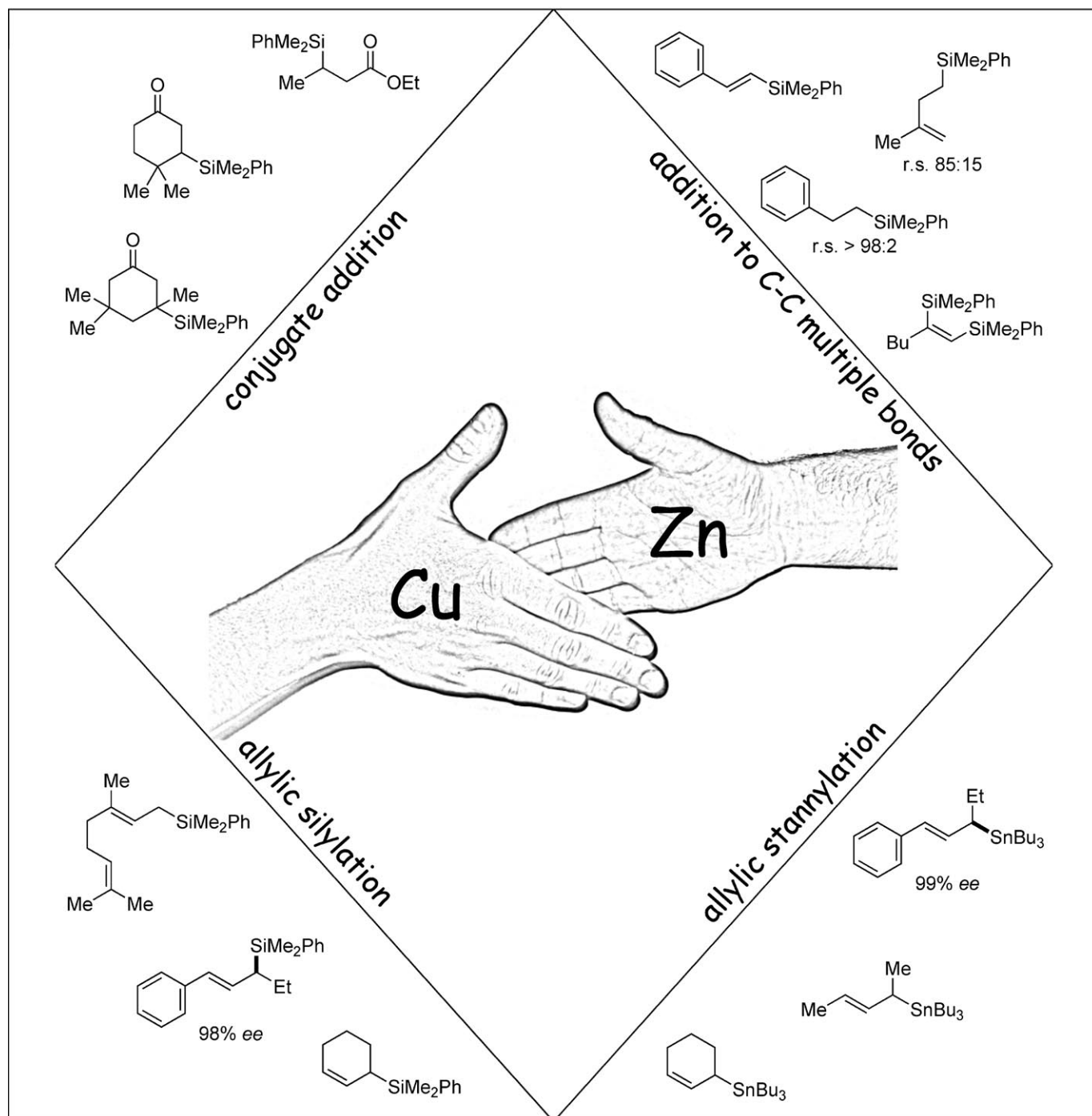


Silicon- and Tin-Based Cuprates: Now Catalytic in Copper!

Andreas Weickgenannt and Martin Oestreich*[a]

Copper and Zinc Hand in Hand



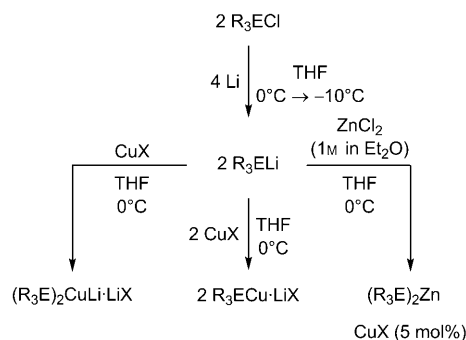
Abstract: Silicon- and tin-containing molecules are versatile building blocks in organic synthesis. A stalwart method for their preparation relies on the stoichiometric use of silicon- and tin-based cuprates, although a few copper(I)-catalyzed or even copper-free protocols have been known for decades. In this Concept, we describe our efforts towards copper(I)-catalyzed carbon–silicon and also carbon–tin bond formations using soft bis-(triorganosilyl) and bis(triorganostannyl) zinc reagents as powerful sources of nucleophilic silicon and tin. Conjugate addition, allylic substitution, and carbon–carbon multiple bond functionalization is now catalytic in copper!

Keywords: allylic substitution • catalysis • conjugate addition • copper • main group elements • zinc

Introduction

Transition-metal-catalyzed reactions greatly influence our way of (retro)synthetic planning and thinking.^[1] In many cases, a catalytic process developed from the cognate stoichiometric transformation. It is therefore remarkable that there are commonly used transition-metal-promoted reactions, which still require stoichiometric amounts of the transition metal. One example of that is the chemistry of silicon- and, certainly to lesser extent, tin-based cuprate reagents.^[2] This situation is somewhat surprising in the light of the ubiquity of silicon- and tin-containing synthetic building blocks, which are often prepared by using exactly these cuprate reagents. Both carbon–silicon and carbon–tin bonds are established linchpins for subsequent carbon–carbon^[3,4] and carbon–oxygen bond^[5,6] formation. Aside from the sheer demand for copper(I)-catalyzed carbon–silicon (and carbon–tin) bond forming reactions, there is an even more startling aspect, we think. “Carbon-based” cuprates also used to be stoichiometric in copper^[7] but the logical switch to copper(I) catalysis was accomplished by a clever yet simple maneuver. The conventional preparation of these cuprates involves the transmetalation from lithium to copper,^[8] owing to the strong nucleophilicity and basicity of the requisite organolithium reagents.^[9] Conversely, these detrimental properties are markedly attenuated if the organolithium reagents are replaced by the corresponding organozinc and organomagnesium reagents, thereby allowing the

catalytic use of copper.^[10] As silicon-based and likewise tin-based cuprates are accessed by exactly the same procedure,^[2] we had anticipated that moving from lithium to zinc might be equally effective ($2\text{R}_3\text{ELi} \rightarrow (\text{R}_3\text{E})_2\text{Zn}$, Scheme 1).



Scheme 1. Silicon- and tin-based cuprate reagents (E = Si or Sn, R = versatile aryl or alkyl groups, X = I, CN or OTf).

This Concept summarizes half a decade of our research towards copper(I)-catalyzed carbon–silicon as well as carbon–tin bond formations. We also establish a long overdue link between the handful of isolated but significant reports, which had remained almost unnoticed for years if not decades. Our survey comprises conjugate addition, allylic substitution, and addition reactions to multiple-bond systems, all of which are now copper(I)-catalyzed...or even free of copper!

Conjugate Addition

The conjugate transfer of silicon nucleophiles onto α,β -unsaturated acceptors is a prominent transformation, and several silicon reagents are available for it.^[3] It started with the clean 1,4-addition of Me_3SiM (M = Li^[11a] but also Na^[11b] and K^[11b]) to cyclic enones without the aid of copper.^[11] While the reaction itself or in itself was a direct hit, the impractical preparation of the reagent(s) and the failure of the Me_3Si unit to participate in the Fleming oxidation thwarted further use. These disadvantages were overcome by employing easy-to-make Me_2PhSiLi ,^[12] which also adds smoothly to enones but in 1,2- rather than 1,4-fashion.^[13] These opposite reaction pathways illustrate that R_3SiLi reagents are afflicted with insufficient chemoselectivity and, connected to that, poor functional group tolerance.^[11,14,15] To counteract this drawback, transmetalation from lithium to copper was identified as the ideal solution,^[2] thereby steering the reaction with electron-deficient acceptors towards selective 1,4-addition. Several protocols were elaborated to generate and transfer these soft silicon nucleophiles (Figure 1).

These cuprate reagents were extensively used in carbon–silicon bond-forming reactions regardless of parallel findings

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$(\text{Me}_2\text{PhSi})_2\text{CuLi}\cdot\text{LiX}$ (1.0 equiv) (from 2 Me_2PhSiLi + CuX with X = I and CN) THF -23°C or -78°C Fleming (1978 and 1987) ^[16,17]	$(\text{Me}_3\text{Si})_2\text{CuLi}\cdot\text{LiX}$ (1.2 equiv) (from 2 Me_3SiLi + CuI or 2 $\text{Me}_3\text{SiSiMe}_3$ + 2 MeLi + CuCN) THF -23°C Fleming (1981 and 1984) ^[16,18]	$(\text{Me}_2\text{PhSi})(\text{Me})\text{CuLi}\cdot\text{LiCN}$ (1.0 equiv) (from Me_2PhSiLi + MeLi + CuCN) THF -23°C Fleming (1984) ^[18]
$(t\text{BuMe}_2\text{Si})(\text{Bu})\text{CuLi}\cdot\text{LiCN}$ (1.3 equiv) (from $t\text{BuMe}_2\text{SiSnMe}_3$ + $\text{Bu}_2\text{CuLi}\cdot\text{LiCN}$) THF -78°C Lipshutz (1989) ^[19]	$(\text{Me}_2\text{PhSi})\text{Cu}\cdot\text{LiCN}$ (1.2 equiv) (from Me_2PhSiLi + CuCN) THF -45°C Oehlschlager (1989) ^[20]	$(\text{Me}_2\text{PhSi})_2\text{CuLi}\cdot\text{LiCN}\cdot\text{Me}_2\text{PhSiLi}$ (1.2 equiv) (from $(\text{Me}_2\text{PhSi})_2\text{CuLi}\cdot\text{LiCN}$ + Me_2PhSiLi + CuCN) THF -45°C Oehlschlager (1989) ^[20]
$[(\text{Et}_2\text{N})\text{Ph}_2\text{Si}]_2\text{CuLi}\cdot\text{LiBr}$ (2.0–3.0 equiv) (from 2 $(\text{Et}_2\text{N})\text{Ph}_2\text{SiLi}$ + CuBr·Me ₂ S) THF -78°C Hoveyda (1994) ^[21]	$(\text{Me}_2\text{PhSi})\text{CuLi}$ (10 equiv) (from Me_2PhSiLi + CuI) Bu ₃ P (10 equiv) THF -78°C Palomo (1994) ^[22]	$(\text{Me}_2\text{PhSi})\text{CuLi}\cdot\text{SMe}_2$ (1.4–2.0 equiv) (from Me_2PhSiLi + CuI·SMe ₂) THF $-78^\circ\text{C} \rightarrow 0^\circ\text{C}$ Bergdahl (2003) ^[23]

Figure 1. Silicon-based cuprates stoichiometric in copper.

that copper is not required for chemoselective 1,4-addition (Figure 2A).^[24] A seminal report was published by Oshima et al.,^[25] in which it was shown that mixed zincates $(\text{Me}_2\text{PhSi})\text{ZnR}_2\text{Li}$ ($\text{R} = \text{Me}$ or Et) add to enones without any catalyst! Different cyclic and acyclic α,β -unsaturated carbonyl and carboxyl acceptors reacted in reasonable yields. Fleming et al. and Singer et al. further broadened the scope using the same zincate; α,β -unsaturated ketones,

amides, nitriles, and aldehydes afforded improved yields,^[26] and even the β,β -disubstituted isophorone underwent the conjugate addition, albeit in low yield. The Lipshutz group then overcame this limitation by again using $(\text{Me}_2\text{PhSi})\text{ZnMe}_2\text{Li}$ in the presence of $\text{Me}_2\text{CuLi}\cdot\text{LiCN}$ as catalyst (Figure 2B).^[27] In this important paper, insufficient reactivity is overridden by the copper catalyst. An alternative copper(I)-catalyzed procedure starting from Si–Si precur-

A) Copper-free protocols

$(\text{Me}_2\text{PhSi})\text{ZnMe}_2\text{Li}$ (1.2–1.4 equiv)
 (from Me_2PhSiLi + Me_2Zn)
 THF
 -78°C
 Oshima (1986)^[25]
 Fleming (1994)^[26a]
 Singer (1995)^[26b]

$(\text{Me}_2\text{PhSi})_2\text{Zn}$ (1.0 equiv)
 (from Me_2PhSiLi + ZnCl_2)
 THF–Et₂O
 -78°C
 Oestreich (2006)^[34]

Topic of this Concept!

B) Copper-accelerated and -catalyzed protocols

$\text{Me}_2\text{Cu}(\text{CN})\text{Li}$ (3.0 mol%)
 $(\text{Me}_2\text{PhSi})\text{ZnMe}_2\text{Li}$ (1.2 equiv)
 (from Me_2PhSiLi + Me_2Zn)
 THF
 -78°C
 Lipshutz (1998)^[27]

$\text{CuOTf}\cdot\text{C}_6\text{H}_6$ (5.0 mol%)
 Bu₃P (11 mol%) or pyridine (10 mol%)
 $\text{Me}_2\text{PhSiSiMe}_2\text{Ph}$ (1.2 equiv)
 (commercially available)
 DMF solvent mixtures
 100°C
 Hosomi (1998)^[28a]
 Scheidt (2004)^[28b]

CuI or CuCN (5.0 mol%)
 $(\text{Me}_2\text{PhSi})_2\text{Zn}$ (1.0 equiv)
 (from Me_2PhSiLi + ZnCl_2)
 THF–Et₂O
 -78°C
 Oestreich (2004)^[33]

Topic of this Concept!

C) Transition metal-catalyzed protocols

$[(R)\text{-binap}]\text{PdCl}_2$ (0.50 mol%)
 $\text{Cl}_2\text{PhSiSiMe}_3$ (1.5–2.0 equiv)
 (several steps)
 C₆H₆
 Δ
 Hayashi and Ito (1988)^[29a]

$\text{Pd}(\text{OAc})_2$ (10 mol%)
 Me_3SiOTf (10 mol%)
 $\text{Me}_2\text{PhSiSiMe}_2\text{Ph}$ (1.2 equiv)
 (commercially available)
 C₆D₆
 r.t.
 Ogoshi and Kurosawa (2002)^[29b]

$[(S)\text{-binap}]\text{Rh}(\text{cod})\text{ClO}_4$ (5.0 mol%)
 (S)-binap (5.0 mol%)
 $\text{Me}_2\text{PhSiBpin}$ (2.5 equiv)
 (from Me_2PhSiLi + HBpin)
 1,4-dioxane–H₂O
 50°C
 Oestreich (2006)^[30]

Figure 2. Copper-free (A), copper(I)-catalyzed and -accelerated (B), and transition-metal-catalyzed protocols (C) for the conjugate addition of silicon nucleophiles.

sors was introduced by Hosomi et al. and later extended by Scheidt et al. (Figure 2B).^[28] This process hinges upon triflate-mediated activation of the silicon–silicon bond followed by transmetalation. Unhindered cyclic and acyclic α,β -unsaturated acceptors including alkylidene malonates performed well.

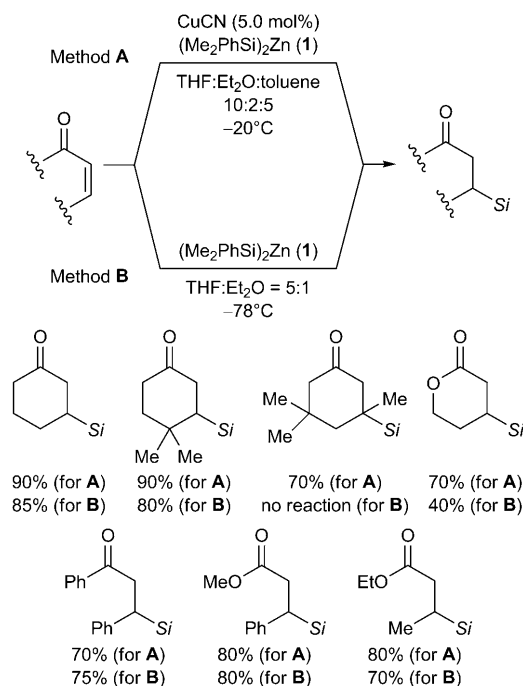
A handful of transition-metal-catalyzed 1,4-additions also rely on the activation of an interelement linkage, either by transmetalation or oxidative addition (Figure 2C). The former is also the central step in the palladium-catalyzed conjugate addition reported by Ogoshi and Kurosawa et al., likely to follow the aforementioned triflate-promoted silicon–silicon bond activation. Conversely, the palladium catalysis devised by Hayashi and Ito et al. involves oxidative addition of a silicon–silicon bond to palladium(0).^[29] The significance of this contribution manifested itself in the fact that it had remained the only example of an asymmetric conjugate carbon–silicon bond formation for a long time. Later, we succeeded in accomplishing a general rhodium-catalyzed process for the enantioselective 1,4-addition of silicon nucleophiles released from an Si–B precursor.^[30]

We were aware of the reports by Oshima et al.^[25] and Lipshutz et al.^[27] when we considered revisiting silicon–copper reagents. Our thinking was however guided by the lessons learned from “carbon-based” cuprate chemistry^[7,31] (vide supra), and we decided to investigate bis(triorganosilyl) zinc reagents as mild sources of nucleophilic silicon (Scheme 1). A brief survey of the literature revealed that $(\text{Me}_2\text{PhSi})_2\text{Zn}$ had already been prepared by Oshima et al. but was merely tested once in a screening of transition-metal-catalyzed allene silylations.^[32] In retrospect, we wonder why the $(\text{Me}_2\text{PhSi})_2\text{Zn}$ reagent was abandoned by the Oshima laboratory. Its preparation from ZnCl_2 is unpretentious unlike the handling of pyrophoric Me_2Zn for accessing $(\text{Me}_2\text{PhSi})_2\text{ZnMe}_2\text{Li}$.

With the chemistry of $(\text{R}_3\text{Si})_2\text{Zn}$ unexplored, we set out to examine the generation of $(\text{R}_3\text{Si})_2\text{Zn}$ ^[32–34] and that of the related $(\text{R}_3\text{Sn})_2\text{Zn}$ ^[35,36] (Scheme 2). For this, corresponding R_3SiCl and R_3SnCl are treated with lithium to form R_3SiLi and R_3SnLi ,^[31] respectively. Subsequent transmetalation from lithium to zinc using ZnCl_2 yields the desired $(\text{R}_3\text{Si})_2\text{Zn}$ and $(\text{R}_3\text{Sn})_2\text{Zn}$ along with a fourfold excess of lithium chloride. Contamination with lithium chloride as a result of reductive metalation (and transmetalation) is often

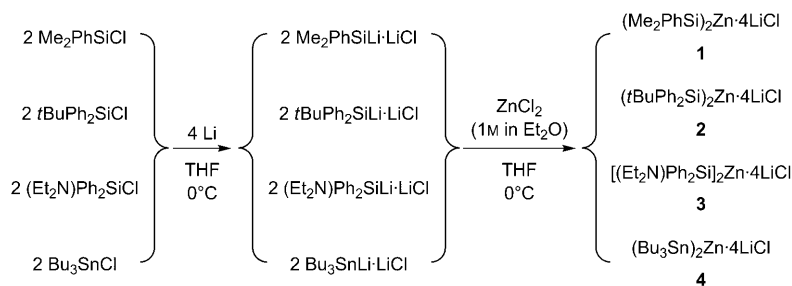
ignored in silicon-based cuprate chemistry. Both the lithium cation (as a Lewis acid) and the chloride anion (as a ligand) might interfere with the reaction outcome (vide infra), which is why $(\text{R}_3\text{E})_2\text{Zn}$ instead of $(\text{R}_3\text{E})_2\text{Zn} \cdot 4\text{LiCl}$ is a rather careless omission. By this, we were able to access $(\text{Me}_2\text{PhSi})_2\text{Zn}$ (**1**)—a source of the Fleming silane^[16]—, $(t\text{BuPh}_2\text{Si})_2\text{Zn}$ (**2**), and $[(\text{Et}_2\text{N})\text{Ph}_2\text{Si}]_2\text{Zn}$ (**3**)—a source of the Tamao silane^[37]—as well as $(\text{Bu}_3\text{Sn})_2\text{Zn}$ (**4**).^[35]

We began to test **1** in the copper(I)-catalyzed conjugate addition to cyclohexenone (Scheme 3). After only a little ex-



Scheme 3. Copper(I)-accelerated and copper-free 1,4-addition using $(\text{Me}_2\text{PhSi})_2\text{Zn}$ (**1**) ($\text{Si} = \text{Me}_2\text{PhSi}$).

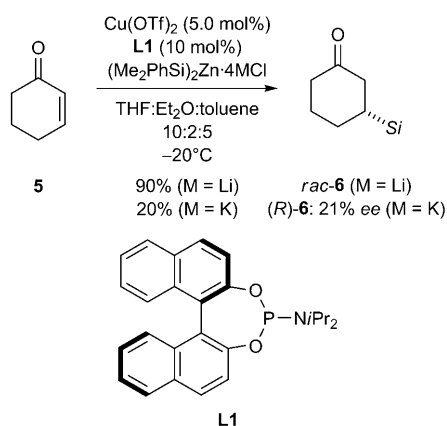
perimentation, we learned that the 1,4-addition proceeds smoothly in the presence of CuCN at low temperatures.^[33,34] Several cyclic and acyclic α,β -unsaturated carbonyls and carboxyls, and even challenging acceptors such as isophorone and γ,γ -dimethyl-substituted cyclohexenone, participated in excellent chemical yields. We were the first to report the β -silylation of the latter, and De-slongchamps et al. immediately used it in a steroid total synthesis.^[38] As mentioned before, the $(\text{R}_3\text{Si})_2\text{Zn} - \text{CuX}$ system in combination with chiral ligands might open the door to a catalytic asymmetric conjugate silylation. To exclude the possibility of an uncatalyzed background reaction, we performed a simple control experiment in the absence of a copper salt.



Scheme 2. Preparation of bis(triorganosilyl) and bis(triorganostannyl) zinc reagents.

We were more than surprised to find that high-yielding 1,4-addition occurred *without any (deliberately added) copper catalyst* even at -78°C !^[34] The isolated yields in these reactions were comparable to those obtained in the copper(I)-catalyzed series. Again, sterically congested γ,γ -dimethyl-substituted cyclohexenone reacted cleanly yet at lower reaction rate with no copper present at all!^[39]

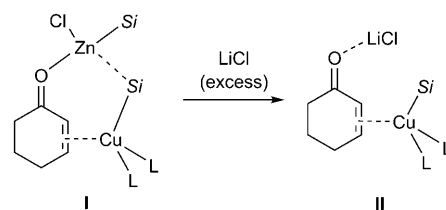
On the one hand, we were enthusiastic about the copper-free conjugate addition but on the other hand, we knew that an enantioselective copper catalysis was put well out of reach by this, unless (chiral) ligand acceleration would be operative. We nevertheless tested the copper(I)-catalyzed reaction in the presence of catalytic amounts of a representative chiral ligand, monodentate phosphoramidite **L1** (**5** $\rightarrow$ *rac*-**6**, Scheme 4).^[40] As we had suspected, no stereoinduc-



Scheme 4. Enantioselective conjugate addition of $(\text{Me}_2\text{PhSi})_2\text{Zn}$ to cyclohexenone: The role of the counter cation.

tion was observed. The complete failure as well as the ease of the reaction itself made us think about the role of the excess lithium chloride in $(\text{Me}_2\text{PhSi})_2\text{Zn}\cdot 4\text{LiCl}$ (**1**). In particular, we were interested in the influence of the Lewis acidity of the lithium cation on its ability to coordinate to the carbonyl oxygen, thereby increasing the susceptibility of the α,β -unsaturated acceptor to nucleophilic attack. For this, we prepared the related zinc reagent $(\text{Me}_2\text{PhSi})_2\text{Zn}\cdot 4\text{KCl}$, using the C_8K intercalation compound.^[41] To our delight, there was indeed asymmetric induction of 21% ee [**5** $\rightarrow$ (*R*)-**6**, Scheme 4]! This enantiomeric excess is certainly not synthetically useful but it clearly demonstrated that it might be possible to compete with the copper-free background reaction.

The pronounced influence of the alkali metal chloride on the stereochemical outcome might be rationalized on the basis of the proposed mechanism for the asymmetric copper(I)-catalyzed 1,4-addition of R_2Zn .^[42] The formation of a chelate complex is assumed to impart the conformational rigidity necessary for high enantiocontrol. In our scenario (**I**, Scheme 5), copper(I) decorated with two monodentate ligands **L** will also be coordinated by the carbon–carbon double bond and a silicon unit, bridging to the carbonyl-coordinated zinc atom. A sufficiently Lewis acidic cation



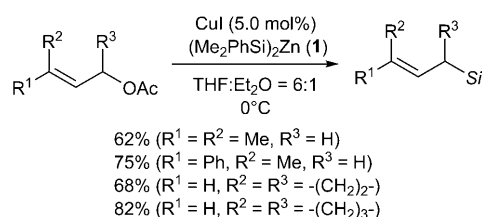
Scheme 5. External Lewis acid interfering with the chelate prior to the stereochemistry-determining step (**L** = ligand).

might then be able to break that vital chelate ring (**I** $\rightarrow$ **II**, Scheme 5). That situation is exactly seen with lithium but not with potassium cations. The use of so far elusive, salt-free zinc reagents might circumvent that issue.

The related tin reagent $(\text{Bu}_3\text{Sn})_2\text{Zn}$ (**4**) adds to α,β -unsaturated acceptors without any catalyst (not shown).^[43,44] We decided not to investigate this any further as there is solid precedence for chemoselective 1,4-addition of Bu_3SnLi , already a soft nucleophile itself.^[31,45] Nevertheless, the 1,4-addition of stoichiometric copper–tin reagents was intensively studied in the past.^[2,45,46]

Allylic Substitution

Allylic silanes are versatile intermediates in organic transformations.^[47] One of the many protocols for their synthesis^[18,47b,48] is the stoichiometric addition of silicon-based cuprates to allylic benzoates developed by Fleming and Marchi.^[2,49] For a long time, the cuprate-catalyzed opening of allylic epoxides introduced by Lipshutz et al. had been the only catalytic method ($\text{Me}_2\text{CuLi}\cdot\text{LiCN}$ with $(\text{Me}_2\text{PhSi})_2\text{ZnR}_2\text{Li}$, cf. Figure 2B).^[27] We asked ourselves whether we could adopt our standard protocol for a general synthesis of allylic silanes from allylic esters and carbamates. Gratifyingly, the standard reaction conditions brought about carbon–silicon bond formation by allylic substitution (Scheme 6).^[50] Allylic silanes were obtained in good chemi-

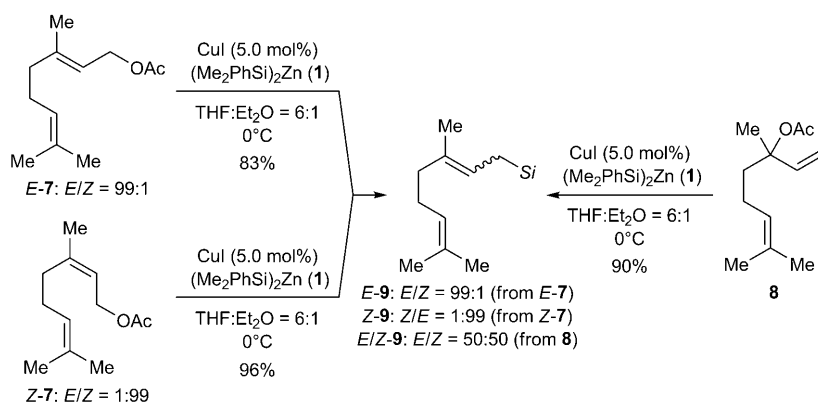


Scheme 6. Copper(I)-catalyzed allylic substitution of simple allylic acetates.

cal yields when simple allylic acetates as well as carbamates (not shown) were subjected to the $(\text{Me}_2\text{PhSi})_2\text{Zn}\text{--CuI}$ combination.

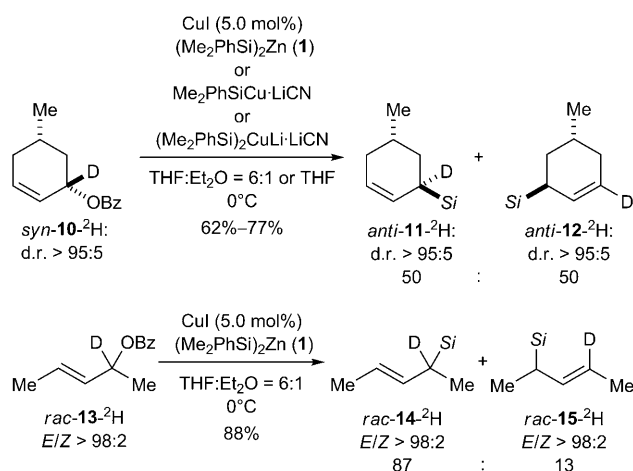
The substitution proceeded with complete preservation of the double-bond geometry with biased primary allylic pre-

cursors (*E*-7→*E*-9 and *Z*-7→*Z*-9, Scheme 7). In turn, a tertiary acetate produced the primary allylic silane without any diastereocontrol (8→*E*-9, Scheme 7), which is consistent with earlier reports.^[2b]



Scheme 7. Regioselective and diastereospecific allylic substitution of structurally biased allylic acetates.

Aside from the facile access to primary allylic silanes, an equally facile stereocontrolled preparation of α -chiral allylic silanes^[47c,51] is synthetically even more attractive. To elucidate the regiochemical course (S_N versus S_N'), we desymmetrized allylic model compounds by deliberate introduction of an ^2H label (Scheme 8).^[52,53] Moreover, allylic benzoate



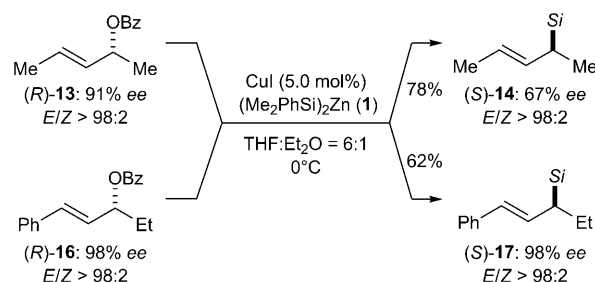
Scheme 8. Elucidation of the regiochemical course by isotopic desymmetrization (Bz=benzoate).

syn-10- ^2H contains a perfectly positioned methyl group to distinguish between *syn* or *anti* substitution mechanisms.^[52] Three different cuprate reagents were used, and a 50:50 mixture of diastereomerically pure *anti*-11- ^2H and *anti*-12- ^2H was obtained in all cases (*syn*-10- ^2H →*anti*-11- ^2H /*anti*-12- ^2H , Scheme 8). This transformation is diastereospecific as *anti*-10 afforded *syn*-11 (not shown).^[50] These data revealed that the reaction follows both formal S_N and S_N' pathways. Con-

sequently, if a cyclic allylic precursor were enantiopure, it would racemize. We next examined ^2H -labeled acyclic substrate *rac*-13- ^2H . Unexpectedly, it underwent the same reaction with reasonable regiocontrol, clearly favoring a formal

S_N -type over a formal S_N' -type displacement (*rac*-13- ^2H →*rac*-14- ^2H /*rac*-15- ^2H , Scheme 8).

The preference for S_N instead of S_N' substitution prompted us to repeat the latter experiment with unlabeled but enantioenriched (*R*)-13 [(*R*)-13→(*S*)-14, Scheme 9]. The slightly eroded enantiomeric excess of allylic silane (*S*)-14 agrees with the regioisomeric ratio obtained from the isotopic labeling. While 10 (cyclic) and 13 (acyclic) were “symmetrically” alkyl-substituted allylic systems, we also in-



Scheme 9. Enantiospecific allylic substitution: Formation of an enantioenriched α -chiral allylic silane.

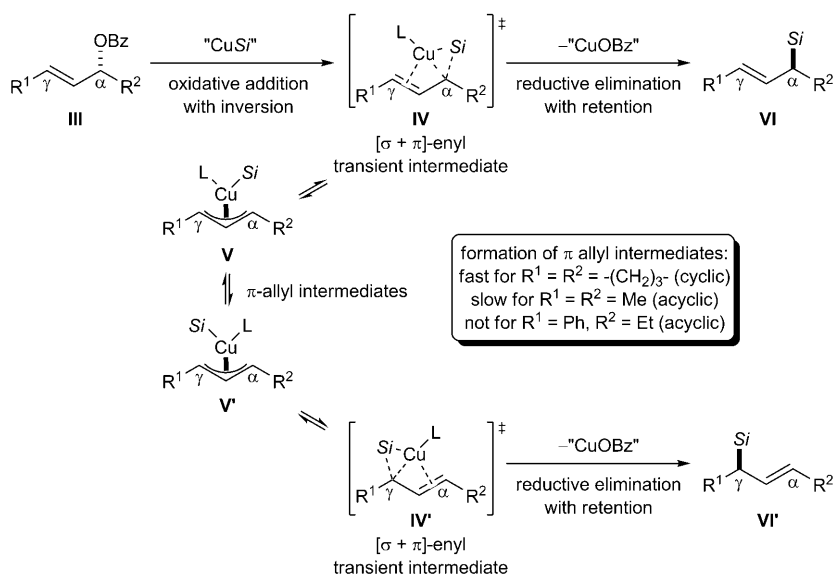
cluded “non-symmetrical” 16 into our survey, and this was a major step forward. (*R*)-16 was converted into allylic silane (*S*)-17 without any loss of stereochemical information [(*R*)-16→(*S*)-17, Scheme 9].^[52]

Based on these findings, we proposed a unified reaction mechanism (Scheme 10).^[52] The reaction starts with oxidative addition of the C–O bond in **III** to catalytically active Me_2PhSiCu (vide infra) (=“ CuSi ”) in an *anti*- S_N fashion (**III**→**IV**). The transient intermediate **IV** might enter two different reaction channels, either immediate reductive elimination (**IV**→**VI**) or formation of a π -allyl intermediate (**IV**→**V**). Depending on the substitution pattern of **IV**, one of these pathways is favored. The net result of direct reductive elimination is an enantiospecific allylic substitution (**III**→**IV**→**VI**). Conversely, the stereochemical integrity of **IV** dwindles by reversible σ - π - σ -isomerization (**IV**→**V**→**V'**→**IV'**) through formation of π -allyl intermediates **V**. The aryl group in “non-symmetrical” systems is vital for the enantiospecificity (**III**→**VI**) due to its stabilization of **IV**. Conjugation with the alkene imparts lifetime,^[54] long enough for the reductive elimination (**IV**→**VI**) to occur prior to π -allyl formation (**IV**→**V**). The situation changes

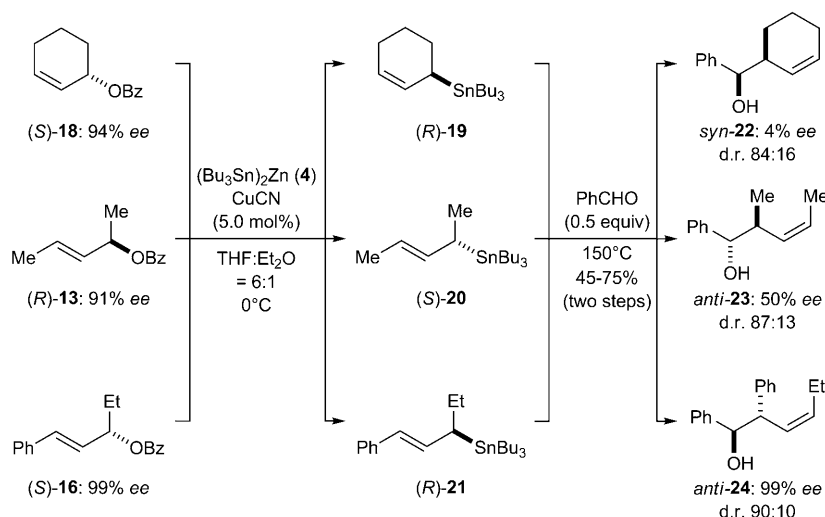
with alkyl substitution, and **IV**, which is devoid of any stabilization, will isomerize to **V** and then to **V'**. Its reaction rate is governed by the structure (cyclic or acyclic) of **IV**.

Both α -chiral allylic silanes and (intrinsically more reactive) stannanes are certainly important allyl transfer reagents.^[47,55] It is therefore somewhat unexpected that all-carbon-substituted α -chiral allylic stannanes had been elusive prior to our work.^[56,57] Their pronounced chemical instability makes them difficult to synthesize, to purify and to store. Oxygenation at the α - or γ -carbon atom greatly enhances their stability, and these reagents have been extensively used in carbonyl allylations.^[55] For us, the obvious next step was to apply our facile copper(I)-catalyzed allylic substitution to that problem. Employing $(\text{Bu}_3\text{Sn})_2\text{Zn}$ (**4**) (cf. Scheme 2) instead of $(\text{Me}_2\text{PhSi})_2\text{Zn}$ (**1**) ought to provide an enantiospecific access to all-carbon-substituted α -chiral allylic stannanes. We chose the same substrates as for the related carbon–silicon bond formation (Scheme 11).^[33,34] Initial screening showed that it was indeed possible to generate allylic stannanes **19–21** in near quantitative yields but their isolation and determination of their enantiomeric excesses by GLC or HPLC failed.^[36] We

therefore processed fragile **19–21** directly in thermal allylation reactions with benzaldehyde.^[58] The corresponding homoallylic alcohols **22–24** were obtained in moderate yields, typical for this transformation.^[57a,59,60] We were delighted that the stereochemical course of the allylic displacements (*S*)-**18**→*syn*-**22**, (*R*)-**13**→*anti*-**23**, and (*S*)-**16**→*anti*-**24** was in full agreement with the silicon series (cf. Scheme 8–10). In one pot, “non-symmetrical” (*S*)-**16** (99% *ee*) was transformed into *anti*-**24** (99% *ee*) via two enantiospecific steps. The diastereospecificity, namely *anti* relative configuration and *Z* geometry of the alkene from an *E*-configured allylic reagent, is explained by a cyclic six-membered transition state with axial orientation of the ethyl group (not shown).^[61]



Scheme 10. Unified mechanistic picture of the regioselective allylic displacement (L = ligand).

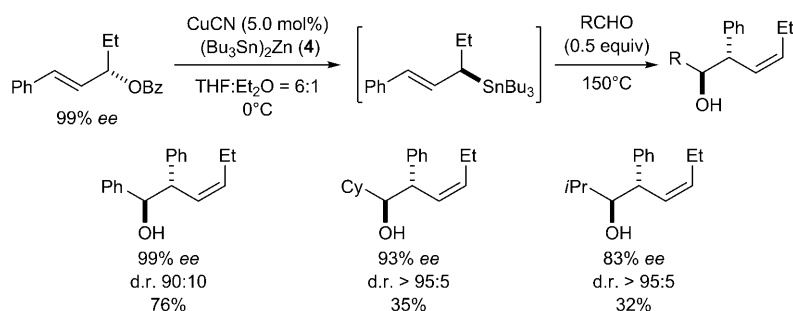


Scheme 11. Copper(I)-catalyzed allylic substitution using $(\text{Bu}_3\text{Sn})_2\text{Zn}$ (**4**): Formation of an enantioenriched α -chiral allylic stannane.

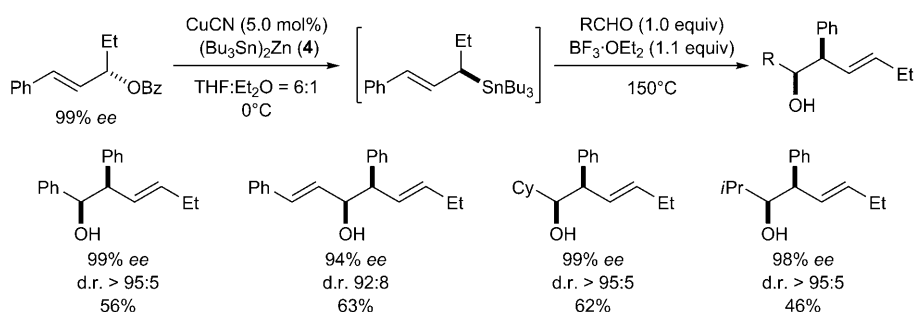
The scope of this reaction was illustrated by a few more *anti*-selective thermal (Scheme 12)^[59] and by several *syn*-selective $\text{BF}_3\cdot\text{OEt}_2$ -promoted carbonyl allylations (Scheme 13). As a consequence of the reaction mechanism,^[62] the Lewis acid-mediated allylation reaction provides an entry into the complementary series of homoallylic alcohols.

Additions to Carbon–Carbon Multiple Bonds

The silyl metalation of carbon–carbon triple bonds offers a practical access to stereodefined vinylic silanes.^[2b,63] These metalations are often realized by the stoichiometric addition of silicon-based cuprate reagents (cf. Figure 1),^[63] yet again

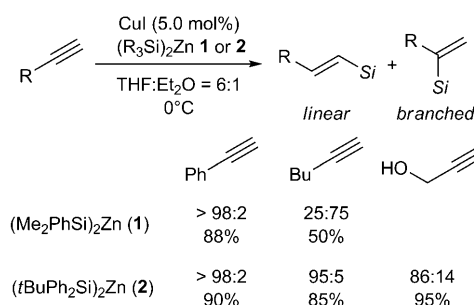


Scheme 12. Enantiospecific and highly *anti*-diastereoselective thermal S_E2' reactions of α -chiral allylic stannanes with aldehydes.

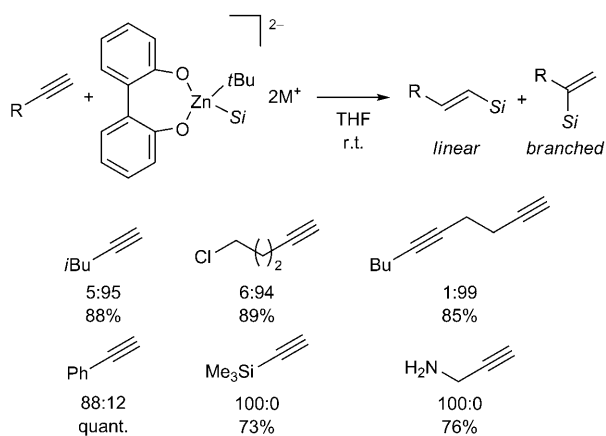


Scheme 13. Enantiospecific and highly *syn*-diastereoselective $BF_3 \cdot OEt_2$ -promoted S_E2' reactions of α -chiral allylic stannanes with aldehydes.

a catalytic variant is known.^[64] The regioselectivity was optimized for selected substrates using sterically hindered reagents. This limitation was eliminated by Uchiyama et al. as part of their seminal work on the silylzincation of terminal alkynes in the absence of any catalyst (Scheme 14).^[65,66b] Their so-called SiBNOL-Zn-ate served as the silicon nucleophile source. Terminal alkynes participated in good to excellent yields with remarkable regioselectivities. Alkyl-substituted alkynes gave branched vinylic silanes, leaving an internal carbon-carbon triple bond intact. Electronic factors



Scheme 15. Copper(I)-catalyzed silylation of terminal alkynes ($Si = Me_2PhSi$ or $tBuPh_2Si$).



Scheme 14. Regioselective silylation of terminal alkynes by Uchiyama et al.

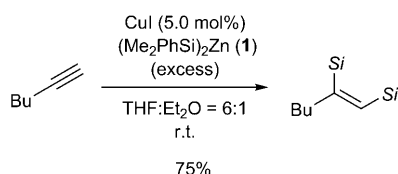
steered the addition towards the linear products with a phenyl or a Me₃Si group attached to the alkyne. Heteroatom-directed silylzincation afforded the linear vinylic silane as well.^[66]

Our approach was identical to the procedures for conjugate addition and allylic substitution (vide supra). We treated terminal alkynes with (Me₂PhSi)₂Zn (1) and more hindered (tBuPh₂Si)₂Zn (2) in the presence of copper(I) iodide (Scheme 15).^[67,68] With 1, the linear:branched ratio was fine with phenylacetylene but poor with 1-hexyne. The latter observation is consistent with Fleming's results, showing that (Me₂PhSi)₂CuLi-LiCN favors the linear, whereas Me₂PhSiCu-LiCN produces the branched isomer. Among a few other clues, this supports the assumption that our

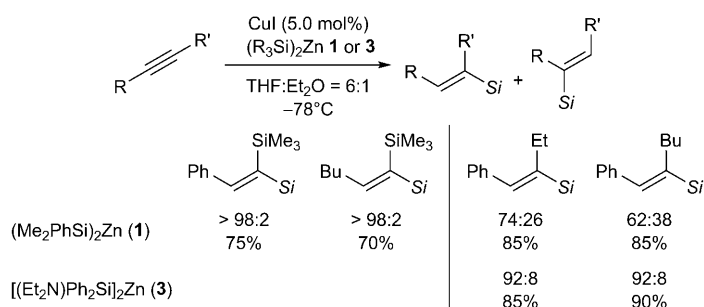
(Me₂PhSi)₂Zn-CuX reagent generates Me₂PhSiCu as the catalytically active compound (vide infra). When (tBuPh₂Si)₂Zn (2) was used, the level of regiocontrol improved substantially.

We also found during our investigations that an excess of (Me₂PhSi)₂Zn (1) and elevated reaction temperature results in bis(silylation) of terminal alkynes (Scheme 16).

Our next goal, the regioselective silyl metalation of internal alkynes, was far more challenging, and we were glad to find that regiocontrol was excellent (r.s. > 98:2) for silylated alkynes (left, Scheme 17). Encouraged by that, we continued to test internal alkynes but the level of regioselectivity (r.s. = 74:26 and 62:38) was poor (right, Scheme 17).^[69] Using conventional (Me₂PhSi)₂Zn (1), these selectivities were not



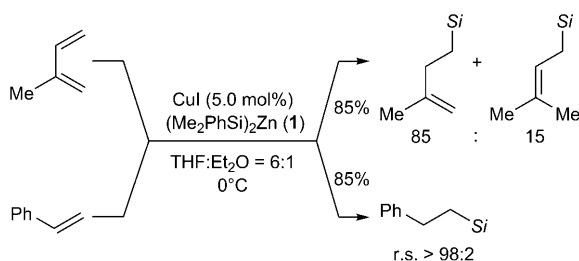
Scheme 16. Unexpected bis(silylation) of an alkyne.



Scheme 17. Regioselective silyl metalation of internal alkynes (Si = Me₂PhSi or (EtO)Ph₂Si derived from (Et₂N)Ph₂Si after treatment with ethanol).

at all surprising,^[70] whereas the ones obtained with [(Et₂N)Ph₂Si]₂Zn (**3**) were! For unknown reasons, the copper reagent derived from heteroatom-substituted **3** added across the carbon–carbon triple bond with decent regiocontrol (r.s. 92:8).^[69] We later demonstrated that the (EtO)Ph₂Si unit (generated from (Et₂N)Ph₂Si by treatment with ethanol) smoothly transmetalates in Hiyama cross-couplings.^[69]

Finally, we subjected isoprene and styrene to our standard protocol, and the desired products were obtained in high yields (Scheme 18).^[71] The styrene experiment lent further



Scheme 18. Copper(I)-catalyzed silylmatalation of isoprene and styrene.

support to our hypothesis that Me₂PhSiCu is formed from the (Me₂PhSi)₂Zn–CuX reagent. Liepins and Bäckvall had found that (Me₂PhSi)₂CuLi–LiCN polymerizes styrene.^[71a]

Conclusions

A general catalysis for carbon–silicon and carbon–tin bond formation using cuprate-type reagents was a much sought-

after goal. Isolated reports had described attractive individual solutions to the problem. Our simple idea, that is the use of soft bis(triorganosilyl) and bis(triorganostannyl) zinc reagents, led to a number of highly effective copper(I)-catalyzed protocols for the silylation and stannylation of organic compounds. We discovered that even uncatalyzed addition of these nucleophiles is possible in some cases. We think that several findings are particularly noteworthy: 1) Copper-free conjugate addition to (hindered) α,β-unsaturated acceptors. 2) Understanding of the mechanism of the copper(I)-catalyzed allylic substitution. 3) Enantiospecific access to α-chiral all-carbon substituted allylic silanes and stannanes. 4) Regioselective silylzincation of internal carbon–carbon triple bonds. The remaining downside of these zinc reagents is certainly the loss of one equivalent of the silicon or the tin group, an issue that might be resolved in the future by using mixed zinc compounds decorated with a non-transferable dummy ligand.^[2b]

The convenience of our protocol is about to find its way into the standard synthetic repertoire, and it is nice to see the chemistry now being picked up by others.^[38,66b]

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