

Synthesis and properties of [PCP] pincer silylene cobalt(I) complexes†

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In this study, two [PCP] pincer silylene cobalt(I) complexes [((Ph₂POCH₂)₂CH)Co(PMe₃)(SiCl((N^tBu)₂CAr))] (Ar = Ph (**2**) and 4-MePh (**3**)) were synthesized through the substitution reaction of the [PCP] pincer cobalt(I) complex [((Ph₂POCH₂)₂CH)Co(PMe₃)₂] (**1**) with silylene ligands: SiCl((N^tBu)₂CAr) (Ar = Ph (**L1**) and 4-MePh (**L2**)). The reaction of complex **2** with CO afforded the carbonyl silylene cobalt(I) complex [((Ph₂POCH₂)₂CH)Co(CO)(SiCl((N^tBu)₂CPh))] (**4**), while complex **2** reacted with CH₃I to give rise to cobalt(II) iodide [((Ph₂POCH₂)₂CH)Co(II)(PMe₃)] (**6**). With a catalyst loading of 2 mol%, complex **6** displayed efficient catalytic activity for hydrosilylation of alkenes by using Ph₂SiH₂ as the hydrogen source under mild conditions. The molecular structures of complexes **2**, **3**, **4** and **6** were determined by single crystal X-ray diffraction analysis.

Introduction

As an analogue of N-heterocyclic carbene (NHC), N-heterocyclic silylene (NHSi) has unique σ -donating/ π -accepting properties. Therefore, NHSi has attracted more and more attention. Since Schmid and Welz synthesized the first NHSi metal complexes in 1977,¹ many stable NHSi metal complexes have been prepared.² In 2015, the Szilvási group proved through theoretical calculations from four aspects (σ -donating ability, π -accepting ability, ligand–metal charge transfer and steric effect) that NHSi may be a potential ligand with better performance than common organo phosphine and carbene ligands in the construction of organometallic catalysts.³ Up to now, the metal complexes of NHSi have been widely used as catalysts in the chemical conversion of carbon–carbon bond formation reactions, carbon–hetero bond formation reactions and reduction reactions, and show excellent performance in catalytic efficiency and chemical selectivity.^{4,5} Compared with NHC and organophosphine ligands, the synthesis and properties of

NHSi metal complexes need further development. In recent years, our group has carried out a study in this field, which shows that the cobalt hydrides formed by replacing trimethylphosphine with the NHSi ligand display better catalytic performance for the Kumada cross-coupling reaction.⁶ In addition, we also found that bis-silylene ligands with the dipyrromethane skeleton are more beneficial to the synthesis of dinitrogen metal complexes and the activation of dinitrogen than bisphosphine ligands.⁷ In order to further study the effect of silylene and trimethylphosphine ligands on the properties of the complexes, two new chloro NHSi coordinated cobalt complexes **2** and **3** were synthesized by using silylene instead of trimethylphosphine. The reactivity of the silylene complexes with CO and CH₃I was studied, and the related complexes **4** and **6** were isolated, respectively. The experimental results also show that complex **6** can catalyze hydrosilylation of alkenes.

Results and discussion

Synthesis of silylene cobalt(I) complexes **2** and **3**

Ligands **L1** and **L2** were synthesized according to the method used for the synthesis of ligand **L1** (Scheme 1).⁸ Ligand **L2** is a new compound and has been fully characterized by spectroscopic methods.

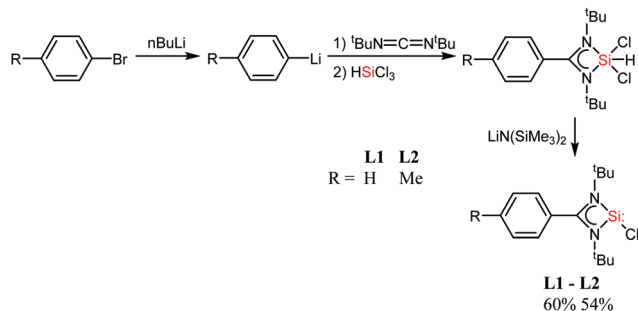
Silylene cobalt(I) complexes **2** and **3** as yellow crystals were isolated from the reaction of cobalt(I) complex **1**⁹ with ligands **L1** and **L2** *via* ligand replacement in the yields of 75% and 70%, respectively (Scheme 2).

Complexes **2** and **3** were new compounds and fully characterized using spectroscopic methods (Table 1). In the IR

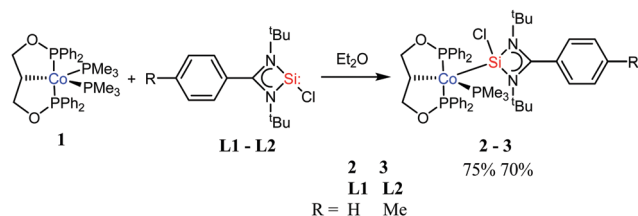
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† Electronic supplementary information (ESI) available: The table of selected crystallographic data and original IR, ¹H, ³¹P, ¹³C and ²⁹Si NMR spectra of complexes **2**, **3**, **4** and [compoundref>/compoundref>](#) and catalytic products. CCDC 1894297, 1947320, 1958714 and 1947318. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1nj02982g



Scheme 1 Synthesis of silylene ligands **L1** and **L2**.



Scheme 2 Preparation of silylene cobalt(I) complexes **2** and **3**.

Table 1 Spectroscopic characterization of complexes **2** and **3**

		2	3	
IR (cm ⁻¹)	$\nu(\text{C}=\text{Y})$ (Y = C, N)	1612	1612	
		1584	1585	
NMR (ppm)	$\rho(\text{PMe}_3)$	951	950	
	¹ H			
		CCH ₃	1.12(s)	1.16(s)
		PCH ₃	1.67(d)	1.69(d)
	³¹ P	PPh ₂	157.4(s)	157.4(s)
	PCH ₃	5.7(t)	5.7(t)	
¹³ C	NCN	174.0(s)	174.1(s)	
		25.8(dt)	25.8(dt)	
	PCH ₃			
Bond length (Å)	²⁹ Si	52.0	54.5	
	Co1 Si1	2.181(1)	2.176(1)	
	Co1 P1	2.158(1)	2.157(1)	
	Co1 P2	2.153(1)	2.1575(5)	
	Co1 P3	2.192(1)	2.1943(7)	
	Co1 C	2.075(4)	2.080(2)	

spectra of complexes **2** and **3** the signals of the double bonds (C=C and C=N) were recorded between 1584 and 1612 cm⁻¹, while the rocking vibrations of PMe₃ were found at 951 (**2**) and 950 cm⁻¹ (**3**). In the ¹H NMR spectra of complexes **2** and **3** the signals of ^tBu groups were registered at 1.12 (**2**) and 1.16 ppm (**3**) as singlets, while the resonances of PMe₃ ligands were located at 1.67 (**2**) and 1.69 ppm (**3**) as doublets, respectively. The ³¹P NMR spectra of these two complexes are the same. The ³¹P NMR spectra indicated that signals of -PPh₂ groups were found at 157.4 ppm as singlets, while those of PMe₃ were recorded at 5.7 ppm as triplets. The ¹³C NMR signals of NCN were registered at 174.0 (**2**) and 174.1 ppm (**3**) as singlets, while the resonances of PMe₃ were located at 25.8 ppm as dt peaks. The ²⁹Si NMR signals of complexes **2** and **3** were located at 52.0 and 54.5 ppm, respectively.

The molecular structures of complexes **2** and **3** were confirmed by single crystal X-ray diffraction analysis (Fig. 1 and 2). Both complexes have trigonal bipyramidal coordination geometries. The P_{PMe₃}-Co-C is the axial direction and [Si, P_{Ph₂}, P_{Ph₂}] is the equatorial plane. The Co1-Si1 bond distances in complexes **2** and **3** are 2.181(1) (**2**) and 2.176(1) Å (**3**), which are typical for the Co-Si(II) bond (Table 1).⁶ The Co-C distances (2.075 (**2**) and 2.080 Å (**3**)) are within the range of the Co-Csp³ bond length (2.03–2.15 Å).¹⁰ Co1-P3 bonds are slightly longer than both Co1-P1 and Co1-P2 due to the strong *trans*-influence of the carbon atom.

The reactions of silylene cobalt(I) complex **2**

CO gas (1 atm) was slowly introduced into the diethyl ether solution of complex **2**. In this process, the color of the solution changed from orange red to orange yellow. After the diethyl ether solvent was evaporated under reduced pressure, the residual solid was extracted with *n*-pentane. Complex **4** was precipitated as yellow block crystals from the *n*-pentane extract at 0 °C in the yield of 65% (Scheme 3). Complex **4** is very air-sensitive and starts to decompose after exposure to air for a few minutes.

In the IR spectrum of **4** the signal of CO was recorded at 1967 and 1897 cm⁻¹, while the vibration of C=N was located at 1586 cm⁻¹. In the ¹H NMR spectrum of **4** the signal of the ^tBu group is a singlet at 0.98 ppm. In comparison with that of complex **2** this upfield shift is 0.14 ppm. The resonance of methyne is located at 3.96 ppm with a downfield shift of

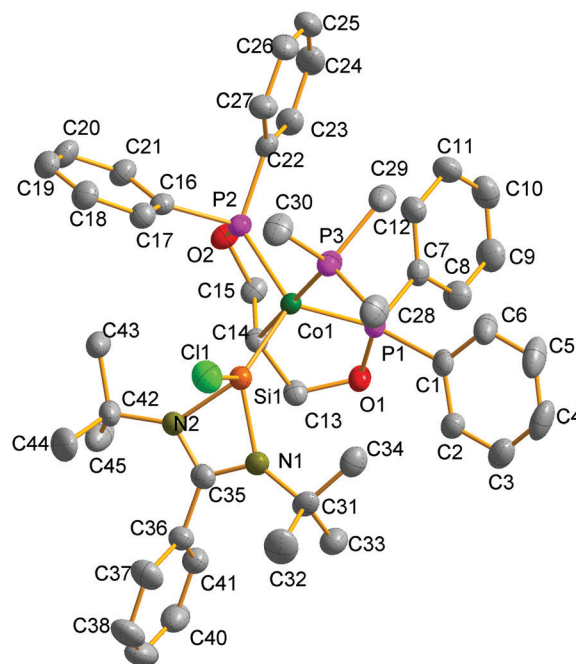


Fig. 1 Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1 P1 2.1583(10), Co1 P2 2.1525(10), Co1 P3 2.1920(11), Co1 Si1 2.181(1), Co1 C14 2.075(4); Si1 Co1 P3 97.14(4), P1 Co1 P2 117.73(4), P2 Co1 P3 98.92(4), C14 Co1 Si1 84.60(11).

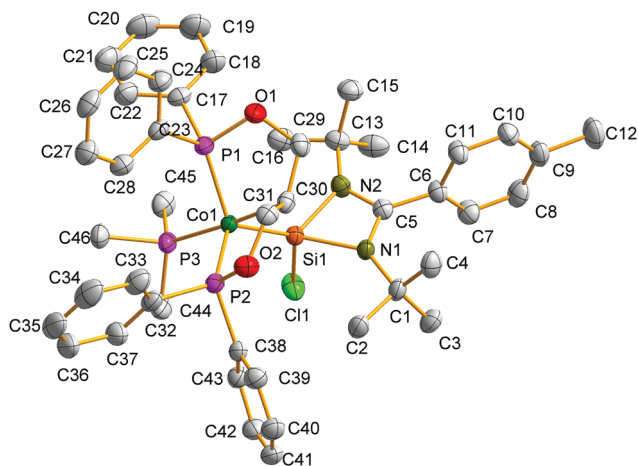


Fig. 2 Molecular structure of complex **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1 P1 2.1564(5), Co1 P2 2.1575(5), Co1 P3 2.1943(5), Co1 Si1 2.176(1), Co1 C30 2.0802(16); Si1 Co1 P3 96.766(19), P1 Co1 P2 117.105(19), P2 Co1 P3 100.534(19), C30 Co1 Si1 84.28(5).

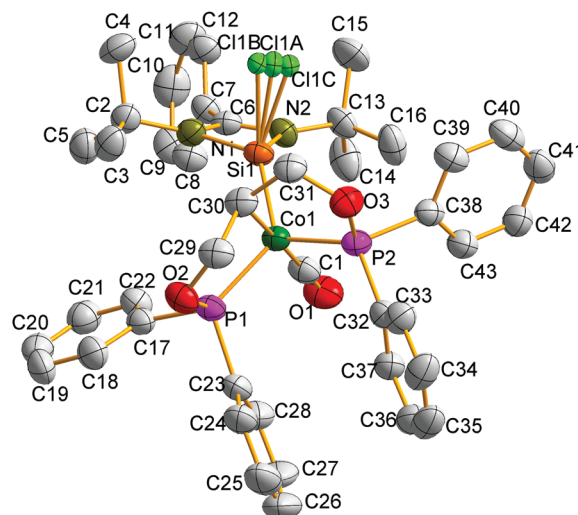
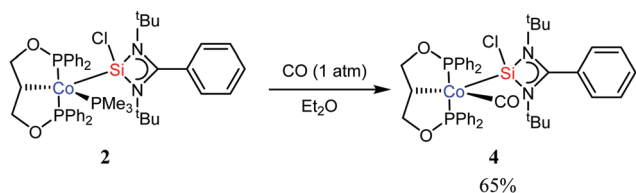


Fig. 3 Molecular structure of complex **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1 P1 2.1384(11), Co1 P2 2.1441(12), Co1 Si1 2.1797(11), Co1 C28 1.733(4), Co1 C2 2.078(4); Si1 Co1 P1 125.81(5), Si1 Co1 P2 117.25(5), C28 Co1 P1 96.60(14), C28 Co1 P2 99.58(15).



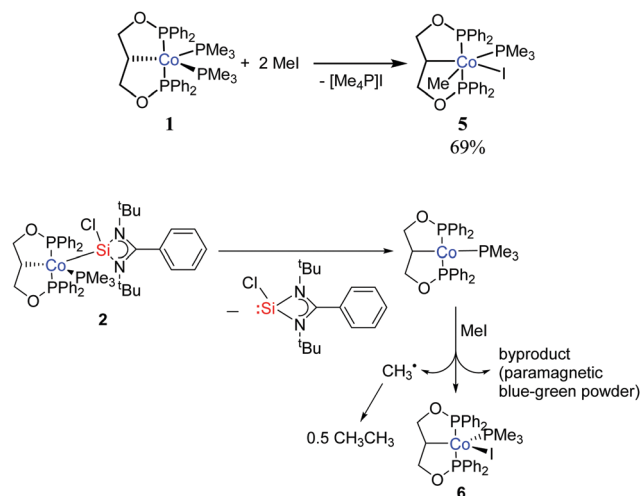
Scheme 3 Reaction of complex **2** with CO.

0.27 ppm in comparison with that of complex **2**. This may be due to the decrease of the electronic cloud density of the Co center caused by π -backdonation from Co to CO. One ^{31}P NMR signal at 167.8 ppm implies that the PMe_3 ligand was replaced by the CO ligand. The ^{29}Si NMR resonance was found at 60.9 ppm as a triplet caused by Si, P-coupling. Compared with that of complex **2**, the downfield shift of 8.9 ppm also indicates that the introduction of CO makes the cobalt center electron-poor.

The X-ray diffraction analysis confirmed that complex **4** is a penta-coordinate compound with trigonal bipyramidal geometry (Fig. 3). C2–Co1–C28 ($178.90(18)^\circ$) is the axial direction, while [Si1, P1, P2] is the equatorial plane. In the equatorial plane the sum of the coordination bond angles (P1–Co1–P2 = $114.63(4)^\circ$; P2–Co1–Si1 = $117.25(4)^\circ$; P1–Co1–Si1 = $125.81(5)^\circ$) is 357.69° , slightly deviated from 360° . The Co1–Si1 bond length is close to those of the Co–Si bonds in complexes **2** and **3**. Co1–C2 ($2.078(4)$ Å) is significantly longer than Co1–C28 ($1.733(4)$ Å). This shows that the π -backdonation makes Co1–C28 have a certain double bond component. The Cl1 atom in the molecule is disordered. As no bromine compound was used during the synthesis, it is impossible that the halogen position is partly occupied by the bromine atom.

We reported that the reaction of complex **1** with MeI delivered methyl cobalt(III) iodide **5** via PMe_3 dissociation and

oxidative addition (Scheme 4) with $[\text{Me}_4\text{P}]\text{I}$ as the byproduct.⁹ Under the same reaction conditions, the reaction of complex **2** with MeI gave rise to cobalt(II) iodide **6** as red crystals via single-electron oxidative addition (Scheme 4). The first step is dissociation of the silylene ligand. After that single-electron oxidative addition took place to form the main product **6** with the release of ethane, produced from the dimerization of methyl radical. In addition to product **6** and ethane, we also found a blue-green powder as the cobalt byproduct. The infrared spectra showed that the byproduct contained silylene and trimethylphosphine, but it was a paramagnetic substance. We failed to make further characterization. The formation of ethane was confirmed by an *in situ* ^1H NMR spectrum with a chemical shift of 0.78 ppm in C_6D_6 . It is obvious that the



Scheme 4 Reactions with MeI.

replacement of PMe_3 by silylene makes the cobalt center less electron-rich due to the π -backdonation from Co to the silylene. Therefore, complex **2** could only react with MeI in the form of single-electron oxidative addition. This result shows that the reducibility of **1** is stronger than that of **2**. Complex **6** is stable in air.

Complex **6** also has a penta-coordinate trigonal bipyramidal geometry (Fig. 4). C14–Co1–P3 ($178.54(9)^\circ$) is the axial direction, while [I1–P1–P2] is the equatorial plane. The sum of the coordination bond angles (P1–Co1–P2 = $114.07(4)^\circ$; P1–Co1–I1 = $115.69(3)^\circ$; P2–Co1–I1 = $125.05(3)^\circ$) in the equatorial plane is 354.81° , deviated from 360° . Co1–P3 ($2.2247(6) \text{ \AA}$) is obviously longer than Co1–P1 ($2.1748(9) \text{ \AA}$) and Co1–P2 ($2.1567(9) \text{ \AA}$) because of the strong *trans*-influence of the carbon atom. Co1–I1 ($2.5934(5) \text{ \AA}$) in complex **6** is shorter than Co–I ($2.6678(7) \text{ \AA}$) in complex **5**. Complex **5** is a hexa-coordinate Co(III) compound, while complex **6** is a penta-coordinate Co(II) compound.

Hydrosilylation of alkenes catalyzed by complex **6**

Organosilicon materials have important applications in industry, agriculture, medicine and other fields. Hydrosilylation of alkenes is the most direct method to synthesize organosilicon compounds. Platinum catalysts, such as Speier's and Karstedt's catalysts, were widely used for hydrosilylation of alkenes.¹¹ Although platinum catalyst systems show high activity and good chemical selectivity, platinum catalysts are toxic, expensive and not recyclable. With the concept of green chemistry and sustainable development being put forward, catalytic

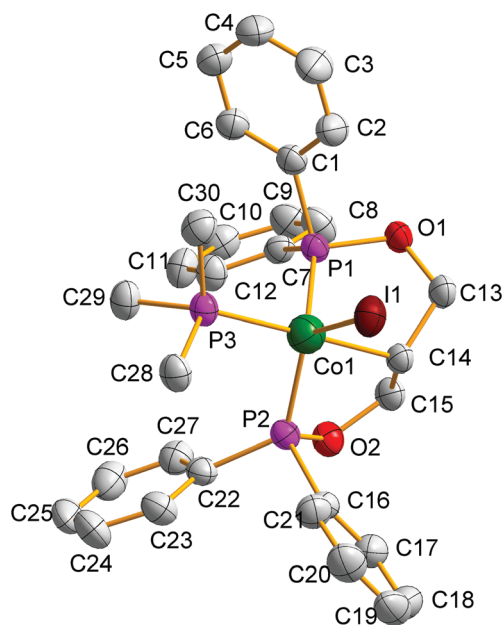


Fig. 4 Molecular structure of complex **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1 I1 $2.5934(5)$, Co1 P1 $2.1748(9)$, Co1 P2 $2.1567(9)$, Co1 P3 $2.2247(6)$, Co1 C14 $2.064(3)$; P1 Co1 I1 $115.68(3)$, P1 Co1 P3 $100.74(4)$, P2 Co1 I1 $125.05(3)$, C14 Co1 I1 $91.32(9)$.

Table 2 Optimization of reaction conditions^a

Entry	Catalyst	Loading NaBH ₄ (mol%)	NaBH ₄ (mol%)	Solvent	Temp. (°C)	Time (h)	Conversion (%) ^b
1	6	0	10	THF	70	10	0
2	6	1	10	THF	70	10	49
3	6	1	10	Toluene	70	10	38
4	6	1	10	Dioxane	70	10	45
5	6	1	10	DMSO	70	10	40
6	6	1	10	THF	70	24	67
7	6	2	10	THF	70	24	82
8	6	2	10	THF	70	30	85
9	2	2	10	THF	70	30	20
10	4	2	10	THF	70	30	45
11	6	2	10	THF	90	30	99
12	6	2	10	THF	50	30	45
13	6	2	10	THF	r.t.	30	<10
14	6	2	5	THF	70	30	85

^a Styrene (1.0 mmol), Ph₂SiH₂ (1.2 mmol) and 1 mL solvent. ^b Determined by GC with *n* dodecane as an internal standard.

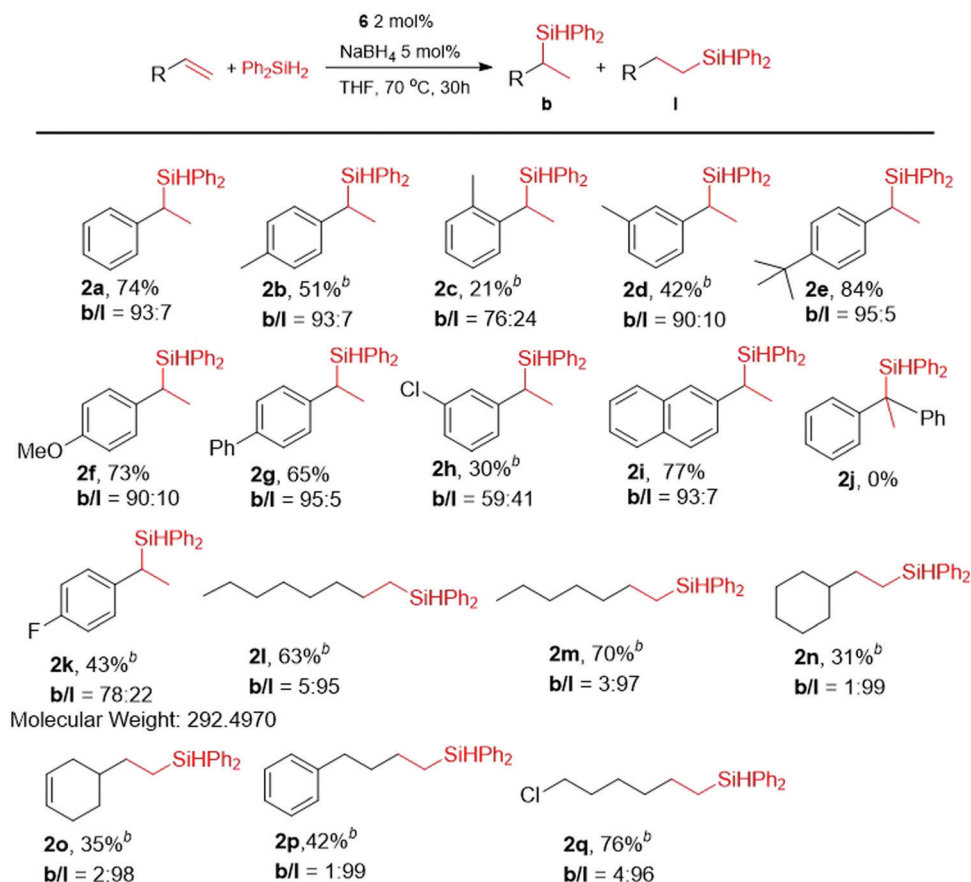
systems based on base metals, such as iron, cobalt and nickel, have been reported continuously. Therefore, it is one of the major challenges for chemists to find alternatives to platinum catalysts.

According to literature reports, metal halides could be used as precursors of catalysts and could form active species for catalytic reactions after combining with activators. For example, (^{Et}PDI)FeCl₂/EtMgBr,¹² (^RBIP^{Ar})FeBr₂/NaBEt₃H,¹³ (P^ONN)FeX₂/NaBEt₃H,¹⁴ (^tBuPCN N^{iPr})FeCl₂,¹⁵ (ⁱPr₂IPO^{iPr})FeCl₂/NaBEt₃H¹⁶ and [iPr₂-(*S,S*)-Bopa]NiCl/NaOtBu¹⁷ catalytic systems have good catalytic activity and selectivity for hydrosilylation of alkenes.

We speculated that complex **6** might have catalytic activity for hydrosilylation of alkenes. Therefore, we chose NaBH₄ as the activator, styrene as the template substrate, and Ph₂SiH₂ as the hydrosilylation reagent to explore the hydrosilylation of alkenes (Table 2). The experiments confirmed that no product was detected without catalyst (entry 1, Table 2). When the loading of the catalyst was 1 mol%, the conversion was 49% in 10 h, and the main product was Markovnikov (entry 2, Table 2). Under the same conditions, when toluene, dioxane and DMSO were used as solvents, the conversions were not as high as that in THF (entries 3–5, Table 2). When the reaction time was extended to 24 h, the conversion increased to 67% (entry 6, Table 2). When the loading of the catalyst was increased to 2 mol%, the conversion increased to 82% (entry 7, Table 2). After that, when the reaction time was extended to 30 h, the conversion increased to 85% (entry 8, Table 2). When complexes **2** and **4** were used as catalysts, the conversions were not as high as that of complex **6** (entries 9 and 10, Table 2). When the reaction temperature was increased to 90 °C, the conversion is complete but the selectivity was poor (entry 11, Table 2). As the reaction temperature decreased, the conversion also decreased (entries 12 and 13, Table 2). The reduction of the amount of activator to 5 mol% had no effect on the reaction. Therefore, the optimized catalytic conditions are those shown in entry 14 of Table 2.

The scope of the substrates was explored under the optimized catalytic conditions (Table 3). In general, for most of the

Table 3 The scope of the substrates^{ab}



^a Catalytic reaction conditions: alkene (1.0 mmol), Ph_2SiH_2 (1.2 mmol), $NaBH_4$ (5 mol%) and **6** (2 mol %) were stirred under neat conditions at 70 °C for 30 hours. Product ratios were determined by GC using *n* dodecane as an internal standard and yields were determined by isolation.

^b $NaBH_4$ (10 mol%), Cat (4 mol%)

substrates, although the isolated yields are moderate, the selectivities are good to excellent. The main products are Markovnikov addition compounds. For styrene, 4-*tert*-butyl styrene, 4-methoxy styrene and 2-vinyl naphthalene, the yields are between 73 and 84%. The corresponding isolated yields of *p*-methyl styrene (51%), *m*-methyl styrene (42%) and *o*-methyl styrene (21%) gradually decreased due to steric hindrance. *m*-Chloro benzene has a 30% yield and *p*-fluoro benzene has a 43% yield. For 1,1-diphenyl ethene there was no reaction. For six aliphatic alkenes, although the yields are moderate, selectivities are very high. Compared with aromatic alkenes, the difference is that the main products are anti-Markovnikov compounds. This means that there is a selectivity reversal from the Markovnikov product to an anti-Markovnikov product for aliphatic alkenes. This phenomenon of selectivity reversal has been reported in cobalt catalyzed hydrosilylation of alkenes.^{18,19}

We consider that the first step of the catalytic mechanism is the formation of a hydrido-cobalt complex from the reduction reaction of complex **6** with $NaBH_4$. The mechanism of the catalytic reaction is the same as that of the

hydrosilylation of alkenes catalyzed by [CNC] pincer cobalt hydride¹⁹ because the selectivity of the two catalytic systems is the same.

Conclusion

In summary, a new chloro silylene ligand **L2** was prepared for a silylene cobalt complex. The reactions of chloro silylene ligands **L1** or **L2** with [PCP] pincer cobalt(i) complex **1** supported by the trimethylphosphine ligand afforded novel [PCP] silylene cobalt(i) complexes **2** or **3** *via* ligand replacement. Complex **2** reacted with CO to give rise to carbonyl silylene [PCP] pincer cobalt(i) complex **4**, while the reaction between complex **2** and MeI produced [PCP] pincer cobalt(ii) iodide **6** *via* single-electron oxidative addition. It was found that complex **6** could catalyze the hydrosilylation of alkenes with good selectivity. The influence of the silylene ligand on the properties of the complexes was discussed and the properties of silylene complexes and phosphine complexes were compared. The molecular structures of complexes **2**, **3**, **4** and **6** were determined by single crystal X-ray diffraction.

Experimental section

General procedures and materials

All air-sensitive reactions were carried out under anhydrous and nitrogen atmosphere conditions by the standard Schlenk technique. Solvents were dried by standard methods and freshly distilled prior to use. Chloro silylene **L1**⁸ and complex **1**⁹ were prepared according to the known literature methods. All other chemicals were purchased and used as received without further purification. Infrared spectra (4000–400 cm⁻¹) were obtained from Nujol mulls between KBr disks and recorded on a Bruker ALPHA FT-IR instrument. ¹H, ¹³C {¹H}, ³¹P {¹H} and ²⁹Si {¹H} NMR spectra were recorded on Bruker Avance 300 MHz and 600 MHz spectrometers. GC was carried out on a Fuli 9790 chromatograph with *n*-dodecane as an internal standard. Elemental analyses were carried out on an Elementar Vario ELIII instrument.

Synthesis of L2. In a nitrogen atmosphere, *n*-BuLi (2.5 M, 20 mL) was slowly added to the diethyl ether solution of *p*-methyl bromo benzene (8.55 g, 50.00 mmol) at 0 °C. The temperature of the reaction solution was slowly increased to room temperature and the solution was stirred for 2 hours. During this process, the reaction solution gradually turned light yellow. Then, ^tBuN C N^tBu (7.71 g, 50.00 mmol) was slowly added to the reaction solution at -78 °C and the reaction solution was stirred for 4 h at room temperature. After that, SiHCl₃ (8.80 g, 65.00 mmol) was slowly added to the resulted reaction solution at -78 °C and the reaction solution was stirred overnight at room temperature. In this process, the color of the reaction solution gradually changed from light yellow to milky white. The diethyl ether was removed under reduced pressure and the residue was extracted with toluene (60 mL). The precursor of **L2** as white crystals was precipitated from the toluene extract at -20 °C (12.09 g, 70%).

LiN(SiMe₃)₂ (3.24 g, 19.34 mmol) in toluene (40 mL) was slowly added to the toluene solution (40 mL) of the precursor of **L2** (6.61 g, 19.15 mmol) at -78 °C under a nitrogen atmosphere. After the temperature of the reaction mixture was increased to room temperature, the color of the reaction solution changed from light yellow to orange yellow. After filtration, the toluene solvent was removed under vacuum and the residue was extracted by *n*-pentane (50 mL × 3). **L2** as a yellow solid (3.19 g, 54%) was crystallized from the *n*-pentane solution at -20 °C. IR (Nujol mull, KBr, cm⁻¹): 1646 (C N), 1611 (C C). ¹H NMR (300 MHz, benzene-d₆, 300 K, δ/ppm): 1.24 (s, 18H, C(CH₃)₃), 2.07 (s, 3H, CH₃), 7.07–6.83 (m, 4H, Ar-H). ¹³C {¹H} NMR (75 MHz, benzene-d₆, 300 K, δ/ppm): 167.1, 139.9, 129.9, 129.1, 128.7, 128.4, 128.1, 127.8, 127.5, 127.4, 53.5 (s, (CH₃)₃C), 31.2 (s, (CH₃)₃C), 21.0 (s, CH₃). ²⁹Si NMR (79 MHz, C₆D₆, 298 K, ppm): 13.8.

Synthesis of complex 2. Under the protection of nitrogen, the diethyl ether solution (30 mL) of **L1** (0.30 g, 1.0 mmol) was slowly added into the diethyl solution (50 mL) of complex **1** (0.65 g, 1.0 mmol). After stirring the solution for 24 hours, the solution changed from dark red to light red, accompanied by precipitation of a large number of yellow crystals. After

filtration, both the yellow crystals obtained from filtration and the yellow crystals precipitated from the filtrate (0 °C) are complex **2** (0.65 g, 75%). Anal. calcd for C₄₅H₅₇ClCoN₂O₂P₃Si (873.35 g mol⁻¹): C, 61.89; H, 6.58; N, 3.21. Found: C, 61.51; H, 6.42; N, 3.28. IR (Nujol mull, KBr, cm⁻¹): 1612, 1584 (C N/C C), 951 (PMe₃). ¹H NMR (300 MHz, benzene-d₆, 300 K, δ/ppm): 1.12 (s, 18H, C(CH₃)₃), 1.67 (d, *J*_{PH} = 9 Hz, 9H, PCH₃), 3.69 (br, 1H, CH), 4.01 (br, 2H, CH₂), 4.31 (br, 2H, CH₂), 6.93–7.19 (m, 17H, Ar-H), 7.68 (s, 4H, Ar-H), 8.18 (s, 4H, Ar-H). ³¹P {¹H} NMR (121 MHz, benzene-d₆, 300 K, δ/ppm): 5.7 (t, *J*_{PP} = 26 Hz, 1P, PMe₃), 157.4 (s, 2P, PPh₂). ¹³C {¹H} NMR (75 MHz, benzene-d₆, 300 K, δ/ppm): 174.0 (s, N-C-N), 149.1 (t, *J*_{PC} = 10 Hz), 146.6 (t, *J*_{PC} = 20 Hz), 132.2, 131.7, 130.6, 129.6, 129.2, 74.0 (t, *J*_{PC} = 12 Hz, CH), 54.0 (s, CH₂), 44.2 (s, (CH₃)₃C), 31.6 (s, (CH₃)₃C), 25.8 (dt, *J*_{PC} = 24 Hz, *J*_{PC} = 6 Hz, PCH₃). ²⁹Si NMR (79 MHz, benzene-d₆, 300 K, δ/ppm): 52.0 (m).

Synthesis of complex 3. The synthesis method of **3** is the same as that of complex **2**. **3** as yellow crystals was obtained (0.62 g, 70%). Anal. calcd for C₄₆H₅₉ClCoN₂O₂P₃Si (887.38 g mol⁻¹): C, 62.26; H, 6.70; N, 3.16. Found: C, 62.01; H, 6.82; N, 3.21. IR (Nujol mull, KBr, cm⁻¹): 1612, 1585, 1535 (C N/C C), 950 (PMe₃). ¹H NMR (300 MHz, benzene-d₆, 300 K, δ/ppm): 1.16 (s, 18H, C(CH₃)₃), 1.69 (d, *J*_{PH} = 9 Hz, 9H, PCH₃), 2.06 (s, CH₃, 3H), 3.71 (br, 1H, CH), 4.01 (br, 2H, CH₂), 4.32 (br, 2H, CH₂), 6.80–7.19 (m, 16H, Ar-H), 7.68 (s, 4H, Ar-H), 8.19 (s, 4H, Ar-H). ³¹P {¹H} NMR (121 MHz, benzene-d₆, 300 K, δ/ppm): 5.7 (t, *J*_{PP} = 25 Hz, 1P, PMe₃), 157.4 (s, 2P, PPh₂). ¹³C {¹H} NMR (75 MHz, benzene-d₆, 300 K, δ/ppm): 174.1 (s, N-C-N), 149.1 (t, *J*_{PC} = 10 Hz), 146.6 (t, *J*_{PC} = 20 Hz), 139.8, 131.8, 130.7, 129.2, 129.0, 74.0 (t, *J*_{PC} = 12 Hz, CH), 53.7 (s, CH₂), 44.3 (s, (CH₃)₃C), 31.7 (s, (CH₃)₃C), 25.8 (dt, *J*_{PC} = 29 Hz, *J*_{PC} = 6 Hz, PCH₃). ²⁹Si NMR (79 MHz, benzene-d₆, 300 K, δ/ppm): 54.5 (m).

Synthesis of complex 4. An atmospheric pressure of CO was introduced into the diethyl ether solution (50 mL) of complex **2** (0.60 g, 0.69 mmol) in a nitrogen atmosphere. After 24 hours, the color of the solution became lighter and complex **2** dissolved gradually. The diethyl ether solvent was removed under reduced pressure and the residue was extracted with *n*-pentane. Complex **6** was precipitated from the extract at 0 °C. Product **4** was obtained as yellow crystals (0.37 g, 65%). Anal. calcd for C₄₃H₄₈ClCoN₂O₃P₂Si (825.28 g mol⁻¹): C, 62.58; H, 5.86; N, 3.39. Found: C, 62.76; H, 5.74; N, 3.31. IR (Nujol mull, KBr, cm⁻¹): 1967, 1897 (C O), 1615, 1586, 1570 (C N/C C). ¹H NMR (300 MHz, benzene-d₆, 300 K, δ/ppm): 0.98 (s, (CH₃)₃C, 18H), 3.96 (s, CH, 1H), 4.07 (s, CH₂, 2H), 4.54 (s, CH₂, 2H), 6.90–7.22 (m, Ar, 17H), 7.74 (s, Ar, 4H), 8.13 (s, Ar, 4H). ³¹P {¹H} NMR (121 MHz, benzene-d₆, 300 K, δ/ppm): 167.8 (s, PPh₂). ¹³C {¹H} NMR (75 MHz, benzene-d₆, 300 K, δ/ppm): 172.1 (s, N-C-N), 145.8 (t, *J*_{PC} = 22 Hz), 144.7 (t, *J*_{PC} = 15 Hz), 131.6, 129.7, 129.4, 128.2, 76.0 (t, *J* = 11 Hz, CH), 54.1 (s, CH₂) 50.8 (s, (CH₃)₃C), 30.6 (s, (CH₃)₃C). ²⁹Si NMR (79 MHz, benzene-d₆, 300 K, δ/ppm): 60.9 (t, *J* = 82 Hz).

Synthesis of complex 6. Under the protection of a nitrogen atmosphere, MeI (0.26 g, 1.84 mmol) was added into the THF solution (50 mL) of complex **2** (0.80 g, 0.92 mmol) using a syringe. When the reaction solution was stirred for 48 h, the

solution changed from light red to dark red. All volatile substances in the solution were removed under reduced pressure, and the residual solid was washed with ether to obtain a purple solid. The purple solid was recrystallized with ether at $-20\text{ }^{\circ}\text{C}$ to obtain compound **6** as purple crystals (0.42 g, 65%). IR (Nujol mull, KBr, cm^{-1}): 1612, 1584 (C C), 950 (PMe₃). Anal. calcd for C₃₀H₃₄CoIO₂P₃ (705.36 g mol⁻¹): C, 51.08; H, 4.86. Found: C, 50.89; H, 4.77. Complex **6** is paramagnetic.

General procedure for hydrosilylation reactions. Under a N₂ atmosphere, 2 mol% catalyst and 5 mol% NaBH₄ were added into a 20 mL Schlenk tube containing a magnetic stirrer with 1 mL THF. The reaction mixture was stirred at 70 °C for 1 h. Then alkene (1.00 mmol), *n*-dodecane (170 mg, 1.00 mmol), and Ph₂SiH₂ (221 mg, 1.2 mmol) were added in order. The reaction mixture was stirred at 70 °C for 30 h and the resulting solution was quenched with ethyl acetate. The organic fractions were concentrated in vacuum and the crude product was purified by column chromatography on silica gel with petroleum ether as the eluent. The pure products were characterized by NMR analysis.

X-Ray structure determination

The intensity data and cell parameters of complexes **2**, **3**, **4** and **6** were recorded using a Stoe Stadi Vari diffractometer equipped with graphite-monochromatized Ga K α radiation ($\lambda = 1.34143\text{ \AA}$), while the intensity data and cell parameters of complex **4** were recorded using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer, employing a Cu K α radiation source ($\lambda = 1.54184\text{ \AA}$). Crystallographic data for complexes **2**, **3**, **4** and **6** are summarized in the ESI.† The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 using the SHELXL program²⁰ through the OLEX interface.²¹ All non-hydrogen atoms were refined anisotropically. CCDC 1894297 (**2**), 1947320 (**3**), 1958714 (**4**) and 1947318 (**6**) contain the supplementary crystallographic data for this paper.†

Conflicts of interest

There are no conflicts to declare.

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