C–H Activation

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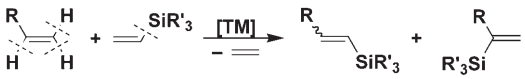
A New Catalytic Route for the Activation of sp-Hybridized Carbon–Hydrogen Bonds**

Bogdan Marciniec, Beata Dudziec, and Ireneusz Kownacki*

In the last two decades we have developed a new type of transition-metal (TM)-catalyzed reaction of vinyl-substituted organosilicon compounds with olefins, known as a silylative coupling (SC, or *trans*-silylation; Scheme 1), that is complementary to metathesis. This reaction occurs by cleavage of the =C–H bond of an olefin and the =C–Si bond of a vinylsilane, in contrast to cross-metathesis, which uses the same substrates and also gives the same products (except the *gem*-isomer), by cleavage of the C=C bond. Various TM complexes (i.e. Ru, Rh, Ir, and Co) containing an M–H and M–Si bond initially, or one generated in situ, catalyze this process.[1,2])



R = alkyl, phenyl, OR, SiR_3, 2-pyrrolidinone, carbazole
R'= alkyl, aryl, alkoxy

Scheme 1. Silylative coupling of olefins with vinylsilanes.

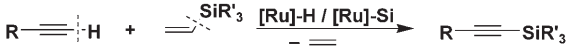
The mechanism for SC catalyzed by ruthenium complexes elucidated by Wakatsuki[3] and by us[4] involves insertion of a vinylsilane into the M–H bond and β-Si transfer to the metal, with elimination of ethylene, to generate M–Si species, then insertion of the alkene into the M–Si bond and β-H transfer to the metal, with elimination of a substituted vinylsilane as product, and regeneration of the catalyst.

The SC process under optimum conditions has become an excellent synthetic tool for the regio- and stereoselective synthesis of functionalized vinylsilicon compounds such as (*E*)-*N*-(silyl)vinylcarbazole,[5a] amides,[5b] 1-silyl-1-(boryl)-ethenes,[5c] functionalized cyclosiloxanes, cyclosilazanes,[5d] and silsesquioxanes[5e] as well as macromolecular organosilicon compounds containing (*E*)-1,2-bis(silyl)fragments.[6] These compounds can be used as synthetic reagents for organic synthesis and as materials precursors and are difficult to prepare by other TM-catalyzed reactions such as cross-metathesis. The *trans*-silylation reaction has recently been extended to other metalloids such as boron[7] and germanium.[8]

The catalytic addition of the =C–H bond in aromatic ketones, esters, and amines to vinylsilanes has been reported by Murai et al. to yield compounds of the type $ArCH_2CH_2SiR_3$.[9a,b] These authors have also reported a $[Ru_3(CO)_{12}]$-catalyzed coupling (silylation) of 3-acetylthiophene with trimethylvinylsilane that gives 3-acetyl-2-(trimethylsilyl)thiophene (64%, toluene, 20 h, 115 °C),[9c] and Park et al. have reported a rhodium-catalyzed silylation of benzyl alcohol with trimethylvinylsilane that yields a siloxy derivative (93%, toluene, 2 h, 200 °C).[9d] Ethylene was produced in both reactions as a secondary product. In view of all the results cited above it is worth emphasizing that the vinylsilicon compounds function as a silylating agent and a hydrogen acceptor.

Herein we present a new catalytic reaction that involves a coupling of terminal alkynes with vinylsilanes of the general formula $H_2C{=}CHSiR_3$ (where SiR_3 is $SiMe_2Ph$, $Si(OEt)_3$, $SiMe(OSiMe_3)_2$, and $SiMe_2(OSiMe_3)$ as well as divinyltetramethyldisiloxane and divinyltetramethyldisilazane), which, by analogy, can be considered a silylative coupling of alkynes and which proceeds in the presence of complexes containing [Ru]–H and/or [Ru]–Si bonds, such as $[RuHCl(CO)(PCy_3)_2]$ (**I**, Cy = cyclohexyl), $[RuHCl(CO)(iPr_3)_2]$ (**II**), $[RuH(CO)(MeCN)_2(PCy_3)_2][BF_4]$ (**III**), $[Ru(SiMe_3)Cl(CO)(PPh_3)_2]$ (**IV**),[10] and $[RuHCl(CO)(PPh_3)_3]$ (**V**), and leads to the evolution of ethylene and formation of the silyl-substituted derivatives (Scheme 2). Interestingly, the hexacoordinate complex **V** appears to be inactive in this reaction.

Substituted alkynylsilanes are commonly used as alkynylating agents in the synthesis of organic and natural prod-



R = alkyl, cycloalkyl, trialkylsilyl
R' = alkyl, aryl, alkoxyl

Scheme 2. Coupling of terminal alkynes with vinylsilanes.

[*] Prof. Dr. B. Marciniec, B. Dudziec, Dr. I. Kownacki
Department of Organometallic Chemistry
Faculty of Chemistry, Adam Mickiewicz University
Grunwaldzka 6, 60-780 Poznan (Poland)
Fax: (+48) 618-291-508
E-mail: Bogdan.Marciniec@amu.edu.pl

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ucts[11] as well as precursors of optoelectronic materials.[12] They can be prepared by classical stoichiometric routes from organometallic reagents and, more recently, by metal-complex-catalyzed silylation of terminal alkynes with aminosilanes[13a] and chlorosilanes,[13b] dehydrogenative silylation with hydrosilanes,[13c] or other transformations of silyl-substituted alkynes.[13d] These reactions have been reviewed recently.[14]

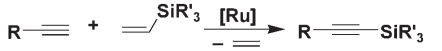
The use of ruthenium catalysts **I**–**IV** for silylative cross-coupling of the selected alkynes, that is, alkyl, cycloalkyl, and silyl ethynes, gives, under the optimum conditions, the respective alkynylsilane, alkynylvinyltetramethyldisiloxane, and alkynylvinyltetramethyldisilazane as the main or exclusive product (see Tables 1 and 2), in some cases accompanied by the products of homo-coupling of the vinylsilicon compounds used in excess. The turnover frequency (TOF) parameters are of the order of 16–27 h^{-1} (Table 1).

All the products were detected by GC and GC-MS methods and identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The reaction was examined in the presence of catalysts **I**–**V** in an open system in toluene, or without solvent, under a gentle stream of argon, although when volatile 3,3-dimethyl-1-butyne was used the reaction was conducted in a closed system. The equimolar reaction of vinylsilanes with alkynes yields some enynes as a result of the dimerization of alkynes, therefore an excess of vinylsilane (two- to fivefold) is necessary to prevent the formation of these enynes. Silylation of 1-ethynyl-1-(trimethylsiloxy)cyclohexane with divinylsiloxane and divinylsilazane, even with a 6- or 10-fold excess of vinylsilicon compound, yields exclusively the monoalkynylvinyldisiloxane and -disilazane with high yield and selectivity (Table 2), accompanied by the homocoupling product of the vinylsilicon substrates. It is noteworthy that, under the conditions examined, the silylation of phenylacetylene with vinylsilane does not occur (only traces).

To explain the mechanism of this new alkyne transformation a series of experiments involving the equimolar reactions of $[Ru(SiMe_3)Cl(CO)(PPh_3)_2]$ (**IV**) with phenylacetylene and silylacetylene were carried out to yield the respective main insertion products (identified by ^{1}H NMR spectroscopy and GC-MS) according to Scheme 3. The spectra taken at various temperatures between −20 and +30 °C unexpectedly show an important difference in the reaction of **IV** with the given acetylenes. Thus, while the reaction with phenylacetylene occurs immediately, even at −20 °C, to form the vinylenephenylruthenium complex **VI** and no [Ru]–H is detected (see Figure 1), the same process with silylacetylene at low temperatures allows the formation of a [Ru]–H complex to be detected, as confirmed by the appearance of a doublet of triplets at $\delta = -6.63$ ppm ($J_{H,P} = 105.2$, $J_{H,P} = 24.3$ Hz), which at room temperature yields the vinylenesilylruthenium analogue **VII** (see Figure 2).

The [Ru]–H complex is apparently produced in both experiments at elevated temperatures (similar to the insertion of olefins into a Ru–Si bond[3,4]). This complex is active (in the absence of vinylsilane) for the hydrogenation of acetylenes as well as for transformations of ruthenium complexes into

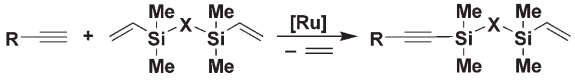
Table 1: Silylative coupling of terminal alkynes with vinylsilanes.



R	R'_3	Cat. (Temp. [°C])	Cat./alkyne/vinylsilane	Conversion [%] (TOF [h^{-1}])	Yield [%]
*t*Bu[a]	Me_2Ph	**I** (100)	10^{-2}:1:5[b]	100	100
		I (110)	10^{-2}:1:3.15[c]	93 (21)	88[d]
		II (100)	10^{-2}:1:2[c]	93	90[e]
$SiEt_3$		**I** (120)	10^{-2}:1:2[c]	100 (27)	94[d]
$SiEt_3$		**I** (100)	10^{-2}:1:4[b]	43	43
$SiEt_3$		**I** (120)	5×10^{-3}:1:2[c]	63	63
$SiEt_3$		**IV** (120)	10^{-2}:1:2[c]	35	35
$SiEt_3$		**IV** (120)	2×10^{-2}:1:5[f]	67	67[e]
Si(*t*Bu)Me_2		**I** (120)	10^{-2}:1:2.3[f]	70	70[d]
*t*Bu[a]	$(OEt)_3$	**I** (100)	10^{-2}:1:10[g]	92	92
		I (110)	10^{-2}:1:4[c]	100 (16)	92[d]
		III (120)	10^{-2}:1:5[h]	100	100
		II (110)	10^{-2}:1:4[b]	50	50
$SiEt_3$	**I** (120)	10^{-2}:1:3.5[c]	90	74[d,e]	
	$Me(OSiMe_3)_2$	**I** (120)	10^{-2}:1:4[c]	100	91[d,e]
	$Me_2(OSiMe_3)$	**I** (120)	10^{-2}:1:4[c]	100	90[d,e]

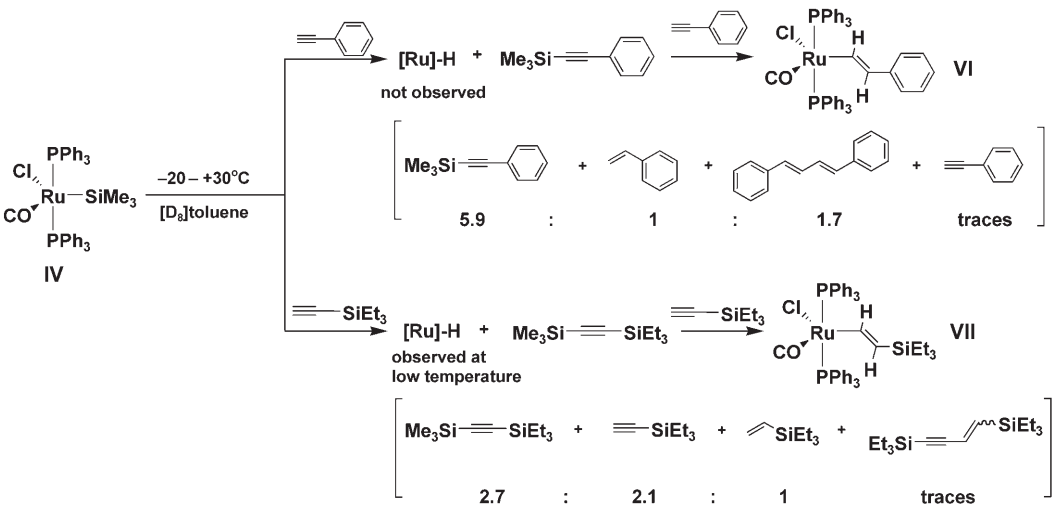
[a] Closed reaction vessel. [b] CH_2Cl_2 (0.5 M), closed reaction vessel. [c] Toluene (0.5 M). [d] Yield of isolated product. [e] Accompanied by traces of vinyl-substituted silane homo-coupling product. Initial TOF measured after 0.5 h of reaction and expressed in moles of alkyne per mole of Ru per hour. Reaction time: 24 h. Yields were determined by GC analysis. [f] Toluene (0.6 M). [g] Toluene (0.35 M). [h] Without solvent.

Table 2: Silylative coupling of terminal alkynes with divinyldisiloxane and -disilazane.



R	X	Cat./alkyne/divinylsilicon compound	Conversion [%]	Yield [%]
$SiEt_3$	O	2×10^{-2}:1:10[a]	100	100[b]
	O	10^{-2}:1:2[c]	52	52[d]
	NH	10^{-2}:1:2[c]	45	45[d]
	NH	10^{-2}:1:6[c]	64	64[b]
	NH	2×10^{-2}:1:10[a]	68	68[b]
	O	10^{-2}:1:5[e]	95	95[b]
	O	2×10^{-2}:1:10[a]	100	100[b]
	O	10^{-2}:1:2[c]	94	94[d]
	NH	10^{-2}:1:6[c]	97	97[d]
	NH	2×10^{-2}:1:10[a]	100	87[d,f]

[a] Toluene (0.3 M). [b] Accompanied by divinylsilicon compound homo-coupling products. [c] Toluene (0.6 M). [d] Accompanied by traces of divinylsilicon compound homo-coupling products. [e] Toluene (0.5 M). [f] Yield of isolated product. Reaction time: 24 h. Yields were determined by GC analysis. Cat.: $[RuHCl(CO)(PCy_3)_2]$ (**I**); temperature: 120 °C.



Scheme 3. Equimolar reactions of **IV** with acetylenes.

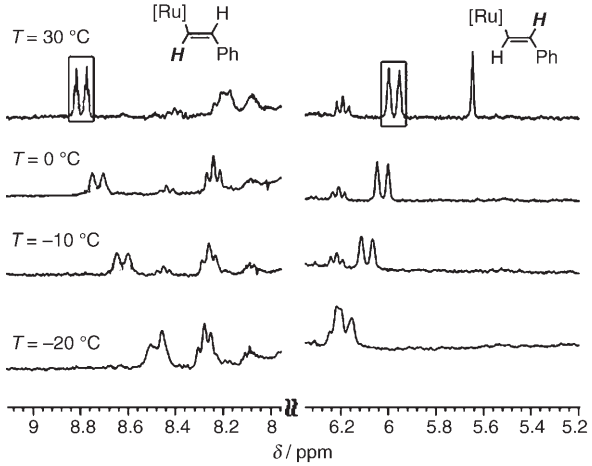


Figure 1. Temperature dependence of the ^{1}H NMR spectra of the reaction of **IV** with phenylacetylene. The boxed signals correspond to those of the vinyl hydrogen atoms shown in italics.

clusters. Acetylene dimerization and co-dimerization with styrene is also observed as a result of the well-known catalysis of these reactions by ruthenium complexes.[15]

In separate experiments, we monitored the equimolar reaction of the hexacoordinate complex **V** with silylacetylene and phenylacetylene at room temperature. These reactions lead to the formation of vinylene complexes **VI** and **VII**, both of which were isolated. The evidence for their vinyleneruthenium structure comes from the ^{1}H NMR spectra of the isolated complexes, in which two doublets of triplets for the vinylene signals appear at $\delta = 8.93$ ($J_{H,H} = 13.3$, $J_{H,P} = 2.3$ Hz) and 6.09 ppm ($J_{H,H} = 13.2$, $J_{H,P} = 2.0$ Hz; phenylvinylene) and $\delta = 8.84$ ($J_{H,H} = 13.0$, $J_{H,P} = 1.7$ Hz) and 5.70 ppm ($J_{H,H} = 13.0$, $J_{H,P} = 2.1$ Hz; triethylsilylvinylene). The NMR spectroscopic data for both isolated vinylene complexes are identical to those reported in references [16, 17]. The above experiments provide evidence that the insertion of acetylene into the Ru–Si bond occurs in a similar manner to the insertion of alkenes.[3, 4b] Under stoichiometric conditions (i.e. in the absence of vinylsilicon compounds) the [Ru]–H complex formed reacts with acetylenes to give dimers and hydrogenated products as well as vinyleneruthenium complexes,

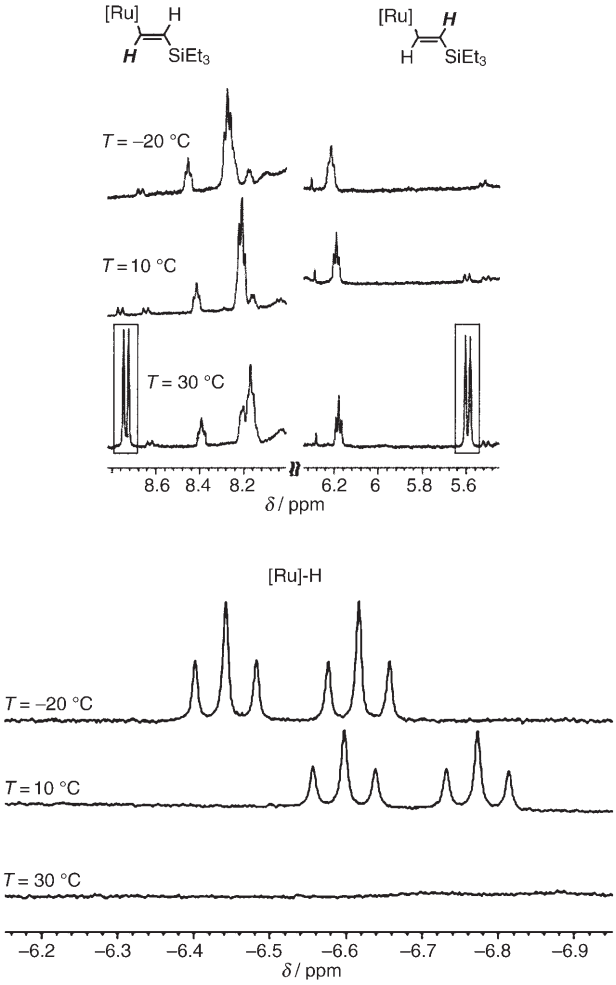
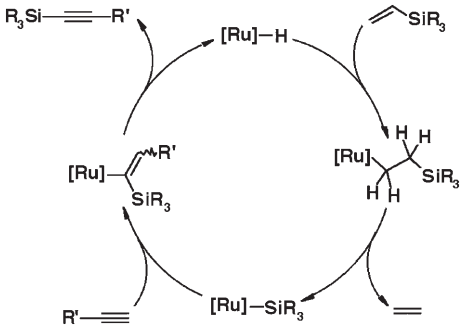


Figure 2. Temperature dependence of the ^{1}H NMR spectra of the reaction of **IV** with $HC{\equiv}CSiEt_3$. The boxed signals correspond to those of the vinyl hydrogen atoms shown in italics.

whereas under the conditions of catalysis (80–120 °C) vinylsilane, particularly if added in excess, reacts preferentially with the ruthenium hydride complex according to a well-documented process to yield a [Ru]–Si complex (see, for example, references [3,4]) and ethylene (see Scheme 4),



Scheme 4. Mechanism of the silylative coupling of alkynes with vinylsilicon compounds.

which explains the catalytic activity of the [Ru]–H/[Ru]–Si systems in the SC of alkynes. However, in the case of phenylacetylene, the ^{1}H NMR spectra of the equimolar experiments indicate that its reaction with the [Ru]–H complex to form the vinylene complex occurs much faster than with the [Ru]–Si moiety and therefore we do not observe the silylation of phenylacetylene under the conditions studied.

The results of the above experiments allow us to propose a mechanism for the reaction of vinylsilicon compounds with substituted acetylenes. The SC of alkynes with vinylsilane involves insertion of the alkyne into the [Ru]–Si bond with subsequent β-H elimination to give silyl-substituted ethyne and the well-known insertion of a vinylsilicon compound into the [Ru]–H bond, and subsequent β-Si elimination of ethylene. Dissociation of a phosphane (observed by GC-MS) from the pentacoordinate [Ru] complexes **I**–**IV** and the inactivity of the hexacoordinate [Ru] species **V** under these reaction conditions suggest that only four-coordinate ruthenium complexes are active catalysts for this process (Scheme 4). This general mechanism is demonstrated by the stoichiometric study of the insertion of a vinylsilicon compound into the ruthenium hydride bond and the above-described insertion of acetylene into the [Ru]–Si bond.

In conclusion, we have shown that the general reaction reported herein opens up a new catalytic route for the activation of ≡C–H bonds and, in combination with the well-known activation of =C–Si bonds, is an efficient method for the selective synthesis of a variety of molecular compounds with an acetylene functionality. The silylalkynyl derivatives synthesized in this manner could play a very important role as organometallic reagents in organic synthesis.[11a]

Experimental Section

General procedure: All experiments were performed under dry and oxygen-free argon using standard Schlenk techniques for the organometallic synthesis.

See Supporting Information for full experimental procedures and the ^{1}H, ^{13}C, and ^{29}Si NMR spectra, the GC-MS traces, and the elemental analysis data of the products.

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Keywords: alkynes · C–H activation · homogeneous catalysis · ruthenium · silanes

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