# Solvent-Free Hydrosilylation of Alkenes Catalyzed by Well-Defined Low-Valent Cobalt Catalysts

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ABSTRACT: A solvent free cobalt catalyzed highly selective hydrosilylation of alkenes has been developed. It was found that both $Co(PMe_3)_4$ and $CoCl(PMe_3)_3$ are highly active catalysts for hydrosilylation of alkenes. The former promoted Markovnikov type hydrosilylation of the aryl alkenes, while the latter catalyzed *anti* Markovnikov type hydrosilylation of the alkyl alkenes. These

two catalytic systems tolerate a variety of functional groups and provide high selectivity and medium to high yield. In the exploration of the reaction mechanism, a dinuclear silyl cobalt(I) complex $[(PMe_3)_2Co(\mu-\eta^2 HSiPh_2)_2Co(PMe_3)_2]$ (**4**) from the $Co(PMe_3)_4$ system and a silyl cobalt dihydride $[(PMe_3)_3Co(H)_2SiClPh_2]$ (**5**) from the $CoCl(PMe_3)_3$ system were obtained. It is proposed that the silyl cobalt(I) intermediate, $[Co(PMe_3)_3(SiHPh_2)]$, is the real catalyst for the $Co(PMe_3)_4$ system, while the hydrido cobalt(I) intermediate, $[HCo(PMe_3)_3]$, is the real catalyst for the $CoCl(PMe_3)_3$ system. Complexes **4** and **5** were characterized by spectroscopic methods and single crystal X ray diffraction.
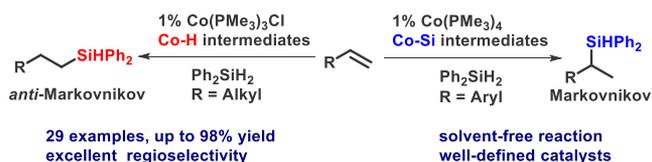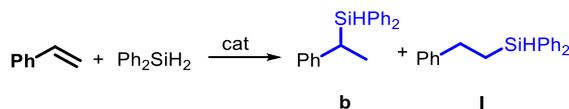
1. INTRODUCTION

Over the past few decades, hydrosilylation has emerged as one of the most successful industrialization examples in organic chemistry.[1] Hydrosilylation products are widely used in the fields of contact lenses,[2] silicone rubber,[3] commodity silicones,[4] etc. Noble metal catalysts represented by Pt based catalysts rank as an important role in silicone industry, but this brings great pollution and cost.[5] In order to overcome the shortcomings of the noble metal catalysts, a series of base metal catalysts have been designed.[6]

Compared with iron complexes, cobalt complexes have more advantages in the diversity of reaction selectivity.[7,8] The pioneering work reported by Chalk and Harrod is the reaction of alkyl alkene with silane catalyzed by $Co_2(CO)_8$ to form *anti* Markovnikov products.[9] However, in the next 50 years the related progress is very slow. Until Deng reported a silyl NHC Co catalyst in 2013,[10] there are some reports on cobalt catalyzed alkene hydrosilylation.[7] The cobalt complexes with different ligands such as phosphine,[11] NHC,[12] 2,6 diiminopyridine,[13] and β diketiminato[14] were reported to catalyze alkene hydro silylation. Most of these reports involve *anti* Markovnikov selectivity, while selective Markovnikov alkene hydrosilylation remains a challenge.[8] In 2016, Huang reported the [PNN] pincer cobalt(II) complexes could afford branched products by the Markovnikov addition.[15] In the same year, Ge found the huge impact of ligands in controlling the reaction selectivity.[11] Lu disclosed an [NNN] pincer cobalt complex catalyzed highly enantioselective Markovnikov type hydrosilylation of alkenes.[16] Deng believed that the selectivity of the hydrosilylation reaction might be controlled by the different steric nature of the NHC

ligands and the capability of incurring $\pi-\pi$ interaction between the substituents.[12] Recently, our group also found that a cobalt hydride with an unsymmetrical NHC [CNC] pincer ligand is an effective catalyst for alkene hydrosilylation.[17] The experimental results showed that Markovnikov products were formed with aryl alkenes, and *anti* Markovnikov silanes were prepared using alkyl alkenes. Although several examples of cobalt catalyzed Markovnikov type alkene hydrosilylation have been known, the mechanisms of these processes were rarely studied. Therefore, it is of great significance to study the mechanism of alkene hydrosilylation.

Phosphines are good auxiliary ligands in organometallic chemistry. The cobalt complexes supported by phosphines were also used for alkene hydrosilylation.[18] As early as 1971, Parish confirmed that a cobalt complex containing Ph_3P ligands could promote the *anti* Markovnikov addition of 1 hexene with $(EtO)_3SiH$.[19] This experiment gives us the initial inspiration that a simple low valent cobalt complex could react with silane to obtain a silyl cobalt complex, which might have a good catalytic effect on alkene hydrosilylation. In 2016, Ge reported that for the alkene hydrosilylation catalyzed by $Co(acac)_2$ Markovnikov products were formed with xantphos, and *anti* Markovnikov silanes were produced with the dppf ligand.[11]

Table 1. Optimization of Reaction Conditions[a]

$$Ph\diagdown \!\!\diagup + Ph_2SiH_2 \xrightarrow{cat} Ph\text{-}\overset{SiHPh_2}{\underset{b}{\diagup}} + Ph\diagup\!\!\diagdown\text{-}SiHPh_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad b \qquad\qquad l$$

entry	catalyst	catalyst loading(mol %)	silane	solvent	temp (°C)	time (h)	convn (%)	selectivity (b/l)
1	Co(PMe$_3$)$_4$	5	PhSiH$_3$	toluene	70	10	37	
2	Co(PMe$_3$)$_4$	5	Ph$_2$SiH$_2$	toluene	70	10	85	89:11
3	Co(PMe$_3$)$_4$	5	Ph$_3$SiH	toluene	70	10	40	
4	Co(PMe$_3$)$_4$	5	(EtO)$_3$SiH	toluene	70	10	53	
5	Co(PMe$_3$)$_4$	5	Et$_3$SiH	toluene	70	10	28	
6	CoCl(PMe$_3$)$_3$	5	PhSiH$_3$	toluene	70	10	18	
7	CoCl(PMe$_3$)$_3$	5	Ph$_2$SiH$_2$	toluene	70	10	96	83:17
8	CoCl(PMe$_3$)$_3$	5	Ph$_3$SiH	toluene	70	10	37	
9	CoCl(PMe$_3$)$_3$	5	(EtO)$_3$SiH	toluene	70	10	65	
10	CoCl(PMe$_3$)$_3$	5	Et$_3$SiH	toluene	70	10	43	
11	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	toluene	70	10	83	93:7
12	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	THF	70	10	88	88:12
13	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	dioxane	70	10	79	92:8
14	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	DME	70	10	53	76:24
15	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	CH$_3$CN	70	10	41	95:5
16	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	neat	70	10	99	98:2
17	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	neat	70	6	99	98:2
18	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	neat	70	4	99	98:2
19	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	neat	70	2	95	98:2
20	Co(PMe$_3$)$_4$	0.5	Ph$_2$SiH$_2$	neat	70	4	73	98:2
21	Co(PMe$_3$)$_4$	0.1	Ph$_2$SiH$_2$	neat	70	4	51	98:2
22	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	neat	50	4	84	98:2
23	Co(PMe$_3$)$_4$	1	Ph$_2$SiH$_2$	neat	25	4	55	98:2
24	CoCl(PMe$_3$)$_3$	1	Ph$_2$SiH$_2$	neat	70	4	85	91:9

[a]Catalytic reaction conditions: styrene (1.0 mmol), Ph$_2$SiH$_2$ (1.2 mmol), and solvent (if needed, 1 mL). Conversions and product ratios were determined by GC using *n* dodecane as an internal standard.

Recently, the catalytic applications of metal complexes containing PMe$_3$ ligands have been reported.[18,20−23] The studies indicate that PMe$_3$ ligands may have good effects in the control of reaction selectivity.[23,24] Based on this inference and as part of our ongoing work on hydrosilylation reactions, we herein report the highly regioselective hydrosilylation of alkene catalyzed by well defined low valent cobalt catalysts Co(PMe$_3$)$_4$ and Co(PMe$_3$)$_3$Cl. The former displayed Markovnikov type regioselectivity for aryl alkenes, while the latter had *anti* Markovnikov type regioselectivity for alkyl alkenes. In addition, compared to the complicated pincer complexes, both Co(PMe$_3$)$_4$ and Co(PMe$_3$)$_3$Cl are easily prepared. The separation of the products of the reaction between Co(PMe$_3$)$_4$ (or Co(PMe$_3$)$_3$Cl) with diphenylsilane is helpful for us to understand the mechanism of the hydrosilylation reaction.
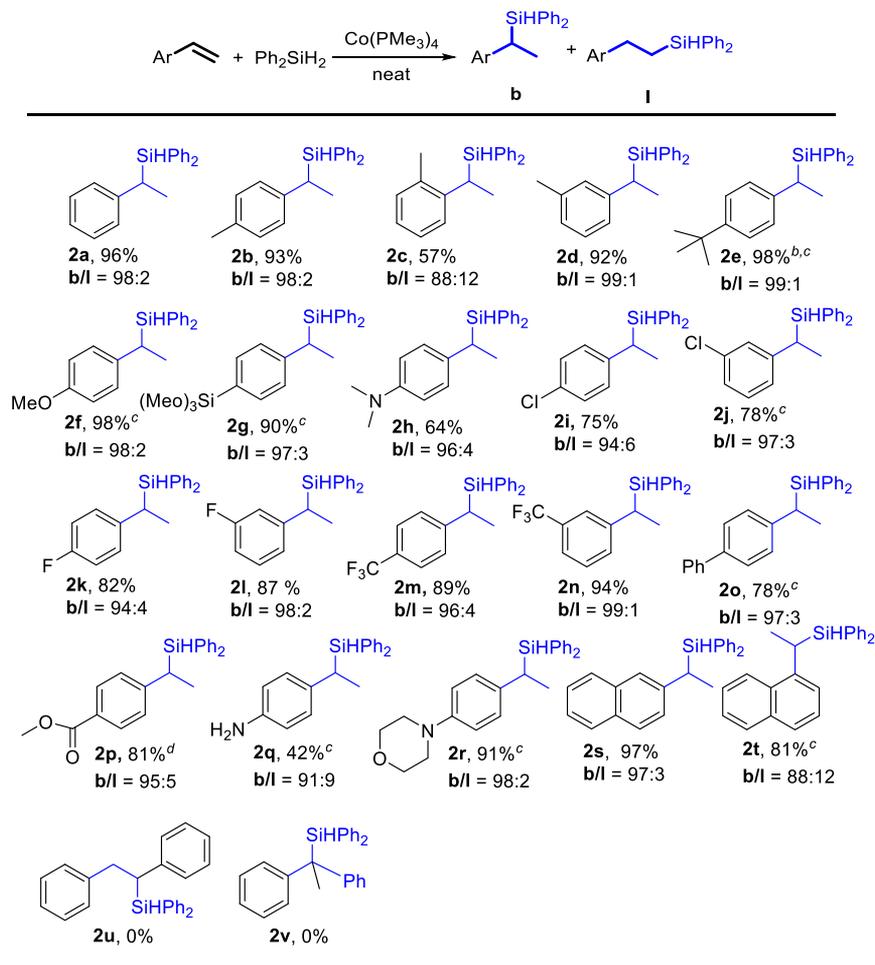
2. RESULTS AND DISCUSSION

2.1. Hydrosilylation of Alkenes Catalyzed by Co-(PMe$_3$)$_4$ and CoCl(PMe$_3$)$_3$. In our previous study, we found that the unsymmetrical NHC [CNC] pincer cobalt complex could promote hydrosilylation of styrene with diphenylsilane to afford the branched product as a major one.[17] Considering the complexity of synthesizing the asymmetric pincer ligand, we use PMe$_3$ as the ligand in this article.

At the beginning, several silanes were screened because this was considered to be an important factor for hydrosilylation in the previous report (entries 1−10, Table 1).[11] It was found that the reaction of styrene with Ph$_2$SiH$_2$ using Co(PMe$_3$)$_4$ (or CoCl(PMe$_3$)$_3$) as the catalyst afforded the Markovnikov

product at 70 °C in medium to high conversion, while the reactions of styrene with other silanes could not give rise to any products that could be separated and characterized. This difference is due to the different electronic properties and steric hindrance of different silanes. Although CoCl(PMe$_3$)$_3$ showed higher conversion than Co(PMe$_3$)$_4$, the latter gave better selectivity with a branched product as the major product. This indicates that Co(PMe$_3$)$_4$ might be a more suitable catalyst for this system (entries 2 and 7, Table 1). This speculation is confirmed by the results of subsequent screening of reaction conditions (entry 24, Table 1). When the catalyst loading was reduced to 1 mol %, the conversion did not decrease significantly. However, when the catalyst loading was further reduced to 0.5 mol %, the conversion decreased significantly (entries 11, 20, and 21, Table 1). The reaction temperature has a great influence on the reaction. A slightly higher temperature is required for this system (entries 16, 22, and 23, Table 1). The possible reason is that the higher temperature is conducive to the dissociation of the PMe$_3$ ligand and the formation of the active real catalyst.[23] In addition to the reaction temperature, the solvents also have a great impact on the reaction (entries 11−16, Table 1). The experimental results show that the catalytic reaction did not need any solvent (entry 16, Table 1). The addition of the solvent in the reaction resulted in a reduction of conversion and selectivity. This is the same as our previous report.[17] Encouragingly, it was found that 99% conversion and 98:2 selectivity were obtained within only 4 h (entries 16−19, Table 1). Therefore, the optimized conditions are alkene (1

**Table 2. Scope of Aryl Alkenes for Co(PMe₃)₄ Catalyzed Hydrosilylation[a]**

2a, 96%
b/l = 98:2

2b, 93%
b/l = 98:2

2c, 57%
b/l = 88:12

2d, 92%
b/l = 99:1

2e, 98%[b,c]
b/l = 99:1

2f, 98%[c]
b/l = 98:2

2g, 90%[c]
b/l = 97:3

2h, 64%
b/l = 96:4

2i, 75%
b/l = 94:6

2j, 78%[c]
b/l = 97:3

2k, 82%
b/l = 94:4

2l, 87 %
b/l = 98:2

2m, 89%
b/l = 96:4

2n, 94%
b/l = 99:1

2o, 78%[c]
b/l = 97:3

2p, 81%[d]
b/l = 95:5

2q, 42%[c]
b/l = 91:9

2r, 91%[c]
b/l = 98:2

2s, 97%
b/l = 97:3

2t, 81%[c]
b/l = 88:12

2u, 0%

2v, 0%

[a]Catalytic reaction conditions: alkene (1.0 mmol), Ph₂SiH₂ (1.2 mmol), and Co(PMe₃)₄ (1 mol %) were stirred in neat conditions at 70 °C for 4 h. Yields were determined by isolation and product ratios were determined by GC using n dodecane as an internal standard. [b]GC yield, 6 h. [c]6 h. [d]24 h.

mmol), diphenylsilane (1.2 mmol), Co(PMe₃)₄ (1 mol %), neat, 70 °C, and 4 h.

2.2. The Scope of Alkenes for the Co-Catalyzed Hydrosilylation. Under the optimized reaction conditions 22 terminal aryl alkenes as substrates were investigated (Table 2). At first, some electron donating functional groups are well tolerated. The substituted styrenes with the methyl (**2b**), tert butyl (**2e**), methoxy (**2f**), trimethoxysilyl (**2g**), dimethylamino (**2h**), amino (**2q**), and morpholino (**2r**) groups at the *para* positions provided good yields with excellent regioselectivities, and several electron withdrawing functional groups are also well tolerated. The substituted styrenes with halide (**2i–2l**), trifluoromethyl (**2m** and **2n**), phenyl (**2o**), and ester (**2p**) groups had good yields with excellent selectivities. Second, the substituents at both *meta* and *para* positions on the phenyl group of styrene are also tolerated. However, with the substituent at the *ortho* position (**2c**), only medium yield (57%) was reached with a decreased selectivity (**b/l = 88:12**). This result may be due to the steric hindrance of the *ortho* group. Besides, the reaction of 2 vinylnaphthalene could also afford the branched product (**2s**) in 97% yield with high selectivity (**b/l = 97:3**), while the reaction of the 1 vinylnaphthalene gave rise to the branched product (**2t**) with a lower yield (81%) in a decreased selectivity (**b/l = 88:12**) . Unfortunately, this system
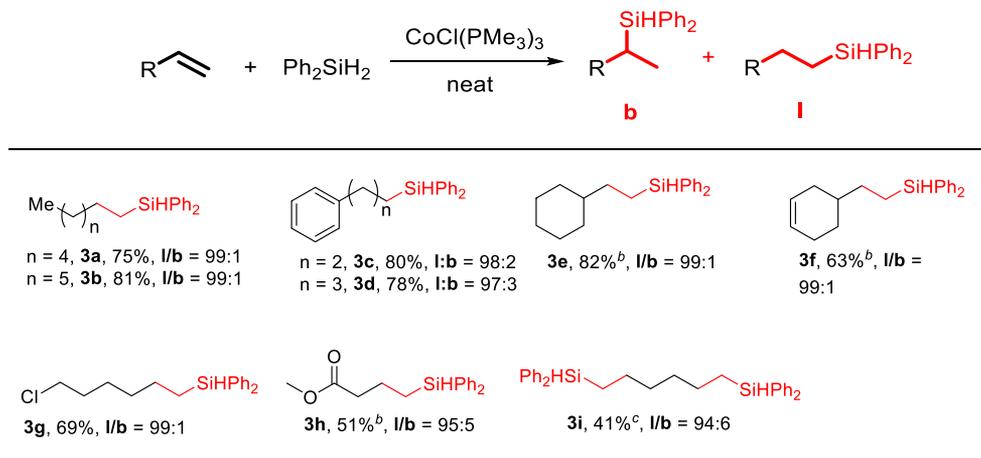
is not suitable for alkyl alkene, and the isomerized product was confirmed with 1 octene as a substrate. This is similar to Field's report.[25] This system is also not suitable for disubstituted alkenes, such as 1,1 diphenylethylene (**2v**) and *trans* stilbene (**2u**).

The gram scale reaction using 1 mol % catalyst loading could be smoothly performed to afford **2a** in 88% yield with excellent Markovnikov selectivity (**b/l = 98:2**) (eq 1).

(1)
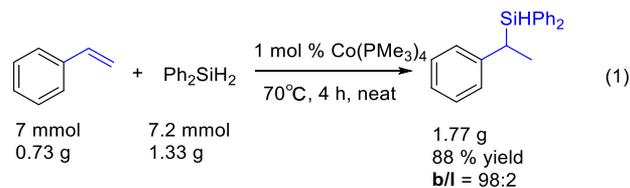
Although Co(PMe₃)₄ could not promote the hydrosilylation of alkyl alkenes, we found that CoCl(PMe₃)₃ could be used as a catalyst to realize the *anti* Markovnikov hydrosilylation of alkyl alkenes. Field also tried to use CoCl(PMe₃)₃ as a catalyst for hydrosilylation of alkenes in 2003. However, only Et₃SiH was tested, and only alkene isomerization products were obtained.[25] After optimization of the catalytic conditions, it was found that n octene could react with Ph₂SiH₂ to convert into correspond

Table 3. Scope of Alkyl Alkenes for CoCl(PMe₃)₃ Catalyzed Hydrosilylation[a]

Me–(CH₂)ₙ–SiHPh₂	Ph–(CH₂)ₙ–SiHPh₂	cyclohexyl–SiHPh₂	cyclohexenyl–SiHPh₂
n = 4, **3a**, 75%, **l/b** = 99:1 n = 5, **3b**, 81%, **l/b** = 99:1	n = 2, **3c**, 80%, **l:b** = 98:2 n = 3, **3d**, 78%, **l:b** = 97:3	**3e**, 82%[b], **l/b** = 99:1	**3f**, 63%[b], **l/b** = 99:1
Cl–(CH₂)–SiHPh₂ **3g**, 69%, **l/b** = 99:1	MeO₂C–(CH₂)–SiHPh₂ **3h**, 51%[b], **l/b** = 95:5	Ph₂HSi–(CH₂)–SiHPh₂ **3i**, 41%[c], **l/b** = 94:6	

[a]Catalytic reaction conditions: alkene (1.0 mmol), Ph₂SiH₂ (1.2 mmol), and CoCl(PMe₃)₃ (1 mol %) were stirred in neat conditions at 70 °C for 14 h. Yields were determined by isolation and product ratios were determined by GC using n dodecane as an internal standard. [b]24 h. [c]2 equiv of silane were added.

ing tertiary silane with high selectivity (**l/b** = 98:2) at 70 °C within 14 h (Table S1). Table 3 summarizes the scope of alkyl alkenes for the Co catalyzed *anti* Markovnikov hydrosilylation. The substrates bearing functional groups were effectively hydrosilylated to the related linear products. A variety of functional groups, such as benzyl (**3c**), cyclohexyl (**3e**), cyclohexene (**3f**), chloro (**3g**), and ester (**3h**), are compatible with the reaction conditions. This result is similar to the report by Holland.[14] When 1,5 hexadiene was used as a substrate, **3i** was obtained successfully.

2.3. Mechanistic Investigation. The mechanism of the Co catalyzed alkene hydrosilylation with Markovnikov selectiv ity has been studied in detail. Generally, cobalt catalyzed alkene hydrosilylation follows either the Chalk−Harrod or modified Chalk−Harrod mechanism.[26] In order to understand the mechanism of the reaction, two stoichiometric reactions were examined. A rapid color change from orange to green was observed when styrene was mixed with Co(PMe₃)₄, but the expected alkene coordinated cobalt complex could not be confirmed (eq 2). The similar alkene coordinated cobalt
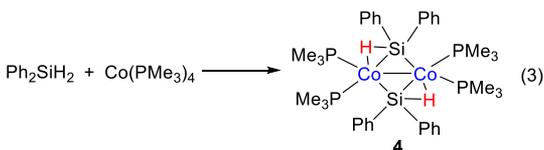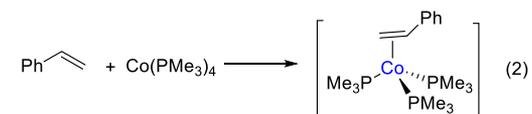
complex was reported by Klein.[27] When Ph₂SiH₂ was added to the n pentane solution of Co(PMe₃)₄, the reaction solution gradually changed from orange to red, accompanied by the precipitation of red crystals of dinuclear cobalt(I) hydride **4** (eq 3). In the IR spectrum of **4**, the ν(Co−H) band is located at 1959 cm⁻¹. This is comparable to the ν(Co(I)−H) (1948 cm⁻¹) for the silyl cobalt hydride.[28] The ¹H NMR spectrum of **4** provides the evidence for the hydrido ligand at −13.01 ppm as a

singlet. In ³¹P NMR spectrum of **4**, two peaks appear at 2.65 and −3.62 ppm, respectively.

The molecular structure of complex **4** (see Figure 1) was confirmed by single crystal X ray diffraction analysis. Surpris
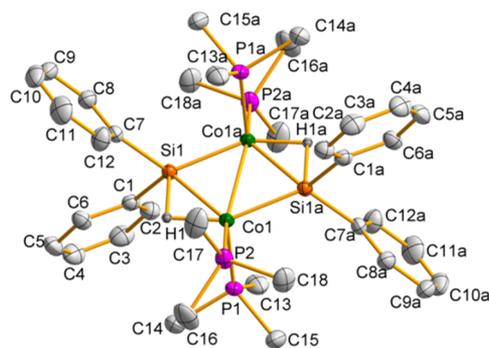

Figure 1. Molecular structure of **4** at the 50% probability level. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−Co1a 2.6451(8), Co1−Si1 2.2352(8), Co1−Si1a 2.3177(8), Co1−H1 1.58(5), Si1−H1 1.60(3); Si1−Co1−Co1a 55.95(2), Si1a−Co1−Co1a 53.04(2), Si1−Co1−Si1a 108.99(3), Si1−Co1−H1 44(1), Si1a−Co1−H1 152(1), P2−Co1−P1, 97.61(3).

ingly, complex **4** is a dinuclear complex with inversion symmetry. Each cobalt atom has a distorted tetrahedral coordination geometry. Deng reported a series of dinuclear cobalt(I) complexes with similar structures in 2017.[28] Compared with the complexes reported by Deng, the Co−Co bond length (2.6451(8) Å) of complex **4** is longer than those complexes (2.599(1) Å for [(cyIDep)Co(μ−η^2 HSiPh₂)₂Co (cyIDep)] and 2.497(1) Å for [(IPr)Co(μ HSiPh₂)₂Co(IPr)]). This distance also indicates a weaker Co−Co interaction. The distances of Co1−Si1 (2.2352(8) Å), Co1−Si1a (2.3177(8) Å), Co1−H1 (1.58(5) Å), and Si1−H1 (1.60(3) Å) also imply the 3c 2e bond nature of the Co−H−Si interactions (Table 4). This is consistent with Deng's view. Another cobalt complex with a similar structure was disclosed in 2015.[29] The difference in complex **4** is that the Co−Co bond (2.3670 (8) Å) in the bis(l diphenylphosphanyl)bis[(trimethylphosphane)cobalt(I) com plex lies within the range of Co═Co bonds.

Table 4. Comparison of Bond Length (Å) in Dicobalt(I) Complexes

	4	**[(cyIDep)Co(μ η^2-HSiPh$_2$)$_2$Co-(cyIDep)][29]**	**[(IPr)Co(μ-HSiPh$_2$)$_2$Co(IPr)][29]**
Co Co	2.6451(8)	2.599(1)	2.4971(5)
Co H	1.58(5)	1.58(3)	1.63(2)
Co Si1	2.2352(8)	2.246(1)	2.2280(6)
Co Si2	2.3177(8)	2.336(1)	2.3165(6)
Si H	1.60(3)	1.66(3)	1.59(2)

To our surprise, complex **4** was also detected from the three component stoichiometric reaction of styrene and Co(PMe$_3$)$_4$ as well as Ph$_2$SiH$_2$ (eq 4). Unfortunately, using 0.5% mol of **4**
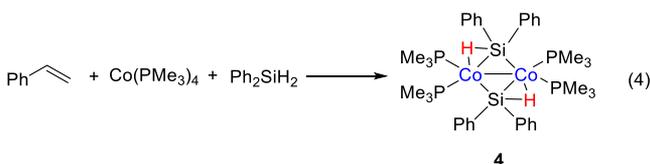
(1% mol cobalt) as a catalyst, only 49% of styrene could convert into the corresponding tertiary silane (**b/l** = 86:14) at 70 °C within 4 h. This result indicates that **4** is not the active intermediate in this catalytic process. In order to further understand the mechanism of the catalytic reaction, the effect of the addition sequence of the styrene and Ph$_2$SiH$_2$ was also studied (Table 5). The results in Table 5 indicate that if the

Table 5. Effect of Addition Sequence of Styrene and Ph$_2$SiH$_2$[a]

| entry	pre-reaction time of Co(PMe$_3$)$_4$ and Ph$_2$SiH$_2$	pre-reaction of Co(PMe$_3$)$_4$ and styrene	convn (%)	product ratios (b/l)
1	0 min	0 min	99	98:2
2	2 min		94	98:2
3	5 min		90	97:3
4	15 min		86	94:6
5	30 min		76	91:9
6	10 h		22	85:15
7		10 h	99	98:2

[a]Catalytic reaction conditions: styrene (1.0 mmol), Ph$_2$SiH$_2$ (1.2 mmol), catalyst loading (1.0 mol %), neat, 70 °C. Conversions and product ratios are determined by GC analysis using dodecane as internal standard.

catalyst reacts with silane for a certain time and then alkene is added, the yield and selectivity of the reaction are closely related to the reaction time of the catalyst and silane. It can be seen from Table 5 that when the prereaction time of the catalyst and silane is 0 min, 2 min, 5 min, 15 min, 30 min, and 10 h, respectively, the conversion of the reaction decreases from 99% to 94%, 90%, 86%, 76%, and 22%. Although the selectivity of the product did not change, the conversion decreased from 99% to 94% in the case of a 2 min prereaction with silane. With the extension of the prereaction time, the selectivity of the product decreases from 98/2 to 97/3, 94/6, 91/9, and 85/15. On the contrary, the yield and selectivity were not affected by the prereaction of the catalyst and styrene even if the reaction time reaches 10 h. The experimental results clearly show that the active intermediate or real catalyst of the catalytic system should be the product of the reaction between Co(PMe$_3$)$_4$ with diphenylsilane. In addition,

hydrogen gas was detected, even if the prereaction time of Co(PMe$_3$)$_4$ with diphenylsilane is only 2 min.

Based on the above experimental results and literature reports,[12] a possible catalytic reaction mechanism is proposed (Scheme 1). At the beginning of the reaction, intermediate **A** as a

Scheme 1. Mechanisms for Markovnikov Hydrosilylation and Formation of 4
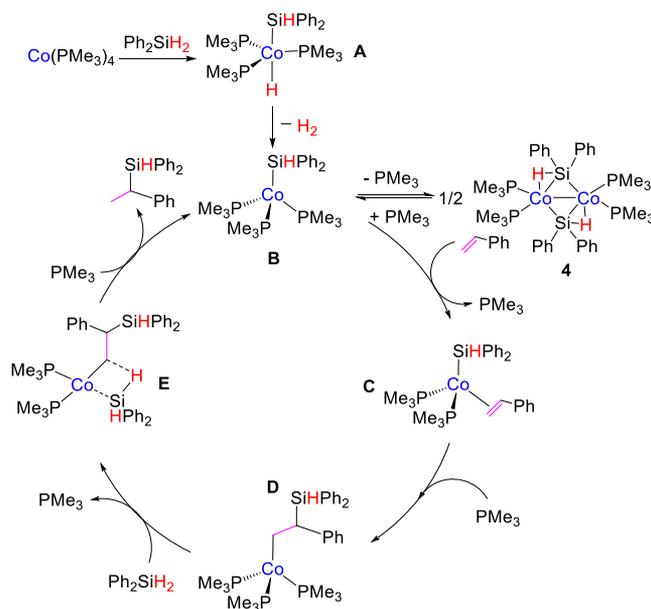
cobalt(II) hydride is produced by the reaction of Co(PMe$_3$)$_4$ with Ph$_2$SiH$_2$ through Si−H bond activation. **A** is not stable and transforms to **B** via single electron reductive elimination with the release of H$_2$. In the absence of alkene, complex **4** is formed through the dimerization of two molecules of **B**. The coordination of alkene to **B** affords intermediate **C** with the dissociation of a PMe$_3$ ligand. The migratory insertion reaction of the coordinated styrene into the Co−Si bond delivers intermediate **D** according to the modified Chalk−Harrod mechanism.[26] The second Ph$_2$SiH$_2$ coordinates to the Co center of **D** to form a four membered ring transition state **E**. The final silane product is generated through σ bond metathesis with the regeneration of real catalyst **B**. Unlike our previous report, the unstable silyl cobalt(I) intermediate **B** is proposed as the real catalyst in this system.[17] This view has been widely accepted in recent years. Both Lu and Deng considered the silicon based cobalt complexes as the real catalysts for the reactions.[12,16]

In order to understand the mechanism of *anti* Markovnikov hydrosilylation of alkyl alkenes catalyzed by CoCl(PMe$_3$)$_3$, the stoichiometric reaction of CoCl(PMe$_3$)$_3$ with diphenylsilane was explored (eq 5). After workup, a silyl cobalt dihydride **5** (see

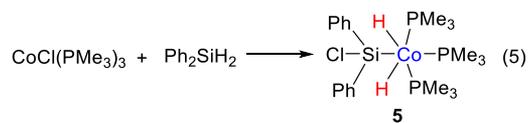Figure 2) was isolated. The similar complex (Ph$_3$P)$_3$Co(H)$_2$Si(OEt)$_3$, obtained from the reaction of (Ph$_3$P)Co(N$_2$)H with (EtO)$_3$SiH, was reported by Parish in 1971.[30] Although complex **5** shows two (Co−H) signals in the IR spectrum at 1931 and 1975 cm^{-1}, respectively, only one singlet was observed at −14.96 ppm with the integral of 2H in the ^{1}H NMR spectrum.
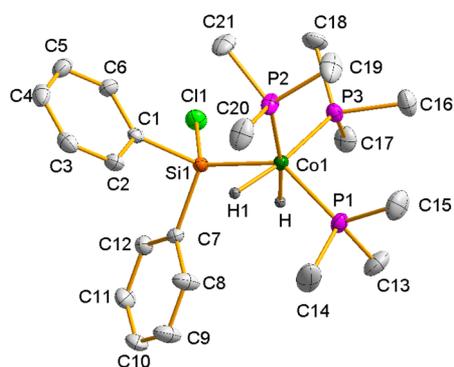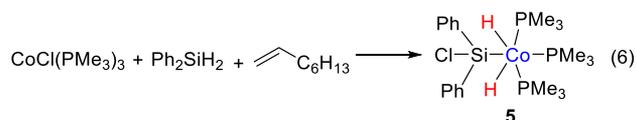
Figure 2. Molecular structure of **5** at the 50% probability level. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−Si1 2.1932(9), Co1−H 1.44(4), Co1−H1 1.47(4); P1−Co1−Si1 136.77(4), P2−Co1−Si1 105.47(3), P2−Co1−P1 103.11(4), P3−Co1−Si1 105.12(3), P3−Co1−P1 101.92(3), P3−Co1−P2 98.48(4), Si1−Co1−H 67(2), P3−Co1−H 86(2), P2−Co1−H 172(2), P1−Co1−H 81(2), Si1−Co1−H1 61(2), P3−Co1−H1 166(2), P2−Co1−H1 86(2), P1−Co1−H1 90(2), H−Co1−H1 88(2).

This result is consistent with that reported by Huttner in 2008.[31,32] In the ^{31}P NMR spectrum of **5**, one phosphine signal appears at 6.51 ppm as a singlet. In the ^{29}Si NMR spectrum of **5**, the resonance appears at 37.72 ppm.

The single crystal X ray diffraction data of complex **5** confirm a distorted octahedral geometry around the Co(III) center. The axial bond angle P2−Co1−H is 172(2)°, deviated from 180°. The sum of the bond angles in the equatorial plane (Si1, H1, P1, P3, and Co1) is 358.04°, close to 360°. The distance of the Co−H bond is 1.44(4) Å for Co1−H and 1.47(4) Å for Co1−H1, respectively. They are slightly longer than the Co−H bond in [*tripod*Co(H)$_2$(SiPh$_3$)] (1.37(4) and 1.35(4) Å).[31] Both Si1−H1 (1.970(4) Å) and Si1−H (2.111(6) Å) are 0.5−0.6 Å longer than the regular Si−H single bond.[33] They are situated between the Si−H bonds of the σ hydrosilanes and the classic silyl hydrides, defined as nonclassical hydrosilane complexes by Emslie.[33] The range of these distances is generally considered to be 1.8 to 2.1 or 2.4 Å.[33,34] The distance of the Co1−Si1 (2.1932(9) Å) is a slightly shorter than those of some silyl cobalt(III) hydrides.[35] That the three trimethylphosphine ligands in different chemical environments in the solid structure have only one singlet in the ^{31}P NMR spectrum indicates that there is a rapid kinetic exchange process for the trimethylphosphine ligands in the solution.

Using complex **5** as the catalyst (1 mol %) with 1 octene as the substrate, the decreased conversion (74%) with excellent selectivity (**b/l** = 1:99) was obtained under optimized conditions. This result indicates that **5** is not an active intermediate in the reaction. Complex **5** could be also isolated from a three component reaction (eq 6). Based on the above

$$CoCl(PMe_3)_3 + Ph_2SiH_2 + \overset{}{\diagup}C_6H_{13} \longrightarrow \underset{\textbf{5}}{\overset{Ph\quad H\quad PMe_3}{\underset{Ph\quad H\quad PMe_3}{Cl-Si-Co-PMe_3}}} \quad (6)$$

experimental results and previous report,[7] we propose a possible reaction mechanism for the *anti* Markovnikov process and formation of **5** (Scheme 2). In the first step, the oxidative addition of the Si−H bond at the Co(I) center gives rise to Co(III) hydride **F**. The reductive elimination between the Co−

Scheme 2. Mechanisms for *anti* Markovnikov Hydrosilylation and Formation of 5
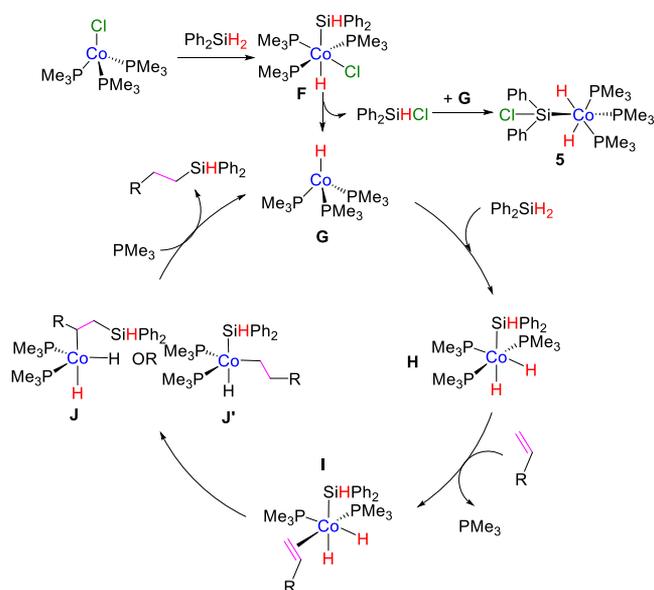
Si and Co−Cl bonds of **F** affords Co(I) hydride **G** with the formation of Ph$_2$SiClH. Silyl dihydrido Co(III) complex **5** is formed through the reaction of Co(I) hydride **G** with Ph$_2$SiClH as the oxidation addition product of the Si−H bond activation in Ph$_2$SiClH. In this catalytic system, cobalt hydride **G** is considered to be the real catalyst. Ph$_2$SiH$_2$ reacts with **G** to afford cobalt(III) intermediate **H** via oxidative addition of the Si−H bond. Ligand exchange between PMe$_3$ and alkene delivers intermediate **I**. The insertion of alkene into the Co−Si bond (modified Chalk−Harrod process) or into the Co−H bond (Chalk−Harrod process) gives rise to intermediate **J** or **J'**. **J** or **J'** transfers to the final hydrosilylation product via reductive elimination with the recovery of real catalyst **G**.

3. CONCLUSIONS

In summary, Co(PMe$_3$)$_4$ and CoCl(PMe$_3$)$_3$ could serve as catalysts for hydrosilyation of alkene under neat conditions. Co(PMe$_3$)$_4$ could promote Markovnikov hydrosilylation of the aryl alkenes, while CoCl(PMe$_3$)$_3$ could catalyze *anti* Markovnikov hydrosilylation of the alkyl alkenes. Both processes provide high yields and excellent selectivity. The gram scale reaction of styrene with Ph$_2$SiH$_2$ using 1 mol % Co(PMe$_3$)$_4$ as the catalyst could afford the Markovnikov product in 88% yield with excellent selectivity (**b/l** = 98:2). In the study of the reaction mechanism, a silyl bridged dicobalt(I) complex [(PMe$_3$)$_2$Co(μ−η^2 HSiPh$_2$)$_2$Co(PMe$_3$)$_2$] (**4**) was isolated for the Co(PMe$_3$)$_4$ system, while a silyl cobalt dihydride [(PMe$_3$)$_3$Co(H)$_2$(SiClPh$_2$)] (**5**) was separated for the CoCl(PMe$_3$)$_3$ system. Both **4** and **5** provide the information to understand the catalytic mechanisms for these two systems. Two mechanisms are proposed based on the experimental results and the literature reports.

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Notes

The authors declare no competing financial interest.

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