IR, and mass spectroscopy and X-ray crystallography (see the Supporting Information). Crystal structures of **1-Pyrr** and **1-Pip** (Figures S2 and S3, respectively, in the Supporting Information) revealed that these molecules adopt a square-pyramidal geometry (the apical position was occupied by a silyl silicon atom), which are similar to those of the trialkylphoshine analogues **1-Cyp** and **1-Cy**.

Reaction of PhC≡CPh with 1.1 equiv of $HSiMe(OSiMe_3)_2$ catalyzed by trialkylphosphine complexes **1-Cy** and **1-Cyp** gave (*E*)-2-silylstilbene **3a** as the main product (Table 1, entries 1 and 2). However, in the case of **1-Cyp** bearing $PCyp_3$ with a smaller Tolman cone angle (165° < 170° (for PCy_3)),[12a,b] the novel (*Z*)-2,α-bis(silyl)stilbene **2a** was also formed as a minor product. During the formation of **2a**, a part of the PhC≡CPh was consumed as a hydrogen acceptor, and (*E*)-/(*Z*)-stilbene was formed in an amount equimolar with **2a**. The selectivity of the formation of **2a** was significantly improved by use of **1-Pyrr** and **1-Pip** having slightly less electron-donating[11] P(amino)$_3$ ligands (see entries 3 and 4) and especially in the case of **1-Pyrr** bearing less bulky $P(NC_4H_8)_3$ (cone angle ca. 145°),[12c] **2a** was formed in 50% (quantitative) yield based on PhC≡CPh. Bis(silyl)stilbene **2a** is considered to be produced via trans-selective hydrosilylation of the C≡C triple bond and *o*-C−H silylation of an aryl group in a consecutive process. This C−H silylation proceeds under relatively mild conditions (40 °C) in comparison with those of metal-catalyzed dehydrogenative arene C−H silylation using $HSiMe(OSiMe_3)_2$ (45−200 °C).[13]

To explore the scope of substrates, we examined the reactions of some arylalkynes, i.e. diarylalkynes ArC≡CAr (Ar = Ph, *p*-Tol, *o*-Tol, C_6H_4-4-OMe, C_6H_4-4-CF_3) and monoarylalkyne EtC≡CPh, with several hydrosilanes $HSiR^2_3$ (R^2_3 = Me(OSiMe$_3$)$_2$, (OEt)$_3$, (OSiMe$_3$)$_3$, (OMe)$_3$, Me_2Ph, Me_2Et) in the presence of 5 mol % of **1-Pyrr** (Table 2). Among the reactions of PhC≡CPh with $HSiR^2_3$ (see entries 1−6), those with moderately bulky hydrosilanes having electron-withdrawing $OSiMe_3$ and OEt groups resulted in high selectivity of the formation of (*Z*)-2,α-bis(silyl)stilbenes **2a**,**b** (entries 1 and 2). In contrast, the reaction with bulkier $HSi(OSiMe_3)_3$ produced (*E*)-2-silylstilbene **3c** quantitatively without production of bis(silyl)-stilbene **2c** (entry 3). It is worth noting that the reaction with less bulky $HSi(OMe)_3$ led to decomposition of catalyst **1-Pyrr**, and no detectable silylated stilbene derivatives were formed (entry 4). $HSiMe_2Ph$ and $HSiMe_2Et$, which have no siloxy or alkoxy groups, are also applicable as substrates to the hydrosilylation/*o*-C−H silylation in modest selectivity (entries 5 and 6). The scope of arylalkynes was also investigated by use of $HSiMe(OSiMe_3)_2$ (see entries 7−11). The reactions of para-substituted diarylalkynes (Ar = *p*-Tol, C_6H_4-4-OMe, C_6H_4-4-CF_3) with HSiMe-

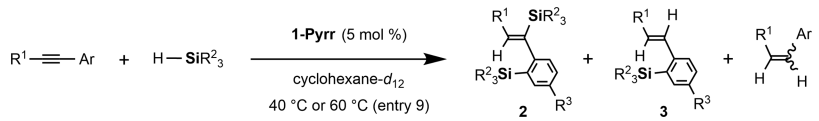
Table 1. Reaction of PhC≡CPh with $HSiMe(OSiMe_3)_2$ Catalyzed by Complexes 1-R



				NMR yield (%)[a]		
entry	cat. **1-R**	temp (°C)	time (h)	**2a**	**3a**	(*E*)-/(*Z*)-stilbene
1[b]	**1-Cy**	40	6		74	trace (<1)
2[b]	**1-Cyp**	room temp	2	6	46	6
3	**1-Pip**	40	2	21	19	21
4	**1-Pyrr**	40	0.5	50		50

[a]Based on PhC≡CPh. [b]The hydrosilylation product (*E*)-Ph(H)C=C(Ph)$SiMe(OSiMe_3)_2$ was also formed as a minor product (see the Supporting Information).

Table 2. Scope of Substrates for Hydrosilylation/*o*-C−H Silylation Catalyzed by 1-Pyrr



					NMR yield (isolated yield) (%)[a]		
entry	alkyne substituents R^1, Ar	hydrosilane ($HSiR^2_3$)	major product	time (h)	**2**	**3**	(*E*)-/(*Z*)-alkene
1	Ph, Ph	$HSiMe(OSiMe_3)_2$	**2a**	0.5	50 (32[d])		50
2[b]	Ph, Ph	$HSi(OEt)_3$	**2b**	22	30 (28[d])		30
3	Ph, Ph	$HSi(OSiMe_3)_3$	**3c**	0.25		~100 (84)	
4[c]	Ph, Ph	$HSi(OMe)_3$		24			
5[b]	Ph, Ph	$HSiMe_2Ph$	**2d**	7	20 (20[d])	8	20
6[b]	Ph, Ph	$HSiMe_2Et$	**2e**	6	19 (18)	4	19
7	*p*-Tol, *p*-Tol	$HSiMe(OSiMe_3)_2$	**2f**	20	50 (36)		50
8[e]	*o*-Tol, *o*-Tol	$HSiMe(OSiMe_3)_2$		24			
9[f,g]	C_6H_4-4-OMe, C_6H_4-4-OMe	$HSiMe(OSiMe_3)_2$	**2g**	4	25 (25)		25
10[b]	C_6H_4-4-(CF_3), C_6H_4-4-(CF_3)	$HSiMe(OSiMe_3)_2$	**2h**	20	10 (6)	4	10
11	Et, Ph	$HSiMe(OSiMe_3)_2$	**2i**	96	30 (24[d])		30

[a]Based on arylalkyne. [b]Hydrosilylation products (*E*)-/(*Z*)-Ar(H)C=C(Ar)SiR^2_3 were also formed (see the Supporting Information). [c]Catalyst deactivation. [d]Cyclohexane or hexane was used as a solvent instead of cyclohexane-d_{12}. [e]Since no reaction occurred at 40 °C, the reaction was performed at 70 °C. [f]The reaction was conducted at 60 °C because the reaction rate was too slow at 40 °C. [g]Some unidentified minor products were also formed.

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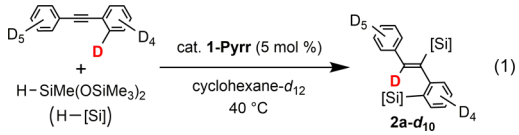
$(OSiMe_3)_2$ gave bis(silyl)stilbenes **2f–h**, although a longer reaction time and/or higher reaction temperature (60 °C for Ar = C_6H_4-4-OMe) was required in comparison with the reaction of entry 1 for PhC≡CPh (entries 7, 9, and 10). When ortho-substituted di-*o*-tolylacetylene was used, no reaction proceeded even at 70 °C (entry 8) probably because the steric hindrance of the *o*-Me groups of the alkyne inhibits the coordination of the C≡C triple bond to the Ru center of **1-Pyrr**. Monoarylalkyne EtC≡CPh also reacted with $HSiMe(OSiMe_3)_2$ in the presence of **1-Pyrr** to give (*Z*)-2,*α*-bis(silyl)styrene **2i** in 30% NMR yield (entry 11), although the reaction time (96 h) was much longer than that for PhC≡CPh (0.5 h, entry 1).[14] Applying reaction conditions similar to those of entry 1 using 2 mol % of **1-Pyrr** and hexane (solvent), we succeeded in gram-scale synthesis of **2a** that gave 1.03 g of **2a** in 42% isolated yield (see the Supporting Information for details).

Novel organosilicon compounds **2a,b,d–i** were fully characterized by spectroscopy and elemental analysis and by crystallography for **2d** (see the Supporting Information). The ^{1}H NMR spectra of (*Z*)-2,*α*-bis(silyl)stilbenes **2a,d–g** show one alkenyl proton signal as a singlet in the range of 7.11–7.22 ppm. Two sets of signals assignable to two inequivalent silyl groups are observed in the ^{1}H and ^{29}Si{^{1}H} NMR spectra of **2a,b,d–i**. The molecular structure of **2d** (SiR^2_3 = $SiMe_2Ph$) was also determined by single-crystal X-ray analysis, showing that **2d** has a *trans*-stilbene skeleton with two silyl groups located at the 2-aryl and *α*-alkenyl carbons (Figure S4 in the Supporting Information).[15,16]

To determine the source of the alkenyl hydrogen of (*Z*)-2,*α*-bis(silyl)stilbenes **2**, we examined a deuterium labeling experiment, i.e. the reaction of PhC≡CPh-d_{10} with $HSiMe(OSiMe_3)_2$ catalyzed by complex **1-Pyrr**, under conditions identical with those for the corresponding reaction of PhC≡CPh (eq 1). As a

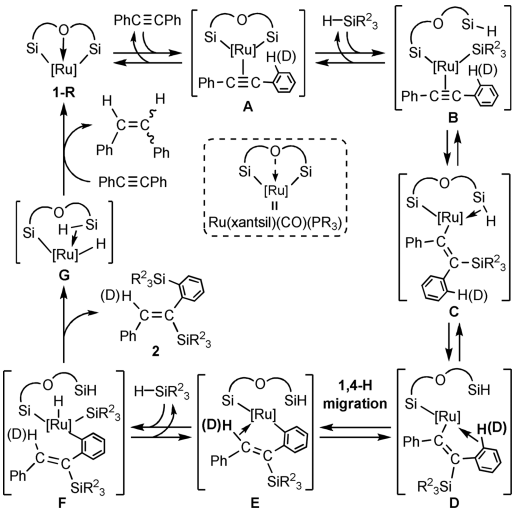


(1)

result, decadeuterated **2a-d_{10}** was formed in 50% NMR yield via selective deuterium migration from the ortho aromatic carbon to the *β*-alkenyl carbon (1,4-hydrogen migration accompanied by concurrent migration of ruthenium,[17] vide infra). The kinetic isotope effect on the hydrosilylation/*o*-C–H silylation was also investigated by ^{1}H NMR monitoring of the two separate reactions with PhC≡CPh and PhC≡CPh-d_{10} (Figure S1 in the Supporting Information). The k_H/k_D value was calculated to be 1.37(4) from the rate constants k_H(obs) = 0.177(4) and k_D(obs) = 0.129(3) that were estimated by the initial rate method.[18]

Although experimental investigations for understanding the mechanism of the hydrosilylation/*o*-C–H silylation are insufficient,[19,20] we tentatively suggest a possible catalytic cycle for this reaction as illustrated in Scheme 2. In the first stage, arylalkyne coordinates to the Ru center of **1-R** via dissociation of the xantsil oxygen to give η^2-alkyne complex **A**.[8] Si–H oxidative addition of hydrosilane $HSiR^2_3$ to **A** followed by Si–H reductive elimination of a silyl ligand moiety of xantsil then occurs to generate intermediate **B**. Insertion of the C≡C triple bond into the Ru–SiR^2_3 bond followed by *E*-/*Z*-isomerization[21] of the resulting (*β*-silyl)alkenyl ligand of intermediate **C** generates alkenyl complex **D**. Subsequently, 1,4-migration of an ortho hydrogen of the phenyl group at the position *β* to the Ru-bound alkenyl carbon occurs to give aryl complex **E**. Related 1,4-

Scheme 2. Proposed Mechanism for Hydrosilylation/*o*-C–H Silylation of Arylalkynes[a]



[a]PhC≡CPh was used as a representative example of arylalkynes in the mechanism.

hydrogen (or -metal) migration in the conversion from ruthenium(II) alkenyl to aryl complexes has been reported by Ishii and co-workers.[17a] Si–H oxidative addition of the second hydrosilane molecule then forms intermediate **F**, and subsequent Si–C reductive elimination gives product **2** accompanied by hydrido η^2-silane complex **G**. Finally, the second alkyne molecule accepts two hydrogen atoms from **G** to regenerate **1-R**.[22]

We have previously proposed that a possible mechanism of the *o*-C–H silylation/hydrogenation reaction to give (*E*)-arylalkene **3** involves *o*-C–H oxidative addition of the coordinated arylalkyne in η^2-alkyne complex intermediate **A**.[8] This C–H cleavage is considered to compete against the Si–H oxidative addition of hydrosilane to **A** in Scheme 2, giving bis-silylated product **2**. We speculate that the C–H cleavage would be slowed down if the Ru–xantsil catalyst contains a less-electron-donating triaminophosphine. On the other hand, the Si–H oxidative addition of hydrosilane to **A** would be facilitated in the case of moderately bulky $HSiMe(OSiMe_3)_2$ and $HSi(OEt)_3$, having electron-withdrawing groups. These speculations are consistent with an increase in the selectivity of **2** vs **3** when catalysts **1-Pyrr** and **1-Pip** and the above hydrosilanes were used.

In summary, the tandem trans-selective hydrosilylation and *o*-C–H silylation of arylalkynes with tertiary silanes was achieved by use of the ruthenium catalyst **1-Pyrr** or **1-Pip** containing the xanthene-based bis(silyl) ligand xantsil and an aminophosphine ligand to produce 2,*α*-bis-silylated (*Z*)-stilbene or (*Z*)-styrene derivatives **2**. In this reaction, both aryl and alkenyl carbons were silylated regioselectively under mild conditions (40–60 °C).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00528.

Experimental procedures, crystal structures, and NMR spectra of new compounds (PDF)

Accession Codes

CCDC 1552334–1552336 contain the supplementary crystallographic data for this paper. These data can be obtained free of

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charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(12) Reported Tolman cone angles PCy_3 170°, $PCyp_3$ 165°, and $P(NC_4H_8)_3$ ca. 145° show that the bulkiness of these phosphines are in the order $PCy_3 > PCyp_3 > P(NC_4H_8)_3$. See: (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Chaplin, A. B.; Weller, A. S. *J. Organomet. Chem.* **2013**, *730*, 90. (c) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696.

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(14) We also examined the reactions of MeC≡CPh and HC≡CPh with $HSiMe(OSiMe_3)_2$, but in both cases, target 2,α-bis(silyl)styrenes were not obtained (see the Supporting Information).

(15) The final *R* factors for the crystal structure analysis of **2d**, i.e. R1 ($I > 2\sigma(I)$) = 0.1247 and wR2 (all data) = 0.2825, are slightly higher than the usual upper limits of 0.10 and 0.25, respectively, for a reliable crystallographic model. This is possibly caused by the low quality of the single crystal (a thin plate). Nevertheless, this analysis clearly showed that **2d** adopts a 2,α-bis-silylated *trans*-stilbene structure with reasonable bond distances and angles (see the Supporting Information for details).

(16) Crystals of (*Z*)-2,α-bis(silyl)stilbene **2d** showed blue fluorescence upon irradiation with 254 nm UV light.

(17) (a) Takano, K.; Ikeda, Y.; Kodama, S.; Ishii, Y. *Chem. Commun.* **2015**, *51*, 4981 and references therein. (b) Ikeda, Y.; Takano, K.; Kodama, S.; Ishii, Y. *Chem. Commun.* **2013**, *49*, 11104. (c) Ma, S.; Gu, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 7512. (d) Shi, F.; Larock, R. C. *Top. Curr. Chem.* **2009**, *292*, 123.

(18) The k_H/k_D value is small but significantly larger than unity, implying that the C−H cleavage process (1,4-H migration) would affect the turnover-limiting step (TLS) in some way. We are thinking at present that the C−H cleavage may be involved in the TLS or occur in the pre-equilibrium steps of the TLS. See also: Simmons, E. M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 3066.

(19) Stoichiometric reaction of complex **1-Pip** with PhC≡CPh (1 equiv) for 24 h at room temperature consumed ca. 50% of **1-Pip** and gave a complicated mixture of unidentified products and **1-Pip** (see the Supporting Information). That of **1-Pip** with $HSiMe(OSiMe_3)_2$ (1 equiv) at room temperature was slower, which consumed only 4% of **1-Pip** after 24 h to give 9,9-dimethyl-4,5-bis(dimethylsilyl)xanthene ($xantsilH_2$). On the basis of these results, we proposed a catalytic mechanism that involved the reaction of **1-R** with arylalkyne in the first step as illustrated in Scheme 2.

(20) When the reaction of PhC≡CPh with $HSiMe(OSiMe_3)_2$ catalyzed by **1-Pyrr** (5 mol %) was conducted in the presence of ca. 20 mol % of $P(NC_4H_8)_3$, the reaction rate considerably decreased. This result implies that phosphine dissociation or coordination possibly takes place in the TLS or in the pre-equilibrium of the TLS.

(21) (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (b) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984.

(22) We have previously reported a dehydrogenation reaction of a hydrido(η^2-silane)ruthenium complex by alkene, which is closely related to the last step (from **G** to **1-R**) of the mechanism (Scheme 2). See: Komuro, T.; Arai, T.; Kikuchi, K.; Tobita, H. *Organometallics* **2015**, *34*, 1211.

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