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Transition-metal-catalyzed *trans*-bis-silylation of alkynes: development, mechanistic insights, and synthesis of fused siloles

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Review

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Abstract

Transition-metal-catalyzed bis-silylation of alkynes is an atom-economical strategy for constructing two carbon–silicon bonds in a single transformation. Classical bis-silylation reactions generally proceed through *cis* addition of a Si–Si bond to an unsaturated substrate, whereas *trans*-bis-silylation is much less common and requires control of both Si–Si bond activation and the stereochemical course of C–Si bond formation. Intramolecular *trans*-bis-silylation has emerged as a particularly useful route to fused siloles. This review traces the development of transition-metal-catalyzed *trans*-bis-silylation from the rhodium(I)-catalyzed cyclization of (2-alkynylphenyl)disilanes to palladium- and rhodium-catalyzed syntheses of pyridine- and thiophene-fused siloles. Density functional theory studies show that a formal *trans* product does not necessarily imply a direct elementary *anti*-addition event; palladium and rhodium systems can reach the same net stereochemical outcome through distinct multistep organometallic pathways. Ruthenium-catalyzed intramolecular hydrosilylation is discussed as a mechanistically distinct but structurally related route to pyridine-fused siloles. The review also places these ring-forming reactions in the broader context of intermolecular *trans*-bis-silylation, including rhodium-catalyzed *trans*-disilylation of alkynones with unactivated disilanes and palladium-catalyzed reactions enabled by coordinating unsymmetrical disilanes. Recent reagent-design studies, particularly those employing quinoline-containing disilanes, demonstrate that coordination, substrate polarization, and cooperative catalysis can control regio- and stereoselectivity without the geometric constraint of ring closure. Current limitations – including narrow substrate and disilane scope, reliance on precious metals, elevated reaction temperatures, and limited functional evaluation – are critically assessed. Opportunities for catalyst and

reagent design, predictive computational analysis, broader heteroarene scope, and integration with functional-materials studies are highlighted.

Introduction

Organosilicon compounds occupy a distinctive position at the interface of synthetic chemistry and materials science. Incorporation of silicon can modify molecular geometry, orbital energies, lipophilicity, and chemical reactivity, while silicon-containing π-conjugated frameworks have found broad application in optoelectronic and functional materials. Among these frameworks, siloles (silacyclopenta-2,4-dienes) are particularly notable because σ*–π* interaction involving the silicon center and the conjugated diene contributes to a relatively low-lying LUMO. This electronic feature has stimulated extensive investigation of silole-containing molecules and polymers for light-emitting, photovoltaic, and semiconducting applications [1-5].

A wide range of synthetic strategies has been developed for silole construction, including reactions of dilithiobutadienes with halosilanes, transition-metal-catalyzed cyclizations, reductive cyclizations of diynes, C–H silylation, hydrosilylation, and transformations that exploit Si–Si bonds [6-12]. Among these approaches, bis-silylation is attractive because two C–Si bonds can be formed by addition of a single Si–Si bond across an unsaturated unit. More broadly, transition-metal-catalyzed addition of element–element bonds to alkynes provides a versatile platform for the stereodefined synthesis of highly substituted alkenes [13]. Most established alkyne bis-silylation reactions proceed with *cis* selectivity. In the conventional mechanistic picture, oxidative addition of a Si–Si bond to a low-valent metal is followed by alkyne coordination, migratory insertion, and reductive elimination; the geometric requirements of these elementary steps generally favor delivery of the two silyl groups to the same face of the alkyne-derived framework. *trans*-Bis-silylation therefore represents both a synthetic challenge and a mechanistic departure from the canonical pathway. A key advance was reported by Matsuda and Ichioka in 2012, who demonstrated that rhodium(I)-catalyzed intramolecular addition of a Si–Si bond across the alkyne of (2-alkynylphenyl)disilanes afforded 3-silyl-1-benzosiloles with a net *trans* relationship [14]. This work established that the usual stereochemical preference of bis-silylation can be overridden when substrate preorganization, catalyst identity, and favorable ring formation act cooperatively. An important intermolecular precedent followed in 2018, when He and co-workers reported a rhodium(I)-catalyzed *trans*-disilylation of alkynones with unactivated disilanes [15]. Subsequent studies extended the intramolecular concept to heteroaromatic fused siloles and to distinct catalytic manifolds. An earlier contribution by Matsuda, Kadowaki, and Murakami in 2007 demonstrated ruthenium-catalyzed double *trans*-hydrosilylation of 1,4-diarylbuta-1,3-diynes with dihydrosilanes to afford 2,5-diarylsiloles [16]. Although distinct from intramolecular bis-silylation involving Si–Si bond cleavage, this work provided an important precedent for ruthenium-catalyzed *trans*-selective silole formation. Ruthenium-catalyzed intramolecular hydrosilylation of 3-dimethylsilyl-2-ethynylpyridines provided a related route to pyridine-fused siloles [17]. Although this reaction does not involve bis-silylation, it offers a useful comparison between Si–H and Si–Si activation. Palladium-catalyzed intramolecular *trans*-bis-silylation subsequently afforded pyridine-fused siloles from 2-bromo-3-(pentamethyldisilanyl)pyridines under Sonogashira-type conditions [18]. Rhodium catalysis then enabled *trans*-bis-silylation of preformed 2-ethynyl-3-(pentamethyldisilanyl)pyridines [19], and the strategy was further extended to thiophene-fused siloles [20]. More recently, Zhao and co-workers achieved a palladium-catalyzed intermolecular *trans*-bis-silylation of terminal alkynes using a designed quinoline-containing disilane and subsequently established the regio- and stereodivergent bis-silylation of alkynoates through cooperative palladium/Lewis acid catalysis [21,22]. Together, these studies show that net *trans* selectivity can be generated by several distinct combinations of substrate design, catalyst, and disilane reagent.

This review critically examines the development, scope, and mechanistic understanding of transition-metal-catalyzed *trans*-bis-silylation of alkynes, with particular emphasis on the synthesis of fused siloles. The discussion is organized around the interplay among substrate topology, metal catalyst, Si–Si versus Si–H activation, and computed reaction pathways. Particular attention is given to the distinction between the observed *trans* stereochemistry and the elementary steps by which that stereochemical outcome is generated. Current limitations in substrate scope, catalyst efficiency, disilane design, and functional evaluation are then considered to identify directions for further development. Recent reviews have surveyed either disilylation chemistry broadly [23] or *trans*-selective addition of diverse element–element bonds to alkynes, including Si–Si, B–B, Si–B, P–B, Se–B, and B–Sn [24]. In contrast, this review focuses specifically on the transition-metal-catalyzed *trans*-bis-silylation of alkynes, emphasizing its mechanistic diversity, the distinction between net *trans* selectivity and the underlying elementary steps, and its development as a ring-forming strategy for fused siloles. The historical development of the field and the related Ru-catalyzed pathway are summarized in Figure 1.

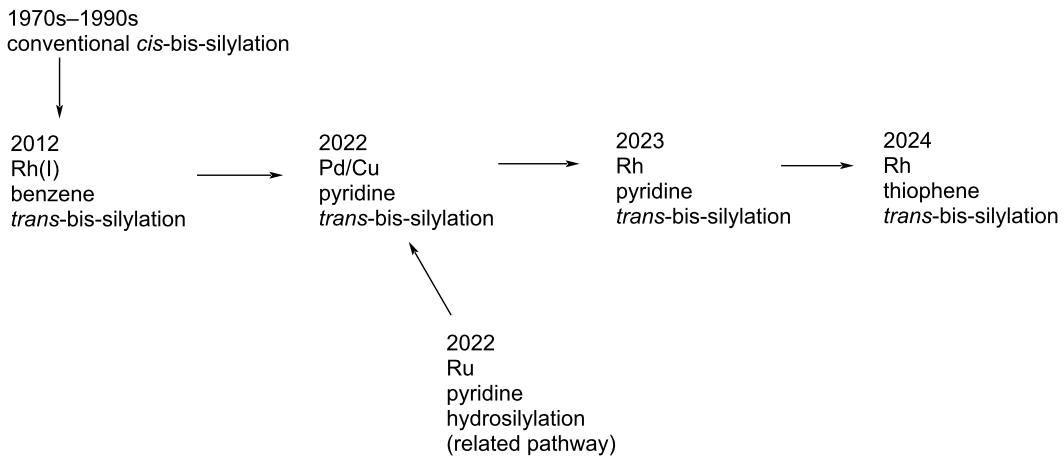


Figure 1: Historical development of intramolecular transition-metal-catalyzed *trans*-bis-silylation leading to fused siloles, with ruthenium-catalyzed intramolecular hydrosilylation shown as a related pathway.

Review

Background: transition-metal-catalyzed silylation approaches to fused siloles

Conventional bis-silylation and the predominance of *cis* addition

Transition-metal-catalyzed bis-silylation has been investigated for several decades. Early palladium- and platinum-catalyzed studies established that disilanes can add across unsaturated carbon–carbon bonds, and subsequent works broadened both the range of disilane reagents and the available catalyst classes [13,25-29]. Activated disilanes, strained cyclic disilanes, and well-defined palladium silyl complexes have all been employed in alkyne bis-silylation. A recent comprehensive review has summarized the rapid expansion of methods leading to *cis*/*trans*-1,2-disilylated and *gem*-disilylated alkenes [23]. Despite this mechanistic and structural diversity, the classical reaction landscape remains dominated by *cis* products.

The predominance of *cis* addition is consistent with the canonical catalytic sequence. Oxidative addition of a Si–Si bond generates a bis(silyl)metal species, after which alkyne insertion into one M–Si bond and subsequent C–Si reductive elimination can preserve a *syn*-relationship between the two silicon substituents. Formation of a *trans* product therefore requires the system to deviate from this trajectory, for example through a different sequence of elementary steps, geometric reorganization of an intermediate, or stereochemical inversion before the formation of the second C–Si bond. Intramolecular substrates introduce an additional driving force because the formation of a favorable five-membered ring can compensate for otherwise disfavored geometric changes.

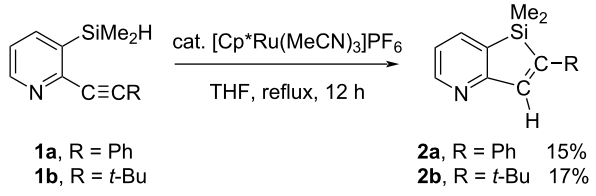
Ru-catalyzed intramolecular hydrosilylation as a related route

Before considering Si–Si-based cyclizations, a related Si–H-based reaction is informative because it provides access to the same class of heteroarene-fused products through a distinct bond-activation mode. 3-Dimethylsilyl-2-ethynylpyridine derivatives undergo intramolecular hydrosilylation in the presence of $[Cp^*Ru(MeCN)_3]PF_6$ to furnish pyridine-fused siloles [17]. Phenyl- and *tert*-butyl-substituted alkynes gave the corresponding cyclic products in 15% and 17% isolated yields, respectively, whereas an *n*-butyl-substituted substrate produced a complex mixture and the trimethylsilyl-substituted alkyne was recovered without cyclization.

The proposed Ru pathway involves substrate coordination, oxidative hydrometalation to a σ-vinyl intermediate, and reductive elimination to form the C–Si bond. This mechanism differs fundamentally from the bis-silylation because Si–Si bond cleavage is not involved. Nevertheless, the reaction establishes that appropriately positioned pyridylalkynylsilanes can undergo five-membered-ring closure to the silolo[3,2-*b*]pyridine framework. The modest yields and pronounced substituent dependence also illustrate a recurring limitation in fused-silole synthesis: productive intramolecular cyclization must compete with oligomerization, polymerization, and other unselective alkyne reactions.

The Ru study also examined the photophysical properties of the products. The phenyl-substituted derivative exhibited a longer-wavelength absorption than the *tert*-butyl analogue, consistent with enhanced π conjugation, and time-dependent density functional theory (TD-DFT) calculations were used to interpret the

observed electronic transitions. These results are relevant to the broader context of *trans*-bis-silylation because they connect the ring-forming methodology with the electronic consequences of fused-silole construction. Representative Ru-catalyzed cyclizations are shown in Scheme 1.



Scheme 1: Ruthenium-catalyzed intramolecular hydrosilylation of 3-dimethylsilyl-2-ethynylpyridine derivatives **1** leading to pyridine-fused siloles **2**.

Emergence of intramolecular *trans*-bis-silylation

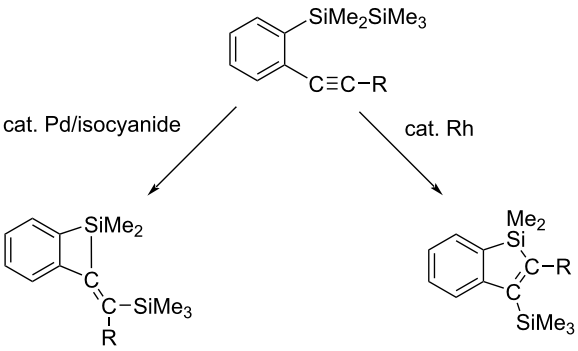
Rhodium-catalyzed formation of benzosiloles

The 2012 study by Matsuda and Ichioka provided the key proof of concept for the intramolecular *trans*-bis-silylation [14]. Rhodium(I)-catalyzed cyclization of (2-alkynylphenyl)disilanes furnished 3-silyl-1-benzosiloles through formal *trans* addition of the Si–Si bond across the alkyne. Importantly, the outcome was strongly catalyst-dependent: related palladium/isocyanide chemistry favored *cis*-bis-silylation and formation of a different ring system, whereas rhodium promoted formation of the five-membered benzosilole through *trans* addition.

This catalyst-dependent divergence established two principles that remain central to the field. First, *trans*-bis-silylation is not simply a stereochemical variant of conventional *cis* addition; a change in the stereochemical course can alter skeletal connectivity and ring size. Second, the substrate functions as a preorganized reaction platform in which Si–Si activation, alkyne insertion, and ring closure are coupled. These features make intramolecular systems particularly useful for probing how catalyst identity and substrate geometry govern the formal *trans* outcome. The catalyst-controlled divergence between the *cis* and *trans* pathways is illustrated in Scheme 2.

Palladium-catalyzed intramolecular *trans*-bis-silylation of pyridine substrates

A complementary route to pyridine-fused siloles was developed from 2-bromo-3-(pentamethyldisilanyl)pyridine and terminal alkynes under $PdCl_2(PPh_3)_2$/CuI conditions [18]. The transformation combines the formation of the C(sp^2)–C(sp) bond characteristic of a Sonogashira coupling with the subsequent intramolecular *trans*-bis-silylation of the resulting alkynylpyridine framework. Ethynylbenzene derivatives afforded the corresponding pyridine-fused siloles, and the study constituted the first reported successful use of a palladium catalyst for a *trans*-bis-silylation of alkynes with disilanes.



Scheme 2: Catalyst-controlled intramolecular bis-silylation of (2-alkynylphenyl)disilanes reported by Matsuda and Ichioka [14]: *cis*-bis-silylation with a Pd/isocyanide system and *trans*-bis-silylation with a Rh(I) catalyst.

The tandem nature of this process is synthetically significant because the alkynyldisilane intermediate can be generated in situ rather than isolated in advance. Mechanistically, however, the simultaneous presence of Pd and Cu introduces additional complexity relative to a single-metal cyclization. Any mechanistic description must account for the cross-coupling event, Si–Si bond activation, alkyne coordination and insertion, and closure of the five-membered silole ring.

Density functional theory (DFT) calculations were used to investigate possible pathways leading to the *trans*-bis-silylated product. The calculations suggested a sequential mechanism in which a *cis*-bis-silylation species is initially formed and subsequently converted into the thermodynamically more stable *trans* product. However, the proposed *cis* species has not been experimentally observed or isolated, and its conversion into the *trans* product has not been experimentally demonstrated. Thus, the *cis*-to-*trans* pathway should be regarded as a computationally proposed mechanism rather than an experimentally established isomerization. This distinction emphasizes that the stereochemistry of the isolated product does not necessarily reveal the stereochemical course of the initial Si–Si bond addition.

The palladium system also illustrates that the pyridine ring is not merely a passive fused aromatic component. Its nitrogen atom modifies substrate electronics and can influence coordination behavior, while the resulting pyridine-fused silole introduces an electron-deficient heteroaromatic unit into the conjugated framework. Thus, the reaction addresses both a mechanis-

tic problem in organosilicon catalysis and a structural objective in heteroaromatic silole synthesis. The tandem Pd/Cu transformation and the simplified DFT-derived pathway are summarized in Scheme 3.

Rhodium-catalyzed *trans*-bis-silylation of heteroaromatic alkynes

Pyridine-fused siloles

To separate the cyclization step from the preceding cross-coupling chemistry and to evaluate a distinct transition-metal platform, preformed 2-ethynyl-3-(pentamethyldisilanyl)pyridines were subjected to rhodium catalysis [19]. Heating at 110 °C in the presence of a rhodium complex afforded pyridine-fused siloles through intramolecular *trans*-bis-silylation. The results demonstrated that formation of the pyridine-fused framework is not specific to the Pd/Cu tandem system and that Rh-mediated Si–Si activation, previously established for the benzosilole formation, can be extended to a nitrogen-containing heteroaromatic substrate.

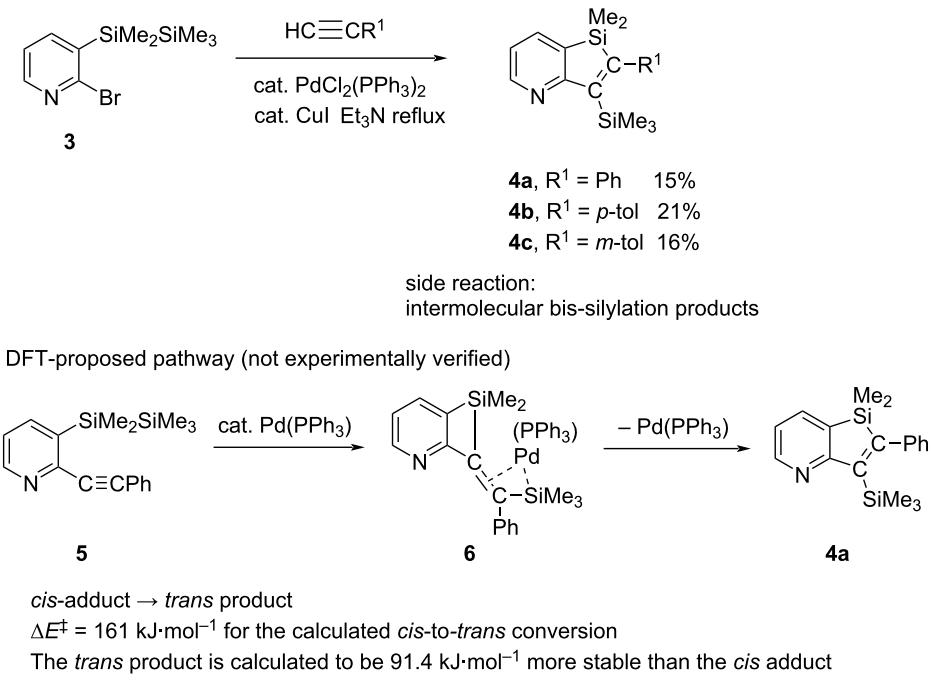
The study also addressed the mechanistic origin of the *trans* product. DFT calculations compared *trans*- and *cis*-bis-silylation routes using RhCl(CO) and $RhCl(CO)_2$ catalyst models. In both models, the calculated activation barriers favored the *trans* pathway, consistent with the experimental outcome. The proposed route involves Si–Si bond cleavage, migration of a trimethylsilyl group to the alkyne-derived carbon framework, and subsequent structural reorganization before release of the fused silole product [19]. Importantly, this mechanism differs from the sequential *cis*-to-*trans* pathway identified for the palladium system.

Comparison of the palladium and rhodium reactions is therefore particularly instructive. Both generate the same general pyridine-fused silole topology from pentamethyldisilanylpyridine precursors, but they do so in different catalytic contexts. The Pd/Cu system couples Sonogashira alkynylation with ring formation, whereas the Rh reaction begins from an isolated alkynyl substrate. The latter consequently provides a more direct platform for examining Si–Si activation and the elementary steps associated with intramolecular *trans*-bis-silylation.

Thiophene-fused siloles

The heteroaromatic scope was subsequently extended from pyridine to thiophene [20]. 3-Ethynyl-2-(pentamethyldisilanyl)thiophene derivatives underwent rhodium-catalyzed cyclization at 110 °C to give thiophene-fused siloles through intramolecular *trans*-bis-silylation. This study represented the first transition-metal-catalyzed bis-silylation route to thiophene-fused siloles and demonstrated that the ring-forming concept is not confined to nitrogen-containing heteroarenes.

This extension is significant from both synthetic and materials perspectives. Thiophene-containing π systems are established



Scheme 3: Palladium-catalyzed synthesis of pyridine-fused siloles **4** through intramolecular *trans*-bis-silylation and a simplified representation of the DFT-derived pathway.

components of electrochromic materials, field-effect transistors, light-emitting systems, and organic photovoltaics. Fusion of a silole unit to thiophene therefore combines two electronically distinctive building blocks within a single conjugated framework. More generally, the pyridine and thiophene examples show that intramolecular *trans*-bis-silylation can operate on heteroarenes with markedly different electronic characteristics.

The materials relevance of thiophene-fused siloles was established in earlier studies of dithienosilole-containing conjugated oligomers and polymers. Ohshita reviewed the synthesis and electronic properties of these materials, including their applications in organic light-emitting diodes, photovoltaic cells, and thin-film transistors [30]. This prior work provides a materials-science context for the later development of rhodium-catalyzed routes to thiophene-fused siloles, although the synthetic methodologies are distinct.

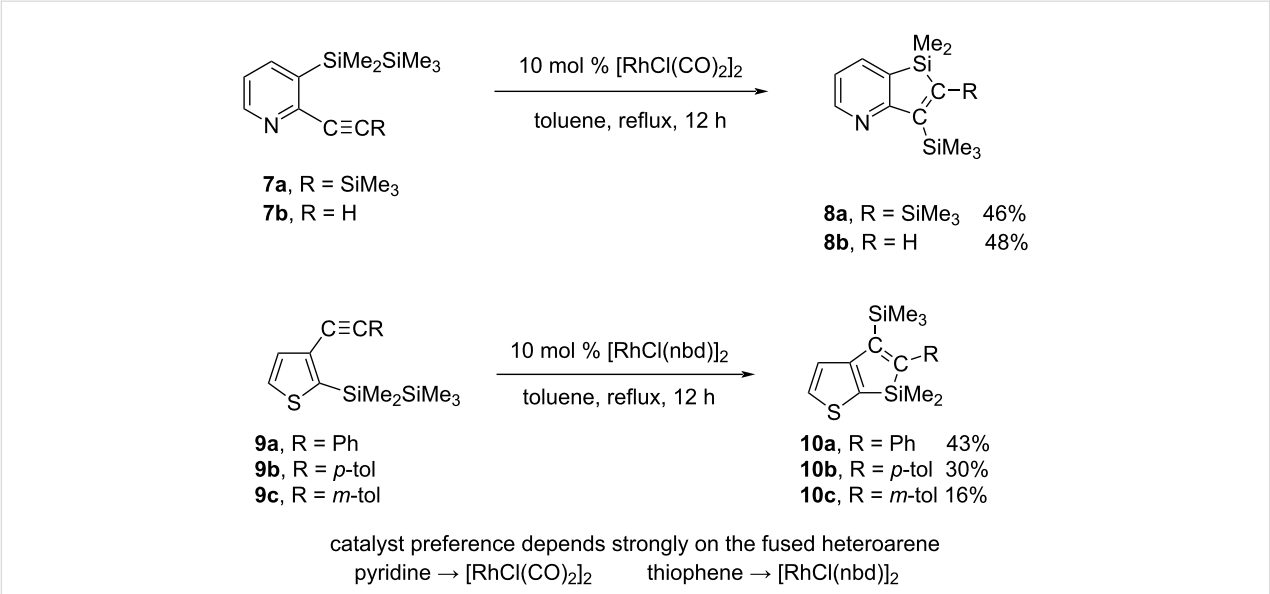
DFT calculations were again employed to analyze formation of the thiophene-fused product. Using RhCl(nbd) (nbd = norbornadiene) as the active catalyst model, a multistep pathway containing several intermediates and transition states was identified, with the calculated rate-determining step occurring late in the sequence [20]. Considered together with the pyridine study, these results support a general methodological point: formal *trans*-bis-silylation should be interpreted in terms of catalyst-dependent organometallic elementary steps rather than assumed to correspond to a single concerted *anti*-addition event. The demonstrated heteroaromatic scope nevertheless remains narrow, and extension to furans, pyrroles, benzothiophenes, azaarenes, and more highly substituted fused systems remains an important objective. Representative Rh-catalyzed pyridine- and thiophene-fused silole syntheses are compared in Scheme 4.

The representative cyclizations also illustrate the present limitations in reaction efficiency. The Pd/Cu tandem synthesis of pyridine-fused siloles afforded isolated yields of 15–21% for three arylalkyne substrates under reflux in triethylamine for 12 h [18]. In contrast, the Rh-catalyzed cyclizations of preformed pyridylalkynes gave 46–48% yields with 10 mol % $[RhCl(CO)_2]_2$ in refluxing toluene for 12 h [19], whereas the corresponding thiophene series furnished 16–43% yields using 10 mol % $[RhCl(nbd)]_2$ under toluene reflux [20]. Because these results involve different substrates and reaction sequences, the yields should not be interpreted as a direct comparison of intrinsic Pd and Rh catalyst efficiencies.

Mechanistic understanding of *trans*-bis-silylation

Why is *trans* addition unusual?

In a simplified *cis*-bis-silylation cycle, oxidative addition of a disilane to a low-valent metal generates a bis(silyl)metal species. Alkyne coordination and migratory insertion then place a silyl group and the metal on the developing alkene framework, after which reductive elimination forms the second C–Si bond. In the absence of additional reorganization, this sequence tends to preserve a *cis* relationship between the two silicon substituents. A formal *trans* outcome therefore requires the cat-



Scheme 4: Rhodium-catalyzed intramolecular *trans*-bis-silylation leading to pyridine- and thiophene-fused siloles **8** and **10**. Mechanistic investigations employed RhCl(CO) and $RhCl(CO)_2$ models for the pyridine system and a RhCl(nbd) model for the thiophene system. These computational models should be distinguished from the experimentally employed rhodium catalyst precursors.

alytic system to depart from this default stereochemical trajectory.

Intramolecular ring formation provides one means of overcoming this constraint. Tethering the alkyne and disilane increases effective molarity and creates a thermodynamic incentive for five-membered-ring formation. The catalyst can therefore access pathways involving insertion, rotation, metal migration, or other structural reorganization before formation of the final C–Si bond. Accordingly, the term "*trans*-bis-silylation" describes the overall stereochemical outcome without necessarily specifying an elementary *anti*-addition step.

Comparative analysis of Pd- and Rh-catalyzed reaction pathways

The DFT studies of the Pd- and Rh-catalyzed reactions provide insight into the possible origins of *trans* selectivity, although the proposed pathways differ among the catalytic systems [18-20]. For the Pd-catalyzed pyridine system, a sequential pathway involving a computationally identified *cis*-bis-silylation species followed by conversion into the *trans* product was proposed. The calculated activation barrier for this conversion was 161 kJ·mol^{-1}, and the *trans* product was calculated to be 91.4 kJ·mol^{-1} more stable than the *cis* species [18]. Importantly, neither the *cis* species nor its conversion into the *trans* product has been experimentally demonstrated. For the Rh-catalyzed pyridine system, calculations using RhCl(CO) and RhCl(CO)$_2$ models favored the *trans*-bis-silylation pathway over the competing *cis* pathway [19]. In the Rh-catalyzed thiophene system, a different catalyst model, RhCl(nbd), was employed to investigate a multistep pathway leading to the *trans* product [20]. Because these calculations involve different substrates, ligand environments, and computational models, their activation energies cannot be compared directly to establish the relative catalytic activities of Pd and Rh complexes. Rather, the results indicate that *trans*-bis-silylation can proceed through distinct mechanistic pathways depending on the substrate and catalytic system. For the RhCl(CO) model of the pyridine reaction, the reported activation energies were 169 and 189 kJ·mol^{-1} for the *trans* and *cis* pathways, respectively. With RhCl(CO)$_2$, the corresponding values were 123 and 170 kJ·mol^{-1}, although the rate-determining transition states differed between the two pathways [19]. The RhCl(nbd) model used for the thiophene reaction gave a calculated free-energy barrier of 176 kJ·mol^{-1} at 383.15 K [20]. These values describe different substrates, catalyst coordination environments, and computational treatments; in particular, the number and identity of coordinated ligands may affect steric congestion and the accessibility of competing transition states. Therefore, the numerical barriers should not be used to rank the experimental catalysts directly.

This mechanistic diversity has direct implications for catalyst design. Ligands and substrate substituents can influence Si–Si bond activation, alkyne insertion, intermediate geometry, and the barriers associated with subsequent bond formation or reorganization. Consequently, catalyst identity can alter ring size or stereochemical outcome even within closely related substrate classes. Mechanistic conclusions should therefore be established for each catalytic manifold rather than transferred uncritically from one metal system to another.

The Ru hydrosilylation reaction provides a useful mechanistic contrast [17]. In that system, oxidative hydrometalation of the Si–H/alkyne unit followed by reductive elimination can generate the cyclic C–Si bond without Si–Si cleavage. Comparison with the Pd and Rh bis-silylation systems emphasizes that similar fused silole architectures can be reached through fundamentally different activation modes. A unified computational analysis employing consistent DFT calculations, solvation treatments, and ligand models across Ru, Pd, and Rh systems would be valuable for more quantitative comparison of these pathways.

Intermolecular *trans*-bis-silylation and stereodivergent reactions

The transition from intramolecular to intermolecular *trans*-bis-silylation reaction is a critical test of generality because regioselectivity and stereoselectivity must be controlled without the geometric assistance of a tether. A notable early intermolecular example was reported by He and co-workers in 2018: the rhodium(I)-catalyzed disilylation of alkynones with unactivated disilanes furnished *trans*-disilylated products with high stereoselectivity [15]. The reaction demonstrated that *trans* selectivity can be achieved intermolecularly when an electronically biased alkyne and an appropriate rhodium catalyst are combined. Mechanistic studies also revealed facile Si–Si activation and crossover of the disilane components under the reaction conditions, highlighting the dynamic behavior of the Si–Si bond before product formation. A mechanistically distinct but related approach was reported by Yamagishi, Shimokawa, and Yorimitsu, who developed a Cu-catalyzed twofold silylmetalation of diarylacetylenes using silylpotassium species generated in situ from a disilane and *t*-BuOK [31]. Because this transformation proceeds through a sequential silylmetalation rather than a direct addition of an intact Si–Si bond, it lies outside the strict definition of bis-silylation adopted here, but it provides a useful complementary strategy for vicinal disilylation of alkynes.

A conceptually different solution emerged from reagent design. Zhao and co-workers employed strongly coordinating unsymmetrical disilanes 8-(2-substituted-1,1,2,2-tetramethyldisilanyl)quinoline (TMDQ) to achieve the palladium-catalyzed

intermolecular *trans*-bis-silylation of terminal alkynes [21]. Experimental and computational studies indicated that the observed *trans* product is generated through a sequence involving initial *cis*-bis-silylation followed by *Z*/*E* isomerization, rather than by a simple direct *anti*-addition event. This result closely parallels a central theme of the intramolecular chemistry: the net stereochemistry of the isolated product does not necessarily identify the stereochemistry of the initial Si–Si-addition step.

The development of TMDQ was itself enabled by earlier advances in unsymmetrical disilane design. Song and co-workers showed that an amide-functionalized unsymmetrical disilane could undergo a highly regio- and stereoselective palladium-catalyzed bis-silylation of terminal alkynes [32], while Zhao and co-workers later demonstrated a Ni(0)-catalyzed *cis*-bis-silylation of internal alkynes using strongly coordinating TMDQ reagents [33]. These studies established that a coordinating substituent attached to the disilane can profoundly affect Si–Si activation, catalyst association, regioselectivity, and downstream differentiation of the two silyl groups. Building on this concept, a subsequent palladium/Lewis acid catalytic system enabled regio- and stereodivergent bis-silylation of alkynoates with TMDQ [22]. Modulation of the catalytic environment provided access to distinct 1,2-bis(silyl)alkene products, including a *trans* isomer, demonstrating that regioselectivity and *cis*/*trans* stereoselectivity are interdependent variables that can be controlled through cooperative catalyst and reagent design. More recently, Chen and co-workers reported the Pd-catalyzed *trans*-silaboration of terminal alkynes using a quinoline-directed Si–B reagent [34]. In a related development in reagent design, Liu and co-workers demonstrated a regioselective bis-silylation of terminal alkenes with unsymmetrical disilanes [35]. Although these reactions involve Si–B addition or alkene substrates rather than *trans*-bis-silylation of alkynes, respectively, they further illustrate the utility of coordinating reagent design for selectivity control.

For fused-silole synthesis, these intermolecular advances are important for two reasons. First, they demonstrate that *trans* selectivity is not intrinsically dependent on ring closure. Second, they identify complementary strategies – substrate polarization, coordinating disilane design, and cooperative catalysis – that may ultimately reduce the dependence of intramolecular methods on highly preorganized substrates. Conversely, insights into intermediate reorganization and ring-closure energetics may inform the design of intermolecular *trans*-bis-silylation systems. Representative intermolecular reactions based on these reagent-design concepts are shown in Scheme 5.

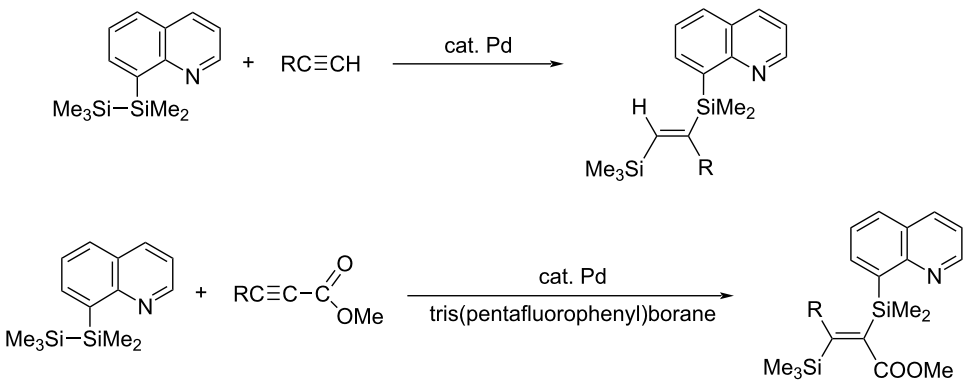
Scope, limitations, and opportunities

Substrate scope and reaction efficiency

Intramolecular *trans*-bis-silylation has so far been demonstrated mainly for *ortho*-related alkynyl and disilanyl groups on benzene, pyridine, and thiophene rings. The limited heteroarene scope and pronounced substituent dependence remain important constraints: in the related Ru-catalyzed hydrosilylation, phenyl- and *tert*-butyl-substituted alkynes cyclized, whereas the *n*-butyl substrate gave no isolable cyclic product and the trimethylsilyl-substituted substrate did not cyclize [17]. Systematic comparisons of alkyne substituents under a common catalyst system, followed by tests with furan, pyrrole, and benzothiophene substrates, would establish which steric and electronic factors control ring closure.

Catalyst and disilane design

Current intramolecular methods rely largely on Pd or Rh catalysts, often at elevated temperatures and substantial catalyst loadings. In the reported heteroaromatic examples, the preferred Rh precatalyst differs between pyridine and thiophene sub-



Scheme 5: Representative palladium-catalyzed intermolecular *trans*-bis-silylation of terminal alkynes and regio- and stereodivergent bis-silylation of alkynoates using designed disilane reagents.

strates [19,20]. Direct comparisons of ligand sets, catalyst loadings, and temperatures within each substrate series would therefore be more informative than extrapolating from different catalytic systems. Pentamethyldisilanyl groups also dominate the reported fused-silole syntheses. Coordinating disilanes, including amide-functionalized reagents and quinoline-based TMDQ, have demonstrated control of Si–Si activation and selectivity in intermolecular chemistry [21,22,32,33]; testing analogous designs in intramolecular cyclizations is a specific opportunity, rather than an established solution. Functionalization of the residual silyl substituent could further diversify the resulting siloles.

Functional evaluation and outlook

The materials potential of these fused siloles remains less developed than their synthesis. The Ru-derived pyridine-fused siloles showed substituent-dependent absorption and fluorescence [17], while related fused oligosiloles prepared by a distinct synthetic route displayed changes in optical and electrochemical properties with increasing fusion [36]. A useful next step would be to measure absorption, emission, and redox properties for matched pyridine- and thiophene-fused silole series and correlate these data with substitution and molecular structure. Combined with consistently modeled reaction pathways and experimentally measured selectivities, such comparisons would identify both the practical limits of *trans*-bis-silylation and the functional value of its products. The representative catalytic routes are summarized in Table 1. Systematic absorption, emission, and electrochemical comparisons of the Pd- and Rh-derived fused siloles have not yet been reported in the studies discussed here [18-20].

Conclusion

Transition-metal-catalyzed *trans*-bis-silylation of alkynes constitutes a still-limited but conceptually important area of organosilicon chemistry. In 2012 a rhodium-catalyzed synthesis of 3-silyl-1-benzosiloles established that a Si–Si bond can be incorporated across an alkyne with a net *trans* relationship under intramolecular conditions. Subsequent palladium and rhodium studies extended this reactivity to pyridine-fused siloles, and rhodium catalysis further enabled the synthesis of thiophene-fused siloles. Mechanistic and computational studies have shown that these formal *trans* products can arise through catalyst-dependent multistep organometallic pathways and therefore should not be interpreted automatically as the products of a simple concerted *anti* addition.

The ruthenium-catalyzed intramolecular hydrosilylation of pyridine substrates provides a useful mechanistic and synthetic comparison, illustrating how Si–H and Si–Si activation can converge on related fused-silole architectures through distinct pathways. At the same time, the intermolecular *trans*-bis-silylation with designed disilanes demonstrates that *trans* selectivity can be achieved without the geometric constraint imposed by ring closure and substantially broadens the conceptual scope of the field.

The principal challenge is now one of generality. Expansion of substrate and disilane scope, improved catalyst efficiency, mechanistically guided ligand and reagent design, and closer integration with structure–property studies will be required for *trans*-bis-silylation to develop from a mechanistically distinctive transformation into a broadly useful synthetic strategy.

Table 1: Representative transition-metal-catalyzed routes discussed in this review.

catalyst	key substrate	activation mode	net outcome	product class	ref.
Rh(I)	(2-alkynylphenyl)disilane	Si–Si	intramolecular *trans*-bis-silylation	3-silyl-1-benzosilole	[14]
$[Cp^*Ru(MeCN)_3]PF_6$	3-dimethylsilyl-2-ethynylpyridine	Si–H	intramolecular hydrosilylation	pyridine-fused silole	[17]
$PdCl_2(PPh_3)_2$/CuI	2-bromo-3-(pentamethyldisilanyl)-pyridine + terminal alkyne	C–C coupling + Si–Si	tandem coupling/*trans*-bis-silylation	pyridine-fused silole	[18]
$[RhCl(CO)_2]_2$	2-ethynyl-3-(pentamethyldisilanyl)-pyridine	Si–Si	intramolecular *trans*-bis-silylation	pyridine-fused silole	[19]
$[RhCl(nbd)]_2$	3-ethynyl-2-(pentamethyldisilanyl)-thiophene	Si–Si	intramolecular *trans*-bis-silylation	thiophene-fused silole	[20]
Rh(I)	alkynone + unactivated disilane	Si–Si	intermolecular *trans*-disilylation	*trans*-1,2-disilylalkene	[15]
Pd	terminal alkyne + TMDQ	Si–Si	intermolecular *trans*-bis-silylation	*trans*-1,2-bis(silyl)alkene	[21]
$Pd/B(C_6F_5)_3$	alkynoate + TMDQ	Si–Si	regio-/stereodivergent bis-silylation	1,2-bis(silyl)alkenes	[22]

Progress along these directions should enable access to a wider range of structurally and electronically differentiated organosilicon molecules and clarify the role of *trans*-bis-silylation in both synthetic and materials chemistry.

Author Contributions

Akinobu Naka: conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization; writing – original draft; writing – review & editing. Hisayoshi Kobayashi: conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization; writing – original draft; writing – review & editing.

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Data Availability Statement

Data sharing is not applicable as no new data was generated or analyzed in this study.

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