Dehydrogenative Coupling of Terminal Alkynes with O/N-Based Monohydrosilanes Catalyzed by Rare-Earth Metal Complexes

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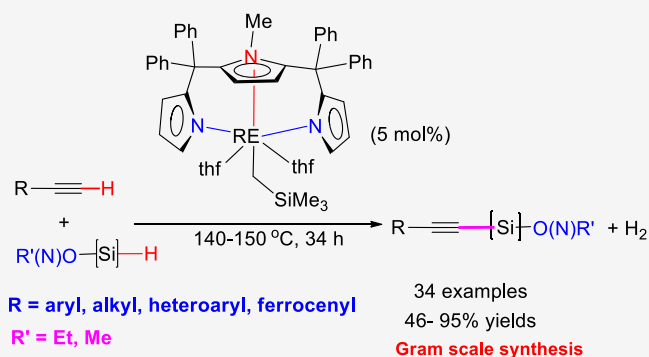
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ABSTRACT: Newly synthesized rare-earth metal alkyl complexes bearing a tripyrrolyl ligand act as excellent precatalysts for the cross-dehydrogenative coupling between various terminal alkynes and O/N-based monohydrosilanes of $HSi(OEt)_3/HSi(NMe_2)_3$, leading to the formation of a variety of alkoxysilylalkyne and aminosilylalkyne derivatives in good to high yields. The precatalysts $LRE(CH_2SiMe_3)(thf)_2$ (RE = Y(**1a**), Er(**1b**), Yb(**1c**), L = 2,5-$[(2\text{-}C_4H_3N)CPh_2]_2(C_4H_2NMe)$, thf = tetrahydrofuran) were easily prepared in high yields via the reactions of $RE(CH_2SiMe_3)_3(thf)_2$ with the proligand H_2L in a single step. Mechanistic studies reveal that treatment of **1** with phenylacetylene could generate the active catalytic species: dinuclear rare-earth metal alkynides ($L(thf)_n[RE(\mu\text{-}C\equiv CPh)]_2L$) (RE = Y(**5a**), n = 1; Yb(**5c**), n = 0), which could react with $HSi(OEt)_3$ to produce the coupling product **4aa** and the dinuclear rare-earth metal hydrides ($L(thf)[RE(\mu\text{-}H)]_2L$) (RE = Y(**6a**); Yb(**6c**)). By contrast, prior treatment of **1c** with $HSi(OEt)_3$ proceeds via cleavage of the Si—O bond to produce the dinuclear ytterbium alkoxide ($LYb(\mu\text{-}OEt))_2$ **7c**, which is inert in the dehydrogenative coupling reaction. The results of the mechanistic studies are consistent with the observation that the reaction is greatly influenced by the addition sequence of precatalyst/alkynes/silanes.

Me
Ph   N   Ph
Ph   Ph
N   RE   N   (5 mol%)
thf   thf
SiMe₃

R≡═─H
+   140-150 °C, 34 h   R─≡─[Si]─O(N)R' + H₂
R'(N)O─[Si]─H

R = aryl, alkyl, heteroaryl, ferrocenyl
R' = Et, Me

34 examples
46- 95% yields
Gram scale synthesis

INTRODUCTION

The development of highly selective and efficient catalysts for the chemical transformation of C–H bonds into valuable materials is of significant importance. Silylalkynes are an important class of organic synthons for the construction of C–C and C–X (X = heteroatom) bonds.[1] These compounds are commonly prepared by the deprotonation of terminal alkynes with Grignard reagents or organolithium, followed by coupling with silyl electrophiles.[2] Nevertheless, issues such as atom- and step-economy and functional group compatibility with the highly nucleophilic metal-acetylides limit the applicability of this method.

The catalytic cross-dehydrogenative coupling of terminal alkynes with hydrosilanes presents the most attractive and atom-economic synthetic route, because the only byproduct is H_2. Thus, several catalytic systems including transition-metal,[3] alkaline-metal,[4] alkaline-earth metal,[5] main-group element,[6] and a divalent ytterbium-imine complex[7] have been successfully developed for this reaction system in the previous work (Scheme 1). Despite these impressive advances, such reaction systems suffer more or less from some side reactions associated with this cross-coupling, for example, competitive hydrosilylation of alkynes,[8] isomerization, and dimerization of terminal alkynes.[4a,e,9] Moreover, most reaction systems have
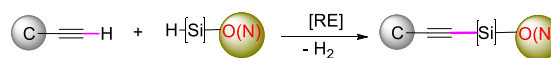
Scheme 1. Dehydrogenative Coupling Reaction of Terminal Alkynes with Hydrosilanes

Previous work

C≡═─H + H─[Si]─C $\xrightarrow[-H_2]{Cat}$ C≡═─[Si]─C
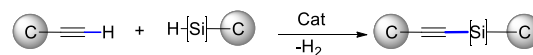
Cat: transition metal; alkaline-metal; alkaline-earth-metal; $B(C_6F_5)_3$; Yb(II) complex

This work

C≡═─H + H─[Si]─O(N) $\xrightarrow[-H_2]{[RE]}$ C≡═─[Si]─O(N)

• Additive-free   • High efficiency
• No H_2 acceptor   • Wide substrate scope   • Gram-scale synthesis

relied on hydrocarbon silanes as a reaction partner, while the heteroatom-substituted hydrosilanes, such as alkoxysilanes and aminosilanes, have been rarely used, probably due to the presence of more polarized Si−O and Si−N bonds,[10] as observed in the stoichiometric reactions of a scandium phosphinoalkylidene complex with triethoxysilane or the reactions of yttrium hydride with methoxysilane, involving the cleavage of the Si−O bond to form scandium or yttrium alkoxides,[11] while alkoxysilylalkynes are an important building block, utilized in a range of transformations, such as the Hiyama alkynylation/cyclization reaction,[12a,b] [4 + 2] cyclo-addition,[12c] and alkynylation of ketones.[12d,f] Recently, RC≡CSi(OMe)$_3$ was used in trifluoromethylalkynylation of alkenes via a copper-catalyzed radical relay process.[12g] However, synthetic approaches to such a type of alkoxysilylalkyne and aminosilylalkyne via a cross-dehydrogenative coupling strategy has remained largely unexplored.[3a,4a,6] Here, we report the first example of C(sp)−H/Si−H dehydrogenative coupling of terminal alkynes with hydrosilanes containing Si−O and Si−N bonds in the presence of rare-earth metal precatalysts to afford alkoxysilylalkynes and aminosilylalkynes in good to high yields with a broad functional-group tolerance. Alkynyl and hydrido species, representing the resting-state complexes in the catalytic cycle, were successfully isolated and characterized to shed light on the reaction mechanisms.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes. N-Heterocyclic pyrrolyl ligands have attracted particular research interest in organometallic chemistry due to their η^5/η^1 bonding capability, and they are anticipated to be alternatives to cyclopentadienyl ligands.[13] Rare-earth metal alkyl complexes supported by a tripyrrolyl ligand **L**RE(CH$_2$SiMe$_3$)(thf)$_2$ (RE = Y(**1a**), Er(**1b**), Yb(**1c**), **L** = 2,5-[(2-C$_4$H$_3$N)CPh$_2$]$_2$-(C$_4$H$_2$NMe), thf = tetrahydrofuran) were synthesized in high yields (90% for **1a**; 88% for **1b**; 89% for **1c**) from the reactions of RE(CH$_2$SiMe$_3$)$_3$(thf)$_2$ with the proligand H$_2$**L** in thf (Scheme 2). Complexes **1a**−**1c** have a good solubility in

Scheme 2. Preparation of the Rare-Earth Metal Alkyl Complexes
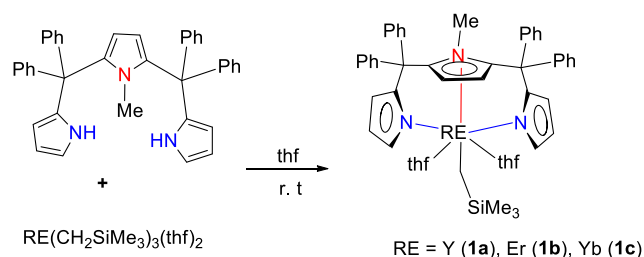
toluene and were characterized by single-crystal X-ray crystallography and elemental analysis. The representative structure of **1a** is shown in Figure 1, and those of **1b** and **1c** are provided in the Supporting Information (Figures S1 and S2). X-ray analysis revealed that the central N-methylated pyrrole ring adopts a η^5-bonding mode to the yttrium ion with the bond length of the Y−Pyr ring, ranging from 2.876(5) to 2.943(5) Å, which are longer than those in [2-(2-CH$_3$OC$_6$H$_3$NC(H)CH$_2$SiMe$_3$)C$_4$H$_3$N]$_2$Y$_2$(CH$_2$SiMe$_3$)$_2$-(DME), DME = dimethoxyethane(2.632(4) Å to 2.773(5) Å).[13c] The two terminally positioned pyrrolyl rings adopt η^1-
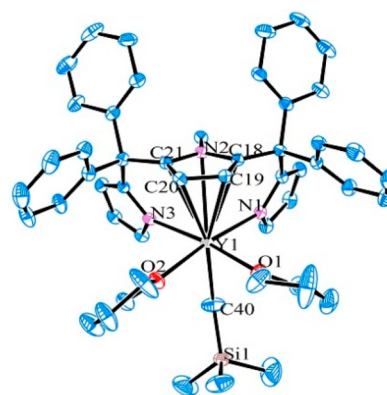

Figure 1. Molecular structure of complex **1a** with ellipsoids at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Y−N1 2.359(5), Y−N2 2.903(4), Y−N3 2.380(4), Y−C18 2.902(5), Y−C19 2.876(5), Y−C20 2.899(5), Y−C21 2.943(5), Y−C40 2.383(13), Y−O1 2.411(5), Y−O2 2.411(5).

bonding modes to the metal ion with bond lengths of Y1−N1 2.359(5) Å and Y1−N3 2.380(4) Å, which are shorter than those of 2.392(2) Å in N-arylaminomethyl-substituted pyrrolyl yttrium complex[14a] and 2.446(2) Å in [(2-(Me$_2$NCH$_2$)-C$_4$H$_3$N)Y(CH$_2$SiMe$_3$)$_2$]$_2$;[14b] even when different coordinate numbers were taken into account.[14c] The geometry of the central metal ion can be described as a distorted octahedron. The ^{1}H NMR spectrum of **1a** clearly proves the presence of the Y−CH$_2$SiMe$_3$ species, showing a doublet at −0.95 ppm ($^2J_{Y-H}$ = 2.5 Hz), which was further confirmed by a doublet at 31.5 ppm ($^1J_{Y-C}$ = 37.5 Hz) in the ^{13}C{^{1}H} NMR spectra (Figures S3 and S4).

Catalytic Activity. Phenylacetylene was chosen as a model substrate to react with triethoxysilane, and the results were listed in Table 1. The results show that both high temperature and long reaction time are beneficial to improve the yields of triethoxy(phenylethynyl)silane: ~70% yield of the product **4aa** could be obtained at 80 °C for 80 h, 100 °C for 34 h, and 120 °C for 22 h (entries 1−4). When the reaction temperature was elevated to 150 °C, a higher 92% yield was obtained within 34 h (entry 6). However, a higher temperature of 160 °C resulted in a slight decrease in the yield (90%), while the hydro-silylation product of phenylacetylene was detected (entry 7). Of the three rare-earth metal complexes examined, the Er complex **1b** proved to be the best one to afford the coupling product in 95% yield under the same conditions, while the Yb complex **1c** also provided 92% yield (entries 8 and 9). Er(CH$_2$SiMe$_3$)$_3$(thf)$_2$, as **1b** precursor has no activity in this dehydrogenative coupling mainly due to its high thermal instability (entry 10),[15a] indicating the essential role of the tripyrrolyl ligand. Decreasing the loading amount of the precatalyst was detrimental to the reaction efficiency (entries 12 and 13). On consideration of economy and activity, 5 mol % catalyst loading with respect to alkyne was used in the next study. It is notable that an extra amount of triethoxysilane is required, and the suitable stoichiometric ratio of the triethoxysilane and phenylacetylene is 2:1 due to the redistribution of the HSi(OEt)$_3$ into SiH$_4$ and Si(OEt)$_4$ in this reaction,[15b] as revealed by gas chromatography-mass spectrometry (GC-MS) analysis (entries 14 and 15). Figure 2 shows the yields of PhC≡CSi(OEt)$_3$ and Si(OEt)$_4$ versus the reaction time at different temperatures. The yields of the

Table 1. Optimization of Reaction Conditions[a]

entry	[RE] (mol %)	[Si]/ [alkyne]	T (°C)	t (h)/yield[b] (%)	t (h)/yield[b] (%)
1	**1a** (5)	2	80	34/47	80/73
2	**1a** (5)	2	90	34/50	80/80
3	**1a** (5)	2	100	34/67	80/84
4	**1a** (5)	2	120	22/70	34/81
5	**1a** (5)	2	140	22/84	34/89
6	**1a** (5)	2	150	22/90	34/92
7	**1a** (5)	2	160	22/87	34/90
8	**1b** (5)	2	150	22/89	34/95
9	**1c** (5)	2	150	22/89	34/92
10[c]	complex(5)	2	150	22/0	34/0
11	**1b** (6)	2	150	22/89	34/95
12	**1b** (4)	2	150	22/90	34/93
13	**1b** (3)	2	150	22/88	34/90
14	**1b** (5)	1.5	150	22/83	34/88
15	**1b** (5)	2.5	150	22/90	34/92

[a]Reaction conditions: To a Schlenk glass reactor were successively placed [RE], 200 μL of toluene, **2a** (0.40 mmol), and HSi(OEt)$_3$ under Ar. [b]Yields were based on **2a** and determined by GC analysis with mesitylene as an internal standard, and the product was characterized by NMR spectroscopy. [c]Er(CH$_2$SiMe$_3$)$_3$(thf)$_2$ as the catalyst.
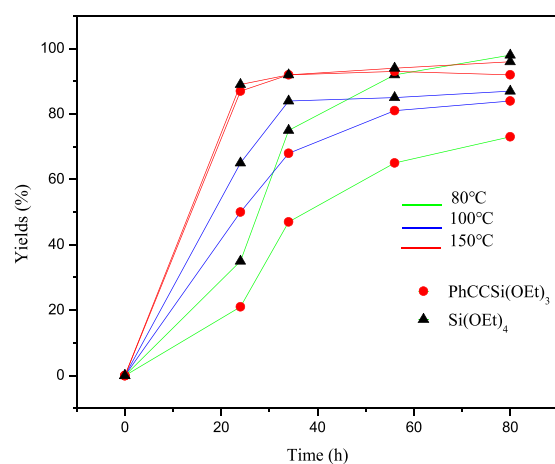
Figure 2. Yields of the alkoxysilylalkyne and Si(OEt)$_4$ vs reaction time at different temperatures. The yield was determined by GC analysis.

redistribution product are obviously faster than those of alkoxysilylalkyne at 80 and 100 °C, respectively (green and blue lines in Figure 2). When the reaction temperature was raised to 150 °C, both PhC≡CSi(OEt)$_3$ and Si(OEt)$_4$ can reach up to more than 90% yields within a relatively short time (red line). A gram-scale reaction was performed, and the crude product was purified by fractional distillation at 120 °C under reduced pressure to afford the triethoxy(phenylethynyl)silane as a pure colorless liquid in 90% yield.
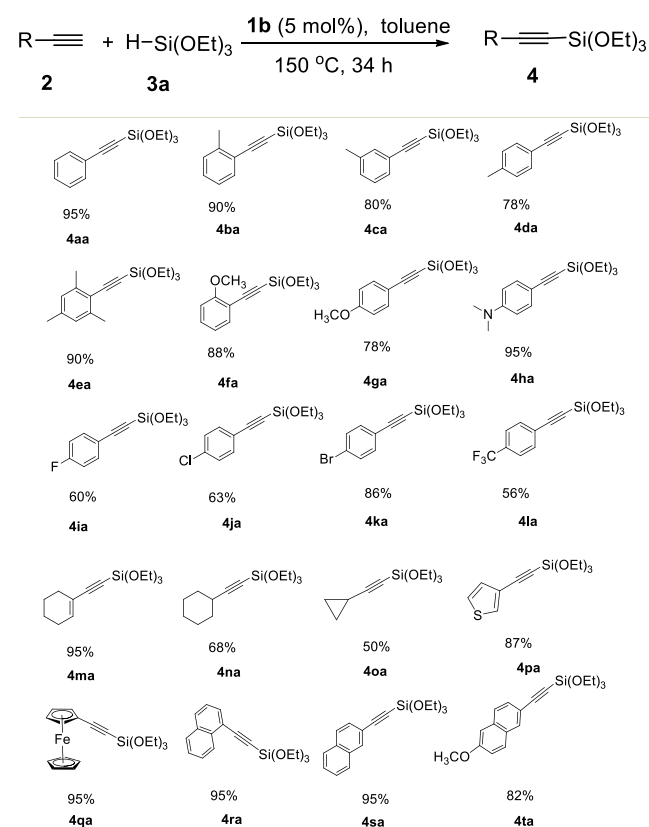
Next, the scope of the hydrosilanes using phenylacetylene **2a** as an alkyne partner in the presence of 5 mol % **1b** was investigated, and the results are shown in Table 2. In addition to HSi(OEt)$_3$, heteroatom-substituted hydrosilanes, such as HMeSi(OEt)$_2$ and HSi(NMe$_3$)$_3$, processed well in this

Table 2. Scope of the Hydrosilanes[a]
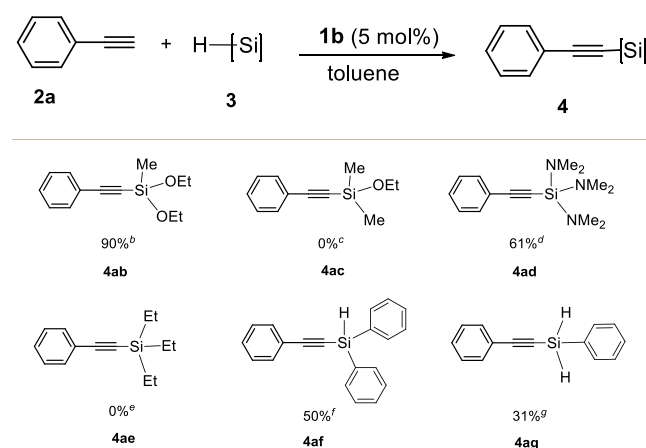
[a]Reaction conditions: Cat **1b** (20.0 μmol), **2a** (0.40 mmol), toluene (200 μL) under Ar for 34 h. Yields were based on **2a** and determined by GC analysis with mesitylene as an internal standard. [b]HSiMe(OEt)$_2$ (1.2 mmol) at 140 °C. [c]HSiMe$_2$OEt (0.8 mmol) at 140 °C. [d]HSi(NMe$_2$)$_3$ (0.4 mmol) at 140 °C. [e]HSiEt$_3$ (0.8 mmol) at 150 °C. [f]H$_2$SiPh$_2$ (0.8 mmol) at 80 °C for 40 h. [g]H$_3$SiPh (0.4 mmol) at 50 °C for 40 h

coupling reaction, affording the corresponding products of **4ab** and **4ad** in 90% and 61% yields under similar conditions. However, attempts to synthesize the monoalkoxysilylalkyne **4ac** and trialkylsilylalkyne **4ae** by using monohydrosilanes, such as HMe$_2$SiOEt and HSiEt$_3$, failed. The secondary hydrosilane of H$_2$SiPh$_2$ and the primary hydrosilane of H$_3$SiPh can be coupled with **2a** to afford the products **4af** and **4ag** in 50% and 31% yields under appropriate temperature for 40 h, respectively. The results show that the rare-earth metal alkyl complexes with a tripyrrolyl ligand as precatalysts have a good advantage for the preparation of alkoxysilylalkynes and aminosilylalkynes via the cross-dehydrogenative coupling.

Thus, we proceeded to evaluate the scope of terminal alkynes with HSi(OEt)$_3$ as the hydrosilane partner (Table 3). The results showed that both electron-donating and electron-withdrawing substituents on the benzene ring were tolerated, affording the corresponding alkoxysilylalkyne products in good to high yields. It is interesting to find that substitution on the *ortho* position of the benzene ring has an advantageous effect on this transformation. For example, mesitylacetylene and 2-methyl phenylacetylene produced the corresponding products in 90% yields (**4ba**, **4ea**), while 3-methyl and 4-methyl phenylacetylene only provided 80% and 78% yields (**4ca**, **4da**), respectively. A similar phenomenon was also observed in methoxy-substituted aryl alkynes (**4fa**, **4ga**). Moreover, this reaction system showed an excellent tolerance of functional groups, as the dimethylamino, halogen (F, Cl, Br), and trifluoromethyl-substituted phenylacetylenes participated in the reaction well to afford the corresponding ethoxysilyl-substituted alkynes (**4ha**–**4la**) in 56−95% yields. Besides, alkyl-substituted alkynes including cyclohexenyl, cyclohexyl, and cyclopropyl groups worked successfully in this reaction (**4ma**–**4oa**). The heteroarylacetylene also reacted well with HSi(OEt)$_3$, affording the desired product **4pa** in 87% yield. Moreover, metallosilylacetylene **4qa**, an important compound having a potential application in optoelectronic materials,[16] was obtained in 95% yield in this reaction. Three different naphthalenylacetylenes could also be silylated efficiently to
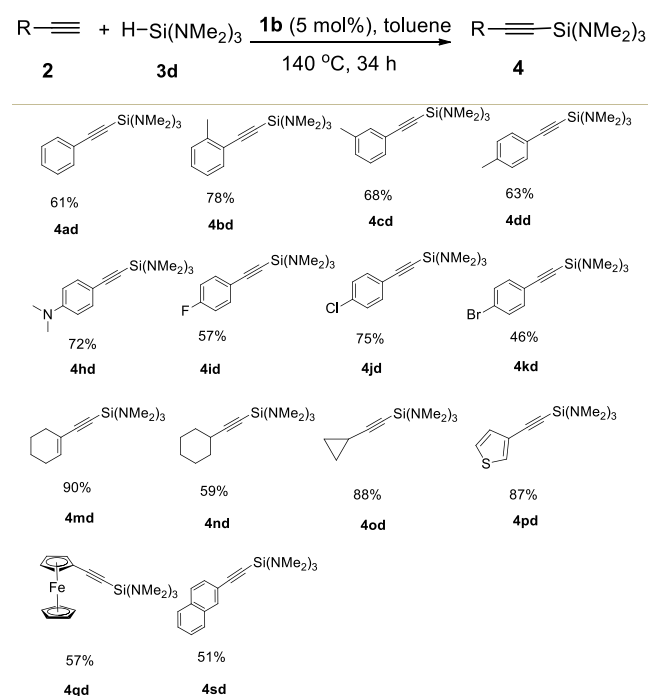
Table 3. Scope of the Coupling of Terminal Alkynes with HSi(OEt)$_3$[a]

R─≡ + H─Si(OEt)$_3$ $\xrightarrow[\text{150 °C, 34 h}]{\textbf{1b} (5 \text{ mol\%}), \text{ toluene}}$ R─≡─Si(OEt)$_3$

2   **3a**   **4**

95% **4aa**	90% **4ba**	80% **4ca**	78% **4da**
90% **4ea**	88% **4fa**	78% **4ga**	95% **4ha**
60% **4ia**	63% **4ja**	86% **4ka**	56% **4la**
95% **4ma**	68% **4na**	50% **4oa**	87% **4pa**
95% **4qa**	95% **4ra**	95% **4sa**	82% **4ta**

[a]Reaction conditions: To a Schlenk glass reactor were successively placed **1b** (5 mol % based on the alkynes), **2** (4.0 mmol), toluene (2.0 mL), and **3a** (8.0 mmol) under Ar at 150 °C for 34 h. Yields were based on **2** and determined by GC analysis with mesitylene as an internal standard.

Table 4. Scope of the Coupling of Terminal Alkynes with HSi(NMe$_2$)$_3$[a]

R─≡ + H─Si(NMe$_2$)$_3$ $\xrightarrow[\text{140 °C, 34 h}]{\textbf{1b} (5 \text{ mol\%}), \text{ toluene}}$ R─≡─Si(NMe$_2$)$_3$

2   **3d**   **4**

61% **4ad**	78% **4bd**	68% **4cd**	63% **4dd**
72% **4hd**	57% **4id**	75% **4jd**	46% **4kd**
90% **4md**	59% **4nd**	88% **4od**	87% **4pd**
57% **4qd**	51% **4sd**		

[a]Reaction conditions: To a Schlenk glass reactor were successively placed **1b** (5 mol % based on the alkynes), **2** (4.0 mmol), toluene (2.0 mL), and **3d** (4.0 mmol) under Ar at 140 °C for 34 h. Yields were determined by GC analysis with mesitylene as an internal standard.

provide the products in excellent yields under the standard reaction conditions (**4ra**−**4ta**).

The cross-dehydrogenative coupling of various terminal alkynes with HSi(NMe$_2$)$_3$ was investigated under similar conditions. Notably, aminosilanes have been seldom used in the construction of C−Si bonds. In this process, neither the vinylsilane (hydrosilylation) product nor the redistribution product of Si(NMe$_2$)$_4$ was detected in GC-MS analysis, which is different from the cross-dehydrogenative coupling between the terminal alkynes and HSi(OEt)$_3$. The scope of the catalytic reaction of the terminal alkynes with the N-based hydrosilane was evaluated (Table 4). A series of arylsubstituted acetylenes with substituents of different electronic and steric natures on the benzene ring smoothly undergo the coupling reaction, affording the corresponding aminosilylalkyne derivatives **4ad**−**4kd** in moderate to good yields (46−78%). The catalytic system was also compatible with alkyl- and heteroaryl-substituted acetylenes to produce the corresponding products **4md**−**4pd** in 59−90% yields without any detectable hydrosilylation byproducts. Notably, the ferrocenyl and naphthalenyl acetylenes reacted well with HSi(NMe$_2$)$_3$ to afford **4qd** and **4sd** in 57% and 51% yields, respectively.
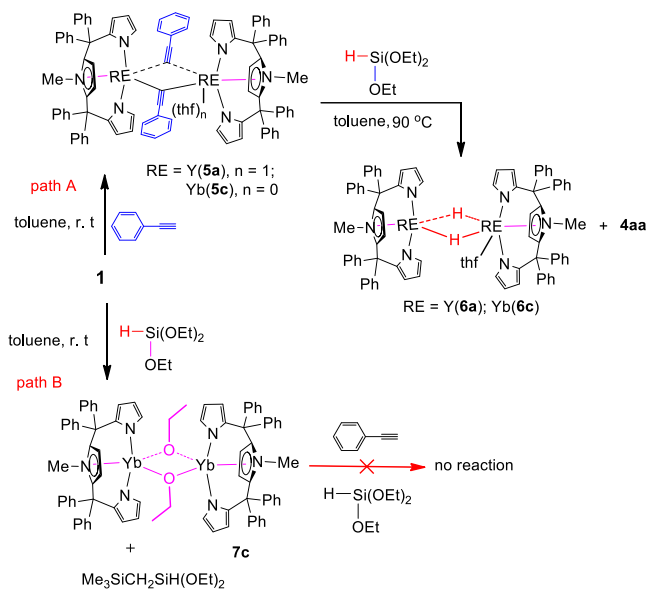
Mechanism Studies. To gain some insights into the mechanism of the present cross-dehydrogenative coupling reaction, some control experiments were performed. It was

interesting to note that, when the reagent addition order was changed from RE/alkyne/silane to RE/silane/alkyne, the yield of the desired alkoxysilylalkyne product diminished greatly, suggesting the in situ generation of RE metal complexes bearing different reactivities. To ascertain this, treatment of **1** with an equimolar amount of phenylacetylene in toluene at room temperature for 12 h, dinuclear rare-earth metal alkynides (**L** (thf)$_n$[RE(μ-C≡CPh)]$_2$**L**) (RE = Y(**5a**), n = 1; Yb(**5c**), n = 0) were isolated in 70% and 62% yields, respectively (Scheme 3, path A). In this process, σ-bond metathesis of **1** with a terminal alkyne produced the alkynide unit followed by reassembly to the dinuclear complexes **5** with the alkynyl groups as bridges. When the complexes **5** were treated with an equimolar amount of HSi(OEt)$_3$ in toluene at 90 °C for 6 h, in addition to the desired product **4aa**, the dinuclear rare-earth metal hydrides (**L** (thf)[RE(μ-H)]$_2$**L**) (RE = Y (**6a**); Yb (**6c**)) were isolated successfully (Scheme 3, path A). By contrast, treatment of **3** with 1 equiv of HSi(OEt)$_3$ in toluene at room temperature generated a dimeric ytterbium complex (**LYb(μ-OEt)**)$_2$ (**7c**) bearing the ethoxyl groups as bridges. The formation of Me$_3$SiCH$_2$SiH(OEt)$_2$ was also detected in the reaction solution by GC-MS (Scheme 3, path B). Obviously, complex **7c** is formed through the cleavage of the Si−O bond of HSi(OEt)$_3$ instead of the Si−H bond in the reaction. It is well-known that the bond dissociation energy (BDE) of the Si−O bond is 548 kJ/mol, while that of the Si−H bond is 400 kJ/mol.[17] The different reactivity displayed by HSi(OEt)$_3$ toward **1** and **5** might be partly attributed to the different activity of the RE−C bonds of RE−CH$_2$SiMe$_3$ and RE−C≡CPh; for example, the Y−C(sp^3) BDE is 398 kJ/mol, far higher than Y−C(sp) BDE 218 kJ/mol.[17] It is found that,
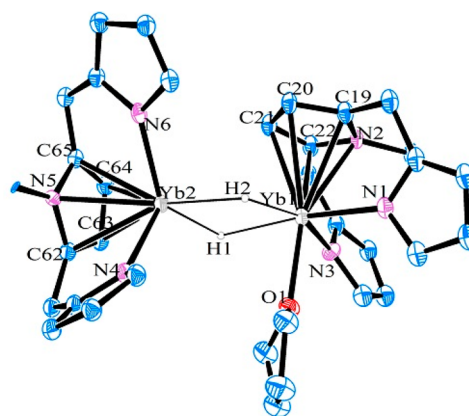
Scheme 3. Stoichiometric Reaction

Figure 4. Molecular structure of complex **6c** with ellipsoids at the 30% probability level. Hydrogen atoms (except for the bridging atoms H1 and H2) and the benzene rings on the ligand were omitted for clarity. Selected bond lengths (Å): Yb1−N1 2.268(11), Yb1−N2 2.627(10), Yb1−N3 2.280(10), Yb2−N4 2.252(11), Yb2−N5 2.592(9), Yb2−N6 2.243(11), Yb1−H1 2.11(8), Yb1−H2 2.32(8), Yb2−H1 2.17(8), Yb2−H2 2.18(8), Yb1−O1 2.312(10), Yb1−C19 2.705(16), Yb1−C20 2.750(16), Yb1−C21 2.705(16), Yb1−C22 2.663(16), Yb2−C62 2.665(13), Yb2−C63 2.686(13), Yb2−C64 2.685(14), Yb2−C65 2.661(13).

when complex **7c** is treated with phenylcaetylene or HSi-(OEt)$_3$, or a mixture of both substrates at 90 °C, no desired product **4aa** was detected. In contrast to **7c**, yttrium complexes **5a** and **6a** exhibited good catalytic activities in cross-dehydrogenative coupling silylation (Figures S4 and S5). Taken together, these experimental results suggest complex **5** as the real catalytic active species in the dehydrogenative cross-coupling reaction.

Solid-state structural analyses revealed that complexes of **5**−**7** are dinuclear complexes (Figures 3−5). The rare-earth metal ions are coordinated by a tripyrrolyl ligand in σ, π, σ fashion, which is similar to that of the mononuclear complexes **1a**−**1c**. In complex **5a**, a molecule of thf is coordinated to one of the yttrium ions, and its geometry is slightly different from that of the ytterbium structure, probably due to the requirement of coordination for larger metal ion radius. The bond lengths of Y2−N4 2.337(6) Å and Y2−N6 2.352(5) Å in **5a** are slightly shorter than those of Y1−N1 2.359(5) Å and Y1−N3 2.380(4) Å in **1a**. The Yb1−C40 and Yb1−C40^i bond lengths are 2.444(7) and 2.445(7) Å in **5c**, which are comparable to the

values of 2.42(2) and 2.47(2) Å in the alkynide-bridged dinuclear erbium complex,[18a] even if the difference in the ionic radii is taken into account.[14c] The bridging Yb−H bond lengths of 2.11(8), 2.32(8), 2.17(8), and 2.18(8) Å in **6c** are longer than the values of Yb−H 1.90 and 2.10 Å in [{Me$_2$Si(η^5-C$_5$H$_4$)$_2$Yb^{III}(thf)}$_2$(μ-H)(μ-Cl)],[19a] but they are shorter than those of 2.57(5), 2.16(9), 2.50(5), and 2.13(9) Å in the dimeric hydride [Yb(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_2$Et)-(thf)(μ-H)]$_2$.[19b] Although the quality of the structural data of **6a** is not satisfied, the hydride resonance showed a triplet ($^1J_{Y-H}$ = 28.0 Hz) at 5.96 ppm in the ^{1}H NMR spectrum in d_8-thf at room temperature, and the coupling constants are similar to those observed for other dimeric yttrium hydrides (Figure S7).[19c] The bond lengths of Yb1−O1 2.225(2) Å and Yb1−O1^i 2.222(2) Å in **7c** are slightly longer than the bridging bond length of 2.126(6) Å in the hetero-bimetallic ytterbium complex supported by a carbon-bridged bis(phenolate)-ligand[20a] and the bond length of Yb−O (Ar) 2.111(6) Å in
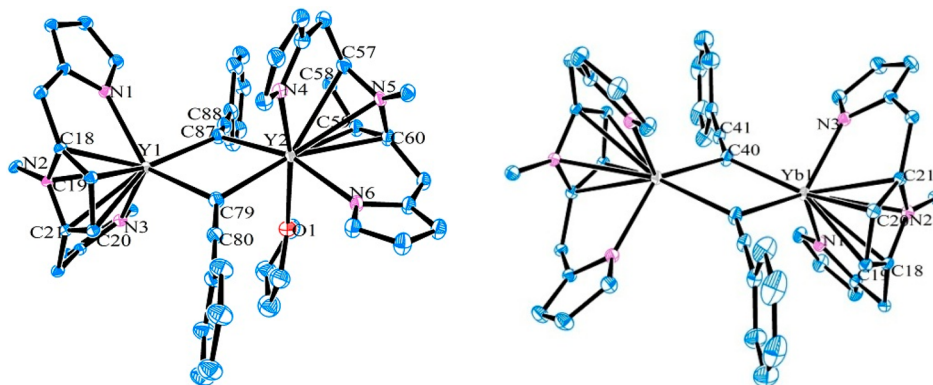

Figure 3. Molecular structure of complexes **5a** (left) and **5c** (right) with ellipsoids at the 30% probability level. Hydrogen atoms and the benzene rings on the ligand were omitted for clarity. Selected bond lengths (Å): **5a** Y1−N1 2.329(4), Y1−N2 2.653(4), Y1−N3 2.293(4), Y2−N4 2.337(6), Y2−N5 2.791(5), Y2−N6 2.352(5), Y1−C79 2.514(6), Y1−C87 2.490(6), Y2−C79 2.500(6), Y2−C87 2.606(6), Y2−O1 2.441(5); **5c** Yb−N1 2.238(6), Yb1−N2 2.634(5), Yb1−N3 2.262(6), Yb1−C18 2.732(5), Yb1−C19 2.791(6), Yb1−C20 2.759(6), Yb1−C21 2.669(6), Yb1−C40 2.444(7), Yb1−C40^i 2.445(7).
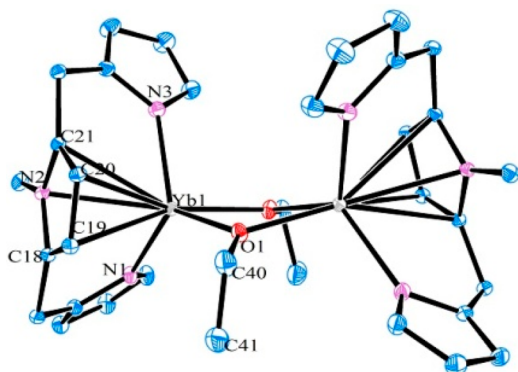
Figure 5. Molecular structure of complex **7c** with ellipsoids at the 30% probability level. Hydrogen atoms and the benzene rings on the ligand were omitted for clarity. Selected bond lengths (Å): Yb1–N1 2.297(2), Yb1–N2 2.682(2), Yb1–N3 2.262(3), Yb1–O1 2.225(2), Yb1–O1^i 2.222(2), Yb1–C18 2.737(3), Yb1–C19 2.807(3), Yb1–C20 2.825(3), Yb1–C21 2.778(3).

the ytterbium alkyl complex stabilized by a piperazidine-bridged bis(phenolato) ligand.[20b]

On the basis of the above experimental results and density functional theory (DFT) calculation (in the Supporting Information), we proposed a plausible reaction mechanism (Scheme 4). The σ-bond metathesis of the rare-earth metal

Scheme 4. A Possible Mechanism of the Catalytic Cross-Coupling Reaction
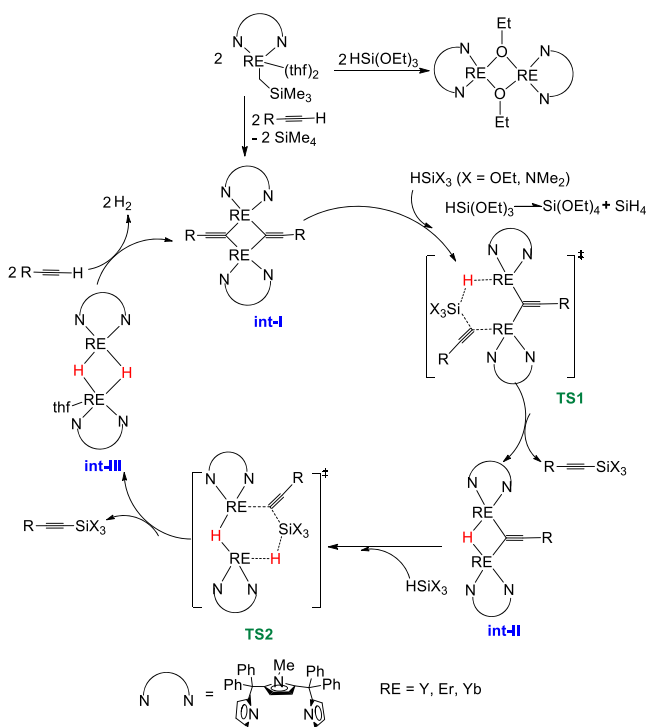
complexes with terminal alkynes produced the dimeric int-**I** bridged by the alkynyl groups, which then reacted with HSi(OEt)$_3$ or HSi(NMe$_3$)$_3$ to give the dimeric int-**II** bridged by an alkynyl group and a hydrogen atom via **TS1** with the release of the product **4aa**. Then a second silane attacks the RE–C(alkynyl) bond of int-**II** to form the int-**III** via **TS2**, together with the catalytic products of alkoxysilylalkynes/

aminosilylalkynes through the coupling reaction. During the transformation, though the theoretical calculation of 1.9 eV is unfavorable, improving the reaction temperature and prolonging time could overcome the energy barrier, which is in good line with the experimental observation (Figure S11). The crucial inte-**III** then reacted with terminal alkynes to regenerate the catalytically active species **I** with the release of H$_2$ to fulfill a catalytic cycle. In this process, the redistribution of the triethoxysilane was a major competitive reaction detrimental to the desired cross-coupling. Furthermore, kinetic isotope effect (KIE = k_H/k_D = 3.83) studies suggest that the C(sp)–H bond cleavage of the terminal alkyne is involved in the rate-determining step in the present catalytic reaction (see the Supporting Information).

CONCLUSION

In summary, we have successfully realized the cross-dehydrogenative coupling of terminal alkynes with HSi(OEt)$_3$ or HSi(NMe$_3$)$_3$ in the presence of rare-earth metal alkyl complexes ligated by the tripyrrolyl ligand as precatalysts for the first time. This catalytic system can tolerate many functional groups, thus making this method an effective strategy for the preparation of a variety of alkoxysilylalkynes and aminosilylalkynes. A probable mechanism has been proposed for this reaction, and some key intermediates have been corroborated by the control experiments and DFT calculations. We believe that this method has high potential for application as a unique and complementary synthetic approach to different types of silylalkynes.

EXPERIMENTAL SECTION

General Procedures. All manipulations of air- and moisture-sensitive materials were performed under a dry argon atmosphere using standard Schlenk techniques or in a glovebox. All solvents were dried by refluxing over sodium/benzophenone ketyl under argon and distilled prior to use unless otherwise noted. 2,5-[(2-C$_4$H$_3$NH)-CPh$_2$]$_2$(C$_4$H$_2$NMe) (H$_2$L),[21] and RE(CH$_2$SiMe$_3$)$_3$(thf)$_2$ were synthesized according to the literature methods.[22] Triethoxysilane and tris(dimethylamino)silane were distilled prior to use. Alkynyl compounds were purchased from TCI and used without further purification. IR spectra were recorded on a Shimadzu FTIR-Prestige-21 spectrometer (KBr pellets). Elemental analyses data were obtained on a PerkinElmer model 2400 Series II elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker model AV-500 NMR spectrometer (500 MHz for ^{1}H; 125.0 MHz for ^{13}C) in C$_6$D$_6$ for rare-earth metal complexes and in CDCl$_3$ for organic compounds. Chemical shifts (δ) were reported in parts per million. The J values are reported in hertz. The organic products were analyzed by GC7890F equipped with a flame ionization detector and a GC (Thermo TRACE 1300)-MS (Thermo ISQ QD) system. High-resolution (HR) MS measurements were conducted with a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Suitable crystals of rare-earth metal complexes were sealed in a thin-walled capillary. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An empirical absorption correction was applied using the SADABS program.[23] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[24a,c] The solvents of some structures were moved by Platon Squeeze.[24d]

Synthesis of LY(CH$_2$SiMe$_3$)(thf)$_2$ (1a). To a clear colorless solution of the tripyrrole proligand H$_2$L (1.00 g, 1.84 mmol) in 7.0 mL of thf was added a clear colorless solution of Y(CH$_2$SiMe$_3$)$_3$(thf)$_2$(0.91 g, 1.84 mmol) in 7.0 mL of thf at room temperature. Then 7.0 mL of n-hexane was added, and the resulting mixture was stirred

vigorously for 2 min before being allowed to stand still for 12 h. During this course, crystals precipitated and were collected by filtration, washed with 5 mL of *n*-hexane, and dried in vacuo (1.42 g, 90%). ^{1}H NMR (500 MHz, C$_6$D$_6$, ppm): δ 7.45 (s, 4H, Ar*H*), 7.24–7.18 (m, 8H, Ar*H*), 7.10–7.05 (m, 8H, Ar*H*), 6.99–6.97 (m, 2H, Pyr*H*), 6.58 (s, 4H, Pyr*H*), 6.22 (s, 2H, Pyr*H*), 3.75 (s, 8H, thf), 2.40 (s, 3H, N*Me*), 1.35 (s, 8H, thf), −0.08 (s, 9H, Si*Me*$_3$), −0.95 (d, $^2J_{Y-H}$ = 2.5 Hz, 2H, C*H*$_2$SiMe$_3$). ^{13}C NMR (125 MHz, C$_6$D$_6$, ppm): 149.7, 149.6, 144.9, 144.2, 130.2, 127.2, 127.1, 126.2, 113.7, 110.0, 108.3, 69.4 (thf), 58.3 (CPh$_2$), 35.4 (NCH$_3$), 31.5 (d, $^1J_{Y-C}$ = 37.5 Hz, Y-CH$_2$SiMe$_3$), 25.4 (thf), 4.2 (SiMe$_3$). Anal. Calcd for C$_{51}$H$_{58}$N$_3$O$_2$SiY: C, 71.06; H, 6.78; N, 4.87. Found: C, 70.51; H, 6.77; N, 4.73%. IR (KBr pellets, cm^{-1}): ν 3058, 3028, 2954, 2807, 2804, 2501, 1955, 1902, 1641, 1597, 1551, 1491, 1444, 1441, 1392, 1299, 1248, 1220, 1170, 1115, 1082, 1033, 1002, 962, 904, 863, 799, 763, 745, 702, 655, 568, 548.

Synthesis of LEr(CH$_2$SiMe$_3$)(thf)$_2$ (1b). Following the same procedure as described for the preparation of 1a, the reaction of H$_2$L (1.00 g, 1.84 mmol) with Er(CH$_2$SiMe$_3$)$_3$(thf)$_2$ (1.05 g, 1.84 mmol) afforded 1b as pink crystals (1.54 g, 88%). Anal. Calcd for C$_{51}$H$_{58}$N$_3$O$_2$SiEr: C, 65.14; H, 6.22; N, 4.47. Found: C, 64.78; H, 6.21; N, 4.42%. IR (KBr pellets, cm^{-1}): ν 3085, 3057, 3028, 2869, 2808, 2664, 2507, 2344, 1956, 1900, 1817, 1774, 1672, 1653, 1596, 1550, 1490, 1444, 1441, 1394, 1321, 1298, 1248, 1231, 1184, 1155, 1115, 1094, 1033, 862, 763, 745, 704, 567, 548.

Synthesis of LYb(CH$_2$SiMe$_3$)(thf)$_2$ (1c). Following the same procedure as described for the preparation of 1a, the reaction of H$_2$L (1.00 g, 1.84 mmol) with Yb(CH$_2$SiMe$_3$)$_3$(thf)$_2$ (1.07 g, 1.84 mmol) afforded 1c as brown crystals (1.55 g, 89%). Anal. Calcd for C$_{51}$H$_{58}$N$_3$O$_2$SiYb: C, 64.74; H, 6.18; N, 4.44. Found: C, 64.97; H, 6.38; N, 4.52%. IR (KBr pellets, cm^{-1}): ν 3088, 3057, 3028, 2955, 2869, 2664, 2506, 1956, 1901, 1817, 1774, 1652, 1596, 1550, 1490, 1444, 1394, 1320, 1298, 1248, 1231, 1155, 1115, 1078, 1041, 904, 862, 800, 768, 745, 702, 567, 548.

Synthesis of (L(thf)[Y(μ-C≡CPh)]$_2$L) (5a). To a clear solution of the complex 1a (0.23 g, 0.26 mmol) in 14.0 mL of toluene was added a clear solution of phenylacetylene (29 μL, 0.26 mmol) in 14.0 mL of toluene at room temperature. Colorless crystals appeared after the solution was allowed to stand for 12 h. The solids were collected by filtration, washed with 7 mL of *n*-hexane, and dried in vacuo (0.28 g, 70%). ^{1}H NMR (500 MHz, thf-d_8, ppm): δ 7.80 (s, 4H, Ar*H*), 7.30 (s, 6H, Ar*H*), 7.22 (s, 12H, Ar*H*), 7.07 (s, 16H, Ar*H*), 6.99–6.96 (m, 16H, Ar*H* and Pyr*H*), 6.24 (s, 4H, Pyr*H*), 6.11 (s, 4H, Pyr*H*), 5.77 (s, 4H, Pyr*H*), 3.51 (s, 4H, thf), 2.37 (s, 6H, N*Me*), 1.66 (s, 4H, thf). ^{13}C NMR (125 MHz, thf-d_8, ppm): 149.8, 149.5, 146.5, 145.9, 142.4, 132.1, 131.3, 130.6, 130.0, 128.5, 128.0, 127.5, 126.2, 125.4, 108.8, 108.1, 105.8, 67.6 (thf), 58.3 (CPh$_2$), 36.3 (NCH$_3$), 25.7 (thf). Anal. Calcd for C$_{98}$H$_{80}$N$_6$OY$_2$·C$_6$H$_{14}$: C, 77.02; H, 5.84; N, 5.18. Found: C, 77.21; H, 5.58; N, 4.99%. IR (KBr pellets, cm^{-1}): ν 3084, 3057, 3030, 2956, 2871, 1955, 1901, 1819, 1776, 1595, 1553, 1490, 1443, 1414, 1392, 1320, 1298, 1231, 1222, 1184, 1115, 1094, 963, 907, 887, 851, 797, 759, 744, 703.

Synthesis of (LYb(μ-C≡CPh))$_2$ (5c). Following the same procedure as described above for the preparation of 5a, the reaction of 1c (0.23 g, 0.24 mmol) with phenylacetylene (27 μL, 0.24 mmol) afforded 5c as yellow crystals (0.23 g, 62%). Anal. Calcd for C$_{94}$H$_{72}$N$_6$Yb$_2$·C$_6$H$_{14}$: C, 69.91; H, 5.05; N, 4.89. Found: C, 69.54; H, 5.33; N, 4.53%. IR (KBr pellets, cm^{-1}): ν 3084, 3057, 3030, 2958, 2869, 1953, 1899, 1814, 1595, 1550, 1492, 1445, 1416, 1389, 1332, 1296, 1260, 1229, 1182, 1153, 1119, 1036, 963, 902, 887, 853, 795, 764, 744, 704.

Synthesis of (L(thf)[Y(μ-H)]$_2$L) (6a). The complex 5a (0.50 mg, 0.32 mmoL) was dissolved in hot toluene (15.0 mL). Next, triethoxysilane (60 μL, 0.32 mmoL) was added, and the reaction mixture was stirred at 90 °C for 6 h. The colorless solution was concentrated to ~10 mL and filtered, and then 5.0 mL of *n*-hexane was added to the clear solution. Colorless crystals appeared after the solution was allowed to stand at 0 °C for 12 h. The solids were collected by filtration, washed with 7.0 mL of cold *n*-hexane, and dried in vacuo (0.14 g, 30%). ^{1}H NMR (500 MHz, thf-d_8, ppm): δ 7.30 (s,

4H, Ar*H*), 7.24 (t, *J* = 7.5 Hz, 8H, Ar*H*), 7.11 (t, *J* = 7.5 Hz, 4H, Ar*H*), 6.99–6.92 (m, 12H, Ar*H*), 6.76 (d, *J* = 7.5 Hz, 8H, Ar*H*), 6.61 (s, 4H, Pyr*H*), 5.96 (t, $^1J_{Y-H}$ = 28.0 Hz, 2H, Y-*H*), 5.95–5.94 (m, 4H, Pyr*H*), 5.84 (s, 4H, Pyr*H*), 5.77 (t, *J* = 3.0 Hz, 4H, Pyr*H*), 3.47 (s, 4H, thf), 2.25 (s, 6H, N*Me*), 1.61 (s, 4H, thf). ^{13}C NMR (125 MHz, thf-d_8, ppm): 149.5, 149.3, 144.7, 144.2, 130.2, 128.2, 127.6, 126.8, 126.5, 124.9, 111.5, 109.3, 108.7, 67.6 (thf), 58.2 (CPh$_2$), 37.1 (NCH$_3$), 25.7 (thf). Anal. Calcd for C$_{82}$H$_{72}$N$_6$OY$_2$·C$_6$H$_{14}$: C, 74.36; H, 6.10; N, 5.91. Found: C, 74.10; H, 5.96; N, 5.63%. IR (KBr pellets, cm^{-1}): ν 3084, 3067, 3025, 2953, 2868, 2129, 1664, 1583, 1491, 1445, 1413, 1297, 1258, 1219, 1184, 1117, 1095, 1038, 983, 963, 885, 848,,798, 762, 745, 703, 563, 543, 486, 466.

Synthesis of (L(thf)[Yb(μ-H)]$_2$L) (6c). Following the same procedure as described above for the preparation of 6a, the reaction of 5c (0.51 mg, 0.30 mmoL) with triethoxysilane (55 μL, 0.30 mmoL) afforded 6c as pale yellow crystals (0.12 g, 32%). Anal. Calcd for C$_{82}$H$_{72}$N$_6$OYb$_2$·C$_6$H$_{14}$: C, 66.48; H, 5.45; N, 5.29. Found: C, 66.66; H, 5.52; N, 4.80%. IR (KBr pellets, cm^{-1}): ν 3100, 3057, 2954, 2870, 1956, 1899,1815,1597, 1553, 1491, 1445, 1322, 1297, 1231, 1217, 1184, 1157, 1117, 1094, 1038, 1002, 976, 963, 903, 798, 763, 745, 703, 652, 622, 544, 486.

Synthesis of (LYb(μ-OEt))$_2$(7c). To a clear brown solution of the complex 1c (0.30 g, 0.31 mmol) in 10.0 mL of toluene was added a clear colorless solution of triethoxysilane (57 μL, 0.31 mmol) in 5.0 mL of toluene. The color of the solution changed from brown to yellow quickly. Yellow crystals precipitated after the solution was allowed to stand for 12 h, and they were collected by filtration, washed with 5.0 mL of *n*-hexane, and dried in vacuo (0.42 g, 80%). Anal. Calcd for C$_{82}$H$_{72}$N$_6$O$_2$Yb$_2$·C$_6$H$_{14}$: C, 65.82; H, 5.40; N, 5.23. Found: C, 66.05; H, 5.16; N, 5.15%. IR (KBr pellets, cm^{-1}): ν 3084, 3057, 3025, 2955, 2924, 2856, 1956, 1895, 1814, 1654, 1597, 1552, 1491, 1444, 1413, 1389, 1321, 1296, 1259, 1231, 1184, 1150, 1115, 1094, 1038, 963, 903, 885, 797, 763, 744, 703, 622, 545, 484.

General Catalytic Procedures for the Dehydrogenative Coupling Reaction. In a glovebox, to a 15 mL Schlenk tube equipped with a magnetic stir bar was added the catalyst 1b (0.18 g, 0.20 mmol), toluene (2 mL), and the terminal alkyne (4.00 mmol) via syringe sequentially, and the resulting solution was stirred for 5 min before the addition of triethoxysilane (1.47 mL, 8.00 mmol). The sealed tube was taken out of the glovebox and heated at 150 °C for 34 h. After that, the mixture was cooled to room temperature. The reaction tube was uncapped carefully in a ventilated cabinet and stirred for 5 min to release the flammable gas SiH$_4$ in the case of triethoxysilane being employed in the reaction. An aliquot (30 μL) was taken out and diluted with hexane to 2 mL. After filtration, the aliquot was subjected to GC-MS analysis to determine the yield with mesitylene as an internal standard. Analytically pure samples of the products suitable for spectroscopic analysis were obtained by concentration of the reaction mixture under vacuum, and the residue was extracted with hexane (10.0 mL). The extraction was purified by fractional distillation under reduced pressure to give the product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01902.

Structures of complexes 1b–c; Crystallographic data of 1 and 5-7; Compounds data and ^{1}H and ^{13}C NMR spectra; CCDC: 1943681−1943683 (1b-c), 1943684 (5a), 2010984 (5c), 1943685−1943686 (6c and 7c) (PDF)

Accession Codes

CCDC 1943681−1943686 and 2010984 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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