A New Synthetic Route to Heteroarylsilanes via Ruthenium-Catalyzed C-H/SiR_3 Coupling

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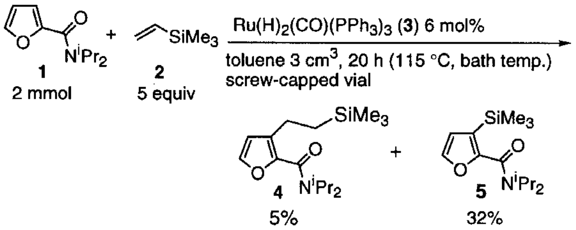
Heteroarylsilanes can be synthesized by the reaction of heteroaromatic compounds with triorganovinylsilanes with the aid of a $Ru_3(CO)_{12}$-catalyst. A variety of heteroaromatic compounds can be used in this C–H/SiR_3 coupling. The coupling reaction was observed to take place at a position β to the directing carbonyl group, e.g., ketone, ester, and amide, in the case of heteroaromatic compounds.

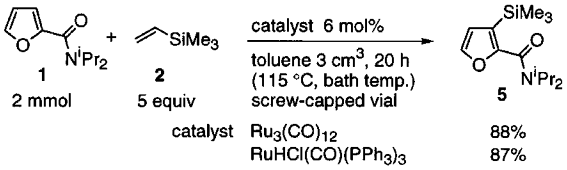
In the course of our studies of the catalytic C–H/olefin coupling reaction,[1] we discovered a new type of reaction which enables direct conversion of a C–H bond into a C–Si bond with the aid of a $Ru(H)_2(CO)(PPh_3)_3$-catalyst. In this reaction, the silyl group is delivered via a vinylsilane. This is the subject of the present communication. Two aspects of our findings are significant. First, the results demonstrate a new option for catalytic C–H/olefin coupling by means of alternating the steps in the catalytic cycle, thus rendering a new, unique opportunity for the design of a catalytic cycle. Second, the results represent a new method for the introduction of organosilyl groups into heteroaromatics. Aryl- and heteroarylsilanes are usually synthesized by a reaction of an organometallic reagent such as Grignard and lithium reagents with halo- and alkoxysilanes.[2] In these cases, organic halides are typically required for generating the corresponding organometallic reagents. In this context, the catalytic silylation with hexaorganodisilanes (R_3SiSiR_3) reported recently is of importance.[3c]

As a part of the study of the ruthenium-catalyzed C–H/olefin coupling reactions,[1] we carried out a reaction of furan-2-carboxylic acid diisopropylamide (**1**) with trimethylvinylsilane (**2**) in the presence of $Ru(H)_2(CO)(PPh_3)_3$ (**3**) as a catalyst and found that the C-H/olefin coupling product **4** and the dehydrogenative silylation product **5** were formed in 5% and 32% yields, respectively (Eq 1). The formation of the latter product was unexpected, but easily explained (*vide infra*). It is noteworthy that this reaction subsequently became a useful synthetic method for the preparation of heteroarylsilanes under neutral reaction conditions. Although there are several precedents for the silylation of aromatic rings using hydrosilanes[4] or disilanes,[3] this represents a unique method for silylation employing vinylsilanes.

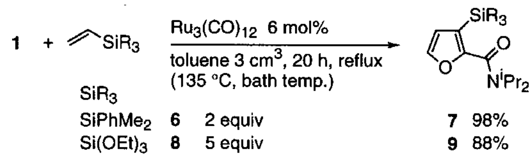


(1)

The catalytic activities of a variety of transition metal complexes were examined (Eq 2). Complexes $Ru(H)_2(CO)(PPh_3)_3$ (**3**), $Ru_3(CO)_{12}$,[5] and $RuHCl(CO)(PPh_3)_3$[6–9] exhibited catalytic activity but $RuCl(SiMe_3)(CO)(PPh_3)_2$,[7] $Rh_4(CO)_{12}$, and $RhH(CO)(PPh_3)_3$ did not. It is interesting that $RuHCl(CO)(PPh_3)_3$ shows good activity while this complex is not effective for the catalytic addition of aromatic C–H bonds to vinylsilanes. Dimethylphenylvinylsilane (**6**) exhibited a higher activity than that of **2**. In the case of the reaction with **6**, the use of 2 equiv of the vinylsilane **6** was sufficient to attain a nearly quantitative yield (98% yield) (Eq 3). The reaction of furan **1** with the triethoxyvinylsilane (**8**) afforded the corresponding silylated product **9** in 88% yield.



(2)



(3)

We have examined the present C–H/SiR_3 coupling reaction using a variety of aromatic compounds, which are shown in Figure 1. Unfortunately, however, these compounds failed to react with vinylsilane **2** using a $Ru_3(CO)_{12}$-catalyst under the reaction conditions shown in Eq 1. At present, it is difficult to explain the difference in reactivities between the heteroaromatic and the aromatic compounds.

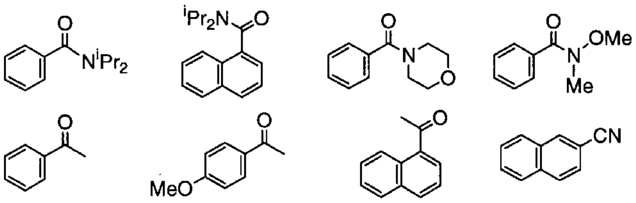
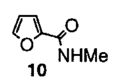
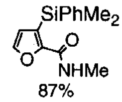
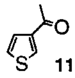
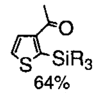
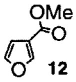
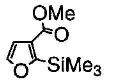
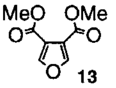
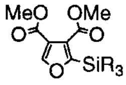
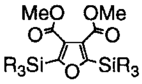
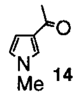
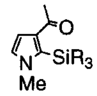
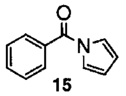
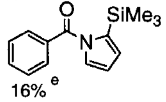


Figure 1. Aromatic compounds which do not react with **2**.

Selected results obtained for various types of heteroaromatic compounds with vinylsilanes **2** and **6** are listed in Table 1.

The diisopropyl group on the nitrogen atom of the amide moiety is not essential. The reaction of *N*-methyl-2-furancarboxamide (**10**) with **6** proceeded smoothly to give the corresponding silylated product in 87% yield (run 1). The silylation of 3-acetylthiophene (**11**) using vinylsilanes **2** and **6** afforded

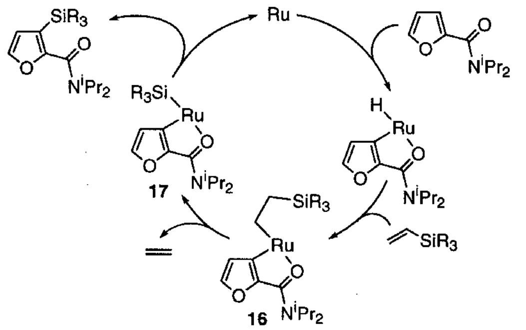
Table 1. Ru$_3$(CO)$_{12}$-Catalyzed silylation of heteroaryl compounds with vinylsilanes[a]

Run	Heteroaryl compound	Vinylsilane	Time	Products	
1	 10	6	20 h	 87%	
2[b]	 11	2	20 h	 64%	
3[b]		6	20 h	60%	
4	 12	2	72 h	 22%[c]	
5	 13	2	72 h	 35%	 47%
6		6	48 h	61%	0%
7	 14	2	20 h	 no reaction	
8		6	20 h	21%[d]	
9	 15	2	72 h	 16%[e]	

[a]Reaction conditions. For vinylsilane **2**, the reaction was carried out in a screw-capped vial at 115 °C (oil bath temperature): heteroaryl compound (1-2 mmol), vinylsilane (5 equiv), Ru$_3$(CO)$_{12}$ (6 mol%), toluene. For vinylsilane **6**, the reaction was carried out in a refluxing toluene solution: heteroaryl compound (1-2 mmol), vinylsilane (5 equiv), Ru$_3$(CO)$_{12}$ (6 mol%), toluene. [b]Vinylsilane (2 equiv). [c]The ester **12** remained in 75% yield. [d]A large mount of the ketone **14** was converted to unknown product. [e]The ketone **15** remained in 80% yield.

the corresponding silylated products in 64% and 60% yields, respectively (runs 2 and 3). In addition to a ketone and an amide, an ester functionality was also effective as a directing group, albeit the yield was low (run 4). When an additional ester group was introduced on the furan ring, i.e., ester **13**, the reactivity of the furan was increased (runs 5 and 6) compared with that of **12**. In the case of the reaction of 1-methyl-3-acetylpyrrole (**14**), no coupling product was observed with **2** (run 7), but the corresponding coupling product was obtained from **6** in 21% yield (run 8). 1-Benzoylpyrrole (**15**) has two different reaction sites, one being the *ortho* C–H bond of the phenyl group and the other one, the α C–H bond of the pyrrole group (run 9). The silylation took place on the pyrrole ring. It is noteworthy that, although in the ruthenium-catalyzed chelation-assisted C–H/olefin coupling, π-conjugation between the π-electrons of the double bond and the C=X (X = O, N) bond of the directing group is thought to be essential, the silylation of the amide **15** occurred at the α carbon of the pyrrole ring which is not involved in the π-conjugation.

The mechanism for the reaction is outlined in Scheme 1. The initial reaction appears to involve C–H bond cleavage by the ruthenium complex. Insertion of the vinylsilane into the Ru–H bond to give **16**, followed by β-silyl elimination results in formation of an aryl(silyl)Ru species **17**.[10] The subsequent reductive elimination, giving rise to a C–Si bond from the ruthenium center gives rise to the coupling product and regenerates the ruthenium(0) species. Note that the silylethyl complex **16** is similar to the one that gives rise to the C–H/olefin coupling product upon reductive elimination. Actually, in the reaction of Eq 1, both C–H/olefin coupling and C–H/SiR$_3$ coupling products were obtained. This result suggests the participation of intermediate **16** in the present catalytic reaction. The factors which determine the course of the silylethyl reductive elimination or β-silyl group elimination seem intriguing and are now under investigation.



Scheme 1. Plausible Reaction Pathway.

Supporting Information (4 pages) including typical experimental procedures and spectral data for the new compounds are available on request to the author by telefax (+81-6-6879-7396).

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9 Although, for the reaction of Eq 2, RuHCl(CO)(PPh$_3$)$_3$ also exhibited a high activity, this complex was not good catalyst for other substrates. For example, in the case of the reaction of 1-methyl-3-acetylpyrrol **14** with the vinylsilane **6**, the yield was decreased to 6%.

10 In the ruthenium-catalyzed dehydrogenative silylation of olefins using triorganovinylsilanes, β-silyl elimination has been documented by Wakatsuki and co-workers. See, Ref 7a.