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Communication

Nucleophilic Activation of Hydrosilanes via a Strain-Imposing Strategy Leading to Functional Sila-aromatics

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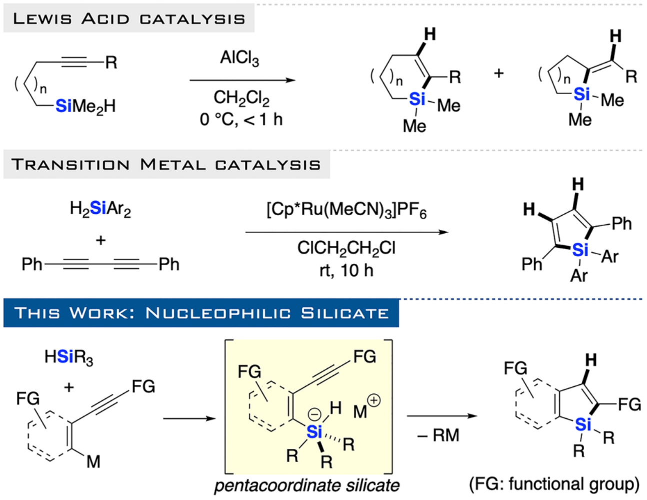
ABSTRACT: Carefully designed cyclic hydrosilanes enable *trans*-selective hydrosilylation of unactivated alkynes without transition metal catalysts via silicate formation. Employment of sterically demanding bidentate ligands of silicon increases steric congestion upon silicate formation, and this strain-imposing strategy facilitates hydride transfer. This hydrosilylation provides efficient access to diverse benzosiloles, silaphenalenes, and related silacycles.

Silicon-centered penta- or hexacoordinate ate complexes, *i.e.* silicates, are fascinating reactive species that can mediate various organic transformations.[1] Carbonyl allylation,[2] enolate addition,[3] and reduction[4] have been especially well studied, and the increased Lewis acidity of the pentacoordinate silicon atom upon silicate formation plays a pivotal role in these reactions.[5] On the other hand, ligand transfer from the pentacoordinate silicate to unpolarized functionalities, such as carbon−carbon triple bonds, is not promoted by the Lewis acidity of the silicon center and, thus, is especially challenging.[6] Herein, we report a design strategy for highly nucleophilic pentacoordinate silicates that enable efficient *trans*-selective hydrosilylation of unactivated internal alkynes,[7,8] leading to benzosiloles[9] and unprecedented sila-aromatics.

Hydrofunctionalization reactions of alkynes provide efficient and straightforward access to functionalized alkenes and have, thus, been extensively investigated.[10] However, *trans*-selective transformations remain difficult and further development is still needed.[11,12] *Trans*-selective hydrosilylation of alkynes is an attractive approach to construct silacycles. Lewis acid catalyzed highly *trans*-selective intermolecular hydrosilylation of unactivated internal alkynes was pioneered by Yamamoto et al. employing trialkylsilanes, and aluminum(III) proved to be particularly effective.[7a] They extended this chemistry to the synthesis of various aliphatic silacycles including a single example of benzosilole.[7b] As for transition-metal-catalyzed processes, Trost extensively developed the Ru-catalyzed methodology,[7c−f] which was utilized for the synthesis of siloles via sequential *trans*-selective hydrosilylations of diynes by Murakami et al.[7g] As a base-promoted example, Lee reported a tandem process of alkynylation of carbonyl compounds and *trans*-hydrosilylation using alkynylhydrosilanes to form oxasilacyclopentenes involving pentacoordinated silicate.[8] We have recently reported a *pseudo*-intramolecular strategy for activation of boron reagents leading to the formation of various boracycles via *trans*-selective interelement boration reactions.[13] This entropic activation strategy may also be applicable for activation of the Si−H bond of hydrosilanes especially with an sp^2-carbanion via pentacoordinate silicate formation to achieve catalyst-free *trans*-selective hydrosilylation reaction leading to functional sila-aromatics (Scheme 1).

Scheme 1. *Trans*-selective Hydrosilylation of Alkynes for Silacycle Formation



Another key to success is the use of sterically demanding diols as the bidentate ligand of the silicon reagents. Initial experiments using commonly employed hydrosilanes such as $HSiEt_3$ and $HSi(OEt)_3$ were not fruitful due to the poor silicate-forming ability of the former and undesired ligand exchange of the latter. For reference, a simple model calculation for acyclic $H_2Si(MeO)_2$ and MeLi showed that the least basic MeO ligand is far more easily substituted than

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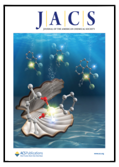

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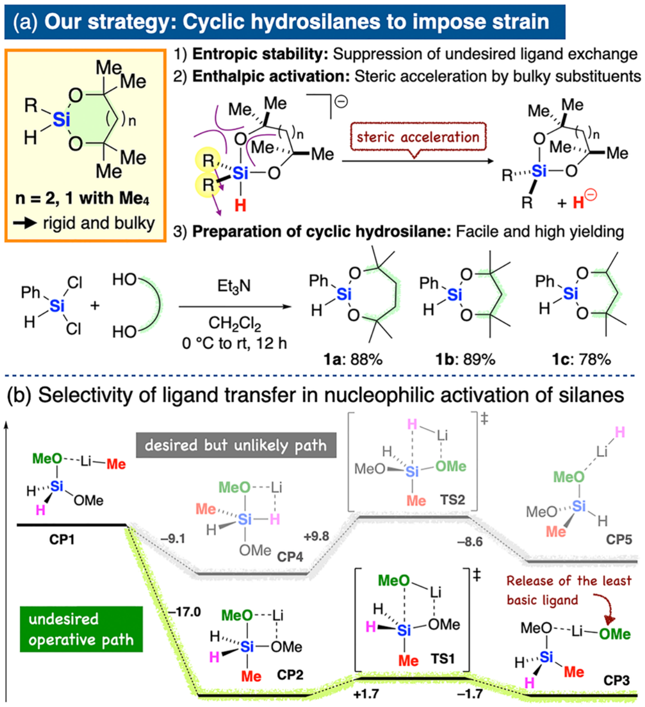
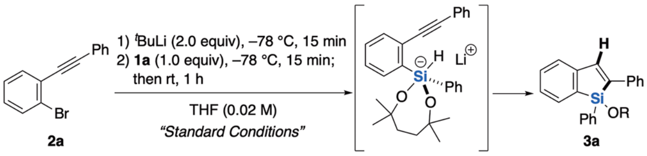


Figure 1. Toward nucleophilic activation of hydrosilanes: (a) our strategy and (b) selectivity of ligand transfer in nucleophilic activation of silanes, with ΔG values (kcal/mol) calculated at the level of B3LYP/6-31+G*.

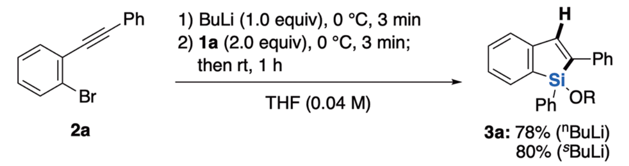
Table 1. Optimization of Reaction Conditions



Entry	Variation from Standard Conditions	Yield (%)
1	none	58[a]
2	**1b** in lieu of **1a**	49[a]
3	**1c** in lieu of **1a**	n.d.
4	$HSiPh_2(O^tBu)$ in lieu of **1a**	37[b,c]
5	**1a**: 1.6 equiv in lieu of 1.0 equiv	87[b]
6	**1a**: 2.0 equiv in lieu of 1.0 equiv	94[b]
7	Quenching without warming up	<5[b]
8	THF: 0.04 M in lieu of 0.02 M, otherwise under the conditions of entry 6	98[b]
9	TEMPO (3.0 equiv), otherwise under the conditions of entry 8	93[b]
10	9,10-Dihydroanthracene (3.0 equiv), otherwise under the conditions of entry 8	97[b]
11	^{i}PrMgCl·LiCl (1.0 equiv) in lieu of ^{t}BuLi, 1-I-2-(phenyl ethynyl)benzene in lieu of **2a**, otherwise under the conditions of entry 8	n.d.
12	Et_2O in lieu of THF	<5[b]

[a] Isolated yields. [b] NMR yields determined using mesitylene as an internal standard. [c] The product has two phenyl groups on silicon as exocyclic substituents. THF = tetrahydrofuran. n.d. = not detected.

Circumvention of ^{t}BuLi and cryogenic conditions:



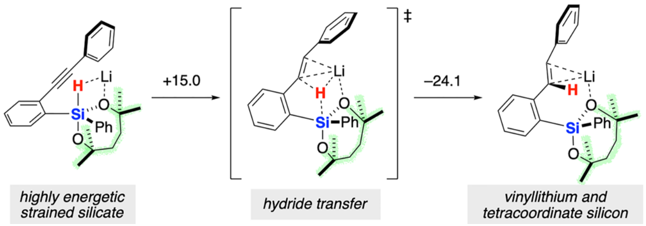
the hydride ($\Delta G^{\ddagger}_{TS1}$ = 1.7 kcal/mol vs $\Delta G_{CP2\text{-}CP4}$ + $\Delta G^{\ddagger}_{TS2}$ = 17.7 kcal/mol) (Figure 1b). Thus, we adopted a strategy of tying back two of the alkoxy ligands on the silicon by using diols. Moreover, envisioning enthalpic activation of hydride, we adopted a *strain-imposing strategy* with a multiply methylated ligand for steric acceleration (Figure 1a-2). To test this design strategy, we prepared seven- and six-membered hydrosilanes containing diols equipped with multiple methyl groups (**1a**−**1c**), as shown in Figure 1a-3. Notably, these silanes, which were obtained in high yields, are stable to air and moisture, in contrast to frequently employed diols such as pinacol and 2,2-dimethyl-1,3-propanediol.[14]

Next, we selected 2-phenylethynylphenyllithium, prepared from bromoarene **2a**, as a model substrate (Table 1). Upon treatment of the aryllithium with **1a** (1.0 equiv) hydride transfer proceeded efficiently and subsequent cyclization gave the desired benzosilole **3a** in 58% yield (entry 1). The regio- and stereoselectivity of hydrosilylation were perfectly controlled, whereas such control is sometimes problematic in the case of transition metal or Lewis acid catalysis. Use of **1b** slightly decreased the yield of benzosilole to 49% (entry 2). In the case of **1c**, the product was observed by GCMS analysis of the crude mixture, but the silylether was cleaved during chromatographic purification on silica gel (entry 3). The use of $HSiPh_2(O^tBu)$, which is involved in Lee's hydrosilylation,[8] afforded the corresponding benzosilole in 37% yield accompanied by the formation of the silylated diphenylacetylene in 12% yield via undesired substitution of ^{t}BuO ligand (entry 4). The poor ligand transfer selectivity observed here can be attributed to the lack of entropic stabilization of the pentacoordinate silicate with the monodentate alkoxide ligand upon activation with the highly basic carbanion. A higher loading of **1a** improved the yield of **3a** (entries 5 and 6). Hydride transfer was very slow at −78 °C and warming to rt was required for smooth progress (entry 7). The yield reached the maximum under the conditions of entry 8. Use of 3 equiv of TEMPO or 9,10-dihydroanthracene under the optimized reaction conditions had no effect, and **3a** was obtained in 93% and 97% yields, respectively (entries 9 and 10). These results strongly indicate that the present process does not involve free radicals as key species promoting the reaction. Use of magnesiated species only gave diphenylacetylene and unchanged **1a**, with no silicate formation (entry 11). Diethyl ether basically shut down the reaction, whereas THF was extremely effective (entry 12). Although ^{t}BuLi was found to be the most suitable metalating agent in this system, we also evaluated less aggressive ^{n}BuLi and ^{s}BuLi. The use of these alkyllithiums under optimized conditions afforded **3a** in good yield under noncryogenic conditions.

DFT calculations revealed that the activation energy for hydride transfer from the silicon center to the carbon−carbon triple bond is 15.0 kcal/mol with a large energy gain of −24.1 kcal/mol resulting from strain release (Scheme 2). The silicate-forming step and the ring-closing step are highly reversible and essentially barrierless processes with activation energy values of 1.8 and 2.4 kcal/mol, respectively (for the entire reaction pathway; see Scheme S1).

With the optimal set of reaction conditions in hand, the scope of the benzosiloles was investigated (Table 2). This reaction can be easily scaled up, and **3a** was obtained on a gram scale in 88% yield. The fluorescence quantum yield of **3a**

Scheme 2. DFT Calculations on Hydride Transfer[a]

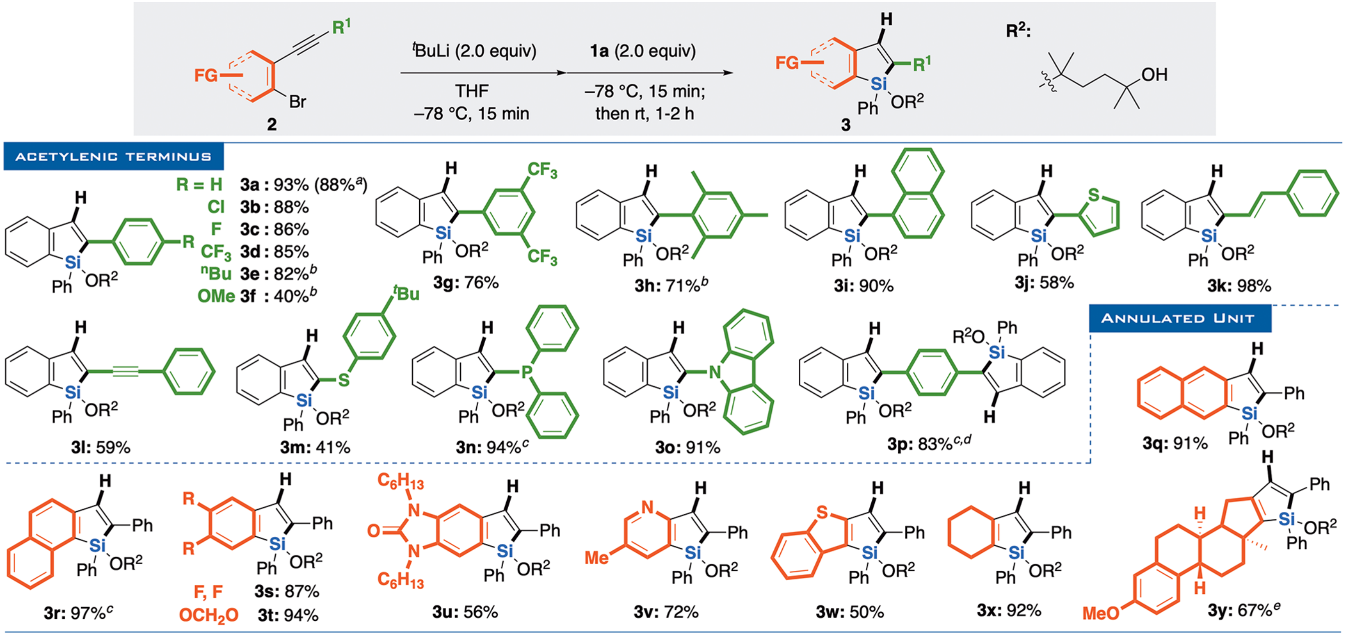


[a]Calculated at the level of M06-2X/6-31+G* with PCM (THF). Numerical values are ΔG (kcal/mol). One molecule of THF on a Li atom is omitted for clarity.

is almost quantitative (Φ_{FL} = 98% in $CHCl_3$) with an emission wavelength of 410 nm. The electronic character of the *para*-substituent on the aryl group at the 2-position was first examined. The electron-neutral parent phenyl group gave **3a** in 93% yield, and the electron-withdrawing Cl-, F-, and CF_3-substituted benzosiloles were obtained in high yields as well (**3b**–**3d**). The substrates with electron-donating substituents (^{n}Bu, OMe) required heating for good conversion (**3e**, **3f**). Highly electron-deficient 3,5-bis(trifluoromethyl)phenyl and sterically encumbered mesityl and naphthyl groups were also tolerated (**3g**–**3i**). A heteroaromatic ring was also applicable (**3j**). The triple bond proximal to the aryllithium was the reactive site in the case of enyne and diyne substrates (**3k**, **3l**). This methodology offers facile access to unique benzosiloles bearing a heteroelement directly at the 2-position (**3m**–**3o**). Double hydrosilylation of the 1,4-diethynylbenzene-based substrate afforded **3p** in 83% yield. As for annulated aromatic units, extension of the π-conjugated system (**3q**, **3r**) and substitutions with heteroelements (**3s**–**3u**) proceeded in high yields. Heteroarene-annulated siloles were also obtained (**3v**, **3w**). This silacycle formation is not limited to benzosiloles, and 1-bromo-2-phenylethynylcyclohexene gave the tetrahydrobenzosilole **3x** in 92% yield. The silole ring was also installed in a steroid, affording the pentacyclic estrogen analogue **3y** in good yield. In contrast, hydrosilylation of the double bond using (*E*)-1-bromo-2-styrylbenzene was not successful under the current conditions. Compounds of the silole family are attracting increasing attention, especially in materials science, owing to potential applications for organic light-emitting diodes (OLEDs), organic light-emitting field-effect transistors (OLEFETs), organic solid-state luminescent sensors, photovoltaic cells, *etc.*[15] Thus, we believe the present methodology is of high value in offering access to a range of unprecedented structures.

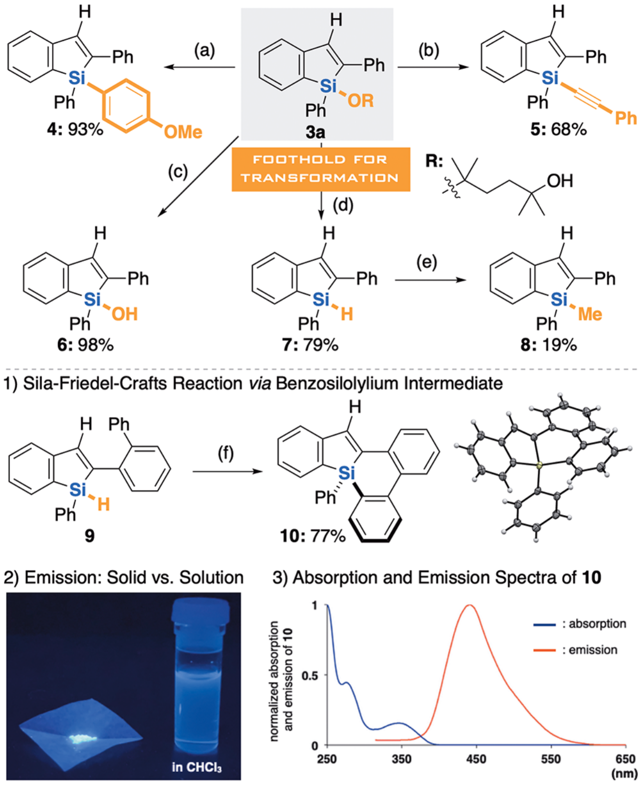
One of the major advantages of this silacycle-forming reaction is its modularity for modification of the substituent on the silicon atom owing to the silylether unit acting as a leaving group (Scheme 3). The reaction with 4-anisyllithium gave the unsymmetrically substituted benzosilole **4** in 93% yield. Quantitative fluorination with $BF_3{\cdot}OEt_2$[16] and subsequent alkynylation proceeded in 68% yield (**5**). Treatment of the fluorinated intermediate with silica gel afforded the corresponding silanol **6** quantitatively. Hydrosilane **7**, obtained by reduction of **3a** with DIBAL, is an intriguing chemical scaffold. Anionic activation of **7** was achieved by deprotonation of the Si–H bond employing TMP-Li, and the generated silyl anion was captured by methyl iodide. Although the yield of **8** is low due to competing TMP-silicate formation, this is, to our knowledge, the first example of deprotonation of an Si–H bond with lithium amide.[17] The relatively high acidity of the Si–H bond of **7** suggests that there may be some degree of aromatic stabilization of the benzosilolide (or silolide) anion by the 10π (or 6π) electron system. Utilization of unprecedented benzosilolylium species was also demonstrated. Treatment of hydrosilane **9** with triphenylmethyl cation, followed by sila-Friedel–Crafts reaction[18] with the pendent biphenyl moiety provided another benzosilole structure **10** in

Table 2. Hydrosilylation Leading to Diverse Benzosiloles



Isolated yields. [a]Run at 70 °C on 3.0 mmol scale. [b]Run at 60 °C. [c]Run at 70 °C. [d]Run with ^{t}BuLi (4.0 equiv) and **1a** (4.0 equiv). [e]Mixture of diastereomers (3:1).

Scheme 3. Transformation of Benzosilole[a]



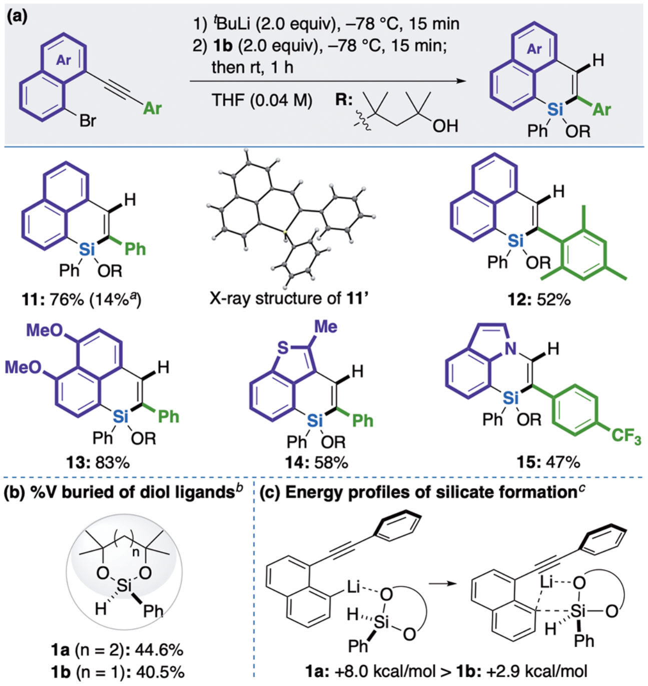
[a]Isolated yields. R: 1,1,4-trimethyl-4-hydroxypenthyl. (a) 4-MeO-C_6H_4Li (2.2 equiv), THF, 80 °C, 72 h. (b) $BF_3{\cdot}EtO_2$ (2.0 equiv), THF, rt, 20 h, then phenylethynyllithium (5.0 equiv), THF, 60 °C, 12 h. (c) $BF_3{\cdot}EtO_2$ (2.0 equiv), THF, rt, 20 h, then SiO_2. (d) DIBAL (4.0 equiv), THF, 80 °C, 20 h. (e) TMPLi (2.0 equiv), THF, −78 °C, 15 min, then CH_3I (10 equiv), rt, 15 min. (f) $Ph_3CB(C_6F_5)_4$ (2.0 equiv), 2,6-lutidine (2.0 equiv), CH_2Cl_2, rt, 16 h.

77% yield. Compound **10** is weakly fluorescent in solution (Φ_{FL} = 5% in $CHCl_3$), but is strongly fluorescent in the solid state. This compound might thus find an application as a dye with AIEE character.

Finally, this hydrosilylation reaction was extended to the synthesis of six-membered sila-aromatics (Table 3a). Naphthyllithium prepared from 1-bromo-8-phenylethynylnaphthalene was converted to the silaphenalene **11** (Φ_{FL} = 57% in $CHCl_3$) in 76% yield by employing **1b**. The structure was unambiguously determined by single-crystal X-ray diffraction analysis of compound **11′** obtained by reduction of **11** with DIBAL. Contrary to the case of benzosilole formation, use of **1a** significantly decreased the yield of the silaphenalene to 14% (Table 1, entry 1 vs entry 2).

In order to shed light on the reason for this drastic difference, the %V buried[19] values of the ligands of **1** were calculated using Samb*V*ca, developed by Cavallo.[20] The results suggest that **1a** is sterically more congested than **1b** in the coordination sphere of the silicon center (Table 3b). This is consistent with the difference in the stability of silicate formed from the naphthyllithium and **1** (Table 3c). More facile silicate formation with **1b** due to the smaller repulsive interaction with the sterically demanding peri-substituted naphthyllithium, as compared with **1a**, should be one of the reasons for the much better conversion with **1b**. As for silaphenalenes, a large substituent such as a mesityl group at the 2-position and methoxy groups on the naphthyl moiety were tolerated (**12** and **13**). The silacycle fused with benzothiophene **14** was obtained in 58% yield. Ynamide was also a competent substrate and was smoothly hydrosilylated to give an unprecedented 1*H*-[1,4]azasilino[3,2,1-*hi*]indole framework (**15**). There are a few early reports on silaphenalene dealing with the physical and chemical properties of its cationic, anionic, and radical forms.[21] However, the reported preparation required a severe pyrolytic condition (685 °C) and afforded the silaphenalene in only 10% yield.[21a] Our methodology is incomparably milder and is compatible with peripherally decorated silaphenalenes.

Table 3. Hydrosilylation for Other Silacycles



Isolated yields. [a]Run with **1a** (2.0 equiv). [b]Optimized Cartesian coordinates obtained at the level of M06-2X/6-311++G** with PCM (THF) were used. [c]Δ*G* values at the level of M06-2X/6-31+G* with PCM (THF).

In conclusion, we report an efficient hydrosilylation reaction of unactivated carbon−carbon triple bonds via silicate formation. The keys to success were the use of unprecedented seven- and six-membered dialkoxyhydrosilanes designed for entropic stabilization in the silicate state, and the strain-imposing strategy to enhance the nucleophilicity of hydride. The diol ligand is also beneficial as a leaving group for subsequent chemical transformations of the obtained benzosiloles at the silicon center. The present methodology provides a powerful tool for flexible design of functional silacycles. Detailed analyses of the optical and physical properties of the novel silacycles and applications of the cyclic hydrosilanes for construction of other ring systems are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c12619.

> Experimental procedures, characterization data, computational details (PDF)

Accession Codes

CCDC 2021313 and 2046045 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For excellent reviews on Lewis base catalyzed reactions involving hypervalent silicates, see: (a) Rendler, S.; Oestreich, M. Hypervalent Silicon as a Reactive Site in Selective Bond-forming Processes. *Synthesis* **2005**, 1727−1747. (b) Orito, Y.; Nakajima, M. Lewis Base Catalyzed Asymmetric Reactions Involving Hypervalent Silicate Intermediates. *Synthesis* **2006**, 1391−1401. (c) Denmark, S. E.; Beutner, G. L. Lewis Base Catalysis in Organic Synthesis. *Angew. Chem., Int. Ed.* **2008**, *47*, 1560−1638.

(2) For seminal publications, see: (a) Kira, M.; Kobayashi, M.; Sakurai, H. Regiospecific and Highly Stereoselective Allylation of Aldehydes with Allyltrifluorosilane Activated by Fluoride Ions. *Tetrahedron Lett.* **1987**, *28*, 4081−4084. (b) Kira, M.; Sato, K.; Sakurai, H. Pentacoordinate Allylsilicates: Characterization and Highly Stereoselective Reaction with Aldehydes. *J. Am. Chem. Soc.* **1988**, *110*, 4599−4602. (c) Kobayashi, S.; Nishio, K. Facile and Highly Stereoselective Allylation of Aldehydes Using Allyltrichlorosilanes in DMF. *Tetrahedron Lett.* **1993**, *34*, 3453−3456. (d) Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. Asymmetric Allylation of Aldehydes with Chiral Lewis Bases. *J. Org. Chem.* **1994**, *59*, 6161−6163. (e) Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S. (*S*)-3,3′-Dimethyl-2,2′-biquinoline *N*,*N*′-Dioxide as an Efficient Catalyst for Enantioselective Addition of Allyltrichlorosilanes to Aldehydes. *J. Am. Chem. Soc.* **1998**, *120*, 6419−6420. (f) Denmark, S. E.; Fu, J. On the Mechanism of Catalytic, Enantioselective Allylation of Aldehydes with Chlorosilanes and Chiral Lewis Bases. *J. Am. Chem. Soc.* **2000**, *122*, 12021−12022. For a review, see: (g) Sakurai, H. Metamorphosis of Synthetic Strategies with Allylic Silanes: Tetracoordinated Allylic Silanes into Pentacoodinated Allylic Silicates. *Synlett* **1989**, 1−8.

(3) For comprehensive studies on aldol reaction with a combination of trichlorosilylenolates and phosphoramidite by Denmark, see: (a) Denmark, S. E.; Winter, S. B. D.; Su, X.; Wong, K.-T. Chemistry of Trichlorosilyl Enolates. 1. New Reagents for Catalytic, Asymmetric Aldol Additions. *J. Am. Chem. Soc.* **1996**, *118*, 7404−7405. (b) Denmark, S. E.; Wong, K.-T.; Stavenger, R. A. Chemistry of Trichlorosilyl Enolates. 2. Highly-selective Asymmetric Aldol Additions of Ketone Enolates. *J. Am. Chem. Soc.* **1997**, *119*, 2333−2334. (c) Denmark, S. E.; Ghosh, S. K. The First Catalytic, Diastereoselective, and Enantioselective Crossed-aldol Reactions of Aldehydes. *Angew. Chem., Int. Ed.* **2001**, *40*, 4759−4762. (d) Denmark, S. E.; Stavenger, R. A. Asymmetric Catalysis of Aldol Reactions with Chiral Lewis Bases. *Acc. Chem. Res.* **2000**, *33*, 432−440. For recent contributions on enantioselective aldol reaction of unprotected carboxylic acid, see: (e) Kotani, S.; Yoshiwara, Y.; Ogasawara, M.; Sugiura, M.; Nakajima, M. Catalytic Enantioselective Aldol Reactions of Unprotected Carboxylic Acids under Phosphine Oxide Catalysis. *Angew. Chem., Int. Ed.* **2018**, *57*, 15877−15881.

(4) (a) Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. Reduction Selective de Composes Carbonyles par Catalyse Heterogene a la Surface des Sels. *Tetrahedron* **1981**, *37*, 2165−2171. (b) Fujita, M.; Hiyama, T. Highly Diastereocontrolled Reduction of Ketones by Means of Hydrosilanes. Practical Synthesis of Optically Active 1,2-Diols and 2-Amino Alcohols of Threo or Erythro Configuration. *J. Am. Chem. Soc.* **1984**, *106*, 4629−4630. (c) Hosomi, A.; Hayashida, H.; Kohra, S.; Tominaga, Y. Pentaco-ordinate Silicon Compounds in Synthesis: Chemo- and Stereo-selective Reduction of Carbonyl Compounds Using Trialkoxy-substituted Silanes and Alkali Metal Alkoxides. *J. Chem. Soc., Chem. Commun.* **1986**, 1411−1412. (d) Kohra, S.; Hayashida, H.; Tominaga, Y.; Hosomi, A. Pentacoordinate Organosilicon Compounds in Synthesis: Asymmetric Reduction of Carbonyl Compounds with Hydrosilanes Catalyzed by Chiral Bases. *Tetrahedron Lett.* **1988**, *29*, 89−92.

(5) For design and utilization of highly Lewis acidic silicon reagents without silicate formation, pioneered by Leighton, see: (a) Kinnaird, J. W. A.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. Strained Silacycles in Organic Synthesis: A New Reagent for the Enantioselective Allylation of Aldehydes. *J. Am. Chem. Soc.* **2002**, *124*, 7920−7921. (b) Wang, X.; Meng, Q.; Nation, A. J.; Leighton, J. L. Strained Silacycles in Organic Synthesis: The Tandem Aldol−Allylation Reaction. *J. Am. Chem. Soc.* **2002**, *124*, 10672−10673. (c) Kubota, K.; Leighton, J. L. A Highly Practical and Enantioselective Reagent for the Allylation of Aldehydes. *Angew. Chem., Int. Ed.* **2003**, *42*, 946−948. (d) Shirakawa, S.; Berger, R.; Leighton, J. L. Enantioselective Friedel−Crafts Alkylations with Benzoylhydrazones Promoted by a Simple Strained Silacycle Reagent. *J. Am. Chem. Soc.* **2005**, *127*, 2858−2859.

(6) Silyl enolates and ketenesilylacetals are well studied as examples of the ligand (enolate) transfer reaction from hypervalent silicates to highly polarized carbonyls. Aldol reaction: (a) Matsukawa, S.; Okano, N.; Imamoto, T. Phosphine Catalyzed Aldol Reaction between Ketene Silyl Acetals and Aldehydes: Nucleophilic O−Si and C−Si Bond Cleavage by Phosphines. *Tetrahedron Lett.* **2000**, *41*, 103−107. (b) Miura, K.; Nakagawa, T.; Hosomi, A. Lewis Base-promoted Aldol

Reaction of Dimethylsilyl Enolates in Aqueous Dimethylformamide: Use of Calcium Chloride as a Lewis Base Catalyst. *J. Am. Chem. Soc.* **2002**, *124*, 536−537. (c) Mukaiyama, T.; Fujisawa, H.; Nakagawa, T. Lewis Base Catalyzed Aldol Reaction of Trimethylsilyl Enolates with Aldehydes. *Helv. Chim. Acta* **2002**, *85*, 4518−4531. (d) Nakagawa, T.; Fujisawa, H.; Nagata, Y.; Mukaiyama, T. Lithium Acetate-catalyzed Aldol Reaction between Aldehyde and Trimethylsilyl Enolate in Anhydrous or Water-containing *N*,*N*-Dimethylformamide. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1555−1567. Mannich reactions: (e) Fujisawa, H.; Takahashi, E.; Mukaiyama, T. Lewis Base Catalyzed Mannich-type Reactions between Trimethylsilyl Enol Ethers and Aldimines. *Chem. - Eur. J.* **2006**, *12*, 5082−5093. Michael reactions: (f) Nakagawa, T.; Fujisawa, H.; Nagata, Y.; Mukaiyama, T. Lewis Base-catalyzed Michael Reactions between Trimethylsilyl Enolate and α,β-Unsaturated Carbonyl Compounds. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 236−246.

(7) Representative examples of Lewis acid catalyses: (a) Asao, N.; Sudo, T.; Yamamoto, Y. Lewis Acid-catalyzed *trans*-Hydrosilylation of Alkynes. *J. Org. Chem.* **1996**, *61*, 7654−7655. (b) Sudo, T.; Asao, N.; Yamamoto, Y. Synthesis of Various Silacycles *via* the Lewis Acid-catalyzed Intramolecular *trans*-Hydrosilylation of Unactivated Alkynes. *J. Org. Chem.* **2000**, *65*, 8919−8923. (c) Trost, B. M.; Ball, Z. T. Markovnikov Alkyne Hydrosilylation Catalyzed by Ruthenium Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 12726−12727. (d) Trost, B. M.; Ball, Z. T. Intramolecular Endo-Dig Hydrosilylation Catalyzed by Ruthenium: Evidence for a New Mechanistic Pathway. *J. Am. Chem. Soc.* **2003**, *125*, 30−31. (e) Trost, B. M.; Ball, Z. T.; Jöge, T. Regioselective Hydrosilylation of Propargylic Alcohols: An Aldol Surrogate. *Angew. Chem., Int. Ed.* **2003**, *42*, 3415−3418. (f) Trost, B. M.; Ball, Z. T. Alkyne Hydrosilylation Catalyzed by a Cationic Ruthenium Complex: Efficient and General *Trans* Addition. *J. Am. Chem. Soc.* **2005**, *127*, 17644−17655. (g) Matsuda, T.; Kadowaki, S.; Murakami, M. Ruthenium-catalysed Double *trans*-Hydrosilylation of 1,4-Diarylbuta-1,3-diynes Leading to 2,5-Diarylsiloles. *Chem. Commun.* **2007**, 2627−2629. Cr-catalysis for *trans*-selective hydrosilylation: (h) Fuchikami, T.; Ubukata, Y.; Tanaka, Y. Group 6 Anionic μ-Hydride Complexes $[\mathrm{HM_2(CO)_{10}}]^-$ (M = Cr, Mo, W): New Catalysts for Hydrogenation and Hydrosilylation. *Tetrahedron Lett.* **1991**, *32*, 1199−1202.

(8) Maifeld, S. V.; Lee, D. Unusual Tandem Alkynylation and *trans*-Hydrosilylation to Form Oxasilacyclopentenes. *Org. Lett.* **2005**, *7*, 4995−4998.

(9) For benzosilole-forming reactions involving vinylic lithium intermediates, see: (a) Yamaguchi, S.; Xu, C.; Tamao, K. Bis-silicon-bridged Stilbene Homologues Synthesized by New Intramolecular Reductive Double Cyclization. *J. Am. Chem. Soc.* **2003**, *125*, 13662−13663. (b) Xu, C.; Wakamiya, A.; Yamaguchi, S. General Silaindene Synthesis Based on Intramolecular Reductive Cyclization toward New Fluorescent Silicon-containing π-Electron Materials. *Org. Lett.* **2004**, *6*, 3707−3710. (c) Ilies, L.; Tsuji, H.; Sato, Y.; Nakamura, E. Modular Synthesis of Functionalized Benzosiloles by Tin-mediated Cyclization of (*o*-Alkynylphenyl)silane. *J. Am. Chem. Soc.* **2008**, *130*, 4240−4241. (d) Ilies, L.; Sato, Y.; Mitsui, C.; Tsuji, H.; Nakamura, E. Modular Synthesis of Polybenzo[*b*]silole Compounds for Hole-blocking Material in Phosphorescent Organic Light Emitting Diodes. *Chem. - Asian J.* **2010**, *5*, 1376−1381. Xi reported a synthetically versatile 2-lithiobenzosilole generated via dilithiated species; see: (e) Wang, C.; Luo, Q.; Sun, H.; Guo, X.; Xi, Z. Lithio Siloles: Facile Synthesis and Applications. *J. Am. Chem. Soc.* **2007**, *129*, 3094−3095.

(10) For a recent comprehensive review on hydrofunctionalization reactions, see: (a) Chen, J.; Guo, J.; Lu, Z. Recent Advances in Hydrometallation of Alkenes and Alkynes via the First Row Transition Metal Catalysis. *Chin. J. Chem.* **2018**, *36*, 1075−1109. For hydrosilylation reactions, see: (b) *Hydrosilylation A Comprehensive Review on Recent Advances*; Marciniec, B., Ed.; Springer-Verlag: New York, 2009.

(11) *trans*-Selective hydroaluminations of alkynes using lithium aluminates are classical and reliable protocols for the synthesis of multiply substituted olefins. For representative seminal contributions, see: (a) Slaugh, L. H. Lithium Aluminum Hydride, A Homogeneous Hydrogenation Catalyst. *Tetrahedron* **1966**, *22*, 1741−1746. (b) Zweifel, G.; Steele, R. B. A Novel Method for the Synthesis of *cis*-α,β-Unsaturated Derivatives via *trans*-Hydroalumination of Disubstituted Alkynes with Lithium Diisobutylaluminum Hydride. *J. Am. Chem. Soc.* **1967**, *89*, 5085−5086. (c) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. A New Stereospecific Synthesis of Trisubstituted Olefins. Stereospecific Synthesis of Farnesol. *J. Am. Chem. Soc.* **1967**, *89*, 4245−4246.

(12) For a review on *trans*-selective hydrometalation of internal alkynes, see: Frihed, T. G.; Fürstner, A. Progress in the *trans*-Reduction and *trans*-Hydrometalation of Internal Alkynes. Applications to Natural Product Synthesis. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 135−160.

(13) (a) Nagashima, Y.; Hirano, K.; Takita, R.; Uchiyama, M. *Trans*-Diborylation of Alkynes: *Pseudo*-Intramolecular Strategy Utilizing a Propargylic Alcohol Unit. *J. Am. Chem. Soc.* **2014**, *136*, 8532−8535. (b) Nogami, M.; Hirano, K.; Kanai, M.; Wang, C.; Saito, T.; Miyamoto, K.; Muranaka, A.; Uchiyama, M. Transition Metal-free *trans*-Selective Alkynylboration of Alkynes. *J. Am. Chem. Soc.* **2017**, *139*, 12358−12361. (c) Nogami, M.; Hirano, K.; Morimoto, K.; Tanioka, M.; Miyamoto, K.; Muranaka, A.; Uchiyama, M. Alkynylboration Reaction Leading to Boron-containing π-Extended *cis*-Stilbenes as a Highly Tunable Fluorophore. *Org. Lett.* **2019**, *21*, 3392−3395. (d) Hirano, K.; Morimoto, K.; Fujioka, S.; Miyamoto, K.; Muranaka, A.; Uchiyama, M. Nucleophilic Diboration Strategy Targeting Diversified 1-Boraphenarene Architectures. *Angew. Chem., Int. Ed.* **2020**, *59*, 21448−21453.

(14) Foley, C. N.; Leighton, J. L. A Highly Stereoselective, Efficient, and Scalable Synthesis of the C(1)−C(9) Fragment of the Epothilones. *Org. Lett.* **2015**, *17*, 5858−5861.

(15) For comprehensive reviews on applications of siloles as functional materials, see: (a) Hissler, M.; Dyer, P. W.; Réau, R. Linear Organic π-Conjugated Systems Featuring the Heavy Group 14 and 15 Elements. *Coord. Chem. Rev.* **2003**, *244*, 1−44. (b) Yamaguchi, S.; Tamao, K. A Key Role of Orbital Interaction in the Main Group Element-containing π-Electron Systems. *Chem. Lett.* **2005**, *34*, 2−7. (c) Yamaguchi, S.; Xu, C.; Yamada, H.; Wakamiya, A. Synthesis, Structure, and Photophysical Properties of Silicon and Carbon-bridged Ladder Oligo(*p*-phenylenevinylene)s and Related π-Electron Systems. *J. Organomet. Chem.* **2005**, *690*, 5365−5377. (d) Shirota, Y.; Kageyama, H. Charge Carrier Transporting Molecular Materials and Their Applications in Devices. *Chem. Rev.* **2007**, *107*, 953−1010. (e) Shimizu, M.; Hiyama, T. Organic Fluorophores Exhibiting Highly Efficient Photoluminescence in the Solid State. *Chem. - Asian J.* **2010**, *5*, 1516−1531. (f) Shimizu, M.; Hiyama, T. Silicon-bridged Biaryls: Molecular Design, New Synthesis, and Luminescence Control. *Synlett* **2012**, *23*, 973−989 and references therein.

(16) Oguri, N.; Takeda, N.; Unno, M. Facile Synthesis of Cyclic Fluorosiloxanes. *Chem. Lett.* **2015**, *44*, 1506−1508.

(17) (a) Corriu, R. J. P.; Guerin, C. Alkali Metal Hydrides: New Metallating Reagents at Silicon. *J. Chem. Soc., Chem. Commun.* **1980**, 168−169. For use of silylanions generated with KH for benzosilole synthesis, see: (b) Ilies, L.; Tsuji, H.; Nakamura, E. Synthesis of Benzo[*b*]siloles via KH-promoted Cyclization of (2-Alkynylphenyl)-silanes. *Org. Lett.* **2009**, *11*, 3966−3968.

(18) For intramolecular sila-Friedel−Crafts reaction for the synthesis of dibenzosiloles, see: Furukawa, S.; Kobayashi, J.; Kawashima, T. Development of a Sila-Friedel−Crafts Reaction and Its Application to the Synthesis of Dibenzosilole Derivatives. *J. Am. Chem. Soc.* **2009**, *131*, 14192−14193.

(19) (a) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. A Combined Experimental and Theoretical Study Examining the Binding of *N*-Heterocyclic Carbenes (NHC) to the Cp*RuCl (Cp* = η^5-$\mathrm{C_5Me_5}$) Moiety: Insight into Stereoelectronic Differences between Unsaturated and Saturated NHC Ligands. *Organometallics* **2003**, *22*, 4322−4326. (b) Clavier, H.; Nolan, S. P. Percent Buried Volume for Phosphine and *N*-heterocyclic Carbene Ligands: Steric Properties in Organometallic Chemistry. *Chem. Commun.* **2010**, *46*, 841−861.

(20) Falivene, L.; Cao, Z.; Petta, A.; Serra, L.; Poater, A.; Oliva, R.; Scarano, V.; Cavallo, L. Towards the Online Computer-aided Design of Catalytic Pokets. *Nat. Chem.* **2019**, *11*, 872−879.

(21) (a) Boudjouk, P.; Kiely, J. S.; Sooriyakumaran, R. The Synthesis of 1-Silaphenalanes from 1,8-Difunctional Naphthalenes. Confirmation of the Structures of the Pyrolysis Products of (1-Naphthyl)-vinyldichlorosilane. *J. Organomet. Chem.* **1981**, *221*, 33−45. (b) Sooriyakumaran, R.; Boudjouk, P. 1-Silaphenalenes, Potential Precursors to Aromatic Silylenium Ions and Aromatic Silyl Anions. Spectroscopic and Chemical Studies. *J. Organomet. Chem.* **1984**, *271*, 289−297.

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