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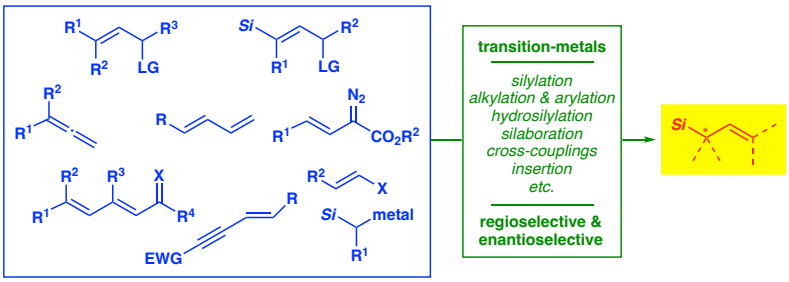

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Abstract Over the past 30 years, the synthesis of α-chiral allylsilanes have attracted much interest. These compounds are indeed versatile building blocks and linchpins ranking among the most useful organic scaffolds due to the large number of transformations that both their C–Si bond and C–C double bond can undergo. They therefore occupy a unique place in the arsenal of the organic chemist, particularly for the synthesis of complex molecules. In this review, an overview of transition-metal-catalysed syntheses of α-chiral allylislanes is presented.

Key words allylsilanes, allylic substitution, conjugate addition, enantioselectivity, hydrosilylation, regioselectivity

1 Introduction

The small electronegativity difference between carbon and silicon results in low polarization of the C–Si bond which makes it a relatively robust covalent bond, providing organosilicon compounds with high bench stability and easy handling. Among organosilicon compounds, allylsilanes hold a unique place in the organic chemist's arsenal and have been used in many synthetic transformations such as carbonyl allylation, fluorodesilylation, ring-closing and cross-metathesis, cross-coupling reactions and annulations to access various carbo- and heterocycles.[1–6] In the past 30 years, allylsilanes have therefore aroused the interest of organic chemists for their preparation.[4,7]

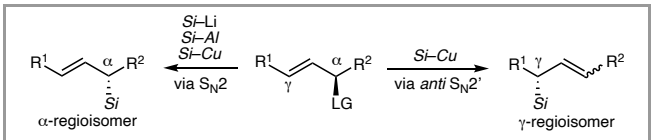
In particular, considerable efforts have been made in recent years to develop stereoselective accesses to α-chiral allylsilanes, containing tertiary or quaternary stereogenic carbon centers in the α-position of silicon. While a few excellent reviews have covered recent advances in the synthesis of allylsilanes, none of them have been however specifically devoted to that of α-chiral allylsilanes. The present review intends to fill the gap in the field by reporting methods based on transition-metal catalysis.

2 Addition of Silylmetals

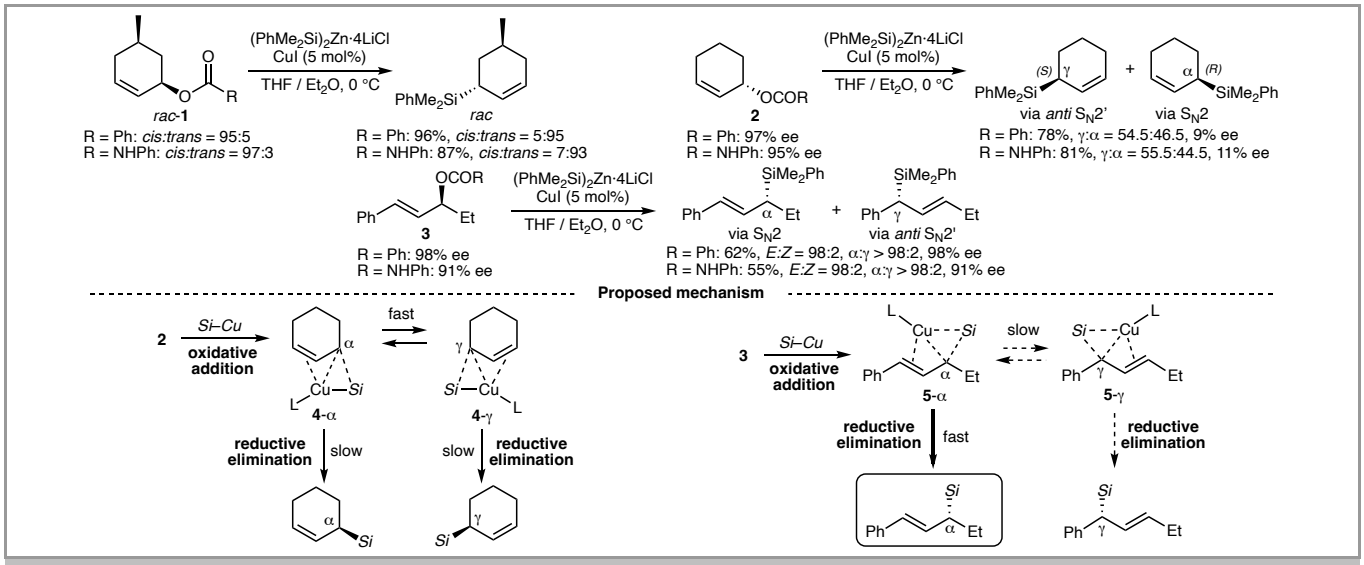
2.1 Silylation of Allylic Electrophiles

2.1.1 Under Copper Catalysis

The synthesis of allylsilanes by addition of silylmetals to allylic electrophiles (mainly allylic halides, acetates, carbamates, sulfonates and phosphates), through either S_N2 or S_N2' pathway, emerged in the early 1980s. As a general trend, silyllithium[8] and silylaluminium[9] reagents provide mainly α-products through S_N2 pathway, while silylcopper reagents,[10] and in particular silylcuprates, afford α- or γ-products as major regioisomers via S_N2 or S_N2' pathways, depending on the conditions (Scheme 1). From chiral allylic electrophiles, both pathways provide α-chiral allylsilanes, the S_N2' process having being demonstrated to take place stereoselectively in *anti* fashion with silylcuprates in most cases.

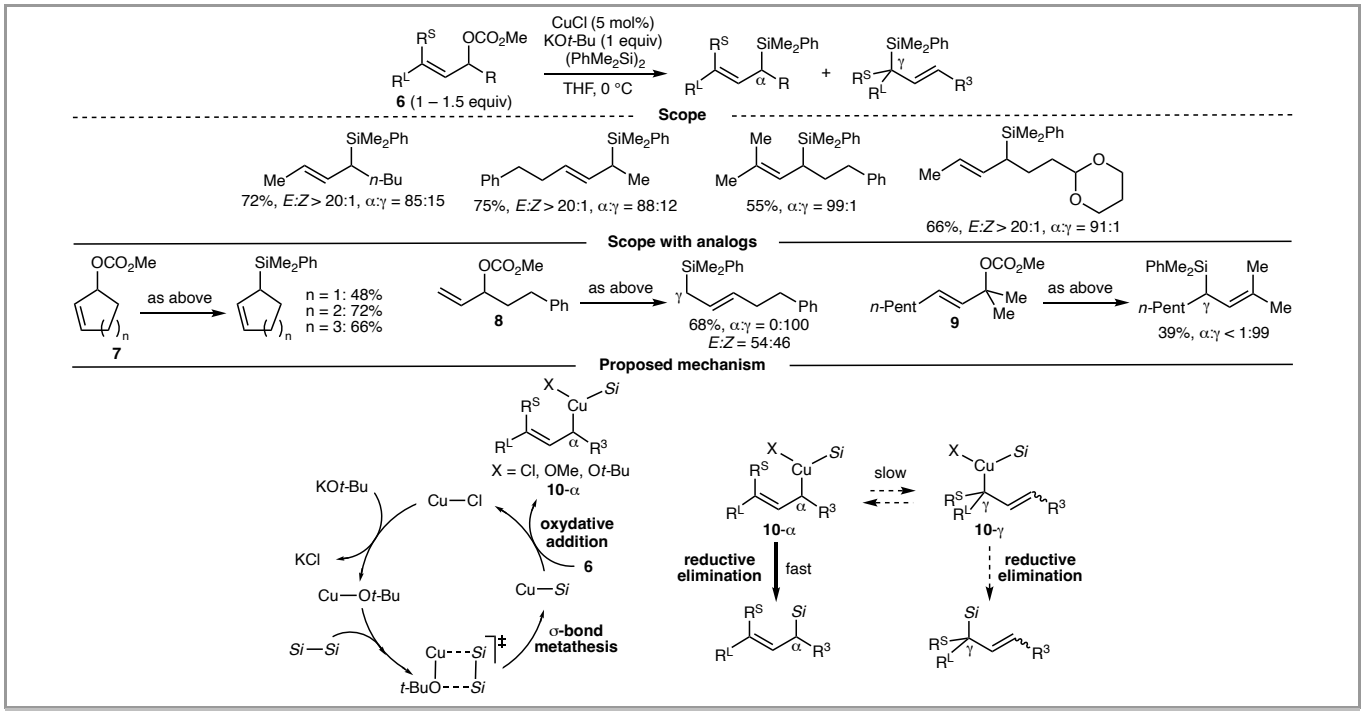


Scheme 1 General trend in silylation of allylic electrophiles

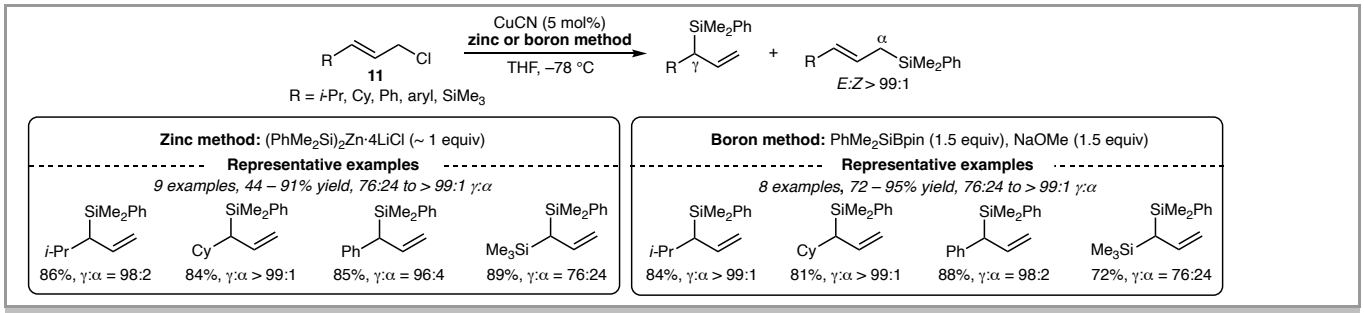


Scheme 2 Copper-catalyzed silylation of chiral allylic esters and carbamates with $(PhMe_2Si)_2Zn·4LiCl$

It is not until 2005 that Oestreich et al. reported the first transition-metal-catalyzed allylic silylation.[11] They showed that the reaction between chiral allylic carbamates or esters and $(PhMe_2Si)_2Zn·4LiCl$, catalyzed by 5 mol% of CuI, enabled the highly diastereoselective formation of α-chiral allylsilanes. More particularly, racemic *cis* substrates **1** were found to afford *trans* α-chiral allylsilanes with clean inversion of the stereogenic carbon (Scheme 2). The authors further extended the reaction to enantioenriched analogs. The stereoselective outcome was then shown to highly depend on the structure of the starting materials.[12] Almost racemic mixtures were obtained from cyclic substrates **2**, via S_N2 and *anti* S_N2' competitive pathways. On the other hand, acyclic substrates **3** provided clean inversion of the configuration of the stereogenic center and perfect control of the (*E*)-configuration, via the S_N2 pathway. All these results were explained by invoking the equilibrium between the two [σ + π] enyl transient intermediates, which are generated by oxidative addition of the C–O bond of the substrates to the metal center of the catalytically silylcopper active species generated in situ. The equilibrium between symmetrical intermediates **4**-α and **4**-γ was assumed to be fast compared to reductive elimination, resulting in quasi-racemization through formation of nearly equimolar mixtures of enantiomeric α- and γ-products, from **4**-α and **4**-γ respectiveley. Conversely, the equilibrium between unsymmetrical intermediates **5**-α and **5**-γ was assumed to be slow, yielding predominantly α-products from **5**-α. More recently, Sawamura et al. reported a related reaction using disilane $(PhMe_2Si)_2$ in the presence of 5 mol% of CuCl and a stoichiometric amount of KO*t*-Bu.[13] Under these conditions, secondary allylic carbonates **6** yielded α-regioisomers as major products (Scheme 3). Cyclic substrates **7** afforded similar



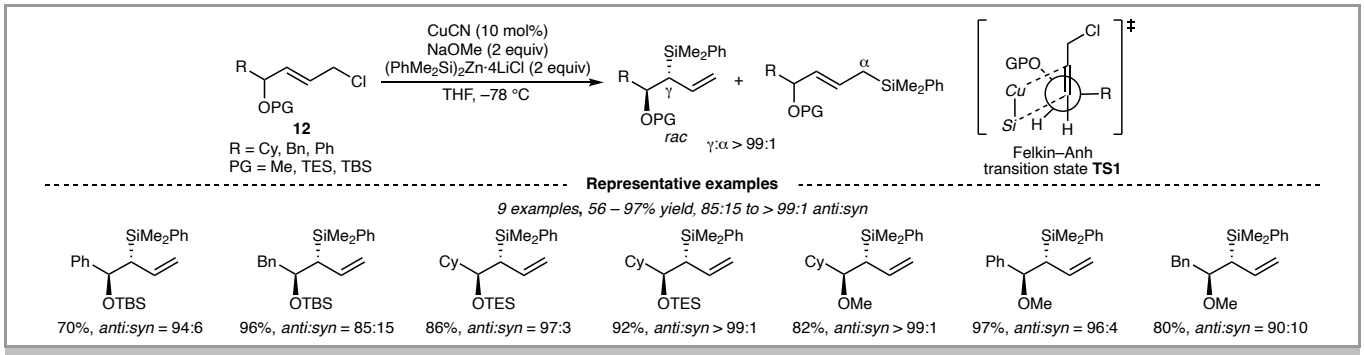
Scheme 3 Copper-catalyzed silylation of chiral allylic carbonates with $(PhMe_2Si)_2$



Scheme 4 Zinc and boron methods with primary allylic chlorides

results,while that containing terminal allylic system **8** as well as tertiary one **9** provided exclusively γ-regioisomers, and (*Z*)-configured substrates were poorly regioselective. The authors rationalized these results by the formation of copper(III) intermediates **10**-α via oxidative addition of the C–O bond of allylic carbonates to the catalytically active silylcopper species generated through σ-bond metathesis. The authors postulated that, when the steric bulk at the α-position is lower than that at the γ-position, **10**-α would undergo fast reductive elimination, giving predominantly α-regiosiomers. Otherwise, isomerization of **10**-α into **10**-γ was assumed to take place faster, which yields γ-regiosiomers as major products through reductive elimination.

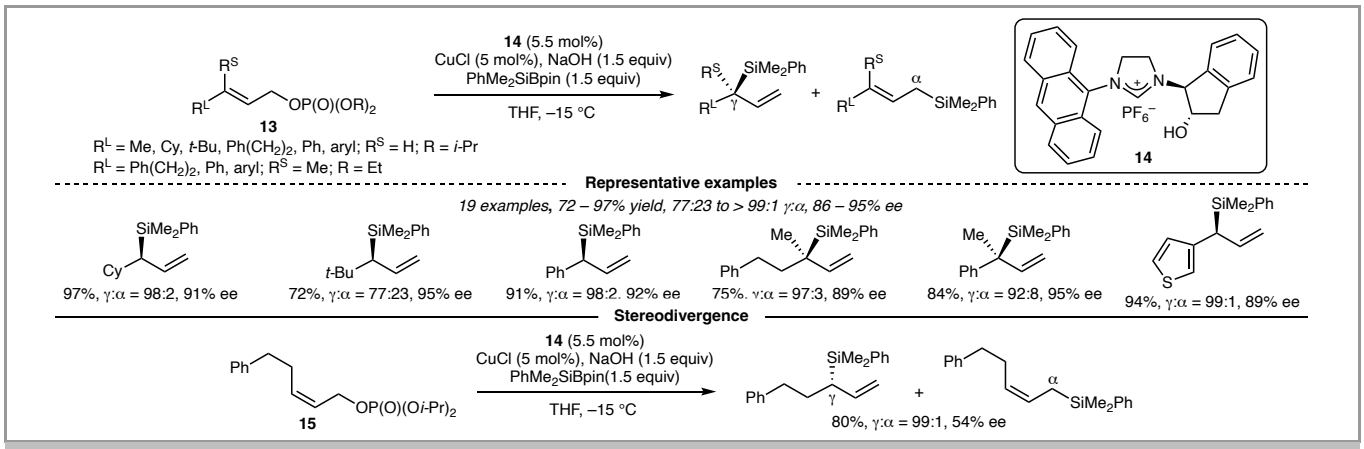
In the continuation of their work, Oestreich et al. showed that the regioselectivity of the reaction of allylic electrophiles with $(PhMe_2Si)_2Zn·4LiCl$ was dependent on the leaving group.[14] When allylic esters, carbamates and carbonates were reacted with $(PhMe_2Si)_2Zn·4LiCl$ in the presence of 5 mol% of CuCN (i.e. the zinc method), α-regioisomers were exclusively obtained. In contrast, allylic phosphates, chlorides and bromides yielded predominantly γ-regioisomers. More particularly, chlorides **11** were found to be the substrates of choice, affording the highest γ-regioselectivity (Scheme 4). The authors obtained similar results through copper-catalyzed activation of the Si–B bond of Suginome silylboronate ($PhMe_2SiBpin$) with an alkoxide base (i.e. the boron method).[15] The the use of a slight excess of the non-bulky NaOMe alkoxide base was then found to be necessary to enable boron-to-copper transmetalation of silicon via σ-bond metathesis. The boron method was also applied with success to chiral δ-alkoxy allylic chlorides **12** (Scheme 5).[16] In all cases, perfect γ-regioselectivity and high *anti* 1,2-diastereoselectivity were observed and rationalized by Felkin–Anh transition state **TS1** in which the alkoxy group was assumed to be smaller than the other substituent of the stereogenic center.



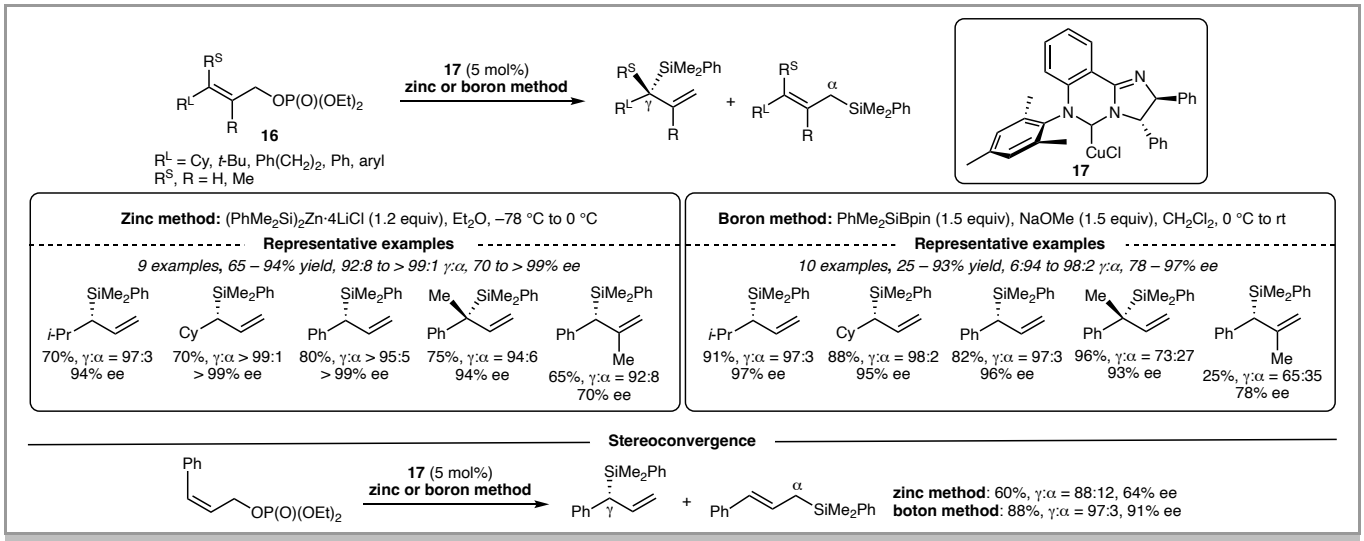
Scheme 5 Boron method with chiral δ-alkoxy primary allylic chlorides

In 2013, Hayashi et al. developed an enantioselective boron method for γ-substitution of allylic phosphates **13** employing 5 mol% of CuCl and 5.5 mol% of imidazolium salt **14** (Scheme 6).[17] Except in the case of the bulky tert-butyl group, the reaction yielded tertiary α-chiral allylsilanes with excellent γ-regio-and enantioselectivity. Combining diisopropyl phosphates and NaOH was shown to offer the best results and also enabled the synthesis of quaternary γ-products from γ,γ-disubstituted substrates. Stereodivergence was found to be a feature of the reaction since (*Z*)-configured allylic phosphate **15** led to the opposite configuration of the newly created stereogenic center, albeit with eroded enantiomeric purity. Around the same time, significant better γ-regio- and enantioselectivity were obtained by Oestreich et al. using 5 mol% of NHC copper catalyst **17** prepared in advance (Scheme 7).[18] Both γ-substituted and γ,γ-disubstituted allylic phosphates **16** gave almost exclusively γ-regioisomers, except with the bulky tert-butyl group at the γ-position, while loss of enantioselectivity was observed with a β-substituted substrate. Catalyst **17** was also used with silylzinc reagents with which it was found that the greater the steric bulk at the silicon, the lower the γ-regio- and enantioselectivity. Thus, $(PhMe_2Si)_2Zn·4LiCl$ was shown to outperform its *t*-$BuPh_2Si$ and Ph_3Si analogs.[19] As before, except in the peculiar case of a β-substituted substrate, the zinc method was notably superior to the boron method. In addition, contrary to the result obtained with the NHC copper complex of **14**, the two methods proved to be stereoconvergent since they gave the same enantiomers with γ-regio- and enantioselectivity in the same order of magnitude from (*E*)- and (*Z*)-configured isomeric substrates. Noteworthy, the same trend was observed with allylic chlorides, although with huge erosion of enantioselectivity.

Although excellent in almost all cases, the enantioselectivity was disappointing with β-substituted substrates. Oestreich et al.

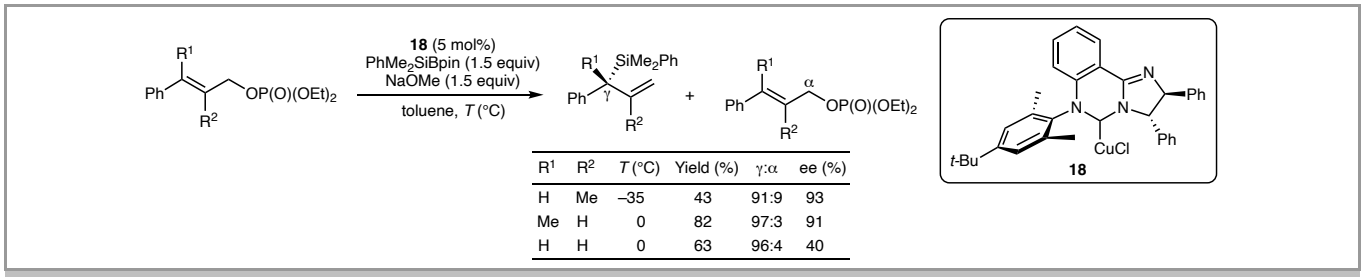


Scheme 6 Enantioselective boron method with primary allylic phosphates



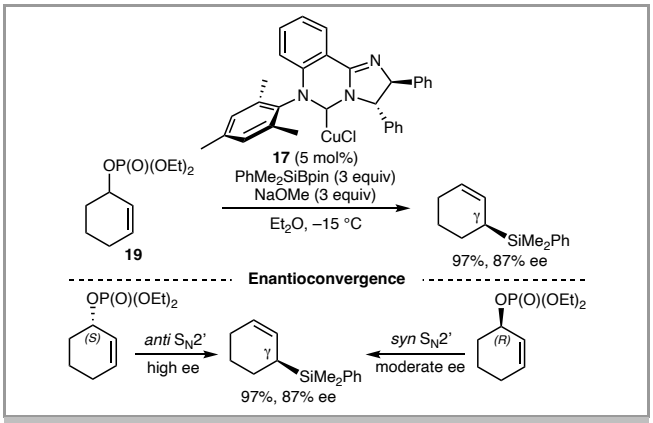
Scheme 7 Enantioselective boron and zinc methods with primary allylic phosphates

managed to improve it using the boron method with the bulkier tert-butyl-substituted NHC copper complex **18**.[18b] A dramatic influence of the solvent was also observed since in toluene γ-regioselectivity was significantly increased at low temperature, with high enantioselectivity, while in THF α-regioselectivity prevailed (Scheme 8). Toluene exhibited the same beneficial effect with γ,γ-disubstituted allylic phosphates. but failed to give accepatble enantioselectivity with γ-substituted substrates. The authors also showed that the boron method, conducted with NHC copper complex **17**, enabled the enantioconvergent γ-silylation of racemic cyclohex-2-enyl diethyl phosphate **19**.[20] A phosphate leaving group, a low temperature and Et_2O as solvent proved to be the optimal combination. Under these conditons, the boron method afforded the (*S*)-enantiomer in high yield with excellent optical purity (Scheme 9). The contribution of the S_N2 pathway to the enantioselectivity was inferred to be negligible by deuterium-labeling experiments. All these results suggested that both enantiomers of **19** were transformed into the same product through two distinctive S_N2' pathways with opposite diastereofacial selectivities. γ-Silylation of the (*S*)-enantiomer of **19** was assumed to occur in highly enantioselective *anti* manner, while γ-silylation of the (*R*)-enantiomer of **19** was assumed to occcur in moderate enantioselective *syn* manner.



R¹	R²	*T* (°C)	Yield (%)	γ:α	ee (%)
H	Me	–35	43	91:9	93
Me	H	0	82	97:3	91
H	H	0	63	96:4	40

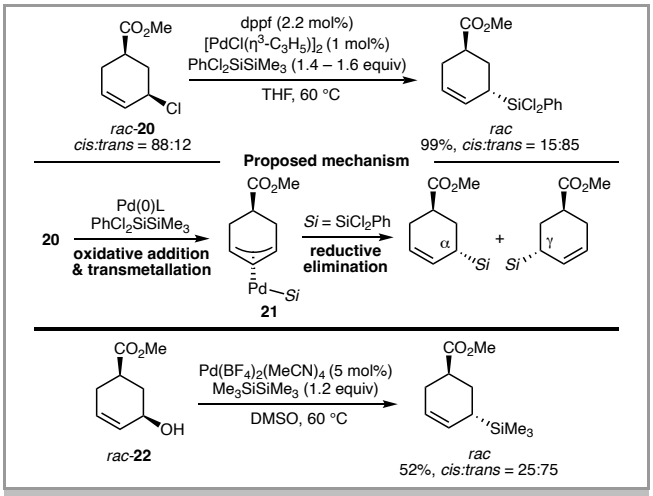
Scheme 8 Influence of the solvent on the enantioselective boron method withprimary allylic phosphates



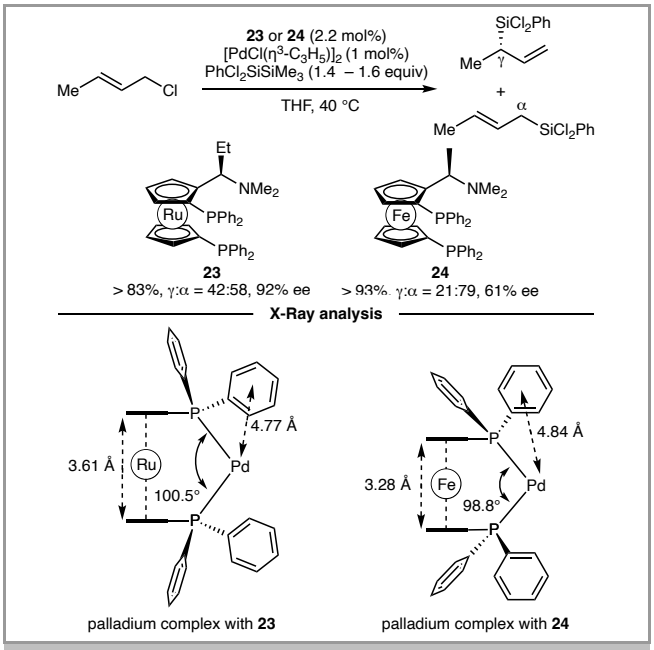
Scheme 9 Convergent enantioselective boron method

2.1.2 Under Palladium Catalysis

Silylation of allylic electrophiles through π-allylmetals was uncovered in the early 1980s. In 1983, Trost et al. described the moderately diastereoselective reaction of optically active allylic acetates with silylaluminium reagents under palladium and molybdenum catalysis.[21] Ten years later, Hayashi et al. reported that unsymmetrical disilane $PhCl_2SiSiMe_3$ allowed silylation of allylic electrophiles when carried out in the presence of 1 mol% of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 2.2 mol% of a tertiary phosphine (Scheme 10).[22] In particular, they showed that $PhCl_2SiSiMe_3$ reacted with racemic *cis* allylic chloride **20** to yield the *trans* product. The reaction was assumed to involve formation, with inversion, of symmetrical π-allylpalladium complex **21** through oxidative addition of the C–Cl bond to palladium(0), generated in situ, and subsequent silicon-to-palladium transmetallation of the $PhCl_2Si$ group. The transfer of the $PhCl_2Si$ group to the α- and/or γ-carbon by reductive elimination then would provide the two enantiomeric *trans* products. More recently, Szabó et al. described the related reaction with racemic *cis* allylic alcohol **22** and symmetrical disilane $Me_3SiSiMe_3$ catalyzed by 5 mol% of $Pd(BF_4)_2(MeCN)_4$.[23] In this reaction, $Me_3SiSiMe_3$ was assumed to behave as a Lewis acid activating the hydroxyl of the substrate, while it was inert under previous Hayashi's conditions. This activation would therefore facilate oxidative addition of the C–O bond of the substrate to palladium(0) generated in situ to afford



Scheme 10 Diastereoselective palladium-catalyzed silylation of cyclic allylic electrophiles with disilanes



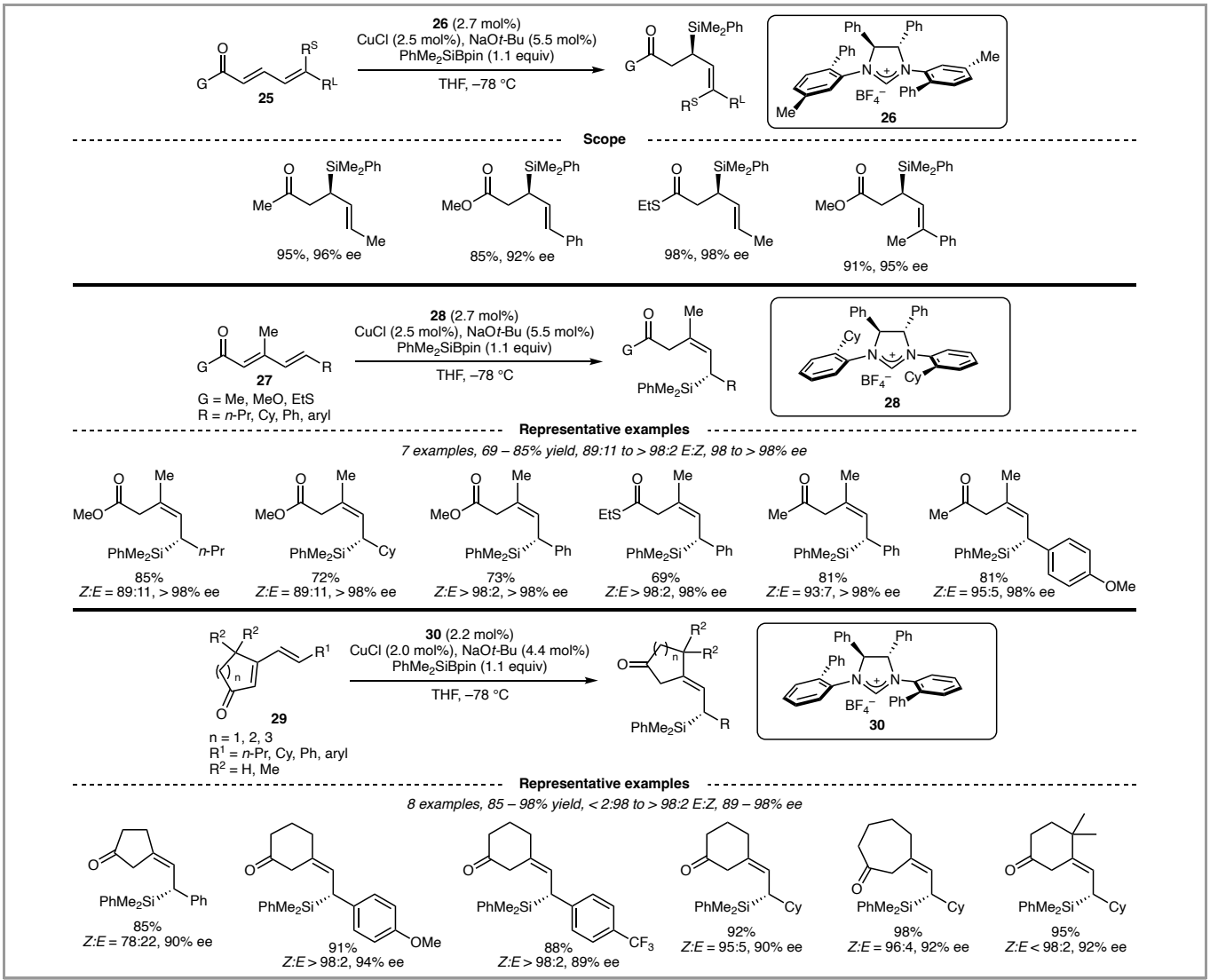
Scheme 11 Enantioselective palladium-catalyzed silylation of primary allylic chlorides with metallocene-based diphosphines

symmetrical π-allylpalladium complex, which in turn would yield the *trans* product through reductive elimination. In the course of their studies, Hayashi et al. managed to carry out γ-silylation of primary allylic chlorides in enantioselective manner with $PhCl_2SiSiMe_3$ by replacing the tertiary phosphine with chiral metallocene-based diphosphines.[22,24] They showed that ruthenocenyl diphosphine **23** offered better enantioselectivity than its ferrocenyl analog **24**. This was explained by a greater bite angle of the diphosphine in the palladium complex formed with **23**, as seen by X-ray analysis, which results in a greater bulk at the palladium and therefore in significant higher enantioselectivity (Scheme 11). However, the γ-regioselectivity remained low in both cases.

2.2 Conjugate Addition

2.2.1 1,4- and 1,6-Conjugate Additions to Dienyl Carbonyls

In 2010, Hoveyda et al. applied the enantioselective boron method to the silylation of dienyl carbonyls (Scheme 12).[25] With substrates **25**, the silylation occured through the 1,4-mode of addition in the presence of 2.7 mol% of CuCl and 2.7 mol% of chiral imidazolium salt **26**. Functionalized β'-carbonyl α-chiral allylsilanes were obtained with high enantiomeric purity and perfect (*E*)-selectivity. In sharp contrast, with substrates **27**, containing a methyl substituent in the β-position, the 1,6-mode of addition predominated. In this case, using chiral imidazolium salt **28** was required to achieve both excellent enantiomeric purity and (*Z*)-selectivity. Roughly similar results were obtained from cyclic dienones **29** with 2.2 mol% of imidazolium salt **30**, except in the case of the cyclopentenyl system which gave lower (*Z*)-selectivity. In these reactions, the (*E*,*E*)-configuration of the dienyl system turned out to be the key since (*Z*,*E*)-isomers were not sastifactorily converted to the expected products.



Scheme 12 Enantioselective boron method with dienyl carbonyls

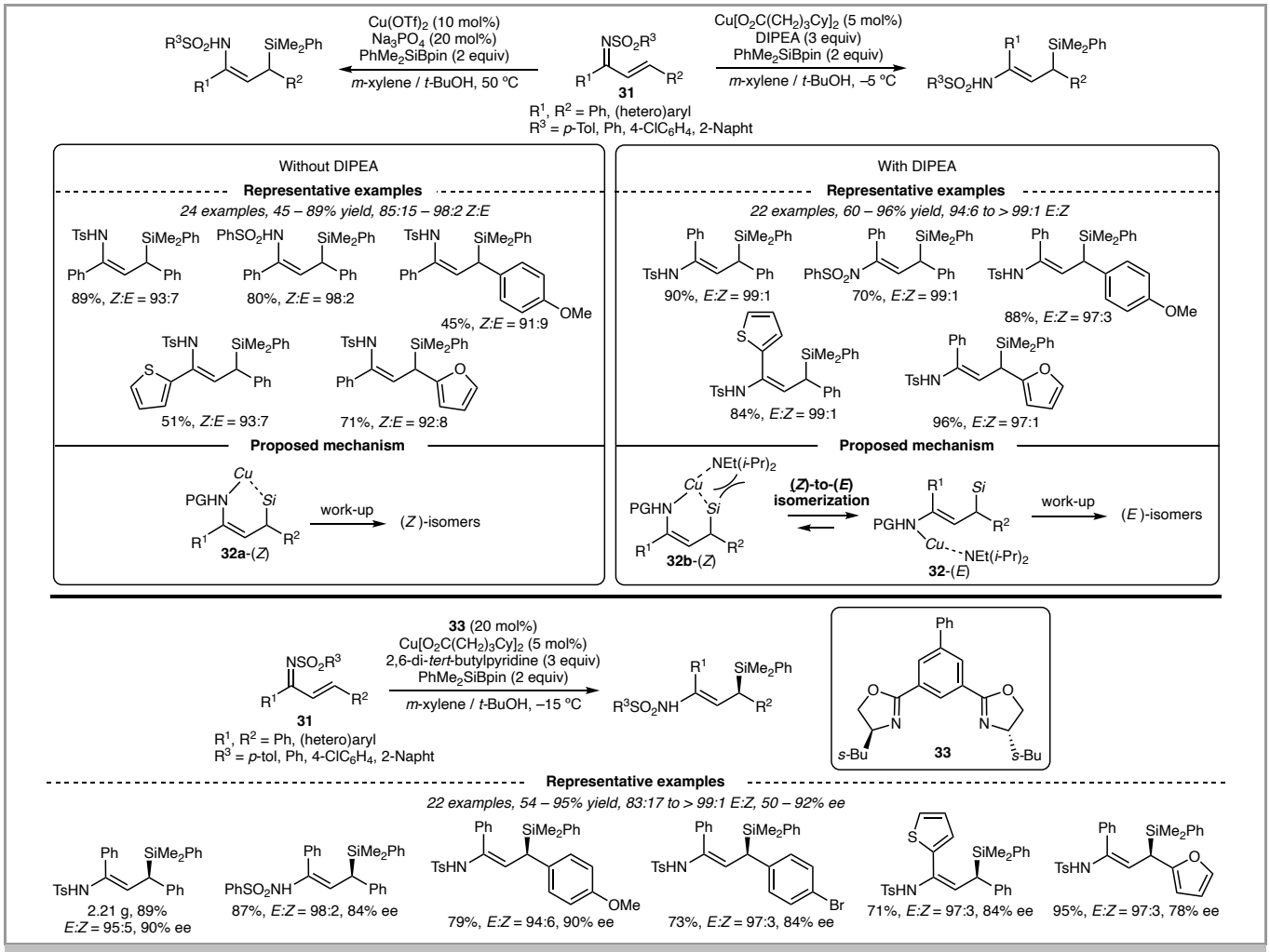
2.2.2 1,4-Conjugate Addition to α,β-Unsaturated Imines and Sulfones

In 2018, Xu et al. reported the enantioselective copper-catalyzed 1,4-conjugate silylation of α,β-unsaturated aryl imines **31** with $PhMe_2SiBpin$ (Scheme 13).[26] The use of 10 mol% of $Cu(OTf)_2$ in the presence of 20 mol% of Na_3PO_4 yielded γ-aminated α-chiral allylsilanes with excellent (*Z*)-selectivity. In contrast, using 5 mol% of copper bis(4-cyclohexylbutyrate) with an excess of DIPEA gave predominantly (*E*)-isomers. The (*Z*)-selectivity observed in the absence of amine was rationalized by the formation of stable copper amides **32a**-(*Z*), via 1,4-silylation, which would provide directly (*Z*)-products upon work-up. The (*E*)-selectivity observed in the presence of DIPEA was assumed to result from the formation of instable copper amides **32b**-(*Z*), due to great steric interations generated by DIPEA coordinated on copper, which would then undergo (*Z*)-to-(*E*) isomerization, yielding (*E*)-isomers upon work-up. The authors also developed an enantioselective version of their reaction using 20 mol% of chiral Pybox **33** with an excess of 2,6-di-tert-butylpyridine which led to (*E*)-configured products with high enantiomeric purity, even on the gram-scale.

Very recently, Yin et al. described a two-step procedure for the enantioselective synthesis of α-chiral allylsilanes from α,β-unsaturated benzo[d]thiazolyl sulfones **34**. This procedure combined the enantioselective boron method, carried out with 5 mol% of chiral NHC copper complex **35**, with Julia–Kociensky olefination of the benzothiazol-2-yl sulfones obtained with various aliphatic and aromatic aldehydes (Scheme 14).[27] The overall transformation, which could also be conducted one-pot, yielded products with perfect (*E*)-selectivity, in most cases, and high enantiomeric purity.

2.2.3 Double Conjugate Addition to Enynes

The same year, Xu et al. also reported the double silylation of enynes **36** with $PhMe_2SiBpin$ catalyzed by 10 mol% of CuCl in the presence of 12 mol% of 4,4′-di-tert-butyl-2,2′-bipyridine (BBBPY) and an excess of DIPEA in MeOH at 30 °C (Scheme 15).[28] The reaction gave a library of γ-silylated α-chiral allylsilanes with perfect (*E*)-selectivity. A wide array of aryl, heteroaryl and alkyl groups were tolerated on the enynes and nitrile, ketone and ester moieties could be used as electron-withdrawing groups. Interestingly, two different silyl groups could be sequentially introduced in one-pot manner using two

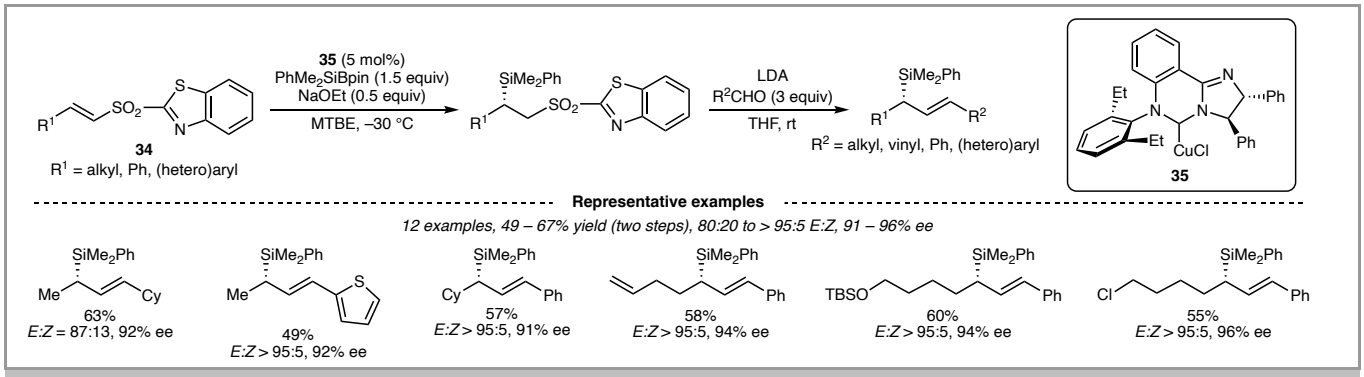


Scheme 13 Enantioselective copper-catalyzed 1,4-conjugate silylation of α,β-unsaturated imines

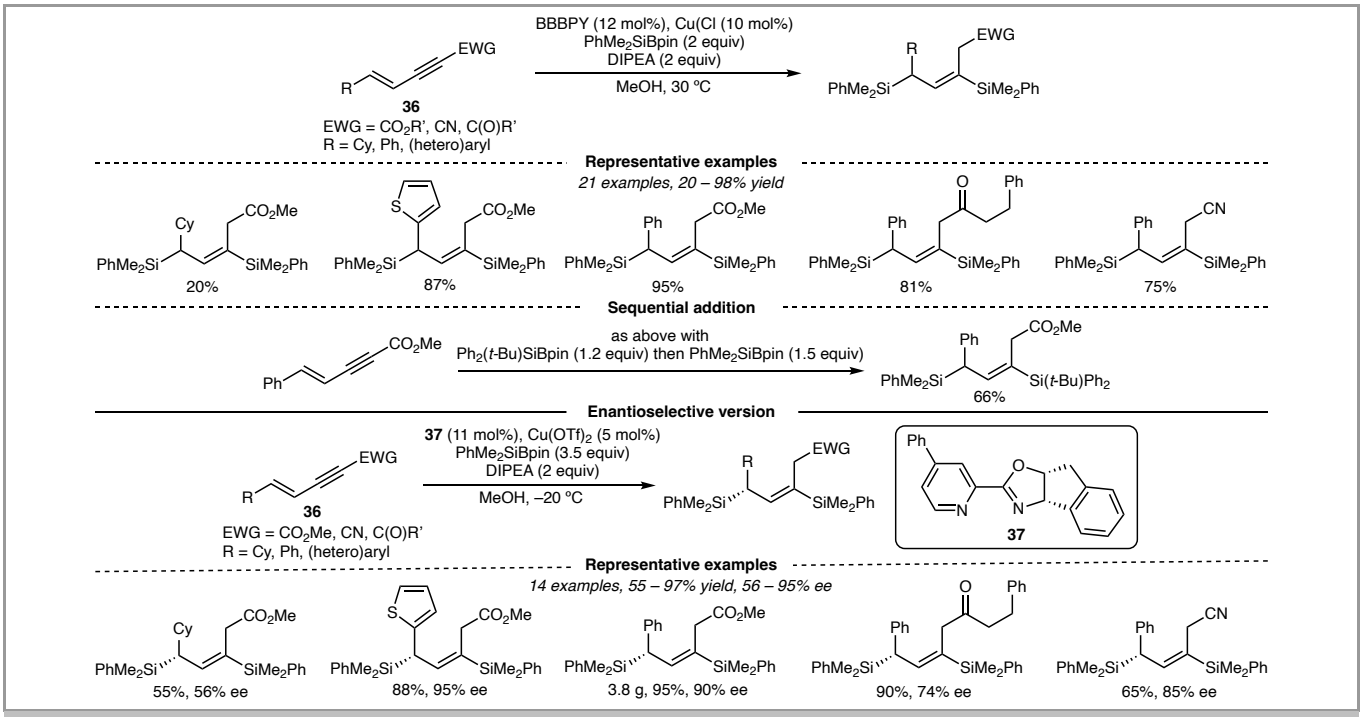
different silylborane reagents. The tranformation was assumed to involve the regioselective silylcupration of the C–C triple bond, giving dienyl intermediates upon methanolysis which would undergo 1,6-conjugate silylation. Under roughly similar conditions at low temperature, 5 mol% of $Cu(OTf)_2$ and 11 mol% of oxazoline **37** yielded (*E*)-products with high enantiomeric purity. In this case, the reaction, which could be scaled up for the gram-scale, was nevertheless rectricted to (*E*)-aryl enynes since (*Z*)-aryl enynes afforded complex mixtures and alkyl enynes led to mediocre enantioselectivity. This time, although ketones and nitriles could still be used as electron-withdrawing groups, enynoates offered the best results.

2.3 1,2-Addition to *N*-tert-Butylsulfonyl Imines

In 2014, Sato et al. reported that the reaction between $PhMe_2SiBpin$ and *N*-tert-butylsulfonyl imines using 10 mol% of $(CuOTf)_2{\cdot}C_6H_6$ in the presence of 20 mol% of chiral diamine **38** and an excess of 2,6-xylenol proceeded enantioselectively through the 1,2-mode of addition.[29] 2,6-Xylenol was shown to be the best proton source, not only to accelerate the regeneration of the catalyst, but also to obtain the desired products with excellent optical purity. When applied to α,β-unsaturated substrates, the reaction yielded α-sulfonylamido α-chiral allylsilanes with high enantioselectivity (Scheme 16).



Scheme 14 Enantioselective boron method on α,β-unsaturated benzo[d]thiazolyl sulfones / Julia–Kociensky olefination

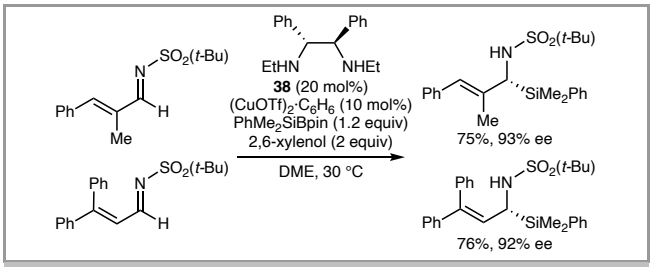


Scheme 15 Enantioselective copper-catalyzed double conjugate silylation of enynes

2.4 Silboration

2.4.1 1,2-Silaboration of Allenes

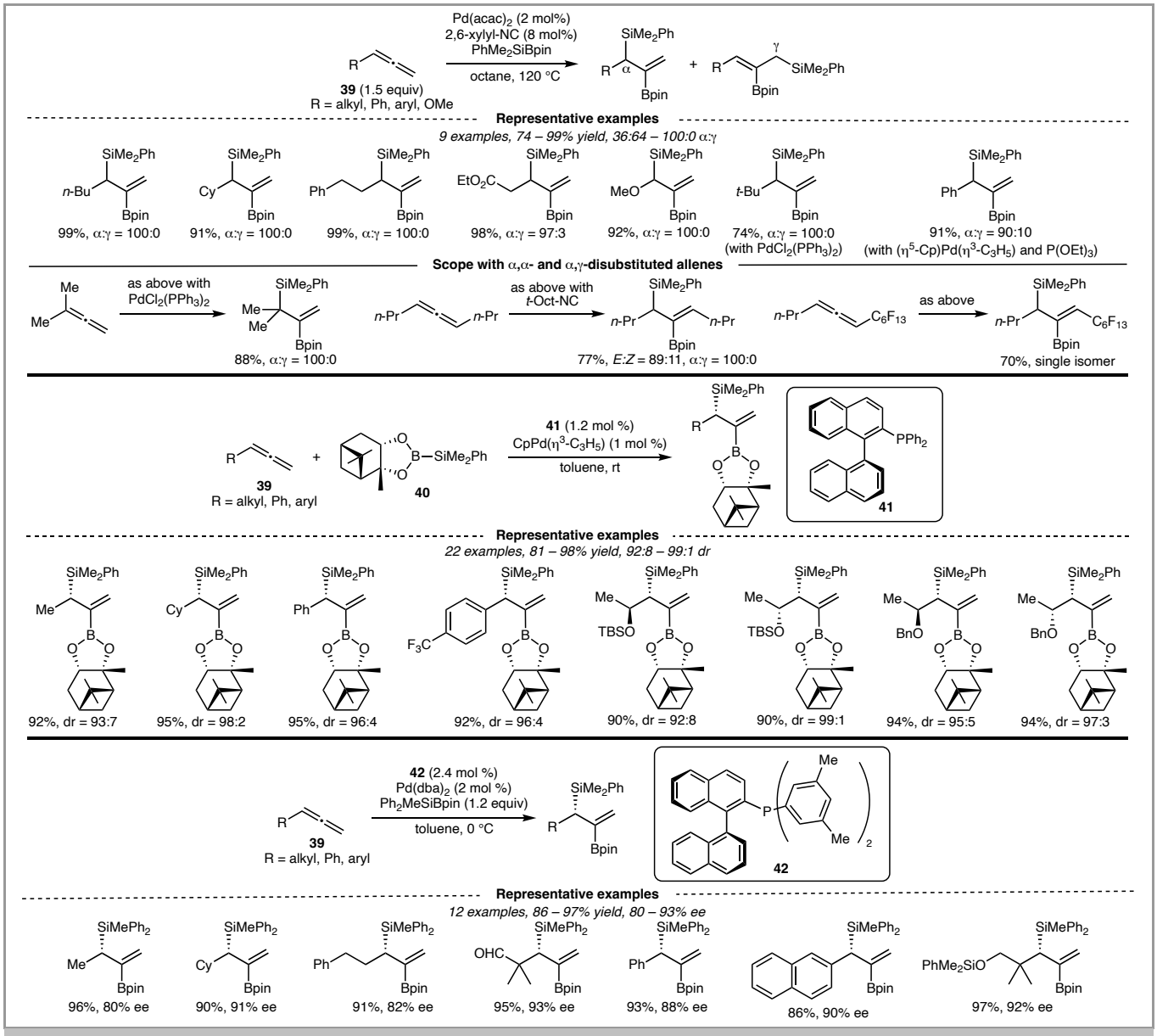
Ito and Suginome reported that the palladium catalyst prepared from 2 mol% of $Pd(acac)_2$ and 8 mol% of 2,6-xylyl isocyanide enabled the reaction between $PhMe_2SiBpin$ and α-substituted terminal allenes **39** through addition of the Si–B bond across the internal C–C bond, at high temperature (Scheme 17).[30] The authors showed that palladium catalysts, prepared from a wide range of ligands such as isonitriles and phosphines, could be used.[31] In this reaction, the silyl group was preferentially delivered to the more substituted allenic carbon, affording predominantly α-regioisomers, except in the case of substrates substituted with electron-withdrawing groups, as perfluoroalkyl groups. These conditions could be applied with success to symmetrical α,α- and α,γ-disubstituted allenes. Unsymmetrical α,γ-disubstituted analogs also underwent Regioselective 1,2-silaboration when bearing an electron-donating group at the α-position and an electron-withdrawing group at the γ-position, and afforded products with the silyl group exclusively introduced at the α-position. Shortly after this work, the use of $CpPd(\eta^3\text{-}C_3H_5)$ and tertiary phosphines was demonstrated to allow the reaction to take place under milder conditions. The authors thus succeeded in reacting allenes **39** with chiral pinanediol-derived silylborane **40** in the presence of 1 mol% of $CpPd(\eta^3\text{-}C_3H_5)$ and 1.2 mol% of chiral phosphine **41** at rt, giving β-borylated products with high diastereoselectivity via double asymmetric induction. Allenes bearing alkoxy β³-stereogenic carbons offered analogous results.[30b,31] With these substrates, the configuration of the newly created silicon-subsituted stereogenic carbon was slightly affected by that of the original stereogenic carbon, albeit match–mismatch effect was observed.[30b,33] When performed with $Ph_2MeSiBpin$ and catalyzed by 2 mol% of $Pd(dba)_2$ in the presence of 2.4 mol% of chiral phosphine **42**, the reaction led to high enantioselectivity, in particular with allenes bearing secondary and tertiary alkyl or aryl groups.[30b,34] As before, a slight match–mismatch effect was observed with allenes that contain β'-alkoxy stereogenic carbons.



Scheme 16 Enantiosleective copper-catalyzed 1,2-silylation of *N*-tert-butylsulfonylimines

2.4.2 1,4-Silaboration of 1,3-Dienes

Silaboration of cyclic 1,3-dienes was reported by Ito et al. to proceed exclusively through the 1,4-mode of addition using 5 mol% of $Ni(acac)_2$ and 10 mol% of both a tertiary phosphine and dibal (Scheme 18).[35] The reaction was however restricted to 1,3-cyclohexadiene and 1,3-cycloheptadiene and required the use of sterically bulky phosphines to observe perfect *cis* stereoselectivity, giving only *cis* δ-borylated products in high yields. Screening of phosphines showed that $PCyPh_2$ was the key to observe high diastereoselectivity presumably by accelerating the reductive elimination step. Later, Moberg et al. disclosed the enantioselective 1,4-silaboration of 1,3-cyclohexadiene using 5 mol% of $Pt(acac)_2$ and 10 mol% of chiral phosphoramidite **43**.[36] The conversion was nevertheless incomplete and yielded the product with modest enantiomeric purity. Surprisingly, all palladium complexes tested by the authors failed to enable the reaction.



Scheme 17 Palladium-catalyzed 1,2-silaboration of allenes

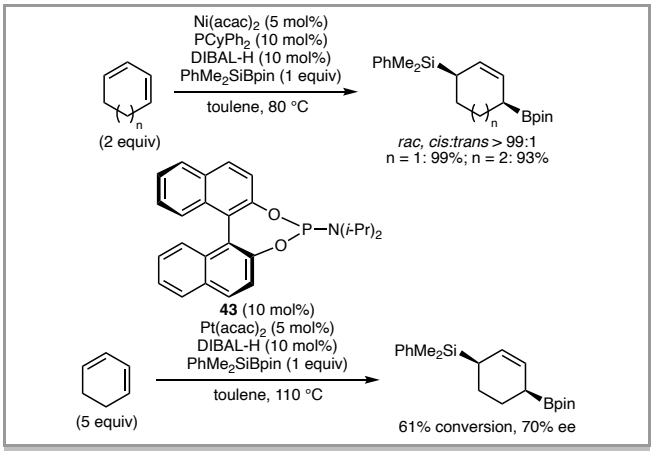
2.4.3 1,5- and 1,6-Silaborations of Vinylcyclopropanes and Vinylcyclobutanes

Ito and Suginone reported that the 1,5-silaboration of vinyl cyclopropanes **44** could be carried out under nickel catalysis. They showed that the nickel(0) catalyst, prepared in situ from 5 mol% of both Ni(acac)$_2$, dibal and PCy$_3$, afforded 5-borylated α-chiral allylsilanes with perfect (*E*)-selectitvity via cleavage of the C–C σ-bond in the ring followed by reductive elimination (Scheme 19).[37] The authors applied the method with success to the synthesis of 6-borylated products from vinyl cyclobutane analogs **45** via 1,6-silaboration, although higher temperature and four times as much catalyst loading were required.

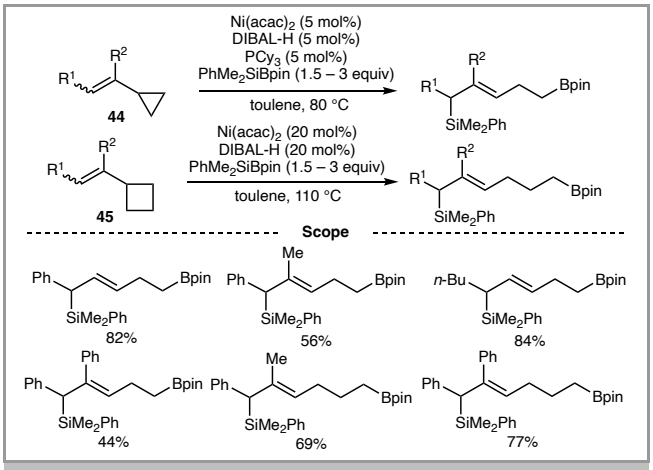
3 Addition of Nucleophiles

3.1 Substitutiion of γ-Silylated Allylic Electrophiles

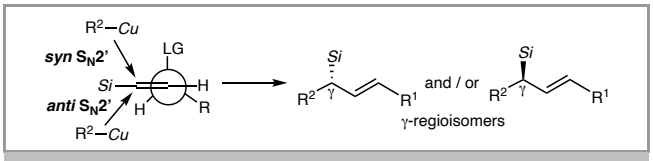
γ-Substitution of chiral γ-silylated allylic electrophiles with nucleophiles, mainly organometallic reagents, is a very useful method for accessing α-chiral allylsilanes that has received much interest from chemists over the last 25 years. For this purpose, organocopper reagents, either prepared in advance or



Scheme 18 Metal-catalyzed 1,4-silaboration of cyclic 1,3-dienes



Scheme 19 Nickel-catalyzed silaboration of small-ring vinyl cycloalkanes



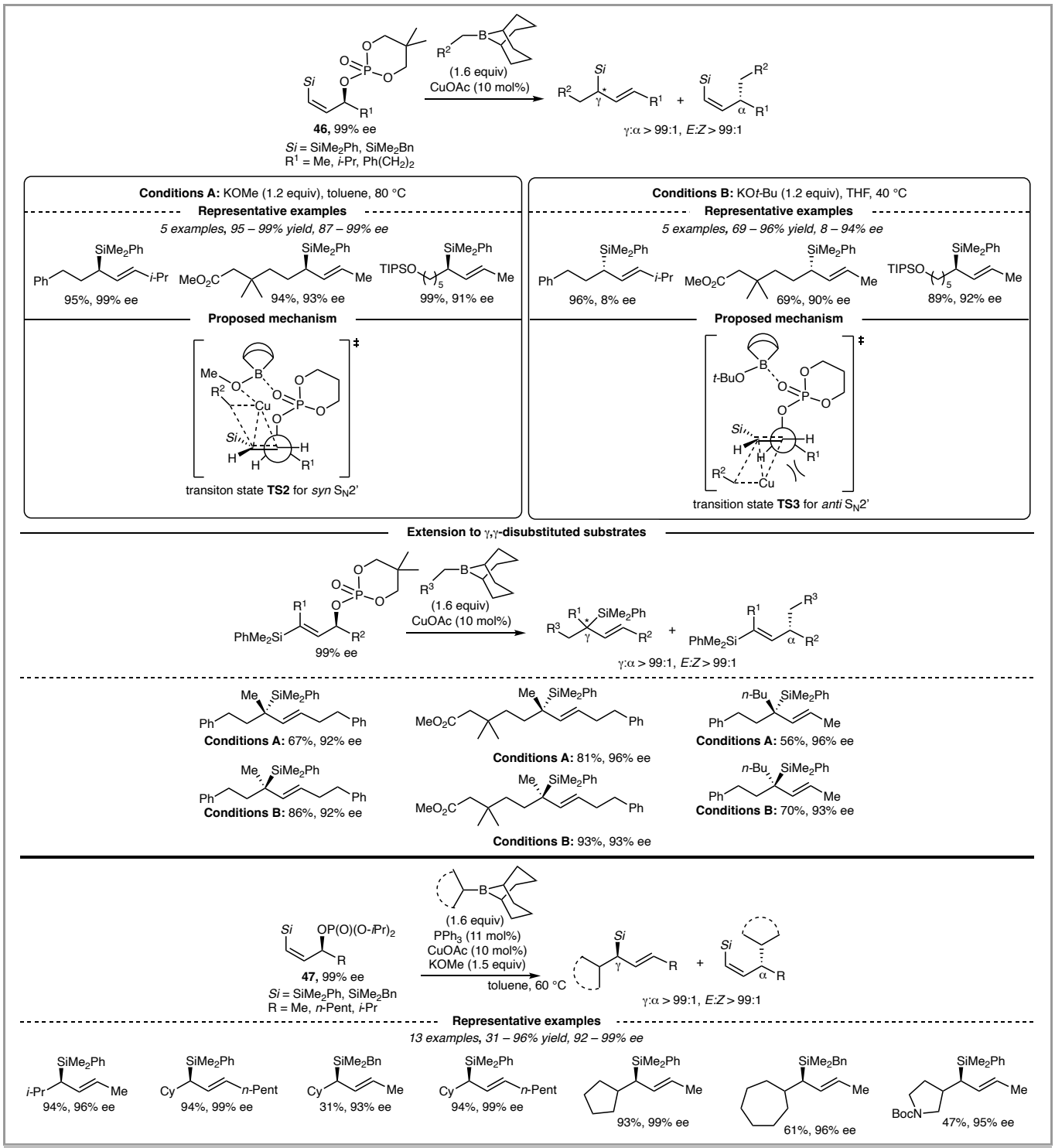
Scheme 20 Allylic substitution of chiral γ-silylated allylic electrophiles with organocopper reagents

generated in situ, are the reagents of choice which generally react stereoselectively via *syn* or *anti* S_N2' pathway (depending on the conditions) to afford predominantly γ-regioisomers (Scheme 20).

In 1998, Woerpel et al. disclosed the diastereoselective γ-addition of isobutylcopper to optically active γ-silylated allylic carbamates, giving α-chiral allylsilanes with high 1,3-chirality transfer.[38] More than 10 years later, Sawamura et al. reported this type of reaction with boranes under copper-catalysis. They showed that primary alkylboranes, derived from 9-BBN, reacted with chiral γ-silylated allylic phosphates **46** with perfect γ-regioselectivity in the presence of 10 mol% of CuOAc and a slight excess of alkoxide base (Scheme 21).[39] The stereochemistry of the reaction was shown to highly depend on the nature of the alkoxide base required for the activation of the alkylborane reagent. In the presence of KOMe, the reaction occurred in *syn* S_N2' fashion while with the bulkier base KO*t*-Bu it proceeded in *anti* S_N2' fashion, giving the enantiomeric products with optical purities in the same order of magnitude. Except with the bulky isopropyl group at the α-position, the reaction took place with excellent 1,3-chirality transfer under both conditions. Silylether, chloroaryl or ester moieties were tolerated on the primary alkyl chain of the boranes and either $SiMe_2Ph$ or $SiMe_2Bn$ groups could be used. The reversal of the diastereofacial selectivity was also observed with γ,γ-disubstituted substrates which provided quaternary α-chiral allylsilanes. This reversal was rationalized by transition states **TS2** and **TS3**, operating respectiveley with KOMe and KO*t*-Bu. The oxygen of KOMe was assumed to be able to coordinate on copper, which would enable γ-addition across the C–C double bond followed by *syn* β-elimination through cyclic transition state **TS2**. In contrast, the bulky tert-butyl group of KO*t*-Bu would prevent this coordination, which would result in γ-addition across the C–C double bond and subsequent *anti* β-elimination through acyclic transition state **TS3**. With a bulky substituent at the α-position of the leaving group, **TS2** was assumed to be constrained, giving low enantioselectivity as with the isopropyl group. The authors later extended the reaction to secondary alkylboranes using KOMe and 11 mol% of a tertiary phosphine, in particular PPh_3.[40] The reaction with substrates **47** thus occurred with perfect γ-regioselectivity via the preferential *syn* S_N2' fashion. In this case, experimental and theoretical studies showed that the addition of a tertiary phosphine was the key for the boron-to-copper transmetallation of the $PhMe_2Si$ group to take place and then to generate the catalytically active alkylcopper species.

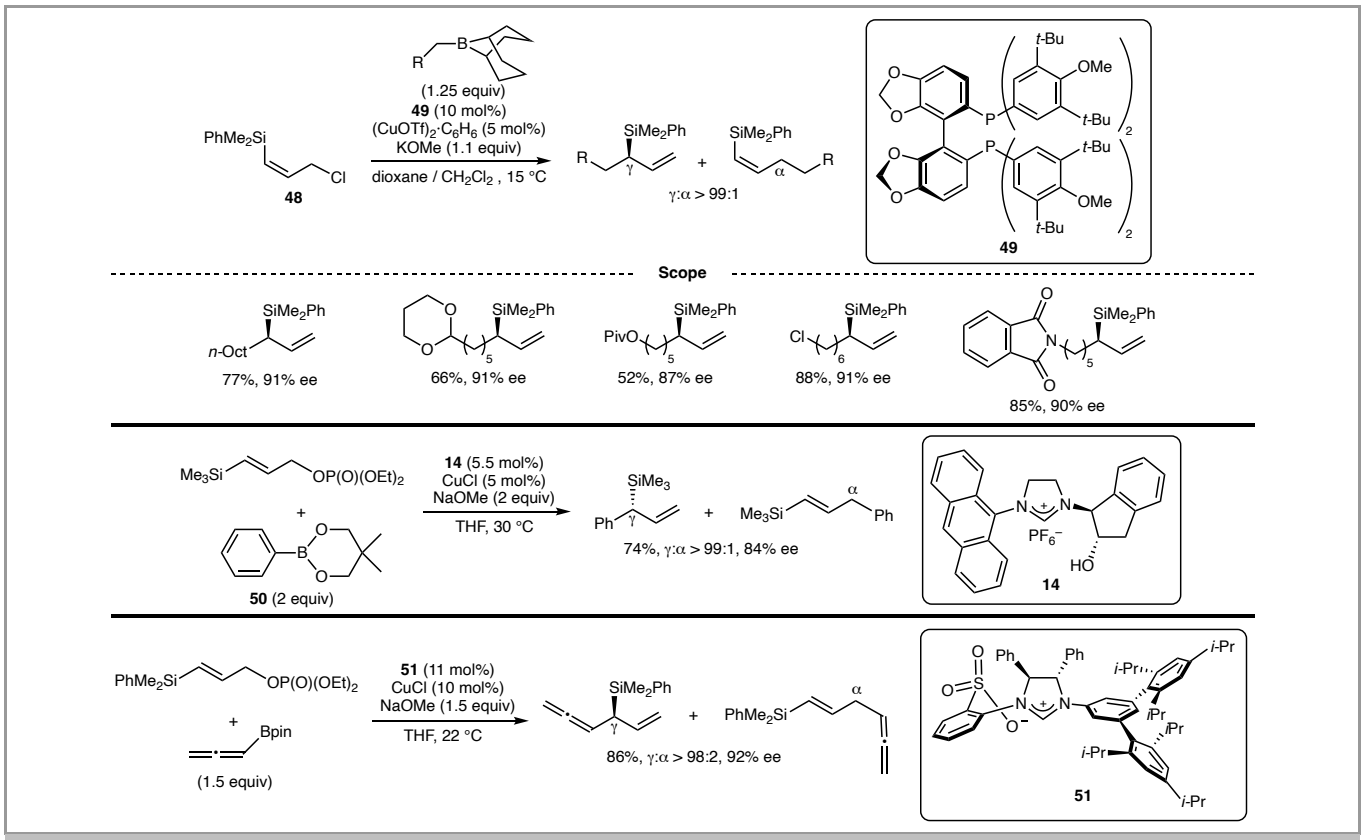
Following these works, Sawamura et al. managed to apply the method with primary alkylboranes enantioselectively to chloride **48** with 5 mol% of $(CuOTf)_2{\cdot}C_6H_6$ in the presence of 10 mol% of DTBM-modified Segphos **49** and a slight excess of KOMe, giving α-chiral allylsilanes with perfect γ-regioselectivity and high enantiomeric purity (Scheme 22).[41] Under similar reaction conditons, aryl- and allenylboron reagents also offered excellent results from primary allylic phosphates. For instance, Hayashi et al. performed the reaction with phenylboronate **50** in the presence of 5 mol% of CuCl and 5.5 mol% of imidazolium salt **14** to yield the desired enantioenriched α-chiral allylsilane through perfect γ-phenylation.[42] In another example disclosed by Hoveyda et al., an allenic α-chiral allylsilane was synthetized with high enantiomeric purity by reaction with allenylboronic acid pinacol ester catalyzed by 10 mol% of CuCl in the precence of 11 mol% of sulfonate-containing imidazolium salt **51**.[43]

In the past 15 years, intensive studies have been carried out by Hoveyda et al. in the field of γ-addition of organometallics to γ-silylated allylic electrophiles under NHC copper catalysis. In the course of their studies, they showed that dialkylzincs could react with γ-substituted allylic phosphates **52** in the presence of less than 2 mol% of a copper salt, $(CuOTf)_2{\cdot}C_6H_6$ or CuOAc, and chiral NHC silver complex **53** with perfect γ-regioselectivity and excellent enantioselectivity (Scheme 23).[44] The reaction also provided quaternary γ-products with similar results from less reactive γ,γ-disubstituted allylic phosphates with up to 10 mol% increase in loadings of both silver complex **53** and copper salt. It was also shown that the use of a transition-metal catalyst was not necessary for the reaction to occur, although lower yield and enantioselectivity were obtained in this case.[45] With diarylzinc reagents, 1 mol% of NHC silver complex **54** was required to perform the reaction with γ-substituted substrates, while γ,γ-disubstituted analogs required to employ up to 2.5 mol% of sulfonate-containing NHC silver complex **55,** although a slight erosion of enantiomeric purity was observed in this case, even at low temperature. The authors also reported that as little as 1 mol% of complex **55** was able to catalyze the reaction with (heteroaryl)aluminium reagents,[46] and found that less than 1 mol% of the two parent NHC silver complexes **56** and **57** was enough to perform the reaction with vinylaluminium reagents.[47] In all cases, both perfect γ-regioselectivity and retention of the C–C double bond geometry of the vinylaluminium reagents were observed. The reaction with (*E*)-vinylaluminium reagents was performed in the presence of as little as 1 mol% of $CuCl_2{\cdot}2H_2O$ and 0.5 mol% of complex **56**. It was completed within less than 12 h at –15 °C and gave bis(allyl)silanes with high enantiomeric purity. On the other hand, (*Z*)-configured reagents required the use of complex **57** at lower temperature (–50 °C) for longer reaction time (24 h) to prevent the (*Z*)-to-(*E*)-isomerization of the vinylaluminum reagents.

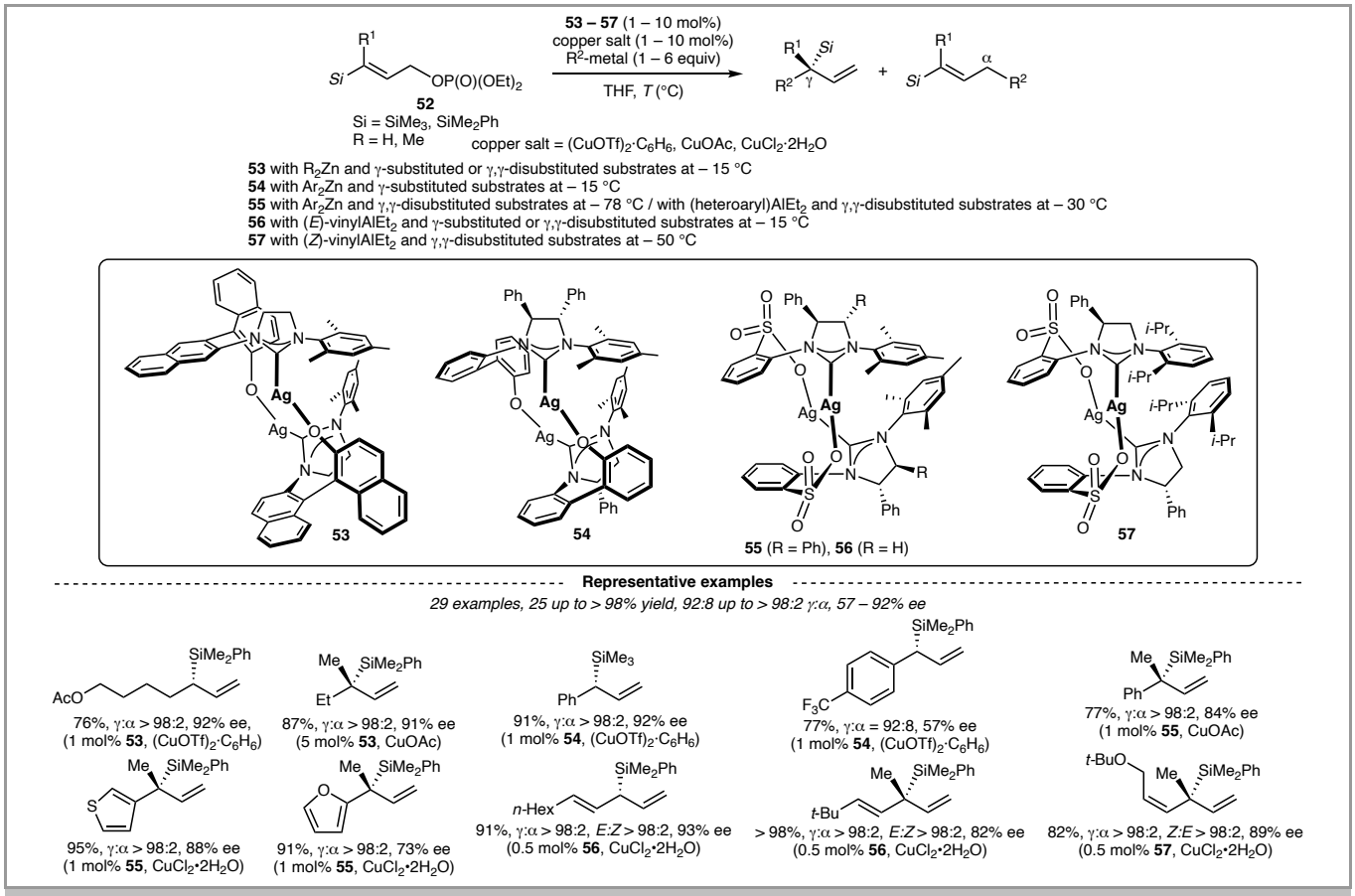


Scheme 21 Copper-catalyzed γ-alkylation of γ-silylated allylic phosphates with alkylboranes

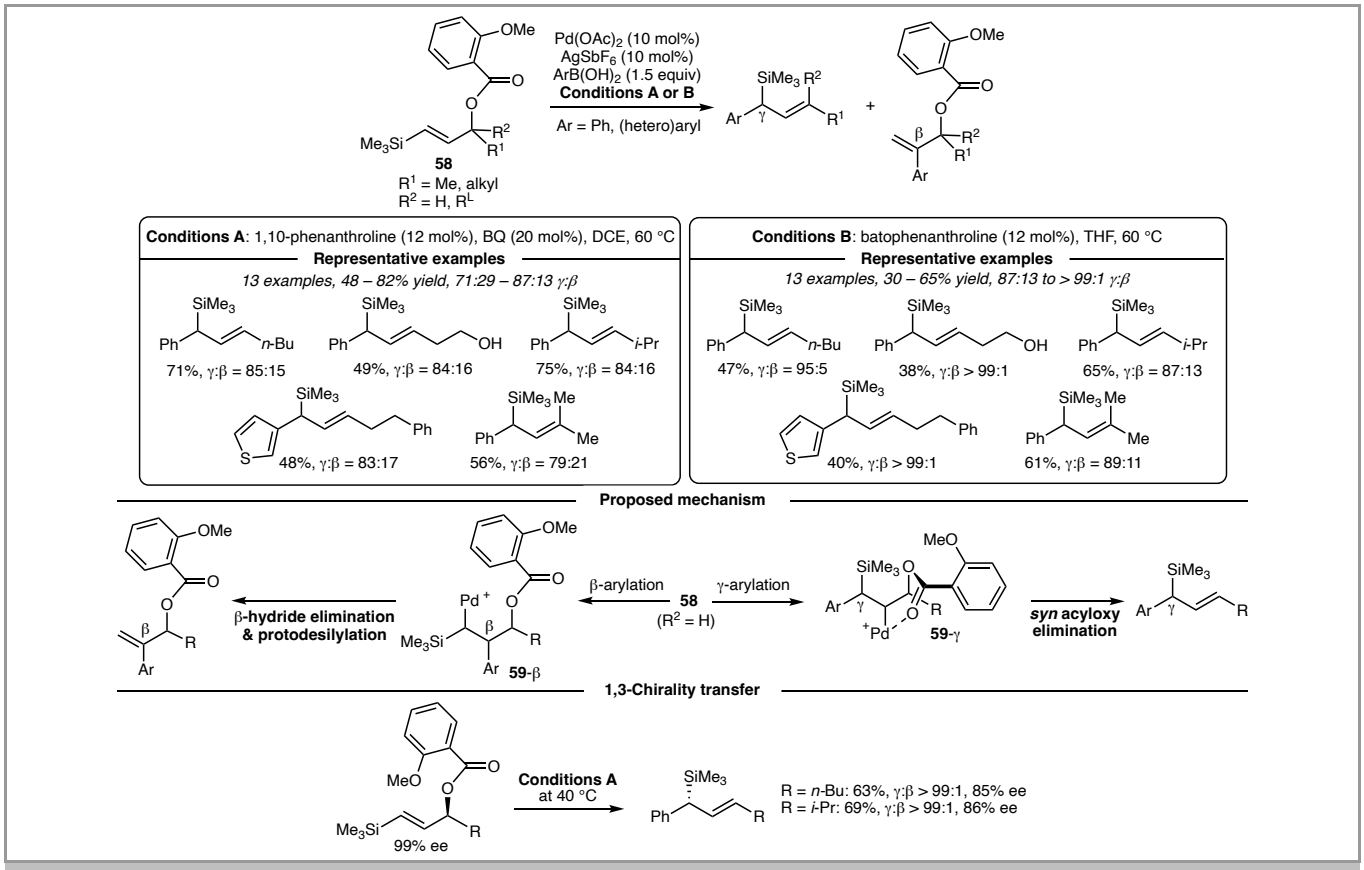
In 2010, Sawamura et al. reported the palladium-catalyzed γ-arylation of chiral γ-silylated allylic esters **58** with $ArB(OH)_2$. The reaction could be carried out with 10 mol% of $Pd(OAc)_2$ and $AgSbBF_6$ in the presence of 12 mol% of 1,10-phenanthroline and 20 mol% of 1,4-benzoquinone, giving α-chiral allylsilanes with perfect (*E*)-selectivity and quite good γ-regioselectivity (Scheme 24).[48] Alternatively, 1,10-phenanthroline and 1,4-benzoquinone could be replaced by 12 mol% of batophenanthroline, affording improved γ-regioselectivity, albeit with generally slightly lower yield. Under these two conditions, various functional groups in both $ArB(OH)_2$ and allylic esters **58** were tolerated and the reaction took place through *syn* insertion of the catalytically active (aryl)palladium species, generated in situ, across the C–C double bond. The authors rationalized the excelent γ-regioselectivity by the formation of six-membered cationic palladacycles **59**-γ, resulting from γ-arylation, which were assumed to be more stable than intermediates **59**-β, resulting. from β-arylation, and to undergo subsequent *syn* acyloxy elimination. From optically active substrates, the reaction was found to proceed in *syn* fashion with excellent 1,3-chirality transfer.



Scheme 22 Enantioselective copper-catalyzed γ-alkylation of γ-silylated allylic electrophiles with alkyl-, aryl- and allenylboranes



Scheme 23 Enantioselective copper-catalyzed γ-substitution of γ-silylated primary allylic phosphates with diorganozinc reagents



Scheme 24 Palladium-catalyzed γ-arylation of chiral γ-silylated allylic esters

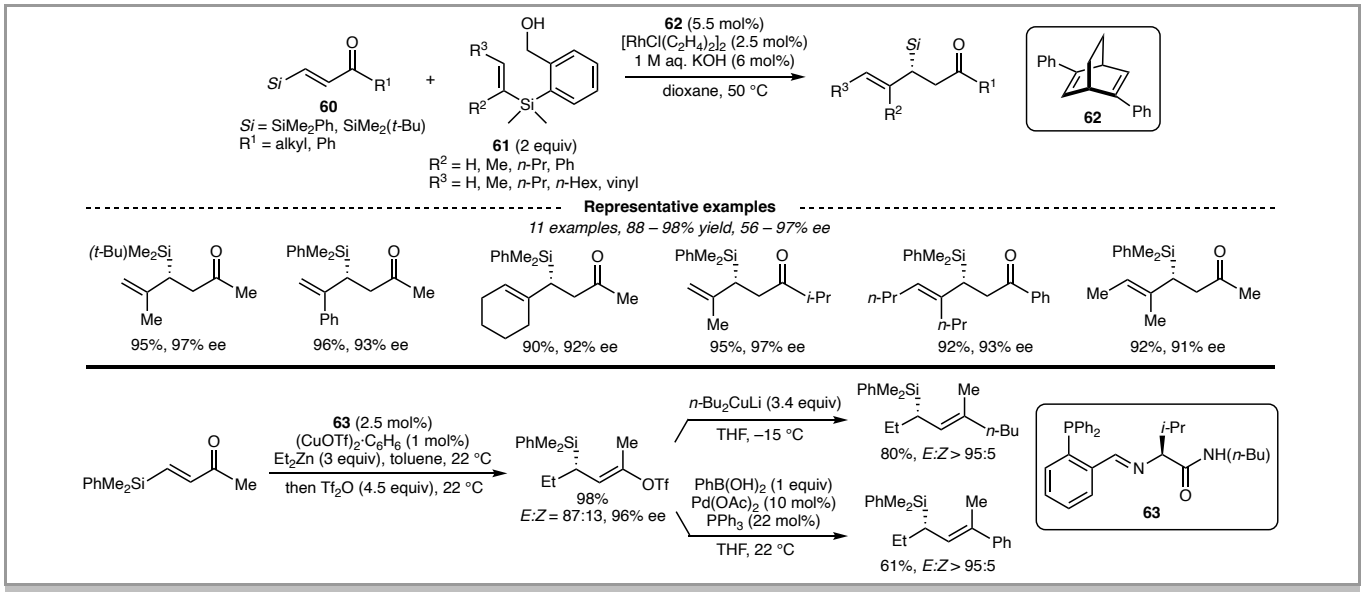
3.2 1,4-Conjugate Addition to β-Silyl Enones and Enoates

In 1990, Fleming et al. described the diastereoselective 1,4-conjugate addition of a copper reagent on an enantioenriched β-silyl acryloyl lactam.[49] The first example of such a reaction in an enantioselective manner was, however, only reported in 2007 by Hayashi et al. who developed the 1,4-conjugate vinylation of β-silyl enones **60** employing vinylic pronucleophile reagents **61** with 2.5 mol% of $[RhCl(C_2H_4)_2]_2$ in the presence of 5.5 mol% of chiral diene **62** (Scheme 25).[50] The use of 6 mol% of aqueous KOH was also required in order to activate the rhohium catalyst as rodium hydroxide. Only α-substituted reagents **61** were found to give γ'-oxo α-chiral allylsilanes with high enantiomeric purity. The same year, Hoveyda et al. also described that the reaction of such an enone with Et_2Zn could be catalyzed by 1 mol% of $(CuOTf)_2{\cdot}C_6H_6$ in the presence of 2.5 mol% of valine-based phosphine **63**.[51] Quenching with excess Tf_2O afforded a γ-triflate derivative with excellent enantioselectivity and good (*E*)-selectivity, which was further transformed into other γ,γ-disubstituted α-chiral allylsilanes with perfect (*E*)-selectivity without erosion of enantiomeric purity, through Suzuki cross-coupling with $PhB(OH)_2$ or alkylation with *n*-Bu_2CuLi.

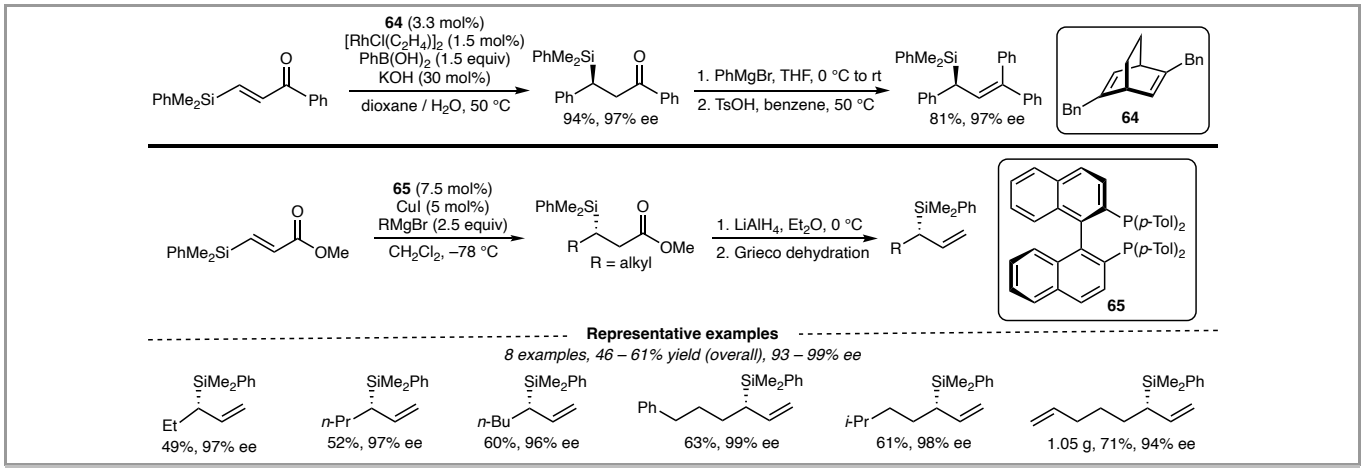
In 2007, Hayahi et al. also developed a multi-step synthesis involving a key-step of rhodium-catalyzed enantioselective 1,4-conjugate phenylation of a γ-silylated enone with $PhB(OH)_2$ and 1.5 mol% of $[RhCl(C_2H_4)_2]_2$ in the presence of 3.3 mol% of chiral diene **64** and 30 mol% of KOH in aqueous medium. Subsequent treatment with PhMgBr followed by acidic dehydration yielded an α-chiral allylsilane with high enantiomeric purity (Scheme 26).[52] Another multi-step synthesis was reported by Loh et al. who combined the enantioselective 1,4-conjugate alkylation of γ-silyl methyl acrylate, by reaction with alkyl Grignard reagents catalyzed by 5 mol% of CuI in the presence of 7.5 mol% of (*R*)-Tol-Binap **65**, with ester reduction and dehydration under Grieco's conditions.[53] The overall synthetic sequence was applicable on the gram-scale without deterioration of yield or enantiomeric purity.

3.3 Reduction of γ-Silylated Allylic Carbonates

In the mids 1990s, Hayashi et al. shown that γ-silylated (*Z*)-configured allylic carbonates **66** were reduced with formic acid in the presence of proton sponge, 3 mol% of $Pd_2(dba)_3{\cdot}CHCl_3$ and 6 mol% of chiral monodentate phosphine ligands (MOP ligands).[54] The reaction tolerated a wide array of silyl groups and offered the best enantioselectivity with biphenanthryl MOP ligand **67** (Scheme 27). The reaction was found by the authors to be enantiodivergent, (*E*)-configured substrates yielding the enantiomeric products, although with significant lower optical purity. On the basis of NMR studies, the authors rationalized the higher enantioselectivity observed with (*Z*)-isomers by the large difference in stability between the two diastereomeric pairs of *anti* π-allylpalladium complexes. The epimerization equilibrium between these two diastereoisomers would be directed towards **68**-(*S*)-*anti* which would then undergo reductive elimination to give (*S*)-enantiomers with high enantiomeric purity. Conversely, the difference in stability between the two diastereomeric pairs of *syn* π-allylpalladium complexes would be smaller, affording mixtures of both enantiomers via reductive elimination.



Scheme 25 Enantioselective transition metal-catalyzed 1,4-conjugate addition to β-silyl enones



Scheme 26 Multi-step syntheses involving enantioselective metal-catalyzed 1,4-conjugate addition to β-silyl enones and enoates

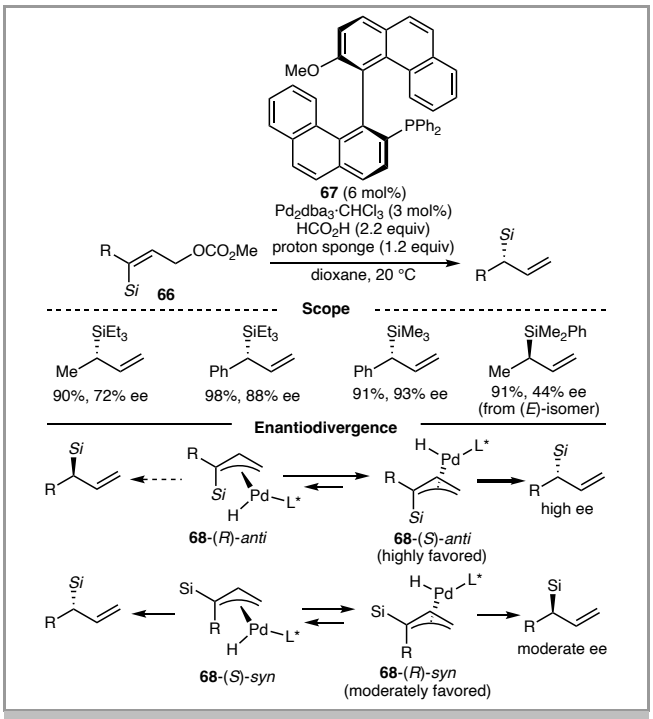
4 Hydrosilylation

4.1 1,4-Hydrosilylation of 1,3-Dienes

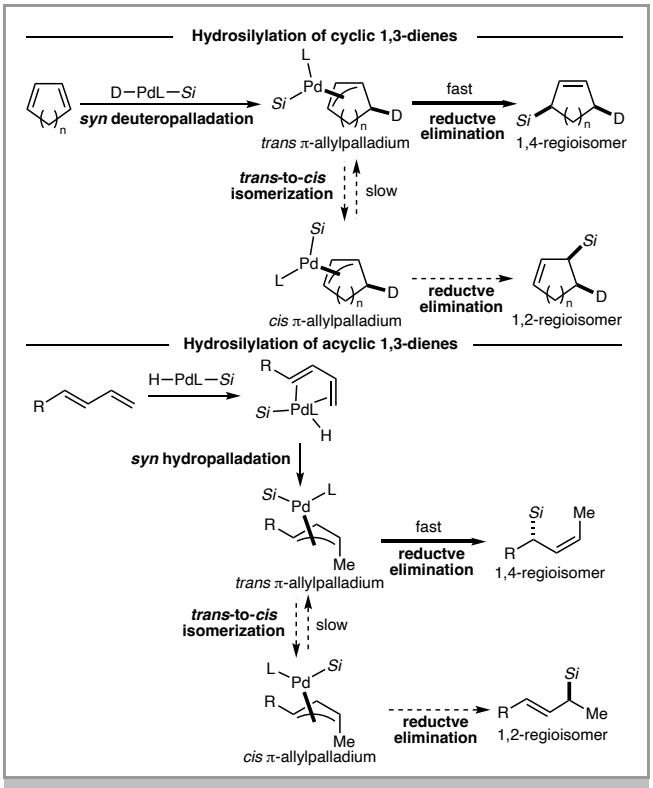
Hydrosilylation of cyclic 1,3-dienes is known to proceed in 1,4-fashion under palladium catalysis. The use of deuterium-labeled silanes showed that *trans* π-allylpalladium complexes, in which the silyl group is located at the *trans* position to the allylic carbon next to the deuterated carbon, are formed through *syn* hydropalladation (Scheme 28).[55] The 1,4-mode of addition was assumed to result from these complexes undergoing reductive elimination faster than isomerization into *cis* π-allylpalladium complexes which would give 1,2-regioisomers. With acyclic 1,3-dienes, hydrosilylation also proceeds with the preferred 1,4-regioselectivity from the cisoid conformation of the starting materials via an analogous mechanism.[56]

The first work on enantioselective palladium-catalyzed 1,4-hydrosilylation of cyclic 1,3-dienes is due to Kumada, Yamamoto and Hayashi. in the early 1980s.[57] Soon after, a great leap forward was made using chiral ferrocenyl phosphine-derived palladium complexes.[58] In particular, hydrosilylation of cyclopentadiene with $HSiCl_3$, catalyzed by 0.02 mol% of palladium catalyst **69** prepared in advance, yielded only 1,4-regioisomers, albeit with moderate enantioselectivity (Scheme 29).[56] The perfluoroalkyl group on the nitrogen atom was found to be benefical for the enantioselectivity by increasing the solubility of the catalyst and thus enhancing its activity. With 1,3-cyclohexadiene, the best results were reported in the mid-1990s by Hiyama et al. who performed the reaction with $HSiF_2Ph$ and the palladium catalyst generated in situ from 0.5 mol% of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 2 mol% of chiral ferrocenyl phosphine **70**.[59] Around the same time, other ligands such as β-*N*-sulfonyl(aminoalkyl)phosphines **71** and **72**[60] as well as menthyl-derived phosphetane **73**,[61] were developed and offered roughly equivalent enantiomeric purity. However, as early as 1996, Hayashi et al. reported the beneficial use of MOP ligands in 1,4-hydrosilyaltion of cyclic 1,3-dienes.[62] In the early 2000s, their intensive studies led to the design of chiral MOP ligand **74** containing an electron-donating group at the C4-position of the aryl moiety and two *n*-octyl substituents at the C6-positions of the two binaphtyl groups, which increases the solubility of the catalyst and therefore enhances its catalytic activity (Scheme 30).[63] Thus, when the reaction was carried out with as little as 0.125 mol% of $PdCl(\eta^3\text{-}C_3H_5)]_2$ in the presence of 0.5 mol% of ligand **74**, 1,4-hydrosilylated cyclopentadiene was obtained with excellent enantiomeric purity. Later, the

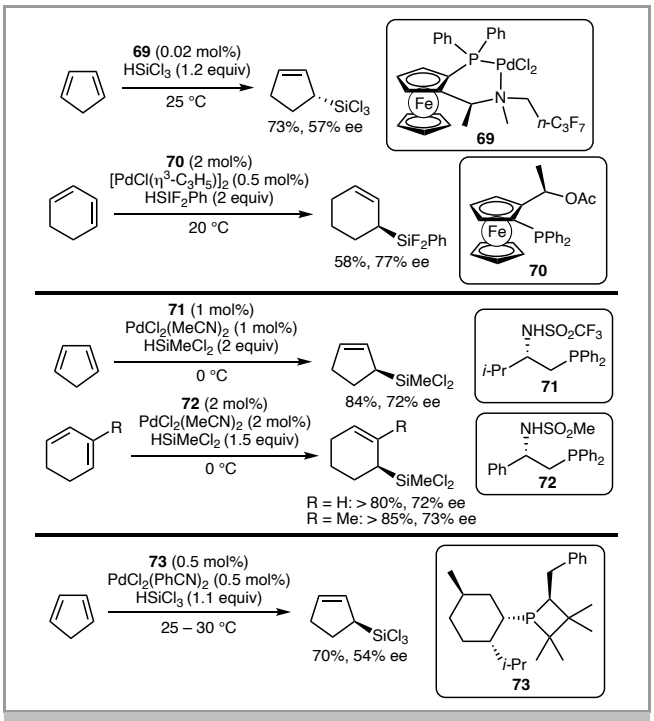
authors showed that slightly better enantioselectivity could be obtained for hydrosilylation of 1,3-cyclohexadiene using 1 mol% of the same palladium catalyst and 2 mol% of chiral phosphoramidite **75**.[64] Both the steric bulkiness and electronic effects of the two benzhydryl groups of ligand **75** were evidenced to play a crucial role in the magnitude of enantioselectivity.



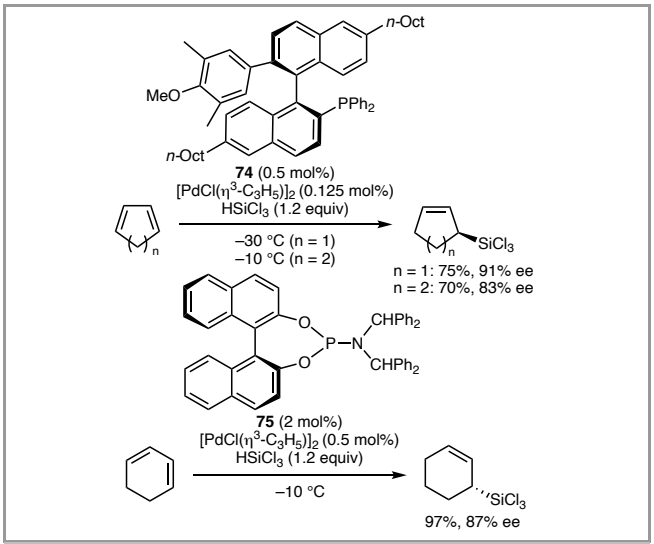
Scheme 27 Enantioslective palladium-catalyzed reduction of β-silylated allylic carbonates



Scheme 28 Palladium-catalyzed 1,4-hydrosilylation of 1,3-dienes



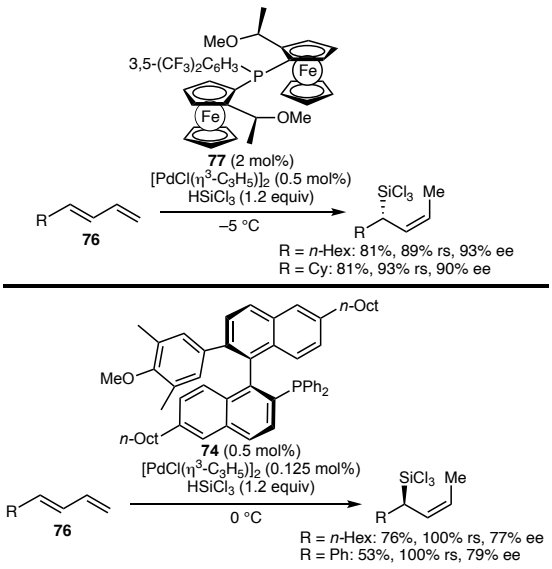
Scheme 29 Seminal enantioselective palladium-catalyzed 1,4-hydrosilylation of cyclic 1,3-dienes



Scheme 30 Enantioselective palladium-catalyzed 1,4-hydrosilylation of cyclic 1,3-dienes

In the mid-1980s, pioneering work on enantioselective 1,4-hydrosilylation of acyclic 1,3-dienes was undertaken by Hayashi et al. who used chiral ferrocenyl phosphine-derived palladium catalysts with halosilanes, albeit with low enantioselectivity.[65] Roughly similar results were obtained by Hatanaka et al. with chiral MOP ligands.[66] About ten years later, Hayashi et al. showed that hydrosilylation of 1-substituted 1,3-butadienes **76** could be advantageously carried out with $HSiCl_3$ in the presence of 0.5 mol% of $PdCl(\eta^3\text{-}C_3H_5)]_2$ and of 2 mol% of chiral bis(ferrocenyl)phosphine ligand **77**, which offered α-chiral allylsilanes with excellent enantiomeric purity (Scheme 31).[67] However, although also excellent, the 1,4- regioselectivity was not perfect unlike previously reported with MOP ligands.[66] Gratifyingly, when carrying out the reaction with 0.125 mol% of

$[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 0.5 mol% of highly soluble MOP ligand **74**, the authors succeeded in achieving perfect 1,4-regioselectivity, albeit with significant erosion of enantiomeric purity compared to that observed with ligand **77**.[63b]



Scheme 31 Enantioselective palladium-catalyzed 1,4-hydrosilylation of 1-substituted 1,3-butadienes

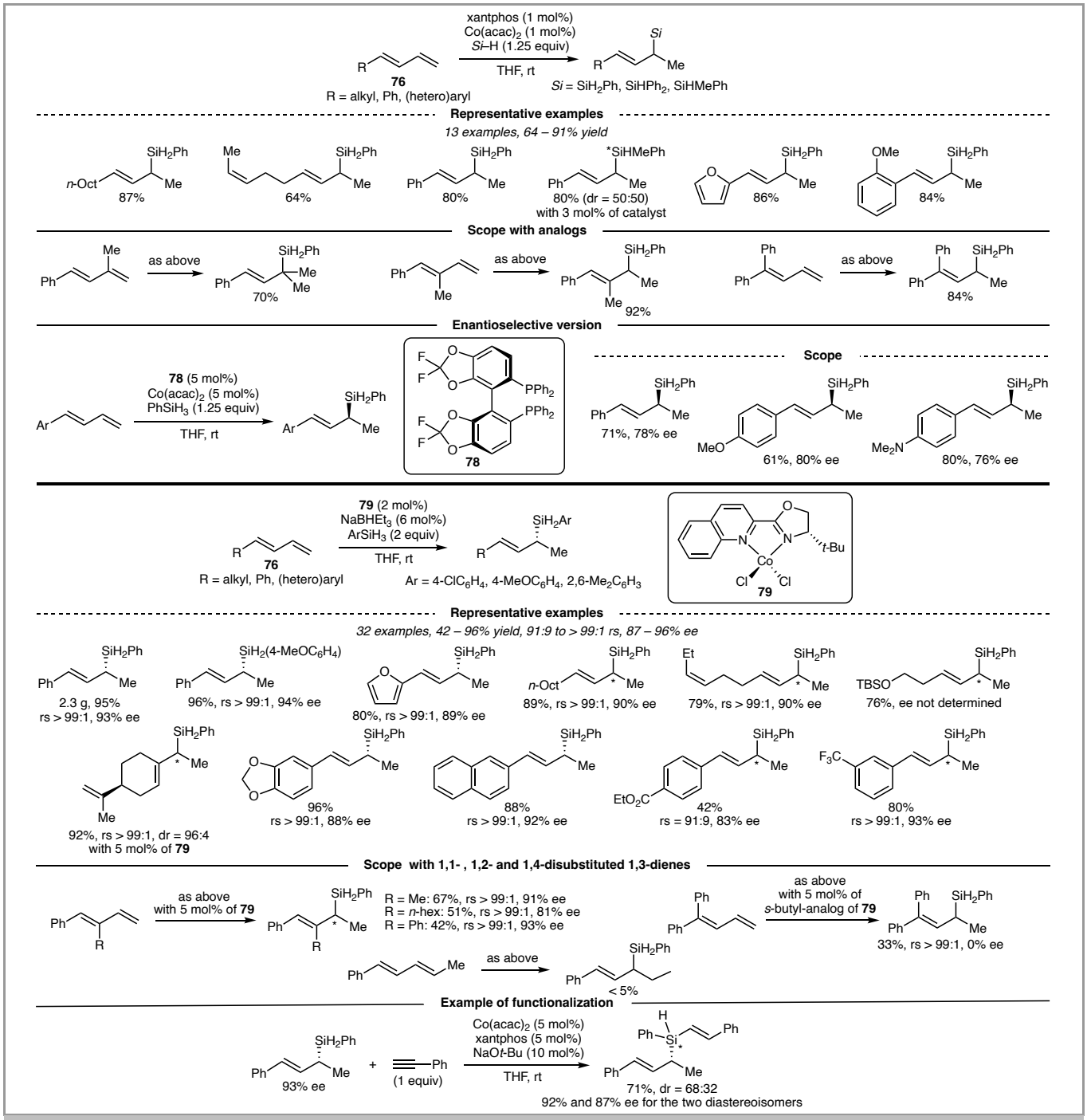
4.2 1,2-Hydrosilylation of 1,3-Dienes

In 2018, cobalt-catalyzed hydrosilylation of 1-substituted 1,3-butadienes **76** and their 1,1-and 1,3-disubstituted analogs was described by Ge et al. to occur with perfect Markovnikov 1,2-regioselectivity by reaction with silanes in the presence of 1 mol% of $Co(acac)_2$ and xantphos (Scheme 32).[68] The reaction, tolerated various silanes and was shown to be stereoconvergent since both (*E*)- and (*Z*)-configured substrates gave (*E*)-products. The authors rationalized the regioselectivity of the reaction by a modified Chalk–Harrod mechanism, supported by deuterium-labelling experiments with $PhSiD_3$, involving insertion of the Co–Si bond across the terminal C–C double bond with delivery of cobalt at the terminus. Enantioenriched products could also be obtained, with fairly good enantiomeric purity, using 5 mol% of (*R*)-difluorphos **78**. Soon after this work, the enantioselectivity was improved by Huang et al. who used catalysts prepared in advance by reaction of $CoCl_2$ with chiral quinoline-oxazoline ligands. Upon activation of 2 mol% of tert-butyl-substituted ligand **79** with 6 mol% of $NaBHEt_3$, the reaction with substrates **76** offred the best results, even on the gram-scale. The absolute configuration of the new stereogenic carbon was however only assigned for 1-aryl-substituted products.[69] The protocol was also applicable to 1,2-disubstituted 1,3-dienes without erosion of enantiomeric purity, but a 5 mol% higher catalytic loading was required and lower yield was obtained. In sharp contrast, the reaction yielded racemic products from 1,1-disubstituted 1,3-dienes and dit not work at all with 1,4-disubstituted analogs. Synthetically interesting, the products obtained could further be converted in other highly functionalized α-chiral allylsilanes. In particular, the cobalt-catalyzed vinylation of the silicon afforded access to vinylic α-chiral allylsilanes, containing a stereogenic silicon, with complete retention of the configuration of the stereogenic carbon.

Very recently, Meng et al. reported a related reaction with various prochiral silanes and 4 mol% of diphosphine **80**.[70] The reaction afforded a library of α-chiral allylsilanes, containing a stereogenic silicon, with high diastereo- and enantioselectivity, even on the gram-scale (Scheme 33). Only prochiral alkylic and vinylic arylsilanes were found efficient, (alkyl)vinyl and diaryl analogs leading to very low yields, and only (*E*)-configured substrates were found reactive. The authors speculated that the stereogenic silicon configuration could be controlled during the formation of the catalytically active chiral cobalt–silicon species upon activation by $NaBHEt_3$ of the cobalt complex formed from $Co(acac)_2$ and **80**. Alternatively, they envisioned the formation of a mixture of two diastereoisomers, the reaction then taking place via dynamic kinetic resolution. To get more insight into the mechanism, the authors also undertook extensive deuterium-labelling and kinetic experiments that demonstrated deuterium incorpation at the silicon, with retention of its configuration, suggesting that σ-bond metathesis occurred at silicon. As before, further palladium and platinium-catalyzed transformations at silicon enabled access to other highly functionalized α-chiral allylsilanes, having tetrasubstituted stereogenic silicon, without loss of diastereo- and enantioselectivity.

4.3 1,2-Hydrosilylation of Allenes

Palladium-catalyzed 1,2-hydrosilylation of terminal allenes **81** was reported by Montgomery et al. to proceed by addition of the Si–H bond of silanes across the internal C–C bond of allenes, yielding α-chiral allylsilanes.[71] The reaction could be performed with various silanes, including sterically demanding ones such as *t*-Bu_2SiH_2, and was catalyzed by 5 mol% of $Pd_2(dba)_3$ in the presence of 10 mol% of both imidazolium salt **82** and KO*t*-Bu (Scheme 34). The silyl group was preferentially delivered to the substituted allenic carbon, which is the more electron-rich sp^2-carbon, giving α-products without detection of β-regioisomeric vinylsilanes coming from addition of the silyl group to the central allenic carbon. Similarly, symmetrical α,γ-disubstituted allenes **83** led to α-products with roughly equivalent results and perfect (*E*)-selectivity employing 5 mol% of imidazolim salt **84**. Conversely, the reaction failed to afford α-chiral allylsilanes from α,α-disubstituted allenes, γ-regioisomers with the C–Si bond created at the least substituted allenic carbon being formed. Similar results were obtained by Schmidt et al. who performed 1,2-hydrosilylation of cyclohexylallene catalyzed by 1 mol% of (3-iminophosphine)-derived palladium complex **85** prepared in advance.[72] Under these reaction conditions, the regioselectivity was proved to be correlated to the steric bulk of the silane since only primary and secondary silanes afforded the desired α-products, tertiary silanes providing β-regioisomeric vinylsilanes. The α-regioselectivity of all these reactions was assumed to result from oxidative addition of the Si–H bond of silanes to palladium(0) followed by delivery of hydride to the allenic central carbon, giving π-allylpalladium complexes which in turn would undergo reductive elimination. Very recently, Xu and Fu carried out the reaction in enantioselective manner with α-aryl-substituted terminal allenes **81** by the use of $PhSiH_3$ in the presence of 1 mol% of $Cu(OAc)_2$ and chiral diphosphine **86**, which gave predominantly α-products with less than 10% yield of γ-regioisomers.[73] The reaction could be conducted on the gram-scale with identical results and the silicon of the products

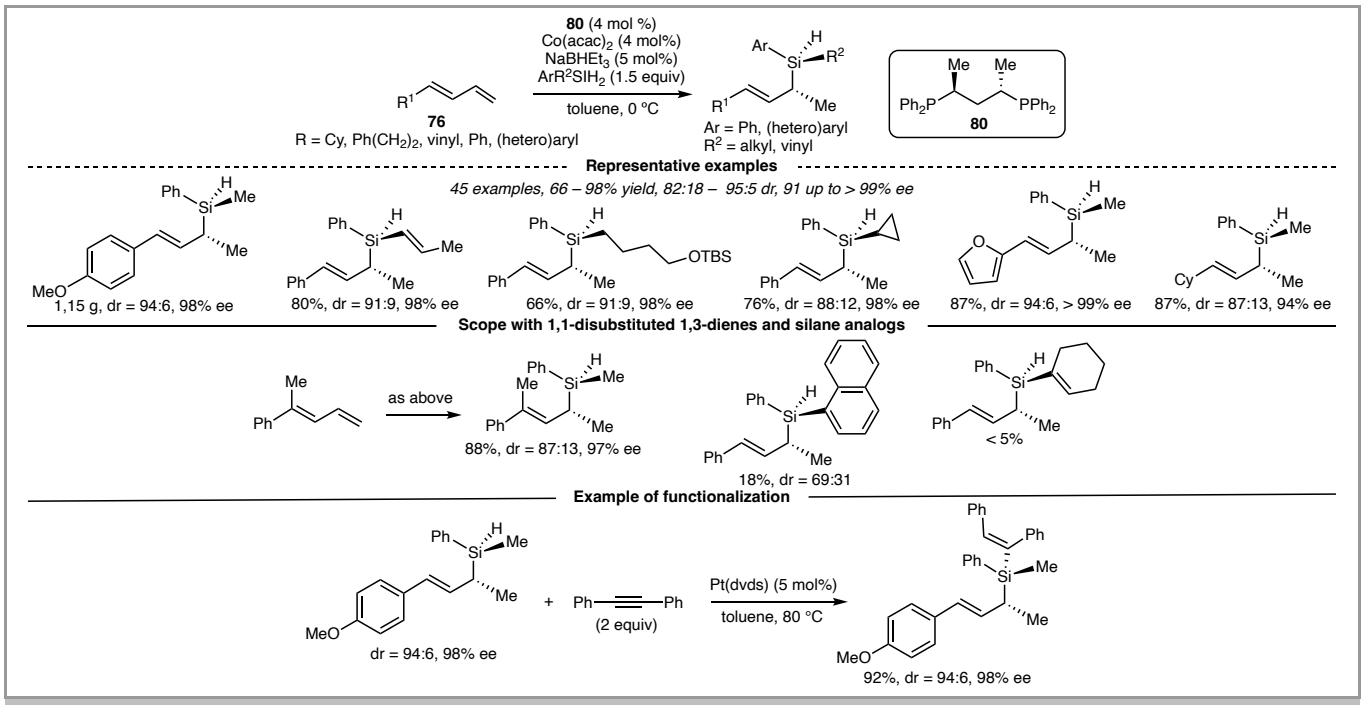


Scheme 32 Cobalt-catalyzed Markovnikov 1,2-hydrosilylation of 1,3-dienes

could be futher functionalized, for instance into bis(allyl)silanes, without loss of enantiomeric purity. With 1-alkyl-substituted analogs, the use of 2 mol% of both $Cu(OAc)_2$ and diphosphine **87** was required, although notaly lower enantioselectivity was observed, even at lower temperature.

The α-regioselective 1,2-hydrosilyation of α,α-disubstituted terminal allenes was found to be more challenging. In 2015, Schmidt et al. described the palladium-catalyzed 1,2-hydrosilyation of dimethylallene, yielding achiral quaternary allylsilanes.[72] As before, only primary and secondary silanes afforded exclusively α-products. More recently, Tang et al. used a wider array of unsymmetrical α,α-disubstituted terminal allenes **88** with Ph_2SiH_2 and 1 mol% of $Pd_2(dba)_3$ in the presence of 2.5 mol% of racemic BI-DIME and obtained also exlusively α-products (Scheme 35).[74] With enantiopure BI-DIME-derived ligand **89**, the reaction afforded products with perfect α-regioselectivity but moderate enantiomeric purity which could be improved with the combination of Ph_3SiH and enantiopure ligand **90**, albeit in moderate isolated yield due to the lack of regioselectivity under these conditions.

In 2023, Wang and Xu reported the first nickel-catalyzed enantioselective 1,2-hydrosilylation of allenes **88** with alkyl- and arylsilanes (Scheme 36).[75] The key to obtain quatrenary α-chiral allylsilanes with perfect α-regioselectivity and excellent enantiomeric purity was to perform the reaction in the presence of 6 mol% of chiral SPSiOL-derived bisphosphite ligand **91** with



Scheme 33 Enantioselective cobalt-catalyzed Markovnikov 1,2-hydrosilylation of 1,3-dienes with prochiral silanes

5 mol% of $NiBr_2$·DME and 20 mol% of LiO*t*-Bu. The reaction was found to tolerate broad substrate scope and could be applied on the gram-scale without any loss of efficiency. However, only primary silanes enabled hydrosilyation, secondary and tertiary analogs being unreactive, presumably due to steric hindrance. The reaction was also carried out successfully using $Ni(cod)_2$, instead of $NiBr_2$·DME/LiO*t*-Bu combination, suggesting that low-valent nickel was involved in the catalytic cycle. To gain more insights into the reaction mechanism, the authors undertook deuterium experiments and DFT calculations that unveiled that the Si–H bond cleavage probably occurred in the rate determining step. In addition, the products could be further functionnalized, for instance by hydrosilylation of aldehydes catalyzed by cobalt complex **92**, giving compounds containing a stereogenic silicon atom, with excellent diastereoselectivity.

5 Cross-Coupling Reaction

5.1 Cross-Coupling of Vinyl Halides

In 1982, Kumada et al. reported the first synthesis of optically active α-chiral allylsilanes by enantioselective cross-coupling between (*E*)-configured vinyl bromides **93** and α-trimethylsilybenzyl magnesium bromide (Scheme 37).[76] The reaction was catalyzed by 0.5 mol% of ferrocenyl phosphine-derived palladium complex **94**, prepared in advance, and gave (*E*)-products with excellent enantiomeric purity and complete retention of the C–C double bond geometry. In contrast, with (*Z*)-configured vinyl bromides, (*Z*)-products were obtained with the same configuration of the new stereogenic carbon, but lower enantiomeric putity. More recently, Reisman et al. developed the enantioselective nickel-catalyzed alkylation of substrates **93** with a diverse array of α-silylated benzylic chlorides **95** using 5 mol% of cobalt-phthalocyanine(CoPc), as co-catalyst, 10 mol% of preformed chiral Box-derived nickel complex **96** and an excess of manganese.[77] The reaction yielded α-chiral allylsilanes with high enantiomeric purity and moderate-to-good yield. It could also be carried out with other reactants such as α-silylated mesylates, instead of chlorides **95**, and enol triflates, instead of vinyl bromides **93**, and could be applied on the gram-scale with quite similar enantioselectivity but slightly lower yield.

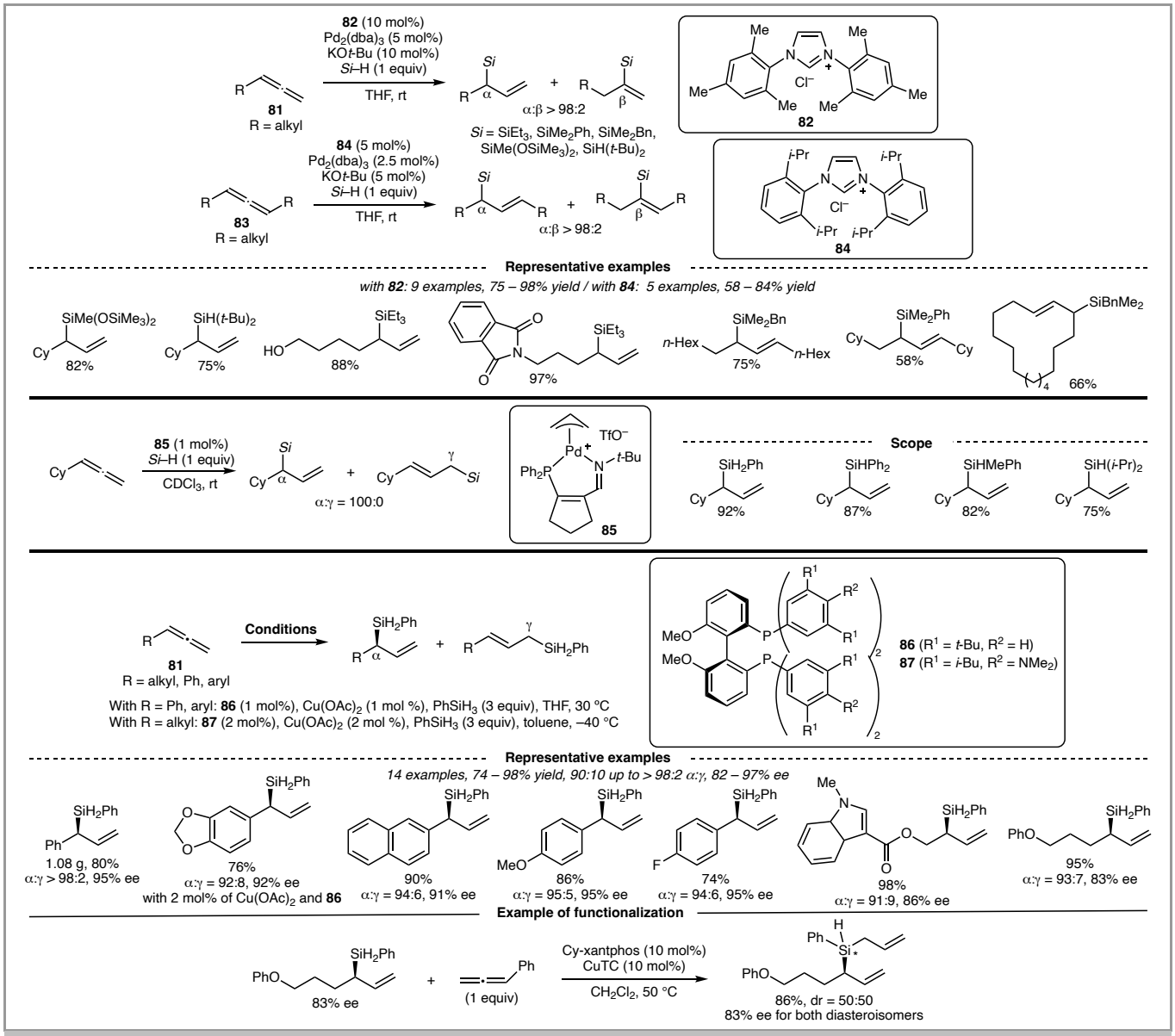
5.2. Retroallylation of δ-Silylated Homoallylic Alcohols

In 2007, Oshima and Yorimitsu developed the palladium-catalyzed intramolecular retroallylation of chiral δ-silylated homoallylic tertiary alcohols with aryl bromides.[78] The reaction was conducted with 2.5 to 5 mol% of $Pd(OAc)_2$ in the presence of 5 to 20 mol% of a tertiary arylphosphine and a sligh excess of Cs_2CO_3. Diverse silyl groups were tolerated, giving α-chiral allylsilanes with high (*E*)-selectivity (Scheme 38). With enantioenriched substrate **97**, excellent 1,3-chirality transfer and perfect (*E*)-selectivity were observed, and products were obtained with excellent enantiomeric purity. The authors postulated that the reaction involved oxidative addition of the C–Br bond of aryl bromides to palladium(0), generated in situ, bromine-exchange of palladium with alcohol, and then retroallylation, via chair-like transition state **TS4**, followed by reductive elimination.

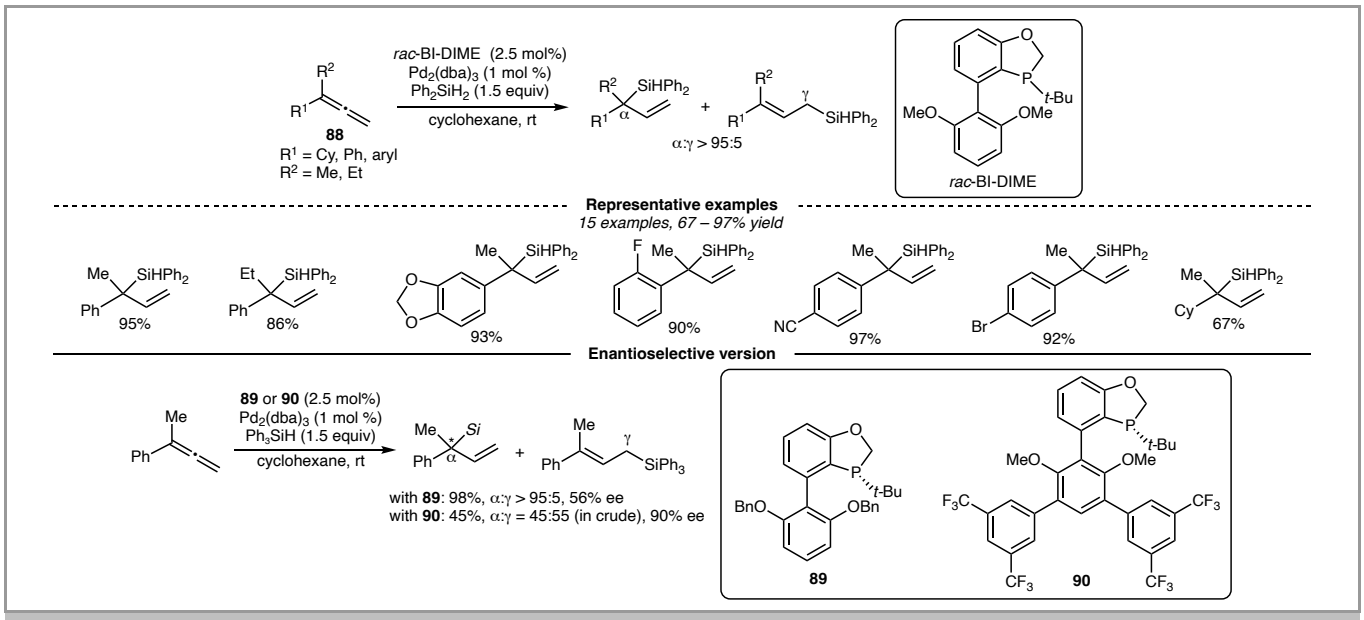
5.3 Multi-Component Cross-Coupling of 1,3-Dienes

Sato et al. reported that the three-component coupling between 1,3-dienes **76,** aliphatic and aromatic aldehydes and $PhMe_2SiBpin$, catalyzed by 10 mol% of $Ni(cod)_2$ in the presence of 10 mol% of chiral phosphoramidite **98,** provided γ'-hydroxyl α-chiral allylsilanes with perfect *syn* 1,3-diastereoselectivity and high enantiomeric purity (Scheme 39).[79] The reaction could also be performed with 1,4-disubstituted 1,3-dienes, yielding products containing three continuous stereogenic centers in *anti*,*anti* relationship as single diastereoisomers, albeit with

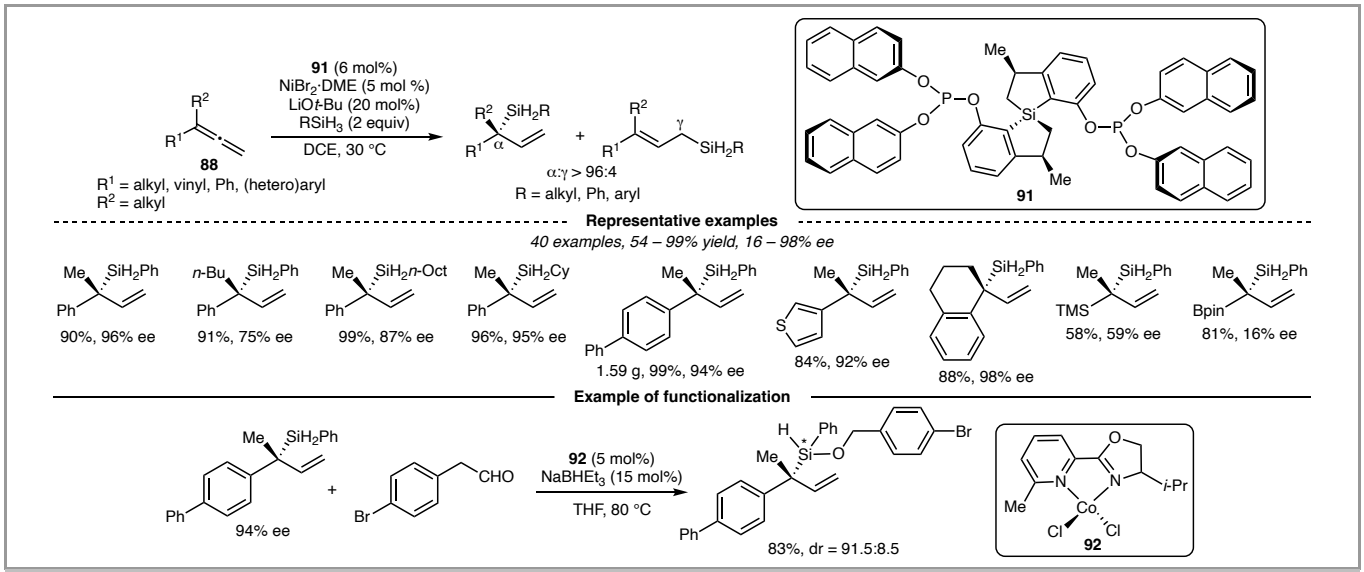
greatly eroded enantiomeric purity or yield. The mechanism



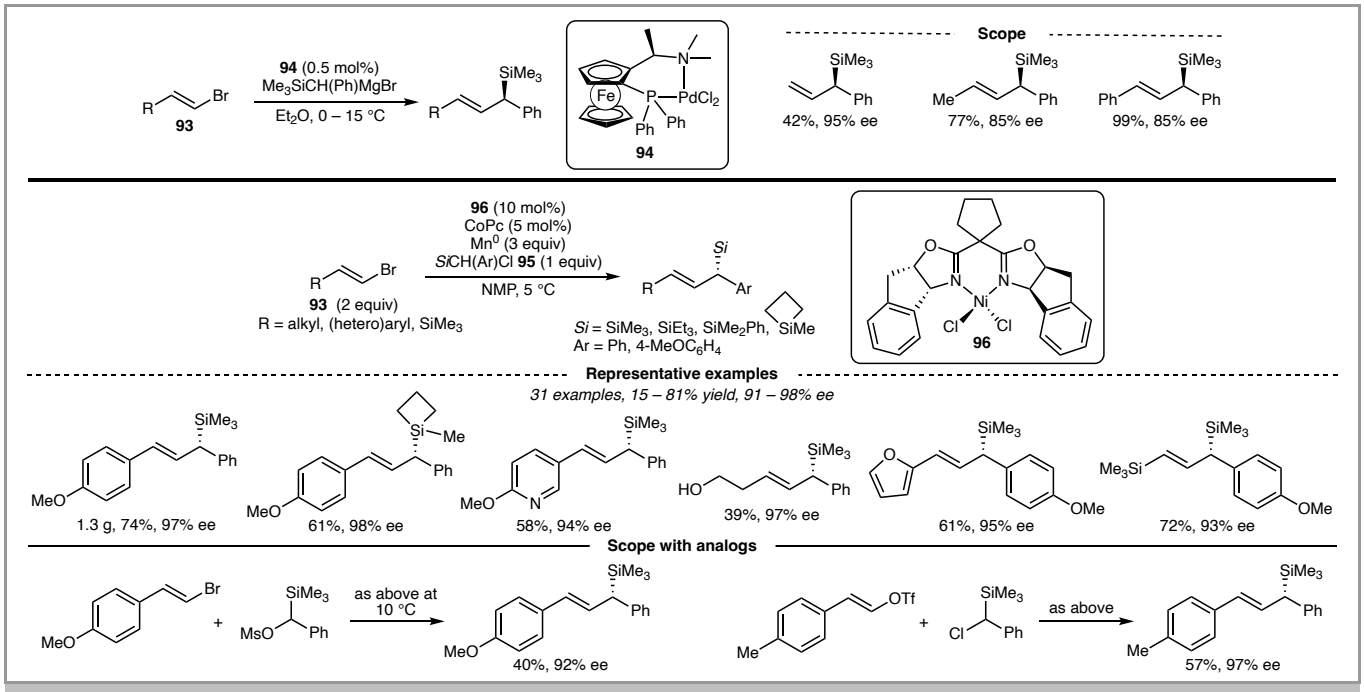
Scheme 34 Palladium and copper-catalyzed 1,2-hydrosilylation of α-substituted and α,γ-disubstituted terminal allenes



Scheme 35 Palladium-catalyzed 1,2-hydrosilylation of α,α-disubstituted terminal allenes



Scheme 36 Enantioselective nickel-catalyzed 1,2-hydrosilylation of α,α-disubstituted terminal allenes



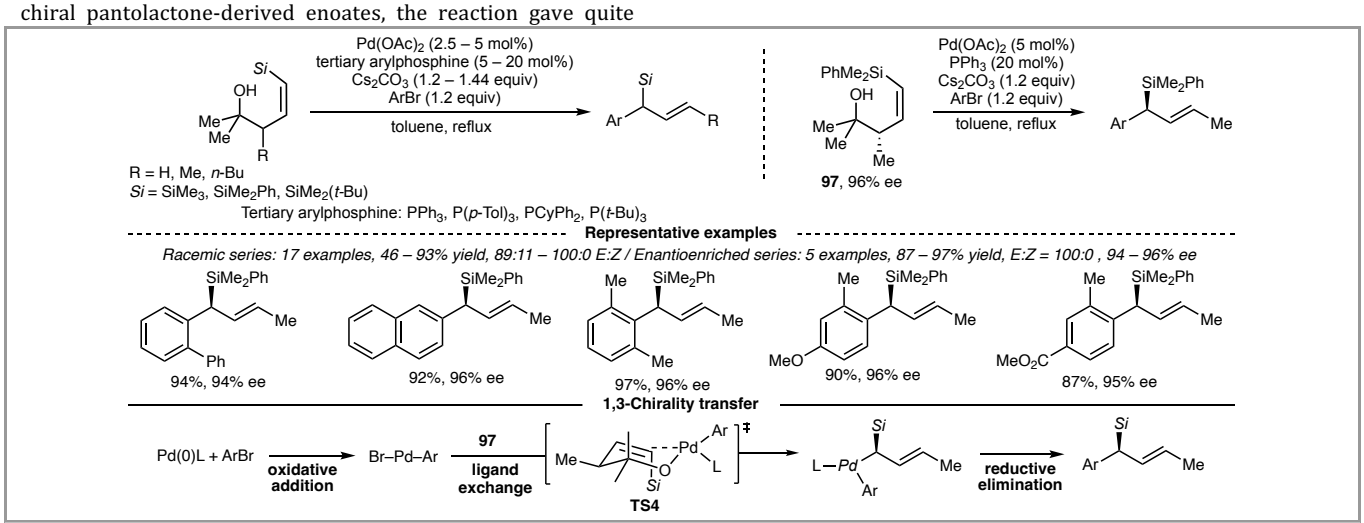
Scheme 37 Enantioselective palladium and nickel-catalyzed cross-coupling of vinyl electrophiles

proposed by the authors would involve the formation of five-membered oxanickelacycle intermediates by oxidative addition of aldehydes and 1,3-dienes to nickel(0). These intermediates then would undergo σ-bond metathesis with $PhMe_2SiBpin$ and subsequent reductive elimination.

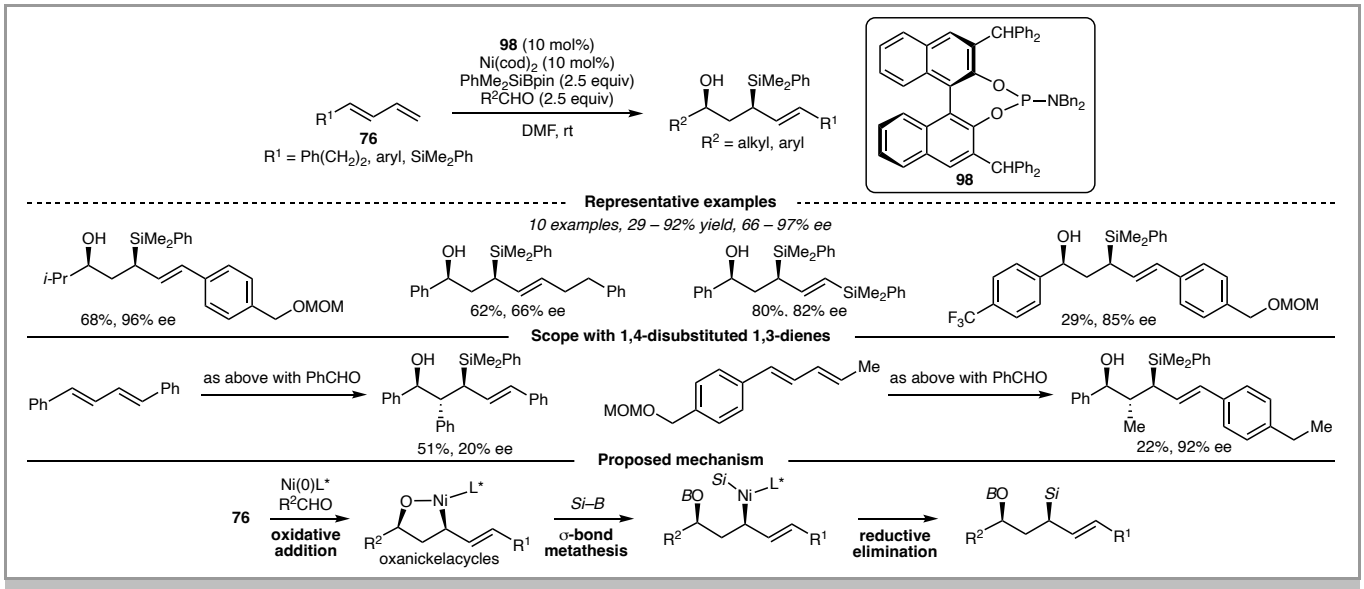
6 Insertion Reactions

6.1. Vinylcarbenoid Insertion into Si–H Bonds

In 1994, Landais et al. demonstrated that α-diazo carbonyl derivatives **99** were able to generate vinylrhodium carbenoids, in the presence of 1 mol% of $Rh_2(OAc)_4$, which underwent insertion into the Si–H bond of a wide array of silanes, yielding β'-carbonyl α-chiral allylsilanes (Scheme 40).[80a] Applied to chiral pantolactone-derived enoates, the reaction gave quite moderate diastereoselectivity. Soon after, the same authors reported two examples of the reaction of α-diazo enoates with $PhMe_2SiH$ catalyzed by 1 mol% of $Rh_2(5S\text{-MEPY})_4$ at rt with low yield and low-to-moderate enantioselectivity.[80b] At the same time, better enantioselectivity was obtained by Davies et al. who succeeded in carrying out the reaction with $Rh_2(S\text{-DOSP})_4$ and substrates **100** at lower temperature in pentane due to the high solubility of this rhodium catalyst in hydrocarbon solvents.[81] More recently, in a continuation of their work on carbenoid insertion into Si–H bond,[82] Panek et al. found that under Davis' conditions the reaction with *n*-Bu_3SiH gave products with quite similar enantiomeric purity but reduced yield.[83] They also showed that the reaction provided unsatisfactory results with $(Me_3Si)_3SiH$ and did not work at all with Ph_3SiH. However, they succeeded in



Scheme 38 Palladium-catalyzed retroallylation of δ-silylated homoallylic alcohols



Scheme 39 Enantioselective nickel-catalyzed three-component coupling of 1,3-dienes, aldehydes and $PhMe_2SiBpin$

using Ph_3SiH by performing the insertion with 5 mol% of $Cu(MeCN)_4(BF_4)$ in the presence of 7 mol% of dichlorodiimine **101**, giving the expected product with moderate enantiomeric purity. Nevertheless, further recrystallization from petroleum ether allowed the product to be isolated with high enantiomeric purity, albeit in low yield.

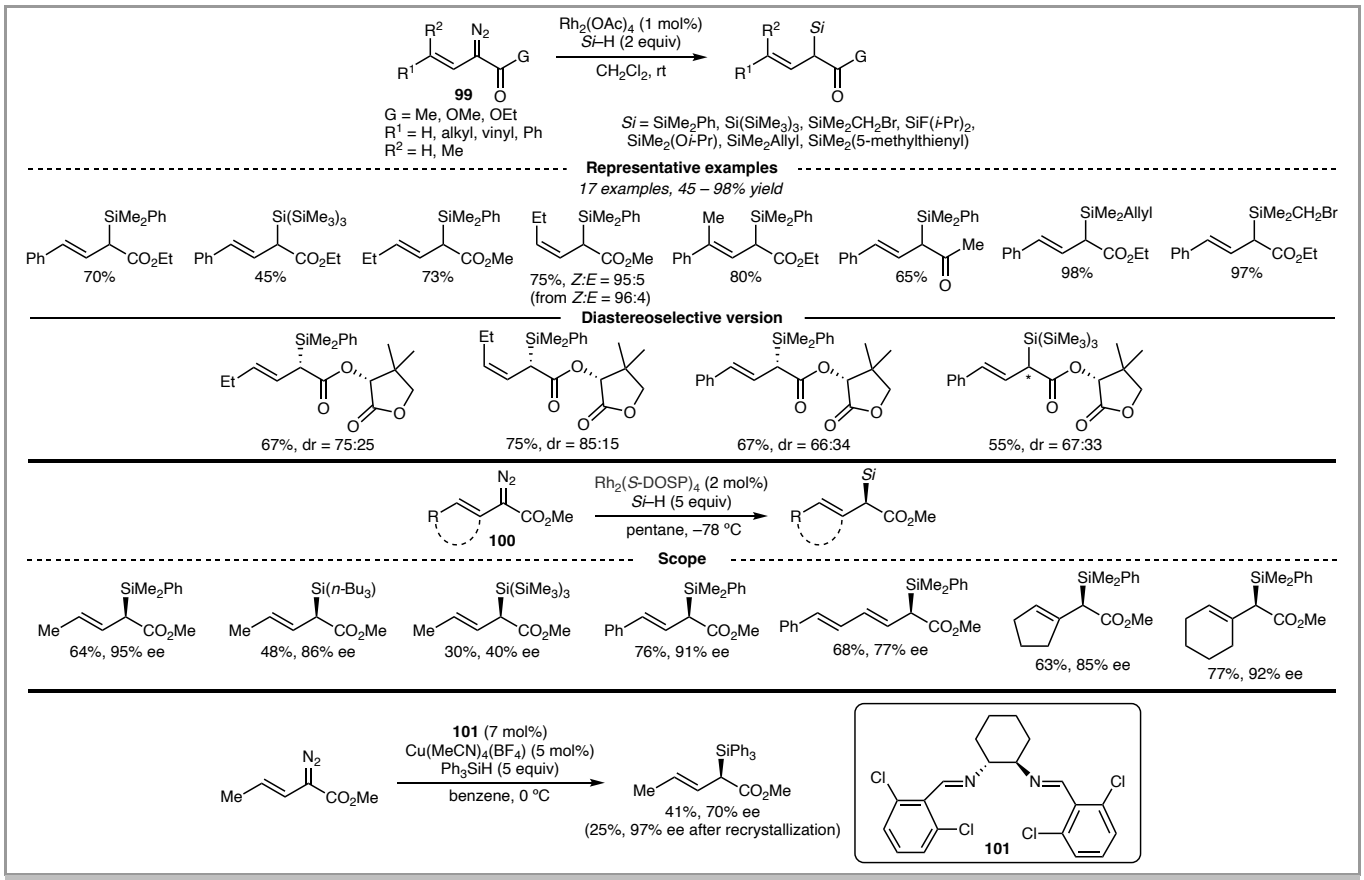
6.2. Silylene Insertion into Allylic C–O Bonds

In the mid 2000's, Woerpel et al. developped the copper-catalyzed insertion of silylenes into allylic C–O bonds.[84] They found that the decomposition of cyclohexene silacyclopropane **102** in the presence of 1 mol% of $(CuOTf)_2$·toluene generated di-tert-butylsilylene which then reacted with chiral allylic ethers to provide α-chiral allylsilanes (Scheme 41). When replacing the copper catalyst with 0.5 mol% of AgO_2CCF_3, the reaction gave an allylic disilane via insertion of two di-tert-butylsilylene groups. From enantioenriched *cis* allylic benzylic ether **103**, the reaction took place with significant loss of enantiomeric purity. In this reaction, the sole formation of *cis* products indicated that the new C–Si bond was formed with retention of the C–O bond that was broken. This result led the authors to explain the loss of enantioselectivty by allylic transposition occuring via *syn* [2,3]-sila-Wittig rearrangement and giving the enantiomeric product.

7 Rearrangments

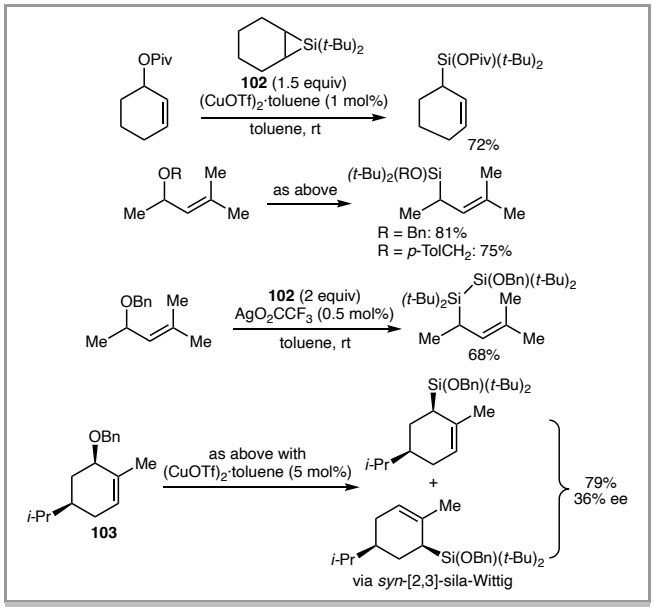
7.1 Intramolecular γ-Silylation of Allylic Disilanyl Ethers

Suginome et al. showed that palladium-catalyzed thermal rearrangement of achiral allylic disilanyl ethers and subsequent Peterson-type elimination led to racemic α-chiral allylsilanes.[85] Carried out with 2 mol% of $Pd(acac)_2$ in the presence of 8 mol% of 1,1,3,3-tetramethylbutyl isocyanide (TMBC), the reaction was applicable to enantioenriched substrates **104**, which contain various silyl groups, yielding products with high 1,3-chirality transfer and perfect (*E*)-selectivity (Scheme 42). The reaction was found to be enantiodivergent since (*E*)-and (*Z*)-substrates afforded enantiomeric products with roughly equivalent optical purity. The high 1,3-chirality transfer was assumed to result from intramolecular *cis* addition of the Si–Pd bond, formed by oxidative addition of the Si–Si bond to palladium(0), across the



Scheme 40 Rhodium-catalyzed reaction of α-diazo carbonyl derivatives with silanes

C–C double bond through chair-like transition state **TS5**. When performing the reaction in refluxed hexane, the authors showed that dimerized compounds could be isolated, recrystallized and subjected to Peterson-type elimination by treatment with *n*-BuLi. Following this protocol, they succeeded in synthetizing a product with 99.4% ee from a starting allylic disilanyl ether with 79.2% ee by enantiomeric enrichment.



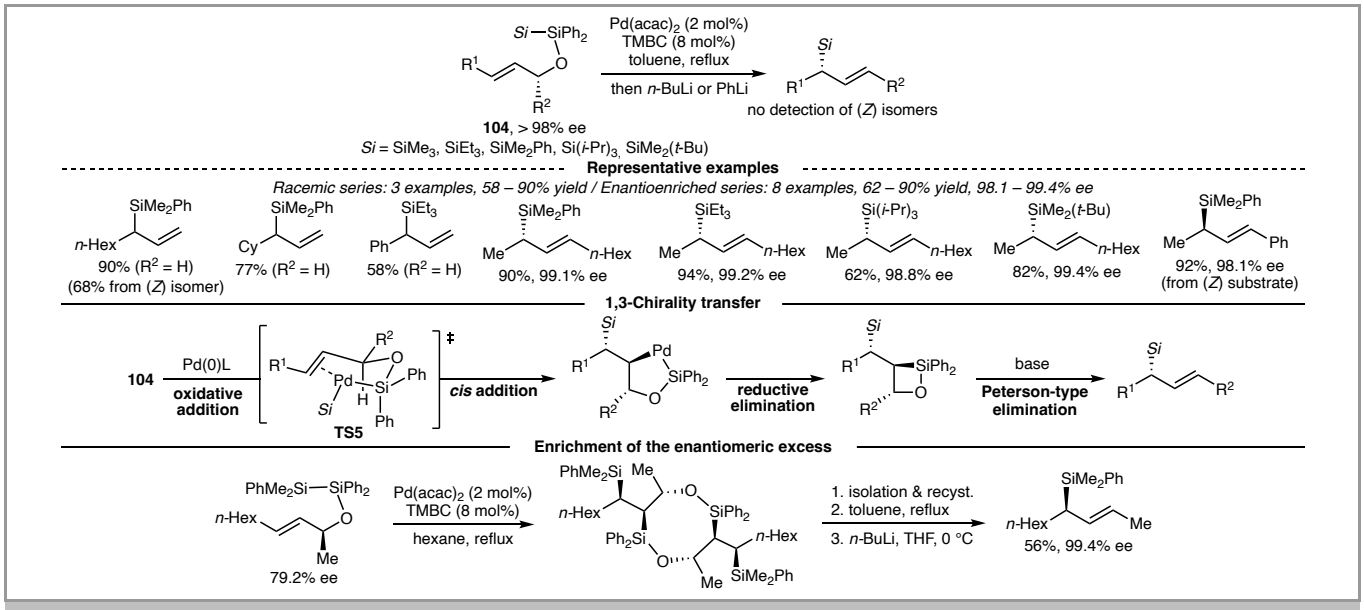
Scheme 41 Insertion of di-*tert*-butylsilylene into allylic C–O bonds

7.2. Domino Isomerization–Claisen Rearrangement of γ-Silylated Bis(allylic) Ethers

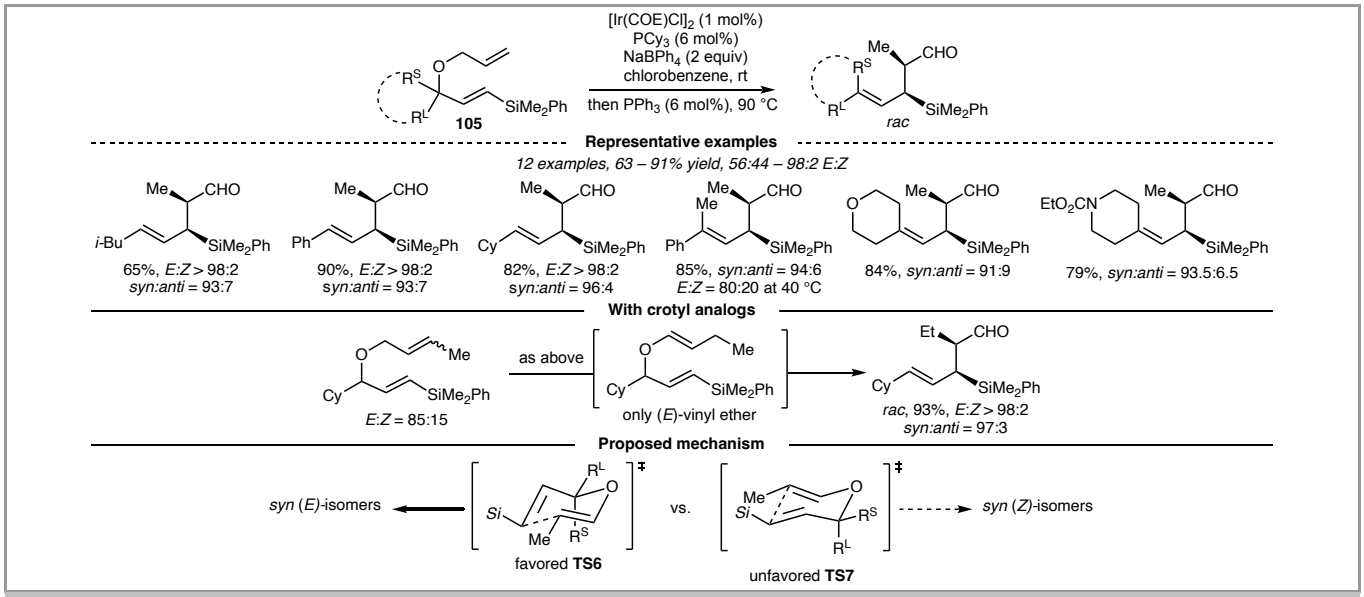
In 2012, Cook et al. reported that isomerization of γ-silylated bis(allylic) ethers **105** was catalyzed by 1 mol% of $[Ir(COE)Cl]_2$ in the presence of 6 mol% of PCy_3 and 2 mol% of $NaBPh_4$ at rt. When followed by thermal Claisen-rearrangement mediated by 6 mol% of PPh_3, β'-formyl α-chiral allylsilanes were obtained with high *syn* 1,2-diastereoselectivity (Scheme 43).[86] Excellent (*E*)-selectivity was observed from secondary substrates, while unsymmetrical tertiary ones yielded mixtures of isomers, even at lower temperature. With crotyl analogs, the authors showed that only (*E*)-vinyl ethers were formed during the isomerization process, regarless the C–C double bond geometry of the starting materials, affording exlusively (*E*)-products through Claisen-rearrangement. This result led the authors to rationalize both the (*E*)-selectivity and the *syn* 1,2-diastereoselectivty by chair-like transition state **TS6**, which is preferred over **TS7** due to less steric interactions. The energy difference between these two transition states was thought to be lower with unsymmetrical bis(allylic) ethers, making unfavored **TS7** more competitive and leading to low (*E*)-selectivity

8 Miscellaneous

Reaction of aldehydes with α-trimethylsilyl allylic acetate **106** was reported by Krische et al. to be catalyzed by 5 mol% of (*R*)-segphos- or (*R*)-C3-tunephos-derived iridium complexes **107** and **108** in the presence of stoichiometric K_3PO_4, to prevent



Scheme 42 Palladium-catalyzed intramolecular γ-silylation of allylic disilanyl ethers

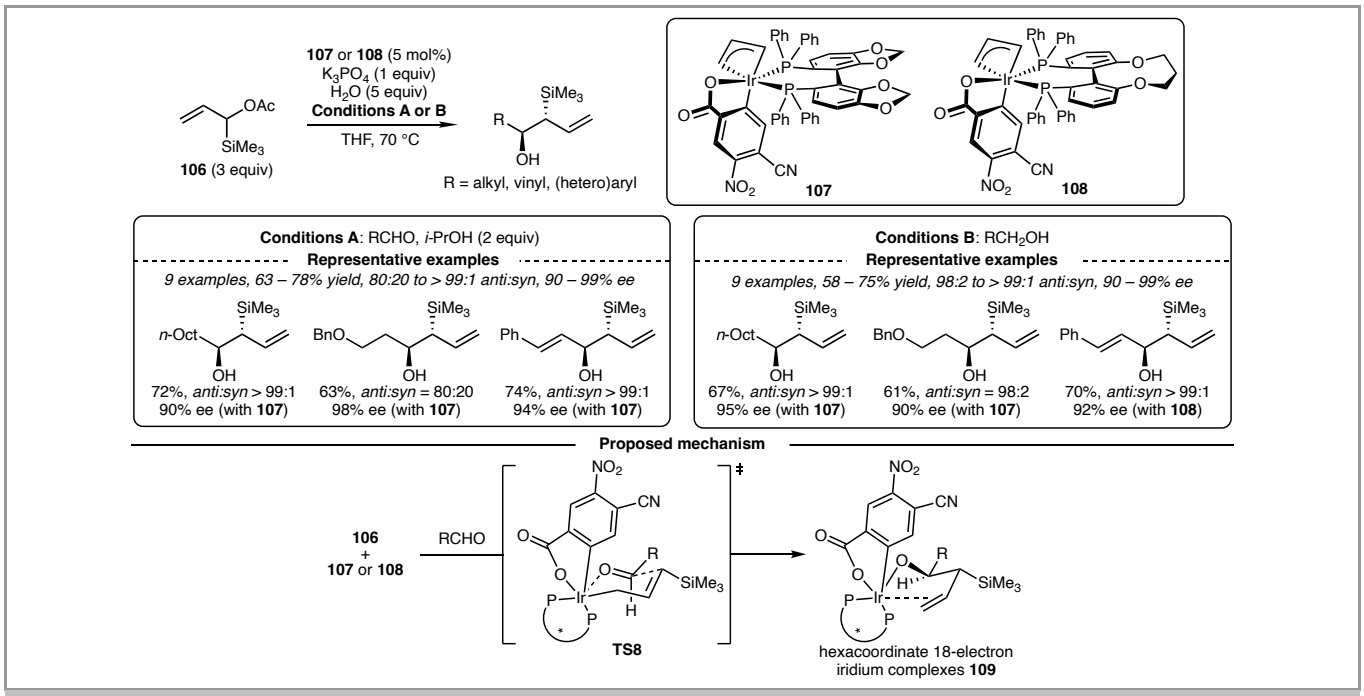


Scheme 43 Iridium-catalyzed domino isomerisation–Claisen rearrangement of γ-silylated bis(allylic) ethers

Peterson olefination, and an excess of isopropyl alcohol (Scheme 44).[87] In all cases, β'-hydroxy α-chiral allylsilanes were obtained with excellent enantioselectivity and good-to-high *anti*:*syn* ratio. In the absence of isopropyl alcohol, these iridium complexes enabled the direct coupling of primary alcohols, via dehydrogenation into aldehydes, with equivalent diastereo- and enantioselectivity. The predominant formation of *anti* 1,2-adducts suggested that carbonyl addition occurred via chair-like transition state **TS8** involving (*E*)-γ-silylated allyliridium intermediates. Key to the reaction is the fact that no oxidation of the products into aldehydes, through dehydrogenation, took place, which led the authors to postulate the formation of inactive hexacoordinate 18-electron iridium complexes **109** that thus cannot engage in β-hydride elimination. Subsequent ligand exchange with reactant alcohol or isopropyl alcohol would afford the product and allow regeneration of the catalyst.

9 Conclusion

This review highlights research in the development of the regio- and stereoselective synthesis of α-chiral allylsilanes under transition-metal catalysis. Particular emphasis was placed on specific enantioselective processes using chiral cobalt, copper, silver, iridium, nickel, palladium, platinum and rhodium catalysts, providing access to optically active tertiary α-chiral allylsilanes, and in a lesser extent, to quaternary ones. These processes involve α- or γ-silylation of allylic electrophiles, γ-alkylation and γ-arylation of γ-silylated allylic electrophiles, hydrosilylation of 1,3-dienes and allenes, carbene insertion into Si–H bonds of silanes and silylene insertion into allylic C–O bonds, as well as rearrangements. Although this review does not cover synthetic methods that are not catalyzed by transition-metal complexes, as for instance the useful allylation of carbonyl derivatives with γ-silylated allylboron reagents, we trust that it



Scheme 44 Enantioselective iridium-catalyzed carbonyl silyl allylation

will be of use to organic chemists who are interested in the synthesis of this important class of silicon compounds. We also hope this review will encourage further developments in the field, in particular to access the more complex enantioenriched quaternary α-chiral allylsilanes.

Acknowledgment

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Conflict of Interest

The authors declare no conflict of interest.

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Biosketches

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