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Gold-Catalyzed Dehydrogenative Cycloaddition of Tethered 1,*n*-Dihydrodisilanes to Alkynes

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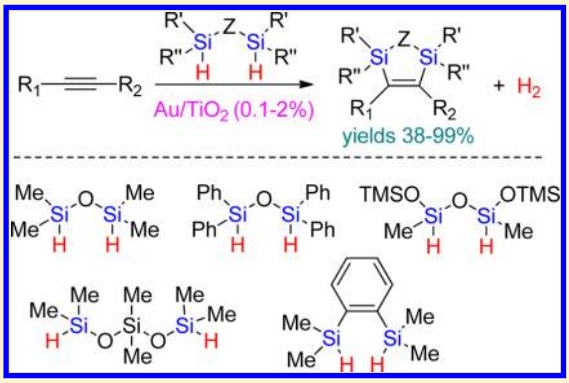
Supporting Information

ABSTRACT: Gold nanoparticles supported on TiO_2 (0.1−2% mol) catalyze at mild conditions the dehydrogenative addition of tethered 1,*n*-dihydrodisilanes, such as 1,1,3,3-tetramethyldisiloxane (**1**), 1,1,3,3-tetraphenyldisiloxane (**2**), 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (**3**), 1,1,3,3,5,5-hexamethyltrisiloxane (**4**), and 1,2-bis(dimethylsilyl)benzene (**5**), to alkynes, forming cycloadducts and releasing H_2. Under the same conditions, polymeric methylhydrosiloxane is completely unreactive. For the majority of terminal alkynes and 1,*n*-dihydrodisilanes the yields are excellent (up to 99%). In general, terminal alkynes are more reactive as compared to internal. The reaction tolerates several functional groups and can be performed in a variety of solvents. In the case of 1,1,3,3-tetramethyldisiloxane, it is proposed that gold nanoparticles form intermediate *cyclo*-gold-tetramethyldisiloxane via a dehydrogenative pathway, which undergoes a formal [3+2] cycloaddition to alkynes.

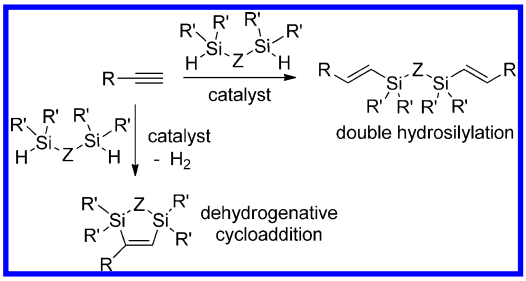


INTRODUCTION

The gold-catalyzed reaction of hydrosilanes with alkynes has attracted the interest of organic chemists over the past few years, especially under heterogeneous conditions using nano gold substances.[1] It has been recognized that the hydrosilylation pathway is predominant, as occurs under catalysis by a variety of metals including Pt, Pd, Rh, or Ru. Among the different variants of gold catalysts, acetone-solvated gold nanoparticles supported on carbon or γ-alumina[2] and Au/CeO_2[3] afford exclusively hydrosilylation products with β-(*E*) selectivity. On the contrary, a homogeneous Au(III) catalyst[3] provides unselectively products of β-(*E*) and β-(*Z*) addition. A thin gold film on the surface of boronsilicate capillaries was also proven as an active catalyst for the hydrosilylation of terminal alkynes in a continuous-flow reactor under microwave irradiation.[4] Additionally, we have recently shown that Au/TiO_2 catalyzes the β-(*E*)-selective hydrosilylation of terminal alkynes, forming minor *cis*-disilyl alkenes as side-products.[5] On the other hand, in the presence of an unsupported nanoporous gold catalyst[6] the hydrosilylation pathway does not takes place. Instead, facile semihydrogenation of alkynes into alkenes occurs, with one hydrogen atom provided by the hydrosilane, while the second arises from a water molecule. A surprising differentiation takes place upon using 1,1,3,3-tetramethyldisiloxane (TMDS) as a reactant. Although under Pt(0) catalysis conditions TMDS affords the typical double hydrosilylation products with terminal alkynes,[7] in the presence of Au/TiO_2 dehydrogenative cycloaddition occurs readily, forming substituted 2,5-dihydro-1,2,5-oxadisiloles in excellent yields.[8]

Dehydrogenative cycloaddition of tethered 1,*n*-dihydrodisilanes to alkynes is known in a few cases, under catalysis by Pt, Ni, and Pd,[9] often competing with the hydrosilylation pathway (Scheme 1). TMDS for instance has been reported to afford

Scheme 1. Possible Pathways in the Metal-Catalyzed Reaction of a Terminal Alkyne with Tethered 1,*n*-Dihydrodisilanes



the dehydrogenation cycloadduct with an alkyne (in a single example) as a minor byproduct, while the typical hydrosilylation products prevail.[9b] Formally, 1,2-disilyl addition products to alkynes are derived via the oxidative insertion of metals (e.g., Pd, Pt) into the Si−Si bond of 1,2-disilanes followed by double addition to the triple bond[10] and by other means.[11]

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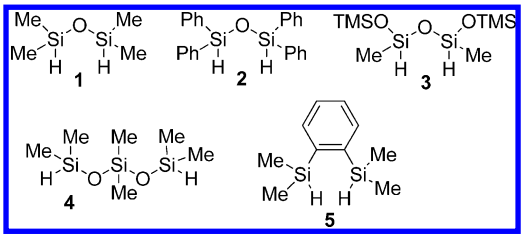
In this article we present a full account of our studies regarding the oxidative cycloaddition of 1,1,3,3-tetramethyldisiloxane, TMDS (**1**), to alkynes,[8] including recent studies that shed light on the reaction mechanism. Additionally, herein we show that a series of tethered 1,*n*-dihydrodisilanes (Chart 1) such as 1,1,3,3-tetraphenyldisiloxane (**2**), 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (**3**), 1,1,3,3,5,5-hexamethyltrisiloxane (**4**), and 1,2-bis(dimethylsilyl)benzene (**5**) follow the same trend as TMDS does, providing in the presence of Au/TiO_2 mainly or exclusively the dehydrogenative cycloaddition pathway with a series of alkynes.

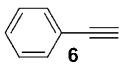
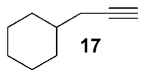
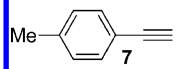
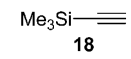
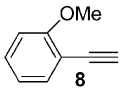
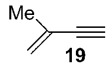
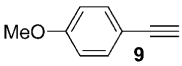
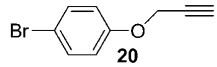
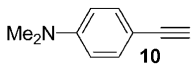
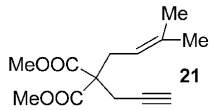
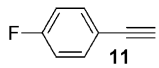
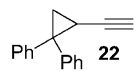
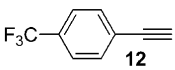
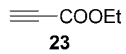
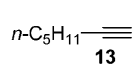
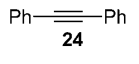
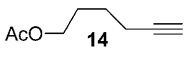
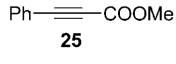
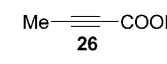
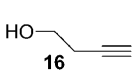
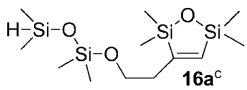
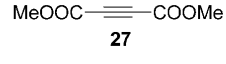
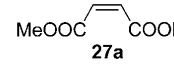
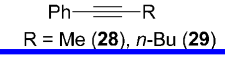
Chart 1. Structures of Tethered 1,*n*-Dihydrodisilanes 1−5



RESULTS AND DISCUSSION

a. Au/TiO_2-Catalyzed Reaction of Alkynes with 1,1,3,3-Tetramethyldisiloxane (1), 1,1,3,3-Tetraphenyldisiloxane (2), and 1,1,1,3,5,7,7,7-Octamethyltetrasiloxane (3). A series of terminal alkynes (1.0 equiv) react smoothly at room temperature with 1,1,3,3-tetramethyldisiloxane (1.0−1.1 equiv only if dry solvent is used) in the presence of 0.3 mol % Au/TiO_2 to afford substituted 2,5-dihydro-1,2,5-oxadisiloles[12] (Table 1) in up to 99% isolated yield. For some of the substrates, minor side-products (up to 10% relative yield) resulting from the competing hydrosilylation and/or semihydrogenation of the triple bond were seen. Only in the case of ethyl propiolate (**23**) do the byproducts become substantial

Table 1. Dehydrogenative Cycloaddition of 1,1,3,3-Tetramethyldisiloxane, 1,1,3,3-Tetraphenyldisiloxane, and 1,1,1,3,5,7,7,7-Octamethyltetrasiloxane to Alkynes Catalyzed by Au/TiO_2[a]

alkyne	products	Yield[b]/Time	alkyne	products	Yield[b]/Time
 **6**	**6a** (R',R"=Me) **6b** (R',R"=Ph)	84%/30 min 38%/8 h	 **17**	**17a** (R',R"=Me)	88%/40 min
 **7**	**7a** (R',R"=Me) **7c** (R'=Me, R"=OTMS)	99%/30 min 78%/14 h	 **18**	**18a** (R',R"=Me)	87%/1 h
 **8**	**8a** (R',R"=Me) **8b** (R',R"=Ph)	99%/40 min 40%/12 h	 **19**	**19a** (R',R"=Me) **19b** (R',R"=Ph)	78%/40 min 38%/10 h
 **9**	**9a** (R',R"=Me)	96%/40 min	 **20**	**20a** (R',R"=Me)	72%/30 min
 **10**	**10a** (R',R"=Me)	81%/40 min	 **21**	**21a** (R',R"=Me)	79%/6 h
 **11**	**11a** (R',R"=Me) **11b** (R',R"=Ph) **11c** (R'=Me, R"=OTMS)	85%/20 min 40%/8 h 94%/12 h	 **22**	**22a** (R',R"=Me)	91%/12 h
 **12**	**12a** (R',R"=Me)	91%/20 min	 **23**	**23a** (R',R"=Me)	42%/1 h
 **13**	**13a** (R',R"=Me) **13b** (R',R"=Ph) **13c** (R'=Me, R"=OTMS)	97%/30 min 42%/10 h 91%/16 h	 **24**	**24a** (R',R"=Me)	88%/24 h
 **14**	**14a** (R',R"=Me)	98%/30 min	 **25**	**25a** (R',R"=Me)	44%/2 h
 **15**	**15a** (R',R"=Me) **15b** (R',R"=Ph) **15c** (R'=Me, R"=OTMS)	92%/30 min 40%/10 h 96%/14 h	 **26**	**26a** (R',R"=Me) **26c** (R'=Me, R"=OTMS)	64%/45 min 85%/16 h
 **16**	 **16a**[c]	95%/30 min	 **27**	 **27a**	82%/24 h
			 R = Me (**28**), *n*-Bu (**29**)	No reaction with TMDS, **2** or **3**	

[a]Reaction conditions for 1,1,3,3-tetramethyldisiloxane (**1**): 1.1 equiv, 25 °C, dry CH_2Cl_2, Au/TiO_2 (0.3 mol %); reaction conditions for 1,1,3,3-tetraphenyldisiloxane (**2**): 2.0 equiv, 25 °C, dry CH_2Cl_2, Au/TiO_2 (1.5 mol %); reaction conditions for 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (**3**): 1.2 equiv, 80 °C, dry 1,2-dichloroethane, Au/TiO_2 (1.2 mol %). In general, if nondried solvent is used, a moisture-dependent excess of hydrosilane should be added to compensate its hydrolysis. [b]Isolated yields after column chromatography. Alkyne conversions were >99% by GC-MS analysis in all cases. [c]2.2 molar equiv of TMDS was used.

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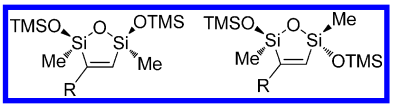
and reduce the isolated yield of cycloadduct **23a**. Even 0.1 mol % of the catalyst can drive the reaction to completion, yet longer reaction times are necessary (>3 h). With 1−2 mol % catalyst loading, the reaction occurs instantaneously with violent evolution of H_2. As for the reaction solvent, dichloromethane, 1,2-dichloroethane, hexane, toluene, diethyl ether, or ethyl acetate can be used with a narrow variation in reaction rate, isolated yield, and product selectivity. Nondried solvents can also be used, simplifying the process. In such case, excess TMDS should be used to compensate its partial hydrolysis from the moisture present in the solvent. GC-MS analysis revealed that in the presence of moisture 1,1,3,3-tetramethyldisiloxane transforms primarily at the initial stages of the reaction into 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (dimer) and minor amounts of trimer, while at a later stage, the dimeric tetrasiloxane transforms into octamethylcyclotetrasiloxane (cyclic dimer) and higher oligomers. The hydrolysis of TMDS by moisture is rapidly catalyzed by Au/TiO_2, as proven by independent experiments in the absence of the alkyne. It is well established in recent years that silanes undergo hydrolytic oxidation catalyzed by gold nanoparticles[13] or nanoporous gold.[14] Byproduct oligosiloxanes are highly nonpolar and therefore can be easily removed by column chromatography, eluting the crude reaction mixture with hexane. Alkynes are completely unreactive to TMDS in the absence of the catalyst, as well as in the presence of unsupported TiO_2 (anatase or rutile). Therefore, the active catalytic sites are undoubtedly provided by the gold nanoparticles. It is also important to emphasize that a series of homogeneous Au(I) catalysts do not provide any product (of either oxidative cycloaddition or hydrosilylation). In the presence of 3 mol % $AuCl_3$ on the other hand (refluxing DCE, 5 h), alkynes such as **6**−**8** were reduced by TMDS to the corresponding styrenes (GC-MS) and gradually to aryl alkanes, while cycloadducts **6a**−**8a** were detected in the crude reaction mixture in up to 10% relative yield. As seen in Table 1, the reaction tolerates a variety of functional groups bound on either the aryl ring or alkyl chains. Notably, in the case of 3-butyn-1-ol (**16**), by using 2.2 equiv of TMDS, **16a** was isolated in almost quantitative yield. Upon using <1.0 equiv of TMDS, the analysis of the crude reaction mixture by ^1H NMR revealed that protection of the hydroxyl group is faster than the addition on the triple bond, which indicates that TMDS rapidly protects alcohols as silyl ethers in a dehydrogenative manner.[15] Additionally, for substrates **19** and **21**, which possess an additional C−C double bond, the cycloaddition proceeds selectively on the triple bond in good yield. Regarding 1,6-enyne **21** no intramolecular cyclization products[16] were detected, nor in the case of aryl propargyl ether **20**.[17] The cyclopropyl-substituted alkyne **22**, which has been used as a highly sensitive probe to study the mechanism of addition on a C−C triple bond,[18] cleanly afforded the cycloadduct **22a** without leading to any rearranged products. This result implies that there is lack of development of a charge or radical (partial or full) on the internal sp-C atom of the alkyne during the transition state of the reaction.

The studies with terminal alkynes were extended to 1,1,3,3-tetraphenyldisiloxane (**2**) and 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (**3**). 1,1,3,3-Tetraphenyldisiloxane[19] was easily prepared from the basic hydrolysis of chlorodiphenylsilane. In general, the reactions of terminal alkynes with **2** proceed much more slowly as compared to TMDS and require increased loading of catalyst (see Table 1). Apart from the mainly formed products of dehydrogenative cycloaddition in relative yield of 55−65% (2,5-dihydro-1,2,5-oxadisiloles), typical β-(*E*)-hydrosilylation adducts in relative yields of 35−45% were also identified. 1,1,3,3-Tetraphenyldisiloxane has a high tendency to hydrolyze in the presence of Au/TiO_2; thus in the case of using nondried solvent up to 3−4 equiv of **2** is necessary to drive the reaction of alkynes to completion. 1,1,1,3,5,7,7,7-Octamethyltetrasiloxane (**3**) is even more slowly reacting with terminal alkynes at ambient conditions and requires refluxing DCE to go to completion (typically 8−12 h). Yet, the reactions are very clean and the dehydrogenative cycloaddition products were formed in 78−96% isolated yields (Table 1) as an equimolar mixture of two diastereomers, shown in Scheme 2. ^{13}C NMR spectroscopy

Scheme 2. Diastereomeric Products from the Reaction of 1,1,1,3,5,7,7,7-Octamethyltetrasiloxane (3) with Terminal Alkynes in the Presence of Au/TiO_2



revealed that **3** also appears as an equimolar mixture of two diastereomers (meso and racemic). In addition, polymethylhydrosiloxane (PMHS), which is a highly reactive polymeric hydrosilane (an extended analogue of TMDS) and has exhibited remarkable enhancement of reaction rates in several metal-catalyzed reductive processes,[20] is surprisingly completely unreactive in our case. It is even almost inert toward hydrolysis catalyzed by Au/TiO_2, in contrast to dimeric TMDS, which is extremely sensitive. Being highly hydrophobic, it is likely that PMHS has a low affinity to the hydrophilic surface of the catalyst, preventing thus its proximal and product-forming interaction with the gold nanoparticles.

Internal alkynes are less reactive against TMDS (1% mol of Au/TiO_2 was used), and the product selectivity is lower (Table 1). Generally, in the entries where the isolated yield of 2,5-dihydro-1,2,5-oxadisiloles is moderate, typical hydrosilylation products are formed via a competing pathway. Surprisingly, while diphenylacetylene (**24**) provided **24a** in high yield, internal alkynes **28** and **29** are completely unreactive. Dimethyl acetylenedicarboxylate (**27**) did not yield either cycloadduct or hydrosilylation product, but was slowly reduced within 24 h to a mixture of dimethyl maleate (∼90%) and dimethyl succinate (∼10%). It is possible that the stereoselective reduction proceeds through a gold-catalyzed semihydrogenation[7] by the slow oxidative hydrolysis of TMDS, as the reaction was performed within an open-air flask. The dihydrosilanes **2** and **3** are either completely unreactive with internal alkynes (e.g., with **28**, **29**), or react extremely slowly (with **24**). A notable exemption is unsaturated ester **26**, which provides with 1,1,1,3,5,7,7,7-octamethyltetrasiloxane the dehydrogenation cycloadduct **26c** in high yield.

b. Au/TiO_2-Catalyzed Reaction of Alkynes with 1,1,3,3,5,5-Hexamethyltrisiloxane (4) and 1,2-Bis(dimethylsilyl)benzene (5). The facile formation of the five-membered ring of 2,5-dihydro-1,2,5-oxadisiloles from the gold-catalyzed reaction among alkynes and TMDS or the structurally similar **2** and **3** (Table 1) possessing two Si−H functionalities at the 1,3-position urged us to examine whether a more remote position of the Si−H groups within the same molecule would lead to the same dehydrogenative cycloaddition pathway. For this purpose we studied the Au/TiO_2-catalyzed reaction of terminal alkynes with 1,1,3,3,5,5-

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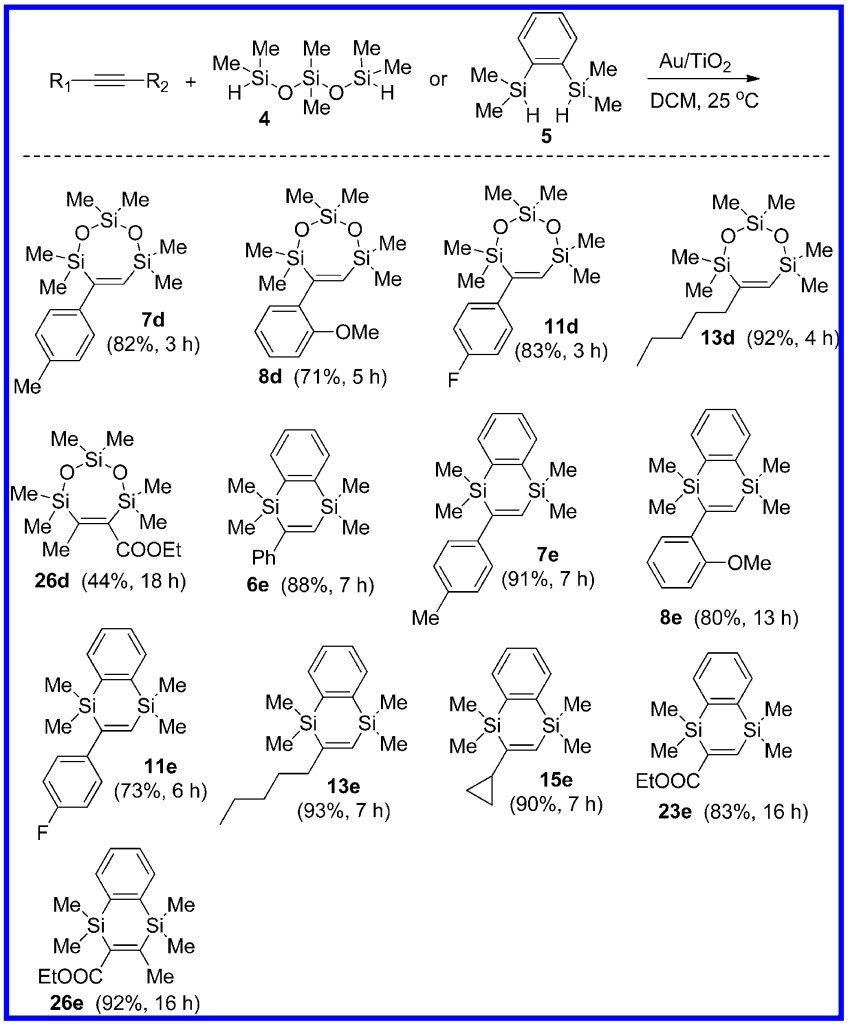
Scheme 3. Products from the Au/TiO_2-Catalyzed Oxidative Cycloaddition of 1,1,3,3,5,5-Hexamethyltrisiloxane (4) and 1,2-Bis(dimethylsilyl)benzene (5) to Alkynes[a]



[a]Reaction conditions for 1,1,3,3,5,5-hexamethyltrisiloxane (**4**): 1.2 equiv, 25 °C, dry CH_2Cl_2, 3 h, Au/TiO_2 (1.2 mol %); reaction conditions for 1,2-bis(dimethylsilyl)benzene (**5**): 1.2 equiv, 25 °C, dry CH_2Cl_2, 6 h, Au/TiO_2 (1.0 mol %). If nondried CH_2Cl_2 is used, a moisture-dependent excess of **4** or **5** should be added to compensate their competing hydrolyses. [b]Isolated overall yields after column chromatography. Alkyne conversions were >99% by GC-MS analysis in all cases.

hexamethyltrisiloxane (**4**) and 1,2-bis(dimethylsilyl)benzene (**5**). 1,1,3,3,5,5-Hexamethyltrisiloxane, the higher analogue of TMDS bearing the Si–H functionalities at the 1,5-position, reacts smoothly at ambient conditions with the alkynes, affording the seven-membered ring 4,7-dihydro-1,3,2,4,7-dioxatrisilepines in 44–92% isolated yields (Scheme 3). The reaction rate as compared to TMDS is approximately 20–30 times lower, possibly due to the higher negative entropy of activation during the formation of the seven-membered ring. This is the first time that the 1,3,2,4,7-dioxatrisilepanic heterocyclic ring appears in the literature. Internal alkynes such as **24**, **28**, and **29** tested in their reaction with **4** proved unreactive, yet **26** provided **26d** in moderate yield. 1,2-Bis(dimethylsilyl)benzene (**5**) is already known to undergo oxidative cycloaddition with alkynes catalyzed by (ethylene)-bis(triphenylphosphine)Pt(0).[9b] Under catalysis by Au/TiO_2, adducts bearing the 1,1,4,4-tetramethyl-1,4-dihydrobenzo[*b*]-[1,4]disiline core skeleton (Scheme 3) were also smoothly formed in yields varying from 73% to 93%. While internal alkynes are in general unreactive or provide hydrosilylation products (e.g., reaction of **5** with 3-hexyne), unsaturated ester **26** gave adduct **26e** in excellent yield. The reactivity of this specific substrate not only with 1,2-bis(dimethylsilyl)benzene but with other 1,*n*-dihydro disilanes (**1**, **3** and **4**) might be related to the intrinsic low energy of its LUMO orbital, as it will be analyzed in the accompanying mechanistic discussion.

c. Mechanistic Studies Regarding the Au-Catalyzed Oxidative Cycloaddition of TMDS to Alkynes. To draw mechanistic conclusions on this quite general cycloaddition, we focused on 1,1,3,3-tetramethyldisiloxane (**1**). A postulated rational mechanism to account for the dehydrogenative cycloaddition of TMDS to alkynes has been already presented earlier by us,[8] through a modification of the Crabtree–Ojima mechanism, as shown in Scheme 4. This mechanism involves insertion of the metal (nanoparticle) on the Si–H bond (intermediate **I**), silylmetalation to the alkyne to form intermediate **II**, followed by an intramolecular elimination of H_2 and [Au]. While this proposal seems reasonable, we went forward examining other alternatives. For example, terminal alkynes that react at a remarkable rate could possibly undergo dehydrogenative silylation, forming silyl alkynes (intermediate **III**), followed by a gold-catalyzed intramolecular hydro-

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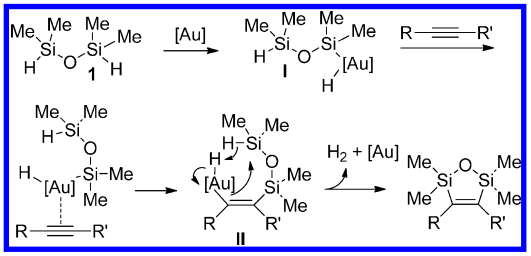
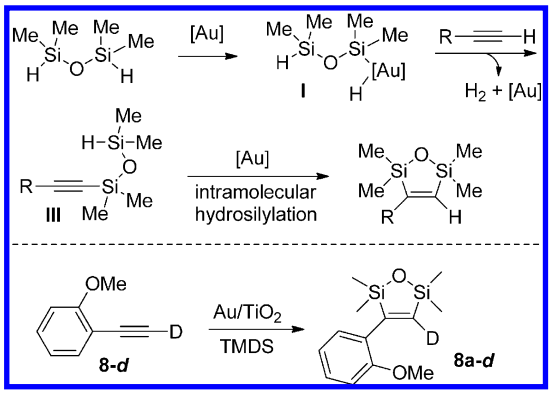
Scheme 4. Postulated Mechanism Regarding the Au-Catalyzed Oxidative Cycloaddition of TMDS to Alkynes through a Modification of the Crabtree−Ojima Mechanism



silylation[3−5] (Scheme 5). The dehydrogenative silylation pathway among terminal alkynes and hydrosilanes is well

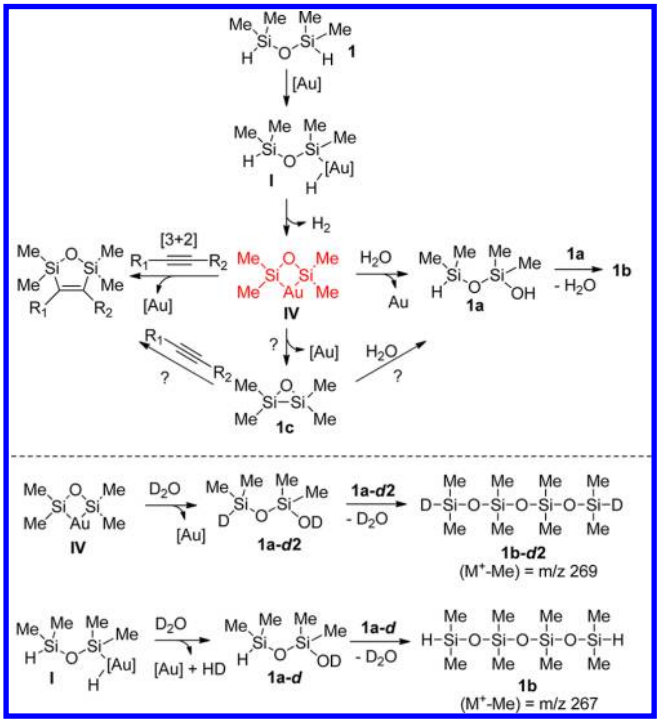
Scheme 5. Unlikeliness of a Possible Mechanism of Cycloaddition of TMDS to Terminal Alkynes, Involving Sequential Dehydrogenative Silylation and Hydrosilylation



established in the literature under Lewis acid catalysis conditions[21] or in the presence of iridium catalysts.[22] We studied the reaction between TMDS and labeled alkyne **8-*d***,[23] which provided 2,5-dihydro-1,2,5-oxadisilole **8a-*d*** with >97% D content (see the Supporting Information (SI)). If the mechanism appearing in Scheme 5 was taking place, no D atom should be seen on the cycloadduct due to the anticipated elimination of HD in the initial dehydrogenative silylation step.

A clue for the possible intermediates was acquired by taking a closer look at the hydrolysis side-products of TMDS. As commented earlier, if traces of water are present in the reaction mixture, at the initial stages of the reaction TMDS undergoes oxidative hydrolysis to the corresponding monosilanol **1a**, which condenses into dimeric 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (**1b**, Scheme 6). At the latter stages, **1b** either oligomerizes or forms octamethylcyclotetrasiloxane (cyclic dimer). In the case where traces of D_2O were added into the reaction mixture, GC-MS analysis revealed the incorporation of two deuterium atoms in **1b** (compound **1b-*d*$_2$** of Scheme 6). The mass spectrum of **1b** shows the typical M^+-Me fragmentation at m/z = 267, while we observed in the presence of deuterium oxide the same fragmentation at m/z = 269, indicative for the formation of **1b-*d*$_2$** (see SI). On the basis of the mechanism presented in Scheme 4, no D incorporation in dimeric side-product **1b** should be expected. The formation of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane-1,7-d_2 (**1b-*d*$_2$**) could be rationalized upon considering the *cyclo*-disilylmetalla intermediate **IV** shown in Scheme 6. *Cyclo*-metalla-oligosiloxanes and *cyclo*-metalladisilabutanes of Pt, Pd, Ir, and Rh are known

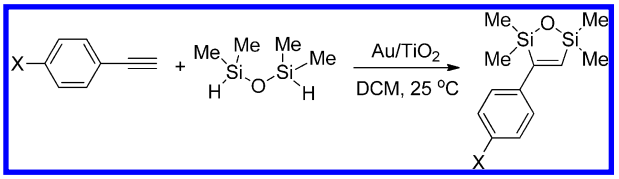
Scheme 6. Proposal Regarding the Intermediacy of a *Cyclo*-gold-disiloxane IV in the Au/TiO_2-Catalyzed Hydrolysis of TMDS and in Its Cycloaddition with Alkynes



compounds, and their formation arises from the dehydrogenative reaction (elimination of H_2) among 1,ω-dihydro tethered oligosilanes and the metal.[24] It is possible that *cyclo*-gold-disiloxane **IV** is formed through an intramolecular elimination of H_2 in intermediate **I** (Scheme 6), through a synergistic effect of the two proximal Si−H bonds and the gold nanoparticle.[25] The existence of gold disilyl species such as **IV** was recently documented from the oxidative insertion of Au(I) into a Si−Si bond.[26] The possibility that *cyclo*-gold-disiloxane **IV** decomposes into tetramethylsilylene oxide (**1c**) cannot be excluded. Silylene oxides[27] are labile compounds and could reasonably undergo a formal [3+2] cycloaddition to the alkynes, forming 2,5-dihydro-1,2,5-oxadisiloles.

A kinetic study regarding the competitive cycloaddition of aryl acetylenes with TMDS was also performed. It was found that electron-withdrawing substituents on the aryl ring accelerate the reaction rate relative to electron-donating ones (Table 2). The competitions were carried out upon reacting an

Table 2. Hammett-Type Kinetics in the Competing Oxidative Cycloaddition of TMDS to Aryl Acetylenes



entry	X	k_X/k_H
1	*p*-Me	0.74
2	*p*-MeO	0.88
3	*p*-NMe_2	0.68
4	*p*-F	1.39
5	*p*-CF_3	4.72

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equimolar mixture of the co-reacting acetylenes with a limited amount of TMDS, at 10−40% conversion.[28] Then the crude reaction mixture was analyzed by GC-MS and ^{1}H NMR. Attempts to fit the kinetic data (k_X/k_H) in a linear Hammett plot versus either σ or σ^+ values gave a poor outcome (R^2 = 0.68 and 0.64, respectively; see SI), indicative of a nonionic or radical-type transition state, as also exemplified by the lack of a rearrangement pathway in the reaction of cyclopropyl alkyne **22** with TMDS (Table 1). The current reactivity trend might be attributed to a LUMO-lowering effect of the electron-withdrawing substituents in reacting alkynes. Goddard and co-workers have calculated and interpreted a similar trend in the Huisgen cycloaddition of some aryl-fused cyclooctynes with alkyl azides.[29]

As supported gold nanoparticles on metal oxide surfaces contain, apart from Au(0) nanoclusters, ionic gold species,[1a,30] we postulate Au(I) bearing NPs (presumably cationic gold clusters Au_n^+ stabilized by the support) as the most reasonable active catalytic sites. Thus, the oxidative insertion of a Au(I) site into the σ Si−H bonds[31] of the hydrosilane will lead to the formation of Au(III) metallacycle **IV**. Following the formal [3+2] cycloaddition of **IV** to the alkyne, the Au(I)-catalytic site will be regenerated. A Au(I)−Au(III) redox sequence involving intramolecular oxidative addition of a Si−Si bond followed by the insertion of an oxygen atom has been recently authenticated.[26]

CONCLUSIONS

In conclusion, we have shown that Au/TiO_2 is a highly efficient catalyst for the dehydrogenative cycloaddition of several 1,*n*-dihydro tethered disilanes to alkynes under mild conditions. Depending on the remoteness of the Si−H functionalities in reacting disilane and the tether as well, this simple protocol provides access to the five-membered ring of 2,5-dihydro-1,2,5-oxadisiloles, to the six-membered ring of 1,1,4,4-tetramethyl-1,4-dihydrobenzo[*b*][1,4]disilines, and to the seven-membered ring of 4,7-dihydro-1,3,2,4,7-dioxatrisilepines. Terminal alkynes are significantly more reactive as compared to internal and provide the cycloadducts in good to excellent yields. It is proposed that ionic gold sites on Au NPs form with 1,1,3,3-tetramethyldisiloxane intermediate *cyclo*-gold-disiloxane via H_2 elimination, which consequently undergoes a formal [3+2] cycloaddition to alkynes.

EXPERIMENTAL SECTION

General Procedure for the Au/TiO_2-Catalyzed Dehydrogenative Cycloaddition Reaction. To a vial containing the alkyne (1.0 mmol) and a suitable amount of the 1,*n*-dihydrodisilane in 0.5 mL of solvent (see Table 1 and Scheme 3) was added Au/TiO_2 (concerning the loading levels of catalyst see Table 1 and Scheme 3). The reaction was monitored by TLC and GC-MS. After the disappearance of the starting material, the slurry was filtered with the aid of 3 mL of solvent through a short pad of silica gel. The filtrate was evaporated under vacuum, and the residue was chromatographed (if necessary).

Characterization of Products. The spectroscopic data of 2,5-dihydro-1,2,5-oxadisiloles **6a−16a**, **18a−21a**, and **23a−27a** have been previously reported.[8]

*2,2,3,5,5-Pentaphenyl-2,5-dihydro-1,2,5-oxadisilole (**6b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.70−7.66 (m, 8H), 7.49−7.33 (m, 17H), 7.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.7, 143.7, 140.6, 135.2, 134.7, 134.5, 134.2, 130.4, 130.4, 128.6, 128.0, 128.0, 127.1, 126.8. HRMS: calcd for $C_{32}H_{26}OSi_2$ + H, 483.1600; found 483.1595.

*2,5-Dimethyl-3-(p-tolyl)-2,5-bis((trimethylsilyl)oxy)-2,5-dihydro-1,2,5-oxadisilole (**7c**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.43 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.00 and 6.99 (two singlets, 1H each, corresponding to the two diastereomers), 0.36, 0.32, 0.30, and 0.25 (four singlets, 3H each, corresponding to the two diastereomers), 0.14, 0.12, 0.11, and 0.09 (four singlets, 9H each, corresponding to the two diastereomers). ^{13}C NMR (75 MHz, $CDCl_3$, equimolar mixture of two diastereomers): 162.9, 162.8, 140.6, 140.5, 137.9, 137.9, 137.0, 136.9, 129.3, 129.3, 126.6, 126.6, 21.2, 21.2, 1.9, 1.8, 1.8, 1.7, −0.2, −0.4, −0.5, −0.7. HRMS: calcd for $C_{17}H_{32}O_3Si_4$ + H, 397.1507; found 397.1502.

*3-(2-Methoxyphenyl)-2,2,5,5-tetraphenyl-2,5-dihydro-1,2,5-oxadisilole (**8b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.85 (s, 1H), 7.72 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.67−7.59 (m, 8H), 7.45−7.28 (m, 12H), 7.23 (dt, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 7.5 Hz, 1H), 3.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.2, 155.7, 143.7, 136.1, 134.9, 134.9, 134.5, 130.1, 129.7, 129.3, 127.8, 127.6, 127.0, 123.7, 121.0, 110.6, 53.4. HRMS: calcd for $C_{33}H_{28}O_2Si_2$ + H, 513.1706; found 513.1704.

*3-(4-Fluorophenyl)-2,2,5,5-tetraphenyl-2,5-dihydro-1,2,5-oxadisilole (**11b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.72−7.65 (m, 8H), 7.62 (s, 1H), 7.48−7.36 (m, 14H), 6.97 (t, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.3 (d, J_{C-F} = 245.0 Hz), 162.1, 143.5 (d, J_{C-F} = 2.0 Hz), 135.1, 134.9, 134.8, 130.5, 130.4, 128.8, 128.7, 128.4 (d, J_{C-F} = 8.0 Hz), 128.1, 128.0, 115.5 (d, J_{C-F} = 21.0 Hz). HRMS: calcd for $C_{32}H_{25}FOSi_2$ + H, 501.1506; found 501.1502.

*3-(4-Fluorophenyl)-2,5-dimethyl-2,5-bis((trimethylsilyl)oxy)-2,5-dihydro-1,2,5-oxadisilole (**11c**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.51−7.44 (m, 2H), 7.04 (t, J = 8.5 Hz, 2H), 6.96 and 6.94 (two singlets, 1H each, corresponding to the two diastereomers), 0.34, 0.30, 0.29, and 0.25 (four singlets, 3H each, corresponding to the two diastereomers), 0.14, 0.11, 0.09, and 0.08 (four singlets, 9H each, corresponding to the two diastereomers). ^{13}C NMR (75 MHz, $CDCl_3$, equimolar mixture of two diastereomers): 162.6 (d, J_{C-F} = 245.0 Hz), 162.6 (d, J_{C-F} = 245.0 Hz), 161.8, 161.8, 141.6 (d, J_{C-F} = 2.0 Hz), 141.5 (d, J_{C-F} = 2.0 Hz), 135.9, 135.9, 128.2 (d, J_{C-F} = 8.0 Hz), 128.1 (d, J_{C-F} = 8.0 Hz), 115.4 (d, J_{C-F} = 21.0 Hz), 115.4 (d, J_{C-F} = 21.0 Hz), 1.8, 1.7, 1.7, 1.6, −0.4, −0.6, −0.6, −0.8. HRMS: calcd for $C_{16}H_{29}FO_3Si_4$ + H, 401.1256; found 401.1252.

*3-Pentyl-2,2,5,5-tetraphenyl-2,5-dihydro-1,2,5-oxadisilole (**13b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.68−7.62 (m, 8H), 7.46−7.35 (m, 12H), 7.09 (s, 1H), 2.48 (t, J = 7.5 Hz, 2H), 1.52−1.42 (m, 2H), 1.25−1.17 (m, 4H), 0.80 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 168.5, 141.4, 135.1, 134.9, 134.8, 134.1, 130.2, 130.1, 127.9, 127.9, 36.1, 31.6, 27.8, 22.4, 13.9. HRMS: calcd for $C_{31}H_{32}OSi_2$ + H, 477.2070; found 477.2063.

*2,5-Dimethyl-3-pentyl-2,5-bis((trimethylsilyl)oxy)-2,5-dihydro-1,2,5-oxadisilole (**13c**).* ^{1}H NMR (300 MHz, $CDCl_3$): 6.39 and 6.38 (two broad singlets, 1H each, corresponding to the two diastereomers), 2.25 (t, J = 7.5 Hz, 2H), 1.52−1.44 (m, 2H), 1.34−1.25 (m, 4H), 0.90 (t, J = 7.5 Hz, 3H), 0.21, 0.20, 0.16, and 0.15 (four singlets, 3H each, corresponding to the two diastereomers), 0.11, 0.10, 0.09, and 0.08 (four singlets, 9H each, corresponding to the two diastereomers). ^{13}C NMR (75 MHz, $CDCl_3$, equimolar mixture of two diastereomers): 168.1, 168.0, 142.0, 142.0, 36.1, 36.1, 31.7, 31.7, 28.1, 28.1, 22.5, 22.5, 14.0, 14.0, 1.8, 1.8, 1.8, 1.8, −0.6, −0.8, −0.9, −1.2. HRMS: calcd for $C_{15}H_{36}O_3Si_4$ + H, 377.1820; found 377.1814.

*3-Cyclopropyl-2,2,5,5-tetraphenyl-2,5-dihydro-1,2,5-oxadisilole (**15b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.73 (d, J = 7.0 Hz, 4H), 7.66 (d, J = 7.0 Hz, 4H), 7.51−7.36 (m, 12H), 6.87 (s, 1H), 1.88−1.82 (m, 1H), 0.87−0.80 (m, 2H), 0.68−0.62 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 170.4, 136.4, 135.1, 135.0, 134.8, 134.2, 130.3, 130.2, 128.0, 127.9, 16.4, 9.7. HRMS: calcd for $C_{29}H_{26}OSi_2$ + H, 447.1600; found 447.1602.

*3-Cyclopropyl-2,5-dimethyl-2,5-bis((trimethylsilyl)oxy)-2,5-dihydro-1,2,5-oxadisilole (**15c**).* ^{1}H NMR (300 MHz, $CDCl_3$): 6.32 and 6.30 (two broad singlets, 1H each, corresponding to the two diastereomers), 1.66−1.47 (m, 1H), 0.81−0.75 (m, 1H), 0.66−0.55 (m, 3H), 0.21, 0.19, 0.17, and 0.15 (four singlets, 3H each, corresponding to the two diastereomers), 0.13, 0.10, 0.10, and 0.08 (four singlets, 9H each, corresponding to the two diastereomers). ^{13}C NMR (75 MHz, $CDCl_3$, equimolar mixture of two diastereomers): 170.0, 169.9, 138.2, 138.1, 16.8, 18.8, 8.2, 8.2, 8.0, 7.9, 1.8, 1.8, 1.8, 1.7,

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−0.3, −0.6, −0.6, −0.9. HRMS: calcd for $C_{13}H_{30}O_3Si_4$ + H, 347.1350; found 347.1346.

*3-(Cyclohexylmethyl)-2,2,5,5-tetramethyl-2,5-dihydro-1,2,5-oxadisilole (**17a**).* ^{1}H NMR (300 MHz, $CDCl_3$): 6.48 (s, 1H), 2.18 (br d, J = 7.0 Hz, 2H), 1.75−1.62 (m, 5H), 1.45−1.35 (m, 1H), 1.29−1.11 (m, 3H), 0.92−0.78 (m, 2H), 0.21 (s, 6H), 0.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 167.6, 144.7, 45.0, 36.9, 33.5, 26.6, 26.3, 1.0, 0.5. MS (EI): 254 (M^+, 2), 239 (M^+ − Me, 16), 172 (22), 157 (46), 133 (33), 83 (45), 73 (34), 55 (100).

*2,2,5,5-Tetraphenyl-3-(prop-1-en-2-yl)-2,5-dihydro-1,2,5-oxadisilole (**19b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.69 (d, J = 7.0 Hz, 4H), 7.62 (d, J = 7.0 Hz, 4H), 7.49−7.35 (m, 12H), 7.28 (s, 1H), 5.19 (br s, 1H), 5.14 (br s, 1H), 2.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.3, 144.2, 142.7, 135.2, 134.8, 134.6, 134.4, 130.3, 130.3, 127.9, 127.9, 120.1, 20.5. HRMS: calcd for $C_{29}H_{26}OSi_2$ + H, 447.1600; found 447.1591.

*3-(2,2-Diphenylcyclopropyl)-2,2,5,5-tetramethyl-2,5-dihydro-1,2,5-oxadisilole (**22a**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.28−7.07 (m, 10H), 5.84 (s, 1H), 2.46 (dd, J_1 = 8.0 Hz, J_2 = 7.5 Hz, 1H), 1.85 (dd, J_1 = 8.5 Hz, J_2 = 8.0 Hz, 1H), 1.59 (dd, J_1 = 8.5 Hz, J_2 = 7.5 Hz, 1H), 0.26 (s, 3H), 0.11 (s, 6H), −0.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.5, 146.8, 142.6, 140.2, 131.2, 128.4, 127.9, 127.7, 126.2, 126.0, 41.0, 30.1, 20.8, 0.6, 0.4, 0.4, −0.0. MS (EI): 350 (M^+, 11), 258 (12), 133 (100), 73 (44).

*Ethyl 2,4,5-Trimethyl-2,5-bis((trimethylsilyl)oxy)-2,5-dihydro-1,2,5-oxadisilole-3-carboxylate (**26c**).* ^{1}H NMR (300 MHz, $CDCl_3$): 4.27−4.14 (m, 2H), 2.22 and 2.21 (two singlets, 3H each, corresponding to the two diastereomers), 1.31 (t, J = 7.5 Hz, 3H), 0.30, 0.26, 0.23, and 0.19 (four singlets, 3H each, corresponding to the two diastereomers), 0.11, 0.10, 0.09, and 0.07 (four singlets, 9H each, corresponding to the two diastereomers). ^{13}C NMR (75 MHz, $CDCl_3$, equimolar mixture of two diastereomers): 172.3. 172.2, 167.2, 167.2, 144.8, 144.8, 59.7, 59.7, 17.3, 17.2, 14.3, 14.3, 1.7, 1.6, 1.6, 1.6, −0.8, −1.2, −2.4, −2.7. HRMS: calcd for $C_{14}H_{32}O_5Si_4$ + H, 393.1405; found 393.1399.

*2,2,4,4,7,7-Hexamethyl-5-(p-tolyl)-4,7-dihydro-1,3,2,4,7-dioxatrisilepine (**7d**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.10 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 2.34 (s, 3H), 0.26 (s, 6H), 0.22 (s, 6H), 0.16 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.0, 147.1, 145.2, 135.7, 128.7, 126.3, 21.0, 1.6, 1.3, 0.7. HRMS: calcd for $C_{15}H_{26}O_2Si_3$ + H, 323.1319; found 323.1314.

*5-(2-Methoxyphenyl)-2,2,4,4,7,7-hexamethyl-4,7-dihydro-1,3,2,4,7-dioxatrisilepine (**8d**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.19 (dt, J_1 = 7.5, J_2 = 2.0 Hz, Hz, 1H), 7.04 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 6.92 (dt, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 6.77 (br d, J = 7.5 Hz, 1H), 6.37 (s, 1H), 3.76 (s, 3H), 0.27 (s, 6H), 0.17 (s, 6H), 0.14 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.7, 155.0, 147.2, 138.2, 128.5, 127.7, 121.0, 109.6, 54.4, 1.4, 1.0, 0.8. HRMS: calcd for $C_{15}H_{26}O_3Si_3$ + H, 339.1268; found 339.1262.

*5-(4-Fluorophenyl)-2,2,4,4,7,7-hexamethyl-4,7-dihydro-1,3,2,4,7-dioxatrisilepine (**11d**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.09−6.93 (m, 4H), 6.32 (s, 1H), 0.26 (s, 6H), 0.20 (s, 6H), 0.15(s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.1, 161.6 (d, J_{C-F} = 245.0 Hz), 148.0 (d, J_{C-F} = 1.0 Hz), 144.1 (d, J_{C-F} = 3.5 Hz), 127.9 (d, J_{C-F} = 8.0 Hz), 114.8 (d, J_{C-F} = 21.0 Hz), 1.5, 1.3, 0.7. HRMS: calcd for $C_{14}H_{23}FO_2Si_3$ + H, 327.1068; found 327.1063.

*2,2,4,4,7,7-Hexamethyl-5-pentyl-4,7-dihydro-1,3,2,4,7-dioxatrisilepine (**13d**).* ^{1}H NMR (300 MHz, $CDCl_3$): 6.15 (s, 1H), 2.10 (t, J = 6.5 Hz, 2H), 1.52−1.35 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H), 0.19 (s, 6H), 0.18 (s, 6H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.2, 142.1, 40.3, 31.7, 29.1, 22.5, 14.0, 1.4, 1.0, 0.7. HRMS: calcd for $C_{13}H_{30}O_2Si_3$ + H, 303.1632; found 303.1626.

*Ethyl 2,2,4,4,6,7,7-heptamethyl-4,7-dihydro-1,3,2,4,7-dioxatrisilepine-5-carboxylate (**26d**).* ^{1}H NMR (300 MHz, $CDCl_3$): 4.19 (q, J = 7.0 Hz, 2H), 1.80 (s, 3H), 1.30 (t, J = 7.0 Hz, 3H), 0.25 (s, 6H), 0.24 (s, 6H), 0.11 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.6, 155.0, 149.1, 60.2, 21.1, 14.3, 0.9, 0.5, 0.1. HRMS: calcd for $C_{12}H_{26}O_4Si_3$ + H, 319.1217; found 319.1213.

*1,1,4,4-Tetramethyl-2-phenyl-1,4-dihydrobenzo[b][1,4]disiline (**6e**) (ref 32).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.64−7.56 (m, 2H), 7.44−7.25 (m, 7H), 6.87 (s, 1H), 0.39 (s, 6H), 0.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.2, 147.2, 145.8, 145.0, 144.2, 133.4, 133.1, 128.3, 128.2, 128.1, 126.5, 126.3, 0.0, −0.5.

*1,1,4,4-Tetramethyl-2-(p-tolyl)-1,4-dihydrobenzo[b][1,4]disiline (**7e**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.64−7.58 (m, 2H), 7.43−7.36 (m, 2H), 7.17 (d, J = 7.0 Hz, 2H), 7.15 (d, J = 7.0 Hz, 2H), 6.84 (s, 1H), 2.37 (s, 3H), 0.38 (s, 6H), 0.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.9, 145.1, 145.1, 144.3, 144.2, 136.1, 133.3, 133.1, 128.9, 128.3, 128.1, 126.2, 21.1, 0.1, −0.5. HRMS: calcd for $C_{19}H_{24}Si_2$ + H, 309.1495; found 309.1490.

*2-(2-Methoxyphenyl)-1,1,4,4-tetramethyl-1,4-dihydrobenzo[b][1,4]disiline (**8e**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.63−7.57 (m, 2H), 7.44−7.36 (m, 2H), 7.22 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 7.04 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.84 (s, 1H), 3.82 (s, 3H), 0.39 (s, 6H), 0.30 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.4, 155.3, 147.0, 146.1, 144.5, 136.8, 133.0, 132.9, 128.9, 128.1, 127.9, 127.7, 121.0, 109.8, 54.7, −0.6, −0.6. HRMS: calcd for $C_{19}H_{24}OSi_2$ + H, 325.1443; found 325.1433.

*2-(4-Fluorophenyl)-1,1,4,4-tetramethyl-1,4-dihydrobenzo[b][1,4]disiline (**11e**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.64−7.58 (m, 2H), 7.43−7.37 (m, 2H), 7.23−7.18 (m, 2H), 7.02 (t, J = 8.5 Hz, 2H), 6.83 (s, 1H), 0.36 (s, 6H), 0.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.8 (d, J_{C-F} = 243.5 Hz), 161.1, 146.0 (d, J_{C-F} = 1.0 Hz), 144.7, 144.0, 143.2 (d, J_{C-F} = 3.0 Hz), 133.4, 133.1, 128.4, 128.2, 127.9 (d, J_{C-F} = 8.0 Hz), 115.0 (d, J_{C-F} = 21.0 Hz), 0.0, −0.5. HRMS: calcd for $C_{18}H_{21}FSi_2$ + H, 313.1244; found 313.1235.

*1,1,4,4-Tetramethyl-2-pentyl-1,4-dihydrobenzo[b][1,4]disiline (**13e**) (ref 32).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.60−7.54 (m, 2H), 7.40−7.33 (m, 2H), 6.57 (s, 1H), 2.30 (br t, J = 6.5 Hz, 2H), 1.52−1.44 (m, 2H), 1.39−1.26 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H), 0.31 (s, 6H), 0.27 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.4, 145.0, 144.8, 140.4, 133.1, 133.0, 128.0, 127.9, 40.0, 31.7, 28.3, 22.6, 14.1, −0.4, −0.8.

*2-Cyclopropyl-1,1,4,4-tetramethyl-1,4-dihydrobenzo[b][1,4]disiline (**15e**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.62−7.54 (m, 2H), 7.41−7.35 (m, 2H), 6.30 (s, 1H), 0.39 (s, 6H), 0.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.9, 144.8, 144.7, 134.1, 133.2, 133.1, 128.1, 128.0, 18.0, 7.0, −0.3, −0.9. HRMS: calcd for $C_{15}H_{22}Si_2$ + H, 259.1338; found 259.1334.

*Ethyl 1,1,4,4-Tetramethyl-1,4-dihydrobenzo[b][1,4]disiline-2-carboxylate (**23e**).* ^{1}H NMR (300 MHz, $CDCl_3$): 8.02 (s, 1H), 7.62−7.55 (m, 2H), 7.44−7.36 (m, 2H), 4.28 (q, J = 7.0 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H), 0.43 (s, 6H), 0.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 168.4, 159.1, 150.3, 144.7, 142.6, 133.7, 133.1, 128.5, 128.2, 60.7, 14.3, −0.2, −1.0. HRMS: calcd for $C_{15}H_{22}O_2Si_2$ + H, 291.1236; found 291.1231.

*Ethyl 1,1,3,4,4-Pentamethyl-1,4-dihydrobenzo[b][1,4]disiline-2-carboxylate (**26e**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.60−7.53 (m, 2H), 7.41−7.36 (m, 2H), 4.28 (q, J = 7.5 Hz, 2H), 2.09 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H), 0.37 (s, 6H), 0.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 170.6, 158.6, 146.3, 143.7, 143.2, 133.1, 133.0, 128.4, 128.3, 60.2, 21,0, 14.5, −0.7, −1.8. HRMS: calcd for $C_{16}H_{24}O_2Si_2$ + H, 305.1393; found 305.1388.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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$$\frac{k_X}{k_H} = \frac{\log(1 - [\mathbf{Pa}]/[\mathbf{R}])}{\log(1 - [\mathbf{6a}]/[\mathbf{6}])}$$

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