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Communication

Rare-Earth-Catalyzed Selective 1,4-Hydrosilylation of Branched 1,3-Enynes Giving Tetrasubstituted Silylallenes

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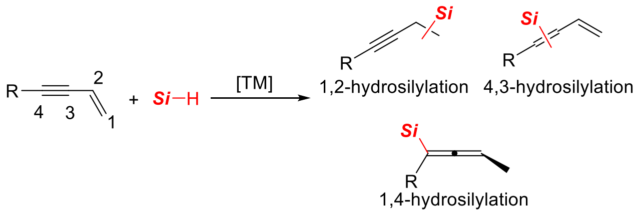
ABSTRACT: Allenes are versatile synthons in organic synthesis and medicinal chemistry because of their diverse reactivities. Catalytic 1,4-hydrosilylation of 1,3-enynes may present the straightforward strategy for synthesis of silylallenes. However, the transition-metal-catalyzed reaction has not been successful due to poor selectivity and very limited substrate scopes. We report here the efficient and selective 1,4-hydrosilylation of branched 1,3-enynes enabled by the ene-diamido rare-earth ate catalysts using both alkyl and aryl hydrosilanes, leading to the exclusive formation of tetrasubstituted silylallenes. Deuteration reaction, kinetic study, and DFT calculations were conducted to investigate the possible mechanism, revealing crucial roles of high Lewis acidity, large ionic radius, and ate structure of the rare-earth catalysts.

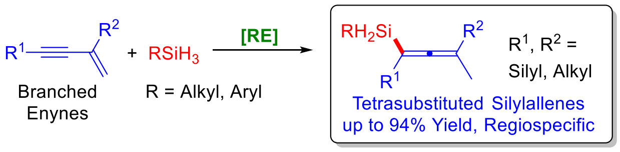
Metal-catalyzed hydrosilylation of unsaturated organic compounds, especially alkenes and alkynes, represents the most efficient and straightforward protocol for the synthesis of various silyl-functionalized organic molecules, which played important roles in organic and materials chemistry.[1] 1,3-Enynes, readily available conjugated organic compounds containing both alkene and alkyne moieties, are basic building blocks in synthetic chemistry.[2] However, catalytic hydrosilylation of 1,3-enynes confronts the issues of regio- and stereoselective control because there exist three mainly competing pathways, namely, 1,2-, 4,3-, and 1,4-hydrosilyation (Scheme 1).[3] As a result, only a few cases of transition-metal-catalyzed 4,3-hydrosilylation of 1,3-enynes for the synthesis of silyldienes have been reported,[4] while catalytic 1,4-hydrosilyation of 1,3-enynes to silylallenes has been met with very little success. There were only a couple of Pt- and Pd-catalyzed asymmetric 1,4-hydrosilylations of 1,3-enynes that have been reported.[3a,b,5] However, these precious-metal-catalyzed reactions suffered from very limited substrate scopes. Because allenes feature unique structures and diverse reactivities and are valuable multifunctional synthons in synthetic and medicinal chemistry,[6] the development of efficient and selective catalysts for 1,4-hydrosilylation of enynes is highly desired.

Scheme 1. Catalytic Hydrosilylation of 1,3-Enynes

Previous Work: Transition-Metal-Catalyzed Hydrosilylation of Enynes



This Work: Rare-Earth-Catalyzed 1,4-Hydrosilylation of Branched Enynes



Rare-earth-catalyzed hydrosilylation of alkenes and alkynes exhibits unique reactivity and selectivity because of their high Lewis acidity and large ionic radii.[7] In particular, we have recently shown that ene-diamido rare-earth (RE) complexes enabled highly regioselective hydrosilylation of internal alkenes and alkynes.[8] Stimulated by the high reactivity of these rare-earth complexes, we are interested in the exploration of rare-earth-catalyzed hydrosilylation of 1,3-enynes with the expectation to realize some novel and selective transformations for the synthesis of valuable synthons and organosilanes.

Herein, we report the employment of ene-diamido rare-earth ate complexes for the successful catalytic 1,4-hydrosilylation of branched 1,3-enynes, leading to the formation of tetrasubstituted silylallenes (Scheme 1). Mechanistic studies and DFT calculations indicated that the high Lewis acidity, large ionic radius, and unique ate structure are key factors for the unprecedented transformation.

Catalytic hydrosilylation of 2-methyl-4-trimethylsilyl-1-butene-3-yne (**7a**) with $n\text{C}_6\text{H}_{13}\text{SiH}_3$ (**6a**) was selected as model reaction (Table 1). Initially, we investigated the ene-diamido

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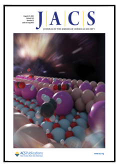

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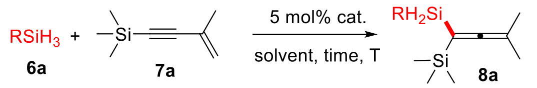
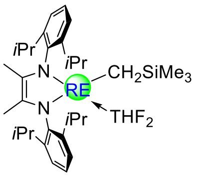
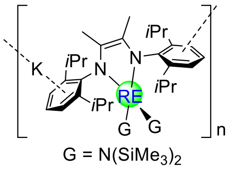
Table 1. Reaction Condition Optimization[a]



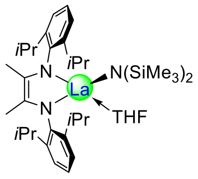


1, RE = Sm
YC, RE = Y



G = N(SiMe$_3$)$_2$

2, RE = La
4, RE = Sm
5, RE = Y



3

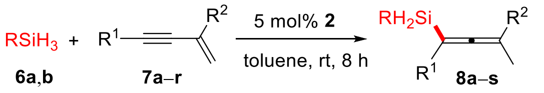
entry	cat	solvent	time (h)	*T* (°C)	yield (%)[b]
1	YC	C_6D_6	12	80	<5
2	**1**	C_6D_6	12	80	<5
3	**3**	C_6D_6	12	80	<5
4	**2**	C_6D_6	4	rt	74
5	**4**	C_6D_6	4	rt	68
6	**5**	C_6D_6	4	rt	21
7	**2**	C_6D_6	8	rt	>99
8	KN[c]	C_6D_6	24	80	29
9	**2**	toluene	8	rt	>99
10	**2**	*n*-hexane	8	rt	52
11	**2**	THF	24	80	<5

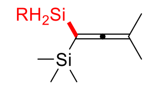
[a] $nC_6H_{13}SiH_3$ **6a** (0.44 mmol), 2-methyl-4-trimethylsilyl-1-butene-3-yne **7a** (0.4 mmol), catalyst (0.02 mmol, 5 mol %), 0.6 mL of solvent. [b] Yields of **8a** were determined by ^{1}H NMR and GC-MS with the crude mixture. [c] KN = KN(SiMe$_3$)$_2$.

rare-earth alkyl and amide complexes LY(CH$_2$SiMe$_3$)(THF)$_2$ (YC, L = ArNC(Me)C(Me)NAr, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, entry 1),[9] LSm(CH$_2$SiMe$_3$)(THF)$_2$ (**1**, entry 2),[8b] and LLa(N(SiMe$_3$)$_2$)(THF) (**3**, entry 3).[8c] However, only very low conversions (<5% yield of geminal disilylallene **8a**) have been observed in 12 h at 80 °C with these neutral catalysts. Prompted by our recent successes in the hydrosilylation of internal alkynes with rare-earth ate complexes, the ene-diamido lanthanum bis(amido) ate complex K[LLa(N(SiMe$_3$)$_2$)$_2$] **2** (entry 4) was employed. Indeed, **2** enabled highly selective hydrosilylation of **7a** with **6a** to give 1,4-hydrosilylation product **8a** in high yield (74%) in 4 h at room temperature without the contamination of the other hydrosilylation products. The samarium and yttrium ate complexes K[LSm(N(SiMe$_3$)$_2$)$_2$] (**4**)[8c] and K[LY(N(SiMe$_3$)$_2$)$_2$] (**5**, see the Supporting Information (SI)) were also examined (entries 5 and 6). Under same reaction conditions, the samarium ate complex **4** gave **8a** in 68% yield whereas the yttrium complex **5** only produced **8a** in 21% yield. This activity trend appeared to be closely correlated with the ionic radii of the elements: the larger the ionic radius is, the higher the activity (La^{3+} > Sm^{3+} > Y^{3+}). When the reaction time was extended to 8 h (entry 7), the lanthanum ate complex **2** gave **8a** almost quantitatively. KN(SiMe$_3$)$_2$ (KN, entry 8) is also active but only gave **8a** in 29% yield at 80 °C in 24 h, and the reaction did not produce any more product after 24 h. These results indicated that the combination of a large rare-earth ion with KN(SiMe$_3$)$_2$ forming ate structure is crucial for the effective catalytic 1,4-hydrosilylation of enynes.

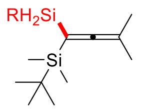
Toluene (entry 9) and C$_6$D$_6$ are the superior solvents for the hydrosilylation of the enyne, whereas the reaction in *n*-hexane (entry 10) only resulted in the 1,4-hydrosilylation product in 52% yield probably because of the poor solubility of **2** in *n*-hexane. In sharp contrast, almost no reaction was observed in THF (entry 11) probably due to the interactions of the solvent molecules with the lanthanum ion, which suppresses the coordination−insertion process.

Table 2. Hydrosilylation with Alkyl Hydrosilanes[a]

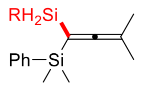




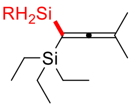
8a, R = *n*C$_6$H$_{13}$, 85% yield
8b, R = Cy, 88% yield (16 h)[b]



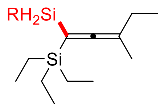
8c, 87% yield



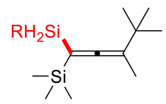
8d, 86% yield



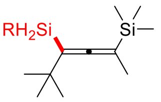
8e, 85% yield



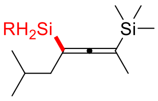
8f, 90% yield



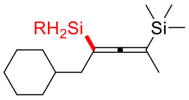
8g, 91% yield



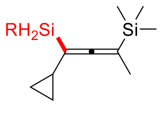
8h, 94% yield



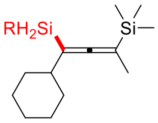
8i, 93% yield



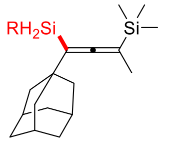
8j, 87% yield



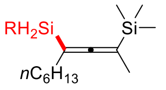
8k, 89% yield



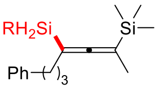
8l, 92% yield



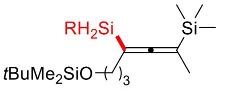
8m, 86% yield



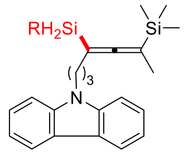
8n, 84% yield



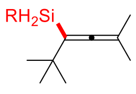
8o, 83% yield



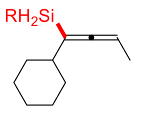
8p, 85% yield (16 h)



8q, 92% yield



8r, 91% yield (12 h)



8s, 92% yield (6 h)

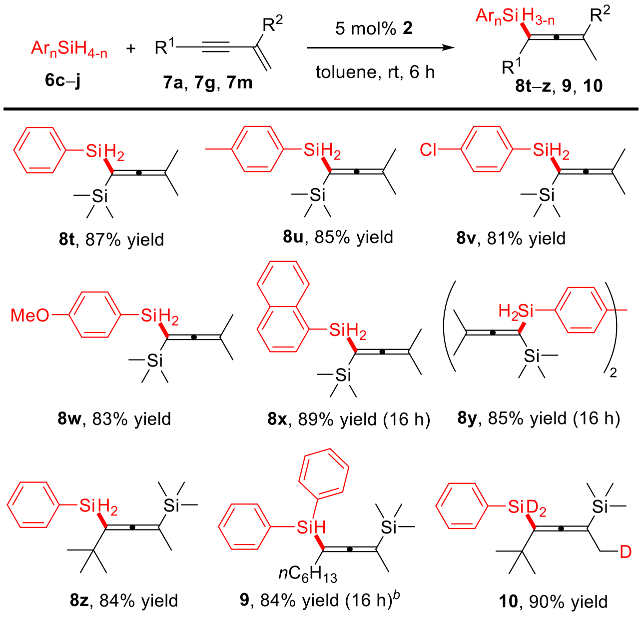
[a] RSiH$_3$ **6a** and **6b** (R = *n*C$_6$H$_{13}$, R = cyclohexyl, 0.44 mmol), enynes **7a−r** (0.4 mmol), catalyst **2** (0.02 mmol, 5 mol %), rt and 1 mL of toluene. Isolated yield. [b] 60 °C.

Under the optimized conditions (Table 1, entry 9), hydrosilylation of a range of branched 1,3-enynes **7a−r** with alkyl-substituted hydrosilanes *n*C$_6$H$_{13}$SiH$_3$ **6a** and CySiH$_3$ **6b** was examined (Table 2). All of the branched enynes underwent selective 1,4-hydrosilylation to afford tetrasubstituted silylallenes **8a−r** in excellent yields (83−94%), while the other hydrosilylation products were not observable. When the internal substituent R^2 on the alkene moiety is alkyl, the catalytic reaction could be applied to enynes containing various silyl-substituted alkyne moieties (R^1) to yield geminal disilylallenes (**8a−g**); when the internal substituent R^2 is silyl, the reaction is viable for enynes containing alkyl-substituted alkyne moieties (R^1) to produce 1,3-disilylallenes (**8h−q**). It is noteworthy that the 1,4-hydrosilylation underwent smoothly in good yields for the enynes with sterically demanding groups (86−87% yields of **8c**, **8d**, and **8m**). The hydrosilylation of enynes with siloxyl and N-heterocyclic substituents (**8p** and **8q**) could also achieve good yields in 16 and 8 h. The enynes with chloro and hydroxyl groups were not compatible with this reaction.

The substituent effects of 1,3-enynes on the hydrosilylation selectivity have been further examined with alkyl substituted enynes and terminal enynes. 1,3-Enynes with *t*-butyl and cyclohexyl groups could also been successfully hydrosilyated to give 1,4-hydrosilylation products (**8r** and **8s**, 91 and 92% yields) in 12 and 6 h. However, *n*-hexyl (R^1) substituted 1,3-enynes (R^2 = H, Me) exhibited poor regioselectivity with the formation of 1,4- and 4,3-hydrosilylation products (Table S1 in the SI). It is very likely that the steric effects of R^1 group could efficiently inhibit the 4,3-insertion but favor 1,4-selectivity.[10] It is noted that **8n** was generated selectively from enynes with R^1 = *n*-hexyl and R^2 = silyl groups because of the inductive effects of the silyl group on the alkene moiety, which could result in high electron density on the silyl carbon atom and facilitate the 1,2-insertion.[8c,11] However, with 1,3-enynes of R^1 = aryl and R^2 = silyl groups, the reactions only yielded polymeric materials and hydrosilylation products could not be observed.[8a,12]

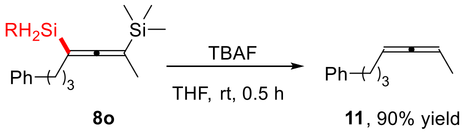
Aryl-substituted hydrosilanes could also be applied to the catalytic reaction (Table 3) with satisfactory yields (81−90%) and excellent regioselectivity. The catalytic protocol is tolerated to some functional groups (chloro **8v** and alkoxy **8w**). In addition, the bis(allene) **8y** can be obtained. It is noted that the substituents of hydrosilanes have significant effect on the catalytic activity: aryl hydrosilanes (phenyl **8t**) are more active than alkyl hydrosilanes (*n*-hexyl **8a** and cyclohexyl **8b**), and bulky hydrosilanes are less active (naphthyl **8x**). To our delight, the 1,4-hydrosilylation with the secondary silane Ph_2SiH_2 proceeded successfully to give the expected product **9** in 84% yield. The hydrosilylation with $PhSiD_3$ yielded the deuteration 1,3-disilylallenes (**10**) exclusively (90% yield), indicating the 1,4-hydrosilylation by D and $RSiD_2$ groups, which was strongly supported by the ^{1}H, ^{2}H, and ^{13}C NMR spectra. The synthetic potentials of silylallenes was demonstrated by the desilylation of **8o** with TBAF (Scheme 2), which afforded 1,3-disubstituted allene **11** in 90% yield.[13]

Table 3. Hydrosilylation with Aryl Hydrosilanes[a]



[a] $ArSiH_3$ **6c–j** (0.44 mmol), 1,3-enyne **7a**, **7g**, and **7m** (0.4 mmol), catalyst **2** (0.02 mmol, 5 mol %), rt and 1 mL of toluene. Isolated yield. [b] 60 °C.

Scheme 2. Derivatization of Silylallene



The reaction of lanthanum ate complex **2** with silane **6** was reported to yield lanthanum hydride $K[L((Me_3Si)_2N)La(\mu\text{-}H)_2La(H)(THF)L]K$.[8c] In contrast, the neutral complex **3** is inactive to the hydrosilane. These results indicated that the negative charge in anionic $[LLa(N(SiMe_3)_2)_2]^-$ of ate complex **2** could facilitate the σ-bond metathesis of **2** with hydrosilane to form active rare-earth hydride intermediate (Figure 1a).[8,14,15] The catalytic cycle may initiate with the selective 1,2-insertion of enyne **7** into the lanthanum hydride **A**, giving the η^3-propargyl/allenyl lanthanum intermediate **B**, similar to the Cu and Mg hydride-catalyzed 1,4-hydroelementation of 1,3-enynes.[10] After that, σ-bond metathesis of **B** with hydrosilane **6** led to the exclusive formation of silylallene **8** and regeneration of the active hydride **A**.

To gain further support for the proposed mechanism, DFT calculations were carried out. First, the LUMO of the 1,3-enyne **7g** was calculated using frontier orbital population analysis (Figure S1 in the SI). The coefficients at the C1 and C2 (0.40, 0.31) atoms of the alkene moiety are larger than those at the C4 and C3 (0.27, 0.13) atoms of the alkyne moiety, which explains, to a certain degree, the preference for initial 1,2-insertion rather than 4,3-insertion.[16] To further understand the mechanism, the calculations were also performed on the 1,4-hydrosilylation of 1,3-enyne **7a** with $MeSiH_3$ using $[LLa(H)(N(SiMe_3)_2]^-$ as the catalyst (Figure 1b). It is predicted that the hydrosilylation was initiated by the facile 1,2-insertion of an enyne via the four-centered TS1 (Figure 1c) with the energy barrier of 21.1 kcal/mol, affording the η^3-propargyl/allenyl lanthanum intermediate **B**. The 4,3-insertion showed higher activation energy ($\Delta\Delta G^\ddagger$ = 0.4 kcal/mol) than that of 1,2-insertion because of the strong steric repulsion between substituents on the internal alkyne moiety and bulky ene-diamido ligand in TS1′ (Figure S2 in the SI). Meanwhile, the calculations suggest that propargyl/allenyl intermediate **B** from 1,2-insertion is more stable ($\Delta\Delta G$ = −4.7 kcal/mol) than dienyl intermediate **B′** from 4,3-insertion. It is worth noting that the η^1-propargyl lanthanum species has not been predicted on the basis of 1,2-insertion, which is probably caused by the large lanthanum ion that could favor the η^3-fashion.[17] In fact, the short distance of La−C4 (2.67 Å) compared to that of La−C2 (3.37 Å), along with the almost linear C2−C3−C4 angle of 171.9°, suggests that the geometry of intermediate **B** lies between η^3-propargyl/allenyl and η^1-allenyl structures. Finally, intermediate **B** underwent σ-bond metathesis with hydrosilane via the TS2 to give the silylallene with the regeneration of the hydride intermediate. This σ-bond metathesis step requires a higher energy barrier (24.1 kcal/mol) and thus becomes the rate-limiting step of the overall reaction.

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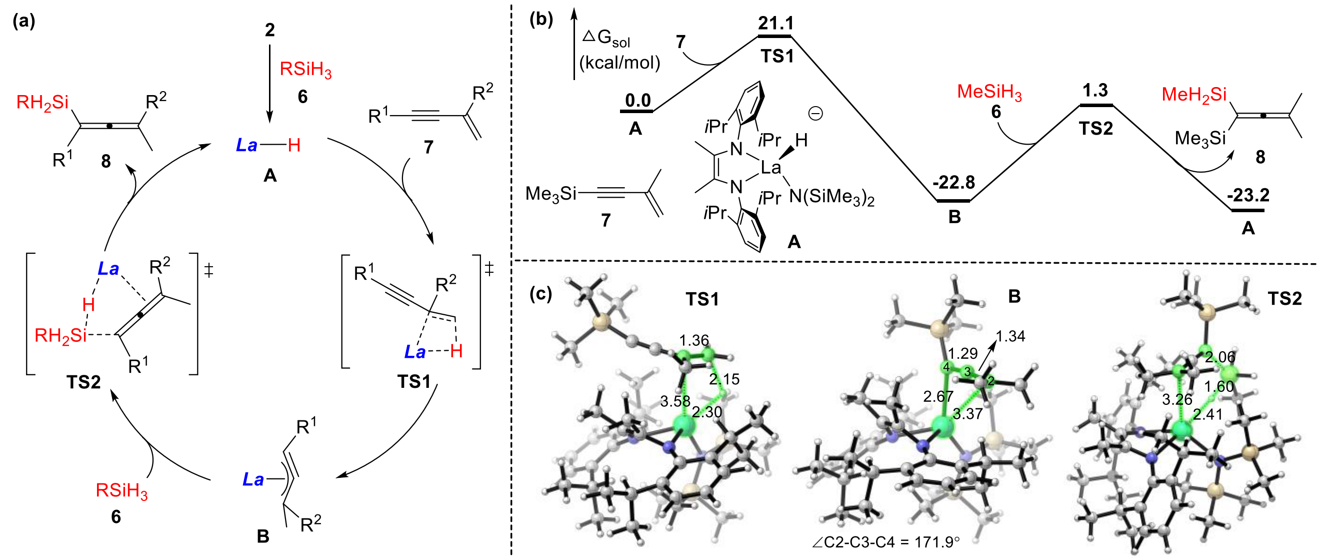

Figure 1. (a) Proposed mechanism. (b) Gibbs free-energy profile. (c) Calculated structures of TS1, **B**, and TS2.

Kinetic studies on 1,4-hydrosilylation were carried out (Table S2 and Figure S3 in the SI) which indicated that the rate law was of first order dependence on the hydrosilane and enyne.[8c] The results suggested that the reaction rate was influenced by both substrates. It is probably attributed to the steric hindrance of the branched 1,3-enynes, which leads to the intermediate **B** with bulky η^3-propargyl/allenyl features having a relatively slow σ-bond metathesis reaction with hydrosilane.

In summary, we have disclosed that the lanthanum ate complex **2** enabled highly efficient and selective 1,4-hydrosilylation of branched 1,3-enynes with various primary and secondary hydrosilanes to yield tetrasubstituted silylallenes. The high activity for sterically demanding branched enynes could be attributed to the high Lewis acidity and large ionic radius of lanthanum ion as well as the highly reactive ate hydride intermediate. Further applications of ene-diamido rare-earth ate catalysts in hydroelementation of bulky unsaturated molecules are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c04689.

Experimental procedures, DFT calculations, and spectroscopic data (PDF)

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Notes

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