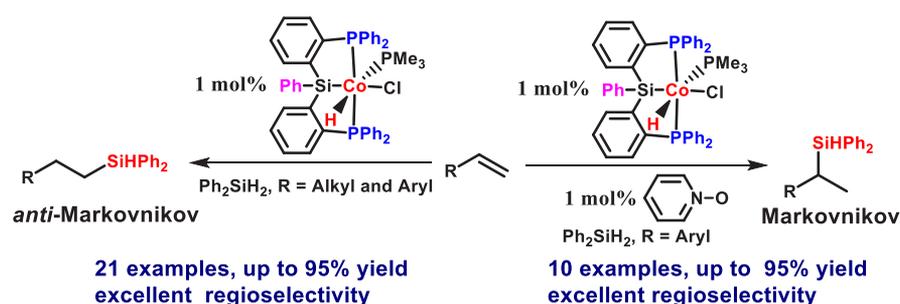


# Selectivity Reverse of Hydrosilylation of Aryl Alkenes Realized by Pyridine N-Oxide with [PSiP] Pincer Cobalt(III) Hydride as Catalyst

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**ABSTRACT:** Six silyl cobalt(III) hydrides **1–6** with [PSiP] pincer ligands having different substituents at the P and Si atoms ([ $(2 \text{ Ph}_2\text{PC}_6\text{H}_4)_2\text{MeSiCo(H)(Cl)(PMe}_3)$ ] (**1**), [ $(2 \text{ Ph}_2\text{PC}_6\text{H}_4)_2\text{HSiCo(H)(Cl)(PMe}_3)$ ] (**2**), [ $(2 \text{ Ph}_2\text{PC}_6\text{H}_4)_2\text{PhSiCo(H)(Cl)(PMe}_3)$ ] (**3**), [ $(2 \text{ }^i\text{Pr}_2\text{PC}_6\text{H}_4)_2\text{HSiCo(H)(Cl)(PMe}_3)$ ] (**4**), [ $(2 \text{ }^i\text{Pr}_2\text{PC}_6\text{H}_4)_2\text{MeSiCo(H)(Cl)(PMe}_3)$ ] (**5**), and [ $(2 \text{ }^i\text{Pr}_2\text{PC}_6\text{H}_4)_2\text{PhSiCo(H)(Cl)(PMe}_3)$ ] (**6**)) were synthesized through the reactions of the ligands (**L1–L6**) with  $\text{CoCl(PMe}_3)_3$  via Si–H bond cleavage. Compounds **1–6** have catalytic activity for alkene hydrosilylation, and among them, complex **3** is the best catalyst with excellent *anti* Markovnikov regioselectivity. A silyl dihydrido cobalt(III) complex **7** from the reaction of **3** with  $\text{Ph}_2\text{SiH}_2$  was isolated, and its catalytic activity is equivalent to that of complex **3**. Complex **7** and its derivatives **10–12** could also be obtained through the reactions of complexes **3**, **1**, **4**, and **5** with  $\text{NaBHET}_3$ . The molecular structure of **7** was indirectly verified by the structures of **10–12**. To our delight, the addition of pyridine N oxide reversed the selectivity of the reaction, from *anti* Markovnikov to Markovnikov addition. At the same time, the reaction temperature was reduced from 70 to 30 °C on the premise of high yield and excellent selectivity. However, this catalytic system is only applicable to aromatic alkenes. On the basis of the experimental information, two reaction mechanisms are proposed. The molecular structures of cobalt(III) complexes **3–6** and **10–12** were determined by single crystal X ray diffraction analysis.

## 1. INTRODUCTION

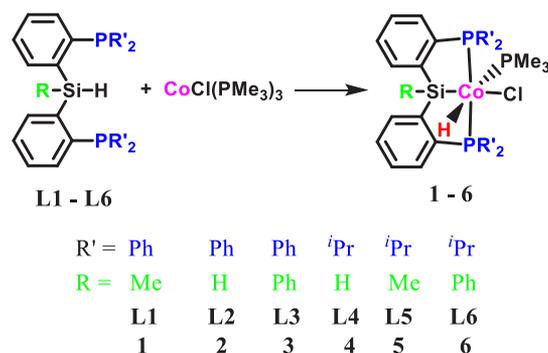
Organosilanes are important starting materials in the fields of silicon rubbers, paper releasing coatings, molding implants, and pressure sensitive adhesives owing to their stability, nontoxicity, and versatile transformations.<sup>1</sup> The alkene hydrosilylation catalyzed by transition metals is a particularly noteworthy method to obtain organosilanes with high atom economy.<sup>2</sup> For over decades, precious metal catalysts, especially Pt and Rh, have been widely used for alkene hydrosilylation.<sup>3</sup> However, the high cost and environmental issues of precious metals have led to extensive study on the development of earth abundant base metal alternatives.<sup>4</sup> Iron, cobalt, and nickel catalysts become the most promising candidates.<sup>5</sup> In recent years, breakthroughs have been made in the research progress of cobalt complexes. A large number of cobalt complexes bearing phosphine,<sup>6</sup> cyclopentadienyl,<sup>7</sup> N heterocyclic carbene,<sup>8</sup> and 2,6 diiminopyridine ligands<sup>9</sup> can promote alkene hydrosilylation.

It is well known that ligand design is the core of transition metal catalysis and plays a critical role in tuning catalyst activity and selectivity.<sup>10</sup> A large number of studies have shown that pincer ligands have unique stereochemical structures, which lead to significant inert bond activation and catalytic properties of the corresponding transition metal complexes.<sup>11</sup> Several cobalt complexes bearing pincer ligands have been used for alkene hydrosilylation. In 2016, Fout disclosed a bis(carbene) Co(I) dinitrogen complex for catalytic *anti* Markovnikov hydrosilylation of terminal alkenes.<sup>12</sup> In the same year, Huang found that the [PNN]

pincer cobalt(III) complexes could provide an unprecedented high level of Markovnikov selectivity (branched/linear up to 99:1).<sup>13</sup> Lu developed a highly enantioselective Markovnikov type alkene hydrosilylation with the [NNN] pincer cobalt(II) complexes as catalysts.<sup>14</sup> Recently, we reported the [CNC] pincer cobalt(III) hydrides have Markovnikov selectivity for aryl olefins and *anti* Markovnikov selectivity for alkyl olefins.<sup>15</sup> Because of the good  $\sigma$  donating ability and strong *trans* influence of [PSiP] pincer ligands, their metal complexes were widely studied and applied for a variety of catalytic reactions.<sup>16</sup> Turculet carried out the study on [PSiP] pincer metals complexes in 2007.<sup>17</sup> We found that [PSiP] pincer metal complexes could catalyze hydrosilylation of carbonyl compounds,<sup>18</sup> dehydration of amides to nitriles,<sup>19</sup> and alkene hydrosilylation as well as nitrogen silylation.<sup>20</sup>

As a continuation of our work in the direction of cobalt catalyzed selective hydrosilylation of alkenes, in this paper, six [PSiP] pincer cobalt(III) hydrides with different substituents at the Si or P atom were prepared (Scheme 1). It was

**Scheme 1. Preparation of Silyl [PSiP] Pincer Cobalt(III) Hydrides 1–6**



confirmed that compound 3 is the best catalyst for alkene hydrosilylation having *anti* Markovnikov selectivity. It is interesting that the addition of pyridine N oxide could not only make the catalytic condition milder but also reverse the selectivity to form Markovnikov products.

## 2. RESULTS AND DISCUSSION

### 2.1. Synthesis of Silyl [PSiP] Pincer Cobalt(III) Hydrides 1–6 via Si-H Activation.

Silyl [PSiP] pincer

cobalt(III) hydrides 1–6 were synthesized from the reactions of [PSiP] pincer ligands L1–L6 and CoCl(PMe<sub>3</sub>)<sub>3</sub> via Si–H bond cleavage (Scheme 1).<sup>21</sup> Five new complexes 2–6 were completely analyzed with spectroscopic techniques.

The characteristic spectroscopic data are summarized in Table 1. The molecular structures of complexes 3–6 were determined by single crystal X ray diffraction analysis. Complexes 3–6 have similar molecular structures (Figures S1–S4) to complex 1.<sup>21</sup> Comparing the selected bond parameters of complexes 1 and 3–6 (Table 1), we find that the Co1–H (1.63(7) Å) of 6 is the longest, while the Co1–H (1.45(3) Å) of 4 is the shortest among the five cobalt complexes. We speculate that the steric hindrance effect of the substituents at both the Si and P atoms plays an important role in this point. Co1–P3 bonds are longer than Co1–P1 and Co1–P2 bonds in the five complexes due to the strong *trans* influence of the hydrido ligands. The bond angles P3–Co1–Cl1 in complexes 4–6 are less than the corresponding values of complexes 1 and 3 because of the spatial baffle effect of the isopropyl substituents at the P atoms. For the same reason, the bond angles P1–Co1–P2 in complexes 4 and 6 are also less than the corresponding values in complexes 1 and 3. The large bond angle P1–Co1–P2 in complex 5 may be related to its symmetry plane.

**2.2. *anti*-Markovnikov Alkene Hydrosilylation with Cobalt(III) Hydrides 1–6 as Catalysts.** It has been confirmed that hydrido cobalt(III) complexes as catalysts could efficiently and selectively promote both aryl and alkyl alkene hydrosilylation.<sup>15</sup> In this paper, the reaction of styrene and Ph<sub>2</sub>SiH<sub>2</sub> was selected as the template reaction with complexes 1–6 as catalysts to explore the optimal catalytic conditions (Table 2). It can be seen that complex 3 is the best catalyst with 97% conversion and good *anti* Markovnikov selectivity (b/l = 11:89) at 70 °C for 24 h (entries 1–6, Table 2). When the reaction time was shortened, the conversion of the reaction decreased significantly (entries 7 and 8, Table 2). It was found that neat reaction has a better effect than the reaction with solvents (entries 3 and 9–15, Table 2). As a silylation agent, Ph<sub>2</sub>SiH<sub>2</sub> has the best effect, which is obviously better than that of (EtO)<sub>3</sub>SiH ~ Ph<sub>3</sub>SiH > Me(EtO)<sub>2</sub>SiH > Et<sub>3</sub>SiH > PhShH<sub>3</sub> (entries 16–20, Table 2). So we have the following optimization conditions: 1 mol % 3, Ph<sub>2</sub>SiH<sub>2</sub>, styrene, without solvent, 24 h, and 70 °C (entry 3, Table 2).

**Table 1. Selected Spectroscopic Data and Structural Parameters (Å and deg) of 1–6**

	1	2	3	4	5 <sup>a</sup>	6
H <sub>hydrido</sub> /ppm	13.68(q)	13.63(q)	13.75(q)	15.60(q)	16.61(q)	16.17(q)
J/Hz	61	63	67	75	75	72
$\nu$ (Co-H)/cm <sup>-1</sup>	1910	1882	1908	1893	1902	1956
Co1 H	1.52(2)		1.51(3)	1.45(3)	1.39(1)	1.63(7)
Co1 P1	2.188(1)		2.1925(6)	2.2275(8)	2.2386(10)	2.2381(14)
Co1 P2	2.188(1)		2.2000(6)	2.2106(8)	2.2386(10)	2.219(14)
Co1 P3	2.259(2)		2.2321(6)	2.2631(9)	2.2712(15)	2.2751(16)
Co1 Si1	2.252(2)		2.2443(6)	2.2195(6)	2.2764(13)	2.2493(16)
Co1 Cl1	2.410(1)		2.424(4)	2.3708(7)	2.3773(14)	2.347(6)
P1 Co1 P2	147.09(7)		147.97(2)	142.34(3)	147.81(5)	138.2(11)
P1 Co1 Si1	86.85		86.28(2)	83.77(3)	84.31(2)	85.95(6)
P2 Co1 Si1	93.76		87.45(2)	86.09(3)	84.31(2)	85.10(2)
P3 Co1 Cl1	92.85(6)		94.65(6)	85.04(3)	82.34(6)	84.3(3)

<sup>a</sup>P1A in complex 5 corresponds to P2 here.

**Table 2. Optimization of Reaction Conditions<sup>a</sup>**


entry	catalyst	loading (mol %)	solvent	silane	temp (°C)	time (h)	conv. (%)	ratio (b/l) <sup>b</sup>
1	1	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	20	90:10
2	2	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	63	33:67
3	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	97	11:89
4	4	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	24	25:75
5	5	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	30	15:85
6	6	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	43	31:69
7	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	6	27	
8	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	12	60	11:89
9	3	1	THF	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	82	23:77
10	3	1	toluene	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	84	33:67
11	3	1	dioxane	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	85	21:79
12	3	1	benzene	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	42	33:67
13	3	1	DMSO	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	10	
14	3	1	DMF	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	98	34:66
15	3	1	acetonitrile	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	28	25:75
16	3	1	neat	Ph <sub>3</sub> SiH	70	24	57	
17	3	1	neat	PhSiH <sub>3</sub>	70	24	12	
18	3	1	neat	Et <sub>3</sub> SiH	70	24	30	
19	3	1	neat	Me(EtO) <sub>2</sub> SiH	70	24	33	
20	3	1	neat	(EtO) <sub>3</sub> SiH	70	24	59	
21	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	50	24	60	16:84
22	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	25	24	21	33:67
23	3	0.5	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	70	18:82
24 <sup>c</sup>	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	70	24	85	70:30
25 <sup>c</sup>	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	30	24	90	96:4
26 <sup>c,d</sup>	3	1	neat	Ph <sub>2</sub> SiH <sub>2</sub>	30	24	99	96:4

<sup>a</sup>Catalytic 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. <sup>b</sup>b/l: branched/linear. <sup>c</sup>With pyridine N oxide (1.0 mol %). <sup>d</sup>Change the order of addition of the reagents: in the presence of pyridine N oxide, styrene reacted with the catalyst at 30 °C for 20 min first; silane was added and reacted at 30 °C for 24 h next.

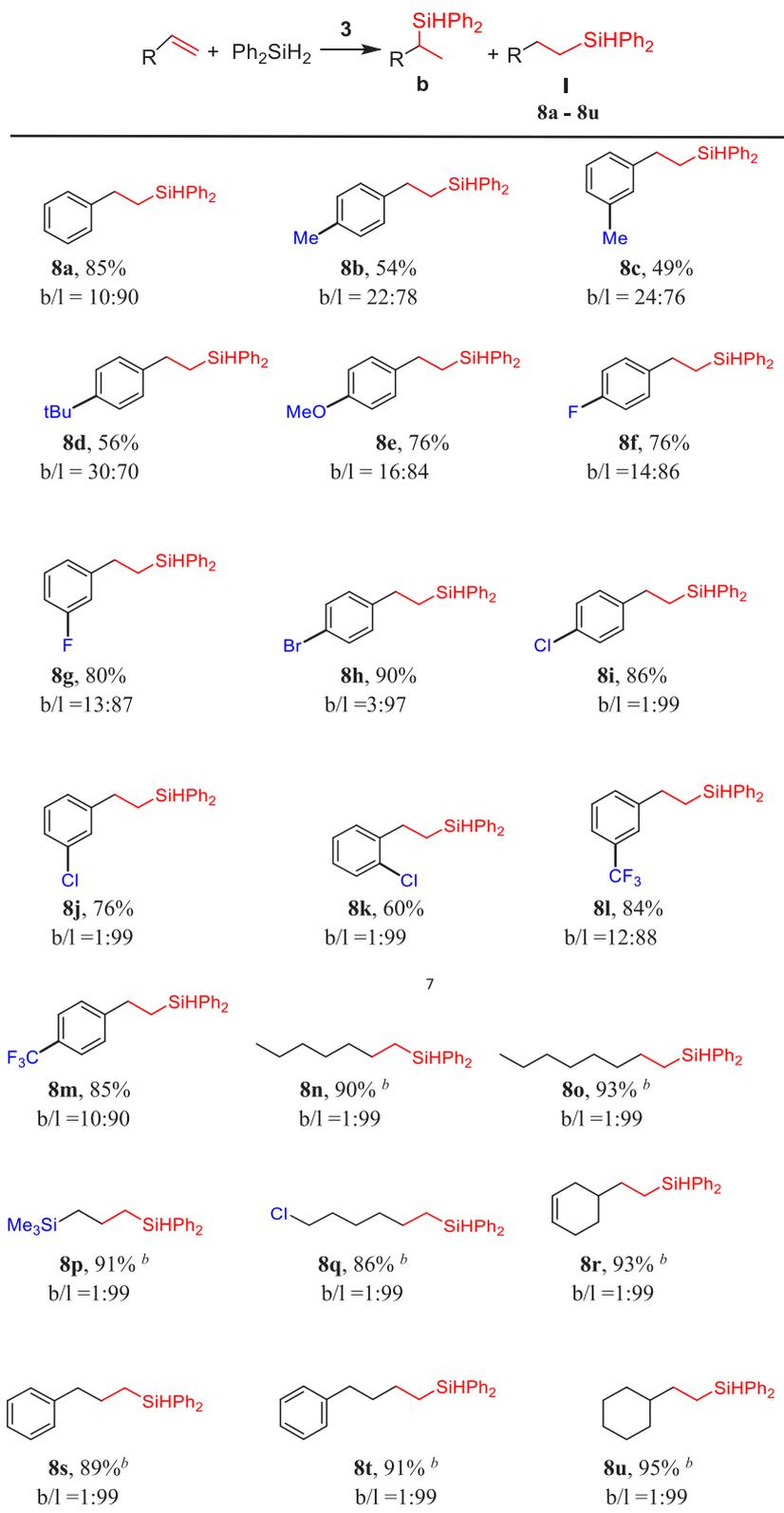
The hydrosilylation of 21 alkene substrates was studied to obtain the products of *anti* Markovnikov addition. Complex **3** was used as catalyst to realize the *anti* Markovnikov hydrosilylation of aromatic alkenes in moderate to high yield, but the selectivity varies with the different substituents on the phenyl ring (**8a–8m**, Table 3). The alkenes with electron withdrawing groups on the phenyl ring (**8f–8m**, Table 3) afforded linear products in slightly better regioselectivity compared with the alkenes bearing electron donating groups on the phenyl ring (**8b–8e**, Table 3). However, the positions of the substituents on the phenyl groups (*ortho*, *meta*, or *para*) have little effect on the experimental results. To our regret, the alkenes bearing reactive functional groups, such as 1 nitro 4 vinylbenzene and methyl 4 vinylbenzoate, have poor selectivity (Table 7). The experimental results show that the catalytic system is tolerant to a variety of substituents and provides moderate to very good yields with excellent regioselectivity. In general, the yield and selectivity of aliphatic alkenes (**8n–8u**, Table 3) are better than those of aromatic alkenes (**8a–8m**, Table 3), except for pent 4 en 2 one (Table 7).

**2.3. Mechanistic Investigation.** To shed light on the mechanism of this Co catalyzed alkene hydrosilylation, the stoichiometric reactions of complex **3** with styrene and complex **3** with Ph<sub>2</sub>SiH<sub>2</sub> were studied, respectively (Scheme 2). The experiments showed that complex **3** did not react

with styrene, but reacted with Ph<sub>2</sub>SiH<sub>2</sub> to form dihydrido cobalt(III) complex **7** as a yellow solid. In the IR spectrum of complex **7**, the typical signals for Co–H bonds were found at 1934 and 1886 cm<sup>-1</sup>, while the  $\nu(\text{Co H})$  vibration of complex **3** at 1908 cm<sup>-1</sup> disappeared. Compared with the hydrido resonance of complex **3** at -13.73 ppm, the hydrido resonance of complex **7** appeared at -12.74 ppm. In the <sup>31</sup>P NMR spectrum of **7**, the peak at 95.3 ppm belongs to two -PPh<sub>2</sub> groups, while the signal at 12.7 ppm is brought by a PMe<sub>3</sub> ligand. Unfortunately, no single crystals of complex **7** suitable for X ray diffraction could be obtained. Dihydrido cobalt(III) complex **7** as a possible intermediate arouses our research interest, while dihydrido complexes of the first row transition metals have been developed in recent years and most of them were prepared by activation of dihydrogen.<sup>22</sup> Alternatively, dihydrido complexes may be directly accessed by the reduction with NaBHET<sub>3</sub>.<sup>23</sup> Therefore, the reaction of complex **3** with NaBHET<sub>3</sub> was carried out to deliver complex **7** (Scheme 3). At the same time, the reaction between complex **1** or **4** or **5** and NaBHET<sub>3</sub> gave rise to the corresponding dihydrido complex **10** or **11** or **12**. The typical spectroscopic data of complexes **7** and **10–12** are listed in Table 4.

Fortunately, the molecular structures of complexes **10–12** were determined by single crystal X ray diffraction analysis (Figure 1 (**10**), Figure S5 (**11**), and Figure S6 (**12**)). In the molecular structures of complexes **10–12**, the cobalt atom is

Table 3. *anti* Markovnikov Alkene Hydrosilylation with Complex 3 as Catalyst<sup>a</sup>

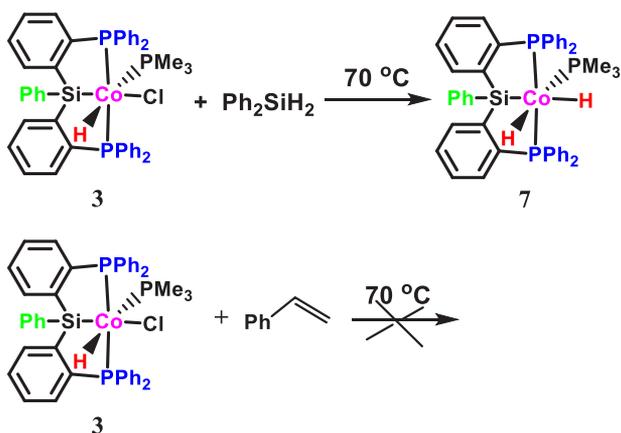


<sup>a</sup>Catalytic conditions: 3 (1 mol %), olefin (1.0 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (1.2 mmol), solvent free at 70 °C for 24 h; isolated yields. <sup>b</sup>30 h.

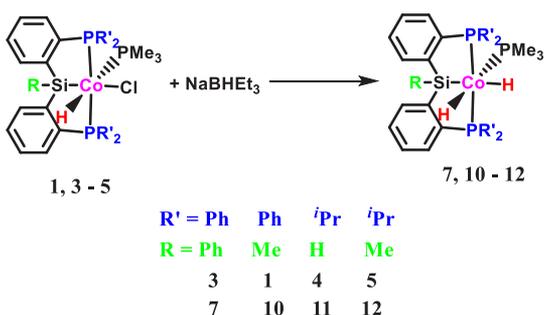
situated in a distorted octahedral coordination geometry. The ligand arrangement of complex 10 is different from those of complexes 11 and 12. In the molecular structure of complex 10, two hydrido ligands are in the *trans* positions of the two

-PPh<sub>2</sub> groups, while, in complexes 11 and 12, two hydrido ligands are in the *trans* positions of the PMe<sub>3</sub> ligand and silyl group, respectively. The selected bond parameters of complexes 10–12 are listed in Table 4. It is also proved

**Scheme 2. Stoichiometric Reactions of Complex 3 with the Substrates**

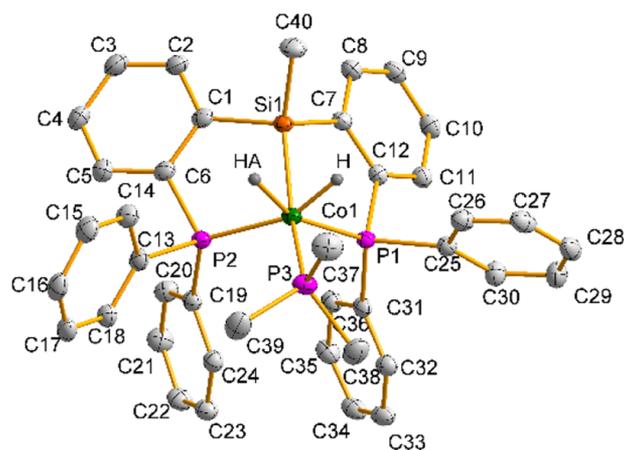


**Scheme 3. Synthesis of Dihydrido Cobalt(III) Complexes 7 and 10–12**



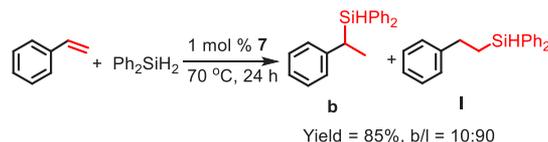
that the structure of complex 7 deduced from the spectroscopic information is correct.

When complex 7 was used to catalyze the reaction of styrene with  $\text{Ph}_2\text{SiH}_2$  under the same catalytic conditions, its catalytic activity is equivalent to that of complex 3 (Scheme 4). It was also found that the reaction of complex 3 with  $\text{Ph}_2\text{SiH}_2$  under the catalytic conditions ( $70^\circ\text{C}$ ) was accompanied by the release of dihydrogen (Scheme 5).<sup>13</sup> The generation of dihydrogen was detected by GC (Figure S113). Complex 7 lost dihydrogen and converted to active unsaturated intermediate A. A is the real catalyst for this catalytic system, and this is similar as our early work.<sup>20</sup> Although the experiment to isolate A failed because of the instability of the tetra coordinate Co(I) species, its existence has been proved indirectly by the isolation of the penta coordinate



**Figure 1.** ORTEP plot of complex 10 at the 50% probability level (most of the hydrogen atoms are omitted for clarity).

**Scheme 4. Catalytic Activity of Complex 7**



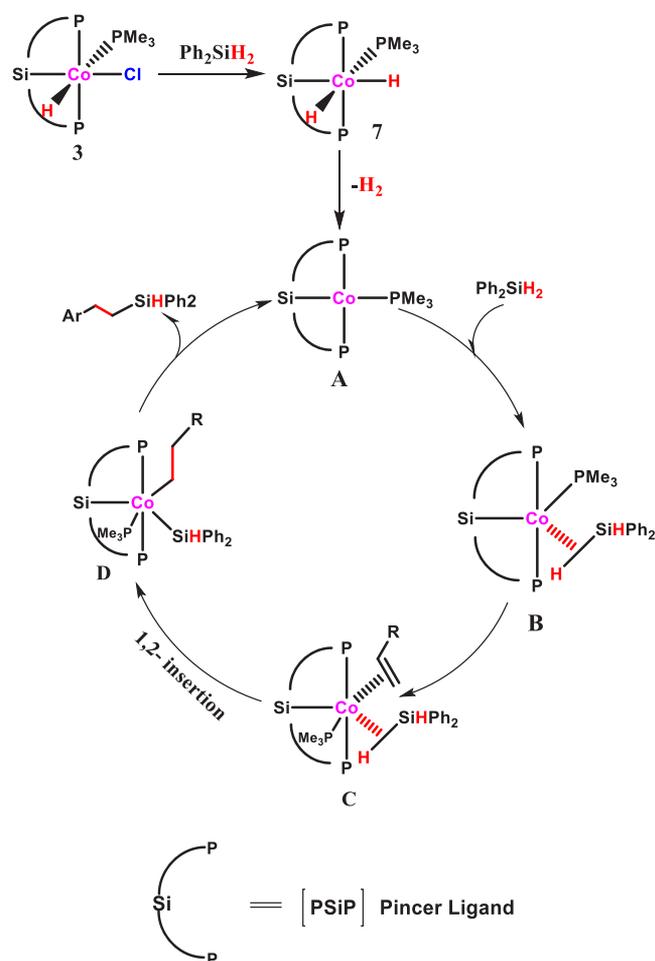
Co(I) complex 13 from the stoichiometric reaction between complex 3 and  $\text{Ph}_2\text{SiH}_2$  in the presence of 1 equiv of trimethylphosphine as a supporting ligand (Scheme 6). Complex 13 was reported in our recent work.<sup>20</sup> A interacts with diphenylsilane to form B having an  $\eta^2$  (Si–H) bond (semi activated).<sup>21</sup> The  $\pi$  coordination of the olefin to B gives rise to C. After 1,2 insertion, C is converted to disilyl alkyl complex D. D undergoes reductive elimination to deliver *anti* Markovnikov silane with the regeneration of A. The 1,2 insertion step is in agreement with the Chalk–Harrod type mechanism.<sup>24</sup> The selectivity of this catalytic system is opposite to that of our early catalytic system.<sup>20</sup> We speculate that the main reason may be the existence of trimethylphosphine dissociated from the catalyst in the previous catalytic system. Free trimethylphosphine may play a role for the selectivity. More experiments and theoretical calculations are needed to further explain the selectivity reverse.

**2.4. Pyridine N-Oxide Realized Selectivity Reverse of Hydrosilylation of Aromatic Alkenes.** In the research of alkene hydrosilylation, how to control the selectivity is always a challenge. Recently, we reported that pyridine N oxide can

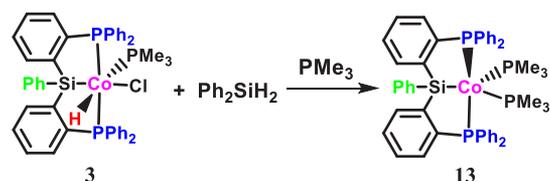
**Table 4. Selected Spectroscopic Data and Structural Parameters (Å and deg) of 7 and 10–12**

	7	10	11	12
$H_{\text{hydrido}}/\text{ppm}$	12.70(s)	13.03(t)	13.41(t)	13.56(m)
$J/\text{Hz}$		13.5	36	
$\nu(\text{Co-H})/\text{cm}^{-1}$	1935, 1886	1915, 1896	1933, 1800	1938, 1790
Co1 H		1.43(3)	1.46(4)	1.54(6)
Co1 H <sub>A</sub>		1.38(3)	1.44(4)	1.54(6)
Co1 P1		2.1786(6)	2.1613(9)	2.1560(12)
Co1 P2		2.1745(6)	2.1572(9)	2.1567(12)
Co1 P3		2.2094(6)	2.1970(10)	2.1976(13)
Co1 Si1		2.2137(6)	2.2587(10)	2.2729(14)
P1 Co1 Si1		89.04(2)	87.47(3)	85.42(5)
P2 Co1 Si2		87.79(2)	85.18(3)	84.65(5)

### Scheme 5. Proposed Mechanism for *anti* Markovnikov Alkene Hydrosilylation



### Scheme 6. Formation of Penta coordinate Complex 13



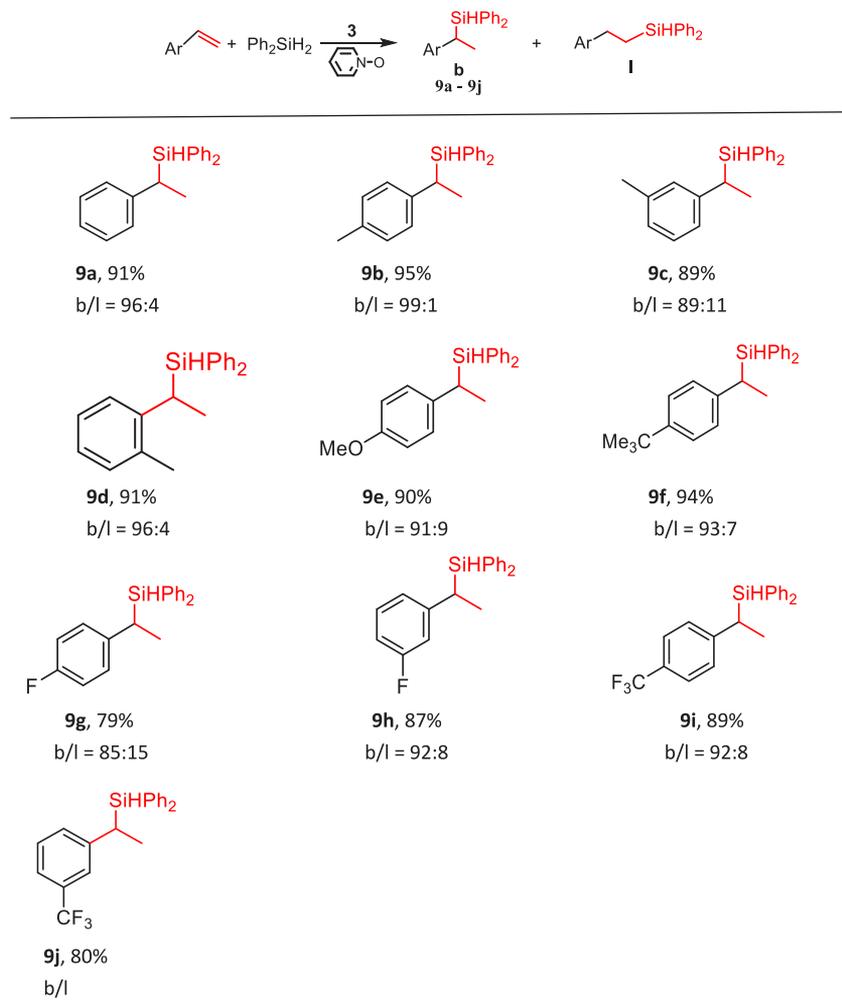
promote iron catalyzed hydrosilylation of carbonyl compounds because it is beneficial to form coordination unsaturated metal complexes.<sup>18</sup> Inspired by this result, we wonder whether pyridine N oxide can influence the regioselectivity of the alkene hydrosilylation reaction by changing the reaction mechanism. With this expectation, pyridine N oxide was added to this catalytic system. It is surprising that, although the conversion was reduced from 97% to 85% by the addition of pyridine N oxide, the selectivity of the reaction was reversed and the main product was the Markovnikov product, instead of the *anti* Markovnikov product without pyridine N oxide (entry 24, Table 2). In addition, we also found that the addition of pyridine N oxide at lower temperature (30 °C) could not only improve the conversion (from 85% to 90%) but also increase the selectivity from (b/l = 70:30) to (b/l = 96:4) (entries 24 and 25, Table 2). If styrene was allowed to react with catalyst 3 in the presence of pyridine N oxide at 30 °C for 20 min,

and then  $\text{Ph}_2\text{SiH}_2$  was added to react for 24 h, the reaction was almost carried out in a quantitative manner with the same selectivity (entry 26, Table 2). These results provide useful support for the exploration of the reaction mechanism. Therefore, we obtained the following optimization conditions: in the presence of pyridine N oxide, styrene reacted with 3 at 30 °C for 20 min first; silane was added and reacted at 30 °C for 24 h next (entry 26, Table 2).

Under the optimized reaction conditions, we further studied the substrate range of the catalytic system for Markovnikov alkene hydrosilylation in the presence of pyridine N oxide (Table 5). It was confirmed that complex 3 catalyzed Markovnikov hydrosilylation of aromatic alkenes with  $\text{Ph}_2\text{SiH}_2$  in the presence of pyridine N oxide in good yields with good selectivity (9a–9j, Table 5). The reaction condition became milder, from 70 °C without pyridine N oxide to 30 °C. The catalytic reactions could be carried out in good yields of 79–95% with high branched/linear ratios (83:17 to 99:1), no matter whether there are electron donating (9b–9f, Table 5) or electron withdrawing (9g–9j, Table 5) groups on the phenyl ring, or whether the substituents on the phenyl rings are in the meta or para positions. The *ortho* substituted aryl alkene could also be hydrosilylated in excellent yield under the same reaction conditions (9d, Table 5). It should be noted that both the yield and the selectivity of the alkenes with electron donating groups (9b–9f, Table 5) are better than those of the alkenes with electron withdrawing groups (9g–9j, Table 5) after addition of pyridine N oxide. Although moderate conversions could be obtained in the presence of pyridine N oxide with 1 nitro 4 vinylbenzene and methyl 4 vinylbenzoate as the substrates, the related products could not be isolated and characterized because of poor selectivity (Table 7). However, this reversal is only suitable for aromatic alkenes. It was also proved that the conversion of the aliphatic alkene decreased significantly with the addition of pyridine N oxide. When pyridine N oxide was added, the conversion of cyclohexyl ethylene at 70 °C decreased from 99% without pyridine N oxide to 49% (b/l = 20:80), and the conversion of cyclohexyl ethylene at 30 °C was 47% (b/l = 5:95) with the addition of pyridine N oxide. These results indicate that the aliphatic alkene in the presence of pyridine N oxide has only moderate conversion without selectivity reverse.

In order to further understand the mechanism of the pyridine N oxide realized Markovnikov hydrosilylation of aromatic alkenes catalyzed with 3, the influence of the addition order of styrene and  $\text{Ph}_2\text{SiH}_2$  was studied in the presence of pyridine N oxide (Table 6). When the pre reaction time of complex 3 and  $\text{Ph}_2\text{SiH}_2$  was 0 min, 10 min, 20 min, 1 h, and 6 h, respectively, the conversion of the reaction decreased from 90% to 89%, 71%, 64%, and 62% and the selectivity of the reaction decreased from 96/4 to 94/6. On the contrary, when the pre reaction time of complex 3 and styrene was 0 min, 10 min, and 20 min, respectively, the conversion of the reaction increased from 90% to 95% and 99%. After 20 min, the yield and selectivity were not influenced by the pre reaction time of complex 3 and styrene even if the pre reaction time reached 6 h. The experimental results clearly show that, in this catalytic system, the intermediate produced by alkene coordination is beneficial to the catalysis. Therefore, we first monitored the stoichiometric reaction of complex 3 with pyridine N oxides by *in situ* <sup>1</sup>H NMR spectroscopy. Although we could not separate the products that can be characterized, we found a new hydrido

Table 5. Markovnikov Alkene Hydrosilylation with Complex 3 as Catalyst<sup>a</sup>



<sup>a</sup>Catalytic reaction conditions: alkene (1.0 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (1.2 mmol), pyridine N oxides (1 mol %), and 3 (1 mol %) were stirred in neat conditions at 30 °C for 24 h; isolated yields.

Table 6. Effect of Addition Sequence of Styrene and Ph<sub>2</sub>SiH<sub>2</sub><sup>a</sup>

entry	pre-reaction time of 3, pyridine N-oxide,s and Ph <sub>2</sub> SiH <sub>2</sub>	pre-reaction time of 3, pyridine N-oxides, and styrene	conv. (%)	product ratios (b/l)
1	0 min	0 min	90	96:4
2	10 min		90	96:4
3	20 min		71	96:4
4	1 h		64	96:4
5	6 h		62	94:6
6		10 min	95	96:4
7		20 min	99	96:4
8		1 h	99	96:4
9		6 h	99	96:4

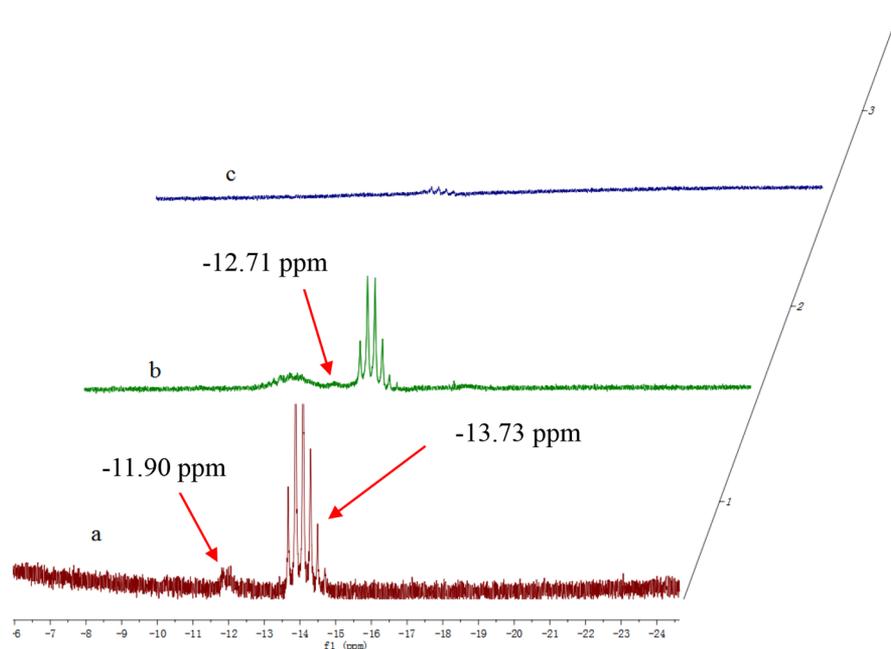
<sup>a</sup>Catalytic reaction conditions: alkene (1.0 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (1.2 mmol), pyridine N oxides (1 mol %), and 3 (1 mol %) were stirred in neat conditions at 30 °C for 24 h. Conversions and product ratios were determined by GC analysis using *n* dodecane as internal standard.

signal at -11.90 ppm ((a), Figure 2) at 2 h after the start of the reaction. We think that this signal belongs to intermediate 3a. When styrene was added to the above reaction mixture, a new hydrido signal at -12.71 ppm ((b), Figure 2) was

detected at 2.5 h. It is supposed to be due to the formation of E. As the reaction proceeded, the hydrido signals almost disappeared at 6 h ((c), Figure 2). It was speculated that intermediate F was formed.

It has been confirmed that pyridine N oxide can accelerate the formation of an unsaturated coordination intermediate.<sup>18</sup> The <sup>31</sup>P NMR signal at 31.73 ppm for O=PMe<sub>3</sub> was found from the solution of the reaction between complex 3 and pyridine N oxide.

On the basis of the experimental results, a catalytic cycle for Markovnikov alkene hydrosilylation is proposed in Scheme 7. At the beginning, the reaction of pyridine N oxide with a dissociated PMe<sub>3</sub> ligand affords O=PMe<sub>3</sub> and free pyridine to form an intermediate 3a with the coordination of pyridine molecule. The replacement of the pyridine ligand by the alkene gives rise to E. The 2,1 insertion of alkene into the Co-H bond occurs subsequently to afford intermediate F, an alkyl cobalt intermediate. This is considered as an important step for the hydrosilylation of alkenes because it determines the selectivity of the reaction. H<sub>2</sub>SiPh<sub>2</sub> coordinates to the Co center in F to form a four membered ring transition state G. The final silane product is generated through σ bond metathesis with the regeneration of real catalyst 3a. This



**Figure 2.** *In situ*  $^1\text{H}$  NMR (a) reaction of **3** with pyridine N oxide for 2 h; (b) reaction of **3** and pyridine N oxide for 2 h, then addition of styrene for 0.5 h; (c) reaction of **3** and pyridine N oxide for 2 h, then addition of styrene for 4 h.

mechanism is similar to that with [CNC] pincer cobalt hydride as catalyst.<sup>15</sup>

**2.5. Hydrosilylation of Alkenes with Reactive Functional Group.** With 1 nitro 4 vinylbenzene, methyl 4 vinyl benzoate, and pent 4 en 2 one as the substrates, the conversions are listed in Table 7. Moderate conversions could be obtained with or without pyridine N oxide. Unfortunately, due to the complexity of many products, we were unable to provide yield and selectivity data because we have not been able to separate out the products that can be characterized.

### 3. CONCLUSIONS

In summary, six silyl cobalt(III) hydrides **1–6** with [PSiP] pincer ligands having different substituents at the P and Si atoms were obtained from the combinations of the ligands (L1–L6) with  $\text{CoCl}(\text{PMe}_3)_3$  by Si–H bond cleavage. Compounds **2–5** are new and were fully characterized. It was verified that **3** is the best catalyst for alkene hydro silylation with very good selectivity. For both aliphatic and aromatic alkenes, *anti* Markovnikov products were isolated. A silyl dihydrido cobalt(III) complex **7** from the reaction of **3** with  $\text{Ph}_2\text{SiH}_2$  was isolated, and its catalytic activity is equivalent to that of complex **3**. Complex **7** and its derivatives **10–12** could also be obtained through the reactions of complexes **3**, **1**, **4**, and **5** with  $\text{NaBHET}_3$ . The molecular structure of **7** was indirectly verified by the structures of **10–12**. What is interesting is that the addition of pyridine N oxide not only makes the reaction conditions milder (from 70 to 30  $^\circ\text{C}$ ) but also reverses the regioselectivity of the reaction by changing the reaction mechanism, resulting in Markovnikov products. However, this reversal is limited to aromatic alkenes. According to the experimental evidence, different reaction mechanisms for the two regioselectivities are proposed. The molecular structures of complexes **3–6** and **10–12** were determined by single crystal X ray diffraction analysis.

### 4. EXPERIMENTAL SECTION

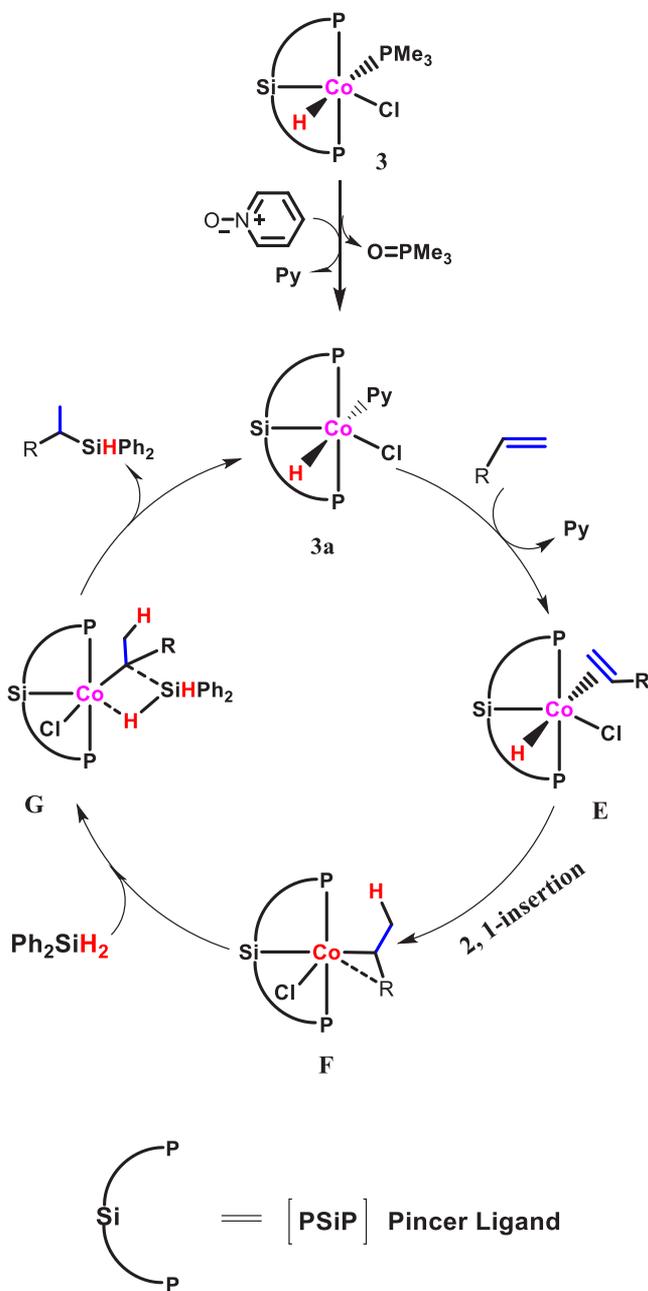
**4.1. General Procedures and Materials.** All manipulations were carried out under a  $\text{N}_2$  (or Ar) atmosphere with the standard Schlenk techniques. Solvents were treated through distillation from Na benzophenone. Ligands L1,<sup>17</sup> L2,<sup>25</sup> L3,<sup>26</sup> L4,<sup>27</sup> L5, L6,<sup>28</sup> complex **1**,<sup>21</sup> and  $\text{CoCl}(\text{PMe}_3)_3$ <sup>29</sup> were obtained with published methods. Infrared spectra (4000–400  $\text{cm}^{-1}$ ) with Nujol mulls between KBr disks were obtained with a Bruker ALPHA FT IR instrument. NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers. GC analysis was realized on a Fuli 9790 chromatograph. The samples were sealed in capillaries for melting point measurement with a WRR instrument.

**Caution!**  $(\text{EtO})_3\text{SiH}$  is flammable and highly toxic by 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  $\text{SiH}_4$ ) 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: 10.1021/cen.v071n013.p002). In addition,  $\text{PhSiH}_3$  and  $\text{Me}(\text{EtO})_2\text{SiH}$  are also highly flammable.

**4.2. Synthesis of Complex 2.** L2 (0.85 g, 1.54 mmol) in 40 mL of THF was added to the solution of  $\text{CoCl}(\text{PMe}_3)_3$  (0.51 g, 1.58 mmol) in 30 mL of THF at 0  $^\circ\text{C}$ . The reaction solution was stirred for 24 h at room temperature. The solution changed from purple to yellow, and a large amount of yellow powder precipitated. **2** (0.74 g, 1.02 mmol) was obtained as yellow powder in a yield of 66%. Dec: > 219  $^\circ\text{C}$ . Calcd for  $\text{C}_{39}\text{H}_{39}\text{ClCoP}_3\text{Si}$  (723.12 g/mol): C, 64.78; H, 5.44. Found: C, 64.57; H, 5.67. IR (Nujol,  $\text{KBr}$ ,  $\text{cm}^{-1}$ ): 2069 (Si H), 1882 (Co H), 957 ( $\text{PMe}_3$ ).  $^1\text{H}$  NMR (300 MHz, benzene  $d_6$ , 300 K,  $\delta/\text{ppm}$ ): -13.63 (q,  $J = 63.0$  Hz, 1H, Co H), 0.62 (d,  $J = 9.0$  Hz,  $\text{PCH}_3$ , 9H), 3.52 (m, 1H, Si H), 7.05–7.11 (m, Ar H, 10H), 7.32–7.37 (m, Ar H, 3H), 7.50–7.54 (m, Ar H, 2H), 7.80–7.86 (m, Ar H, 5H), 8.14–8.19 (m, Ar H, 8H).  $^{31}\text{P}$  { $^1\text{H}$ } NMR (121 MHz, benzene  $d_6$ , 300 K,  $\delta/\text{ppm}$ ): -6.1 (s,  $\text{PMe}_3$ , 1P), 67.0 (s,  $\text{PPh}_2$ , 2P).  $^{13}\text{C}$  { $^1\text{H}$ } NMR (75 MHz, benzene  $d_6$ , 300 K,  $\delta/\text{ppm}$ ): 29.8 (s,  $\text{PCH}_3$ ), 127.0 (s, Ar C), 127.3 (s, Ar C), 127.9 (s, Ar C), 130.2 (s, Ar C), 132.4 (t,  $J = 2.6$  Hz, Ar C), 132.9 (t,  $J = 3.4$  Hz, Ar C).

**4.3. Synthesis of Complex 3.** L3 (0.63 g, 1.00 mmol) in 30 mL of THF was added to the solution of  $\text{CoCl}(\text{PMe}_3)_3$  (0.33 g, 1.02

**Scheme 7. Proposed Mechanism for Markovnikov Alkene Hydrosilylation**



mmol) in 30 mL of THF at 0 °C. The reaction solution was stirred for 24 h at room temperature. The solution changed from purple to

**Table 7. Conversion of Alkenes with Reactive Functional Group<sup>a</sup>**

without pyridine N-oxide <sup>b</sup>	79%	64%	89%
with pyridine N-oxide <sup>c</sup>	70%	59%	-

<sup>a</sup>Conversions were determined by GC analysis using *n* dodecane as an internal standard. <sup>b</sup>Catalytic conditions: olefin (1.0 mmol), diphenylsilane (1.2 mmol), **3** (1 mol %), solvent free at 70 °C for 24 h. <sup>c</sup>Catalytic reaction conditions: alkene (1.0 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (1.2 mmol), pyridine N oxides (1 mol %), and **3** (1 mol %) were stirred in neat conditions at 30 °C for 24 h.

yellow. **3** (0.64 g, 0.8 mmol) was isolated as yellow crystals at -20 °C from *n* pentane solution in a yield of 80%. Dec: > 172 °C. Calcd for C<sub>45</sub>H<sub>43</sub>ClCoP<sub>3</sub>Si (799.23 g/mol): C, 67.63; H, 5.42. Found: C, 68.02; H, 5.55. IR (Nujol, KBr, cm<sup>-1</sup>): 1908 (Co H), 937 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): -13.75 (q, *J* = 67 Hz, 1H, Co H), 0.39 (d, *J* = 9.0 Hz, PCH<sub>3</sub>, 9H), 7.10–7.17 (m, Ar H, 17H), 7.26–7.29 (m, Ar H, 2H), 7.41–7.43 (m, Ar H, 2H), 7.61–7.64 (m, Ar H, 2H), 7.90–7.92 (m, Ar H, 4H), 8.12–8.14 (m, Ar H, 2H), 8.28–8.30 (m, Ar H, 4H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): -7.4 (s, PMe<sub>3</sub>, 1P), 69.2 (s, PPh<sub>2</sub>, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): 16.8 (d, *J* = 24 Hz, PCH<sub>3</sub>), 128.5 (t, *J* = 3.8 Hz, Ar C), 128.7 (s, Ar C), 129.3 (d, *J* = 7.5 Hz, Ar C), 132.6 (t, *J* = 4.5 Hz, Ar C), 132.9 (s, Ar C), 133.4 (t, *J* = 9.8 Hz, Ar C), 133.9 (t, *J* = 4.5 Hz, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): 58.9 (s).

**4.4. Synthesis of Complex 4.** **L4** (0.43 g, 1.03 mmol) in 30 mL of THF was added to the solution of CoCl(PMe<sub>3</sub>)<sub>3</sub> (0.35 g, 1.08 mmol) in 30 mL of THF at 0 °C. The reaction solution was stirred for 24 h at room temperature. The solution changed from purple to yellow. **4** (0.47 g, 0.80 mmol) was isolated as yellow crystals at -20 °C from *n* pentane solution in a yield of 78%. Dec: > 160 °C. Calcd for C<sub>27</sub>H<sub>47</sub>ClCoP<sub>3</sub>Si (587.05 g/mol): C, 55.24; H, 8.07. Found: C 55.43; H 8.30. IR (Nujol, KBr, cm<sup>-1</sup>): 2071 (Si H), 1893 (Co H), 951 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): -15.61 (q, *J* = 75.0 Hz, 1H, Co H), 0.87 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 1.11 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 1.35 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 1.55 (d, *J* = 9.0 Hz, PCH<sub>3</sub>, 9H), 1.86 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 2.63–2.73 (m, PCHCH<sub>3</sub>, 2H), 2.76–2.83 (m, PCHCH<sub>3</sub>, 2H), 5.51 (dd, *J* = 3.0 Hz, *J* = 15.0 Hz, Si H, 1H), 7.09–7.15 (m, Ar H, 2H), 7.20–7.30 (m, Ar H, 4H), 7.99–8.01 (d, *J* = 6.0 Hz, Ar H, 2H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): -3.6 (s, PMe<sub>3</sub>, 1P), 83.7 (s, P<sup>*i*</sup>Pr, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): 23.3 (dd, *J* = 6.8 Hz, *J* = 16.5 Hz, PCHCH<sub>3</sub>), 25.5 (s, PCH<sub>3</sub>), 26.6 (dd, *J* = 6.8 Hz, *J* = 12.0 Hz, PCHCH<sub>3</sub>), 126.4 (t, *J* = 3.0 Hz, Ar C), 131.4 (s, Ar C), 132.5 (t, *J* = 9.8 Hz, Ar C), 133.3 (t, *J* = 3.8 Hz, Ar C), 133.9 (t, *J* = 4.5 Hz, Ar C), 154.9 (t, *J* = 26.2 Hz, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): 82.9 (s).

**4.5. Synthesis of Complex 5.** **L5** (0.43 g, 1.02 mmol) in 30 mL of THF was added to the solution of CoCl(PMe<sub>3</sub>)<sub>3</sub> (0.33 g, 1.02 mmol) in 30 mL of THF at 0 °C. The reaction solution was stirred for 24 h at room temperature. The solution changed from purple to yellow. **5** (0.45 g, 0.75 mmol) was isolated as yellow crystals at -20 °C from *n* pentane solution in a yield of 76%. Dec: > 162 °C. Calcd for C<sub>28</sub>H<sub>49</sub>ClCoP<sub>3</sub>Si (601.08 g/mol): C, 55.95; H, 8.22. Found: C 56.28; H 8.60. IR (Nujol, KBr, cm<sup>-1</sup>): 1902 (Co H), 951 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): -16.61 (q, *J* = 75.0 Hz, 1H, Co H), 0.61 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 0.85 (s, SiCH<sub>3</sub>, 3H), 0.89 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 1.12 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 1.19 (s, PCH<sub>3</sub>, 9H), 1.40 (q, *J* = 6.0 Hz, PCHCH<sub>3</sub>, 6H), 1.94–2.03 (m, PCHCH<sub>3</sub>, 2H), 2.71–2.85 (m, PCHCH<sub>3</sub>, 2H), 6.98 (q, *J* = 6.0 Hz, Ar H, 2H), 7.06–7.14 (m, Ar H, 4H), 8.07 (d, *J* = 9.0 Hz, Ar H, 2H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene *d*<sub>6</sub>, 300 K, δ/ppm): -9.6 (s, PMe<sub>3</sub>, 1P), 70.9 (s, P<sup>*i*</sup>Pr, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75

MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 6.4 (s, SiCH<sub>3</sub>), 17.1 (s, PCHCH<sub>3</sub>), 18.1 (s, PCHCH<sub>3</sub>), 18.8 (s, PCHCH<sub>3</sub>), 26.4 (s, PCHCH<sub>3</sub>), 27.5 (t,  $J$  = 11.3 Hz, PCHCH<sub>3</sub>), 32.2 (d,  $J$  = 17.2 Hz), 126.5 (s, Ar C), 128.8 (s, Ar C), 131.2 (t,  $J$  = 6.4 Hz, Ar C), 143.1 (s, Ar C), 158.1 (t,  $J$  = 16.5 Hz, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 51.7 (s).

**4.6. Synthesis of Complex 6.** L6 (0.64 g, 1.30 mmol) in 30 mL of THF was added to the solution of CoCl(PMe<sub>3</sub>)<sub>3</sub> (0.42 g, 1.31 mmol) in 30 mL of THF at 0 °C. The reaction solution was stirred for 24 h at room temperature. The solution changed from purple to yellow. **6** (0.52 g, 0.80 mmol) was isolated as yellow crystals at -20 °C from Et<sub>2</sub>O solution in a yield of 80%. Dec: > 130 °C. Calcd for C<sub>33</sub>H<sub>51</sub>ClCoP<sub>3</sub>Si (663.16 g/mol): C, 59.77; H, 7.75. Found: C, 60.02; H, 7.91. IR (Nujol, KBr, cm<sup>-1</sup>): 1956 (Co H), 951 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): -16.17 (q,  $J$  = 72.0 Hz, 1H, Co H), 0.95–0.99 (m, PCHCH<sub>3</sub>, 6H), 1.22 (s, PCH<sub>3</sub>, 9H), 1.31–1.36 (m, PCHCH<sub>3</sub>, 6H), 1.37–1.46 (m, PCHCH<sub>3</sub>, 6H), 1.85 (s, PCHCH<sub>3</sub>, 6H), 2.62 (s, PCHCH<sub>3</sub>, 2H), 3.02 (s, PCHCH<sub>3</sub>, 2H), 7.17–7.26 (m, Ar H, 7H), 7.42–7.49 (m, Ar H, 4H), 7.84 (s, Ar H, 2H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): -0.5 (s, PMe<sub>3</sub>, 1P), 85.8 (s, P<sup>i</sup>Pr, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 14.0 (s, CHCH<sub>3</sub>), 17.6 (s, CHCH<sub>3</sub>), 19.2 (d,  $J$  = 19.5 Hz, PCH<sub>3</sub>), 21.3 (s, CHCH<sub>3</sub>), 22.4 (s, CHCH<sub>3</sub>), 26.4 (s, CHCH<sub>3</sub>), 28.8 (s, CHCH<sub>3</sub>), 34.2 (s, CHCH<sub>3</sub>), 126.9 (s, Ar C), 128.8 (s, Ar C), 133.3 (s, Ar C), 137.3 (s, Ar C), 145.2 (t,  $J$  = 18.8 Hz, Ar C), 146.4 (s, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 50.3 (s).

**4.7. Synthesis of Complex 7.** (a) Complex 3 (0.40 g, 0.50 mmol) in 20 mL of THF was combined with Ph<sub>2</sub>SiH<sub>2</sub> (0.11 g, 0.6 mmol) in 20 mL of THF. The mixture was stirred for 6 h at 70 °C. The solution changed from yellow to brown red. **7** (0.08 g, 0.10 mmol) was isolated as a yellow powder at -20 °C from Et<sub>2</sub>O solution in a yield of 21%. (b) Complex 3 (0.79 g, 0.98 mmol) in 40 mL of THF was combined with NaBHET<sub>3</sub> (0.120 g, 0.98 mmol) in 30 mL of THF at 0 °C. The solution changed from yellow to red rapidly, and the reaction solution was stirred for 12 h at room temperature. **7** (0.57 g, 0.75 mmol) was isolated as a yellow powder at -20 °C from Et<sub>2</sub>O solution in a yield of 74%. Dec: > 203 °C. Calcd for C<sub>45</sub>H<sub>44</sub>CoP<sub>3</sub>Si (764.79 g/mol): C, 70.67; H, 5.8. Found: C, 70.89; H, 5.81. IR (Nujol, KBr, cm<sup>-1</sup>): 1886, 1934 (Co H), 946 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): -12.7 (s, 2H, Co H), 1.06 (d,  $J$  = 6 Hz, PCH<sub>3</sub>, 9H), 6.69–6.74 (m, Ar H, 5H), 6.94–7.10 (m, Ar H, 15H), 7.19–7.26 (m, Ar H, 3H), 7.31–7.49 (m, Ar H, 3H), 7.97–8.03 (m, Ar H, 4H), 8.19–8.21 (m, Ar H, 3H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 12.7 (s, PMe<sub>3</sub>, 1P), 95.3 (s, PPh<sub>2</sub>, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 24.2 (d,  $J$  = 16.5 Hz, PCH<sub>3</sub>), 127.1 (s, Ar C), 132.1 (d,  $J$  = 24 Hz, Ar C), 133.2 (d,  $J$  = 15.8 Hz, Ar C), 135.4 (s, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 64.5 (s).

**4.8. Synthesis of Complex 10.** Complex 1 (1.10 g, 1.49 mmol) in 30 mL of THF was combined with NaBHET<sub>3</sub> (0.18 g, 1.49 mmol) in 30 mL of THF at 0 °C. The solution changed from yellow to red rapidly and was stirred for 12 h at room temperature. **10** (0.68 g, 0.97 mmol) was isolated as yellow crystals at -20 °C from Et<sub>2</sub>O solution in a yield of 65%. Dec: > 196 °C. Calcd for C<sub>40</sub>H<sub>42</sub>CoP<sub>3</sub>Si (702.72 g/mol): C, 68.37; H, 6.02. Found: C, 68.61; H, 5.90. IR (Nujol, KBr, cm<sup>-1</sup>): 1895, 1915 (Co H), 950 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): -13.03 (t,  $J$  = 13.5 Hz, 2H, Co H), 1.15 (d,  $J$  = 6 Hz, PCH<sub>3</sub>), 6.67–6.72 (m, Ar H, 4H), 6.94–7.05 (m, Ar H, 16H), 7.21–7.26 (m, Ar H, 2H), 7.92 (s, Ar H, 4H), 8.23–8.26 (m, Ar H, 2H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 12.2 (s, PMe<sub>3</sub>, 1P), 95.0 (s, PPh<sub>2</sub>, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 24.3 (d,  $J$  = 15.8 Hz, PCH<sub>3</sub>), 30.0 (s, SiCH<sub>3</sub>), 126.9 (s, Ar C), 127.2 (s, Ar C), 128.4 (s, Ar C), 131.5 (t,  $J$  = 8.3 Hz, Ar C), 132.2 (d,  $J$  = 15.8 Hz, Ar C), 135.4 (s, Ar C), 142.8 (d,  $J$  = 23.0 Hz, Ar C), 149.6 (d,  $J$  = 47.3 Hz, Ar C), 158.6 (d,  $J$  = 44.2 Hz, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 61.6 (d,  $J$  = 90.6 Hz).

**4.9. Synthesis of Complex 11.** Complex 4 (0.38 g, 0.65 mmol) in 40 mL of THF was combined with NaBHET<sub>3</sub> (0.080 g, 0.65

mmol) in 30 mL of THF at 0 °C. The solution changed from yellow to red rapidly and was stirred for 12 h at room temperature. **11** (0.24 g, 0.43 mmol) was isolated as yellow crystals at -20 °C from Et<sub>2</sub>O solution in a yield of 68%. Dec: > 173 °C. Calcd for C<sub>27</sub>H<sub>48</sub>CoP<sub>3</sub>Si (552.58 g/mol): C, 58.68; H, 8.76. Found: C, 68.61; H, 5.90. IR (Nujol, KBr, cm<sup>-1</sup>): 1987 (Si H), 1800, 1933 (Co H), 948 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): -13.41 (t,  $J$  = 36 Hz, 2H, Co H), 0.95 (s, CHCH<sub>3</sub>, 12H), 1.04 (s, CHCH<sub>3</sub>, 6H), 1.33 (m, CHCH<sub>3</sub>, P(CH<sub>3</sub>)<sub>3</sub>, 15H), 2.11 (s, CHCH<sub>3</sub>, 2H), 2.62 (s, CHCH<sub>3</sub>, 2H), 6.38 (s, Si H, 1H), 7.15–7.24 (m, Ar H, 6H), 8.36 (s, Ar H, 2H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 12.8 (s, PMe<sub>3</sub>, 1P), 112.6 (s, P<sup>i</sup>Pr, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 16.9 (s, CHCH<sub>3</sub>), 17.9 (s, CHCH<sub>3</sub>), 18.9 (s, CHCH<sub>3</sub>), 19.6 (s, CHCH<sub>3</sub>), 23.7 (t,  $J$  = 11.3 Hz, CHCH<sub>3</sub>), 25.9 (d,  $J$  = 15.8 Hz, P(CH<sub>3</sub>)<sub>3</sub>), 28.7 (s, CHCH<sub>3</sub>), 126.7 (s, Ar C), 133.2 (t,  $J$  = 6.8 Hz, Ar C), 146.3 (td,  $J$  = 18.0, 5.3 Hz, Ar C), 157.4 (t,  $J$  = 18.8 Hz, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 38.8 (s).

**4.10. Synthesis of Complex 12.** Complex 5 (0.38 g, 0.63 mmol) in 40 mL of THF was combined with NaBHET<sub>3</sub> (0.076 g, 0.63 mmol) in 30 mL of THF at 0 °C. The solution changed from yellow to red rapidly and was stirred for 12 h at room temperature. **12** (0.23 g, 0.41 mmol) was isolated as yellow crystals at -20 °C from Et<sub>2</sub>O solution in a yield of 65%. Dec: > 171 °C. Calcd for C<sub>28</sub>H<sub>50</sub>CoP<sub>3</sub>Si (566.61 g/mol): C, 59.35; H, 8.89. Found: C, 59.13; H, 9.01. IR (Nujol, KBr, cm<sup>-1</sup>): 1790, 1938 (Co H), 946 (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): -13.56 (m, 2H, Co H), 0.4 (s, SiCH<sub>3</sub>, 3H), 0.9–1.02 (m, CHCH<sub>3</sub>, 12H), 1.06–1.11 (m, CHCH<sub>3</sub>, 6H), 1.30 (s, CHCH<sub>3</sub>, 6H), 1.34 (d,  $J$  = 6.0 Hz, P(CH<sub>3</sub>)<sub>3</sub>, 9H), 2.05–2.10 (m, CHCH<sub>3</sub>, 2H), 2.67–2.70 (m, CHCH<sub>3</sub>, 2H), 7.15–7.20 (m, Ar H, 2H), 7.26–7.36 (m, Ar H, 4H), 8.27–8.29 (d, Ar H, 6H). <sup>31</sup>P {<sup>1</sup>H} NMR (121 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 0.89 (s, PMe<sub>3</sub>, 1P), 98.91 (s, P<sup>i</sup>Pr, 2P). <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 17.0 (s, CHCH<sub>3</sub>), 18.2 (s, CHCH<sub>3</sub>), 19.1 (s, CHCH<sub>3</sub>), 20.0 (s, CHCH<sub>3</sub>), 23.7 (t,  $J$  = 15.8 Hz, CHCH<sub>3</sub>), 26.3 (d,  $J$  = 20.3 Hz, P(CH<sub>3</sub>)<sub>3</sub>), 28.6 (s, CHCH<sub>3</sub>), 125.7 (s, Ar C), 128.3 (s, Ar C), 131.7 (t,  $J$  = 8.3, Ar C), 145.4 (td,  $J$  = 21.8, 7.5 Hz, Ar C), 160.7 (t,  $J$  = 46.5 Hz, Ar C). <sup>29</sup>Si NMR (79 MHz, benzene  $d_6$ , 300 K,  $\delta$ /ppm): 39.1 (s).

**4.11. Synthesis of Complex 13.**<sup>20</sup> Complex 3 (0.60 g, 0.75 mmol) in 40 mL of THF was combined with Ph<sub>2</sub>SiH<sub>2</sub> (0.17 g, 0.90 mmol) in 30 mL of THF and PMe<sub>3</sub> (0.08 g, 1.1 mmol). The reaction solution was stirred for 8 h at 70 °C. **13** (0.35 g, 0.41 mmol) was isolated as a red powder from *n* pentane solution in a yield of 55%.

**4.12. General Procedure for anti-Markovnikov Alkene Hydrosilylation with Co(III) Hydride as Catalyst.** Cobalt complex **3** (1 mol %) was loaded into a Schlenk tube (20 mL) with a magnetic stirrer without any solvent under a nitrogen atmosphere. After that, olefin (1.00 mmol), *n* dodecane (170 mg, 1.00 mmol), and diphenylsilane (221 mg, 1.2 mmol) were successively added. The reaction solution was stirred at 70 °C for 24 h and treated with CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>. The resulting solution was concentrated in vacuum, and the crude product was purified by column chromatography on silica gel with petrol ether as eluent. The pure product was characterized by NMR analysis.

**4.13. General Procedure for Markovnikov Alkene Hydrosilylation with Co(III) Hydride as Catalyst in the Presence of Pyridine N-oxide.** Under a N<sub>2</sub> atmosphere, 1 mol % cobalt complex **3** and 1 mol % pyridine N oxide were added to a 20 mL Schlenk tube containing a magnetic stirrer without any solvent. Then, the alkene (1.00 mmol) and *n* dodecane (170 mg, 1.00 mmol) were added in order. The mixture was stirred at 30 °C for 20 min first. Ph<sub>2</sub>SiH<sub>2</sub> (1.2 mmol) was added and reacted at 30 °C for 24 h next. The reaction solution was treated with ethyl acetate. The resulting solution was concentrated in vacuum. The crude product was purified by column chromatography with petroleum ether as eluent on silica gel. The product was analyzed by NMR spectroscopy.

**4.14. X-ray Structure Determinations.** Single crystal X ray diffraction data for the complexes were collected on Stoe Stadi Vari (3 and 4), Bruker APEX2 microsourc (5), XtaLAB AFC12 (RINC)

(6), and XtaLAB Synergy Dualflex HyPix (10, 11, and 12) diffractometers equipped with graphite monochromatized Ga K $\alpha$  radiation ( $\lambda = 1.34143 \text{ \AA}$ ) (3), Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) (5), or Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) (4, 6, 10, 11, and 12). 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 program<sup>30</sup> and refined on F<sup>2</sup> with SHELXL.<sup>31</sup> 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.

#### Accession Codes

CCDC 1576219, 1587505, 1885505, 2010723, 2024765, 2043316, and 2043317 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](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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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