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Iron-Catalyzed Dihydrosilylation of Alkynes: Efficient Access to Geminal Bis(silanes)

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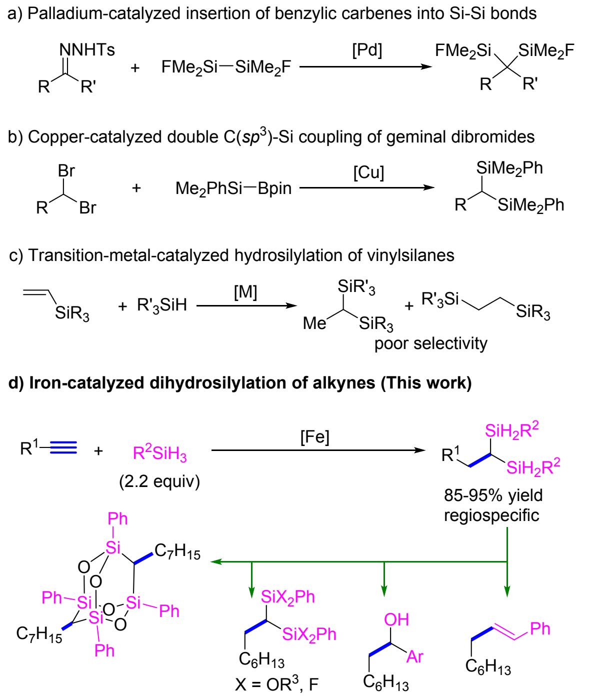
Supporting Information Placeholder

ABSTRACT: Geminal bis(silanes) are versatile synthetic building blocks owing to their stability and propensity to undergo a variety of transformations. However, the scarcity of catalytic methods for their synthesis limits their structural diversity and thus their utility for further applications. Herein we report a new method for synthesis of geminal bis(silanes) by means of iron-catalyzed dihydrosilylation of alkynes. Iron catalysts were distinctly superior to the other tested catalysts, which clearly demonstrates that novel reactivity can be found by using iron catalysts. This method features 100% atom economy, regiospecificity, mild reaction conditions, and readily available starting materials. Using this method, we prepared a new type of geminal bis(silane) with secondary silane moieties, the Si–H bonds of which can easily undergo various transformations, facilitating the synthetic applications of these compounds. Preliminary mechanistic studies demonstrated that the reaction proceeds via two iron-catalyzed hydrosilylation reactions, the first generating β-(*E*)-vinylsilanes and the second producing geminal bis(silanes).

Iron catalysis has attracted considerable attention for two main reasons: (1) iron is abundant, inexpensive, and biocompatible, and thus iron catalysts meet the requirements for green and sustainable chemistry applications, and (2) the unique electronic structures of iron give it the potential to mediate transformations that cannot be achieved with other catalysts. The development of new iron-catalyzed reactions and elucidation of the mechanisms of iron catalysis are among the most important topics in this field.[1]

Organosilanes are widely used in organic synthesis and materials science.[2] In particular, geminal bis(silanes) are versatile synthetic building blocks owing to their stability and propensity to undergo a variety of transformations.[3] However, the scarcity of reliable catalytic methods for their preparation has limited their structural diversity and thus the development of new transformations of these compounds. Syntheses based on stoichiometric reactions generally use ^{t}BuLi, ^{s}BuLi, or other bases, which either show poor selectivity or generate large quantities of waste.[4] Geminal bis(silanes) have also been prepared by means of palladium-catalyzed insertion of benzylic carbenes into Si–Si bonds (Scheme 1a)[5] and by copper-catalyzed double C(sp^3)–Si coupling of geminal dibromides (Scheme 1b),[6] but these two methods have poor atom economy and produce only geminal bis(silanes) with quaternary silyl groups, which are difficult to transform further. Hydrosilylation is a promising method for forming C–Si bonds owing to its high efficiency and 100% atom economy,[7] and in fact hydrosilylation of quaternary vinylsilanes has been studied by several research groups; however, the regioselectivity of these reactions is generally poor (Scheme 1c).[8] Herein we report a new method of synthesizing geminal bis(silanes) by means of iron-catalyzed dihydrosilylation of alkynes. Iron catalysts were distinctly superior to the other types of catalysts that we tested, a result that clearly demonstrates that novel reactivities can be found by using iron catalysts. Our method features 100% atom economy, regiospecificity, mild reaction conditions, and readily available starting materials. More important, this method allows the highly efficient synthesis of previously unreported geminal bis(silanes) with secondary silyl groups, the Si–H bonds of which can undergo various transformations, giving this method great potential synthetic utility.



Scheme1. Catalytic Synthesis of Geminal Bis(silanes).

Figure 1. Catalysts used in this study.

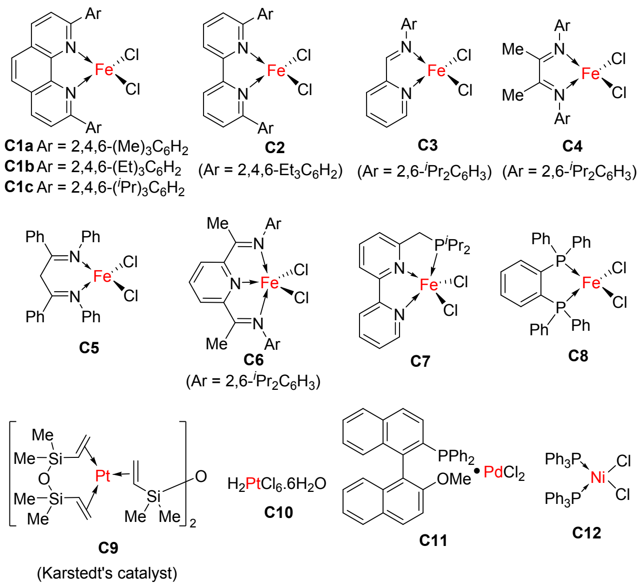
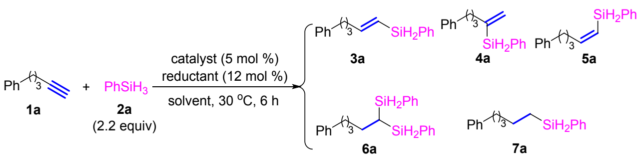


Table 1. Iron-Catalyzed Dihydrosilylation of Pent-4-yn-1-ylbenzene with PhSiH$_3$: Optimization of Reaction Conditions.

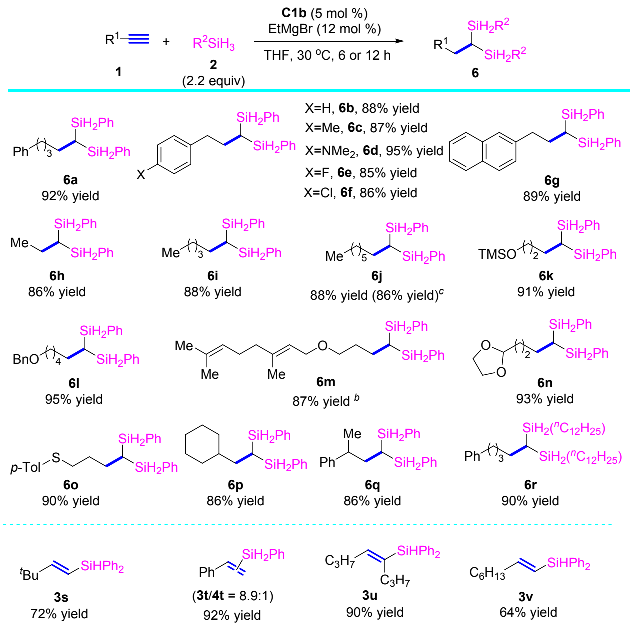


entry[a]	catalyst	reductant	conv. (%)[b]	3a/4a/5a/6a/7a[b]
1	**C1a**	EtMgBr	100	26/0/0/69/0
2[c]	**C1b**	EtMgBr	100	0/0/0/93/0
3	**C1c**	EtMgBr	100	51/0/0/30/15
4	**C2**	EtMgBr	<5	0/0/0/0/0
5	**C3**	EtMgBr	100	62/27/0/0/0
6	**C4**	EtMgBr	30	18/5/0/0/0
7	**C5**	EtMgBr	<5	0/0/0/0/0
8	**C6**	EtMgBr	100	5/0/43/38/0
9	**C7**	EtMgBr	100	45/10/39/0/0
10	**C8**	EtMgBr	<5	0/0/0/0/0
11	**C9**	none	100	22/0/0/0/0
12	**C10**	none	100	15/0/0/0/0
13	**C11**	none	100	33/0/0/0/0
14	**C12**	none	100	27/5/0/0/0
15	**C1b**	MeMgCl	100	35/0/0/58/0
16	**C1b**	NaBHEt$_3$	20	17/0/0/0/0
17	**C1b**	LiAlH$_4$	100	68/0/0/25/0
18	**C1b**	LiCH$_2$TMS	100	69/0/0/24/0
19[d]	**C1b**	EtMgBr	100	0/0/0/93/0
20[e]	**C1b**	EtMgBr	100	0/0/0/88/0

[a] Reaction conditions: **2a** (0.35 mmol), PhSiH$_3$ (0.8 mmol), catalyst (5 mol %), reductant (12 mol %) in THF (1 mL) at 30 °C. [b] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield of **6a** is 90%. [d] Benzene as solvent. [e] Toluene as solvent.

We started by carrying out hydrosilylation reactions between pent-4-yn-1-ylbenzene (**1a**) and PhSiH$_3$ in THF (Table 1). First, we evaluated iron catalysts with various ligands (Figure 1, **C1**–**C8**). EtMgBr was used to reduce the Fe(II) complexes to the active low-valent iron species.[9] These reactions can generate many possible products: monohydrosilylated products **3a**, **4a**, and **5a** (depending on the regioselectivity and stereoselectivity), desired dihydrodsilylation product **6a**, and hydrogenation product **7a**. Controlling the selectivity is the key to making this reaction useful. Although most of the tested iron catalysts showed poor activity or selectivity, catalyst **C1b**, which has a 2,9-diaryl-1,10-phenanthroline ligand,[10] gave desired geminal bis(silane) **6a** in 93% yield by NMR and 90% isolated yield (Table 1, entries 1–10). It is worth mentioning that catalysts based on other metals, which have been widely used in hydrosilylation,[7] gave only complex mixtures containing none of the desired product (entries 11–14). Replacing the iron in **C1b** with other metals afforded complexes that were inactive for the hydrosilylation reaction (see Table SI for details). In addition to EtMgBr, reductants such as MeMgCl, NaBHEt$_3$, LiAlH$_4$, and LiCH$_2$TMS also promoted the hydrosilylation but gave only moderate to poor selectivity for geminal bis(silanes) (Table 1, entries 15–18). Hydrosilylation promoted by **C1b** in the presence of EtMgBr could also be performed in benzene or toluene with satisfactory yields (entries 19 and 20).

Scheme 2. Iron-Catalyzed Dihydrosilylation of Terminal Alkynes: Substrate Scope[a]



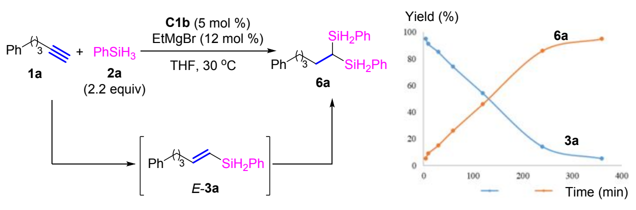
[a] Reaction conditions: **1** (0.35 mmol), R^{2}SiH$_3$ (0.8 mmol), **C1b** (0.0175 mmol, 5 mol %), EtMgBr (0.042 mmol, 12 mmol %) in THF (1 mL) at 30 °C. [b] Used 10 mol % **C1b** and 24 mol % EtMgBr. [c] Game-scale experiment: **1j** (10 mmol), PhSiH$_3$ (22 mmol), **C1b** (0.5 mmol, 5 mol %), EtMgBr (1.2 mmol, 12 mmol %) in THF (25 mL) at 30 °C.

Under the optimal reaction conditions (Table 1, entry 2), reactions of PhSiH$_3$ with various terminal alkyne substrates were then evaluated (Scheme 2). All the tested substrates with linear alkyl substituents (**1a–1o**) underwent dihydrosilylation to generate the corresponding geminal bis(silanes) (**6a–6o**) as the sole hydrosilylation products in good to high yields. Various functional groups, including amino (**6d**), fluoro (**6e**), chloro (**6f**), siloxy (**6k**), alkoxy (**6l** and **6m**), alkenyl (**6m**), acetal (**6n**), and thioether (**6o**), were tolerated. Reactions of terminal alkynes having bulkier, branched alkyl substituents also ran smoothly under the standard conditions and gave satisfactory yields of the desired products (**6p** and **6q**). In addition to phenylsilane, an alkylsilane (n-$C_{12}H_{25}SiH_3$) could also be used as a silylation reagent to afford **6r**. The reaction of $PhSiH_3$ and substrate **1j** was carried out on a gram scale with no loss in yield, and the ligand of **C1b** could be recovered in 87% yield after work-up (see SI for details). The catalyst was sensitive to the steric hindrance of the substrates: the reactions of $PhSiH_3$ with *tert*-butylacetylene (**1s**), 1-arylacetylenes (**1t**), and internal alkynes (**1u**) only afforded mono-hydrosilylation products **3s**, **3t**/**4t**, and **3u**, respectively; the reaction of 1-octyne (**1i**) with secondary silane (e.g. Ph_2SiH_2) afforded the monohydrosilylation product **3v**, while the reactions with tertiary silanes, including $(EtO)_3SiH$ and Et_3SiH were totally inactive. The catalyst was sensitive toward functional groups that can generate free protons or with strong coordinating ability (e.g. hydroxy, carbonyl, nitro, nitrile, and amide).

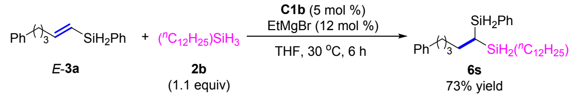
To elucidate the mechanism, we monitored the reaction by ^1H NMR (Scheme 3a). Kinetic plots revealed the hydrosilylation of **1a** initially gave vinylsilane *E*-**3a** (within 10 min),[11] which was then transformed to geminal bis(silane) **6a** via a second hydrosilylation in a regiospecific manner. Interestingly, the mono-hydrosilylation of **1a** with $PhSiH_3$ promoted by the iron catalyst modified with a tridentate pyridine diamine ligand (**C9**) conducted by Tomas and coworkers resulted in *Z*-**3a** instead.[9] These results indicate that different ligands might lead to different mechanisms in iron-catalyzed alkyne hydrosilylation. Reaction of *E*-**3a** with *n*-dodecylsilane under standard conditions afforded the geminal bis(silane) **6s** in 73% yield (Scheme 3b). When deuterated silane ($PhSiD_3$) was used instead of $PhSiH_3$, the corresponding geminal bis(silane) (**6g-*d***) was obtained without obvious redistribution of the deuterium between the products (Scheme 3c). These results clearly indicate that the reaction proceeded via two highly regioselective iron-catalyzed hydrosilylation reactions to produce the geminal bis(silane).

Scheme 3. Control Experiments

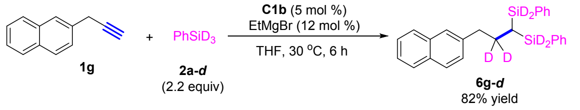
a) Monitoring the reaction process



b) Iron-catalyzed hydrosilylation of silyl alkene 3a

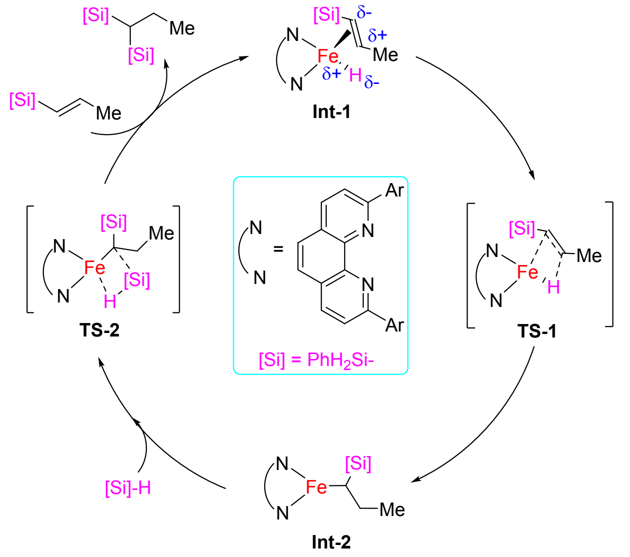


c) Deuterium labelling experiment



Based on the control experiments and by analogue with the hydrosilylation of unfunctionalized internal alkenes catalyzed by similar iron catalysts,[10] we proposed a catalytic cycle for the second hydrosilylation (Scheme 4). The process of hydrogen migration (from **Int-1** to **Int-2** via **TS-1**) is the regioselectivity-determining step. We attribute this selectivity mainly to the α-silicon effect of vinyl silane intermediate. Because the electronegativity of Si atom is smaller than that of C atom, the charge density of β-position of the vinyl silane is significantly lower than its α-position. Thus, the hydride of iron catalyst prefers to attacked β-position of the vinyl silane to give geminal bis(silane) accordingly. The density functional calculation also suggests that the energy barrier of α-selectivity is 6.9 kcal/mol lower than that of β-selectivity (see Figure SX for details).

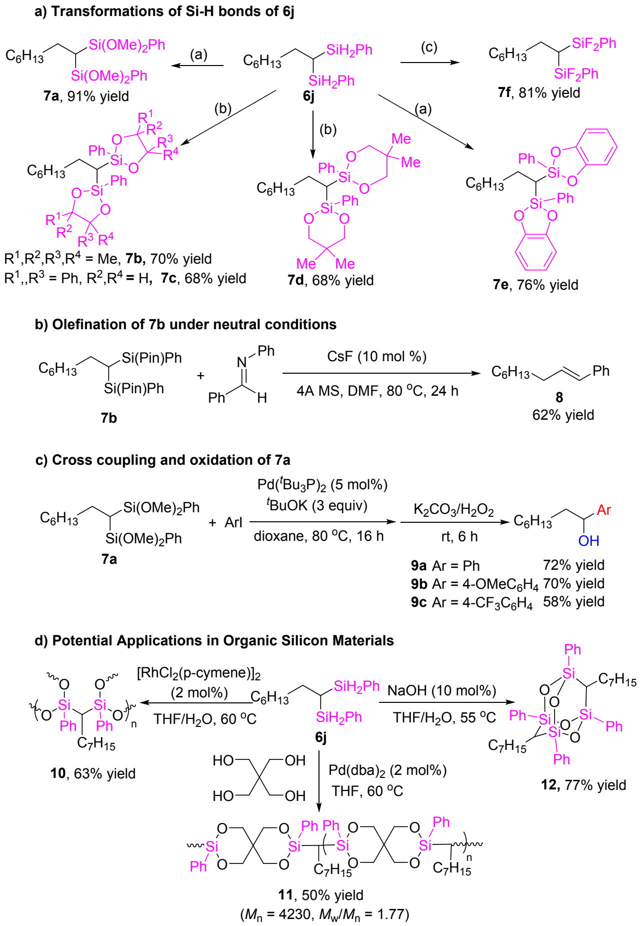
Scheme 4. Proposed Mechanism of Second Hydrosilylation



Unlike the known geminal bis(silanes) with quaternary silyl groups,[3–6] the geminal bis(silanes) produced in this study have secondary silyl groups. The four Si–H bonds of **6** can undergo various transformations, which makes them synthetically useful. For instance, the Si–H bonds of **6j** could be transformed to Si–O bonds (**7a**–**7e**) or Si–F (**7f**) bonds with good yields (Scheme 5a). After the modification of the silyl groups of the geminal bis(silanes), their C–Si bonds became easy to functionalize. For instance, pinacol-hmodified compound **7b** could easily be converted to alkene **8** with excellent *E*-selectivity in the presence of CsF (Scheme 5b).[12] More interestingly, methoxy-modified compound **7a** underwent a tandem Hayama coupling/oxidation reaction to give **9**. In addition, the two C–Si bonds of **7a** could **be** transformed into a C–C bond and a C–O bond, respectively (Scheme 5c). Finally, geminal bis(silane) **6j** could be used to synthesize new polydentate hybrid organic–inorganic xerogels (**10** and **11**)[13] or spherosilicone **12**[14] through simple condensation with water or 2,2-bis(hydroxymethyl)propane-1,3-diol in the presence of a $[RuCl_2(p\text{-cymene})]_2$, $Pd(dba)_2$ or NaOH as a catalyst, respectively (Scheme 5d). The diamantane-like **12** represent a new type spherosilicone. Again, these results demonstrate that this iron-catalyzed dihydrosilylation of alkynes affords a new type of geminal bis(silane) and accordingly opens up the possibilities for other uses of geminal bis(silanes).

In summary, we have described a protocol for iron-catalyzed dihydrosilylation reactions between aliphatic terminal alkynes and primary silanes, which produces geminal bis(silanes) with secondary silyl groups. Because the products contain Si–H bonds, which permit various previously unreported transformations, this protocol not only provides a straightforward route to geminal bis(silanes) but also enhances the utility of these silane reagents. Work on extending the substrate scope of the reaction and transforming the geminal bis(silane) products obtained by means of this protocol is underway in our laboratory and will be reported in due course.

Scheme 5. Transformations of the Products.



Reaction conditions: (a) 0.5-2 mol % $[RuCl_2(p\text{-}cymene)]_2$, diol, THF/Et_2O; (b) 10 mol % NaOH, pinacol, THF, 65 °C; (c) 5 mol % CuI, 4 equiv $CuCl_2$, 4 equiv CsF, Et_2O.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral data, and computational study results. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Graphic for TOC