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Communication

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Regio- and Stereoselective Hydrosilylation of Alkynes Catalyzed by Three-Coordinate Cobalt(I) Alkyl and Silyl Complexes

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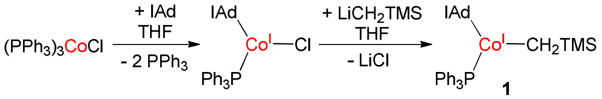
Supporting Information Placeholder

ABSTRACT: A three-coordinate cobalt(I) complex exhibits high catalytic efficiency and selectivity as well as good functional-group compatibility in alkyne hydrosilylation. The three-coordinate cobalt(I) complex [Co(IAd)(PPh$_3$)(CH$_2$TMS)] (**1**) (IAd = 1,3-diadamantylimidazol-2-ylidene) facilitates regio- and stereoselective hydrosilylation of terminal, symmetrical internal, and trimethylsilyl-substituted unsymmetrical internal alkynes to produce single hydrosilylation products in the forms of β-(*E*)-silylalkenes, (*E*)-silylalkenes, and (*Z*)-α,α-disilylalkenes, respectively, in high yields. The comparable catalytic efficiency and selectivity of the cobalt(I) silyl complex [Co(IAd)(PPh$_3$)(SiHPh$_2$)] (**2**) that was prepared from the reaction of **1** with H$_2$SiPh$_2$, and the isolation of an alkyne-cobalt(I) complex [Co(IAd)(η^2-PhC≡CPh)(CH$_2$TMS)] (**3**) from the reaction of **1** with the acetylene point out a modified Chalk-Harrod catalytic cycle for these hydrosilylation reactions. The high selectivity is thought to be governed by steric factors.

The quest for a new generation of economic and environmentally benign catalysts for important chemical transformations has intrigued intensive exploration on non-precious metal catalysis.[1] Transition-metal-catalyzed hydrosilylation of alkyne[2] is a useful synthetic method for vinylsilanes that are versatile and valuable starting materials in organic synthesis.[2, 3] Consequently, great efforts have been excised on the development of non-precious metal alternatives for classic noble metal catalysts. So far, a handful of Fe,[4] Co,[5] and Ni[6] complexes have been found effective to facilitate alkyne hydrosilylation, but these known systems generally exhibit low catalytic efficiency and poor regio- and stereoselectivity. For examples, the hydrosilylation reactions of terminal alkynes using Co$_2$(CO)$_6$(HC≡CCMe$_2$OH)[5b] and (Bu$^t_2$PCH$_2$CH$_2$C$_5$H$_4$)Co(CH$_2$=CH$_2$)[5c] as catalysts produce mixtures of the regio-isomers, *syn-α* and *syn-ß* adducts. The [FeH(CO)(NO)(PPh$_3$)$_2$]-catalyzed hydrosilylation of disubstituted alkynes gives mixtures of stereo-isomers, *syn*- and *anti*-adducts.[4b] Aside from regio- and stereoselectivity issue, the concurrence of alkyne oligmerization,[6] and alkyne hydrogenation[7] also complicates late 3d metal-catalyzed hydrosilylation of alkynes.

Recently, Chirik,[8] Hanson,[9] Holland,[10] and we[11] found that low-coordinate cobalt alkyl complexes can serve as effective catalysts for hydrogenation, hydrosilylation, hydroboration, dehydrogenative silylation, and isomerization of olefins as well as C-H bond borylation. Inspired by these, we target low-coordinate cobalt alkyl complexes bearing *N*-heterocyclic carbene ligands[12] as catalysts for selective hydrosilylation of alkynes with the aim to exploit the steric bulk of NHC ligands to induce selectivity. In this regard, we report the achievement of highly regio- and stereoselective hydrosilylation of alkynes with a structurally well-defined cobalt(I) complex [Co(IAd)(PPh$_3$)(CH$_2$TMS)] (IAd = 1,3-diadamantylimidazol-2-ylidene) as precatalyst.

Scheme 1. Preparation Route for the Cobalt Catalyst



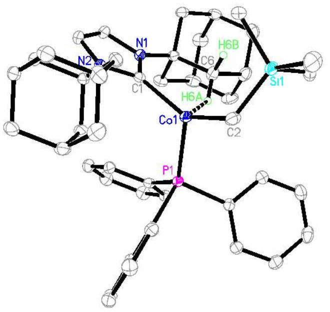
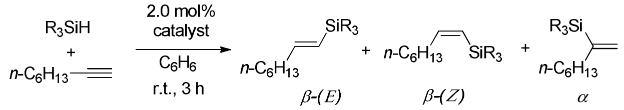


Figure 1. Molecular structures of [Co(IAd)(PPh$_3$)(CH$_2$TMS)] (**1**) showing 30% probability ellipsoids and the partial atom numbering scheme.

The low-coordinate cobalt(I) alkyl complex [Co(IAd)(PPh$_3$)(CH$_2$TMS)] (**1**) was prepared by alkylation of [Co(IAd)(PPh$_3$)Cl] with LiCH$_2$TMS (Scheme 1). It has been fully characterized by ^{1}H NMR, UV-vis-NIR, elemental analyses, as well as single-crystal X-ray diffraction studies.[13] Complex **1** is paramagnetic and has a solution magnetic moment of 3.7(1) μB in C$_6$D$_6$.[14] Its molecular structure established by an X-ray diffraction study shows a distorted trigonal planar CoPCC core with a large C(carbene)-Co-C(alkyl) angle (137.32(7) °) (Figure 1).[13] The Co-C(alkyl) bond distance of 2.041(2) Å is longer than that in the cobalt(II) complex [(nacnac)Co(CH$_2$TMS)] (1.999(15) Å).[15] The steric demanding nature of IAd ligand renders a large dihedral angle (79.5 °) between its imidazole plane and the CoPCC coordination plane. Short contact between the cobalt center and one of the C-H bonds of an adamantyl group has also been noticed in the structure.

Complex **1** proved an efficient catalyst for hydrosilylation of alkynes. As shown in Table 1, the reaction of 1-octyne with H$_2$SiPh$_2$ (1.2 equiv.) and 2 mol% of **1** in 3 h at room temperature can yield, exclusively, the *ß*-(*E*) adduct (*E*)-*n*-C$_6$H$_{13}$CH=CHSiHPh$_2$ in 96% yield (entry 1). The identity of the *ß*-(*E*) adduct has been authenticated by comparing its NMR data and GC retention time with those of the sample prepared by the

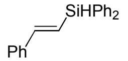
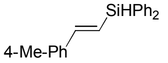
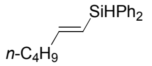
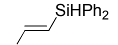
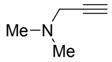
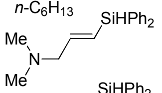
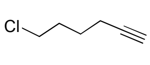
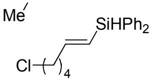
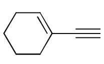
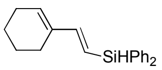
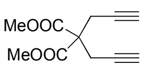
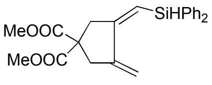
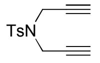
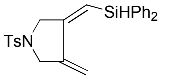
Table 1. Catalytic Performance of Some Metal Complexes in Hydrosilylation of 1-Octyne [a]



Entry	Catalyst	Hydrosilane	GC Yield (%) [b]		
			β-(E)	β-(Z)	α
1	**1**	H_2SiPh_2	96	0	0
2 [c]	**1**	H_2SiPh_2	95	0	0
3 [d]	**1**	H_2SiPh_2	12	0	0
4 [e]	**Co(IMes')(IMes)(N_2)**	H_2SiPh_2	39	0	9
5 [e]	**(IPr)Co(CH_2SiMe_3)$_2$**	H_2SiPh_2	16	0	0
6	**$Co_2(CO)_8$**	H_2SiPh_2	12	5	5
7	**$Rh(PPh_3)_3Cl$**	H_2SiPh_2	65	8	0
8	**$Pt_2(dvtms)_3$**	H_2SiPh_2	32	0	6
9	**2**	H_2SiPh_2	94	0	0
10 [f]	**1**	H_3SiPh	45	15	30
11 [g]	**1**	$HSiPh_3$	0	0	0

[a] 1-Octyne (0.20 mmol) and H_2SiPh_2 (0.24 mmol) at room temperature in C_6H_6 (0.2 mL). [b] Yields based on 1-octyne. [c] 0.1 mol% catalyst loading, 12 h. [d] 0.01 mol% catalyst loading, 48 h. [e] [Co(IMes')(IMes)(N_2)], and [(IPr)Co($CH_2TMS)_2$] were prepared according to ref. 12a and 12b, respectively. [f] 8 h. [g] At 70 °C.

Table 2. Hydrosilylation of Terminal Alkynes with Catalyst **1** [a]

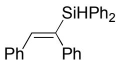
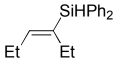
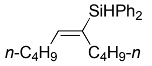
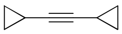
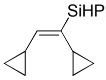
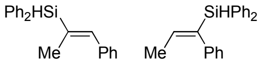
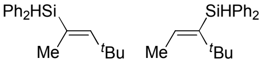
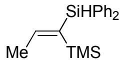
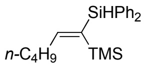
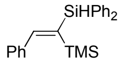
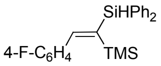
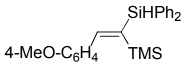
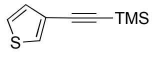
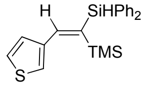
Entry	Alkynes	Product	Yield [b]
1	Ph—≡		96% (88%)
2	4-Me-Ph—≡		88% (78%)
3	n-C_4H_9—≡		99% (84%)
4	n-C_6H_{13}—≡		96% (85%)
5			92% (70%)
6			94% (82%)
7 [c]			86% (78%)
8 [c,d]			62%
9 [c,d]			56%

[a] Alkynes (1.0 mmol) and Ph_2SiH_2 (1.2 mmol) with 2 mol% **1** at room temperature in 0.5 mL C_6H_6. [b] GC yield (isolated yield) based on alkynes. [c] At 70°C. [d] Isolated yield.

reported method. Deuterium labeling experiment using D_2SiPh_2 as the hydrosilane further confirmed the syn-β nature of the vinylsilane.[13] Reducing the catalyst loading to 0.1 mol%, the catalytic system can still produce the vinylsilane in 95% yield in 12 h without losing selectivity (entry 2). With a 0.01 mol% catalyst loading, the reaction afforded the vinylsilane in 12% yield in 48 h (entry 3). The high efficiency and selectivity of catalyst **1** form a sharp contrast to other potential cobalt-NHC catalysts and the traditional alkyne hydrosilylation catalysts. For examples, under paralleled reaction conditions all the reactions with Co(IMes')(IMes)(N_2),[12a] $Co_2(CO)_8$, $Rh(PPh_3)_3Cl$, and $Pt_2(dvtms)_3$ afforded mixtures of the vinylhydrosilanes (entries 4, 6-8); and the reactions with the three-coordinate cobalt(II) complex (IPr)Co($CH_2TMS)_2$ [12b] (IPr = 1,3-bis-2,6-diisopropylphenylimidazol-2-ylidene) gave the β-(E) adduct in low yield (entry 5).

Encouraged by the high activity of catalyst **1** in hydrosilylation of 1-octyne, the reactions with other terminal alkynes were examined, which revealed that all the reactions could selectively produce β-(E) adducts in high yields (Table 2). Hydrosilylation of phenyl and alkyl substituted alkynes can afford E-vinylsilanes in yields high than 88% (entries 1-6, Table 2). Alkynes bearing chloro, protected amine, olefin, and ester functionalities can all be successfully employed (entries 5, 6-9), which demonstrates the good functional group-compatibility of the catalytic system. Intriguingly, the hydrosilylation of 1,6-diynes can also be achieved with the formation of the silylated 1,2-dialkylidenecyclopentanes in good yields with high selectivity (entries 8 and 9).

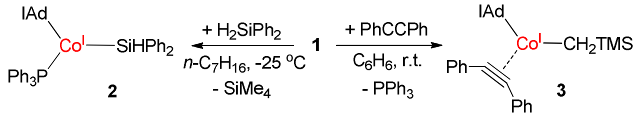
Table 3. Hydrosilylation of Internal Alkynes [a]

Entry	Alkynes	Product	Yield [b]
1	Ph—≡—Ph		96% (83%)
2	Et—≡—Et		92% (85%)
3	n-C_4H_9—≡—C_4H_9-n		94% (89%)
4			90% (75%)
5	Me—≡—Ph	 1:1	96% (70%)
6	Me—≡—^{t}Bu	 1:1.4	96% (95%)
7	Me—≡—TMS		94% (90%)
8	n-C_4H_9—≡—TMS		96% (90%)
9	Ph—≡—TMS		96% (90%)
10	4-F-C_6H_4—≡—TMS		95% (92%)
11	4-MeO-C_6H_4—≡—TMS		98% (92%)
12			88% (86%)

[a] Alkynes (1.0 mmol) and Ph_2SiH_2 (1.2 mmol) with 2 mol% **1** at 70°C in 0.5 mL C_6H_6. [b] GC yield (isolated yield) based on alkynes.

In addition to the reactions with terminal alkynes, selective *syn*-addition of internal alkynes with H_2SiPh_2 could also be achieved with **1** as catalyst at elevated temperature (70 °C). As shown in Table 3, hydrosilylation of symmetrical alkynes with phenyl or alkyl substituents proceeded at 70 °C for 4 hours and afforded (*E*)-vinylsilanes in more than 90% yields (entries 1-4). Dicyclopropylacetylene was compatible without ring opening (entry 4). As for unsymmetrical internal alkynes, the reaction with 1-phenyl-1-propyne afforded the two *E*-isomers in nearly 1:1 ratio (entry 5); the one with 4,4-dimethyl-2-pentyne gave (*E*)-(4,4-dimethylpent-2-en-2-yl)diphenylsilane as the major product (entry 6); and to our delight, the reactions of the unsymmetrical internal alkynes that bear a trimethylsilyl group could give, exclusively, *syn*-adducts in the form of (*Z*)-α,α-disilylalkenes in very high yields (entries 7-12). No significant influence on selectivity and yield was observed in cases of the aryl-substituted alkynes with electro-withdrawing or electro-donating groups attached on aryl (entries 9-11). This observation, in addition with the stepwisely increased selectivity in entries 5-7, suggests that the high regio-selectivity achieved in the reactions with trimethylsilyl-substituted alkynes is controlled by steric factors.[16] Regio- and stereoselectivity control is a challenging task in transition-metal-catalyzed hydrosilylation of alkynes. While a plenty of noble metal catalysts have been developed, few of them could promote high regio- and stereoselective hydrosilylation for both terminal and internal alkynes.[2] In this aspect, the high selectivity achieved in the reactions with both terminal and internal alkynes in the current study signifies the uniqueness of the low-coordinate cobalt catalyst.

Scheme 2. Reactions of 1 with H_2SiPh_2 and PhCCPh



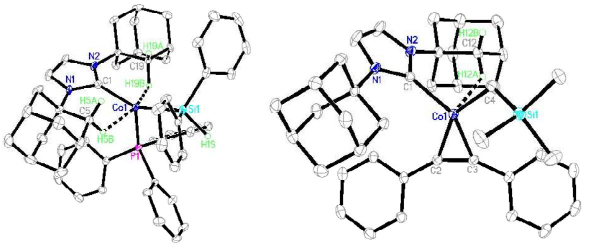
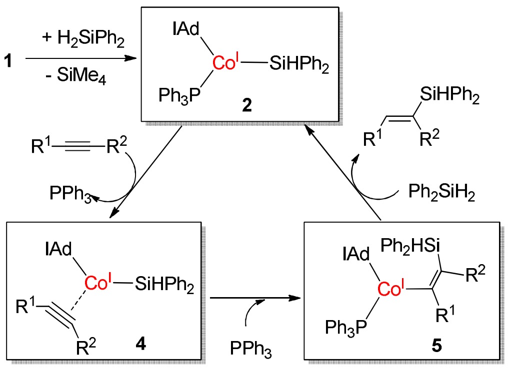


Figure 2. Molecular structures of [Co(IAd)(PPh$_3$)(SiHPh$_2$] (**2**, left) and [Co(IAd)(η^2-PhC≡CPh)(CH$_2$TMS)] (**3**, right) showing 30% probability ellipsoids and the partial atom numbering scheme.

Aiming to throw lights on the reaction mechanism, stoichiometric reactions of **1** with alkynes and hydrosilanes were then studied. Complex **1** proved reactive toward H_2SiPh_2 to yield a three-coordinate cobalt(I) silyl complex, [Co(IAd)(PPh$_3$)(SiHPh$_2$)] (**2**).[13] On the other hand, a cobalt(I) alkyne complex [Co(IAd)(η^2-PhC≡CPh)(CH$_2$TMS)] (**3**) has been isolated from the reaction of **1** with PhC≡CPh (Scheme 2).[13] Figure 2 depicts the molecular structures of both complexes. Complex **2** represents the first example of three-coordinate cobalt silyl complex. Its cobalt center adopts a triganol planar geometry with a large C1-Co-Si angle of 148.4(2) °. The Co-C(carbene) distance (1.980(6) Å) in **2** is shorter than those of the reported low-spin cobalt(I)-NHC complexes,[17] whereas, the Co-Si distance (2.226(2) Å) is comparable to its congeners in low-spin cobalt silyl complexes.[18] Complex **3** is a peculiar low-coordinate complex bearing both an η^2-bonded alkyne ligand and a σ-alkyl group. The long C(alkyne)-C(alkyne) bond distance (1.271(3) Å) and bent C(Ph)-C(alkyne)-C(alkyne) angle (148 °) suggest strong metal-to-ligand backdonation.[19] The unique steric nature of the IAd ligand has induced the near coplanarity of the C(alkyne)-C(alkyne) bond with the C(carbene)-Co-C(alkyl) plane with one of the phenyl groups fitting in the valley between two adamantyl groups.

Scheme 3. Proposed Catalytic Cycle



Testing the catalytic performance of the new cobalt(I) complexes revealed that **2** has comparable catalytic activity and selectivity as that of **1** in the hydrosilylation reaction of 1-octyne with H_2SiPh_2 (entry 9 in Table 1), implying the in-cycle nature of the cobalt(I) silyl species. In contrast, the reaction of PhC≡CPh with H_2SiPh_2 using **3** (2 mol%) as catalyst only gave (*E*-1,2-diphenylvinyl)diphenylsilane in 25% yield after heated at 70 °C for 4 hours. The lower yield, as compared to that of the reaction using **2** as catalyst (96% yield, entry 1 in Table 3), indicates the indispensable role of PPh$_3$ for achieving high catalytic efficiency. Based on these results, a simplified catalytic cycle shown in Scheme 3 is proposed for the hydrosilylation reaction.[20] The interaction of **1** with H_2SiPh_2 yields the silyl intermediate **2**, which then undergoes ligand-substitution reaction with an alkyne molecule to form the alkyne-cobalt(I)-silyl species, Co(IAd)(η^2-R^{1}C≡CR^2)(SiHPh$_2$) (**4**). Once formed, migratory insertion of the silyl moiety to the C≡C triple bond in **4**, triggered probably by the coordination of PPh$_3$, will produce the alkenyl metal species **5** that could further react with H_2SiPh_2 to yield the hydrosilylation product and regenerate **2** (Scheme 3). While our attempts to prepare intermediates **4** and **5** from the reactions of **2** with alkynes were unsuccessful, the isolation of **1** and **3**, which are structurally relevant to **5** and **4**, respectively, hints the capability of the IAd ligand to support low-coordiante silyl-cobalt(I)-alkyne and alkenyl-cobalt(I) intermediates. Notably, the conversion of **1** to **2** and that of **5** to **2** might follow an oxidative addition-reductive elimination mechanism when noting the precedents of oxidative addition of hydrosilanes with cobalt(I) species.[18] On the other hand, considering the steric demanding nature of IAd that might render the formation of a five-coordinate trigonal-bipyramidal Co(III)-species difficult, a sigma-bond metathesis mechanism therefore could not be excluded absolutely.

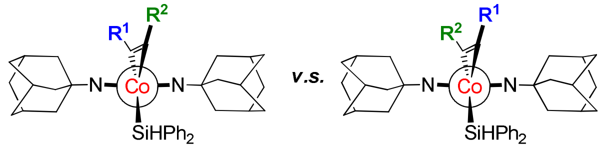


Chart 1. Newman projections of intermediate **4**.

The hydrosilylation products in the reactions with terminal alkynes and silyl-substituted unsymmetrical internal alkynes exhibit different regio-selectivity, which, we thought, should result from the intricate balance of steric repulsion among the IAd group, the silyl group, and the coordinated alkyne in intermediate **4** (Chart 1).[21, 22] For terminal alkynes, the alkyl and phenyl substituents are not bulky and could position toward IAd. Then, the following migratory insertion of the silyl group to the terminal carbon of the alkyne, which is less sterically hindranced, will readily happen and eventually lead to the formation of β syn-adducts. For the trimethylsilyl-substituted internal alkynes, in order to avoiding severe steric repulsion between the trimethylsilyl and IAd groups, the alkynes have to orient their small substituents above the imidazole plane, which, subsequently, will produce *α,α*-disilylalkenyl cobalt intermediate and lead the formation of *α,α*-disilylalkenes. Consistent with this explanation, we found that the catalytic system is invalid for the hydrosilylation of TMSC≡CTMS, and that the steric property of the silyl moiety affects the reaction selectivity. For examples, the hydrosilylation reaction of 1-octyne with the primary silane H_3SiPh (entry 10 in Table 1) exhibits poor selectivity, and the reaction with $HSiPh_3$ (entry 11 in Table 1) could not afford the hydrosilylation product.

In summary, we found a low-coordinate cobalt(I) alkyl complex bearing bulky IAd ligand effects hydrosilylation of alkynes to produce *syn*-adduct of vinylsilanes with high efficiency, selectivity, and good functional group compatibility. Reactivity study on the precatalyst has led to the isolation of the first example of low-coordinate cobalt(I) silyl complex and a novel cobalt(I)-alkyne-alkyl complex. The silyl complex shows comparable activity and selectivity in alkyne hydrosilyation as the alkyl complex. These results collectively point out a modified Chalk-Harrod mechanism for the cobalt-catalyzed reaction. Molecular structure analysis on the low-coordinate cobalt complexes implies that the selectivity is governed by steric factors. Currently, we are exploring the utility of the vinylhydrosilanes for silicon polymer synthesis.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files in CIF format for the new complexes, experimental procedures, and characterization data. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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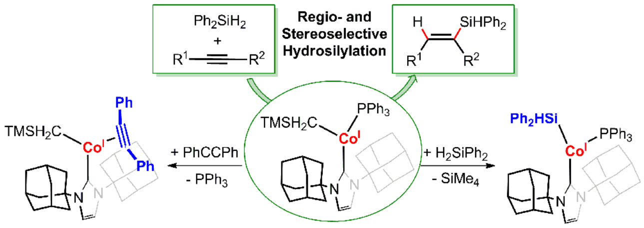
Ph2SiH2
+
R1 R2
Regio- and
Stereoselective
Hydrosilylation
H SiHPh2
R1 R2
TMSH2C
PPh3
CoI
N N
+ PhCCPh
- PPh3
Ph
Ph
+ H2SiPh2
- SiMe4
Ph2HSi