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New hydrosilylation reaction of arylacetylene accompanied by C–H bond activation catalyzed by a xantsil ruthenium complex*

Hiromi Tobita[1,‡], Nobukazu Yamahira[1], Keisuke Ohta[1], Takashi Komuro[1], and Masaaki Okazaki[2]

[1]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan; [2]International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Abstract: A new type of catalytic hydrosilylation of arylalkynes was induced by a 16-electron ruthenium bis(silyl) phosphine complex, resulting in *ortho*-silylation of the aryl group as well as a hydrogenation of the alkyne C≡C bond to give an (*E*)-form of alkene selectively. On the other hand, the same reaction using a related bis(silyl) complex having an η^6-toluene ligand instead of the phosphine ligand as a catalyst led to a normal hydrosilylation reaction to afford silylalkene.

Keywords: hydrosilylation; C–H bond activation; ruthenium complex; reduction; directing group.

INTRODUCTION

Transition-metal-catalyzed silylation of aryl C–H bonds is a valuable reaction for organic synthesis because of the versatility of produced arylsilanes as synthetic intermediates [1]. In this silylation, activation of the aromatic C–H bond by a coordinatively unsaturated complex is a key reaction step. Although several silylation reactions of aromatic compounds have been achieved by use of late transition-metal catalysts, the examples are still limited and, in most cases, high-temperature conditions are required [1–6]. There is also a synthetic challenge: regioselective silylation of substituted arenes [2–6]. As a representative example of this type of reaction, Kakiuchi, Chatani, Murai, and coworkers reported that the reaction of benzene derivatives having a heteroatom-containing directing group with hydrosilane in the presence of ruthenium catalyst and alkene, *tert*-butylethylene or norbornene, at high temperature afforded *ortho*-silylated products selectively in high yield [2–5]. We describe herein that a C≡C triple bond is also effective as another directing group for this type of reaction.

Several years ago, we developed a bis(silyl) chelate ligand xantsil [(9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)] based on a xanthene backbone (Fig. 1) [7,8]. The xantsil ligand has several unique features: (i) xantsil is a rigid chelate ligand, and the chelate effect prevents the easy elimination of silyl groups; (ii) the wide Si–M–Si bite angle prevents the Si–Si reductive elimination; (iii) the silyl ligands work as strong σ-donors with high trans influence; and (iv) the weak M–O dative bond can sta-

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‡Corresponding author

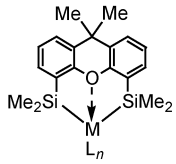


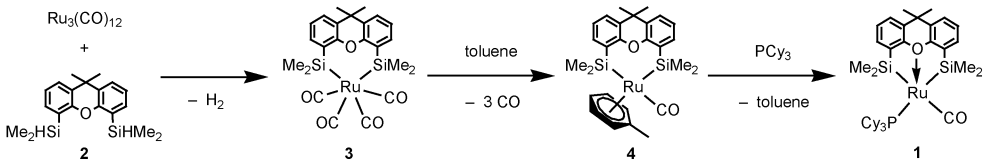
Fig. 1 Xantsil complexes (M = Ru, L_n = various ligands).

bilize coordinatively unsaturated metal center. On the basis of these features, the complexes consisting of the xantsil ligand can possess enhanced reactivity and potential catalytic performance. We recently found that the coordinatively unsaturated ruthenium complex Ru{κ^3(*Si*,*Si*,*O*)-xantsil}(CO)(PCy_3) (**1**) catalyzes a new type of hydrosilylation reaction between a tertiary silane and an arylacetylene under mild heating conditions [9]. In this reaction, an *ortho*-C–H bond of the aryl group in the acetylene is silylated and the C≡C triple bond works as an intramolecular hydrogen acceptor to provide a C=C double bond. The resulting C=C double bond takes (*E*)-configuration selectively.

RESULTS AND DISCUSSION

Preparation of catalysts

The coordinatively unsaturated ruthenium xantsil phosphine complex **1** was synthesized via three reaction steps illustrated in Scheme 1 from $Ru_3(CO)_{12}$ and the ligand precursor xantsilH_2 (**2**) [7,8]. The reaction of $Ru_3(CO)_{12}$ and **2** in toluene at 120 °C for 90 min afforded tetracarbonyl xantsil complex *cis*-Ru{κ^2(*Si*,*Si*)-xantsil}$(CO)_4$ (**3**) in 35 % yield. Complex **3** was then heated in refluxing toluene for 5 h to give the η^6-toluene complex Ru{κ^2(*Si,Si*)-xantsil}(CO)(η^6-toluene) (**4**) in 95 % yield by substitution of three carbonyl ligands with a toluene molecule [7]. The η^6-toluene ligand in **4** is substitution labile and can be substituted cleanly with various ligands at room temperature [8]. We have found that the reaction of **4** with a bulky tricyclohexylphosphine resulted in substitution of one phosphine molecule (2-electron donor) for a toluene ligand (6-electron donor) to give complex **1** [8]. To compensate the decrease of electron count, the bidentate xantsil ligand in **4** is changed to a tridentate ligand in **1**, but still the product **1** has only 16 valence electrons and is coordinatively unsaturated. The second tricyclohexylphosphine molecule was not observed to be coordinated to **1**, probably because the expected product was sterically too congested.



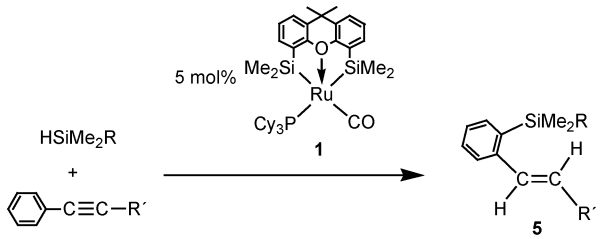
Scheme 1 Synthesis of ruthenium xantsil complexes **3**, **4**, and **1**.

Coordinatively unsaturated complexes are regarded as important intermediates for a variety of catalytic reactions. Therefore, **1** could become a good catalyst for certain transformation reactions. Additionally, coordinatively saturated complex **4** can easily generate coordinatively unsaturated complexes in its reactions because of the lability of the η^6-toluene ligand. Thus, we investigated the hydrosilylation of alkynes using **1** and **4** as catalysts.

Catalytic hydrosilylation of arylacetylenes by ruthenium xantsil complexes

Treatment of the mixture of dimethylphenylsilane and diphenylacetylene with a 5 mol % of **1** in cyclohexane at 40 °C gave an alkene (*E*)-PhC(H)=C(H)(2-$Me_2PhSiC_6H_4$) (**5a**) (Table 1, entry 1) as a main product. The alkene was not a normal hydrosilylation product, but *ortho*-C–H bond activation and silylation of the phenyl group occurred and the C≡C triple bond was reduced to the double bond to give the (*E*)-isomer of **5a** selectively.

Table 1 Hydrosilylation of arylalkynes employing complex **1** as a catalyst.



Entry	Arylalkyne	Hydrosilane	Time (h)	Product	NMR yield (%)	Isolated yield (%)
1	PhC≡CPh	$HSiMe_2Ph$	12	**5a** (R = Ph, R′ = Ph)	84	37
2	PhC≡CPh	$HSiMe_2$(*i*-Pr)	1.5	**5b** (R = *i*-Pr, R′ = Ph)	quant.	83
3	PhC≡CPh	$HSiMe_2Et$	0.5	**5c** (R = Et, R′ = Ph)	quant.	86
4	EtC≡CPh	$HSiMe_2Et$	4	**5d** (R = Et, R′ = Et)	99	52
5	MeC≡CPh	$HSiMe_2Et$	60	**5e** (R = Et, R′ = Me)	95	–

Reaction conditions: alkyne (1 equiv), silane (1–1.2 equiv), **1** (0.05 equiv), 40 °C in cyclohexane or cyclohexane-d_{12}.

The product **5a** was characterized by spectroscopic (NMR, IR, and mass), elemental, and crystallographic analyses. The ^{1}H NMR spectrum in $CDCl_3$ shows two mutually coupled doublet signals at 6.90 and 7.23 ppm with a large coupling constant ($^3J_{HH}$ = 16.0 Hz) assignable to the mutually trans alkenyl protons. The crystal structure of **5a** was determined by the X-ray analysis (Fig. 2) that confirms the silyl group at the *ortho*-position and (*E*)-configuration of the double bond [10].

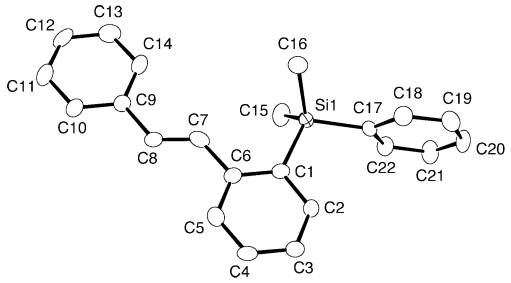
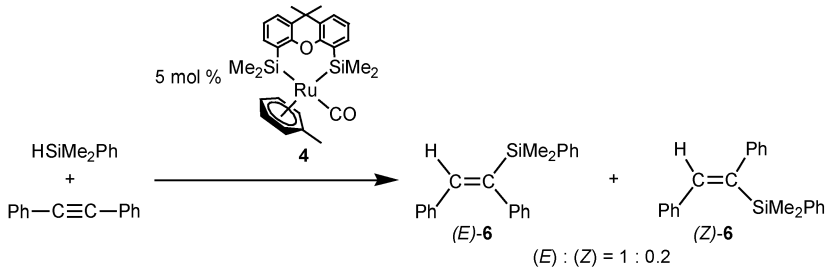


Fig. 2 Crystal structure of **5a** (50 % probability ellipsoids). Hydrogen atoms bound to carbon atoms are omitted for clarity.

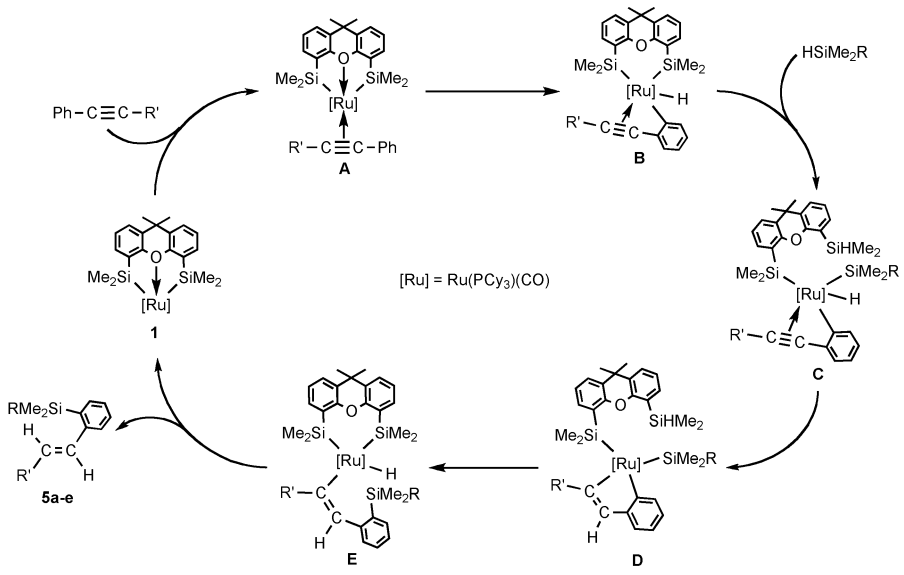
In contrast, when the η^6-toluene complex **4** was used as a catalyst for the same reaction, normal hydrosilylation occurred exclusively to give silylalkene PhCH=C($SiMe_2$Ph)Ph [**6**, (*E*):(*Z*) = 1:0.2] quantitatively (Scheme 2). The striking difference between this reaction and that of entry 1 in Table 1 clearly shows that a relatively small structural change of the catalyst causes a drastic change of the reaction pathway. This fact strongly supports the importance of designing and synthesizing new types of catalyst molecules.



Scheme 2 Hydrosilylation of diphenylacethylene employing the η^6-toluene complex **4** as a catalyst.

We investigated the *ortho*-silylation reaction by varying the substrates to confirm the generality (Table 1, entries 2–5). The reactions with use of hydrosilanes $HSiMe_2R$ (R = *i*-Pr, Et) resulted in the formation of the corresponding *ortho*-silylated alkenes **5b** and **5c** in high yields (entries 2 and 3). The effect of the substituent of hydrosilane can be estimated by comparing entries 1–3: Trialkylsilane reacts faster than phenyldimethylsilane, and, among the trialkylsilanes, the less sterically hindered ethyldimethylsilane reacts faster than isopropyldimethylsilane. Thus, the reaction rate depends on the substituent R on hydrosilane, and the rate decreases in the order: Et > *i*-Pr > Ph. Since the use of ethyldimethylsilane led to better yield and higher reactivity in the reaction with PhC≡CPh, we next investigated the catalytic reactions of other internal alkynes PhC≡CR' (R' = Et, Me) with $HSiMe_2Et$ (entries 4 and 5). These reactions resulted in the same type of hydrosilylation to give the corresponding products **5d** and **5e**, where the reaction rates are both slower than that for the formation of **5c** in entry 3.

A plausible reaction mechanism for the catalytic cycle to form **5a–e** is depicted in Scheme 3. Although we have no experimental evidences for this mechanism, a similar cycle has been proposed by Kakiuchi, Chatani, Murai, and coworkers for the *ortho*-silylation reaction of arenes bearing a heteroatom-containing directing group [2–5]. The first step is considered to be the coordination of the alkynyl group that works as a directing group. Subsequently, *ortho*-metallation occurs accompanied by dissociation of the oxygen atom in the xantsil ligand to give intermediate **B**. The Si–H reductive elimination of one of xantsil silicon in **B** is thought to be necessary to accept the following oxidative addition of an external hydrosilane molecule. Hydrogen migration from ruthenium to the alkynyl carbon then occurs to give intermediate **D**. After that, Si–C reductive elimination, Si–H oxidative addition, and final C–H reductive elimination afford the (*E*)-form of product **5a–e** selectively, and active species **1** is reproduced. In this reaction mechanism, the alkynyl group works not only as a directing group but also as an intramolecular hydrogen acceptor.



Scheme 3 Proposed mechanism for the catalytic cycle to form **5a–e**.

CONCLUSION

The unprecedented hydrosilylation of arylacetylenes with tertiary silanes is induced by a new catalyst, ruthenium xantsil phosphine complex **1**, under mild conditions. This reaction exclusively affords an *ortho*-silylated (*E*)-arylalkene, where the regioselective *ortho*-silylation of an aryl group and trans addition of two hydrogen atoms to a C≡C bond occur. This hydrogenation makes the addition of alkene as a hydrogen acceptor unnecessary, which is indispensable for the efficient reaction progress in most of previously reported *ortho*-silylation reactions between arenes and hydrosilanes [2–5]. In contrast, the same reaction with use of the η^6-toluene xantsil complex **4** as a catalyst leads to the formation of usual hydrosilylation products, i.e., silylalkenes. Mechanistic study and expansion to other substrates for this reaction catalyzed by **1** are in progress.

ACKNOWLEDGMENTS

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10. The unit cell contains two independent molecules, which are related by a pseudocenter on symmetry. Because of the similarity between the individual molecules, only one molecule is depicted in Fig. 2.