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Silylmetalation of Alkenes

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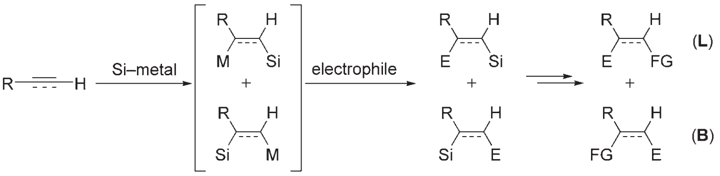
SiBNOL–Zn-ate is a tetracoordinated dianion type zinc ate complex bearing biphenoxide, silyl and tert-butyl ligands.
This complex promotes the chemo- and regio-selective silylzincation of terminal alkynes without any transition metal catalysts under mild conditions.

Abstract: Silylmetalation of alkenes is challenging due to the low reactivity of the substrates. In contrast, carbometalation of alkenes has been realized through several innovative methods, including activation of the reagent and the substrate. A similar approach could be applicable to silylmetalation of alkenes, and we have recently developed a bimetal activation method using zincate complexes for this purpose. Here, we describe how the silylzincation of alkenes was achieved. First, the strategies for carbometalation of alkenes will be summarized. Secondly, the history and development of silylzincation chemistry are briefly described. Then the details of our findings related to two types of silylzincation of alkenes, as well as recent progress in mechanistic studies, are discussed. The key point in the silylzincation of alkenes proved to be the bimetal activation of the substrate. One metal (copper or titanium) strongly coordinates and activates the alkene moiety, and the other metal (zinc) acts as the electron acceptor from the silyl group by way of the alkene moiety. This dual activation concept is expected to be applicable to other combinations of metals, as well as to new types of reactions.

Keywords: copper • silylzincation • titanium • zinc

Introduction

Silylmetalation allows us to introduce both a silyl group and a metal into a substrate in a single operation. The resultant metal–carbon bond can be transformed into a variety of functional groups in a one-pot reaction. Furthermore, the silyl group can also be changed to other functional groups by means of well-known silicon chemistry, such as oxidative cleavage of a carbon–silicon bond, nucleophilic substitution, and cross-coupling reaction. On the other hand, there are some difficulties in silylmetalation of carbon–carbon multiple bonds, including how to control the regio- and chemoselectivity (Scheme 1).



Scheme 1. General scheme for the silylmetalation of alkynes or alkenes leading to branched (B) and linear (L) regioisomers.

Although transition-metal-catalyzed addition of a non-anionic silyl reagent to alkenes, for example, in hydrosilylation,[1] bis-silylation,[2] silylstannylation,[3] and silylboration,[4] is relatively facile and well-developed, addition of an anionic silyl reagent, such as silylcopper and silylzinc complexes, to alkenes has been difficult, due mainly to the low reactivity of alkenes. Indeed, there are plenty of examples of silylmetalation of alkynes,[5–11] allenes,[12,13] and 1,3-dienes,[14,15] but few in the case of alkenes. Carbometalation is also of great interest, and much effort has been directed towards this tough task, although the situation is much the same as with silylmetalation.

In this paper, we first introduce the basic concept of how to achieve carbometalation of alkenes, and describe our success in silylmetalation of alkenes based on this concept. Finally, we look at prospects in this research field.

Carbozincation of Alkenes

Carbometalation of reactive alkenes: Carbometalation of alkenes is known to be a challenging task. One of the reasons for this is the low reactivity of alkenes towards anionic metal reagents. Two different methods, reagent activation and substrate activation, have been examined in order to solve this problem. An example of the substrate activation method is the use of cyclopropene derivatives that are distorted and hence reactive. Nakamura et al. have succeeded in allylzincation using cyclopropenone acetals,[16] and recently Fox et al. have reported the copper-free/catalyzed carbomagnesation of cyclopropenes[17] (Scheme 2). Vinylsilanes are also reactive toward carbometalation.[18] Although the alkene moiety of styrenes and 1,3-dienes is activated by the conjugated aryl group and double bonds, they are too reactive, in that they easily polymerize and thus are difficult to use as substrates for carbometalation. It is inherent in this substrate activation method that the scope of the substrates will be limited. Another difficulty in the carbometalation of alkenes is the retro-reaction (β-carbon elimination), especially in intermolecular reactions, due to the loss of entropy.[19] Reaction using substrates containing adjacent heteroatoms (e.g., allyl alcohols and allylamines) to stabilize the intermediary alkylmetals is one solution to this problem.[20]

Gaudemar–Normant-type allylzincation (G/N reaction): Allylmetalation using a suitable allylmetal reagent is one example of the reagent activation method for the carbometalation of alkenes. Allylmetalation of alkenes might proceed via a six-membered transition state that makes it more facile than usual carbometalation, which might proceed via a four-membered transition state. It is noteworthy that allyl-

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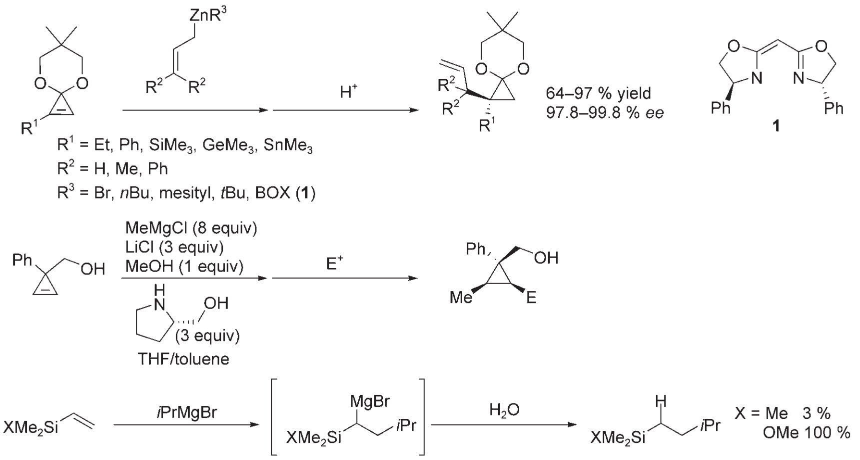


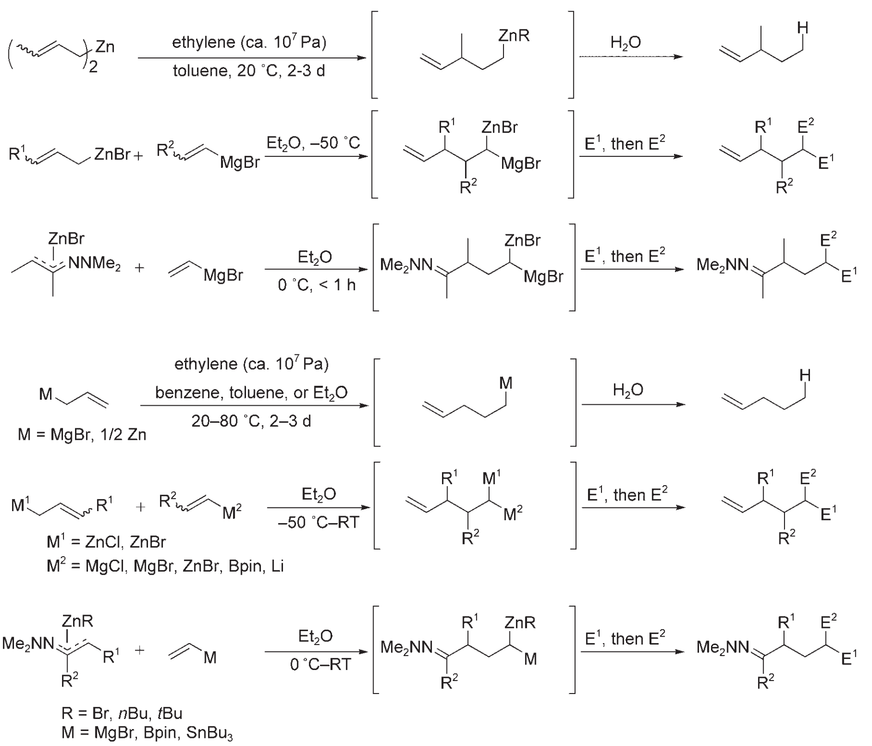
Scheme 2. Carbometalation of reactive alkenes.

zinc reagents were used in most reported allylmetalations of alkenes, while allylmagnesium reagents were used in a few cases, and other allylmetal reagents were rarely used.[21]

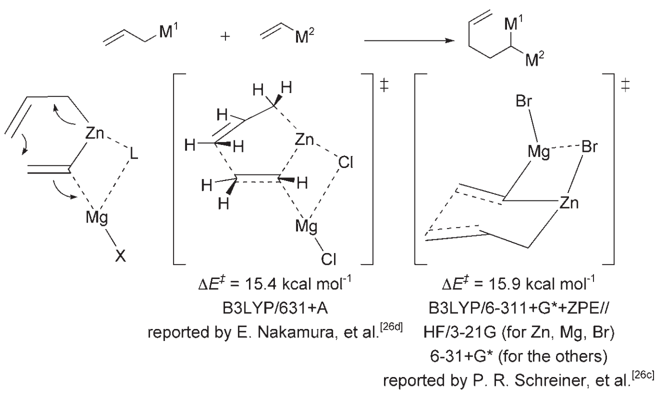
Even though allylmetalation is facile, allylmetalation of simple (i.e., unreactive) alkenes still requires harsh conditions, such as prolonged reaction time, high temperature, and high pressure[22] (Scheme 3). On the other hand, interestingly allylmetalation of vinylmetal compounds (Gaudemar–Normant reaction, denoted as G/N reaction) proceeds smoothly under milder conditions, typically at below ambient temperature for several hours.[23–25] Theoretical analysis indicated the importance of bimetallic activation[26] (Scheme 4) in promoting the formation of the initial complex, and this complexation (or template effect)[27] is the key step of this G/N reaction. Nakamura et al. indicated that the G/N reaction proceeds via metala-Claisen rearrangement on one metal atom (usually zinc) and the other metal atom supports this process as a Lewis acid. These results show the importance of the combination of two metals; that is, combinations such as zinc/magnesium and zinc/zinc work well, whereas zinc/lithium and magnesium/magnesium do not, because strong stabilization of the initial complex makes the activation barrier high and weak stabilization of the product complex is unfavorable for the reaction equilibrium (Table 1). The limitation of this allylmetalation is that only an allyl-type group can be introduced. To overcome this restriction, Nakamura et al. developed carbozincation using zinc enolate derivatives, including zincated amide, ester,[28] and hydrazone,[29,30] with alkenes such as cyclopropenone acetals, vinylmetal reagents, and even unreactive alkenes.

Carbometalation catalyzed by titanocene and zirconocene complexes: Transition-metal-catalyzed carbometalation of alkenes using anionic alkylmetal reagents is also known. Negishi et al. have reported zirconocene-catalyzed carboalumination and carbozincation of alkenes.[31] It is interesting that the proposed mechanisms of the two reactions are completely different and that the combination of metal reagents controls the reaction mode. Carboalumination proceeds via cationic zirconocene complexes or their aluminum adducts. In contrast, carbozincation proceeds via zirconacyclic intermediates (Scheme 5).

More recently, Kambe et al. have reported the titanocene-catalyzed carbometalation of reactive alkenes such as styrenes and vinylsilanes[32] (Scheme 6). It is also noteworthy that the mechanism of this reaction, proposed to be a radical mechanism initiated by titanocene ate complex

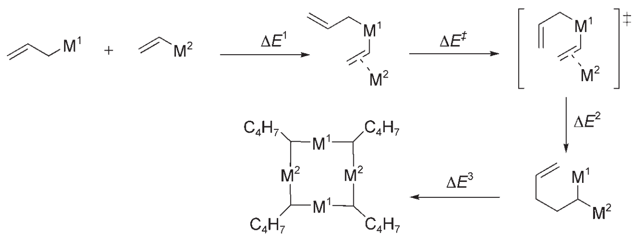


Scheme 3. Allylmetalation of ethylene, G/N reaction, and carbometalation of zincated hydrazone.



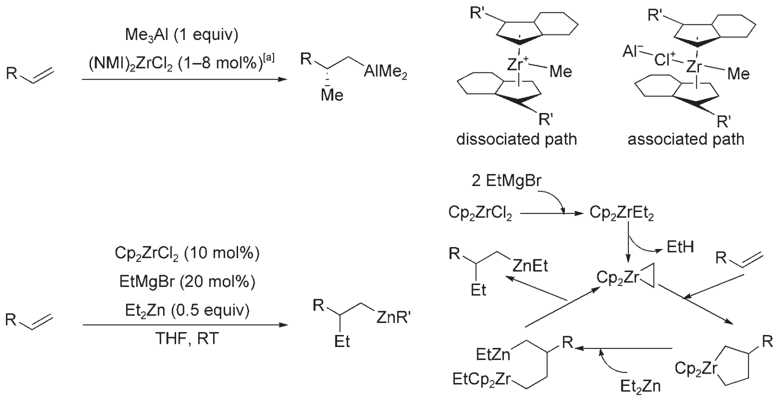
Scheme 4. Predicted transition states of G/N reaction.

Table 1. Theoretical analysis of several combinations of allyl– and vinyl–metal reagents for G/N reaction (B3LYP/631+A unless noted otherwise).



M^1	M^2	ΔE^1 [kcal mol^{-1}]	$\Delta E^{\neq}$ [kcal mol^{-1}]	ΔE^2 [kcal mol^{-1}]	ΔE^3 [kcal mol^{-1}]
ZnBr	H	3.1[a]	11.5[a]	−28.0[a]	n.d.[b]
ZnCl	Li	−52.2	24.5	−1.3	n.d.[b]
ZnCl	MgCl	−5.2	15.4	−11.3	ca. −8–−14
ZnCl	ZnCl	6.8	10.2	−23.2	n.d.[b]
MgCl	MgCl	2.5	13.4	−7.0	ca. −3

[a] B3LYP/6-311+G*+ZPE//HF/3-21G (for Zn, Mg, Br), 6-31+G* (for the others). [b] No data.



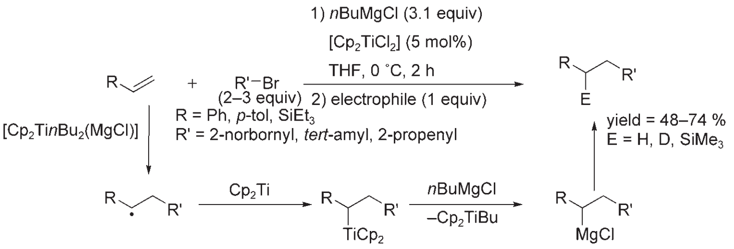
Scheme 5. Zirconocene-catalyzed carbometalation of unreactive alkenes. [a] NMI = 3-neomenthyl-1-indenyl.

($Cp_2TinBu_2(MgCl)$), was not the same as that in the case of zirconocene-catalyzed carbozincations. This mechanism was supported by the use of (bromomethyl)cyclopropane, which is a well-known reagent whose radical quickly opens and gives the 3-butenyl radical. In addition, the regioselectivity of this alkylation is also different from that of the zirconocene-catalyzed reaction, which alkylates at the internal carbon atom. These results indicate that the choice of the transition metal catalyst determines the reaction mode.

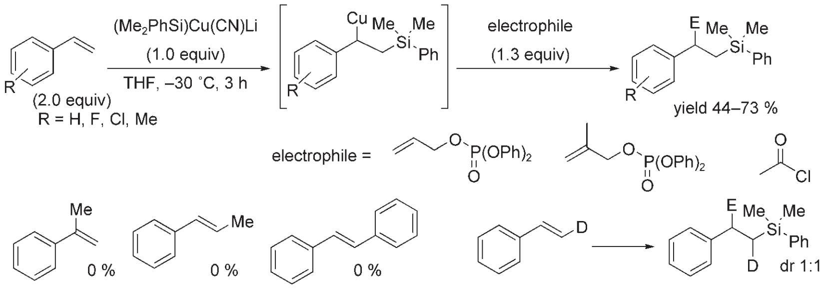
Silylmetalation of Alkenes

Silylzincation and silylcupration of styrenes: Silylmetalation of alkenes using "anionic" silylmetal reagents has been reported by Bäckvall et al.,[33] though the procedure has several limitations: the reaction needs two equivalents of substrate per silylcopper reagent, the substrates that can be used are limited to styrenes (reactive alkenes), and the yield after electrophilic trapping of the intermediates is generally only around 50% (Scheme 7). It is noteworthy that reactions of styrenes are much slower than those of acetylenes and allenes. Silylcupration using $(Me_2PhSi)_2Cu(CN)Li_2$ (so-called higher-order[34] cyanocuprate) gave a poor result because of polymerization of the starting material. Silylcupration of disubstituted alkenes, such as α-methylstyrene, (*E*)-β-methylstyrene, and (*E*)-stilbene also gave poor results, probably due to steric hindrance between the silyl group and the alkene substituents. It is important that, although the silylcupration of other general alkynes proceeds stereospecifically in a *cis*-addition manner, the silylcupration of styrenes proceeds non-stereoselectively. This was confirmed by an isotope labeling experiment with (*E*)-β-deuterated styrene that resulted in 1:1 diastereoisomeric mixtures. This result might suggest that the reaction proceeded via nucleophilic attack of the cuprate complex at the terminal carbon atom of styrene, rather than by concerted four-centered σ-bond metathesis. A radical mechanism was ruled out by the observation that a radical inhibitor had no effect on the rate or stereoselectivity.

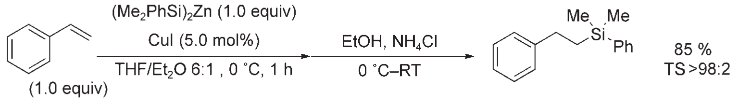
More recently, the copper-catalyzed silylzincation of styrene has been reported by Oestreich et al.[11d] (Scheme 8). This reaction requires only equimolar reagents and the chemical yields are dramatically improved compared with those of silylcupration using a silylcuprate reagent. However, the reaction mechanism has not been established. It has been proposed that the active species is a monosilylcopper complex, such as $Me_2PhSiCu{\cdot}ZnX_2$ (X = Me_2PhSi, Cl, and/or I) based on the similarity in the regioselectivities of alkynes in this method and with $Me_2PhSiCu{\cdot}LiCN$, in contrast to that in the case of $(Me_2PhSi)_2Cu(CN)Li_2$. Further, the bissilylcopper



Scheme 6. Titanocene-catalyzed carbometalation of reactive alkenes.



Scheme 7. Silylcupration of styrenes using silylcuprate $(Me_2PhSi)Cu(CN)Li$.



Scheme 8. Copper-catalyzed silylzincation of styrene.

complex, $(Me_2PhSi)_2Cu(CN)Li_2$, polymerized styrene (see above).

Silylmetalation catalyzed by titanocene complex: Previously, our group has found that the bulky dianion-type zincate having one dimethylphenylsilyl (DMPS) group (DMPS)Zn*t*Bu(OR)$_2$(MM′) ((OR)$_2$ = 2,2′-biphenoxo, M = Li or MgCl, M′ = MgCl, abbreviated as SiBNOL-Zn-ate) is an effective reagent for the chemo- and regioselective silylzincation of terminal alkynes without any transition-metal catalyst[11c] (Table 2). This paper presented the first *di*anion-type zincate-mediated regio- and chemoselective silylzincation reaction of various functionalized alkynes. Only limited success had been reported previously in regioselective silylmetalation to give branched vinylsilanes from terminal alkynes.[35] The report was synthetically complementary to these previous reactions in that we can use various functionalized alkynes as substrates for the first time. In addition, the reaction possesses a number of attractive features as a synthetic reaction. For instance, it can be carried out as a transition metal-free reaction, and therefore its terminal alkyne specificity is very high, that is, other unsaturated bonds, such as internal alkyne, alkene, and diene, are left intact.

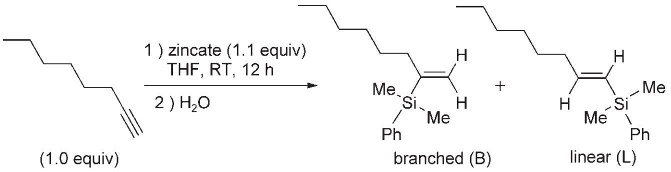
The high reactivities of the new dianion-type silylzincates prompted us to further survey whether the zincates could be used for chemo- and regioselective silylzincation reaction toward alkenes. However, simple applications of this protocol to terminal alkenes by using a SiBNOL-Zn-ate or other zincates proved unsuccessful due to the low reactivity of an isolated carbon–carbon double bond. Therefore, we focused on the screening of catalysts for the silylzincation reaction of terminal alkenes. After several experiments, we found that the silylzincation reaction proceeded with a catalytic amount of titanocene dichloride. Interestingly, this reaction gave not the corresponding alkylsilane, but the γ-allylsilane due to facile β-hydride elimination from the intermediary titanium-carbon bond. Encouraged by this discovery, we continued screening, and finally we found that the combination of 5 mol% $[Cp_2TiCl_2]$ and SiSiNOL-Zn-ate was the best condition for silylating 1-heptene. Although the reaction mechanism is still unclear, Zn-ate is essential for this silylation. The coordination number and the nature of the counter cations of Zn-ate were also critical (Table 3).

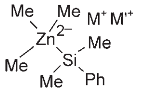
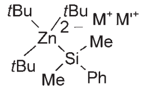
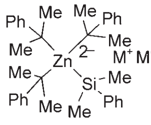
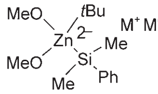
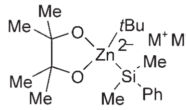
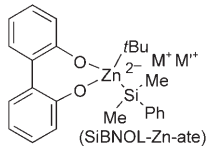
Then, we studied the scope of this new protocol. As well as terminal alkenes bearing simple alkyl chains, those possessing a range of functional groups could be used: suitably protected alcohols, amines, thiol and ketones, as well as cyclohexyl and aryl substitution, are tolerated in the reaction. A variety of electrophilic functional groups, including carbamate, carbonate, and ester, also caused no problems. Substrates containing a free O-H moiety, such as aliphatic alcohols and carboxylic acid could also be utilized, and no self-condensation was observed. This reaction is the first example of an efficient one-step synthesis of γ-substituted allylsilanes with wide substrate generality (Table 4).

Some characteristic aspects of the regio- and stereoselectivity of this silylation can be drawn from the data:

1) *Regioselectivity of addition*: the silylation reaction occurs with very high regiospecificity for monosubstituted alkenes (no regioisomer was detected), probably due to the steric effect.
2) *Direction of β-elimination (allyl/vinyl selectivity)*: as evidenced by runs 1–10, the reactions with terminal alkenes containing any functional group distal from the reaction site (the double bond) gave the allylsilanes preferentially

Table 2. Branch-selective silylzincation of 1-octyne.



Run	Zincate	Yield [%][a]	Ratio (B/L)
1		85[b]	56:44
2		42[c] 89[b]	73:27 74:26
3		100[b]	53:47
4		85[c]	81:19
5		100[c]	92:8
6		100[c]	99:1

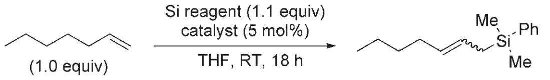
[a] Isolated yield. [b] Countercations (M^+, M'^+) were $2Li^+$. [c] Countercations were Li^+, Mg^+Cl or $2Mg^+Cl$.

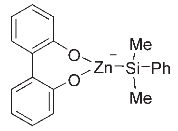
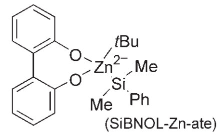
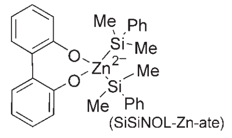
over the corresponding vinylsilanes. On the other hand, in the case of terminal alkenes containing bulky substituents, such as a cyclohexyl, benzyl, or cyclic ketal group, near the reaction site, the allyl/vinyl selectivity showed a declining trend.

3) *Stereoselectivity*: the *E*/*Z* ratios of the allylsilanes were almost constant (except for run 12), with *Z* isomers as the major component.
4) *Isomerization of double bond*: no movement of the C–C double bond of allylsilanes was observed at all, even when a carbonyl or phenyl moiety was present.

Next, we examined the reactivity and chemoselectivity of this reaction with various alkenes. The functional group specificity of this silylation is very high, and internal olefins or 1,1′-disubstituted alkenes did not react at all (Scheme 9). On the other hand, the reaction of styrene provides both alkylsilane and vinylsilane with a quantitative conversion yield. The alkyl/vinyl ratio depends on the reaction temperature to some extent, and when the reaction was carried out at 45 °C, the corresponding vinylsilane and alkylsilane were obtained in 88 and 12 % yields, respectively. In the competitive reaction of internal alkenes in 1,5-heptadiene using SiSiNOL-

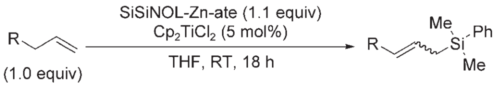
Table 3. Optimization of the silylating reagents for the silylzincation of 1-heptene.

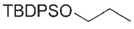
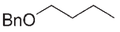
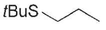
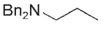
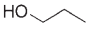
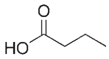
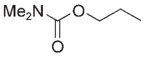
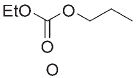
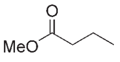
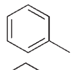
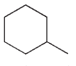
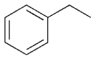
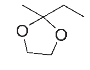


Run	Si Reagent		Catalyst	*E*/*Z*	Yield [%][a]
	anion	cation			
1		Li^+ $ClMg^+$	[Cp_2TiCl_2]	– 28:72	0 37
2		$2Li^+$ $2ClMg^+$	[Cp_2TiCl_2]	– 24:76	0 54
3		$2Li^+$ $2ClMg^+$	[Cp_2TiCl_2]	– 30:70	0 95
4	$Cp_2Ti–SiMe_2Ph$[b]		–	76:24	27

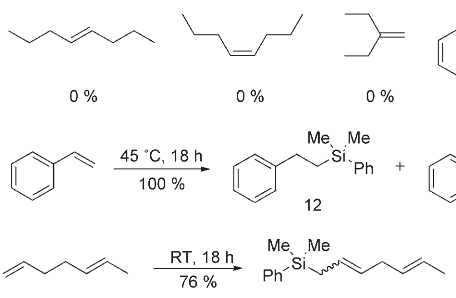
[a] Isolated yield. [b] [Cp_2Ti-$SiMe_2Ph$] was prepared from the reaction of one equivalent of [Cp_2TiCl_2] and two equivalents of $PhMe_2SiLi$; see ref. [9].

Table 4. Silylation of various functionalized terminal alkenes.

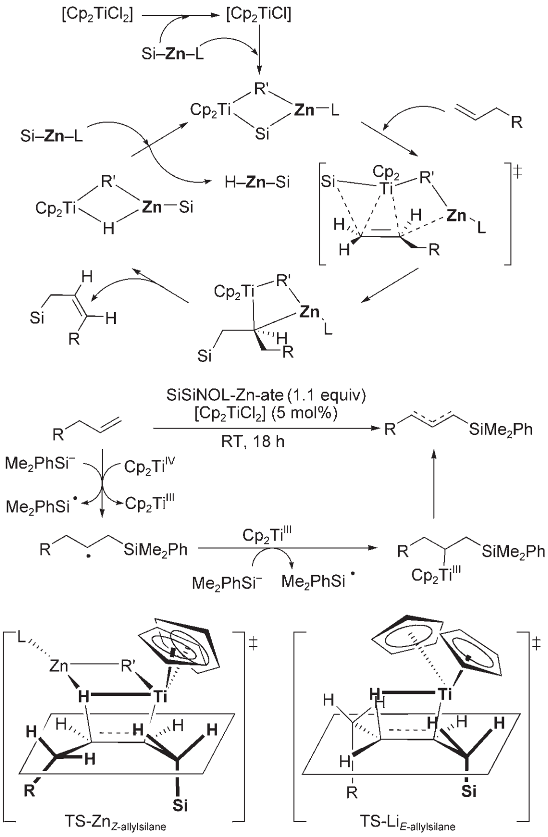


Run	R	E/Z	Yield [%][a]
1		24:76	95
2		28:72	92
3[b]		29:71	94
4		26:74	88
5		21:79	75
6[c]		26:74	55
7[c]		24:76	100
8		24:76	95
9		27:73	79
10		23:77	80
11		n.d.	84
12[d]		49:51	47[e]
13		26:74	71[f]
14		21:79	81[g]

[a] Isolated yield. [b] The reaction was carried out under reflux. [c] 3 equiv zincate was used. [d] The reaction was carried out at 45 °C. [e] Vinylsilane was isolated in 18 % yield (*E*/*Z* 64:36). [f] Vinylsilane was isolated in 8 % yield (*E*/*Z* 58:42). [g] Vinylsilane was isolated in 19 % yield (*E*/*Z* 50:50).



Scheme 9. Reactivity and chemoselectivity of this protocol.

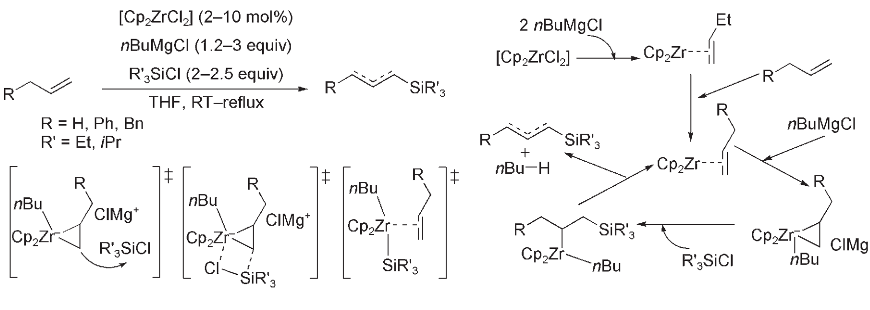


Scheme 10. Possible reaction mechanism of this silylation.

Zn-ate and 5 mol% Cp_2TiCl_2, silylation at the terminal alkene proceeded with complete selectivity. In addition, no isomerization of olefins was observed.

Although details of the reaction mechanism are still unclear, this silylmetalation might not proceed by the same mechanisms as those of titanocene- or zirconocene-catalyzed carbometalation, because the involvement of a titanacycle (Ti^{II})-type intermediate seems unlikely in a reaction with one equivalent of zincate complex prepared from *t*BuMgCl, $Me_2PhSiLi$, ArOMgCl and $ZnCl_2$ at ambient temperature for 18 h. We can not rule out a radical mechanism, such as the initial formation of silyl radical via oxidation of a silyl anion by Ti^{IV} followed by its addition to alkenes and reduction of the resultant (β-silyl)alkyl radical to give a (β-silyl)-carbanion and silyl radical. Nevertheless, by analogy with the copper-catalyzed silylzincation of alkenes, the involvement of a bimetallic activation by titanium and zinc, like that in the reaction catalyzed by copper and zinc, seems plausible, because the addition of zinc is essential for this step. In other words, one equivalent of $Cp_2Ti–SiMe_2Ph$ can silyltitanate alkynes and 1,3-dienes, but alkenes react only sluggishly. It is worth mentioning that the stereoselectivities of allylsilanes obtained from these reactions were different. This indicates that zinc might participate not only in the silylmetalation step, but also in the β-hydride elimination that is thought to be the stereo-determining step. This would not be surprising, because β-hydride elimination is formally the retro reaction of hydrometalation, which is similar to silylmetalation. In fact, many titanocene complexes that are associated with another organo- or inorganometallic reagent, such as $[(Cp_2TiCl_2)_2M]$ (M = Zn, Mg), $[(C_5Me_5)_2TiMH_4]$ (M = Al, B), $[(Cp_2TiH_2)_2AlMe]$ and $[Cp_2TiR_2(MgCl)]$, are known. Possible transition states of β-hydride elimination to explain those different regioselectivies are shown in Scheme 10. In the presence of zinc complex, the substituent of the substrate may be directed so as to avoid one of the ligands on the zinc unit, which is associated with the titanocene unit through one of the ligands on zinc and hydride of the substrate that is to be eliminated, to give the (*Z*)-allylsilane. On the other hand, in the absence of zinc complex, the substituent of the substrate may be directed so as to avoid steric hindrance with the silyl group at the terminal carbon atom, affording the (*E*)-allylsilane.

Though we hesitate to regard this reaction as the same kind of silylmetalation as the titanocene-catalyzed reaction, a similar silylmetalation using zirconocene complex has been developed by Terao et al.[36] It has been proposed that the reaction proceeds via a zirconacyclopropane intermediate that readily associates with one equivalent of Grignard reagent to form a zirconocene ate complex that is able to react with chlorosilane (Scheme 11). Three different mechanisms have been proposed with regard to this last step, that



Scheme 11. Zirconocene-catalyzed silylmetalation of alkenes.

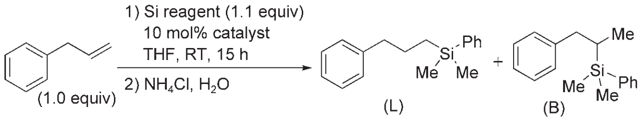
is, nucleophilic attack of the ate complex on chlorosilane, σ-bond metathesis, and oxidative addition of chlorosilane to zirconocene complex affording a Zr^{IV} intermediate and subsequent σ-bond metathesis, and the actual mechanism remains to be established. The resultant zirconium–carbon bond readily undergoes β-hydride elimination to give (*E*)-vinylsilane when the substrate is styrene or ethylene, or (*E*)-allylsilane when the substrate is allylbenzene.

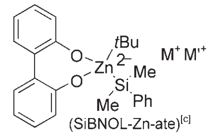
Silylzincation catalyzed by copper salts: Although the titanocene-catalyzed silylzincation reaction is an efficient method for synthesizing functionalized γ-allylsilanes, the intermediates could not be utilized as potent nucleophiles because of the facile β-hydride elimination reaction. However, these intermediates are very attractive for synthesizing multi-functionalized organosilanes. Thus, we next examined how to use these intermediates.

The reaction mechanism of titanocene-catalyzed silylzincation reaction was still unclear, but we assumed that whether the β-hydride elimination reaction proceeds depends upon the kind of intermediary alkyl–metal species. Therefore, we focused on the transition metal catalysts again.

Encouraged by Oestreich's results,[11d] we started to investigate the silylzincation of terminal alkenes, utilizing a catalytic amount of Cu salt and a SiBNOL-Zn-ate. After several experiments, we obtained some interesting results: Cu salts also promote this silylmetalation, and the products were the desired alkylsilanes, that is, in this case, the β-hydride elimination did not proceed (Table 5). We chose CuCN as the best catalyst in respect of low cost, readily availability, and stability.

Table 5. Screening of copper catalysts using allylbenzene.

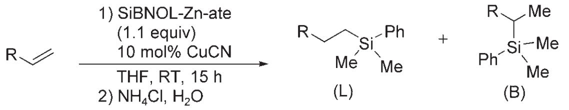


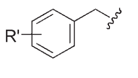
Run	Catalyst	Si Reagent	Yield [%][a]	L/B
1	none	 (SiBNOL-Zn-ate)[c]	37	90:10
2	CuI		73	89:11
3	CuCN		82	83:17
4	CuCN	$Me_2PhSiLi$	<24[b]	0:100

[a] Isolated yield. [b] Several minor products that were difficult to separate were observed, but not identified. [c] Countercations were Li^+, $MgCl^+$, or $2MgCl^+$.

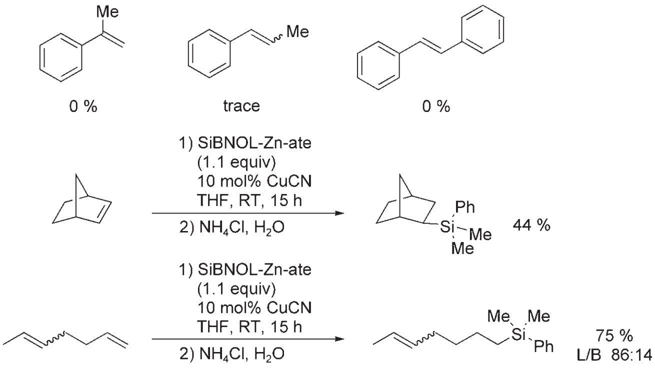
Further investigations revealed wide substrate generality of this new method for the selective silylmetalation reaction of functionalized terminal alkenes (Table 6). Both allylbenzene derivatives and 4-phenyl-1-butene can be used in this reaction, and the yields and selectivities are comparable to the results with allylbenzene. A substrate having a chloro group can also be used. Furthermore, substrates bearing coordinative groups, such as silyl and benzyl ether and thioether, also cause no problems. A variety of electrophilic functional groups including amide, ester, carbamate, carbonate, nitrile, and phosphine oxide are also tolerated in the reaction. Two important conclusions regarding the regioselectivity of this silylmetalation can be drawn from these data. First, the silylation occurs regioselectively with monosubstituted alkenes at the terminal carbon atom. Second, coordinative functional groups have little effect on the regioselectivity. Only when strongly coordinative groups, such as cyano or phosphine oxide, exist at a suitable position does the silylation occur practically regiospecifically at the terminal carbon atom.

Table 6. Silylation of various functionalized terminal alkenes.

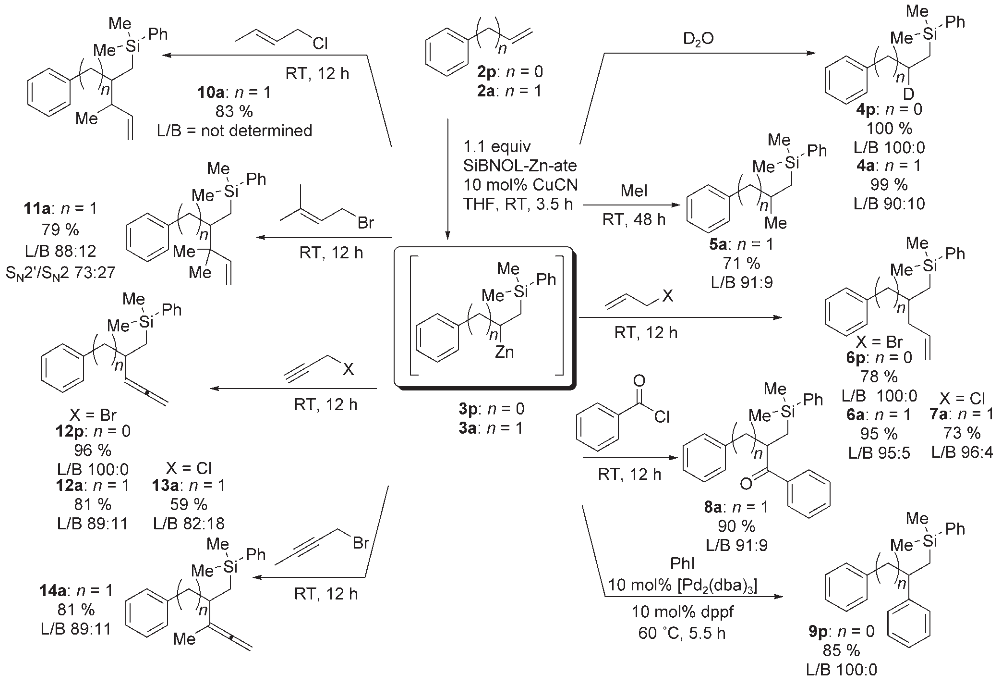


Run	R	Yield [%]	L/B
1	: R′ = 2-OMe	81	90:10
2	: R′ = 4-OMe	97	86:14
3	: R′ = 3,4-OMe	88	84:16
4	$Ph(CH_2)_2$	85	81:19
5	$Cl(CH_2)_4$	73	84:16
6	$TBSO(CH_2)_4$	85	87:13
7	$PhCH_2O(CH_2)_2$	66	86:14
8	$t\text{BuS}(CH_2)_3$	76	79:21
9	$PhCH_2NHC(O)(CH_2)_3$	77	92:8
10	$MeC(O)O(CH_2)_4$	80	83:17
11	$Me_2NC(O)O(CH_2)_3$	90	82:18
12	$EtOC(O)O(CH_2)_3$	94	78:22
13	$NC(CH_2)_2$	85	>99:1
14	$Ph_2P(O)CH_2$	79	>99:1

Next, we investigated the scope of substitution patterns of this reaction. The functional group specificity of this reaction is very high, and α-/β-methyl styrene and *trans*-stilbene, which are among the most reactive disubstituted alkenes, did not react (Scheme 12). However, it is noteworthy that norbornene whose double bond is disubstituted, distorted, and hence reactive, was silylated in moderate yield. In the competitive reaction of terminal and internal alkenes in 1,5-heptadiene, silylmetalation at the terminal alkene proceeded with more than 99 % selectivity.



Scheme 12. Reactivity and chemoselectivity of this protocol.



Scheme 13. Electrophile trapping of the intermediary species. The silylmetalation was carried out using SiBNOL-Zn-ate (1.1 equiv), substrate (**2p**, **2a**) (1.0 equiv), CuCN (10 mol %), and electrophiles (1.5 equiv).

We also demonstrated that the resultant alkyl–metal intermediates could be utilized as carbanion equivalents. The intermediates **3p** and **3a** were treated with D_2O, MeI, allyl halide, or benzoyl chloride to give the corresponding functionalized alkanes in satisfactory yields (Scheme 13). The intermediate **3p** also undergoes Pd-catalyzed C–C bond-forming reactions in high yield and with high regioselectivity. We confirmed that the intermediates react with crotyl chloride, propargyl halide, or their derivatives in a high S_N2' manner. This protocol provides a simple and direct route for the regio-controlled synthesis of α-substituted alkylsilanes and alcohols from various terminal alkenes.

Conclusion and Prospects

The silylmetalation of unreactive alkenes has been difficult. By bringing together several representative recent examples of carbometalation, this article has demonstrated that heterobimetal activation and/or combination with transition metal catalysts opens a new window onto silyl- and carbometalation chemistry. Heterobimetallic reagents such as ate complexes exhibit a synergic chemistry which cannot be replicated by homometallic lithium, magnesium, zinc, or copper compounds. Based on this concept, we have developed efficient reagents, dianion-type silylzincates, for the chemo- and regioselective silylmetalation reaction of functionalized terminal alkenes and alkynes to give corresponding alkylsilanes, allylsilanes, and vinylsilanes. Furthermore, the often milder conditions required for these silylmetalation reactions, which makes them more tolerant of a wider range of functional groups, has opened up new perspectives in synthetic and material chemistry.[37] This improvement allows the elaboration of complex organosilyl molecules.

Since the metal center (zinc, copper, etc.), the counter metal (lithium, magnesium, etc.) and the ligands (alkyl, biphenoxo, etc.), as well as coligands (TMEDA, THF, other amines, ethers, etc.) are all adjustable, the scope for developing new reagents of this type is potentially enormous. Theoretical elucidation of the roles of the metals in the heterobimetal reactions, which is under way in our laboratory, should pave the way for further progress in organosilicon chemistry.

Acknowledgements

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