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

Zhenbo Mo, Jie Xiao, Yafei Gao, and Liang Deng*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China

S *Supporting Information*

ABSTRACT: A three-coordinate cobalt(I) complex exhibits high catalytic efficiency and selectivity as well as good functional group compatibility in alkyne hydrosilylation. $[Co(IAd)(PPh_3)(CH_2TMS)]$ (**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 Co(I) silyl complex $[Co(IAd)(PPh_3)(SiHPh_2)]$ that was prepared from the reaction of **1** with H_2SiPh_2, and the isolation of an alkyne Co(I) complex $[Co(IAd)(\eta^2\text{-}PhC\equiv CPh)(CH_2TMS)]$ 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 inspired intensive exploration into 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 expended 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 example, the hydrosilylation reactions of terminal alkynes using $Co_2(CO)_6(HC\equiv CCMe_2OH)$[5b] and $(Bu^t_2PCH_2CH_2C_5H_4)Co(CH_2=CH_2)$[5c] as catalysts produce mixtures of the regioisomers, *syn-α* and *syn-β* adducts. The $[FeH(CO)(NO)(PPh_3)_2]$-catalyzed hydrosilylation of disubstituted alkynes gives mixtures of stereoisomers, *syn-* and *anti-*adducts.[4b] Aside from regio- and stereoselectivity issues, 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 (NHC) 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 Co(I) complex, $[Co(IAd)(PPh_3)(CH_2TMS)]$ (IAd = 1,3-diadamantylimidazol-2-ylidene), as precatalyst.

The low-coordinate Co(I) alkyl complex $[Co(IAd)(PPh_3)(CH_2TMS)]$ (**1**) was prepared by alkylation of $[Co(IAd)(PPh_3)Cl]$ with $LiCH_2TMS$ (Scheme 1). It has been fully

Scheme 1. Preparation Route for the Cobalt Catalyst
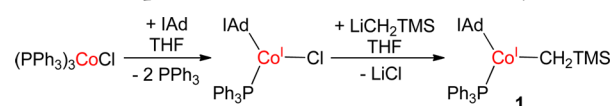
characterized by ^1H NMR, UV-vis-NIR, and elemental analysis, as well as single-crystal X-ray diffraction (XRD) study.[13] Complex **1** is paramagnetic and has a solution magnetic moment of 3.7(1) μB in C_6D_6.[14] Its molecular structure, established by an XRD study, shows a distorted trigonal planar 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 Co(II) complex $[(nacnac)Co(CH_2TMS)]$ (1.999(15) Å).[15] The sterically demanding nature of the IAd ligand renders a large dihedral angle (79.5°) between its imidazole plane and the CoPCC coordination plane. Short contact between the Co 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_2SiPh_2 (1.2 equiv) and 2 mol% of **1** in 3 h at room temperature can yield exclusively the β-(E) adduct (E)-n-$C_6H_{13}CH=CHSiHPh_2$ in 96% yield (entry 1). The identity of the β-(E) adduct has been authenticated by comparing its NMR data and GC retention time with those of the sample prepared by the reported method. A deuterium labeling experiment using D_2SiPh_2 as the hydrosilane further confirmed the *syn-β* nature of the vinylsilane.[13] When the catalyst loading is reduced 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
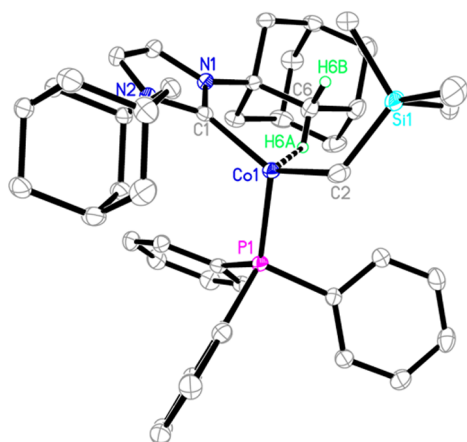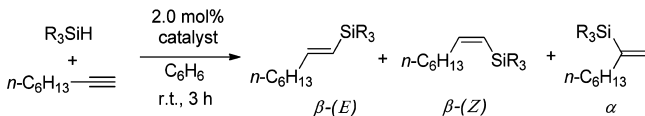
Figure 1. Molecular structures of [Co(IAd)(PPh₃)(CH₂TMS)] (**1**) showing 30% probability ellipsoids and the partial atom numbering scheme.

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

entry	catalyst	hydrosilane	GC yield (%)[b]		
			β-(E)	β-(Z)	a
1	**1**	H₂SiPh₂	96	0	0
2[c]	**1**	H₂SiPh₂	95	0	0
3[d]	**1**	H₂SiPh₂	12	0	0
4[e]	Co(IMes′)(IMes)(N₂)	H₂SiPh₂	39	0	9
5[e]	(IPr)Co(CH₂SiMe₃)₂	H₂SiPh₂	16	0	0
6	Co₂(CO)₈	H₂SiPh₂	12	5	5
7	Rh(PPh₃)₃Cl	H₂SiPh₂	65	8	0
8	Pt₂(dvtms)₃	H₂SiPh₂	32	0	6
9	**2**	H₂SiPh₂	94	0	0
10[f]	**1**	H₃SiPh	45	15	30
11[g]	**1**	HSiPh₃	0	0	0

[a]1-Octyne (0.20 mmol) and H₂SiPh₂ (0.24 mmol) at room temperature in C₆H₆ (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)(N₂)] and [(IPr)Co(CH₂TMS)₂] were prepared according to refs 12a and12b, respectively. [f]8 h. [g]At 70 °C.

12% yield in 48 h (entry 3). The high efficiency and selectivity of catalyst **1** are in sharp contrast to the properties of other potential Co−NHC catalysts and the traditional alkyne hydrosilylation catalysts. For example, under parallel reaction conditions, all the reactions with Co(IMes′)(IMes)(N₂),[12a] Co₂(CO)₈, Rh-(PPh₃)₃Cl, and Pt₂(dvtms)₃ afforded mixtures of the vinylhydrosilanes (entries 4, 6−8), and the reaction with the three-coordinate Co(II) complex (IPr)Co(CH₂TMS)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, we examined the reactions with other terminal alkynes, 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 higher than 88% (entries 1−6, Table 2). Alkynes bearing chloro, protected amine, olefin, and ester functionalities can all

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-C₄H₉≡		99% (84%)
4	n-C₆H₁₃≡		96% (85%)
5	Me–N(Me)≡		92% (70%)
6	Cl		94% (82%)
7[c]			86% (78%)
8[c,d]			62%
9[c,d]			56%

[a]Alkynes (1.0 mmol) and Ph₂SiH₂ (1.2 mmol) with 2 mol% **1** at room temperature in 0.5 mL of C₆H₆. [b]GC yield (isolated yield) based on alkynes. [c]At 70 °C. [d]Isolated yield.

be successfully employed (entries 5−9), 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-dialkylidene-cyclopentanes in good yields with high selectivity (entries 8 and 9).

In addition to the reactions with terminal alkynes, selective *syn*-addition of internal alkynes with H₂SiPh₂ could also be achieved with **1** as catalyst at elevated temperature (70 °C). As shown in Table S2, hydrosilylation of symmetrical alkynes with phenyl or alkyl substituents proceeded at 70 °C for 4 h and afforded (E)-vinylsilanes in more than 90% yields (entries 1−4). Dicyclo-propylacetylene 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-1-t-butyl-2-methylvinyl)diphenylsilane as the major product (entry 6); and, to our delight, the reactions of the unsymmetrical internal alkynes that bear a trimethylsilyl (TMS) 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 the cases of the aryl-substituted alkynes with electron-withdrawing or electron-donating groups attached on aryl (entries 9−11). This observation, in addition to the stepwise increased selectivity in entries 5−7, suggests that the high regioselectivity achieved in the reactions with TMS-substituted alkynes is controlled by steric factors.[16] Regio- and stereoselectivity control is a challenging task in transition-metal-catalyzed hydrosilylation of alkynes. While 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 Co catalyst.

Aiming to shed light on the reaction mechanism, we then studied stoichiometric reactions of **1** with alkynes and hydrosilanes. Complex **1** proved reactive toward H_2SiPh_2 to yield a three-coordinate Co(I) silyl complex, $[Co(IAd)(PPh_3)(SiHPh_2)]$ (**2**).[13] On the other hand, a Co(I) alkyne complex, $[Co(IAd)(\eta^2\text{-}PhC\equiv CPh)(CH_2TMS)]$ (**3**), was isolated from the reaction of **1** with $PhC\equiv CPh$ (Scheme 2).[13] Figure 2 depicts
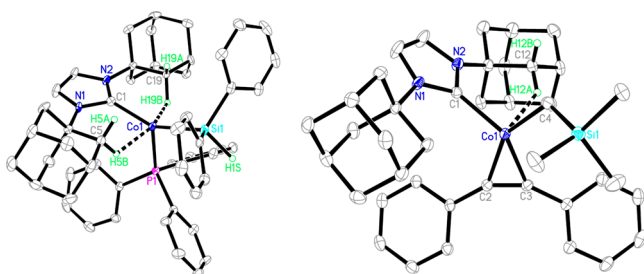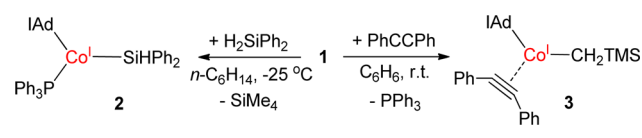
Scheme 2. Reactions of 1 with H_2SiPh_2 and PhCCPh

Figure 2. Molecular structures of $[Co(IAd)(PPh_3)(SiHPh_2)]$ (**2**, left) and $[Co(IAd)(\eta^2\text{-}PhC\equiv CPh)(CH_2TMS)]$ (**3**, right), showing 30% probability ellipsoids and the partial atom numbering scheme.

the molecular structures of both complexes. Complex **2** represents the first example of a three-coordinate cobalt silyl complex. Its Co 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 in the reported low-spin Co(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 back donation.[19] The unique steric nature of the IAd ligand induced 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.

Testing the catalytic performance of the new Co(I) complexes revealed that **2** has catalytic activity and selectivity comparable to 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 Co(I) silyl species. In contrast, the reaction of $PhC\equiv CPh$ with H_2SiPh_2 using **3** (2 mol%) as catalyst only gave (E-1,2-diphenylvinyl)-diphenylsilane in 25% yield after heating at 70 °C for 4 h. The lower yield compared to that of the reaction using **2** as catalyst (96% yield, entry 1 in Table S2) 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 a ligand substitution reaction with an alkyne molecule to form the alkyne-Co(I)-silyl species, $Co(IAd)(\eta^2\text{-}R^1C\equiv CR^2)(SiHPh_2)$ (**4**). Once formed, migratory insertion of the silyl moiety to

**Scheme 3. Proposed Catalytic Cycle**
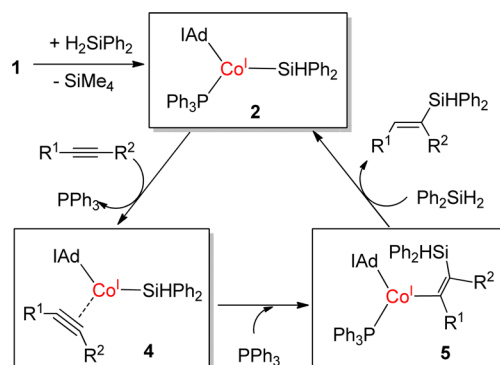
the $C\equiv C$ triple bond in **4**, triggered probably by the coordination of PPh_3, will produce the alkenyl metal species **5** that could further react with H_2SiPh_2 to yield the hydrosilylation product and regenerate **2** (Scheme 3). While our attempts to prepare intermediates **4** and **5** 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 at the capability of the IAd ligand to support low-coordinate 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, noting the precedents of oxidative addition of hydrosilanes with Co(I) species.[18] On the other hand, considering the sterically demanding nature of IAd that might render the formation of a five-coordinate trigonal-bipyramidal Co(III) species difficult, a σ-bond metathesis mechanism therefore could not be excluded absolutely.

The hydrosilylation products in the reactions with terminal alkynes and silyl-substituted unsymmetrical internal alkynes exhibit different regioselectivity, 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

Chart 1. Newman Projections of Intermediate 4
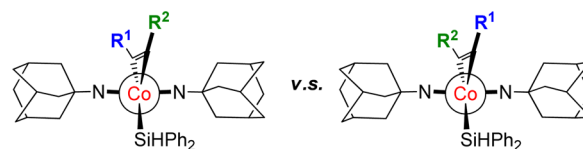
substituents are not bulky and could position toward IAd. The following migratory insertion of the silyl group to the terminal carbon of the alkyne, which is less sterically hindranced, will then readily happen and eventually lead to the formation of β-syn-adducts. For the TMS-substituted internal alkynes, to avoid severe steric repulsion between the TMS and IAd groups, the alkynes have to orient their small substituents above the imidazole plane, which, subsequently, will produce α,α-disilyl-alkenyl cobalt intermediates and lead to the formation of α,α-disilylalkenes. Consistent with this explanation, we found that the catalytic system is invalid for the hydrosilylation of $TMSC\equiv CTMS$, and that the steric property of the silyl moiety affects the reaction selectivity. For example, 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 that a low-coordinate Co(I) alkyl complex bearing bulky IAd ligand effects hydrosilylation of alkynes to produce *syn*-adducts 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 Co(I) silyl complex and a novel Co(I)-alkyne-alkyl complex. The silyl complex shows activity and selectivity in alkyne hydrosilation comparable to that of the alkyl complex. These results collectively point out a modified Chalk−Harrod mechanism for the Co-catalyzed reaction. Molecular structure analysis on the low-coordinate Co 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 (CIF) for the new complexes, experimental procedures, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

deng@sioc.ac.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Bullock, R. M., Ed. *Catalysis without Precious Metals*; Wiley-VCH: Weinheim, 2010. (b) Jaouen, F.; Proietti, E.; Lefèvre, M.; Chenitz, R.; Dodelet, J.-P.; Wu, G.; Chung, H. T.; Johnston, C. M.; Zelenay, P. *Energy Environ. Sci.* **2011**, *4*, 114. (c) Wang, M.; Chen, L.; Sun, L. *Energy Environ. Sci.* **2012**, *5*, 6763.

(2) (a) *Hydrosilyaltion: A Comprehensive Review on Recent Advances*; Marciniec, B., Ed.; Springer: Berlin, 2009. (b) Roy, A. K. *Adv. Organomet. Chem.* **2008**, *55*, 1. (c) Herzig, C. J. In *Organosilicon Chemistry*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1994; p 253.

(3) (a) Lim, D. S. W.; Anderson, E. A. *Synthesis* **2012**, *44*, 983. (b) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375.

(4) (a) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794. (b) Belger, C.; Plietker, B. *Chem. Commun.* **2012**, *48*, 5419.

(5) (a) Isobe, M.; Nishizawa, R.; Nishikawa, T.; Yoza, K. *Tetrahedron Lett.* **1999**, *40*, 6927. (b) Huang, K.-H.; Isobe, M. *Eur. J. Org. Chem.* **2014**, 4733. (c) Yong, L.; Kirleis, K.; Butenschön, H. *Adv. Synth. Catal.* **2006**, *348*, 833. (d) Konno, T.; Taku, K.; Yamada, S.; Moriyasu, K.; Ishihara, T. *Org. Biomol. Chem.* **2009**, *7*, 1167.

(6) (a) Bartik, T.; Nagy, G.; Kvintovics, P.; Happ, B. *J. Organomet. Chem.* **1993**, *453*, 29. (b) Tillack, A.; Pulst, S.; Baumann, W.; Baudisch, H.; Kortus, K.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *532*, 117. (c) Chaulagain, M. R.; Mahandru, G. M.; Montgomery, J. *Tetrahedron* **2006**, *62*, 7560. (d) Berding, J.; van Paridon, J. A.; van Rixel, V. H. S.; Bouwman, E. *Eur. J. Inorg. Chem.* **2011**, 2450.

(7) Enthaler, S.; Haberberger, M.; Irran, E. *Chem.—Asian J.* **2011**, *6*, 1613.

(8) (a) Monfette, S.; Turner, Z. R.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 4561. (b) Obligacion, J. V.; Chirik, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 19107. (c) Friedfeld, M. R.; Shevlin, M.; Hoyt, J. M.; Krska, S. W.; Tudge, M. T.; Chirik, P. J. *Science* **2013**, *342*, 1076.

(d) Obligacion, J. V.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 4133. (e) Atienza, C. C. H.; Diao, T.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P; Boyer, J. L.; Roy, A. K.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 12108.

(9) (a) Zhang, G.; Scott, B. L.; Hanson, S. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 12102. (b) Zhang, G.; Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. *J. Am. Chem. Soc.* **2013**, *135*, 8668.

(10) Chen, C.; Dugan, T. R.; Brennessel, W. W.; Weix, D. J.; Holland, P. L. *J. Am. Chem. Soc.* **2014**, *136*, 945.

(11) Mo, Z.; Liu, Y.; Deng, L. *Angew. Chem., Int. Ed.* **2013**, *52*, 10845.

(12) (a) Mo, Z.; Chen, D.; Leng, X.; Deng, L. *Organometallics* **2012**, *31*, 7040. (b) Przyojski, J. A.; Arman, H. D.; Tonzetich, Z. J. *Organometallics* **2013**, *32*, 723. (c) Danopoulos, A. A.; Braunstein, P. *Dalton Trans.* **2013**, *42*, 7276. (d) Day, B. M.; Pal, K.; Pugh, T.; Tuck, J.; Layfield, R. A. *Inorg. Chem.* **2014**, *53*, 10578.

(13) For details, see Supporting Information.

(14) The large solution magnetic moments suggests the contribution of orbital angular momentum, as observed in other low-coordinate Co-NHC complexes in ref 12.

(15) Young, J. F.; Yap, G. P. A.; Theopold, K. H. *J. Chem. Cryst.* **2009**, *39*, 846.

(16) Similar selectivity has been observed in [Cp*Ru(NCMe)$_3$][PF$_6$]-catalyzed hydrosilylation reactions: Ding, S.; Song, L.-J.; Chung, L. W.; Zhang, X.; Sun, J.; Wu, Y.-D. *J. Am. Chem. Soc.* **2013**, *135*, 13835.

(17) (a) Vélez, C. L.; Markwick, P. R. L.; Holland, R. L.; DiPasquale, A. G.; Rheingold, A. L.; O'Connor, J. M. *Organometallics* **2010**, *29*, 6695. (b) Mo, Z.; Li, Y.; Lee, H. K.; Deng, L. *Organometallics* **2011**, *30*, 4687.

(18) (a) Yong, L.; Hofer, E.; Wartchow, R.; Butenschön, H. *Organometallics* **2003**, *22*, 5463. (b) Whited, M. T.; Mankad, N. P.; Lee, Y.; Oblad, P. F.; Peters, J. C. *Inorg. Chem.* **2009**, *48*, 2507.

(19) Yu, Y.; Smith, J. M.; Flaschenriem, C. J.; Holland, P. L. *Inorg. Chem.* **2006**, *45*, 5742.

(20) Several mechanisms, for examples Chalk−Harrod, modified Chalk−Harrod, σ-bond metathesis, and metal silylene mechanisms, have been proposed for transition-metal-catalyzed hydrosilylation of alkenes and alkynes. See: (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed.* **1988**, *27*, 289. (c) Fu, P. F.; Brard, L.; Li, Y. W.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (d) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640. The modified Chalk−Harrod mechanism or σ-bond metathesis mechanism via Co-silyl intermediates is very likely involved in the current catalytic system. However, with limited information at this stage, we could not exclude one or the other.

(21) Markó et al. developed a similar model for Pt-NHC-catalyzed hydrosilylation reactions: Bo, G. D.; Berthon-Gellzo, G.; Tinant, B.; Markó, I. E. *Organometallics* **2006**, *25*, 1881.

(22) The possible interaction between the Si−H bond and the Co center in intermediate **5** that might prevent the isomerization of vinyl Co intermediates via Crabtree−Ojima mechanism to form *trans*-adduct might be another important factor contributing to the high selectivity of the catalytic system. For Crabtree−Ojima mechanism, see: (a) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.