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Active Low-Valent Niobium Catalysts from $NbCl_5$ and Hydrosilanes for Selective Intermolecular Cycloadditions

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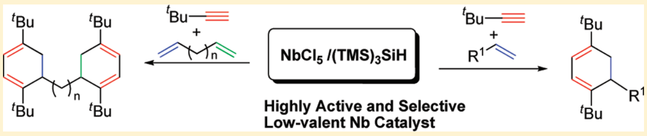
Supporting Information

ABSTRACT: An active niobium catalyst was developed via a simple and nontoxic reduction method from $NbCl_5$/hydrosilane and utilized for the selective [2 + 2 + 2] cycloaddition reaction of terminal alkynes and alkenes/α,ω-dienes, to give 1,3-cyclohexadiene derivatives in high yields with excellent chemo- and regioselectivity.



Low-valent early transition-metal-mediated or -catalyzed organic transformations are intriguing, owing to the inherent ability of these metals to act as reductants for the activation of unsaturated compounds.[1] To date, reactions with Ti(II),[2] Zr(II),[3] Ta(III),[4] and Nb(III)[5] have been intensively explored. Conventionally, these low-valent metals are prepared by reduction, using harsh reducing agents such as elemental metals (Na, Li, Zn), alkyllithiums, Grignard reagents, or $LiAlH_4$.[2−5] In general, these low-valent early transition metal species are thermally unstable, and their preparation and utilization need to be performed at low temperature, hampering their practicality for use in catalytic reactions. Therefore, the development of a method for the generation of thermally stable and catalytically active low-valent early transition metals using stable, safe, and nontoxic reducing agents under mild conditions is highly desirable.

In 1987, Pedersen and co-workers reported the preparation of $NbCl_3(DME)$, a thermally stable low-valent early transition-metal complex, by the treatment of $NbCl_5$ with Bu_3SnH in DME.[6] This complex is currently commercially available and has been utilized as both a reagent and a catalyst in organic transformations.[7] We recently reported the $NbCl_3(DME)$-catalyzed [2 + 2 + 2] cycloaddition reaction between alkynes and alkenes, leading to 1,3-cyclohexadiene derivatives.[8]

In addition, Mashima and co-workers recently reported that a catalytic system consisting of $TaCl_5$ with 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene, or its methyl derivative, in the presence of ethylene led to the ethylene trimerization product.[9]

In this paper, we wish to report a simple and nontoxic method for the generation of low-valent niobium species from $NbCl_5$, using hydrosilanes as reducing agents. This novel $NbCl_5$/hydrosilane catalyst system surpasses the existing $NbCl_3(DME)$ catalyst with regard to both catalytic activity and selectivity in the intermolecular [2 + 2 + 2] cycloadditions of alkynes and alkenes to give 1,3-cyclohexadiene derivatives.[8]

To examine the efficacy of the present Nb catalyst system, the reaction between *tert*-butylacetylene (**1**) and 1-decene (**2a**) was selected as a model reaction and carried out under various conditions (Table 1).

For instance, an active catalyst system, consisting of the salt-free reduction of $NbCl_5$ (0.2 mmol, 10 mol %) with tris(trimethylsilyl)silane ($(TMS)_3SiH$) (0.2 mmol, 10 mol %), in the presence of *tert*-butylacetylene (**1**) (2 mmol), 1-decene (**2a**) (2 mmol), and 1,2-dichloroethane (1 mL) at 40 °C for 3 h, produced 1,4-di-*tert*-butyl-5-octyl-1,3-cyclohexadiene (**3a**) exclusively in 90% yield with excellent chemo- and regioselectivity (Table 1, entry 1). The reaction led exclusively to **3a**, in preference to the formation of any tri-*tert*-butylbenzenes (**4a**), which are produced by the cyclotrimerization of alkynes[10] (**1**) (entry 1). It is noteworthy that when the reaction was performed in the absence of the hydrosilane, that is, with $NbCl_5$ solely, no **3a** formation was observed (entry 2), indicating that hydrosilane is a prerequisite for generating active catalyst. Furthermore, the reaction using the present catalytic system outperformed the conventionally used low-valent Nb complex, $NbCl_3(DME)$, in this transformation (entry 3). When the Ta analogue, $TaCl_5$, was used combined with $(TMS)_3SiH$ under these conditions, **3a** was not obtained at all, but **4a** was preferentially obtained in 54% yield (entry 4). Screening hydrosilanes showed that those bearing bulky substituents, such as $(TMS)_3SiH$ gave the best yields of **3a**. However, besides $(TMS)_3SiH$, a variety of hydrosilanes such as polymethylhydrosiloxane (PMHS), Et_3SiH, $(EtO)_3SiH$, $PhMeSiH_2$, $PhSiH_3$, $(Me_2SiH)_2O$, and $(Me_2SiH)_2NH$ were also good reducing agents for $NbCl_5$ (entries 5−11). The best yield for **3a** was obtained when the reaction between **1** and **2a** was carried out at a 1:1 ratio. However, even when **1** and **2a** were reacted in a stoichiometric ratio (namely, **1**:**2a** = 2:1), the yield for **3a** was still good (entry 12). The reaction is remarkably effective at low catalyst loading (2.5 mol %), giving **3a** in excellent yield (entry 13). The reaction is affected by the solvent employed; halogenated solvents, such as 1,2-dichloroethane, resulted in **3a** in high yield (entry 1). Benzene could also be employed as solvent in this reaction (entry 14). However, the use of 1,2-dimethoxyethane (DME) resulted in a decrease in catalytic activity, since the DME

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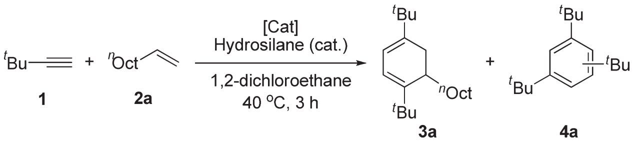
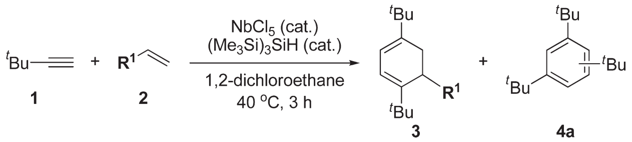
Table 1. $NbCl_5$/Hydrosilane Catalyzed Reaction of *tert*-Butylacetylene (1) and 1-Decene (2a) under Various Conditions[a]



entry	catalyst	hydrosilane	yield (%)[b] 3a (selectivity)[c]	4a
1	$NbCl_5$	$(TMS)_3SiH$	90 [88]	nd[d]
2	$NbCl_5$	none	nd[d]	e
3[f]	$NbCl_3(DME)$	none	61 (91:9)	14
4	$TaCl_5$	$(TMS)_3SiH$	nd[d]	54
5	$NbCl_5$	PMHS	74	8
6	$NbCl_5$	Et_3SiH	57 (88:12)	7
7	$NbCl_5$	$(EtO)_3SiH$	70 (53:47)	18
8	$NbCl_5$	$PhMeSiH_2$	60	trace
9	$NbCl_5$	$PhSiH_3$	58	4
10	$NbCl_5$	$(Me_2SiH)_2O$	84	trace
11	$NbCl_5$	$(Me_2SiH)_2NH$	56 (77:23)	trace
12[g]	$NbCl_5$	$(TMS)_3SiH$	73	nd[d]
13[h]	$NbCl_5$	$(TMS)_3SiH$	90	nd[d]
14[i]	$NbCl_5$	$(TMS)_3SiH$	53	nd[d]
15[j]	$NbCl_5$	$(TMS)_3SiH$	nd[d]	nd[d]

[a] Reaction conditions: **1** (2 mmol), **2a** (2 mmol), 1,2-dichloroethane (1 mL), $NbCl_5$ (0.2 mmol, 10 mol % based on **1**), and hydrosilane (0.2 mmol) at 40 °C for 3 h. [b] GC yields except the values in the square brackets. [c] The regioselectivity of 1,4,5-adducts was >99% unless otherwise noted. The numbers in the parentheses show the regioselectivity ratio (%) (1,4,5-adducts:1,3,5-adducts) determined by GC. [d] Not detected by GC. [e] Small amount (<5%) of a mixture of intractable products including **4a** was detected by GC. [f] Data from ref 8a. [g] **1** (2 mmol) and **2a** (1 mmol) were used. [h] Reaction conditions: **1** (4 mmol), **2a** (4 mmol), 1,2-dichloroethane (1 mL), $NbCl_5$ (0.1 mmol, 2.5 mol % based on **1**), and $(TMS)_3SiH$ (0.1 mmol) at 40 °C for 24 h. [i] Benzene (1 mL) was used as solvent. [j] 1,2-Dimethoxyethane (1 mL) was used as solvent.

Table 2. $NbCl_5$/$(TMS)_3SiH$ Catalyzed Reaction of 1 with Alkenes 2[a]



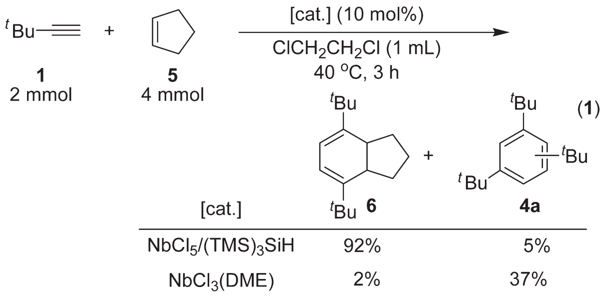
entry	2 (R^1)	yield (%) 3 (selectivity[b])	4a
1	n-C_4H_9 (**2b**)	88 (**3b**)	nd[c]
2	n-C_6H_{13} (**2c**)	93 (**3c**)	nd[c]
3	n-$C_{10}H_{21}$ (**2d**)	89 (**3d**)	nd[c]
4	$(CH_3)_2CHCH_2CH_2$ (**2e**)	77 (**3e**)	nd[c]
5	$PhCH_2$ (**2f**)	63[d] (**3f**)	10
6	$PhCH_2CH_2$ (**2g**)	49 (**3g**)	nd[c]
7	norbornene (**2h**)	99[e] (**3h**)	nd[c]

[a] Reaction conditions: **1** (2 mmol), **2** (2 mmol), 1,2-dichloroethane (1 mL), and $NbCl_5$ (0.2 mmol, 10 mol % based on **1** and $(TMS)_3SiH$ (0.2 mmol) at 40 °C for 3 h. [b] The regioselectivity of 1,4,5-adducts was >99% unless otherwise noted. [c] Not detected by GC. [d] A regioisomer mixture of 1,4,5- and 1,3,5-adducts in an 88:12 ratio. [e] *exo,exo*-Isomer was obtained exclusively.[11]

can coordinate to the Nb metal and form stable and catalytically inert, low-valent niobium species (vide infra) (entry 15) Under the optimized reaction conditions, as shown in Table 1, entry 1, the reaction of **1** with various alkenes (**2**) was examined (Table 2). Reactions using 1-alkenes (**2b**−**2d**) gave the corresponding 1,3-cyclohexadienes (**3b**−**3d**) in 88−93% yield, with excellent chemo- and regioselectivity. Similarly, 5-methyl-1-hexene (**2e**), allylbenzene (**2f**), 4-phenyl-1-butene (**2g**), and norbornene (**2h**) were allowed to react with **1**, affording the corresponding 1,3-cyclohexadiene derivatives (**3e**−**h**) in good yield (entries 4−7).

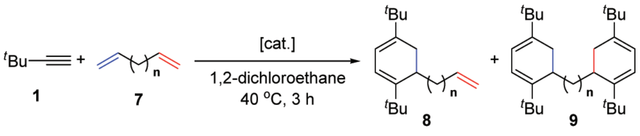
Here, to achieve the cross-cycloaddition of alkyne and alkene, bulky *tert*-butyl acetylene (**1**) is indispensable. Thus, the use of less bulky acetylenes such as 1-hexyne and cyclohexylacetylene exclusively lead to the alkyne cyclotrimerization products.[10]

In sharp contrast to the existing $NbCl_3(DME)$-catalyzed reaction, the present $NbCl_5$/$(TMS)_3SiH$ catalyst system successfully achieved the cycloaddition reaction between **1** and cyclopentene (**5**) (eq 1). Thus, when the $NbCl_5$/$(TMS)_3SiH$ catalyst system was used for the reaction, the desired cycloaddition product, 4,7-di-*tert*-butyl-2,3,3a,7a-tetrahydro-1*H*-indene (**6**),[12] was obtained in 92% yield, along with a small amount of **4a** (5%). However, $NbCl_3(DME)$ showed almost inert catalytic activity for the formation of **6**, and preferentially formed **4a** in 37% yield.



To further explore the synthetic scope and to obtain further information regarding the reactivity of this new catalyst system, the reaction of **1** with several α,ω-dienes (**7a**−**7c**) was examined (Table 3). The selectivity between the monocycloaddition product **8** and the dicycloaddition product **9** was controlled by the substrate ratio (**1**:**7**). Thus, when a reaction between **1** (2 mmol) and **7** (4 mmol) was carried out, only a single alkene within the α,ω-diene is subjected to reaction with **1**, and the corresponding 5-ω-alkenyl-1,3-cyclohexadiene (**8**) is obtained, exclusively (entries 1−3). An almost similar catalytic activity and selectivity are observed for $NbCl_5$/$(TMS)_3SiH$ (entries 1 and 2) and $NbCl_3$(DME) (entry 3). However, it is noteworthy that for the reaction of **1** (2 mmol) and **7** (0.5 mmol) using the $NbCl_5$/$(TMS)_3SiH$ catalyst system both alkene sides of the α,ω-diene react, leading to dicycloaddition products (**9a**−**c**), exclusively, in high yield (entries 4−6). No **9** was obtained at all using $NbCl_3(DME)$ as

Table 3. Nb-Catalyzed Reaction of 1) with α,ω,-dienes (7)[a]

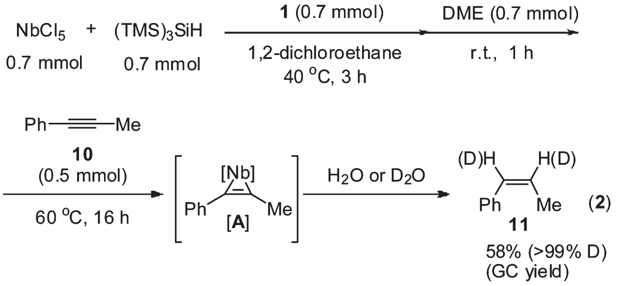


		7		yield (%)	
entry	[cat.]	*n*	**1**:7 (mmol)	**8** (selectivity)[b]	**9**
1	$NbCl_5/(TMS)_3SiH$	4	2:4	77(**8a**)	nd[c]
2	$NbCl_5/(TMS)_3SiH$	6	2:4	90(**8b**)	nd[c]
3[d]	$NbCl_3$(DME)	6	2:4	81(**8b**)[e]	nd[c]
4	$NbCl_5/(TMS)_3SiH$	4	2:0.5	trace	91(**9a**)
5	$NbCl_5/(TMS)_3SiH$	6	2:0.5	trace	79(**9b**)
6	$NbCl_5/(TMS)_3SiH$	8	2:0.5	trace	66(**9c**)
7[f]	$NbCl_3$(DME)	4	2:0.5	11(**8a**)[g]	nd[c]

[a] Reaction conditions: **1** (2 mmol), 7 (0.5−4 mmol), 1,2-dichloroethane (1 mL), $NbCl_5$ (0.2 mmol, 10 mol % based on **1**), and $(Me_3Si)_3SiH$ (0.2 mmol) at 40 °C for 3 h. [b] The regioselectivity of 1,4,5-adducts was >99% unless otherwise noted. [c] Not detected by GC. [d] Data from ref 8b. [e] A regioisomer mixture of 1,4,5- and 1,3,5-adducts in a 92:8 ratio. [f] In addition to the product **8a**, **4a** (27%) was formed. [g] A regioisomer mixture of 1,4,5- and 1,3,5-adducts in a 95:5 ratio.

catalyst. Instead, **8** formed in low yield (11%), along with the alkyne trimerization product **4a** (27%) (entry 7).

The low-valent niobium species appears critical to obtain efficient catalytic activity for the present transformation.[5,8] Indeed, no cycloaddition reaction between alkyne with alkene took place using $NbCl_5$ (Nb(V)) catalyst alone. On the other hand, it is reported that the low-valent niobium complex $NbCl_3$(DME) reacts with internal alkynes to form an Nb-alkyne complex, as confirmed by hydrolysis to give the *cis*-alkene.[6,7a,7b,7d] To obtain structural information regarding the catalytically active low-valent Nb species generated from $NbCl_5$ and $(TMS)_3SiH$, we initially carried out a complexation reaction between a mixture of $NbCl_5/(TMS)_3SiH$ and 1-phenyl-1-propyne (**10**), under the conditions reported for the above-mentioned preparation of the Nb-alkyne complex from $NbCl_3$(DME).[6,7] However, no Nb-alkyne species was verified by hydrolysis of the reaction mixture, and **10** was evidently converted during the reaction course to give an intractable mixture of oligomeric products. This implies that the Nb species generated between $NbCl_5$ and $(TMS)_3SiH$ are too reactive for the analysis of any Nb-alkyne species in a stable form. Indeed, all attempts to isolate or fully characterize the active Nb species have been unsuccessful. However, experimental confirmation for the formation of the low-valent Nb-alkyne complexes has been achieved by adding both **1** (1 equiv) and 1,2-dimethoxyethane (DME) (1 equiv) to a reaction mixture of $NbCl_5/(TMS)_3SiH$ and internal alkyne (eq 2). Thus, **1** (0.7 mmol) and 1,2-dichloroethane (1 mL) was added to a mixture of $NbCl_5$ (0.7 mmol) and $(TMS)_3SiH$ (0.7 mmol). The reaction mixture was stirred at 40 °C for 3 h. Subsequently, DME (0.7 mmol) and **10** (0.5 mmol) were added, and the mixture was stirred at 60 °C for 16 h. Thereafter, the formation of an Nb-alkyne complex was verified by hydrolysis or deuteriolysis of the reaction mixture, affording *cis*-1-phenyl-1-propene (**11**) in substantial yield (>99% D incorporated after deuteriolysis). In the $^{13}C\{^1H\}$ NMR spectrum for the reaction mixture of $NbCl_5/(TMS)_3SiH$/DME-**10**, after the addition of benzene-d_6 at 20 °C, alkyne carbon peaks assignable to the low-valent Nb-alkyne complex [**A**] appear at 236.7 and 255.6 ppm, which agrees with the reported values for the (DME)$NbCl_3$-**10** complex (237.5 and 256.2 ppm)[7a,b] (Figure S1 in Supporting Information). Therefore, the addition of DME to the present highly catalytic active low-valent niobium species would actually lower the activity, resulting in a stable low-valent Nb species, as found for $NbCl_3$(DME).[6,7]



Although it is not possible to confirm a detailed reaction mechanism, $NbCl_5$ could be reduced by $(TMS)_3SiH$ to form **A** (and $(TMS)_3SiCl$); presumably low-valent Nb species are generated, on the basis of the experimental data.[13] The reaction may then proceed via oxidative cyclometalation of the two terminal alkyne molecules (**1**) to give a niobacyclopentadiene intermediate. The subsequent reaction with an alkene would exclusively produce the desired cycloaddition product (Figure S2 in Supporting Information).[8,13]

In conclusion, we have developed an approach for generating low-valent Nb(III) species, via a salt-free reduction method from $NbCl_5$/hydrosilane. These species are active catalysts for the selective [2 + 2 + 2] cycloaddition reactions of terminal alkynes and alkenes, to give 1,3-cyclohexadiene derivatives in high yield. The catalyst system shows remarkable reactivity and selectivity toward the dicycloadditions of α,ω-dienes, as well as the cycloaddition of cyclopentene, with **1**, which could not be achieved using the conventional $NbCl_3$(DME) catalyst system.

■ EXPERIMENTAL SECTION

General. GLC analysis was performed with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). ^{1}H, ^{13}C, and ^{29}Si NMR were measured at 400, 100, and 78.7 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. The products were characterized by ^{1}H NMR, ^{13}C NMR, HMQC and HMBC. Compounds **3a**,[8a] **3b**,[8a] **3c**,[8a] **3f**,[8a] **3h**,[8a] **4a**,[8b] **8a**,[15] **8b**,[15] and **8c**[15] are known compounds and have been previously reported.

Typical Reaction Procedure for the Preparation of 3a (entry 1, Table 1). A mixture of *tert*-butylacetylene (**1a**) (164 mg, 2 mmol), 1-decene (**2a**) (281 mg, 2 mmol), $NbCl_5$ (54 mg, 0.2 mmol), tris(trimethylsilyl)silane (50 mg, 0.2 mmol), and 1,2-dichloroethane (1 mL) was stirred for 3 h at 40 °C under Ar. The yields of the products were estimated from the peak areas, based on the internal standard technique using GC, and **3a** was obtained in 90% yield. The product **3a** was isolated by silica gel column chromatography (*n*-hexane as eluent) in 88% yield (268 mg) a colorless liquid.

Synthesis of 6 from 1a and 5 Using the $NbCl_5/(TMS)_3SiH$ Catalyst System (eq 1). A mixture of *tert*-butylacetylene (**1**) (164 mg, 2 mmol), cyclopentene (**5**) (272 mg, 4 mmol), $NbCl_5$ (54 mg, 0.2 mmol), tris(trimethylsilyl)silane (50 mg, 0.2 mmol), and 1,2-dichloroethane (1 mL) was stirred for 3 h at 40 °C under Ar. The product **6** was isolated by silica gel column chromatography (*n*-hexane as eluent) in 92% yield (214 mg) as a colorless liquid.

Typical Reaction Procedure for the Preparation of 8a (Table 3, entry 1). A mixture of *tert*-butylacetylene (**1**) (164 mg, 2 mmol), 1,7-octadiene (**7a**) (441 mg, 4 mmol), $NbCl_5$ (54 mg, 0.2 mmol), tris(trimethylsilyl)silane (50 mg, 0.2 mmol), and 1,2-dichloroethane (1 mL) was stirred for 3 h at 40 °C under Ar. The product **8a** was isolated by silica gel column chromatography (*n*-hexane as eluent) in 77% yield (211 mg) as a colorless liquid.

Typical Reaction Procedure for the Preparation of 9a (Table 3, entry 4). A mixture of *tert*-butylacetylene (**1**) (164 mg, 2 mmol), 1,7-octadiene (**7a**) (55 mg, 0.5 mmol), $NbCl_5$ (54 mg, 0.2 mmol), tris(trimethylsilyl)silane (50 mg, 0.2 mmol), and 1,2-dichloroethane (1 mL) was stirred for 3 h at 40 °C under Ar. The product **9a** was isolated by silica gel column chromatography (*n*-hexane as eluent) in 91% yield (199 mg) as a colorless liquid.

Reaction of $NbCl_5$/(TMS)$_3$SiH with 10 (eq 2). A solution of $NbCl_5$ (189 mg, 0.7 mmol), $(TMS)_3SiH$ (174 mg, 0.7 mmol), and *tert*-butylacetylene (**1**) (57 mg, 0.7 mmol) in 1,2-dichloroethane (1 mL) was stirred for 3 h at 40 °C under Ar. Subsequently, 1,2-dimethoxyethane (DME) (63 mg, 0.7 mmol) was added to the reaction mixture and stirred for 1 h at room temperature under Ar. Then, 1-phenyl-1-propyne (**10**) (58 mg, 0.5 mmol) was added to the reaction mixture and stirred for 16 h at 60 °C under Ar. The yields of the products were estimated from the peak areas based on the internal standard technique using GC, and **11** was obtained in 58% yield. In the $^{13}C\{^1H\}$ NMR spectrum for the reaction mixture of $NbCl_5$/$(TMS)_3SiH$/DME-**10** inbenzene-d_6 at 20 °C, alkyne carbon peaks assignable to the low-valent Nb-alkyne complex [**A**] appeared at 236.7 and 255.6 ppm, which agrees with the reported values for the $NbCl_3$(DME)-**10** complex (237.5 and 256.2 ppm). The ^{13}C NMR spectrum is shown in Figure S1 in Supporting Information.

3d: colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 5.7 Hz, 3H), 0.97 (s, 9H), 1.06−1.25 (m, 18H), 1.32 (s, 9H), 2.01−2.27 (m, 2H), 2.23, (d, J = 15 Hz 1H), 5.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 27.6 (CH_2), 28.2 (CH_2), 28.3 (CH_2), 28.5 (CH_3), 29.4 (CH_2), 29.6 (CH_3), 29.65 (CH_2), 29.68 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 31.9 (CH_2), 33.3 (CH), 35.0 (C), 35.6 (C), 115.4 (CH), 115.6 (CH) 143.6 (C), 150.2 (C) ; IR (neat, cm^{-1}) 3065, 2924, 1647, 1597, 1465, 1359, 835; GC−MS (EI) m/z (relative intensity) 332 (6) [M^+], 277 (11), 221 (3), 191 (3), 137 (2), 91 (3), 79 (2), 57 (100), 41 (8); HRMS (EI) m/z calcd for $C_{24}H_{44}$ $[M]^+$ 332.3443, found 332.3450.

3e: colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 0.63−0.67 (m, 6H), 0.86 (s, 9H), 0.90 (s, 9H), 1.16−1.36 (m, 4H), 1.83−1.90 (m, 1H), 2.10,2.14 (m, 3H), 5.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 25.9 (CH_2), 28.3 (CH_2), 28.4 (CH_3), 28.5 (CH), 29.6 (CH_3), 33.9 (CH), 35.0 (C), 35.6 (C), 37.2 (CH_2), 115.3 (CH), 115.6 (CH), 143.7 (C), 150.2 (C); IR (neat, cm^{-1}) 3055, 2955, 1645, 1597, 1466, 1367, 1265, 837; GC−MS (EI) m/z (relative intensity) 262 (14) [M^+], 247 (2), 191 (2), 135 (2), 79 (2), 57(100), 43(4). HRMS (EI) m/z calcd for $C_{19}H_{34}$ $[M]^+$ 262.2661, found 262.2663.

3g: colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H), 1.03 (s, 9H), 1.79−1.86 (m, 2H), 2.08−2.41 (m, 2H), 2.34 (d, J = 15.2 Hz 1H), 2.62 (t, J = 7.1 Hz, 2H), 5.62 (s, 2H), 7.05−7.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (CH_2), 28.6 (CH_3), 29.5 (CH_3), 30.4 (CH_2), 32.8 (CH), 34.0 (CH_2), 35.0 (C), 35.6 (C), 115.8 (2CH), 125.6 (CH), 128.2 (CH), 128.4 (CH), 142.6 (C), 143.4 (C), 149.6 (C); IR (cm^{-1}) 3018, 2964, 2041, 1602, 1463, 1367, 1217, 1029, 929, 725; GC−MS (EI) m/z (relative intensity) 296 (13) [M^+], 192 (2), 135 (2), 105 (7), 91 (12), 77(2), 57(100), 41(12). Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.84; H, 10.94.

6: colorless liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 18H), 1.24−1.86 (m, 6H), 2.51−2.56. (m, 2H), 5.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (CH_2), 30.3 (CH_3), 33.5 (CH_2), 35.6 (C), 42.8 (CH), 116.1 (CH), 147.1 (C); IR (cm^{-1}) 3057, 2951, 1463, 1360, 1248, 1198, 851; GC−MS (EI) m/z (relative intensity) 232 (19) [M^+], 217 (18), 175 (17), 119 (15), 79 (3), 57 (100), 41 (17). HRMS (EI) m/z calcd for $C_{17}H_{28}$ $[M]^+$ 232.2191, found 232.2200

9a: white solid, mp 65−67 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 18H), 0.89 (s,18H), 1.10−1.19 (m, 8H), 1.84−2.12 (m, 6H), 5.49 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3 (CH_2), 28.5 (CH_3), 29.6 (CH_3), 31.6 (CH_2), 33.0 (CH), 33.51 (CH_2), 35.0 (C), 35.6 (C), 115.45 (CH), 115.53 (CH), 143.5 (C), 150.5 (C); IR (KBr, neat, cm^{-1}) 3057, 2964, 1645, 1463, 1360, 1265, 833; GC−MS (EI) m/z (relative intensity) 438 (5) [M^+], 382 (4), 248 (2), 218 (2), 192 (30), 79 (2), 57 (100), 41(22). HRMS (EI) m/z calcd for $C_{32}H_{54}$ $[M]^+$ 438.4226, found 438.4222.

9b: white solid, mp 76−78 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 18H), 0.95 (s, 18H), 1.11−1.20 (m, 8H), 1.30−1.42 (m, 4H), 1.90−2.20 (m, 6H), 5.55 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 28.5 (CH_3), 29.6 (CH_3), 31.6 (CH_2), 33.3 (CH), 35.0 (C), 35.6 (C), 115.4 (CH), 115.6 (CH), 143.5 (C), 150.2 (C); IR (KBr, neat, cm^{-1}) 3053, 2964, 1647, 1597, 1463, 1359, 1265, 1198, 837; GC−MS (EI) m/z (relative intensity) 466 (5) [M^+], 353 (1), 207 (1), 175 (4), 131 (1), 91 (2), 57 (100), 41 (6). HRMS (EI) m/z calcd for $C_{34}H_{58}$ $[M]^+$ 466.4539, found 466.4529.

9c: white solid, mp 85−88 °C.^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 18H), 0.96 (s, 18H), 1.11−1.49 (m, 16H), 1.90−2.20 (m, 6H), 5.55 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 28.5 (CH_3), 29.6 (CH_3), 29.8 (CH_2), 31.6 (CH_2), 33.2 (CH), 35.0 (C), 35.6 (C), 115.3 (CH), 115.5 (CH), 143.6 (C), 150.2 (C); IR (KBr, neat, cm^{-1}) 2964, 2853, 2368, 1473, 1359, 1265, 1195, 835; GC−MS (EI) m/z (relative intensity) 494 (4) $[M]^+$, 437 (1), 381 (2), 191 (1), 175 (4), 91 (2), 57 (100), 41 (5). HRMS (EI) m/z calcd for $C_{36}H_{62}$ $[M]^+$ 494.4852, found 494.4874.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Figures S1 and S2. ^1H, ^{13}C, HMQC, and HMBC NMR spectra for products **3a**−**3h**, **6**, **8a**−**8b**, and **9a**−**9c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The stereochemistry of **6** was not determined.

(13) The ^{29}Si NMR(DEPT) measurement of the reaction mixture of $NbCl_5$ and $(TMS)_3SiH$ showed peaks at −11.3 and −13.4 ppm assignable to $(TMS)_3SiCl$, as well as −83.2 and −12.5 ppm (lit.:[14] −85.2 and −12.9 ppm) assignable to t-BuCH=CH$(TMS)_3$ (**12**). Although the role of the bulky substituent on hydrosilane (such as $(TMS)_3SiH$) in the present catalytic system is unclear at present, the **12** may coordinate with the Nb center, increasing the effectiveness of the catalysis.

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