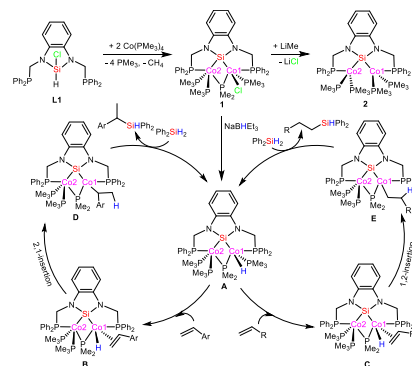


Synthesis of Dinuclear Cobalt Silylene Complexes and Their Catalytic Activity for Alkene Hydrosilylation Reactions

Qingshuang Li, Hongjian Sun, Xiaoyan Li,* Olaf Fuhr, and Dieter Fenske

ABSTRACT: A novel dinuclear silylene cobalt complex $[(\text{Me}_3\text{P})_2\text{Co}(\text{PMe}_2)(\text{CoCl}(\text{PMe}_3))(\text{Si}(\text{NCH}_2\text{PPh}_2)_2\text{C}_6\text{H}_4)]$ (**1**) supported by the $[\text{PSi}(\text{silylene})\text{P}]$ pincer ligand **L1** ($\text{HSiCl}(\text{NCH}_2\text{PPh}_2)_2\text{C}_6\text{H}_4$) with $\text{Co}(\text{PMe}_3)_4$. Complex **1** was formed through the reaction of complex **1** with MeLi . To the best of our knowledge, complexes **1** and **2** are the first examples of dinuclear silylene cobalt complexes supported by the $[\text{PSi}(\text{silylene})\text{P}]$ ligand. A new preligand **L2** ($\text{SiCl}_2(\text{NCH}_2\text{PPh}_2)_2\text{C}_6\text{H}_4$) was synthesized, and the reaction of preligand **L2** with $\text{Co}(\text{PMe}_3)_4$ afforded silyl cobalt complex $[(\text{Me}_3\text{P})_2\text{Co}(\text{SiCl}(\text{NCH}_2\text{PPh}_2)_2\text{C}_6\text{H}_4)]$ (**3**). The reaction of **3** with CO delivered cobalt carbonyl complex $[(\text{Me}_3\text{P})(\text{CO})\text{Co}(\text{Si}(\text{NCH}_2\text{PPh}_2)_2\text{C}_6\text{H}_4)_2\text{O}]$ (**4**). The catalytic activity of cobalt complexes **1–4** on the hydrosilylation of alkenes was explored. Among the four complexes, complex **1** has the best catalytic activity. The catalytic process could be promoted with NaBHET_3 as an additive, and a complete conversion with an excellent selectivity of 98:2 (b/l) could be reached at 120°C within 8 min for aryl alkenes. A possible catalytic cycle was proposed on the basis of the experimental results and literature reports, with a cobalt hydride complex as an active intermediate. The molecular structure of complexes **1–4** was determined by single-crystal X-ray diffraction analysis.



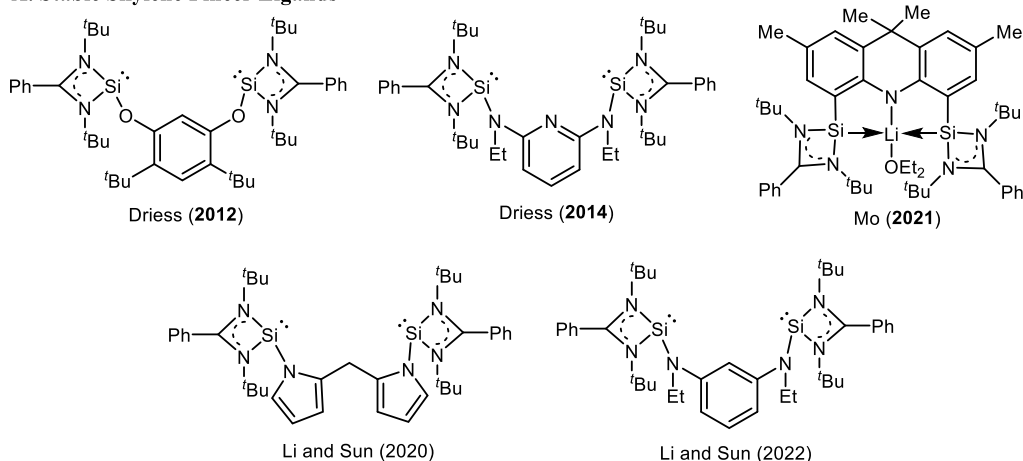
INTRODUCTION

Silylene compounds have high reactivity, and they can realize the activation of small molecules (H_2 ,^{1,2} CO_2 ,³ CS_2 ,⁴ CO ,⁵ P_4 ,⁶ S_8 ,⁷ Se ,⁸ and NH_3 ⁹) and inert bonds (C–F and C–H).¹⁰ With the continuous development in the field of silylene chemistry, many silylene ligand-supported metal complexes have been synthesized, and these metal complexes show excellent properties in the field of homogeneous catalysis.¹¹ The metal complex with a pincer ligand has unique stability and unusual advantages in the field of catalysis.¹² So far, metal complexes supported by pincer silylene ligands are still very rare. Typically, derivatives of Roesky's amidinosilylene (which are exceptionally strong donors) are utilized, serving as building blocks for pincer ligands as well.¹³ Driess' group reported $[\text{SiC}(\text{sp}^2)\text{Si}]$ and $[\text{SiNSi}]$ pincer silylene ligands and used these two ligands to synthesize Ni,¹⁴ Ir,¹⁵ and Fe¹⁶ complexes (A, Figure 1). The Ni complex could realize Sonogashira coupling, and the Fe complex could catalyze hydrosilylation of ketones with a good yield. Mo's group constructed a $[\text{SiNSi}]$ pincer silylene ligand and synthesized an iron complex supported by this ligand (A, Figure 1). The iron complex exhibited a good catalytic effect on the deoxygenation reaction of nitrous oxide and nitro complex with good yields and wide scope of the substrates.¹⁷ In 2020, our research group reported the preparation of a $[\text{SiC}(\text{sp}^3)\text{Si}]$ Bis(silylene) pincer ligand and the corresponding dinitrogen iron hydrido complex through the activation of the $\text{C}(\text{sp}^3)\text{--H}$ bond. To the best of

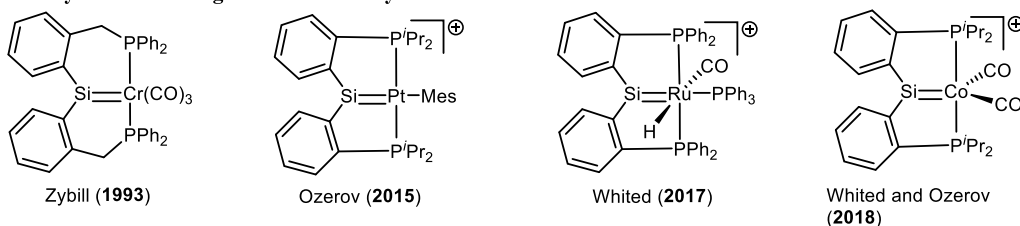
our knowledge, $[\text{SiCHSi}]\text{Fe}(\text{H})(\text{N}_2)(\text{PMe}_3)$ is the first example of a transition metal dinitrogen complex coordinated by the Bis-silylene ligand, and it is an effective catalyst for the silylation of dinitrogen.¹⁸ Recently, we synthesized a $[\text{SiC}(\text{sp}^2)\text{Si}]$ Bis(silylene) pincer ligand, and the related Bis-silylene $[\text{SiCSi}]$ pincer cobalt(III) hydride was prepared and used as an active catalyst in the alkene hydrosilylation reaction. The research results indicate that the introduction of a silylene ligand in the $[\text{SiCSi}]$ pincer cobalt(III) hydride leads to the selectivity reversal in the hydrosilylation of aromatic alkenes from anti-Markovnikov addition with the $[\text{PCP}]$ pincer cobalt(III) hydride as a catalyst to Markovnikov addition with the $[\text{SiCSi}]$ pincer cobalt(III) hydride as a catalyst.¹⁹

In addition to the above isolated silylene pincer ligands, there are several cases with *in situ* generated silylene pincer ligands that are stable in the presence of metals. For example, Zybail's group reported Cr complexes supported by the $[\text{PSi}(\text{silylene})\text{P}]$ pincer ligand.²⁰ Ozerov's group disclosed Co complexes with the $[\text{PSi}(\text{silylene})\text{P}]$ pincer ligand.²¹

A. Stable Silylene Pincer Ligands



B. Silylene Pincer Ligands Stabilized by Metals



C. This Work

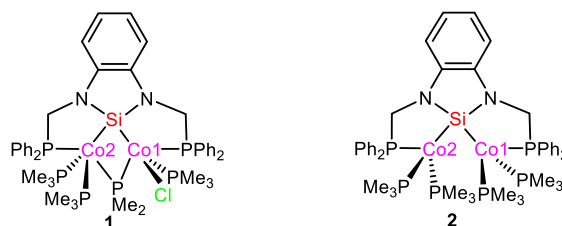


Figure 1. Silylene ligands and silylene metal complexes.

Whited published Ru complexes coordinated by [PSi-(silylene)P] pincer ligands.²² These known silylene pincer ligands are summarized (B, Figure 1). This type of ligand is rare, which limits the development of silylene pincer complexes in the field of organometallic chemistry. It is very important to explore the properties of metal complexes supported by silylene pincer ligands.

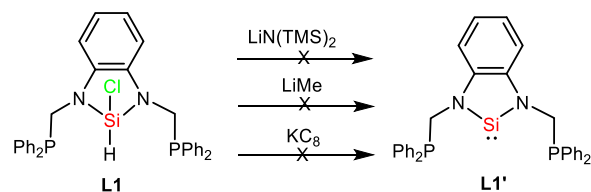
A series of N-heterocyclic [PSiP] pincer ligands, such as (HSiR(R = Me, Ph, and Cl)(NCH₂PPh₂)₂C₆H₄) and (H₂Si(NCH₂P^tBu₂)₂C₆H₄),^{23–25} were synthesized in previous reports. However, this type of [PSi(silylene)P] pincer ligand has rarely been reported. Cabeza's group attempted to synthesize such silylene ligands, but failed.²⁶ In this paper, a novel dinuclear silylene cobalt complex **1** supported by the [PSi(silylene)P] ligand was synthesized through the reaction of N-heterocyclic [PSiP] pincer preligand **L1** (HSiCl(NCH₂PPh₂)₂C₆H₄)²³ with Co(PMe₃)₄ (C, Figure 1). Complex **2** was formed through the reaction of complex **1** with MeLi under similar reaction conditions. The reaction of preligand **L2** (SiCl₂(NCH₂PPh₂)₂C₆H₄) with Co(PMe₃)₄ afforded the silyl cobalt complex **3**. The reaction of **3** with CO delivered the cobalt carbonyl complex **4**. The catalytic activity of cobalt complexes **1–4** on the hydrosilylation of alkenes was explored. Among the four complexes, complex **1**

has the best catalytic activity and could reach a complete conversion with an excellent selectivity of 98:2 (b/l).

RESULTS AND DISCUSSION

Preparation and Structures of Dinuclear Silylene Cobalt Complexes 1 and 2 Supported by the [PSiP] Silylene Ligand. Cabeza's group reported the synthesis of [PGeP] germylene Ge(NCH₂P^tBu₂)₂C₆H₄²⁷ and [PSnP] stannylene Sn(NCH₂P^tBu₂)₂C₆H₄.²⁶ Inspired by the work, we attempted to synthesize similar [PSiP] silylene: Si(NCH₂PPh₂)₂C₆H₄. At first, HSiCl(NCH₂PPh₂)₂C₆H₄ (**L1**)²³ was selected as a precursor to react with LiN(TMS)₂ in toluene (Scheme 1). However, the corresponding target product (**L1'**) was not formed by this way. Then, the reaction of **L1** with MeLi or KC₈ was explored, and the expected silylene

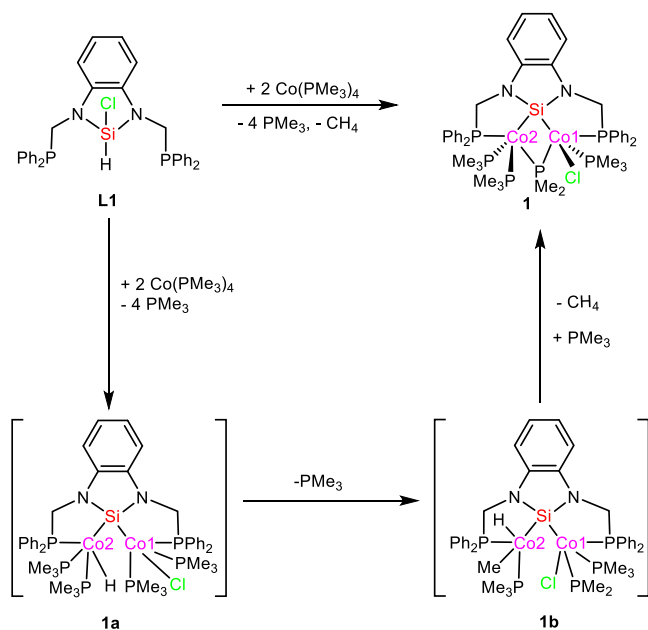
Scheme 1. Attempt to Synthesize Silylene Ligand



product was also not found. Based on the experimental results and the work on the Co complexes supported by silylene ligands by Ozerov's group,²¹ we speculate that such silylene ligand **L'** cannot exist alone. However, the metal complexes with such ligands may be stable, which was confirmed by the following experimental results.

Complex **1** as dark-red crystals was synthesized through the reaction of preligand **L1** with $\text{Co}(\text{PMe}_3)_4$ in diethyl ether with a yield of 76% (Scheme 2). In the IR spectrum of complex **1**,

Scheme 2. Synthesis and Possible Mechanism for the Formation of Complex 1



the typical vibration of the Si–H bond of **L1** at 2247 cm^{-1} disappeared. Single crystals of **1** suitable for X-ray diffraction analysis were obtained from diethyl ether solution. Complex **1** is a dinuclear cobalt complex and is paramagnetic. The magnetic moment ($2.46\ \mu_{\text{B}}$) was tested by Evans' method.²⁸ In the molecular structure of complex **1**, the cobalt atoms are in the center of a distorted square pyramidal with $\tau_5 = 0.05$ for Co1 and 0.06 for Co2 (Figure 2).²⁹ For the Co1 center, P2 is located at the top of the square pyramidal with Cl1, P1, Si1, and P4 atoms at the four vertices of the first square, while for the Co2 center, P6 is located at the top of the square pyramidal with P1, P5, P3, and Si1 atoms at the four vertices of the second square. Due to the strong trans-influence of the Si atom, the bond length of Co2–P5 ($2.2470(5)\text{ \AA}$) is the longest Co–P bond in complex **1**. Similarly, because the trans-influence of the P atom is greater than that of the Cl atom, the Co2–Si1 bond ($2.2602(5)\text{ \AA}$) is longer than the Co1–Si1 bond ($2.1822(4)\text{ \AA}$). These two bonds are similar to those ($2.1949(11)\text{ \AA}$ and $2.2244(11)\text{ \AA}$) reported by Cui's group.³⁰ It is considered that the Co1–Si1 bond length is significantly shorter than the Co2–Si1 bond length due to the electron-withdrawing effect of the chlorine ligand. The distance Co1–Co2 is $2.9773(3)\text{ \AA}$, which is far from bonding.³¹ A possible mechanism for the formation of complex **1** is provided in Scheme 2. The first step is the oxidative addition of Si–H and Si–Cl bonds by two molecules of $\text{Co}(\text{PMe}_3)_4$ with the formation of intermediate **1a**. Then, one P–Me bond is cleaved via single-electron oxidative addition of PMe_3 at the

Co center to form intermediate **1b** with two Co(II) centers. With the reductive elimination of Co–H and Co–Me bonds at the Co2 center, **1b** transforms to **1** with the releasing of one CH_4 molecule in the presence of PMe_3 . Therefore, Co2 could be considered as a Co(0) center, while Co1 could be considered as a Co(II) species. In this case, there should be two unpaired electrons in complex **1**. This result is also consistent with the measurement of the magnetic moment. The signal at -60.2 ppm in the in situ ^{31}P NMR spectrum of the reaction solution provides evidence of free PMe_3 (Figure S7).

The reaction of complex **1** with methyl lithium in THF at room temperature afforded complex **2** (Scheme 3). Complex **2** is also paramagnetic, and no reasonable NMR information could be obtained. Single crystals of complex **2** were obtained from its diethyl ether solution at $-20\text{ }^\circ\text{C}$. Complex **2** is also a silylene dinuclear cobalt complex, and its magnetic moment is $2.70\ \mu_{\text{B}}$. In this case, it is believed that both cobalt centers are in a zero oxidation state. Therefore, complex **2** should have two unpaired electrons. This result is also consistent with the data of the magnetic moment measurement. The structure was determined by X-ray diffraction (Figure 3). In the molecular structure of **2**, the cobalt atom is in the center of a distorted trigonal bipyramid ($\tau_3 = 0.71$).²⁹ Si1–Co1–P2 ($162.05(4)^\circ$) is the axial direction, while P1, P3, and Co1ⁱ atoms are in the triangular plane. The sum of three bond angles [$\text{P1–Co1–P3} = 104.54(4)^\circ$, $\text{P1–Co1–Co1}^i = 115.18(3)^\circ$, and $\text{P3–Co1–Co1}^i = 119.18(3)^\circ$] is 338.90° , deviated from 360° . The Co1–Si1 ($2.1957(9)\text{ \AA}$) bond length of **2** is similar to that in complex **1** ($2.1822(4)\text{ \AA}$). The bond length of Co1–Co1ⁱ is $2.8361(9)\text{ \AA}$, which is shorter than the distance of **1** between Co1 and Co2. Complex **2** has a symmetrical plane. To the best of our knowledge, complexes **1** and **2** are the first examples of dinuclear silylene cobalt complexes supported by the [PSiP] silylene ligand to date.

Synthesis of N-Heterocyclic Silyl Pincer Preligand **L2 and Its Cobalt Complexes.** The Si–H and Si–Cl bonds in the **L1** preligand can be simultaneously activated by two molecules of $\text{Co}(\text{PMe}_3)_4$. Therefore, ligand **2** was synthesized to test whether two Si–Cl bonds could also be concurrently cleaved by two molecules of $\text{Co}(\text{PMe}_3)_4$ to construct a new silylene cobalt complex. According to the previous work,²³ the reaction of *ortho*- $\text{C}_6\text{H}_4(\text{NHCH}_2\text{PPh}_2)_2$ with SiCl_4 in the presence of Et_3N afforded ligand **L2** (Scheme 4). **L2** was obtained as colorless crystals from Et_2O at room temperature in 54% yield and was fully characterized. The ^{31}P NMR spectrum of **L2** shows one singlet at -23.5 ppm for the PPh_2 groups. In the ^{29}Si NMR spectrum, a single resonance was recorded at -29.3 ppm .

When **L2** was combined with $\text{Co}(\text{PMe}_3)_4$ in THF at $-78\text{ }^\circ\text{C}$, the color of the reaction solution changed from yellow-brown to dark-red after 48 h at room temperature. The volatiles were removed in vacuo, leaving a dark-red solid. This residue was extracted with *n*-pentane and diethyl ether. Complex **3** as red rectangle crystals was isolated from the *n*-pentane solution (Scheme 5). Unlike the preparation of complex **1**, only one Si–Cl bond was broken during the formation of complex **3**. At the same time, $(\text{CoCl}(\text{PMe}_3)_3)$ as a byproduct was also isolated. In the ^{31}P NMR spectrum of complex **3**, three distinct signals were detected for the phosphorus groups [at -13.9 ppm (PMe_3), 3.0 ppm (PMe_3), and 65.7 ppm ($-\text{PPh}_2$)]. The relative integral ratio of these signals is 1:1:2. This information is in accord with a

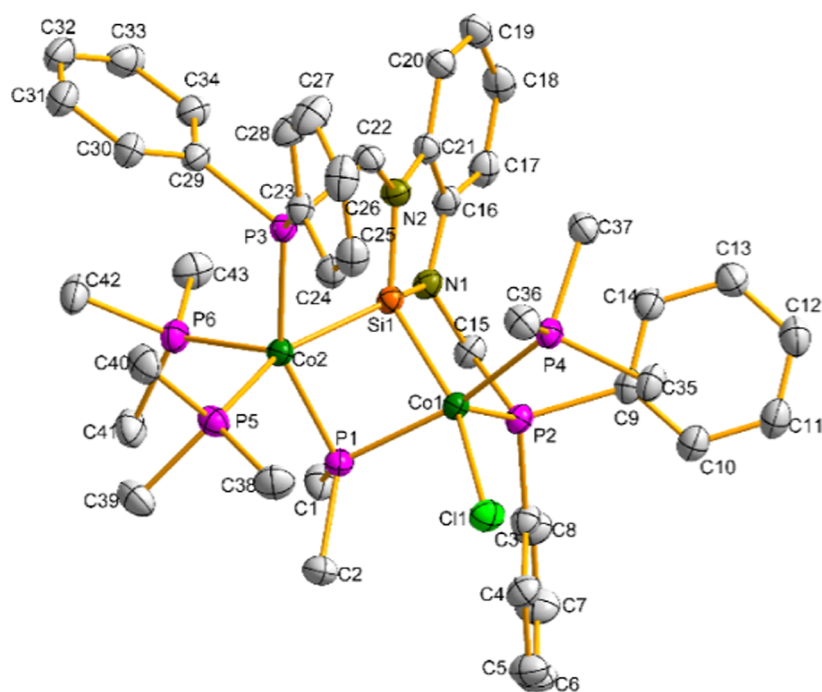
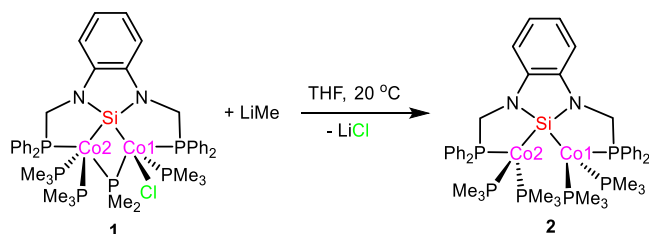


Figure 2. ORTEP plot of complex **1** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (deg): Co1–Co2 2.9773(3), Co1–P1 2.1853(5), Co1–Si1 2.1822(4), Co1–P4 2.2423(4), Co1–P2 2.1422(4), Co1–Cl1 2.3694(4), Co2–P1 2.2112(4), Co2–P3 2.2292(4), Co2–P5, 2.2470(5), Co2–P6 2.2284(4), and Co2–Si1 2.2602(5); P1–Co1–P4 161.639(18), Cl1–Co1–Si1 158.871(18), Co1–Si1–Co2 84.147(16), Co1–P1–Co2 85.250(15), Si1–Co2–P1 75.949(16), P1–Co2–P3 153.077(18), P5–Co2–Si1 156.767(18), and Si1–Co1–P1 78.103(16).

Scheme 3. Synthesis of Complex 2



trigonal bipyramidal coordination geometry because two -PPh_2 groups have the same chemical environment. The structure of complex **3** was determined by single-crystal X-ray diffraction (Figure 4). The Co atom is centered in a distorted trigonal bipyramidal coordination geometry ($\tau_5 = 0.92$)²⁹ with Si1–Co1–P2 ($174.25(3)^\circ$) in the axial direction. The three other P atoms are situated in the equatorial plane, and the sum of the coordination bond angles [$\text{P1–Co1–P3:}119.21(3)^\circ$, $\text{P1–Co1–P4:}113.45(3)^\circ$, and $\text{P3–Co1–P4:}123.80(3)^\circ$] is 356.46° , deviating from 360° . The strong trans-influence of the silyl group results in the longest Co1–P2 (2.2269(8) Å) bond among the four Co–P bonds [Co1–P1: 2.1890(8) Å, Co1–P3: 2.1947(7) Å, and Co1–P4: 2.1968(7) Å]. Although complex **3** is a silyl cobalt complex, the Co1–Si1 bond length (2.2173(8) Å) does not differ significantly from the Co–Si bond lengths of silylene complexes **1** and **2** and is close to that (2.2559(5) Å) in a similar silyl cobalt(I) complex $(\text{Me}_3\text{P})_2\text{Co}(\text{SiMe}(\text{NCH}_2\text{PPh}_2)_2\text{C}_6\text{H}_4)$.²⁴

For the formation of complex **3** and $\text{CoCl}(\text{PMe}_3)_3$, we proposed that at first, $\text{Co}(\text{PMe}_3)_4$ reacted with **L2** to produce intermediate **3a** via ligand substitution, and with the oxidative addition of one Si–Cl bond on the Co center, intermediate **3b**, a cobalt(II) complex, was formed. The comproportionation

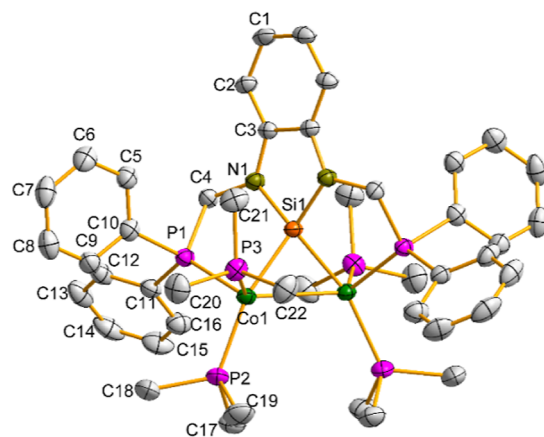
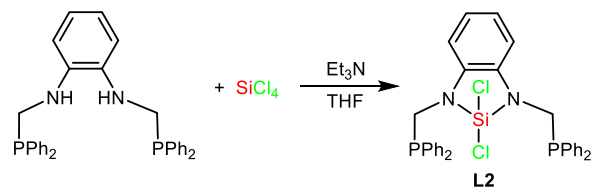


Figure 3. ORTEP plot of complex **2** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (deg). Co1–Co1' 2.8361(9), Co1–P1 2.1784(8), Co1–Si1 2.1957(9), Co1–P3 2.1976(9), Co1–P2 2.2025(9); P1–Co1–Co1' 115.18(3), P1–Co1–Si1 84.06(3), P1–Co1–P3 104.54(4), P1–Co1–P2 103.64(3), Si1–Co1–Co1' 49.77(2), Si1–Co1–P3 94.15(3), Si1–Co1–P2 162.05(4), P3–Co1–Co1' 119.18(3), P3–Co1–P2 99.42(4), and P2–Co1–Co1' 112.70(2). (i) = $1/2 - X$, $3/2 - Y$, $+Z$.

Scheme 4. Synthesis of Preligand L2



Scheme 5. Synthesis of Complex 3

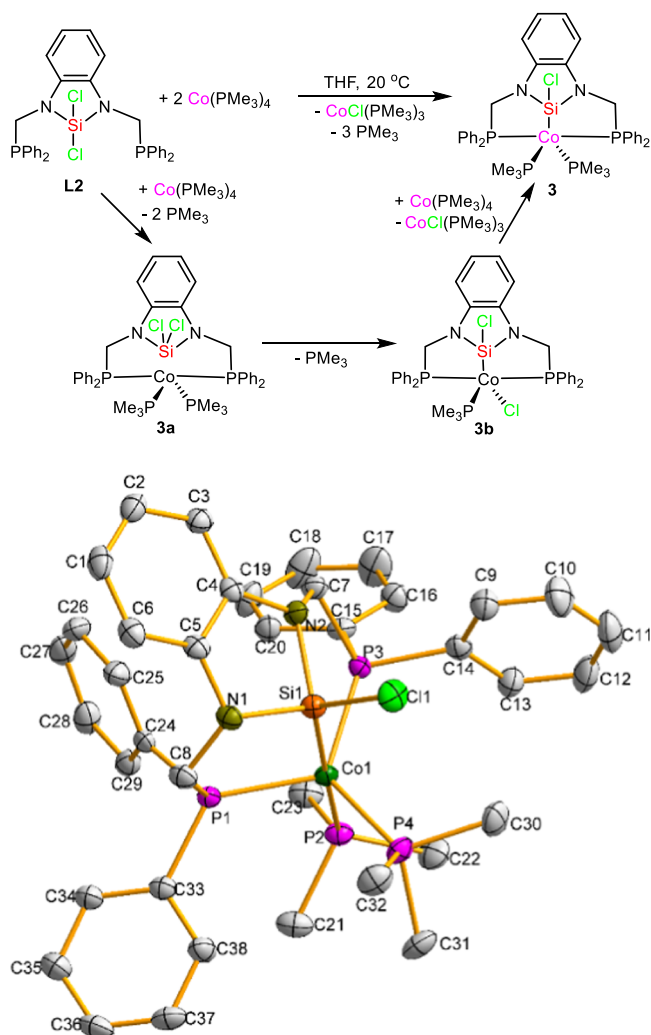


Figure 4. OPTeP plot of complex 3 at the 50% probability level (most of the hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (deg). Co1–P1 2.1890(8), Co1–P3 2.1947(7), Co1–P2 2.2269(8), Co1–P4 2.1968(7), and Co1–Si1 2.2173(8); P1–Co1–P3 119.21(3), P1–Co1–P2 99.35(3), P1–Co1–P4 113.45(3), P1–Co1–Si1 82.15(3), P3–Co1–P2 95.68(3), P3–Co1–P4 123.80(3), P3–Co1–Si1 78.80(3), P4–Co1–P2 93.93(3), P4–Co1–Si1 90.52(3), and Si1–Co1–P2 174.25(3).

reaction between intermediate **3b** and the second $\text{Co}(\text{PMe}_3)_4$ molecule gave rise to complex **3** and $\text{CoCl}(\text{PMe}_3)_3$ (Scheme 5). In order to study the reaction process, the reaction of $\text{Co}(\text{PMe}_3)_4$ and **L2** with a stoichiometric ratio of 1:1 was conducted. The attempt to isolate intermediates **3a** and **3b** was not successful. Complex **3** and unreacted **L2** were detected by the in situ ^{31}P NMR spectrum of the reaction solution (Figure S15).

If the THF solution of complex **3** was exposed to a CO atmosphere (1 atm) at room temperature, the color of the solution changed from dark-red to yellow after 10 h. Complex **4** was separated as yellow crystals from the reaction mixture (Scheme 6). In the IR spectrum of complex **4**, a strong absorption at 1895 cm^{-1} belongs to the terminally coordinated CO ligand. In the ^{31}P NMR spectrum of **4**, the signal of PMe_3 appears at 6.3 ppm, while the resonance of the $-\text{PPh}_2$ group is located at 78.5 ppm. In the ^1H NMR spectrum of **4**, the signal

of PMe_3 as a doublet was detected at 0.32 ppm with a $J_{\text{P-H}}$ coupling of 9.0 Hz. The molecular structure of complex **4** was determined by X-ray crystallography (Figure 5). The symmetrical compound **4** is a dinuclear cobalt complex, in which the cobalt atoms are in the centers of distorted trigonal bipyramids ($\tau_5 = 0.87$).²⁹ The Co1–Si1 bond length (2.2258(17) Å) in complex **4** is significantly longer than that (2.1957(9) Å) in complex **2**. Therefore, complex **4** is a silanide Co compound. Due to the double-bond composition between Co1 and C20, the bond length of Co1–C20 (1.736(6) Å) is significantly shorter than those of the typical Co–C_{alkyl} bonds.³² In the molecular structure of **4**, the O atom acts as a bridging ligand, connecting the two Si atoms with an angle of Si1–O2–Si1ⁱ 172.3(5)°. It is believed that the large Si–O–Si bond angle is caused by the mutual repulsion of large steric hindrance groups on silicon atoms. In fact, the Si–O bond is not very covalent but highly ionic, which also explains near-linear arrangement. The three five-membered rings surrounding the Si atom form a bowl-like structure in the direction away from the central O atom. It is speculated that during the formation of complex **4**, a ligand replacement reaction occurs to generate intermediate **4a**. But the attempt to isolate **4a** was not successful. Complex **4** may be formed through the reaction of **4a** with a trace amount of water in the system. This speculation was further confirmed by the following experiment. We found that the yield of **4** was increased from 31 to 57% when 1 equiv of H_2O was introduced to the reaction system.

Hydrosilylation of Alkenes with Complexes 1–4 as Catalysts. Silylene transition metal complexes have shown excellent catalytic activity for homogeneous catalytic processes.³³ Recently, we have developed a series of phosphine Co complexes for alkene hydrosilylation.^{19,34–39} It was also known that the introduction of silylene ligands can not only improve the catalytic activity of metal complexes but also regulate the catalytic selectivity of metal complexes. As a prolongation of our research work in this area, we explored the catalytic activity and selectivity of cobalt complexes **1–4** for alkene hydrosilylation. Using complexes **1–4** as catalysts, the catalytic activity for the hydrosilylation of styrene and Ph_2SiH_2 was evaluated with a catalyst of 1 mol % and without solvent at 70 °C for 10 h (entries 1–4, Table 1). Except for complex **4**, complexes **1–3** exhibit good activity and selectivity for this reaction, and the Markovnikov product as the major product was obtained. Among the four catalysts, **1** has the best catalytic effect and could reach a conversion of 100% with a selectivity of 95:5 (b/l). Further research has found that using **1** as a catalyst, a complete conversion could also be achieved with unchanged selectivity if the reaction time is shortened to 8 h (entry 5, Table 1). As expected, with NaBH_4Et_3 as an additive, both the conversion and selectivity can be significant improved, a 100% conversion with a selectivity of 98:2 (b/l) was realized within 5 h (entries 6–7, Table 1), and a conversion of 81% with a selectivity of 98:2 (b/l) could also be reached when the reaction time decreased to 2 h (entry 8, Table 1). With a catalyst loading of 0.5%, the same catalytic effect could be achieved as 1% (entries 8–9, Table 1). Several silanes were investigated, and Ph_2SiH_2 shows the best results in catalysis (entries 9–15, Table 1). Neat reactions without additional solvents were found as the best conditions for the production of products (entries 16–20, Table 1). Further experiments demonstrated that when the reaction temperature was increased from 50 to 120 °C, the conversion rate of the reaction increases from 17 to 82% with unchanged selectivity

Scheme 6. Synthesis of Complex 4

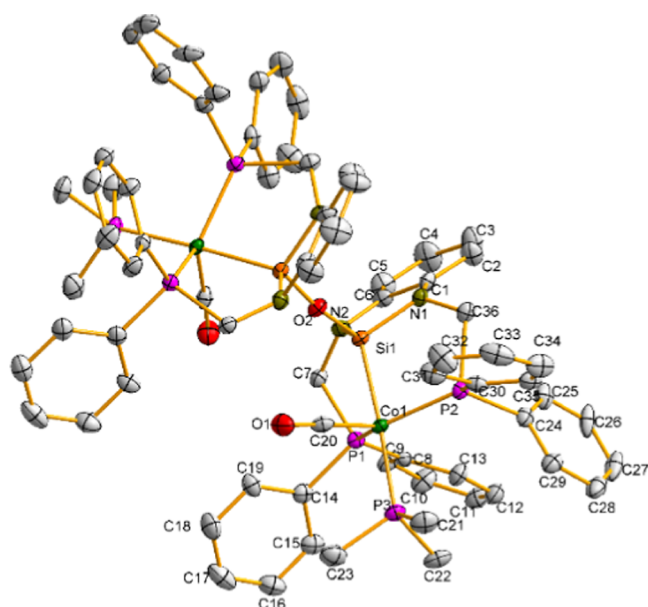
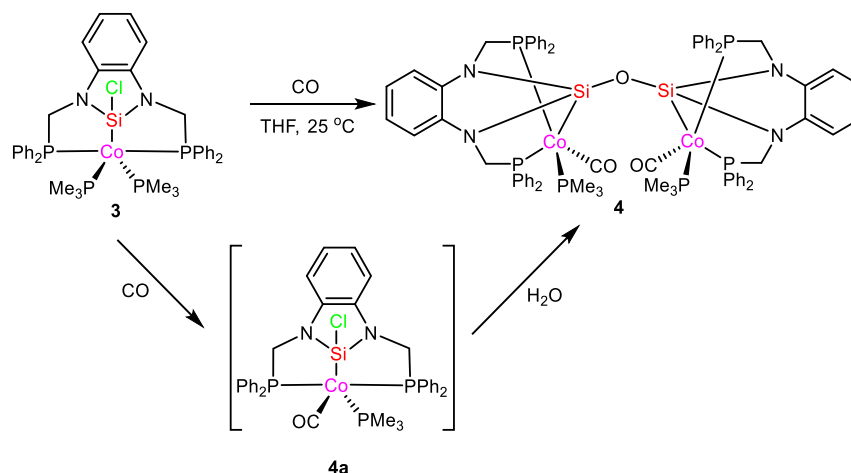


Figure 5. ORTEP plot of complex 4 at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (deg). Co1–P1 2.1884(16), Co1–P2 2.2108(17), Co1–Si1 2.2258(17), Co1–P3 2.1996(17), Co1–C20 1.736(6); P1–Co1–P2 123.21(7), P1–Co1–Si1 83.39(6), P1–Co1–P3 98.76(6), P2–Co1–Si1 82.44(6), P3–Co1–P2 99.36(6), P3–Co1–Si1 175.69(7), C20–Co1–P1 110.8(2), C20–Co1–P2 122.6(2), C20–Co1–Si1 86.06(19), C20–Co1–P3 89.7(2), and Si1–O2–Si1ⁱ 172.3(5). (i) = 1 – X, 1 – Y, +Z.

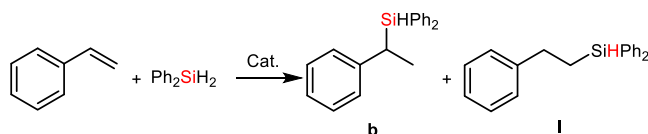
within 15 min and 0.5 mol % catalyst (entries 21–24, Table 1). This indicates that the catalyst is stable at high temperatures. Further investigation was conducted on the influence of the addition order of the substrate on the reaction. When complex 1, NaBHET₃ and Ph₂SiH₂ prereacted for 0 and 5 min, respectively, the conversion decreased from 61 to 52% (entries 25–26, Table 1) within 5 min. On the contrary, when complex 1, NaBHET₃ and styrene prereacted for 0 and 5 min, respectively, the conversion increased from 61 to 82% (entries 25 and 27, Table 1) within 5 min, and a 100% conversion could be reached within 8 min with unchanged selectivity (entry 28, Table 1). Therefore, the best reaction conditions are as follows: 0.5 mol % 1, 0.5 mol % NaBHET₃, prereaction with

alkene for 5 min, solvent-free, 120 °C, and 8 min (entry 28, Table 1).

Under the optimal conditions, the scope of the substrates was further investigated (Table 2). It was found that complex 1 catalyzed Markovnikov hydrosilylation of aromatic alkenes with Ph₂SiH₂ in the presence of NaBHET₃ in excellent yield and selectivity. The substrates with electron-withdrawing groups, such as trifluoromethyl (5e and 5f, Table 2) and halogen (5b–5d, Table 2) groups, have good yields and selectivity. The selectivity and yield of substrates with EWG are superior to those of substrates with EDG. Aryl substrates that possess electron-donating functionalities require an extension of the reaction duration to 3 h to achieve optimal yields. Examples of such groups include methyl (5i, Table 2), methoxy (5j, Table 2), and *tert*-butyl (5k, Table 2). Furthermore, 1-vinylnaphthalene (5g, Table 2) and 4-vinylbiphenyl (5h, Table 2) also have good yields. Unfortunately, this catalytic system is not suitable for aliphatic alkenes. For aliphatic substrates, even if the reaction time is extended to 12 h, the yields are not ideal (5l–5p, Table 2). At the same time, the selectivity of these reactions also decreased. It must be pointed out that for aliphatic substrates, the main products are *anti*-Markovnikov compounds.

To understand the mechanism of the catalytic reaction, we conducted several experiments. Because complex 1 has an excellent catalytic effect in the presence of NaBHET₃, it is speculated that cobalt hydride A is a key intermediate in this proposed process (Scheme 7). Unfortunately, in our hands, the attempt to isolate or characterize A by the stoichiometric reaction of complex 1 and NaBHET₃ was not successful as it rapidly decomposed. This decomposition process was accompanied by the release of H₂ that was detected by GC in this reaction. However, the prereaction of complex 1 with NaBHET₃ impacts the catalytic activity. When the prereaction time of complex 1 and NaBHET₃ was prolonged from 0 to 5 and 10 min, the conversion decreased from 100 to 51% and 47% (entries 28–30, Table 1). This is consistent with the rapid formation and decomposition of metal hydride A. The same reduction of conversion was observed, when the prereaction with Ph₂SiH₂ was conducted (entry 26, Table 1). Thus, A could further react via displacement of PMe₃ by alkene (entries 25–28, Table 1). This is further supported by addition of B(C₆F₅)₃ during the prereaction to capture PMe₃ which increased the conversion (entry 31, Table 1). Hydride

Table 1. Optimization of Reaction Conditions



entry	catalyst	loading (mol %)	silane	solvent	temp (°C)	additive	time (h)	conversion (%)	selectivity b/l
1	1	1	Ph ₂ SiH ₂	neat	70		10	100	95:5
2	2	1	Ph ₂ SiH ₂	neat	70		10	78	94:6
3	3	1	Ph ₂ SiH ₂	neat	70		10	77	92:8
4	4	1	Ph ₂ SiH ₂	neat	70		10	41	
5	1	1	Ph ₂ SiH ₂	neat	70		8	100	95:5
6	1	1	Ph ₂ SiH ₂	neat	70		5	82	95:5
7	1	1	Ph ₂ SiH ₂	neat	70	NaBHET ₃	5	100	98:2
8	1	1	Ph ₂ SiH ₂	neat	70	NaBHET ₃	2	81	98:2
9	1	0.5	Ph ₂ SiH ₂	neat	70	NaBHET ₃	2	80	98:2
10	1	0.5	Et ₃ SiH	neat	70	NaBHET ₃	2	2	
11	1	0.5	Me ₇ PhSiH	neat	70	NaBHET ₃	2	27	
12	1	0.5	Me(EtO) ₂ SiH	neat	70	NaBHET ₃	2	15	
13	1	0.5	(EtO) ₃ SiH	neat	70	NaBHET ₃	2	20	
14	1	0.5	Ph ₃ SiH	neat	70	NaBHET ₃	2	32	
15	1	0.5	PhSiH ₃	neat	70	NaBHET ₃	2	31	
16	1	0.5	Ph ₂ SiH ₂	neat	70	NaBHET ₃	0.5	42	96:4
17	1	0.5	Ph ₂ SiH ₂	DMF	70	NaBHET ₃	0.5	14	
18	1	0.5	Ph ₂ SiH ₂	DMSO	70	NaBHET ₃	0.5	22	
19	1	0.5	Ph ₂ SiH ₂	Toluene	70	NaBHET ₃	0.5	20	
20	1	0.5	Ph ₂ SiH ₂	dioxane	70	NaBHET ₃	0.5	30	
21	1	0.5	Ph ₂ SiH ₂	neat	50	NaBHET ₃	0.25	17	98:2
22	1	0.5	Ph ₂ SiH ₂	neat	70	NaBHET ₃	0.25	37	98:2
23	1	0.5	Ph ₂ SiH ₂	neat	100	NaBHET ₃	0.25	65	98:2
24	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	0.25	82	98:2
25	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	5 min	61	98:2
26 ^a	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	5 min	52	98:2
27 ^b	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	5 min	83	98:2
28 ^b	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	8 min	100	98:2
29 ^c	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	8 min	51	98:2
30 ^d	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	8 min	47	98:2
31 ^e	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	5 min	90	98:2
32 ^f	1	0.5	Ph ₂ SiH ₂	neat	120	NaBHET ₃	5 min	35	98:2

^aComplex 1 and NaBHET₃ prereacted with Ph₂SiH₂ at 120 °C in 5 min. ^bComplex 1 and NaBHET₃ prereacted with styrene at 120 °C in 5 min. ^cComplex 1 was prereacted with NaBHET₃ at 120 °C for 5 min and then prereacted with styrene at 120 °C for 5 min. ^dComplex 1 was prereacted with NaBHET₃ at 120 °C for 10 min and then prereacted with styrene at 120 °C for 5 min. ^eComplex 1, NaBHET₃, and tris(pentafluorophenyl)borane prereacted with styrene at 120 °C in 5 min. ^fComplex 1, NaBHET₃, and trimethylphosphine prereacted with styrene at 120 °C in 5 min.

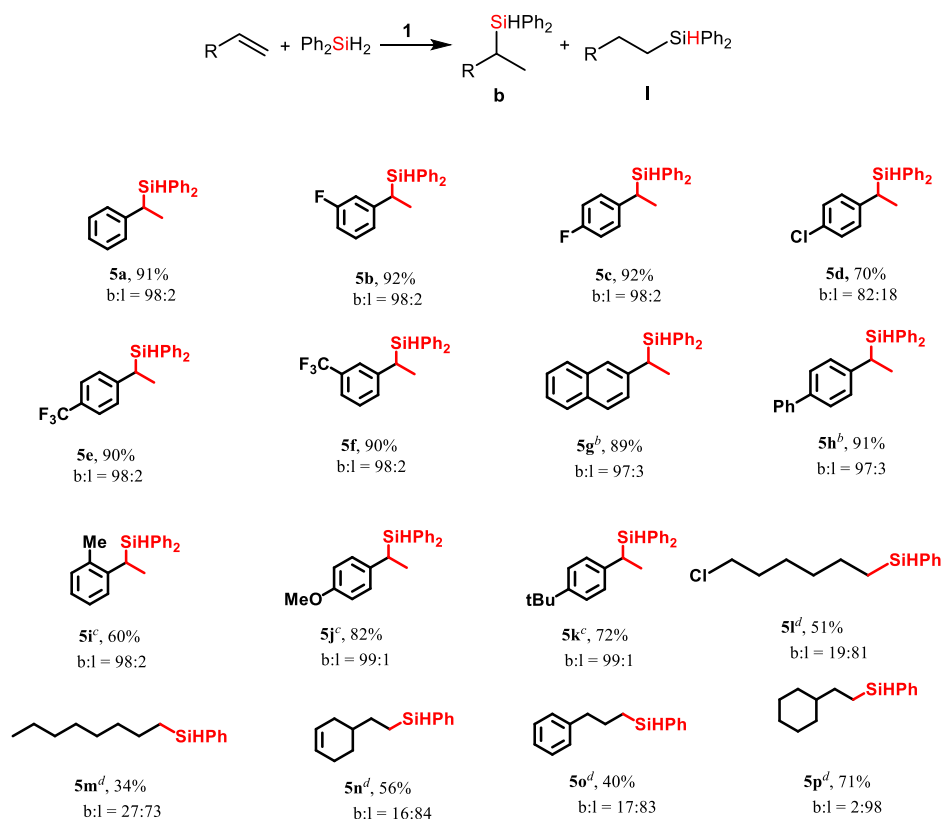
migration to the alkene then can form alkyl complexes which react with Ph₂SiH₂ to regenerate A. This proposal is based on the above experiments and our earlier work,^{19,35,40,41} but the intermediates eluded characterization. Also according to a previous work,^{40,42} we speculate that the change in selectivity between Markovnikov products for aryl- and anti-Markovnikov products for alkyl-substituted alkenes is caused by π - π interactions between the aryl ring of the substrate and the aryl ring of the ligand in the catalyst or the cobalt center itself. Because 1 is a binuclear complex catalyst, other reaction pathways are likely to be involved but are not experimentally corroborated.

CONCLUSIONS

In summary, a novel dinuclear silylene cobalt complex 1 supported by the [PSi(silylene)P] ligand was synthesized through the reaction of N-heterocyclic [PSiP] pincer ligand L1 (HSiCl(NCH₂PPh₂)₂C₆H₄) with Co(PMe₃)₄. Complex 2 was

formed through the reaction of complex 1 with MeLi. To the best of our knowledge, complexes 1 and 2 are the first examples of dinuclear silylene cobalt complexes supported by the [PSiP] silylene ligand. A new preligand L2 (SiCl₂(NCH₂PPh₂)₂C₆H₄) was synthesized, and the reaction of preligand L2 with Co(PMe₃)₄ afforded silyl cobalt complex 3. The expected silylene cobalt complexes 1 and 2 were not formed. The reaction of 3 with CO delivered cobalt carbonyl complex 4. The catalytic activity of cobalt complexes 1–4 on the hydrosilylation of alkenes was explored. Among the four complexes, complex 1 has the best catalytic activity. The catalytic process could be promoted with NaBHET₃ as an additive, and a complete conversion with an excellent selectivity of 98:2 (b/l) could be reached at 120 °C within 8 min for aryl alkenes. A possible catalytic mechanism was proposed on the basis of the experimental results and literature reports, with a cobalt hydride complex as a key active intermediate. Compared with our reported Bis-silylene [SiCSi]

Table 2. Scope of Alkenes for 1-Catalyzed Hydrosilylation^a



^aCatalytic reaction conditions: **1** (0.5 mol %) and NaBHET₃ (0.5 mol %) prereacted with alkene (1.0 mmol) at 120 °C for 5 min, Ph₂SiH₂ (1.2 mmol), solvent-free at 120 °C for 8 min; isolated yields. ^bNo prereaction, **1** (0.5 mol %), NaBHET₃ (0.5 mol %), Ph₂SiH₂ (1.2 mmol), solvent-free at 120 °C for 20 min. ^c3 h. ^d12 h.

pincer cobalt(III) hydride,¹⁹ catalyst **1** has two advantages: (1) it is stable at high temperatures and (2) it has excellent catalytic selectivity for alkene hydrosilylation reactions. The molecular structures of complexes **1**–**4** were determined by single-crystal X-ray diffraction analysis.

EXPERIMENTAL SECTION

General Procedures and Materials. All manipulations were carried out under a N₂ atmosphere with standard Schlenk techniques. Solvents were treated via distillation from Na-benzophenone. **L1**²³ and Co(PMe₃)₄⁴³ were obtained with published methods. Infrared spectra (4000–400 cm^{−1}) with Nujol mulls between KBr disks were obtained with a Bruker ALPHA FT-IR instrument. NMR spectra were recorded on a Bruker Avance 300 and 400 MHz spectrometers. GC analysis was realized on a SHIMADZU GC2014 chromatograph. The samples were sealed in capillaries for melting point measurement with a WRR instrument.

Caution! (EtO)₃SiH is flammable and highly toxic upon inhalation and may cause skin irritation and blindness. Even if during our studies on the hydrosilylation of alkenes we used it without incident, triethoxysilane should be used with precaution. Indeed, due to possible silane disproportionation, the formation of an extremely pyrophoric gas (possibly SiH₄) has led to several fires and explosions reported in the literature. (See the Buchwald Safety Letter: Buchwald, S. L. *Chem. Eng. News* **1993**, 71, 13, 2–3. DOI: [doi:10.1021/cen-v071n013.p002](https://doi.org/10.1021/cen-v071n013.p002)). In addition, PhSiH₃ and Me(EtO)₂SiH are also highly flammable.

Synthesis of Ligand L2. To a solution of C₆H₄(NHCH₂PPh₂)₂ (3.50 g, 6.94 mmol) and triethylamine (1.40 g, 13.87 mmol) in THF (50 mL) was added a solution of SiCl₄ (1.17 g, 6.94 mmol) in THF

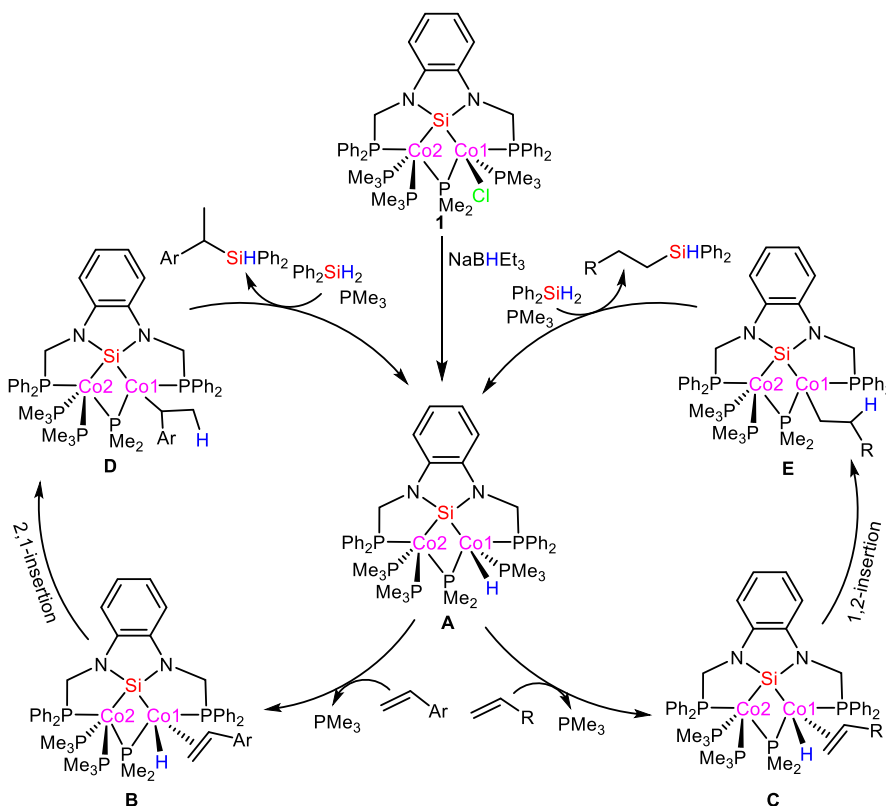
(10 mL) at room temperature. The mixture was stirred for 48 h. The supernatant was isolated by cannula filtration, and the volatiles were removed in vacuo, leaving a sticky solid. This solid was extracted with Et₂O. **L2** was obtained as colorless crystals from diethyl ether at room temperature (2.12 g, 50.7%). mp 61–62 °C. ¹H NMR (300 MHz, CDCl₃, 298 K): δ (ppm) 4.05 (d, *J* = 3.0 Hz, NCH₂, 4H), 6.72–6.81 (m, Ar–H, 4H), 7.24–7.28 (m, Ar–H, 12H), 7.37–7.43 (m, Ar–H, 8H). ³¹P NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 23.47. ²⁹Si NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 28.29(s). ¹³C NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 44.99 (–NCH₂), 109.54 (C₆H₄), 119.18 (C₆H₄), 128.66–136.98 (C₆H₅). HRMS (ESI-TOF): 600.0878 [M + H]⁺ calcd for C₃₂H₂₈Cl₂CoN₂P₄Si, 600.0874.

Synthesis of Complex 1. To a solution of **L1** (0.5 g, 0.88 mmol) in Et₂O (20 mL) was added slowly a solution of Co(PMe₃)₄ (0.64 g, 1.77 mmol) in Et₂O (20 mL) at 0 °C. The reaction solution was warmed to room temperature and stirred for 10 h, resulting in a brown solution. **1** was obtained as dark red crystals from diethyl ether at room temperature (0.65 g, 76%). IR (Nujol mull, KBr, cm^{−1}): 936 ρ (PMe₃). mp 148–149 °C. HRMS (ESI-TOF): 973.1412 [M + H]⁺ calcd for C₄₃H₆₁ClCo₂N₂P₆Si, 973.1416.

Synthesis of Complex 2. MeLi (1.6 M in Et₂O) (0.32 mL, 0.51 mmol) was added slowly to a solution of complex **1** (0.50 g, 0.51 mmol) in THF (20 mL) at 0 °C. The reaction solution was warmed to room temperature and stirred for 10 h. **1** was obtained as dark red crystals from diethyl ether at −20 °C (0.20 g, 42%). IR (Nujol mull, KBr, cm^{−1}): 937 ρ (PMe₃); mp 180–181 °C. HRMS (ESI-TOF): 953.1953 [M + H]⁺ calcd for C₄₄H₆₄Co₂N₂P₆Si, 953.1962.

Synthesis of Complex 3. To a solution of ligand **L2** (0.50 g, 0.83 mmol) in THF (25 mL) was added a solution of Co(PMe₃)₄ (0.60 g, 1.66 mmol) in THF at 0 °C. The reaction solution was warmed to room temperature and stirred for 48 h, resulting in a dark red

Scheme 7. Proposed Mechanism



solution. **3** was obtained as red crystals from *n*-pentane at room temperature (0.26 g, 41%). IR (Nujol mull, KBr, cm^{-1}): 940 ρ (PMe_3); ^1H NMR (300 MHz, C_6D_6 , 298 K): δ (ppm) 0.35 (d, $J = 6.0$ Hz, PCH_3 , 9H), 1.03 (d, $J = 6.0$ Hz, PCH_3 , 9H), 3.68 (m, NCH_2 , 2H), 3.82 (m, NCH_2 , 2H), 6.47–6.62 (m, Ar-H , 10H), 6.81–6.87 (m, Ar-H , 10H), 7.41–7.47 (m, Ar-H , 4H). ^{31}P NMR (400 MHz, C_6D_6 , 298 K): δ 65.74 (m, PPh_2 , 2P), 3.01 (m, PMe_3 , 1P), –13.89 (m, PMe_3 , 1P). ^{13}C NMR (400 MHz, C_6D_6 , 298 K): δ 22.86 (d, PCH_3), 24.28 (d, PCH_3), 59.80 (m, NCH_2), 112.59 (s, Ar-C), 118.28 (s, Ar-C), 127.70 (s, Ar-C), 131.25 (t, Ar-C), 132.20 (t, Ar-C), 139.38 (t, Ar-C), 144.99 (s, Ar-C). ^{29}Si NMR (400 Hz, CDCl_3 , 298 K): δ (ppm) –21.83 (s). Dec >149 °C. HRMS (ESI-TOF): $[\text{M} - \text{Cl}]^+$, 742.1749 calcd for $\text{C}_{38}\text{H}_{46}\text{CoN}_2\text{P}_4\text{Si}$, 742.1746.

Synthesis of Complex 4. To a solution of complex **3** (0.50 g, 0.64 mmol) in THF (25 mL) was exposed to a CO atmosphere at room temperature. The reaction mixture was warmed to room temperature and stirred for 48 h, resulting in a yellow solution. **4** was obtained as yellow crystals from diethyl ether at 0 °C. (0.14 g, 31%). IR (Nujol mull, KBr, cm^{-1}): 1895.94 $\nu(\text{C}\equiv\text{O})$, 947 ρ (PMe_3); ^1H NMR (300 MHz, C_6D_6 , 298 K): δ (ppm) 0.32 (d, $J = 9.0$ Hz, PCH_3 , 18H), 3.78 (m, NCH_2 , 8H), 6.22 (m, Ar-H , 4H), 6.40 (m, Ar-H , 4H), 6.53–6.64 (m, Ar-H , 13H), 6.71–6.76 (m, Ar-H , 8H), 6.79–6.91 (m, Ar-H , 11H), 7.60–7.55 (m, Ar-H , 8H). ^{31}P NMR (400 MHz, C_6D_6 , 298 K): δ (ppm) 78.51 (d, $J = 100$ Hz, PPh_2 , 4P), 6.30 (t, $J = 100$ Hz, PMe_3 , 2P). ^{13}C NMR (400 MHz, C_6D_6 , 298 K): δ 19.78 (dt $J = 96$ Hz, PCH_3), 58.96 (m, NCH_2), 111.75 (s, Ar-C), 117.17 (s, Ar-C), 127.56 (s, Ar-C), 139.08 (t, Ar-C), 140.27 (t, Ar-C), 139.38 (t, Ar-C), 143.95 (s, Ar-C), 203.39 (s, $\text{C}\equiv\text{O}$). ^{29}Si NMR (400 Hz, CDCl_3 , 298 K): δ (ppm) 76.73 (dt, $J = 396$ Hz). Dec pt >159 °C HRMS (ESI-TOF): 1403.2400 $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{72}\text{H}_{74}\text{Co}_2\text{N}_4\text{O}_3\text{P}_6\text{Si}_2$, 1402.2389.

General Procedure for Cobalt-Catalyzed Hydrosilylation Reactions. Under a N_2 atmosphere, 0.5 mol % complex **1** and 0.5 mol % NaBHET_3 were added to a 20 mL Schlenk tube containing a magnetic stirrer, and the solvent was removed immediately by vacuo. Then, alkene (1.00 mmol) was added in the Schlenk tube and prereacted at 120 °C for 5 min. *N*-Dodecane (170 mg, 1.00 mmol)

and Ph_2SiH_2 (1.2 equiv, 221 mg, 1.2 mmol) were added in the order. The reaction mixture was stirred at 120 °C for 8 min. Reaction monitoring with respect to product ratios was conducted by gas chromatography. The reaction solution was quenched with ethyl acetate. The combined organic fractions were concentrated under 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 complex **1** was collected on a Stoe IPDS2 diffractometer equipped with graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Single-crystal X-ray diffraction data for the complexes **2**, **3**, and **4** were collected on XtaLAB Synergy, Dualflex, and HyPix diffractometer equipped with graphite-monochromatized Cu $\text{K}\alpha$ radiation ($\lambda = 1.54184$ Å). During collection of the intensity data, no significant decay was observed. The structures were resolved by direct or Patterson methods with the OLEX2⁴⁴ program and refined on F2 with SHELXL.⁴⁵ All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions.

ASSOCIATED CONTENT

Accession Codes

CCDC 2155875, 2291959, 2327271, and 2327382 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,

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Notes

The authors declare no competing financial interest.

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