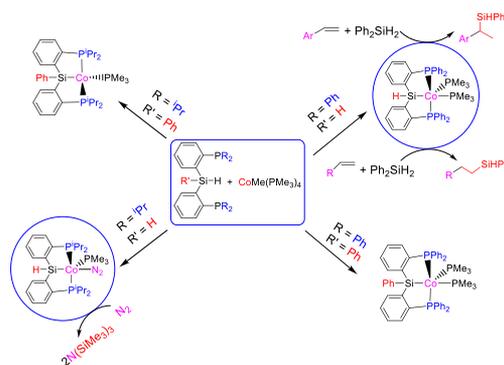


The Effect of Substituents on the Formation of Silyl [PSiP] Pincer Cobalt(I) Complexes and Catalytic Application in Both Nitrogen Silylation and Alkene Hydrosilylation

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ABSTRACT: Four different [PSiP] pincer ligands **L1–L4** ((2 Ph₂PC₆H₄)₂SiHR (R = H (**L1**) and Ph (**L2**)) and (2 ⁱPr₂PC₆H₄)₂SiHR' (R' = Ph (**L3**) and H (**L4**)) were used to investigate the effect of substituents at P and/or Si atom of the [PSiP] pincer ligands on the formation of silyl cobalt(I) complexes by the reactions with CoMe(PMe₃)₄ via Si–H cleavage. Two penta coordinated silyl cobalt(I) complexes, (2 Ph₂PC₆H₄)₂HSiCo(PMe₃)₂ (**1**) and (2 Ph₂PC₆H₄)₂PhSiCo(PMe₃)₂ (**2**), were obtained from the reactions of **L1** and **L2** with CoMe(PMe₃)₄, respectively. Under similar reaction conditions, a tetra coordinated cobalt(I) complex (2 ⁱPr₂PC₆H₄)₂PhSiCo(PMe₃) (**3**) was isolated from the interaction of **L3** with CoMe(PMe₃)₄. It was found that, only in the case of ligand **L4**, silyl dinitrogen cobalt(I) complex **4**, [(2 ⁱPr₂PC₆H₄)₂HSiCo(N₂)(PMe₃)], was formed. Our results indicate that the increasing of electron cloud density at the Co center is beneficial for the formation of a dinitrogen cobalt complex because the large electron density at Co center leads to the enhancement of the π backbonding from cobalt to the coordinated N₂. It was found that silyl dinitrogen cobalt(I) complex **4** is an effective catalyst for catalytic transformation of dinitrogen into silylamine. Among these four silyl cobalt(I) complexes, complex **1** is the best catalyst for hydrosilylation of alkenes with excellent regioselectivity. For aromatic alkenes, catalyst **1** provided Markovnikov products, while for aliphatic alkenes, anti Markovnikov products could be obtained. Both catalytic reaction mechanisms were proposed and discussed. The molecular structures of complexes **1–4** were confirmed by single crystal X ray diffraction.



■ INTRODUCTION

The chemistry of transition metal complexes containing a M–Si bond has achieved rapid development in recent decades because silyl metal complexes are intermediates for catalytic Si–H bond activation and functionalization.^{1,2} Si–H bond activation and functionalization are important for synthesis of new organosilicon compounds as functional materials.³ In addition, the study of silyl metal complexes can provide a deeper understanding of the mechanism of TM catalyzed silylation reactions.⁴ The oxidative addition of the Si–H bond of organosilane at low valent late transition metal centers provides a common and useful way to form silyl metal complexes.^{5,6}

Owing to their stable structure and electronic versatility, pincer ligands have become useful motifs for supporting ligands of transition metal complexes. Strong σ donating ability and *trans* influence of the silyl coordinating moieties also make a metal center electron rich. This causes silyl pincer metal complexes to show a high reactivity toward cleavage of inert bonds such as Si–H bonds via oxidative addition.^{7–9} Among them, [PSiP] pincer metal complexes have been widely used in inert bond activation and metal catalyzed conversion. The

Milstein,¹⁰ Turculet,¹¹ Iwasawa,¹² and Sun¹³ research groups have made great contributions in this regard. In recent years, with the extensive development of nitrogen transition metal compounds,^{14–17} people began to synthesize transition metal complexes supported by [PSiP] pincer ligands and use them in nitrogen activation reactions. In 2018, Turculet reported a bis(dinitrogen) Fe(II) hydride supported by a [PSiP] pincer ligand.¹¹ Nishibayashi studied the preparation and characterization of three cobalt(I) nitrogen complexes bearing [PSiP] pincer ligands and found that none of the three cobalt complexes could catalyze the conversion of nitrogen to ammonia, but under mild conditions, these three cobalt complexes could catalyze the transformation of nitrogen to (Me₃Si)₃N.¹⁸ Since silicon atoms have a strong *trans* influence,

this can increase the electron cloud density of the cobalt center and may enhance the π back donation from the cobalt center to N_2 ligand. Therefore, the coordinated N_2 is significantly activated when N_2 is *trans* positioned to Si atom.

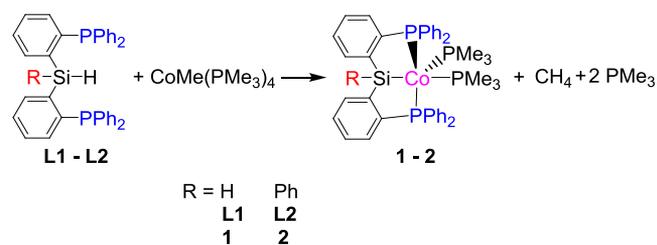
Except for the nitrogen activation reaction, pincer transition metal complexes as catalysts have been gradually applied in alkene hydrosilylation.^{19,20} Fout reported a well defined bis(carbene) [CCC] pincer cobalt(I) dinitrogen complex as a catalyst for the efficient anti Markovnikov hydrosilylation of terminal alkenes, featuring a broad substrate scope.²¹ Our group previously reported the selective hydrosilylation of aromatic and aliphatic olefins using Co hydride supported by [CNC] pincer ligands.²² To our knowledge, there is no transition metal complex supported by a [PSiP] pincer ligand for olefin silylation.

In this paper, we intend to use four different [PSiP] pincer ligands to synthesize silyl [PSiP] pincer cobalt complexes and systematically study the effects of the electronic property of the [PSiP] pincer ligands with different substitutional groups on the formation of silyl complexes. As a matter of fact, four cobalt(I) complexes 1–4 were obtained by the reactions of $CoMe(PMe_3)_4$ with four different [PSiP] pincer ligands. Only one dinitrogen cobalt complex $[(2 \text{ } ^iPrPC_6H_4)_2HSiCo(N_2)(PMe_3)]$ (4) bearing a [PSiP] pincer ligand was isolated. The results show that the formation of nitrogen cobalt complexes is related to the electronic effects of ligands. The catalytic activity of complex 4 toward nitrogen silylation under mild reaction conditions was studied. In addition, silyl [PSiP] pincer cobalt(I) complexes 1–4 as catalysts for alkene hydro silylation were investigated. We also found that complex 1 is the best catalyst for hydrosilylation of alkenes with excellent regioselectivity among these four cobalt complexes. For aromatic alkenes, Markovnikov products as the main products were formed, while anti Markovnikov products as the main products were isolated for aliphatic alkenes. A catalytic reaction mechanism is proposed. It was found that the real catalyst is a cobalt complex with semi activated Si–H bond.

RESULTS AND DISCUSSION

Synthesis of Silyl [PSiP] Pincer Cobalt(I) Complexes 1–4 via Si–H Activation. According to our early report,^{23,24} a novel cobalt(I) complex 1 or 2 with a [PSiP] pincer ligand as Si–H bond activation product was obtained by the reaction of preligand L1²⁵ or L2²⁶ with $CoMe(PMe_3)_4$, respectively (Scheme 1). When preligand L1 or L2 was combined with $CoMe(PMe_3)_4$ in THF at 0 °C, the color of the solution changed from orange to red after 12 h at room temperature. After the volatiles were removed, the residue was extracted with *n* pentane and diethyl ether, respectively. Complex 1 or 2 was obtained as red crystals and was fully characterized by spectroscopic methods.

Scheme 1. Synthesis of Cobalt(I) Complexes 1 and 2



In the IR spectra of complexes 1 and 2, the typical vibrations of the Si–H bond of L1 at 2143 cm^{-1} and L2 at 2186 cm^{-1} disappeared. In the ^{31}P NMR spectra of complexes 1 and 2, three different phosphorus signals were recorded for the phosphorus groups (at -16.4 (PMe_3), 3.5 (PMe_3), and 57.5 ($-\text{PPh}_2$) ppm for 1 and at -19.1 (PMe_3), 3.9 (PMe_3) and 57.8 ($-\text{PPh}_2$) ppm for 2) in the integral ratio of 1:1:2. All the spectroscopic information accords with a trigonal bipyramidal coordination geometry. Single crystal X ray diffraction confirmed the molecular structures of complexes 1 and 2 (Figures 1 and 2). In the molecular structure of complex 1, the cobalt

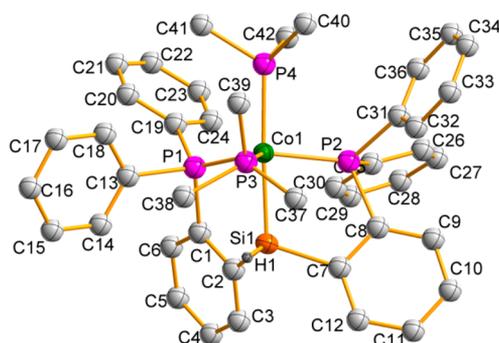


Figure 1. Molecular structure of complex 1. Thermal ellipsoids are drawn at 50% probability level (Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1–P1 2.1869(5), Co1–P2 2.1872(5), Co1–P3 2.1885(5), Co1–P4 2.2132(5), Co1–Si1 2.2599(5); P2–Co1–P3 115.97(2), P1–Co1–P3 114.97(2), P3–Co1–P4 99.47(2), P1–Co1–P2 124.59(2), P2–Co1–P4 94.21(2), P1–Co1–Si1 82.135(19), P4–Co1–Si1 175.60(2), P3–Co1–Si1 84.54(2).

atom is centered in a distorted trigonal bipyramidal coordination geometry with P4–Co1–Si1 ($175.60(2)^\circ$) in the axial direction. Three other coordinated P atoms are located in the equatorial plane with the total sum of the coordination bond angles (P1–Co1–P2 = $124.59(2)^\circ$, P2–Co1–P3 = $115.97(2)^\circ$, and P1–Co1–P3 = $114.97(2)^\circ$)

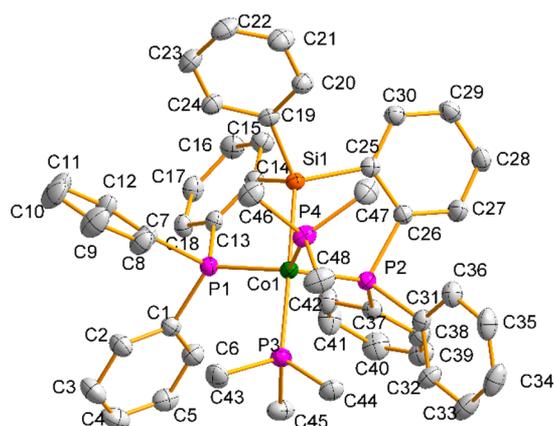
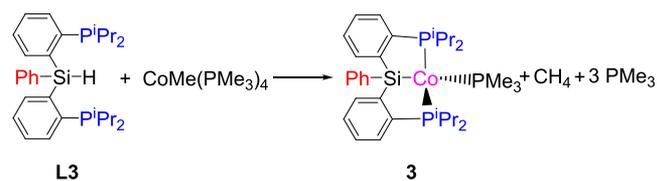


Figure 2. Molecular structure of complex 2. Thermal ellipsoids are drawn at 50% probability level (Hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Co1–P1 2.2048(5), Co1–P2 2.1821(5), Co1–P3 2.2144(5), Co1–P4 2.2013(5), Co1–Si1 2.2878(5); P1–Co1–P3 96.175(1), P1–Co1–Si1 81.260(1), P2–Co1–P1 120.37(2), P2–Co1–P3 96.28(2), P2–Co1–P4 111.04(2), P2–Co1–Si1 83.043(1), P3–Co1–Si1 176.49(2), P4–Co1–Si1 125.22(2).

355.53°, deviated from 360°. Co1–P4 (2.2132(5) Å) is significantly longer than the other three Co–P bonds (Co1–P1 = 2.1869(5), Co1–P2 = 2.1872(5), and Co1–P3 = 2.1885(5) Å) due to the *trans* influence of the silyl group. Two PMe₃ ligands in different spatial positions are also demonstrated by different ¹H NMR signals (0.58 and 1.05 ppm). Complex 2 has the similar structural characteristics with complex 1. However, the Co–Si bond (2.2878(5) Å) in complex 2 is slightly longer than that (2.2599(5) Å) in complex 1. It is proposed that this result is caused by the weak electron donating ability and steric effect of the phenyl group in complex 2. The larger axial bond angle (P3–Co1–Si1 = 176.49(2)°) in complex 2 can be understood by the steric effect of the phenyl group in comparison with that (P4–Co1–Si1 = 175.60(2)°) in complex 1. The iron hydride similar to complex 1 and its structure have been reported.²⁷

If the phenyl groups at the P atoms in L2 are replaced by the isopropyl groups, L2 becomes L3 (Scheme 2).²⁸ The reaction

Scheme 2. Synthesis of Cobalt(I) Complex 3



of CoMe(PMe₃)₄ with L3 in THF afforded the cobalt(I) complex 3. Complex 3 was obtained as yellow crystals from its *n* pentane solution. Complex 3 (d⁸ configuration) with tetrahedral coordination geometry is paramagnetic, and no NMR information could be explained. Single crystal X ray diffraction confirmed that complex 3 has a tetrahedral coordination geometry (Figure 3).

In the molecular structure of complex 3, the cobalt atom is in the center of a distorted tetrahedron. Co1–P3 (2.2137(8) Å) is shorter than the other two Co–P bonds (Co1–P1 = 2.2225(6) and Co1–P2 2.2272(8) Å) because the isopropyl/phenyl groups at P1 and P2 atom have a greater steric hindrance than the methyl groups at the P3 atom. The distance

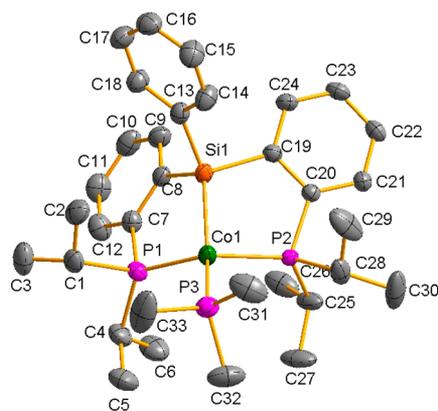
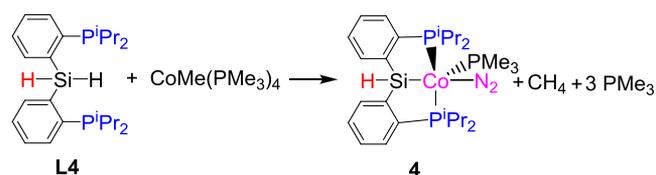


Figure 3. Molecular structure of complex 3. Thermal ellipsoids are drawn at 50% probability level (Hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Co1–P1 2.2225(6), Co1–P2 2.2272(8), Co1–P3 2.2137(8), Co1–Si1 2.2480(6); P1–Co1–P2 122.68(2), P1–Co1–Si1 85.65(2), P2–Co1–Si1 86.01(2), P3–Co1–P1 110.60(2), P3–Co1–P2 105.55(2), P3–Co1–Si1 148.32(3).

of Co1–Si1 (2.2480(6) Å) is slightly shorter than those (2.2599(5) (1) and 2.2878(5) (2) Å) in the penta coordinate silyl Co(I) complexes 1 and 2. Compared with complexes 1, 2, and 4, only complex 3 is tetra coordinate because –ⁱPr is bulkier than –Ph and Si–Ph is bulkier than Si–H.

To our delight, the reaction of L4,²⁹ derived from L3 by the replacement of phenyl group with H atom at the Si atom, with CoMe(PMe₃)₄ in THF afforded the dinitrogen cobalt(I) complex 4 in 61% yield (Scheme 3). Compared with complex

Scheme 3. Synthesis of Dinitrogen Cobalt Complex 4



1, due to the replacement of the phenyl by the isopropyl groups, the density of the electron cloud at the cobalt center is increased. This result indicates that the increasing of electron density at the Co center is beneficial for the formation of dinitrogen cobalt complex because the large electron density at the Co center leads to the enhancement of the π backdonation from cobalt to the coordinated N₂. In the IR spectrum of complex 4, a strong absorption at 2061 cm⁻¹ belongs to the terminal coordinated N₂ ligand, which is comparable with that (2063 cm⁻¹) in the complex [Co(Cy PSiMeP)(N₂)(PMe₃)] reported by Nishibayashi group.¹⁸ A weak absorption at 2020 cm⁻¹ for the unactivated Si–H bond was recorded in complex 4, while the Si–H bond of L4 is situated at 2143 cm⁻¹. Obviously, the coordination of the Si atom to the cobalt center leads to the large bathochromic shift and the weakening of Si–H bond. In the ¹H NMR spectrum of complex 4, the singlet signal at 4.36 ppm is attributed to the Si–H proton, while the Si–H proton of L4 has the resonance at 5.89 ppm. In the ³¹P NMR spectrum of 4, two sets of signals are distinguished at 0.0 (t) and 85.1 (d) ppm, corresponding to the two kinds of the P atoms in an integral ratio of 1 (PMe₃): 2 (–ⁱPr₂).

The molecular structure of complex 4 was determined by single crystal X ray diffraction analysis (Figure 4). Complex 4 has a distorted trigonal bipyramid with the cobalt atom in the center. The N1–N2 bond length of the dinitrogen ligand in 4 is 1.115(2) Å, in the region of those of the terminal dinitrogen ligands in the reported dinitrogen cobalt(I) complexes (0.956–1.125 Å) and close to that (1.131(8) Å) in complex [Co(Cy PSi^{Me}P)(N₂)(PMe₃)].¹⁸ The Si atom in 4 is positioned *trans* to the dinitrogen ligand with a Co1–Si1 distance of 2.2473(5) Å and Co1–N1 distance of 1.8033(2) Å, while the related Co–Si and Co–N distances are 2.2635(19) and 1.787(5) Å in [Co(Cy PSi^{Me}P)(N₂)(PMe₃)]. Obviously, compared with the complex [Co(Cy PSi^{Me}P)(N₂)(PMe₃)], the density of electron cloud on the central cobalt atom in complex 4 with H substituent at the silyl group is lower than that on the cobalt atom in complex [Co(Cy PSi^{Me}P)(N₂)(PMe₃)]. The Co–N bond in complex 4 is also longer than that in [Co(Cy PSi^{Me}P)(N₂)(PMe₃)] due to the decrease of the composition of the π backbonding. This is why the N≡N bond in complex 4 is a little bit shorter than that in complex [Co(Cy PSi^{Me}P)(N₂)(PMe₃)].

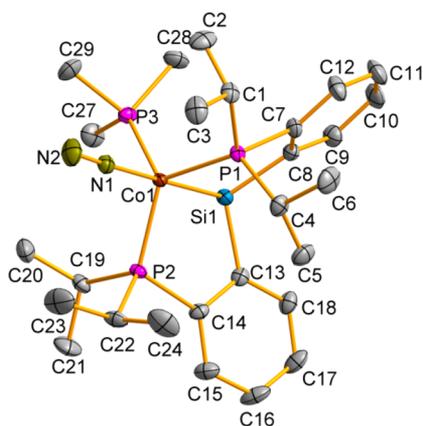


Figure 4. Molecular structure of complex **4**. Thermal ellipsoids are drawn at 50% probability level (Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1–P1 2.2194(5), Co1–P2 2.2062(5), Co1–P3 2.1845(5), N1–N2 1.115(2), Co1–Si1 2.2473(5), Co1–N1 1.8033(16); P2–Co1–P3 119.46(2), P1–Co1–P3 114.55(2), P3–Co1–N1 93.49(5), P1–Co1–P2 121.92(2), P2–Co1–N1 97.95(5), P1–Co1–N1 98.58(5), P3–Co1–Si1 83.98(19), N2–N1–Co1 176.29(17), Si1–Co1–N1 177.39(5).

Catalytic Activity of Dinitrogen Cobalt(I) Complex 4 for Nitrogen Fixation. The catalytic silylation of dinitrogen proceeded smoothly with dinitrogen cobalt complex **4** as a catalyst under ambient reaction conditions (Table 1). For

Table 1. Catalytic Silylation of Dinitrogen with Complex 4^a

$$\text{N}_2 + n \text{ Reductant} + n \text{ Me}_3\text{SiCl} \xrightarrow[\text{Solvent}]{\mathbf{4}} 2 \text{ N}(\text{SiMe}_3)_3$$

(1 atm)

entry	reductant	solvent	T (°C)	reductant/ ClSiMe ₃ (equiv)	N(SiMe ₃) ₃ (equiv) ^d
1 ^b	KC ₈	THF	25	600	0.1
2 ^c	KC ₈	THF	25	600	7.2
3	KC ₈	THF	25	600	8.6
4	Li	THF	25	600	0.2
5	Na	THF	25	600	0.5
6	K	THF	25	600	3.6
7	KC ₈	<i>n</i> - pentane	25	600	5.3
8	KC ₈	toluene	25	600	6.7
9	KC ₈	Et ₂ O	25	600	9.5
10	KC ₈	DME	25	600	9.5
11	KC ₈	dioxane	25	600	15.4
12	KC ₈	dioxane	50	600	13.0
13	KC ₈	dioxane	80	600	12.4
14	KC ₈	dioxane	25	1800	28.8
15	KC ₈	dioxane	25(144h)	1800	52

^a0.01 mmol catalyst, 20 mL solvent, N₂ (1 atm), 24 h. The equivalents of reductant and ClSiMe₃ are based on the catalyst. Yields were determined by GC. ^bWith complex **1**. ^cWith complex **3**. ^dBased on the catalyst.

comparison, we also investigated the behavior of cobalt complexes **1** and **3** without a coordinated dinitrogen ligand. The use of complex **1** or **3** as a catalyst afforded lower equivalents of N(SiMe₃)₃ (entries 1 and 2, Table 1). This indicates that the dinitrogen cobalt complex is an important intermediate for the catalytic reduction of nitrogen. With

excess amounts of KC₈ (600 equiv relative to **4**), Me₃SiCl (600 equiv relative to **4**), and N₂ (1 atm), the catalytic reaction with **4** as a catalyst at room temperature within 24 h gave 8.6 equiv of N(SiMe₃)₃ based on the cobalt atom (entry 3, Table 1). N(SiMe₃)₃ was confirmed as a product by gas chromatography (GC) and HRMS. Due to the lower reducing ability or/and smaller specific surface area, a lower amount of N(SiMe₃)₃ was produced when the active alkali metal (Li, Na or K) was used as a reductant (entries 4–6, Table 1). The use of a strong reductant such as KC₈ was necessary to render the catalytic reaction effective. The amount of produced N(SiMe₃)₃ is also related to the polarity of the solvent (entries 7–11, Table 1). It was confirmed that dioxane was the best reaction medium among the five tested solvents (*n* pentane, toluene, Et₂O, DME, and dioxane). The reaction temperature has a significant impact on the reaction (entry 11–13, Table 1). When temperature rose, the equivalents of N(SiMe₃)₃ significantly reduced. With a larger amount of KC₈ and Me₃SiCl, the catalytic reaction afforded 28.8 equiv of N(SiMe₃)₃ within 24 h, slightly lower than the catalytic effect of complex [Co(CyPSi^{Me}P)(N₂)(PMe₃)]¹⁸ (entry 14, Table 1). Within 144 h under the same conditions (entry 15, Table 1), 52 equiv of N(SiMe₃)₃ were formed. This result further validates the conclusion that the greater the density of electron cloud at the metal center, the better the catalytic effect of the complex. Recently, more reports on dinitrogen silylation catalyzed by mononuclear and multinuclear transition metal complexes were published.^{30–34}

To further explore this reaction, the formation of N(SiMe₃)₃ over time was monitored (Figure 5). This result indicates that

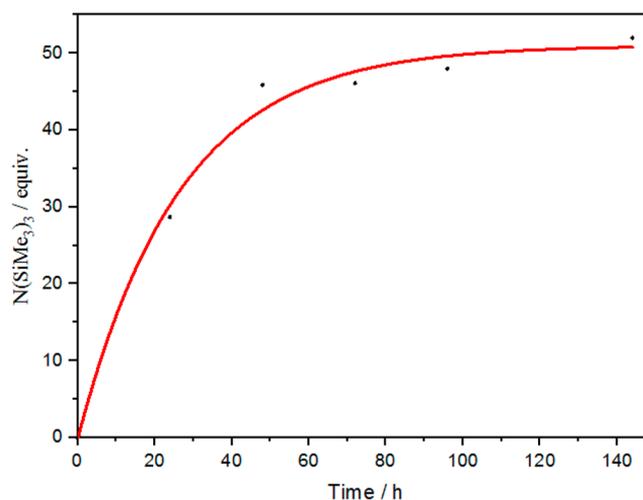
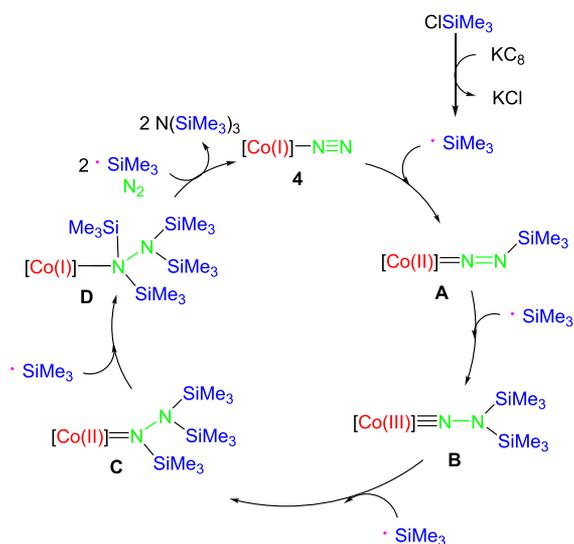


Figure 5. Time profile of formation of N(SiMe₃)₃ with **4** as a catalyst.

the initial formation of N(SiMe₃)₃ proceeded rapidly and the catalytic reaction was almost completed after 144 h. In order to shed light on the mechanism, the stoichiometric reaction of **4** with KC₈ and Me₃SiCl (1:2:2) was examined. Unfortunately, no reaction intermediate could be identified from the reaction mixture.

Based on the literature reports, a catalytic reaction mechanism for this catalytic system is proposed (Scheme 4). At the beginning, the •SiMe₃ radical is formed from the interaction of Me₃SiCl with KC₈ with KCl as a byproduct. The addition of •SiMe₃ to complex **4** gives rise to intermediate **A**, a cobalt(II) species. After the addition of the second •SiMe₃

Scheme 4. A Proposed Catalytic Mechanism for N₂ Silylation



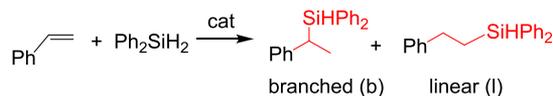
radical A becomes a cobalt(III) intermediate B. The third and fourth radical $\bullet\text{SiMe}_3$ are added to the nitrogen atom connected to cobalt, respectively, so that the valence of cobalt is reduced to form intermediates C and D. In the presence of N₂, the interaction of D with two $\bullet\text{SiMe}_3$ radicals delivers the final product N(SiMe₃)₃ with the recovery of complex 4. Unfortunately, we have not been able to separate and prove these intermediates from experiments.

Hydrosilylation of Alkenes with Silyl [PSiP] Pincer Cobalt(I) Complexes 1–4 as Catalysts. Hydrosilylation of alkenes is an important way to prepare new organosilicon

compounds. In the classical hydrosilylation reaction, platinum and other precious metals have been used as catalysts. In recent years, people began to study the possibility of using base metals, such as iron, cobalt, or nickel, as catalysts for the hydrosilylation of alkenes. Although some cobalt complexes have been reported as catalysts for hydrosilylation,^{20,21,21,35,36} no industrial application for them has been found. We also did some explorations.²² The following work is a continuation of our study in this field.

Initially, styrene was selected as a model substrate to optimize the catalytic conditions. As depicted in Table 2, all cobalt complexes 1–4 gave the Markovnikov product as the major product. In particular, complex 1 was very effective for Markovnikov hydrosilylation and could reach a conversion of 87% with excellent selectivity (b/l = 95:5) (entries 1–4, Table 2). After that we investigated the effect of solvents, silanes, and other experimental parameters, such as temperature and the catalyst loading. It was found that solvent free reaction was identified as the best condition for the formation of hydrosilylation product. Solvents such as THF, toluene, dioxane, *n* pentane, DMSO, DMF, and DME gave unsatisfactory results (entries 1 and 5–11, Table 2). When screening silanes, we found that Ph₂SiH₂ had the best catalytic effect among the five silanes (entries 1 and 12–15, Table 2). When the reaction temperature was reduced to 50 or 30 °C, the conversion decreased to 53% or 8%, respectively (entries 16 and 17, Table 2). This might be the result of the low solubility of the catalyst. When we extended the reaction time to 36 h, the conversion increased from 87% to 93% (entry 18, Table 2). However, when the catalyst loading was 0.5 mol %, the conversion decreased significantly (entry 19, Table 2). When we increased the catalytic loading from 1 mol % to 2 mol %, complete conversion could be achieved within 24 h

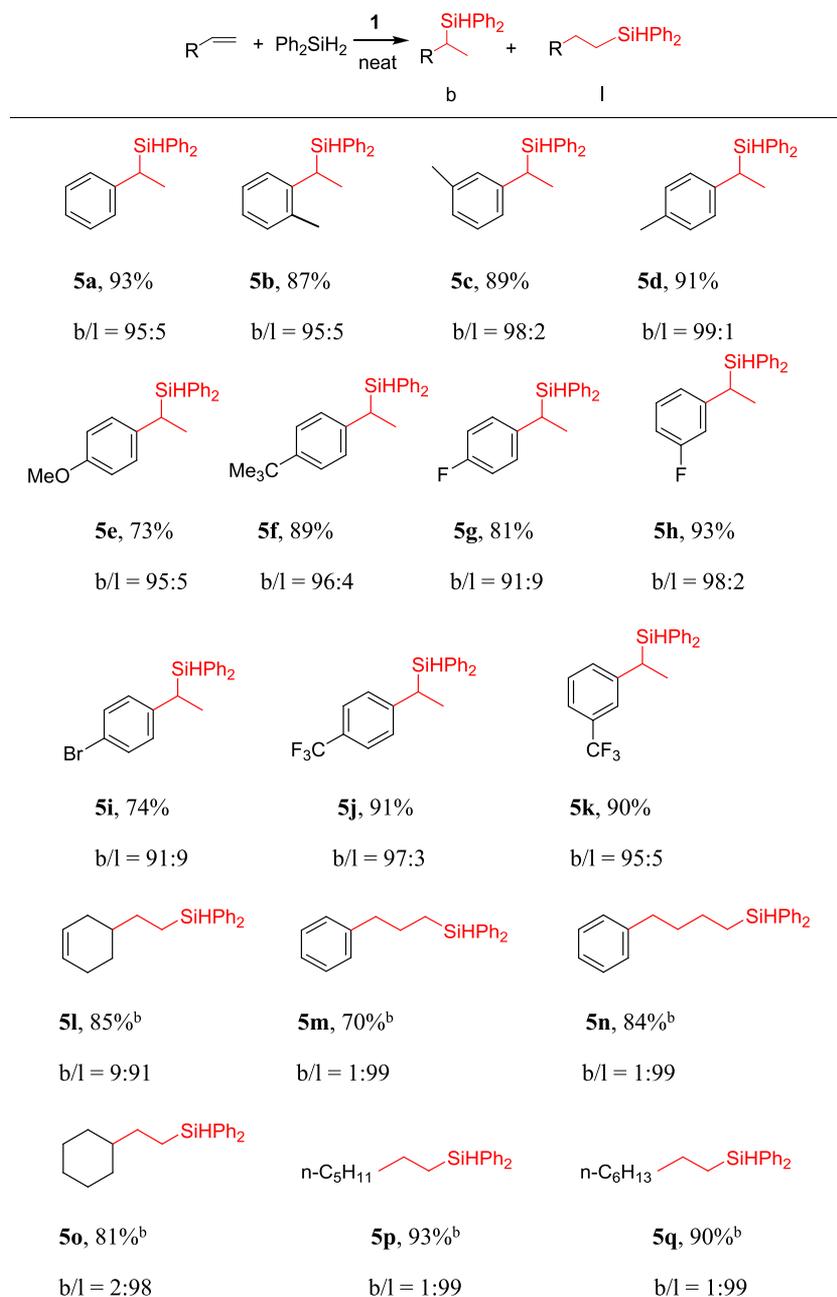
Table 2. Optimization of Reaction Conditions^a



entry	catalyst	loading (mol %)	solvent	silane	temp (°C)	time (h)	conv. (%)	ratio (b/l) ^b
1	1	1	neat	Ph ₂ SiH ₂	70	24	87	95:5
2	2	1	neat	Ph ₂ SiH ₂	70	24	63	87:13
3	3	1	neat	Ph ₂ SiH ₂	70	24	80	45:40
4	4	1	neat	Ph ₂ SiH ₂	70	24	59	83:17
5	1	1	THF	Ph ₂ SiH ₂	70	24	41	70:30
6	1	1	toluene	Ph ₂ SiH ₂	70	24	35	65:35
7	1	1	dioxane	Ph ₂ SiH ₂	70	24	35	66:34
8	1	1	<i>n</i> -pentane	Ph ₂ SiH ₂	70	24	74	77:23
9	1	1	DMSO	Ph ₂ SiH ₂	70	24	49	85:15
10	1	1	DMF	Ph ₂ SiH ₂	70	24	73	88:12
11	1	1	DME	Ph ₂ SiH ₂	70	24	71	45:55
12	1	1	neat	Ph ₃ SiH	70	24	52	--
13	1	1	neat	PhSiH ₃	70	24	40	--
14	1	1	neat	Et ₃ SiH	70	24	68	--
15	1	1	neat	Me(EtO) ₂ SiH	70	24	73	--
16	1	1	neat	Ph ₂ SiH ₂	30	24	8	--
17	1	1	neat	Ph ₂ SiH ₂	50	24	53	95:5
18	1	1	neat	Ph ₂ SiH ₂	70	36	93	95:5
19	1	0.5	neat	Ph ₂ SiH ₂	70	24	30	90:10
20	1	2	neat	Ph ₂ SiH ₂	70	24	99	95:5

^aCatalytic reaction conditions: styrene (1.0 mmol), silane (1.2 mmol), conversions, and product ratios were determined by GC with *n* dodecane as an internal standard. ^bb/l: branched/linear.

Table 3. Scope of Alkenes for Co(I) Catalyzed Hydrosilylation^a



^aCatalytic reaction conditions: alkene (1.0 mmol), Ph₂SiH₂ (1.2 mmol), complex **1** (2 mol %), neat at 70 °C for 24 h; isolated yields. ^b36 h.

(entry 20, Table 2). Therefore, the optimized reaction conditions are as follows: 2 mol % **1**, Ph₂SiH₂, solvent free, 70 °C, and 24 h (entry 20, Table 2).

Under the optimized conditions, the substrate scope was explored (Table 3). The cobalt complex **1** mediated hydrosilylation of aromatic alkenes with Ph₂SiH₂, furnishing Markovnikov branched products with excellent regioselectivity in high isolated yield (**5a–5k**). Various electron donating and electron withdrawing functional groups were well tolerated, such as methyl (**5b–5d**), methoxy (**5e**), *tert* butyl (**5f**), halogen (**5g–5i**), and trifluoromethyl (**5j–5k**) groups. The substituents at *ortho*, *meta*, and *para* position on the phenyl group of styrene were also tolerated. Unexpectedly, the anti Markovnikov linear addition products were obtained from the

hydrosilylation of aliphatic olefins (**5l–5q**). This is similar to the results reported by our group.²² The results indicate that catalyst **1** has Markovnikov selectivity for the aromatic alkenes and anti Markovnikov selectivity for the aliphatic alkenes.

To provide insight into the catalyst activation mode and the nature of the cobalt intermediacy, we conducted the stoichiometric experiments of catalyst **1** and Ph₂SiH₂ as well as **1** and styrene. Although we did not isolate the intermediate, we detected the Co–H signal at 1890 cm⁻¹ by IR during the reaction of catalyst **1** with Ph₂SiH₂ (Figure S50). This value is close to those of the related cobalt complexes.³⁷ Subsequently, we also monitored the reaction of catalyst **1** (1 equiv) with Ph₂SiH₂ (1.2 equiv) by *in situ* ¹H NMR (Figure 6). To our surprise, when the reaction lasted for 1 h, three signals

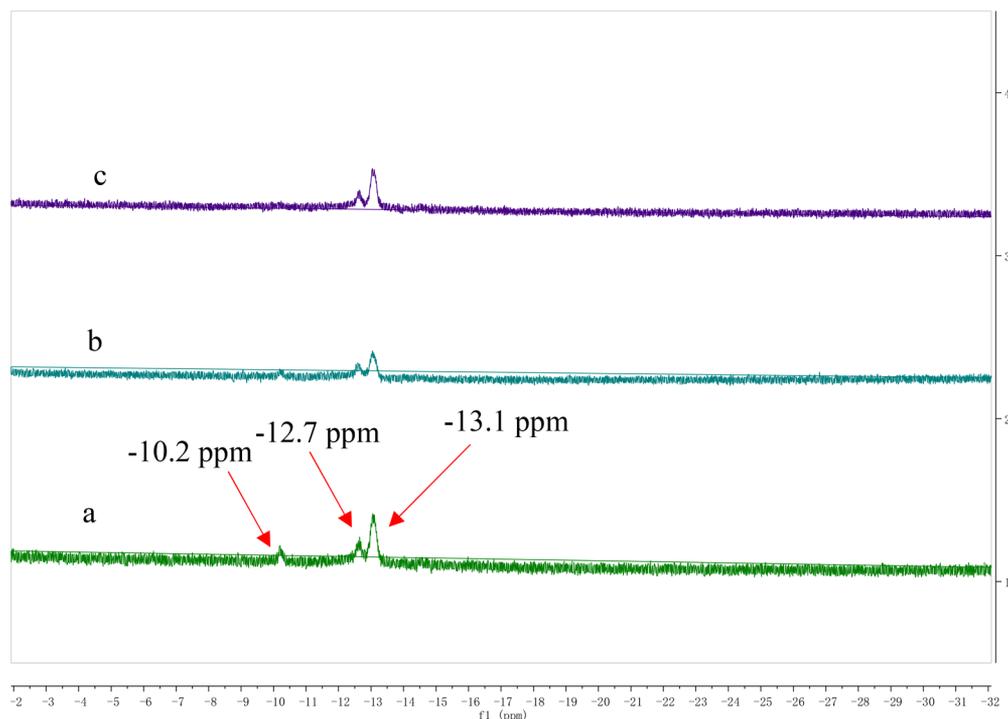


Figure 6. *In situ* ^1H NMR of 1 equiv of **1** reacted with 1.2 equiv of Ph_2SiH_2 : (a) 1 h, (b) 2 h, and (c) 3 h.

appeared in the high field. We speculate that the signal at -10.2 ppm belongs to the intermediate (**E**, Scheme 5) with a semiactivated Si–H bond, while the two peaks at -12.7 ppm and -13.1 ppm belong to a pair of isomers of the cobalt hydrides (**E'**, Scheme 5). As the reaction proceeded, the concentration of the intermediate with a semi activated Si–H bond became less and less. After 3 h, the signal at -10.2 ppm disappeared completely. This indicates that all the species with a semi activated Si–H bond were converted to the cobalt hydrides. These inferences are based on the literature reports.^{38–40} The entire conversion from the semi activated Si–H to Si–H cleavage took 3 h at 70°C . In order to verify the real intermediate of catalytic activity, we also studied the effect of the addition sequence of the reactants. The results show that we could get the same results as in Table 2 if the catalyst **1** reacted with styrene for 30 min or 2 h before adding Ph_2SiH_2 . If the catalyst **1** reacted with Ph_2SiH_2 for 30 min or 2 h before adding styrene, the conversion rate decreased from 99% to 79% or 41% (Table S2). This shows that the real catalyst is a cobalt intermediate with a semi activated Si–H bond. This is similar to the catalytic intermediate reported by Chirik's group.⁴¹

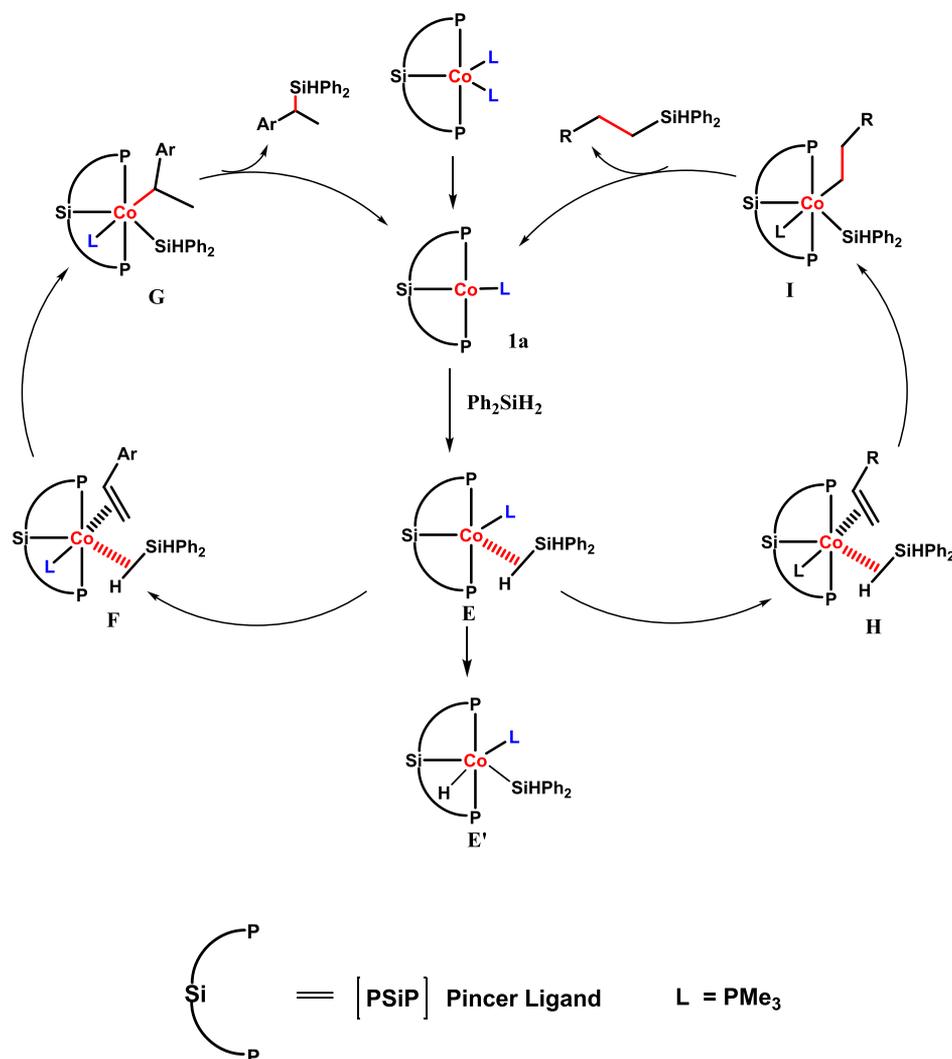
On the basis of the above experimental results and literature reports,^{21,29,42} a possible reaction mechanism for olefin hydrosilylation is proposed (Scheme 5). At the beginning of the reaction, intermediate **1a** with an empty coordination site is formed through the dissociation of PMe_3 ligand from **1**. **1a** reacts with Ph_2SiH_2 to generate active intermediate **E** with a semi activated Si–H bond. **E** was indirectly proved by *in situ* IR and ^1H NMR. The coordination of the substrate alkene to **E** affords intermediate **F** or **H**. If the alkene cannot be quickly captured by **E**, then **E** will undergo an oxidative addition reaction with Ph_2SiH_2 to generate a relatively stable Co(III) hydride **E'**. This is not conducive to the catalytic hydro silylation of alkenes. This inferring was confirmed by the stoichiometric experiments. This step also determines the

regioselectivity of the reaction. For aromatic alkenes, the migration insertion reaction is more inclined to a 2,1 insertion to generate a secondary benzyl cobalt species **G**. In contrast to aromatic alkenes, aliphatic alkenes are more inclined to a 1,2 insertion reaction to form a primary alkyl cobalt species **I**. **G** or **I** undergoes a reductive elimination reaction to deliver Markovnikov (branched) product **J** or anti Markovnikov (linear) product **K** with the recovery of **1a**. This mechanism is different from those proposed by the groups of Fout²¹ and Nakazawa.⁴² They consider that metal hydrides are the key intermediates of the reactions.

CONCLUSIONS

In summary, four different silyl cobalt(I) complexes **1–4** ($[(2\text{-Ph}_2\text{PC}_6\text{H}_4)_2\text{HSiCo}(\text{PMe}_3)_2]$ (**1**), $[(2\text{-Ph}_2\text{PC}_6\text{H}_4)_2\text{PhSiCo}(\text{PMe}_3)_2]$ (**2**), $[(2\text{-}^i\text{Pr}_2\text{PC}_6\text{H}_4)_2\text{PhSiCo}(\text{PMe}_3)]$ (**3**), and $[(2\text{-}^i\text{Pr}_2\text{PC}_6\text{H}_4)_2\text{HSiCo}(\text{N}_2)(\text{PMe}_3)]$ (**4**) bearing [PSiP] pincer ligands with different substitutional groups at the P and Si atom were prepared by the reactions of the preligands (**L1–L4**) with $\text{CoMe}(\text{PMe}_3)_4$ via Si–H bond activation. Among these four complexes, complexes **1**, **2**, and **4** are penta coordinate with a trigonal bipyramidal coordination geometry, while the paramagnetic complex **3** is tetra coordinated with a tetrahedral molecular structure. The difference in coordination number and the coordination of dinitrogen molecule can be explained by the electron effects caused by the replacement of the phenyl group at the Si atom and the isopropyl groups at the P atoms. Our results indicate that the increasing of electron cloud density at the Co center is beneficial for the formation of a dinitrogen cobalt complex because the large electron cloud density at the Co center leads to the enhancement of the π backbonding from cobalt to the coordinated N_2 . It was experimentally confirmed that dinitrogen cobalt(I) complex **4** could be used as a catalyst for nitrogen silylation. Among these four silyl cobalt(I) complexes, complex **1** is the best catalyst for hydrosilylation of alkenes with excellent regioselectivity. For

Scheme 5. Proposed Mechanisms



aromatic alkenes, the reactions obey the Markovnikov rule, while for aliphatic alkenes, the reactions are carried out in the way of the anti Markovnikov rule. The catalytic mechanisms for both nitrogen silylation and alkene hydrosilylation were proposed and discussed by the experimental support. The molecular structures of cobalt(I) complexes **1–4** were determined by single crystal X ray diffraction.

EXPERIMENTAL SECTION

General Procedures and Materials. All reactions were performed under an inert atmosphere utilizing the standard Schlenk techniques. Solvents were dried by distillation from Na benzophenone under nitrogen. Ligands **L1–L4**^{25–29} and $\text{CoMe}(\text{PMe}_3)_4$ ⁴³ were prepared according to literature procedures. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT IR instrument. NMR spectra were obtained by using Bruker Avance 300 and 400 MHz spectrometers. GC MS was recorded on a TRACE DSQ instrument, and GC was recorded on a Fuli 9790 instrument. Melting points (mp) were measured on a WRR instrument with samples in capillaries sealed.

Synthesis of Complex 1. **L1** (0.55 g, 1 mmol) in 30 mL of THF was combined with $\text{CoMe}(\text{PMe}_3)_4$ (0.38 g, 1 mmol) in 30 mL of THF at 0 °C. The mixture was stirred for 14 h at room temperature. After workup, complex **1** (0.57 g, 0.75 mmol) was obtained as red crystals at –20 °C from *n* pentane solution in a yield of 75%. Dec: >174 °C. Anal. calcd for $\text{C}_{42}\text{H}_{47}\text{CoP}_4\text{Si}$ (762.8 g/mol): C, 66.14; H,

6.21. Found: C, 66.54; H, 6.46. IR (Nujol, KBr, cm^{-1}): 2018 (Si–H), 1581 ($\text{ArC}=\text{C}$), 939 (PMe_3). ^1H NMR (300 MHz, benzene d_6 , 300 K, δ/ppm): 0.58 (d, $J = 6.0$ Hz, PCH_3 , 9H), 1.05 (d, $J = 6.0$ Hz, PCH_3 , 9H), 3.97 (q, $J = 15.0$ Hz, Si H, 1H), 6.66–6.74 (m, Ar H, 4H), 6.80–6.82 (m, Ar H, 5H), 6.96–7.02 (m, Ar H, 11H), 7.12–7.18 (m, Ar H, 4H), 7.51–7.57 (m, Ar H, 4H). ^{31}P { ^1H } NMR (121 MHz, benzene d_6 , 300 K, δ/ppm): –16.4 (d, $J = 53.2$ Hz, PMe_3 , 1P), 3.5 (d, $J = 44.8$ Hz, PMe_3 , 1P), 57.5 (m, PPH_2 , 2P). ^{13}C { ^1H } NMR (75 MHz, benzene d_6 , 300 K, δ/ppm): 24.3 (dq, $J = 20.3$, 6.0 Hz, PCH_3), 26.4 (dq, $J = 18.0$, 3.8 Hz, PCH_3), 126.7 (s, Ar C), 126.9 (s, Ar C), 127.2 (t, $J = 3.8$ Hz, Ar C), 130.5 (s, Ar C), 130.9 (t, $J = 11.2$ Hz, Ar C), 132.8 (t, $J = 5.3$ Hz, Ar C), 133.2 (t, $J = 6.8$ Hz, Ar C), 141.6 (qd, $J = 13.9$, 1.5 Hz, Ar C), 142.6 (t, $J = 16.5$ Hz, Ar C), 151.1 (td, $J = 23.3$, 9.8 Hz, Ar C), 157.4 (td, $J = 30.8$, 2.3 Hz, Ar C). ^{29}Si NMR (79 MHz, benzene d_6 , 300 K, δ/ppm): (ddt, $J = 67.5$, 50.8, 33.4 Hz).

Synthesis of Complex 2. **L2** (0.62 g, 1 mmol) in 30 mL of THF was combined with $\text{CoMe}(\text{PMe}_3)_4$ (0.38 g, 1 mmol) in 30 mL of THF at 0 °C. The mixture was stirred for 14 h at room temperature. After workup, complex **2** (0.5 g, 0.6 mmol) was obtained as red power at 0 °C from *n* pentane solution in a yield of 60%. Dec: >160 °C. Anal. calcd for $\text{C}_{48}\text{H}_{51}\text{CoP}_4\text{Si}$ (838.8 g/mol): C, 68.73; H, 6.13. Found: C, 69.22; H, 5.90. IR (Nujol, KBr, cm^{-1}): 1584 ($\text{ArC}=\text{C}$), 940 (PMe_3). ^1H NMR (300 MHz, benzene d_6 , 300 K, δ/ppm): 0.89 (d, $J = 6.0$ Hz, PCH_3 , 9H), 1.26 (d, $J = 6.0$ Hz, PCH_3 , 9H), 6.74–6.77 (m, Ar H, 4H), 6.91–6.96 (m, Ar H, 4H), 7.02–7.33 (m, Ar H, 17H), 7.42–7.44 (m, Ar H, 2H), 8.02–8.04 (d, Ar H, 2H), 8.13–

8.15 (m, Ar H, 4H). ^{31}P {1H} NMR (121 MHz, benzene d_6 , 300 K, δ /ppm): -19.1 (m, PMe_3 , 1P), 3.9 (m, PMe_3 , 1P), 57.7 (m, PPh_2 , 2P). ^{13}C {1H} NMR (75 MHz, benzene d_6 , 300 K, δ /ppm): 28.6 (s, PCH_3), 129.41 (s, Ar C), 131.3 (t, $J = 5.3$ Hz, Ar C), 132.9 (t, $J = 7.5$ Hz, Ar C), 135.9 (s, Ar C), 140.3 (s, Ar C). ^{29}Si NMR (79 MHz, benzene d_6 , 300 K, δ /ppm): 66.28 (s).

Synthesis of Complex 3. L3 (0.68 g, 1.4 mmol) in 30 mL of THF was combined with $\text{CoMe}(\text{PMe}_3)_4$ (0.53 g, 1.4 mmol) in 30 mL of THF at 0 °C. The mixture was stirred for 14 h at room temperature. After workup, complex 3 (0.47 g, 0.76 mmol) was obtained as yellow crystals at 0 °C from *n* pentane solution in a yield of 76%. Dec: >160 °C. Anal. calcd for $\text{C}_{33}\text{H}_{50}\text{CoP}_3\text{Si}$ (626.7 g/mol): C, 63.25; H, 8.04. Found: C, 63.78; H, 8.29. IR (Nujol, KBr, cm^{-1}): 1581 (ArC=C), 944 (PMe_3).

Synthesis of Complex 4. L4 (0.78 g, 1.87 mmol) in 30 mL of THF was combined with $\text{CoMe}(\text{PMe}_3)_4$ (0.74 g, 1.96 mmol) in 30 mL of THF at 0 °C. The mixture was stirred for 48 h at room temperature. After workup, complex 4 (0.66 g, 1.14 mmol) was obtained as red power at 0 °C from *n* pentane solution in a yield of 61%. Dec: >157 °C. Anal. calcd for $\text{C}_{27}\text{H}_{46}\text{CoN}_2\text{P}_3\text{Si}$ (578.6 g/mol): C, 56.05; H, 8.01; N, 4.84. Found: C, 56.31; H, 8.27; N, 4.68. IR (Nujol, KBr, cm^{-1}): 2019 (Si-H), 2061 (N≡N), 1558 (Ar), 948 (PMe_3). ^1H NMR (300 MHz, benzene d_6 , 300 K, δ /ppm): 0.63 (q, $J = 6.0$ Hz, PCHCH_3 , 6H), 0.93 (q, $J = 6.0$ Hz, PCHCH_3 , 6H), 1.14 (q, $J = 6.0$ Hz, PCHCH_3 , 6H), 1.22 (q, $J = 6.0$ Hz, PCHCH_3 , 6H), 1.30 (d, $J = 9.0$ Hz, PCH_3 , 9H), 2.30–2.35 (m, PCHCH_3 , 2H), 2.42–2.54 (m, PCHCH_3 , 2H), 4.36 (s, Si H, 1H), 6.94–6.99 (m, Ar H, 2H), 7.06–7.09 (m, Ar H, 2H), 7.27 (d, $J = 6.0$ Hz, Ar H, 2H), 7.69 (d, $J = 6.0$ Hz, Ar H, 2H). ^{31}P {1H} NMR (121 MHz, benzene d_6 , 300 K, δ /ppm): 0.0 (t, $J = 77.4$ Hz, 1P, PMe_3), 85.1 (d, $J = 65.3$ Hz, 2P, P^iPr_2) ppm. ^{13}C {1H} NMR (75 MHz, benzene d_6 , 300 K, δ /ppm): 23.3 (dd, $J = 16.5, 7.5$ Hz, PCHCH_3), 25.6 (s, PCHCH_3), 26.6 (q, $J = 6$ Hz, PCH_3), 126 (s, Ar C), 131.44 (s, Ar C), 132.5 (t, $J = 9$ Hz, Ar C), 133.3 (t, $J = 4.5$ Hz, Ar C), 133.9 (t, $J = 4.5$ Hz, Ar C), 143.5 (s, Ar C), 155.0 (t, $J = 26.3$ Hz, Ar C). ^{29}Si NMR (79 MHz, benzene d_6 , 300 K, δ /ppm): 57.7 (s).

Catalytic Reduction of Dinitrogen to $\text{N}(\text{SiMe}_3)_3$. A typical process is described as follows. To a solution of KC_8 and Me_3SiCl in solvent (20 mL) was added complex 4 (5.78 mg, 0.01 mmol) at 25 °C under N_2 . After stirring for 24 h, *n* dodecane was added to the reaction mixture as an internal standard. The insoluble substrates were removed by centrifugation, and GC analysis was performed with the supernatant.

General Procedure for Cobalt-Catalyzed Hydrosilylation Reactions. Under a N_2 atmosphere, 2 mol % cobalt complex 1 was added to a 20 mL Schlenk tube containing a magnetic stirrer without any solvent. Then, alkene (1.00 mmol), *n* dodecane (170 mg, 1.00 mmol), and Ph_2SiH_2 (1.2 equiv, 221 mg, 1.2 mmol) were added in order. The reaction mixture was stirred at 70 °C for 24 h. The reaction solution was quenched with ethyl acetate. The combined organic fractions were concentrated in vacuum, and the crude product was purified by column chromatography on silica gel with petrol ether as the eluent. The pure product was characterized by NMR analysis.

X-ray Structure Determinations. Single crystal X ray diffraction data for the complexes were collected on Stoe Stadi Vari diffractometer equipped with graphite monochromatized Ga $K\alpha$ radiation ($\lambda = 0.71073$ Å). During collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentz polarization effects and empirical absorption with the SADABS program. The structures were resolved by direct or Patterson methods with the OLEX2 program⁴⁴ and refined on F^2 with SHELXL.⁴⁵ All non hydrogen atoms were refined anisotropically, and all hydrogen atoms except for those of the disordered solvent molecules were placed using AFIX instructions. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02332>.

The table of selected crystallographic data for 1–4 and original IR, ^1H NMR, ^{31}P NMR, ^{13}C NMR and ^{29}Si NMR spectra of 1, 2, and 4 as well as the catalytic products (PDF)

Accession Codes

CCDC 1548649, 1913002, 1947312, and 1978175 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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