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Cobalt-Catalyzed Cross Addition of Silylacetylenes to Internal Alkynes

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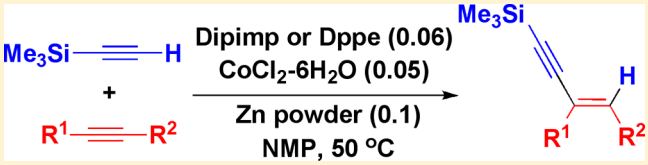
Supporting Information

ABSTRACT: A $CoCl_2 \cdot 6H_2O$/Zn reagent using 2-(2,6-diisopropylphenyl)iminomethylpyridine (dipimp), 1,2-bis(diphenylphosphino)ethane (dppe), or 1,2-bis(diphenylphosphino)benzene (dppPh) as a ligand effectively catalyzed the cross-addition reaction of silylacetylene to internal alkynes. The reaction of some unsymmetrical internal alkynes, such as 3-arylpropargyl alcohols, proceeded in a highly regioselective manner in the presence of dppe or dppPh but gave a nearly 1:1 mixture of regioisomers in the presence of dipimp. The results of reactions using 1-deuterated 2-silylacetylene revealed that the reaction involves a direct oxidative addition of the silylacetylenic C−H bond to cobalt.



INTRODUCTION

Hydroalkynylation of alkynes is a straightforward, atom-economical way to access conjugated enynes, which are versatile as the main structures or substructures of organic materials and biologically important molecules and as synthetic intermediates.[1]

Although the catalytic homodimerization of terminal alkynes has been extensively studied,[2] the cross addition of terminal alkynes to internal alkynes is rather difficult because of competitive homodimerization and oligomerization. Successful cross addition of terminal alkynes to activated internal alkynes bearing an electron-withdrawing group has been developed using palladium,[3] rhodium,[4] iridium,[5] ruthenium,[6] titanium,[7] and uranium[8] catalysts. Alkyne addition to unactivated internal alkynes is not easy and has been relatively less studied. However, some successful examples using this process with terminal silylacetylenes have recently been reported using nickel,[9] ruthenium,[10] rhodium,[11] iridium,[12] and palladium[13] catalysts. Most of these reactions, other than a few exceptions,[9b,c,10] used silylacetylenes with a bulky silyl group, such as $SiMe_2(t\text{-Bu})$, $Si(i\text{-Pr})_3$, and $SiPh_3$, for minimizing the competitive dimerization of the silylacetylene.

In the course of our study on cyclotrimerization reactions of alkynes,[14] we initially found that a 2-(2,6-diisopropylphenyl)-iminomethylpyridine (dipimp)/$CoCl_2 \cdot 6H_2O$/Zn catalyst (for the structure of dipimp, see Figure 1) converted a mixture of trimethylsilylacetylene (**1a**) and diphenylacetylene (**2a**) to the hydroalkynylated product **3aa** (99% *E*) in good yield without any cyclotrimerization products (Scheme 1, R = Me, R′ = Ph). Herein we report the development of the first cobalt-catalyzed cross addition of terminal alkynes to internal alkynes,[15−17] in which **1a** is used as the substrate.

RESULTS AND DISCUSSION

On the basis of the initial results mentioned above, we first optimized the catalyst system and reaction conditions by reacting **1a** or triisopropylacetylene (**1b**) with **2a** or 3-phenyl-2-propyn-1-ol (**2b**) in *N*-methylpyrrolidone (NMP) as benchmark reactions (Scheme 1 and Table 1).

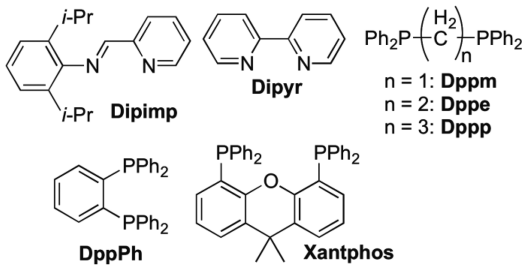


Figure 1. Structures of ligands.

The substrates were recovered when ligands were not used (Table 1, run 1). When dipimp was used as a ligand, (3:1)−(1:3) mixtures of **1a** and **2a** yielded hydroalkynylated product **3aa** in good yield (>84%) with >97% *E* geometric purity (runs 2−5). The use of a slight excess of silylacetylene (1.3 equiv) was thereafter treated as a standard condition. Similarly, **1b** smoothly reacted with **2a** to afford 86% yield of **3ba** but with somewhat reduced geometric purity (run 6).

In the reaction of diarylacetylene **2a**, other ligands, such as 2,2′-bipyridyl, triphenylphosphine, xantphos, 1,2-bis(diphenylphosphino)ethane (dppe), and 1,3-bis(diphenylphosphino)propane (dppp), resulted in comparably low yields (runs 7−11). Reactions with a diphosphine ligand often involved geometric isomerization (runs 8, 9, and 11).

For the reaction of **1** and unsymmetrical internal alkyne **2b**, which may result in the formation of the two regioisomers **3** and **4**, reactions using various ligands were explored (runs 12−19). Catalysis with dipimp, dppe, or dppPh proceeded smoothly and

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Scheme 1. Addition of Silylacetylenes to Diphenylacetylene and 3-Phenylprop-2-yn-1-ol

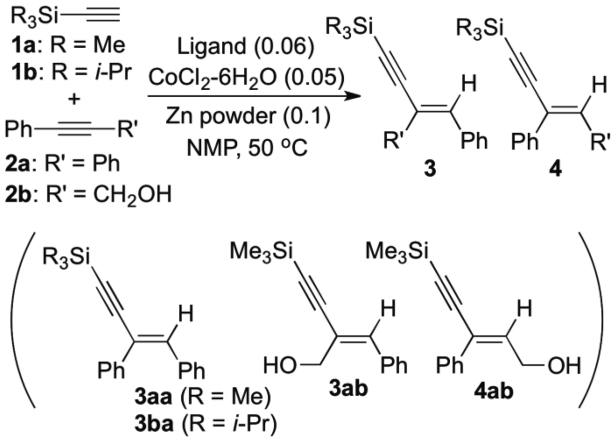


Table 1. Optimization of the Addition of Silylacetylenes to Diphenylacetylene and 3-Phenylprop-2-yn-1-ol[a]

run	ligand[b]	substrate	1:2	3:4[c] (% *E* or *Z* of 3)[c]	total yield, %[d]
1		**1a** + **2a**	1.3:1		trace
2	dipimp	**1a** + **2a**	1:3	(99 *E*)	84[e]
3	dipimp	**1a** + **2a**	1:1.3	(97 *E*)	90[e]
4	dipimp	**1a** + **2a**	1.3:1	(>99 *E*)	99
5	dipimp	**1a** + **2a**	3:1	(98 *E*)	89
6	dipimp	**1b** + **2a**	1.3:1	(92 *E*)	86
7	dipyr	**1b** + **2a**	1.3:1	(96 *E*)	58
8	dppe	**1b** + **2a**	1.3:1	(14 *E*)	50
9	dppp	**1b** + **2a**	1.3:1	(75 *E*)	9
10	2 PPh_3	**1b** + **2a**	1.3:1	(>99 *E*)	6
11	xantphos	**1a**, **2a**	1.3:1	(2 *E*)	67
12	dipimp	**1a** + **2b**	1.3:1	52:48 (>99 *Z*)	99
13	dipyr	**1a** + **2b**	1.3:1	62:38 (>99 *Z*)	26
14	dppm	**1a** + **2b**	1.3:1	>99:1 (>99 *Z*)	15
15	dppe	**1a** + **2b**	1.3:1	96:4 (>99 *Z*)	90
16	dppp	**1a** + **2b**	1.3:1	75:15 (>99 *Z*)	9
17	dppPh	**1a** + **2b**	1.3:1	>99:1 (>99 *Z*)	95
18	xantphos	**1a** + **2b**	1.3:1	>99:1 (>99 *Z*)	6
19	2 PPh_3	**1b** + **2b**	1.3:1		trace

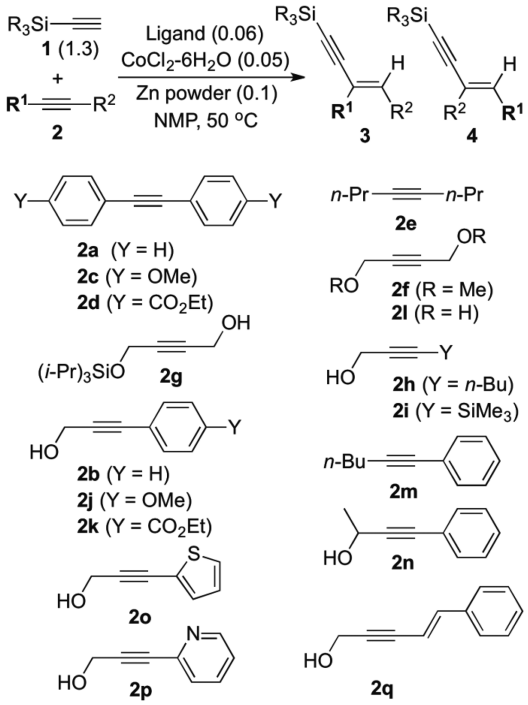
[a]Conditions: **1** (0.50−0.65 mmol), **2** (0.50−3 mmol), $CoCl_2·6H_2O$ (5 mol %), ligand (6 mol %), zinc powder (10 mol %), NMP (2.0 mL), 50 °C, 24 h. [b]See Figure 1 for the ligand structures. [c]Determined by ^1H NMR analysis. [d]Unless otherwise stated, the total yield of **3** and **4** is based on **2**; determined by ^1H NMR analysis using an internal standard. [e]Yield based on **1a**.

quantitatively provided geometrically pure **3ab** and **4ab** (runs 12, 15, and 17). The reactions with dppe and 1,2-bis(diphenylphosphino)benzene (dppPh) showed high regioselectivity, giving (*Z*)-2-benzylidene-4-(trimethylsilyl)but-3-yn-1-ol (**3ab**) (runs 15 and 17); however, a nearly 1:1 mixture of **3ab** and **4ab** was obtained from the reaction with dipimp (run 12).

With these results in hand, we selected the dipimp/$CoCl_2·6H_2O$/Zn, dppe/$CoCl_2·6H_2O$/Zn, and dppPh/$CoCl_2·6H_2O$/Zn catalysts for further exploration of reactions with other representative substrates **2**, as illustrated in Scheme 2.

The results of the reactions of various internal acetylenes **2** using dipimp as a ligand (Scheme 2) are summarized in Table 2. The reactions of **2a** (run 1) and diarylacetylenes with electron-donating and -withdrawing groups (runs 2 and 3, respectively)

Scheme 2. Substrates for Cobalt-Catalyzed Hydroalkynylation



provided the corresponding hydroalkynylated products in good yields and with high geometric purity. The reactions of aliphatic alkynes **2e** and **2h** did not proceed as silylacetylene **1a** was mainly consumed through dimerization[18a] (runs 4 and 8). However, the product **3af** was quantitatively obtained from 1,4-dimethoxybut-2-yne (**2f**), presumably because of the coordinating effect and/or electronic (−I) effect of its propargylic oxygen(s) (run 5). The catalyst loading could be reduced to 2 mol % without any loss of activity (run 6). As shown in runs 9−11, unsymmetrical internal alkynes **2**, bearing an aromatic or silyl substituent, smoothly reacted with **1a** to afford a nearly 1:1 mixture of regioisomers **3** and **4**.

Next, reactions using dppe or dppPh as the ligand were studied, and the results are shown in Table 3 (Scheme 2). Similar to the case for the dipimp/cobalt catalyst, dppe/$CoCl_2·6H_2O$/Zn did not catalyze the reaction of aliphatic internal alkynes **2e** and **2h** (runs 1 and 2),[18b] but 2-butyn-1,4-diol derivatives **2f**, **2l**, and **2g** were smoothly converted to **3af**, **3al**, and **3ag**, respectively, again presumably owing to their coordinating effect and/or the electronic (−I) effect of the oxygen atom (runs 3−7). Reducing the catalyst loading to 2 mol % was possible without any loss of activity (run 4). Aromatic substitution in the internal alkyne promoted the reaction, affording the corresponding adduct(s) in moderate to good yields (runs 8−16). In clear contrast to the reaction with dipimp, the reactions of 3-aryl-2-propyn-1-ols **2j** and **2k** with dppe or dppPh produced the highly predominant regioisomer **3** (runs 8−10). The results of the reactions with substrates bearing an electron-donating or -withdrawing group at the para position of the benzene ring indicate that the electronic nature of the alkynes may affect the regioselectivity. The reactions of phenylbutylacetylene (**2m**) and secondary propargylic alcohol **2n** were slow and gave a mixture of **3** and **4**, respectively, in low yields with moderate regioselectivity (runs 11−14). The use of a 1:3 mixture of **1a** and **2n** as substrates did not improve the yield (run 13). The use of dppPh as a ligand instead of dppe promoted selective formation of **3an** but still in low yield (run 14). However, in addition to phenyl-substituted **2**,

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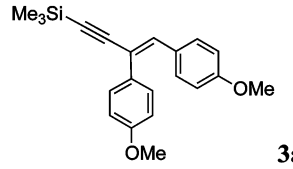
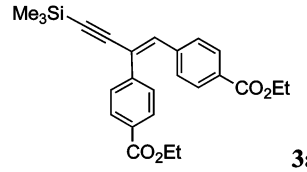
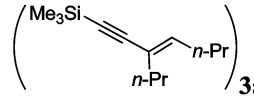
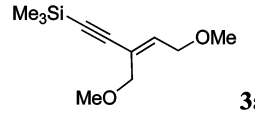
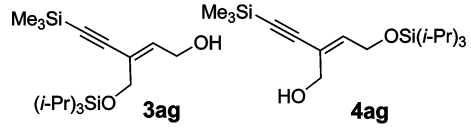
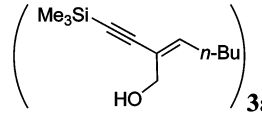
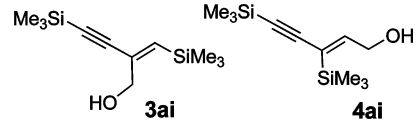
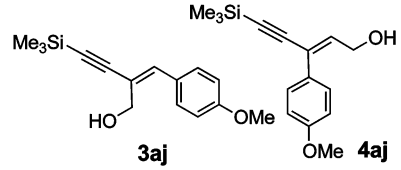
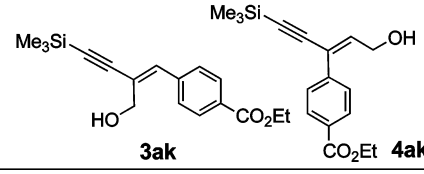
Table 2. dipimp/Cobalt-Catalyzed Hydroalkynylation[a]

Run	2	Product(s)	3:4[b] (*E* or *Z*% of 3)[b]	Total Yield[c]
1	2a	3aa	– (>99%*E*)	98%
2	2c	 3ac	– (91%*E*)	80%
3	2d	 3ad	– (89%*E*)	77%
4	2e	 3ae	– (–)	trace
5	2f	 3af	– (>99%*Z*)	98%
6[d]	2f	3af	– (>99%*Z*)	98%
7	2g	 3ag 4ag	57:43 (>99%*Z*)	26%
8	2h	 3ah	– (–)	trace
9	2i	 3ai 4ai	50:50 (>99%*Z*)	40%
10	2j	 3aj 4aj	45:55 (>99% *Z*)	61%
11	2k	 3ak 4ak	53:47 (>99% *Z*)	70%

[a]Conditions: **1a** (0.65 mmol), **2** (0.50 mmol), $CoCl_2·6H_2O$ (5 mol %), ligand (6 mol %), zinc powder (10 mol %), NMP (2.0 mL), 50 °C, 24 h. [b]Determined by ^1H NMR analysis. [c]Total yield of **3** and **4**. [d]2 mol % of $CoCl_2·6H_2O$ and 2.4 mol % of dipimp were used.

heteroaryl- and alkenyl-substituted propargylic alcohols **2o**, **2p**, and **2q** were exclusively converted to the corresponding **3** in good yields (runs 15–17).

The results depicted in Scheme 3 demonstrate the application of the method to double cross-addition reactions. The reaction of 3,3′-(1,4-phenylene)bis(prop-2-yn-1-ol) (**2r**)

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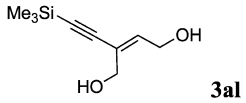
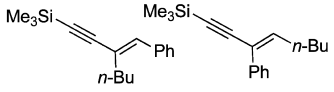
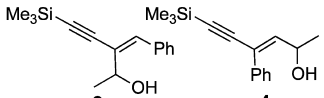
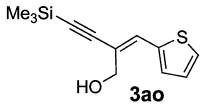
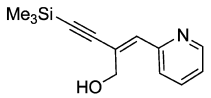
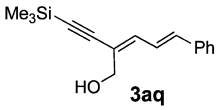
Table 3. (dppe or dppPh)/Cobalt-Catalyzed Hydroalkynylation[a]

Run	2	Product(s)	3:4[b] (*E* or *Z*% of 3)[b]	Yield[c]
1	**2e**	**3ae**	– (–)	trace
2	**2h**	**3ah**	– (–)	trace
3	**2f**	**3af**	– (>99%*Z*)	98%
4[d]	**2f**	**3af**	– (>99%*Z*)	98%
5	**2l**	 **3al**	– (>99% *Z*)	98%
6	**2g**	**3ag** + **4ag**	60:40 (>99%*Z*)	74%
7[e]	**2g**	**3ag** + **4ag**	51:49 (>99% *Z*)	79%
8	**2j**	**3aj** + **4aj**	90:10 (>99% *Z*)	69%
9[e]	**2j**	**3aj** + **4aj**	>99:1 (>99% *Z*)	72%
10	**2k**	**3ak** + **4ak**	>99:1 (>99% *Z*)	98%
11	**2m**	 **3am** **4am**	62:38 (>99% *E*)	35%
12	**2n**	 **3an** **4an**	70:30 (>99% *Z*)	33%
13[f]	**2n**	**3an** + **4 an**	80:20 (>99% *Z*)	32%[g]
14[e]	**2n**	**3an** + **4 an**	>99:1 (>99% *Z*)	18%
15	**2o**	 **3ao**	>99:1 (>99% *Z*)	62%
16	**2p**	 **3ap**	>99:1 (>99% *Z*)	63%
17	**2q**	 **3aq**	>99:1 (>99% *Z*,*E*)	50%

[a]Conditions: **1a** (0.65 mmol), **2** (0.50 mmol), $CoCl_2 \cdot 6H_2O$ (5 mol %), ligand (6 mol %), zinc powder (10 mol %), NMP (2.0 mL), 50 °C, 24 h. [b]Determined by ^1H NMR analysis. [c]Total yield of **3** and **4**. [d]2 mol % of $CoCl_2 \cdot 6H_2O$ and 2.4 mol % of dipimp were used. [e]dppPh was employed as a ligand instead of dppe. [f]A 1:3 mixture of **1a** and **2** was employed. [g]Yields were based on **1a**.

with silylacetylene gave the corresponding bis-enyne compound **3ar** in 68% yield.

Next, reactions with deuterated silylacetylenes using anhydrous $CoCl_2$ were investigated, and the results are illustrated in Scheme 4. Using dipimp as the ligand, the deuterated silylacetylene d-**1b** (>98% D) reacted with **2f** to afford **3bf** (87% isolated yield) with complete deuterium incorporation (>98% D) at the olefinic position. Similar results were obtained using dppe as the ligand instead of dipimp. The reaction of a 1:1 mixture of d-**1b** (0.5 mmol) and **1a** (0.5 mmol) with 1.3 mmol of **2f** produced **3bf** and **3af** in 99% and 98% yields, respectively. The resulting **3bf** showed complete deuterium incorporation, but **3af** was not deuterated at all. The reaction was, therefore, found to be an evident *hydroalkynylation* reaction, in which the olefinic hydrogen in the product comes from silylacetylene, without any scrambling of the hydrogen atoms.[19] Therefore, we suggest that the reaction does not involve a deprotonation/metalation of silylacetylenes **1** and that the C–H cleavage of **1** and formation of the new C–H and C–C bonds must occur on a single metal center of the catalyst.

To investigate the reaction with terminal acetylene substrates other than silylacetylenes (Figure 2), we next performed the reaction of 1-hexyne (**1c**) or 2-methylbut-3-yn-2-ol (**1d**) with

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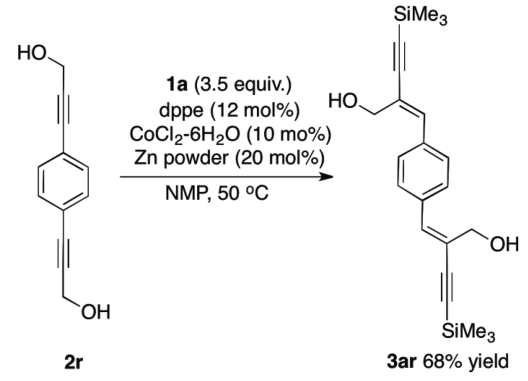
Scheme 3. Double Addition Reaction



Scheme 4. Results of the Reactions with Deuterated Substrates

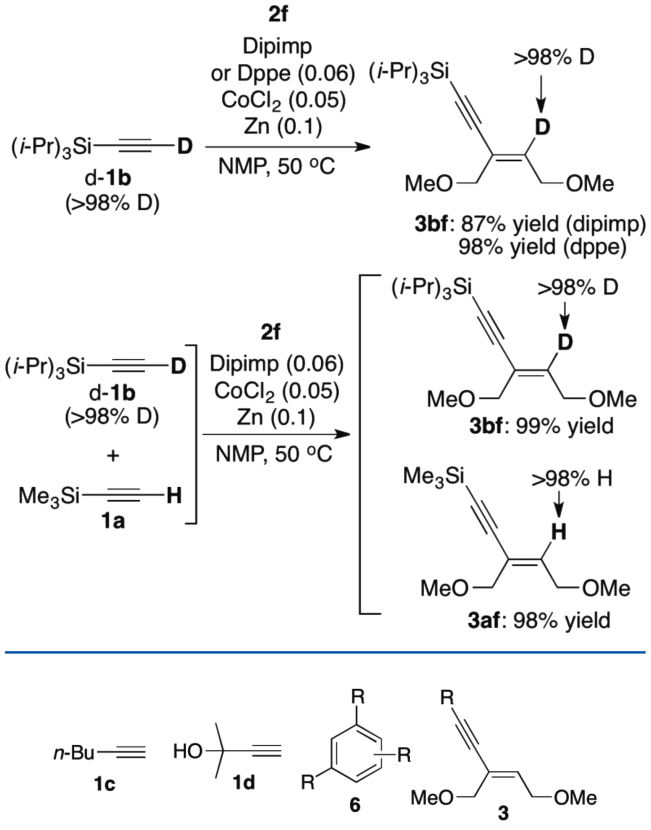
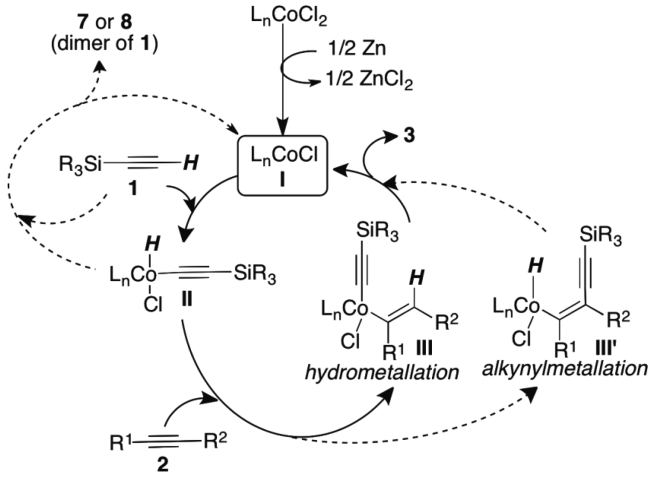


Figure 2. Alkynes other than silylacetylenes.

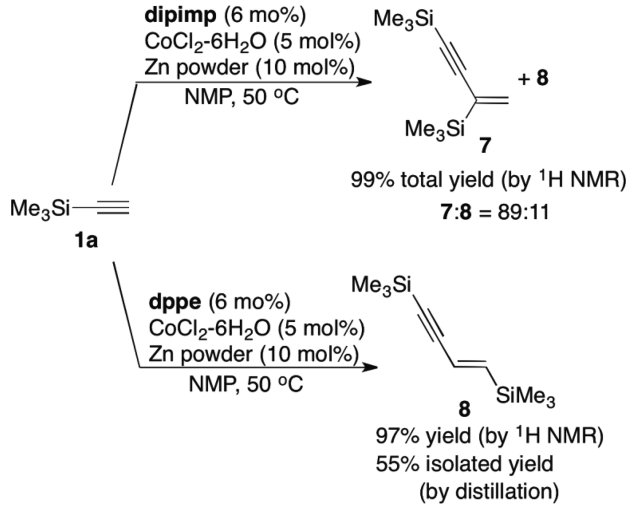
2f in the presence of (dipimip or dppe)/$CoCl_2 \cdot 6H_2O$/Zn in NMP. None of these reactions afforded the corresponding adduct **3**. The reaction of **1c** yielded homocyclotrimerization product(s) **6c**, while no reaction proceeded with alkyne **1d**.

On the basis of these observations, we postulate two possible mechanisms (Scheme 5) for the reaction. As described for other metal catayst,[9−13] cobalt(I) species **I**, generated by reduction of L_nCoCl_2 (L = ligand) with Zn powder, can undergo an oxidative addition reaction with silylacetylenes to generate the alkynylcobalt hydride complexes **II**, followed by a hydrometalation reaction with internal alkynes, giving **III**, the reductive elimination of which produces products **3** and regenerates **I**. Alternatively, **3** can be produced by the reductive elimination of alkenyl hydride complex **III′**, which would be generated via

Scheme 5. Proposed Reaction Mechanism



Scheme 6. Reactions of 1a with a (dipimp or dppe)/$CoCl_2 \cdot 6H_2O$/Zn Catalyst



alkynylmetalation of **II** with the internal alkyne. The results in the tables indicate that the reactivity order of internal alkynes is [ArC≡CAr, ArC≡CCH_2OR, $ROCH_2C{\equiv}CCH_2OR$] > [ArC≡C(alkyl), $Me_3SiC{\equiv}CCH_2OR$] ≫ [(alkyl)C≡C(alkyl), (alkyl)C≡CCH_2OR] for both dipimp/cobalt and dppe/cobalt catalysts and that electrondeficient, less hindered alkynes are more reactive. In the reactions of propargyl alcohols or ethers, coordination by the propargylic oxygen did not affect either the reactivity or the regioselectivity, and the CH_2OR moiety acts as an electron-withdrawing group (−I effect). The difference in steric bulk between the two substituents of the internal alkynes may determine the regioselectivity, and the selectivity was higher in the reactions with dppe or dppPh than in those with dipimp, because dppe and dppPh are more sterically demanding than dipimp.

Although the reactions in the desired catalytic cycle, **I** → **II** → **III** (or **III′**) → **I**, compete with the formation of a silylacetylene dimer(s)[2] via the common intermediate **II**, the reaction rate for the formation of **3** is reasonably faster than that for dimerization of the silylacetylene, although the dimer of the silylacetylene was obtained as a byproduct in each reaction. Interestingly, the coproduced dimer from the dipimp/cobalt system was 2,4-bis(trimethylsilyl)but-1-en-3-yne (**7**), while the dimer obtained

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from the dppe/cobalt system was (*E*)-1,4- bis(trimethylsilyl)but-1-en-3-yne (**8**). As shown in Scheme 6, treatment of **1a** with dipimp/$CoCl_2$·$6H_2O$/Zn or dppe/$CoCl_2$·$6H_2O$/Zn selectively produces **7**[20] and **8**,[21] respectively.

CONCLUSION

In summary, we found that a $CoCl_2$·$6H_2O$/Zn reagent catalyzes addition of trimethylsilylacetylene or triisopropylsilylacetylene to internal alkynes in the presence of a dipimp or 1,2-diphosphine (dppe or dppPh) ligand to afford the corresponding but-1-en-3-yne derivatives with high geometric purity. Some unsymmetrical internal alkynes, such as 3-aryl- and 3-alkenylpropargyl alcohols, were converted to the adduct with high regioselectivity in the presence of dppe or dppPh. To the best of our knowledge, this reaction is the first demonstration of the cobalt-catalyzed hydroalkynylation of internal alkynes.

EXPERIMENTAL SECTION

General Considerations. NMR spectra were recorded with use of a solution in $CDCl_3$ at 600, 500, and 270 MHz for ^{1}H and 150 and 125 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00) or residual $CHCl_3$ (δ 7.26 for ^{1}H NMR) and $CDCl_3$ (δ 77.0 for ^{13}C NMR). IR spectra were recorded on an FT-IR spectrometer. High-resolution mass spectra (HR-MS) were measured on a TOF-MS equipped with an ESI ionization unit. All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. All of the other commercially obtained chemicals, unless otherwise indicated, were used as received. 2-(2,6-Diisopropylphenyliminomethyl)pyridine (dipimp) was prepared from pyridine-2-carboxaldehyde and 2,6-diisopropylaniline by the reported procedure.[22] Compounds **1a**, **1b**, **2a**, **2b**, **2e**, **2f**, **2h**, **2l**, **2m**, and **2n** are available commercially. Compounds **2c** and **2d** and were synthesized according to the procedure reported in the literature.[23] Compounds **2g**, **2i**, **2j**, and **2k** were prepared by conventional reaction procedures. ^{1}H NMR spectra of **7**[20] and **8**[21] obtained were in good agreement with those reported.

Typical Procedure for Hydroalkynylation of Silylacetylenes 1 to Internal Alkynes 2 Catalyzed by a dipimp/$CoCl_2$·$6H_2O$/Zn Reagent (Table 1, Run 3). To zinc powder (3.3 mg, 0.05 mmol) was added a solution of $CoCl_2$·$6H_2O$ (6.0 mg 0.025 mmol) and dipimp (8.0 mg, 0.03 mmol) in NMP (1.0 mL). The resulting mixture was stirred at ambient temperature for 1 h. A solution of trimethylsilylacetylene (**1a**; 90 μL, 0.65 mmol), diphenylacetylene (**2a**; 116 mg. 0.65 mmol), and hexamethylbenzene (40.6 mg, 0.25 mmol, used as an internal standard) in NMP (1.0 mL) was added, and the resulting mixture was stirred at 50 °C for 24 h. After addition of saturated aqueous NH_4Cl, the mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered through a pad of Celite, and concentrated in vacuo to give a crude mixture, which was analyzed by ^{1}H NMR. The residue was purified by column chromatography on silica gel to afford the hydroalkynylated product **3aa** (124 mg, 90% yield with 97% of *E* geometric purity) as a colorless oil.

*(E)-(3,4-Diphenylbut-3-en-1-yn-1-yl)trimethylsilane (**3aa**):*[9b] ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.38−7.33 (*m*, 2H), 7.30−7.26 (*m*, 3H), 7.16−7.12 (*m*, 3H), 7.08 (s, 1H), 7.07−7.02 (*m*, 2H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.3, 136.0, 129.3, 129.1, 128.4, 128.1, 127.8, 127.7, 124.2, 107.6, 94.4, −0.01; IR (KBr) 3019, 2959, 2132, 1594, 1488, 1250 cm^{-1}; HR-MS *m*/*z* calcd for $C_{19}H_{21}Si$ $[M + H]^+$ 277.1413, found 277.1404.

Typical Procedure for Hydroalkynylation of Silylacetylenes 1 to Internal Alkynes 2 Catalyzed by a dppe/$CoCl_2$·$6H_2O$/Zn Reagent (Table 3, Run 10). To zinc powder (3.3 mg, 0.05 mmol) was added a solution of $CoCl_2$·$6H_2O$ (6.0 mg, 0.025 mmol) and dppe (12.0 mg, 0.03 mmol) in NMP (1.0 mL). The resulting mixture was stirred at ambient temperature for 1 h. A solution of trimethylsilylacetylene (**1a**; 90 μL, 0.65 mmol), internal alkyne **2k** (102 mg, 0.50 mmol), and hexamethylbenzene (40.6 mg, 0.25 mmol, used as an internal standard) in NMP (1.0 mL) was added, and the resulting mixture was stirred at 50 °C for 24 h. After addition of saturated aqueous NH_4Cl, the mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered through a pad of Celite, and concentrated in vacuo to give a crude mixture, which was analyzed by ^{1}H NMR. The residue was purified by column chromatography on silica gel to afford the hydroalkynylated product **3ak** (148 mg, 98% yield with >99% of *Z* geometric purity) as a colorless oil.

*Ethyl (Z)-4-(2-(hydroxymethyl)-4-(trimethylsilyl)but-1-en-3-yn-1-yl)benzoate (**3ak**):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.03 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.04 (s, 1H), 4.38 (q, 2H, *J* = 7.2 Hz), 4.34 (d, 2H, *J* = 6.0 Hz), 1.99 (t, 1H, *J* = 6.0 Hz), 1.40 (t, 3H, *J* = 7.2 Hz), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 166.2, 139.8, 137.6, 129.9, 129.7, 129.0, 126.0, 104.7, 98.0, 61.2, 60.8, 14.4, 0.005; IR (neat) 3444, 2959, 2933, 2140, 1714, 1621, 1337, 1276 cm^{-1}; HR-MS *m*/*z* calcd for $C_{17}H_{22}NaO_3Si$ $[M + Na]^+$ 325.1236, found 325.1226.

*Ethyl (E)-4-(5-hydroxy-1-(trimethylsilyl)pent-3-en-1-yn-3-yl)-benzoate (**4ak**):* analytical sample obtained as a colorless oil from the crude mixture by column chromatography (run 11, Table 2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 6.42 (t, 1H, *J* = 6.6 Hz), 4.39 (q, 2H, *J* = 7.2 Hz), 4.31−4.26 (*m*, 2H), 1.47 (t, 1H, *J* = 6.0 Hz), 1.40 (t, 3H, *J* = 7.2 Hz), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 166.2, 140.8, 139.0, 130.0, 129.4, 128.6, 125.3, 105.0, 94.9, 61.1, 59.8, 14.3, −0.17; IR (neat) 3352, 2956, 2930, 2136, 1509, 1298, 1187 cm^{-1}; HR-MS *m*/*z* calcd for $C_{17}H_{22}NaO_3Si$ $[M + Na]^+$ 325.1236, found 325.1242.

*(E)-(3,4-Diphenylbut-3-en-1-yn-1-yl)triisopropylsilane (**3ba**):*.[9b] 177 mg of **3ba** obtained as a colorless oil in 98% isolated yield (run 4, Table 1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.40−7.05 (*m*, 11H), 1.11 (br s, 21H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.5, 136.8, 136.1, 129.3, 129.1, 128.3, 128.1, 127.7, 127.6, 124.5, 109.7, 91.0, 18.7, 11.4; IR (neat) 2952, 2929, 2864, 2140, 1714, 1592, 1487 1288 cm^{-1}; HR-MS *m*/*z* calcd for $C_{25}H_{33}Si$ $[M + H]^+$ 361.2352, found 361.2344.

*(Z)-2-Benzylidene-4-(trimethylsilyl)but-3-yn-1-ol (**3ab**):* 107 mg of **3ab** obtained as a colorless oil in 93% isolated yield (run 17, Table 1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.36 (dd, 2H, *J* = 7.2 Hz, 7.2 Hz), 7.29 (dd, 1H, *J* = 7.2 Hz, 7.2 Hz), 7.26 (d, 2H, *J* = 7.2 Hz), 7.04 (s, 1H), 4.36 (d, 2H, *J* = 6.6 Hz), 1.97 (t, 1H, *J* = 6.6 Hz), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.7, 135.4, 129.0, 128.4, 128.1, 124.0, 105.0, 96.5, 60.7, −0.05; IR (neat) 3370, 3024, 2957, 2139, 1644, 1487, 1249 cm^{-1}; HR-MS *m*/*z* calcd for $C_{14}H_{19}OSi$ $[M + H]^+$ 231.1205, found 231.1213.

*(E)-3-Phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (**4ab**):* analytical sample obtained as a colorless oil from the crude mixture by column chromatography (run 12, Table 1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.40−7.29 (*m*, 5H), 6.36 (t, 1H, *J* = 6.8 Hz), 4.32−4.28 (*m*, 2H), 1.44−1.38 (br, 1H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.9, 136.3, 128.7, 128.2, 128.1, 126.0, 105.7, 94.2, 60.0, −0.11; IR (neat) 3352, 2958, 2897, 2141, 1614, 1493, 1249 cm^{-1}; HR-MS *m*/*z* calcd for $C_{14}H_{18}NaOSi$ $[M + Na]^+$ 253.1025, found 253.1016.

*(E)-(3,4-Bis(4-methoxyphenyl)but-3-en-1-yn-1-yl)trimethylsilane (**3ac**):*.[24] 135 mg of **3ac** obtained as a colorless oil in 80% isolated yield (run 2, Table 2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.32−7.28 (*m*, 2H), 7.04−7.00 (*m*, 2H), 6.96 (s, 1H), 6.84−6.81 (*m*, 2H), 6.71−6.67 (*m*, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.1, 136.2, 130.7, 130.3, 129.9, 128.8, 121.6, 113.8, 113.5, 108.2, 93.3, 55.2 (2C), 0.05; IR (neat) 2960, 2928, 2128, 1505, 1303, 1258 cm^{-1}; HR-MS *m*/*z* calcd for $C_{21}H_{25}O_2Si$ $[M + H]^+$ 337.1624, found 337.1631.

*Diethyl (E)-4,4′-(4-(trimethylsilyl)but-1-en-3-yne-1,2-diyl)-dibenzoate (**3ad**):* 162 mg of **3ad** obtained as a colorless oil in 77% isolated yield (run 3, Table 2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.98−7.93 (*m*, 2H), 7.84−7.80 (*m*, 2H), 7.42−7.37 (*m*, 2H), 7.15 (s, 1H), 7.06 (d, 2H, *J* = 10 Hz), 4.38 (q, 2H, *J* = 7.2 Hz), 4.33 (q, 2H, *J* = 7.2 Hz), 1.39 (t, 3H, *J* = 7.2 Hz), 1.36 (t, 3H, *J* = 7.2 Hz), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 166.2, 166.1, 141.6, 140.0, 137.1, 129.8, 129.4, 129.2, 129.1, 125.5, 106.3, 96.7, 61.04, 60.98, 14.30, 14.27, −0.15; IR (neat) 2956, 2929, 2864, 2140, 1730, 1487, 1340,

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1252 cm^{-1}; HR-MS m/z calcd for $C_{25}H_{28}NaO_4Si$ $[M + Na]^+$ 443.1655, found 443.1663.

*(Z)-(5-Methoxy-3-(methoxymethyl)pent-3-en-1-yn-1-yl)-trimethylsilane (**3af**):*[9b] 104 mg of **3af** obtained as a colorless oil in 98% isolated yield (run 5, Table 2); ^1H NMR ($CDCl_3$, 600 MHz) δ 6.21 (t, 1H, J = 6.6 Hz), 4.09 (d, 2H, J = 6.6 Hz), 4.00 (s, 2H), 3.36 (s, 3H), 3.33 (s, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.8, 122.7, 105.0, 93.8, 70.0, 68.4, 58.2, 58.1, −0.08; IR (neat) 2979, 2928, 2168, 1402, 1266, 1128 cm^{-1}; HR-MS m/z calcd for $C_{11}H_{21}O_2Si$ $[M + H]^+$ 213.1311, found 213.1313.

*(Z)-3-(((Triisopropylsilyl)oxy)methyl)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (**3ag**):* 44 mg of a mixture of **3ag** and **4ag** obtained as a colorless oil in 26% isolated yield (run 7, Table 2); analytical sample obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.25 (t, 1H, J = 6.6 Hz), 4.33 (s, 2H), 4.28 (dd, 2H, J = 6.6 Hz, J = 6.6 Hz), 2.41−2.55 (br, 1H), 1.09 (d, 21H, J = 6.6 Hz), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 139.2, 125.2, 105.3, 94.2, 62.3, 59.2, 17.9, 11.9, −0.16; IR (neat) 3312, 2956, 2934, 2866, 2144, 1733, 1248, 1095 cm^{-1}; HR-MS m/z calcd for $C_{18}H_{36}NaO_2Si_2$ $[M + Na]^+$ 363.2152, found 363.2151.

*(Z)-4-((Triisopropylsilyl)oxy)-2-((trimethylsilyl)ethynyl)but-2-en-1-ol (**4ag**):* mixture of **3ag** and **4ag** obtained as a colorless oil in 26% isolated yield (run 7, Table 2); analytical sample obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.15 (t, 1H, J = 6.0 Hz), 4.38 (d, 2H, J = 6.0 Hz), 4.17 (d, 2H, J = 6.6 Hz), 2.36 (t, 1H, J = 6.6 Hz), 1.06 (d, 21H, J = 6.6 Hz), 0.20 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.9, 124.1, 104.2, 94.8, 60.9, 59.9, 17.9, 11.9, −0.07; IR (neat) 3466, 2952, 2933, 2857, 1714, 1260 1010 cm^{-1}; HR-MS m/z calcd for $C_{18}H_{36}NaO_2Si_2$ $[M + Na]^+$ 363.2152, found 363.2148.

*(Z)-4-(Trimethylsilyl)-2-((trimethylsilyl)methylene)but-3-yn-1-ol (**3ai**):* 45 mg of a mixture of **3ai** and **4ai** obtained as a colorless oil in 40% isolated yield (run 9, Table 2); analytical sample obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.25 (s, 1H), 4.17 (d, 2H, J = 6.6 Hz), 1.77 (t, 1H, J = 6.6 Hz), 0.20 (s, 9H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 141.3, 138.0, 104.9, 95.4, 64.0, −0.10, −0.13; IR (neat) 3368, 2957, 2897, 2868, 2136, 1574, 1306 cm^{-1}; HR-MS m/z calcd for $C_{11}H_{22}NaOSi_2$ $[M + Na]^+$: 249.1107, found 249.1101.

*(Z)-3,5-Bis(trimethylsilyl)pent-2-en-4-yn-1-ol (**4ai**):* mixture of **3ai** and **4ai** obtained as a colorless oil in 40% isolated yield (run 9, Table 2); analytical sample obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.76 (t, 1H, J = 6.6 Hz), 4.29−4.23 (*m*, 2H), 1.39−1.31 (br, 1H), 0.23 (s, 9H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 151.6, 127.3, 107.6, 97.2, 61.9, −0.03, −0.21; IR (neat) 3307, 2958, 2899, 2873, 2121, 1514, 1249 cm^{-1}; HR-MS m/z calcd for $C_{11}H_{23}OSi_2$ $[M + H]^+$ 227.1287, found 227.1290.

*(Z)-2-(4-Methoxybenzylidene)-4-(trimethylsilyl)but-3-yn-1-ol (**3aj**):* 90 mg of a mixture of **3aj** and **4aj** obtained as a colorless oil in 69% isolated yield (run 8, Table 3); analytical sample was obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.22 (d, J = 9.0 Hz, 2H), 6.98 (s, 1H), 6.89 (d, J = 9.0 Hz, 2H), 4.36 (d, 2H, J = 6.0 Hz), 3.82 (s, 3H), 1.97 (t, 1H, J = 6.0 Hz), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.5, 138.5, 130.6, 128.1, 122.0, 113.9, 105.4, 95.9, 60.9, 55.2, 0.009; IR (neat) 3378, 2960, 2928, 2142, 1604, 1339, 1219 cm^{-1}; HR-MS m/z calcd for $C_{15}H_{21}O_2Si$ $[M + H]^+$ 261.1311, found 261.1302.

*(E)-3-(4-Methoxyphenyl)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (**4aj**):* mixture of **3aj** and **4aj** obtained as a colorless oil in 61% isolated yield (run 10, Table 2); analytical sample obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.28 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.29 (t, 1H, J = 6.6 Hz), 4.34−4.28 (*m*, 2H), 3.83 (s, 3H), 1.40 (t, 1H, J = 6.0 Hz), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.4, 136.7, 130.0, 128.7, 125.5, 113.6, 106.0, 93.8, 106.0, 93.8, 60.0, 55.3, −0.08; IR (neat) 3422, 2959, 2923, 2140, 1505, 1278, 1179 cm^{-1}; HR-MS m/z calcd for $C_{15}H_{20}NaO_2Si$ $[M + Na]^+$ 283.1130, found 283.1136.

*(Z)-2-((Trimethylsilyl)ethynyl)but-2-ene-1,4-diol (**3al**):* 90 mg of **3al** obtained as a colorless oil in 98% isolated yield (run 5, Table 3); ^1H NMR ($CDCl_3$, 600 MHz) δ 6.22 (t, 1H, J = 6.6 Hz), 4.28 (d, 2H, J = 6.6 Hz), 4.21 (s, 2H), 2.35−2.25 (br, 1H), 2.09−1.99 (br, 1H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.4, 125.5, 104.2, 95.3, 60.6, 58.5, −0.13; IR (neat) 3176, 2972, 2937, 2156, 1660, 1404, 1243 cm^{-1}; HR-MS m/z calcd for $C_9H_{16}NaO_2Si$ $[M + Na]^+$ 207.0817, found 207.0811.

*(Z)-(3-Benzylidenehept-1-yn-1-yl)trimethylsilane (**3am**):* 45 mg of a mixture of **3am** and **4am** obtained as a colorless oil in 35% yield (run 11, Table 3). ^1H NMR selected peaks for **3am** ($CDCl_3$, 600 MHz): δ 7.37−7.21 (*m*, 5H), 6.90 (s, 1H), 2.39−2.34 (*m*, 2H), 1.65−1.57 (*m*, 2H), 1.42−1.33 (*m*, 4H), 0.90 (t, 3H, J = 7.2 Hz), 0.22 (s, 9H). Selected peaks of ^1H NMR for (*E*)-trimethyl(3-phenyloct-3-en-1-yn-1-yl)silane (**4am**) ($CDCl_3$, 600 MHz): δ δ 7.37−7.21 (*m*, 5H), 6.25 (t, 1H, J = 7.8 Hz), 2.24−2.17 (*m*, 2H), 1.65−1.57 (*m*, 2H), 1.33−1.26 (*m*, 4H), 0.85 (t, 3H, J = 7.2 Hz), 0.19 (s, 9H). ^{13}C NMR of **3am** and **4am** ($CDCl_3$, 150 MHz, measured using a mixture of isomers): δ 141.6, 137.3, 136.7, 136.6, 128.79, 128.75, 128.2, 128.0, 127.3, 127.2, 125.6, 123.4, 107.8, 107.1, 93.8, 91.4, 31.6, 31.0, 30.6, 29.3, 22.4, 22.3, 13.9, 13.8, 0.05. IR (neat, measured using a mixture of isomers): 2957, 2929, 2860, 1614, 1505, 1249 cm^{-1}. HR-MS: m/z calcd for $C_{17}H_{25}Si$ $[M + H]^+$ 257.1726, found 257.1721 (measured using a mixture of isomers).

*(Z)-3-Benzylidene-5-(trimethylsilyl)pent-4-yn-2-ol (**3an**):* 40 mg of a mixture of **3an** and **4an** obtained as a colorless oil in 33% isolated yield (run 12, Table 3); analytical sample obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.35 (dd, 2H, J = 7.2 Hz, 7.2 Hz), 7.31−7.24 (*m*, 3H), 6.97 (s, 1H), 4.80−4.73 (*m*, 1H), 1.84 (d, 1H, J = 7.8 Hz), 1.45 (d, 3H, J = 6.0 Hz), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.2, 135.5, 128.8, 128.7, 128.4, 127.9, 103.2, 97.4, 64.4, 22.7, −0.001; IR (neat) 3361, 2959, 2928, 2139, 1517, 1384, 1250 cm^{-1}; HR-MS m/z calcd for $C_{15}H_{20}NaOSi$ $[M + Na]^+$: 267.1181, found 267.1185.

*(E)-4-Phenyl-6-(trimethylsilyl)hex-3-en-5-yn-2-ol (**4an**):* mixture of **3an** and **4an** obtained as a colorless oil in 33% isolated yield (run 11, Table 3); analytical sample was obtained from the crude mixture by column chromatography; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.39−7.26 (*m*, 5H), 6.17 (d, 1H, J = 9.6 Hz), 4.54−4.47 (*m*, 1H), 1.67−1.56 (br, 1H), 1.32 (d, 3H, J = 6.6 Hz), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 142.1, 136.6, 128.7, 128.3, 128.0, 125.0, 105.9, 94.2, 64.7, 23.3, −0.11; IR (neat) 3271, 2962, 2927, 2143, 1714, 1505, 1250 cm^{-1}; HR-MS m/z calcd for $C_{15}H_{20}NaOSi$ $[M + Na]^+$ 267.1181, found 267.1175.

*(Z)-2-(Thiophen-2-ylmethylene)-4-(trimethylsilyl)but-3-yn-1-ol (**3ao**):* 73 mg of **3ao** obtained as a colorless oil in 62% isolated yield (run 15, Table 3); ^1H NMR ($CDCl_3$, 600 MHz) δ 7.38 (dd, J = 0.6, 4.8 Hz, 1H), 7.08 (br s, 1H), 7.07 (br d, J = 3.6 Hz, 1H), 7.05 (dd, J = 4.2, 5.4 Hz, 1H), 4.48 (dd, J = 1.2, 6.6 Hz, 2H), 1.97 (br t, J = 6.3 H, 1H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.4, 130.1, 129.7, 128.0, 127.6, 121.5, 104.7, 97.9, 60.9, −0.04; IR (neat) 3347, 2953, 2893, 2131, 1591, 1415, 1319, 1247, 1027, 873, 842, 757, 704 cm^{-1}; HR-MS m/z calcd for $C_{12}H_{16}NaOSSi$ $[M + Na]^+$ 259.0589, found 259.0585.

*(Z)-2-(Pyridin-2-ylmethylene)-4-(trimethylsilyl)but-3-yn-1-ol (**3ap**):* 73 mg of **3ap** obtained as a colorless oil in 63% isolated yield (run 16, Table 3); ^1H NMR ($CDCl_3$, 600 MHz) δ 8.58 (br d, J = 4.8 Hz, 1H), 7.72 (dt, J = 1.8, 7.8 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.20 (ddd, J = 1.2, 4.8, 7.8 Hz, 1H), 6.93 (s, 1H), 4.36 (s, 2H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 154.1, 148.9, 137.4, 136.1, 131.0, 125.4, 122.2, 107.0, 98.0, 62.7, −0.13; IR (neat) 3561, 2956, 2896, 2339, 1606, 1587, 1582, 1471, 1427, 1252, 1144 cm^{-1}; HR-MS m/z calcd for $C_{13}H_{17}NNaOSi$ $[M + Na]^+$ 254.0977, found 254.0980.

*(2Z,4E)-5-Phenyl-2-((trimethylsilyl)ethynyl)penta-2,4-dien-1-ol (**3aq**):* 64 mg of **3aq** obtained as a colorless oil in 50% isolated yield (run 17, Table 3); ^1H NMR ($CDCl_3$, 600 MHz) δ 7.43 (d, J = 7.8 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.06 (dd, J = 12, 15.6 Hz, 1H), 6.69 (d, J = 12 Hz, 1H), 6.66 (d, J = 16 Hz, 1H), 4.38 (d, J = 6 Hz, 2H), 1.81 (t, J = 6.3 Hz, 1H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.2, 136.6, 136.4, 128.7, 128.4, 126.9, 123.0, 122.5, 105.5, 97.9, 60.3, −0.02; IR (neat) 3408, 3032, 2958, 2896, 2129, 1612, 1448, 1249, 1158, 1141, 1018, 992, 969, 875, 754, 690 cm^{-1}; HR-MS m/z calcd for $C_{16}H_{20}NaOSi$ $[M + Na]^+$ 279.1181, found 279.1176.

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*(2Z,2′Z)-2,2′-(1,4-Phenylenebis(methanylylidene))bis(4-(trimethylsilyl)but-3-yn-1-ol) (**3ar**):* 130 mg of **3ar** obtained as a colorless oil in 68% yield (Scheme 3); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.26 (s, 4H), 7.01 (s, 2H), 4.36 (d, J = 6 Hz, 4H), 1.97 (t, J = 6.3 Hz, 2H), 0.24 (s, 18H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.0, 135.2, 129.1, 124.6, 104.9, 97.3, 60.8, −0.04; IR (neat) 3434, 2957, 2897, 2864, 2143, 1407, 1249, 1167, 1046, 970, 885, 759, 727 cm^{-1}; HR-MS m/z calcd for $C_{12}H_{16}NaOSSi$ [M + Na]$^+$ 259.0589, found 259.0585.

*(Z)-Triisopropyl(5-methoxy-3-(methoxymethyl)pent-3-en-1-yn-1-yl)-silane (d-**3bf**):*[13] 146 mg of d-**3bf** obtained as a colorless oil in 98% yield (Scheme 4); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.09 (s, 2H), 4.02 (s, 2H), 3.36 (s, 3H), 3.35 (s, 3H, CH_2OCH_3), 1.08 (d, 21H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.8 (t, J = 24 Hz), 123.0, 107.0, 90.3, 70.2, 68.3, 58.3, 58.0, 18.6, 11.2; IR (neat) 2931, 2864, 2144, 1714, 1260, 1192 cm^{-1}; HR-MS m/z calcd for $C_{17}H_{31}DNaO_2Si$ [M + Na]$^+$ 320.2132, found 320.2132.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving spectroscopic data for the compounds. This material 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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