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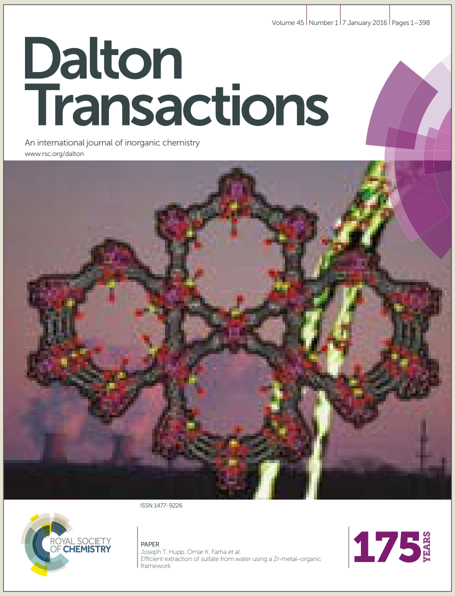

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Synthesis and Catalytic Activity of N-Heterocyclic Silylene (NHSi) Cobalt Hydride for Kumada Coupling Reactions

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Abstract

The electron-rich silylene Co(I) chloride **5** was obtained through the reaction of $CoCl(PMe_3)_3$ with chlorosilylene. Complex **5** reacted with 1,3-siladiazoles $HSiMe(NCH_2PPh_2)_2C_6H_4$ to give the silylene Co(III) hydride **6** through chelate-assisted Si-H activation. To the best of our knowledge, complex **6** is the first example of Co(III) hydride supported by N-heterocyclic silylene. Complexes **5** and **6** were fully characterized by spectroscopic methods and X-ray diffraction analysis. Complex **6** was used as an efficient precatalyst for Kumada cross-coupling reactions. Compared with the related complex **3** supported only by trimethylphosphine, complex **6** as catalyst supported by both chlorosilylene and trimethylphosphine exhibits the more efficient performance for the Kumada cross-coupling reactions. A novel catalytic radical mechanism was suggested and experimentally verified. As an intermediate silylene cobalt(II) chloride **6d** was isolated and structurally characterized.

Keywords: silylene cobalt hydride / N-heterocyclic silylene / silyl cobalt complex / Kumada coupling / radical reaction.

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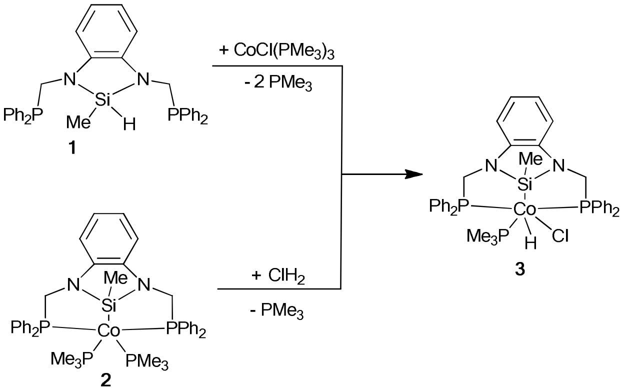
Introduction

The design of ligands plays an important role in controlling the electronic and spatial properties of transition metal (TM) centers. Until now, carbene complexes, especially with N-heterocyclic carbene (NHC),[1-5] have been widely used in coordination chemistry but only a few cases of transition metal compounds containing N-heterocyclic silylene ligand (NHSi) have been reported.[6] Because of the enhanced properties of NHSis as σ-donating / π-accepting ligands with unique steric hindrance compared to NHCs and phosphines, the better performance of the transition metal complexes containing NHSis ligand(s) for catalytic reactions has been revealed.[7,8] And some of these silylene-ligated noble metal complexes have been found as efficient catalysts to catalyze Suzuki[9] or Heck[10] coupling reactions, amide reduction,[11] arene borylation,[12] alkene[13,14] or ketone[15,16] hydrosilyation, Kumada[17,18] or Sonogashira cross-coupling reactions.[19] Driess and co-workers utilized bis(silylene) cobalt(I) complex to achieve an efficient conversion for the [2 + 2 + 2] cyclotrimeriztion reaction of phenylacetylene.[20] More recently, Cui and co-workers reported the remarkable catalytic activity of silylene [SiNSi] pincer-type cobalt(II) complex in the borylation of arenes.[21] However, there are still comparatively few studies on the synthesis and catalytic applications of Fe, Co and Ni complexes containing NHSi ligands.



Scheme 1. Synthesis of Hydrido [PSiP] Pincer Cobalt(III) Chloride

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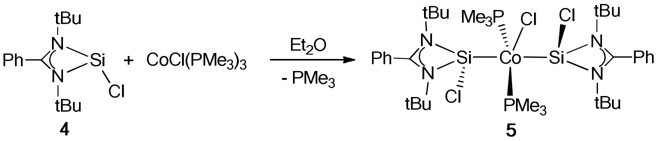
Our research group has done a lot of work on the design and catalytic exploration of Fe, Co and Ni complexes supported by trimethylphosphine ligands. The hydrido iron complexes were found to be excellent catalysts for the hydrogenation of aldehydes and ketones under mild conditions.[22, 23] Recently, we reported synthesis and characterization of a hydrido [PSiP] pincer cobalt(III) chloride **3** (**Scheme 1**).[24] Cobalt complex **3** was found to be a good catalyst for the Kumada cross-coupling reactions of aryl chlorides and aryl bromides with Grignard reagents under mild conditions. In order to investigate the effect of silylene ligand on the property of the cobalt complex, in this paper we disclose the synthesis of cobalt(I) chloride **5** with trimethylphosphine and chlorosilylene as supporting ligands and the silylene hydrido [PSiP] pincer cobalt(Ш) chloride **6** in an unexpected coordination mode. These results reveal the influence of NHSi on the coordination environment of the cobalt center. It is noteworthy that the particular electronic property of NHSi gives the cobalt complex good catalytic activity for the Kumada cross-coupling reactions. It must be highlighted that the hydrido silylene [PSiP] pincer cobalt(III) chloride **6** has better catalytic ability than the hydrido cobalt(III) chloride **3** supported only by trimethylphosphine. A novel catalytic radical mechanism was suggested and experimentally verified. As an intermediate silylene cobalt(II) chloride **6d** was isolated and structurally characterized.

Results and Discussion

Reaction of $CoCl(PMe_3)_3$ with chlorosilylene 4



Scheme 2. Synthesis of Silylene Co(I) Complex **5**

When $CoCl(PMe_3)_3$ was treated with 2 equivalents of chlorosilylene **4** in Et_2O, the reaction solution slowly turned brown and gave rise to a large amount of red solid

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(**Scheme 2**). After 8 h, complex **5** was obtained as red crystals from diethyl ether filtrate at -20 in a yield of 90%. The disilylene cobalt(I) chloride **5** is a ligand replacement product of trimethylphosphine by chlorosilylene. In this reaction, one trimethylphosphine ligand in complex $CoCl(PMe_3)_3$ was replaced by two chlorosilylene ligands and 16e complex $CoCl(PMe_3)_3$ was converted into 18e complex **5**. In the ^1H NMR spectrum of complex **5**, one singlet for ^{t}Bu-groups appears at 0.85 ppm and the signal of PMe_3 is situated at 0.88 ppm. In the VT-31P NMR spectrum of complex **5** (**Figure 1**), the same singlet signals of trimethylphosphine ligands at 25.6 ppm indicate that two PMe_3 ligands are positioned in the same chemical environments. One signal of two silylene ligands exists at 30.0 ppm in the ^{29}Si NMR spectrum. This implies that complex **5** is symmetric about Si atoms.

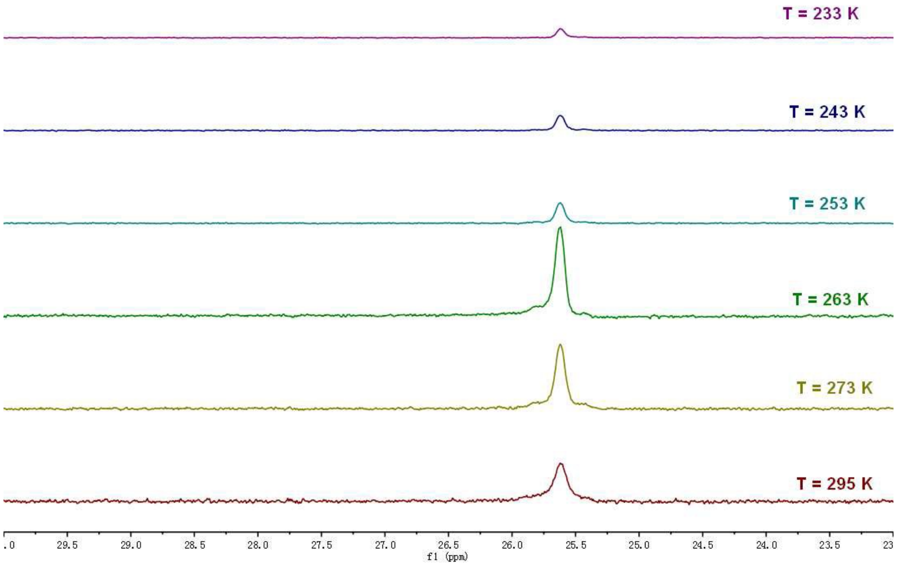

Figure 1. The VT-^{31}P NMR spectra of **5** in THF-d8

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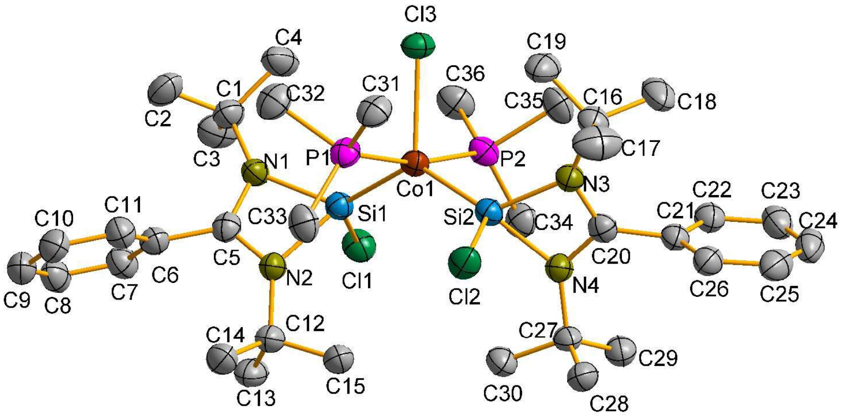

Figure 2. Molecular structure of complex **5**. ORTEP plot of complex **5** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1-Si1 2.175(1), Co1-Si2 2.184(1), Co1-P2 2.195(1), Co1-P1 2.206(1), Co1-Cl3 2.407(1); Si1-Co1-Si2 129.40(5), P2-Co1-P1 168.07(5), Si1-Co1-Cl3 115.88(4), Si2-Co1-Cl3 114.71(4).

The molecular structure of complex **5** was further confirmed by single crystal X-Ray diffraction (**Figure 2**). Complex **5** has a strongly distorted trigonal-bipyramidal geometry around the Co atom. [Co1Si1Si2Cl3] is the equatorial plane and the bond angle P1-Co1-P2 (168.07(5)°) is in the axial position. The sum of the coordination bond angles in the equatorial plane is 359.99°. This implies that the four atoms [Co1Si1Si2Cl3] are almost coplanar. The τ_5 value ((((∠(P2-Co1-P1)-∠(Si1-Co1-Si2))/60) = ((168.07-129.40)/60) = 0.6445) indicates that complex **5** is more like a trigonal-bipyramidal geometry.[25] The bond lengths of Si(II)-Co bonds (Co1-Si1 = 2.175(1) Å and Co1-Si2 = 2.184(1) Å) are significantly shorter than that (2.2480(5) Å) of Si(IV)-Co in complex **3** (**Scheme 1**)[24] owing to the back-bonding from the Co center to the Si atom in complex **5**. One silylene Si2-Cl2 bond extends above the equatorial plane while another silylene Si1-Cl1 bond orientates below the equatorial plane.

Reaction of silylene cobalt complex 5 with [PSiP] preligand 1

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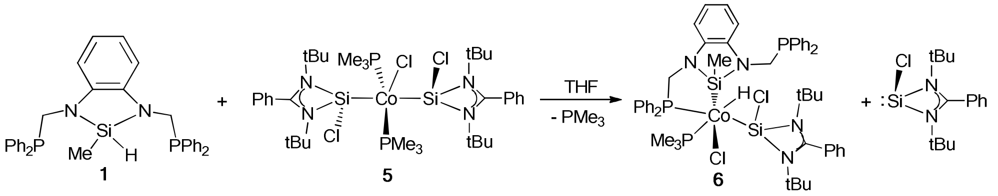

Scheme 3. Synthesis of Silylene Hydrido Co(III) Complex **6**

The reaction of [PSiP] pincer preligand [$HSiMe(NCH_2PPh_2)_2C_6H_4$] **1** with the electron-rich NHSi Co(I) complex **5** in THF resulted in the formation of air sensitive silylene hydrido Co(III) complex **6** via the activation of Si-H bond (**Scheme 3**). Complex **6** was isolated as yellow crystals from diethyl ether at 0 ^{o}C in a yield of 92%. To the best of our knowledge, complex **6** is the first example of hydrido cobalt(III) complex with NHSi ligand.

In the infrared spectrum of complex **6**, there is an obvious stretching band for Co-H bond at 1917 cm^{-1}. Compared to that (1985 cm^{-1}) of complex **3** this is a bathochromic shift due to stronger π-back-donation from Co to Si. The ^{1}H NMR spectrum of complex **6** in C_6D_6 gives evidence for the hydrido ligand at -12.49 ppm as a dd peak due to the coupling of the hydrido H with two coordinated phosphorus atoms with the coupling constants ^{2}J(PH) of 57 Hz and 18 Hz. The signal of PMe_3 ligand is situated at 1.19 ppm. In the ^{31}P NMR spectrum of complex **6**, two types of Ph_2P groups and one kind of PMe_3 group appear at 77.89, 13.28, and -6.0 ppm with a relative integral ratio of 1 : 1 : 1. This reveals that two Ph_2P- groups have different chemical environments. It is conjectured that the steric effect of the chlorosilylene ligand in complex **6** makes one of the two Ph_2P- groups free (uncoordinated). In the ^{29}Si NMR spectrum of complex **6**, the signals of Si(IV) and Si(II) were detected at 68.1 and 10.0 ppm respectively.

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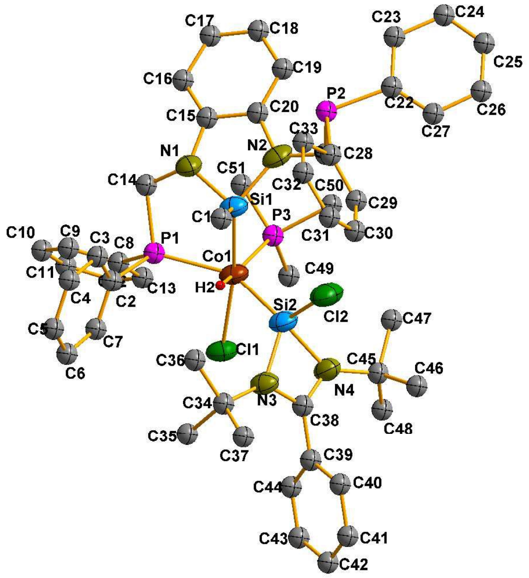

Figure 3. Molecular structure of complex **6**. ORTEP plot of complex **6** at the 50% probability level (most of hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1-Cl1 2.378(2), Co1-P1 2.218(3), Co1-P3 2.205(3), Co1-Si1 2.263(3), Co1-Si2 2.163(3), Co1-H2 1.3(4); Si2-Co1-P3 112.63(12), Si1-Co1-Cl1 168.42(12), P3-Co1-P1 104.30(11), P1-Co1-H2 84(10), Si2-Co1-H2 63(10).

The structure of complex **6** has been elucidated by single crystal X-ray diffraction analysis (**Figure 3**). In the asymmetric unit, two crystallographically independent molecules with the same structural characteristics were observed. Here the structural parameters of one molecule are discussed. As expected from the spectroscopic information, complex **6** did not form a pincer-type coordination structure like complex **3** because one of the two Ph_2P- groups is not coordinated to the cobalt center. In the molecular structure of complex **6**, the cobalt atom is centered in a distorted hexa-coordinate octahedral geometry. The axial Si1-Co1-Cl1 (168.4(1)^o) is almost perpendicular to the equatorial plane formed by [Co1H2P1P3Si2]. The sum of the coordination bond angles in the equatorial plane is 363.93°, close to 360°. In the two structural units, the bond lengths of Co-H are 1.3 Å, slightly shorter than the normal of Co–H bonds (1.40-1.50 Å).[26] Both Si1-Co1-Cl1 (168.4(1)^o) and P1-Co1-Si2 (142.7(1)^o) bond angle bend toward the direction of the hydrido ligand

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due to the small size of the hydrido H. The Co1-Si2 bond distance (2.163(3) Å) is shorter than Co1-Si1 (2.263(3) Å) due to the back-bonding from Co to $Si_{silylene}$ atom.

Catalytic activity of complex 6 for the Kumada coupling reaction

Chloroarenes are important organic substances and widely used in a lot of fields. C-Cl bond is comparatively inert and it is more difficult to activate C-Cl bond. Therefore, how to activate C-Cl bond by transition metal complexes is a big challenge for chemists. Different cross-coupling reactions have been applied for C-Cl activation and functionalization.[27] Recently we have found that complex **3** is a good catalyst for the Kumada coupling reactions.[24] Complex **6** containing [H-Co-Cl] moiety, similar to complex **3**, should also have catalytic activity for the Kumada coupling reaction. Therefore, we explored the catalytic performance of complex **6** for the Kumada C,C-coupling reaction.

We initially examined the catalytic activity of complex **6** for the cross-coupling reaction of chlorobenzene with (4-methylphenyl)magnesium bromide as a probe reaction. After screening reaction temperature, reaction time, solvents and catalyst loading (Table 1), we found that THF was the best reaction medium compared with toluene, dioxane, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (Table1, entries 6, 8 and 10 - 12). A catalyst loading of 2 mol% was also necessary to complete the reaction (Table1, entries 5 - 7). If the temperature increased from 25, 40 to 50 °C, the conversion was changed from 63 to 84, and to 94% (Table1, entries 2, 3 and 6). It is noteworthy that the conversion (85%) at 60 °C was lower than that (94%) at 50 °C (Table1, entries 4 and 6). It must be noted that complex **6** has stronger catalytic activity than complex **3** (Table1, entries 6 and 13). From Table 1 the optimized conditions are summarized as follows: 2mol% catalyst, 50 °C, THF as solvent and reaction time 48h. Under the optimized conditions, the scope of the substrates was expanded (Table 2). It was found that the aryl chlorides with H- or Me-groups have higher yields than those with MeO- groups. With phenyl dichlorides as the substrates, a double Kumada C,C-coupling occurred when 2 equivalents of Grignard reagents were added (Table 3). The results showed that the isolated yields

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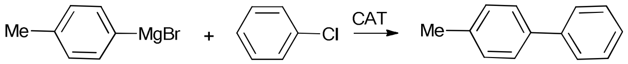
for the reactions with *o*-dichlorobenzene were much lower than those with the *m*-dichlorobenzene and *p*-dichlorobenzene. In these cases the catalytic activity of complex **6** was not as good as that of complex **3**. We speculate that this result is caused by steric hindrance of the silylene ligand.

Table 1. Catalytic Results of the Probe Reaction between Chlorobenzene and (4-Methylphenyl)magnesium Bromide



entry	Catalyst	Time (h)	Cat. (mol%)	Temperature (℃)	solvent	Conversion^{a}(%)
1	**6**	24	2	50	THF	45
2	**6**	48	2	25	THF	63
3	**6**	48	2	40	THF	84
4	**6**	48	2	60	THF	85
5	**6**	48	0.5	50	THF	69
6	**6**	48	2	50	THF	94
7	**6**	48	1	50	THF	80
8	**6**	48	2	50	Dioxane	14
9	**6**	48	2	80	Dioxane	18
10	**6**	48	2	50	Toluene	54
11	**6**	48	2	50	DMSO	<10
12	**6**	48	2	50	DMF	<10
13	**3**	48	2	50	THF	35

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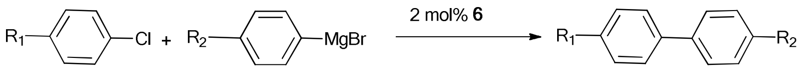
[a] Determined by GC with *n*-dodecane as an internal standard.

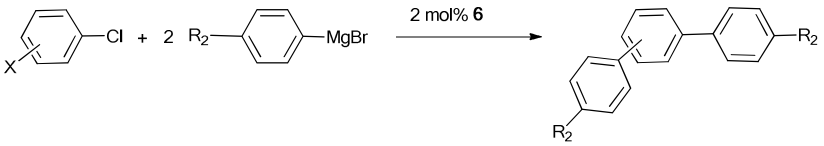
Table 2. Kumada Cross-Coupling Reaction of Aryl Chlorides with Grignard Reagents Catalyzed by **6**[a].



entry	R_1	R_2	yield[b]（%）
1	*p*-CH_3	H	88
2	*p*-OCH_3	H	71
3	H	CH_3	87
4	*p*-OCH_3	CH_3	74
5	H	CH_3O	74
6	*p*-CH_3	CH_3O	76

[a]50□, 48h. [b]Isolated yields.

Table 3. Kumada Cross-coupling Reactions of Phenyl Dichlorides with Grignard Reagents Catalyzed by **6**[a]



entry	X	R_2	yield[b]（%）
1	*o*-Cl	H	< 10[c]
2	*o*-Cl	CH_3	< 10[c]

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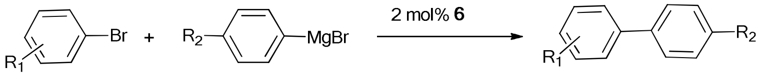
3	*m*-Cl	H	67
4	*m*-Cl	CH_3	78
5	*p*-Cl	H	74
6	*p*-Cl	CH_3	80

[a]50□, 48h. [b]Isolated yields. [c] GC yield with *n*-dodecane as an internal standard.

Table 4. Kumada Cross-Coupling Reaction of Aryl Bromides with Grignard Reagents



entry	R_1	R_2	yield[b]（%）
1	*p*-CH_3	H	82
2	*p*-OCH_3	H	76
3	*o*-CH_3	H	63
4	H	CH_3	83
5	*p*-OCH_3	CH_3	84
6	*o*-CH_3	CH_3	69
7	H	CH_3O	70
8	*p*-CH_3	CH_3O	83

[a]40□, 24h. [b]Isolated yields.

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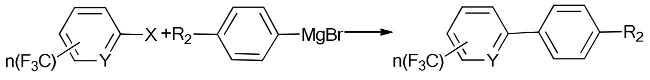
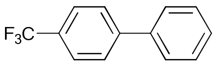
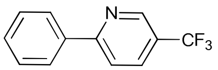
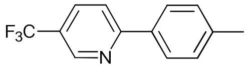
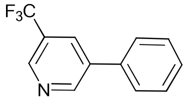
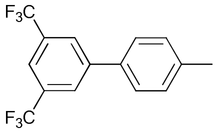
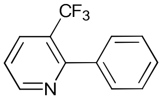
As expected, the catalytic reactions of the derivatives of bromobenzene took place at lower temperature in the moderate yields because they are more active than aryl chlorides (Table 4).

Although trifluoromethyl aromatic compounds have high application value, how to effectively prepare them is still a challenge. Inspired by the efficient performance of **6** for the Kumada cross-coupling reactions, we expanded the substrate scope to a variety of trifluoromethyl aromatic compounds. Under the optimized reaction conditions (2 mol % catalyst **6** in THF at 50℃), the corresponding trifluoromethyl aromatic products were readily generated in higher yield (**7a** −**7e**). The low yield (45%) for the formation of **7f** might be caused by steric effect.

Table 5. Kumada Cross-Coupling Reaction of Trifluoromethyl Aromatic Halides with Grignard Reagents Catalyzed by **6**[a,b].



Y = C or N; X = Cl or Br; n = 1 or 2;

 **7a** 86%, 48 h, X = Cl	 **7b** 90%, 48 h, X = Cl	 **7c** 94%, 48 h, X = Cl
 **7d** 77%, 48 h, X = Cl	 **7e** 88%, 24 h, X = Br	 **7f** 45%, 48 h, X = Cl

[a]50℃. [b]Isolated yields.

Study on the catalytic reaction mechanism

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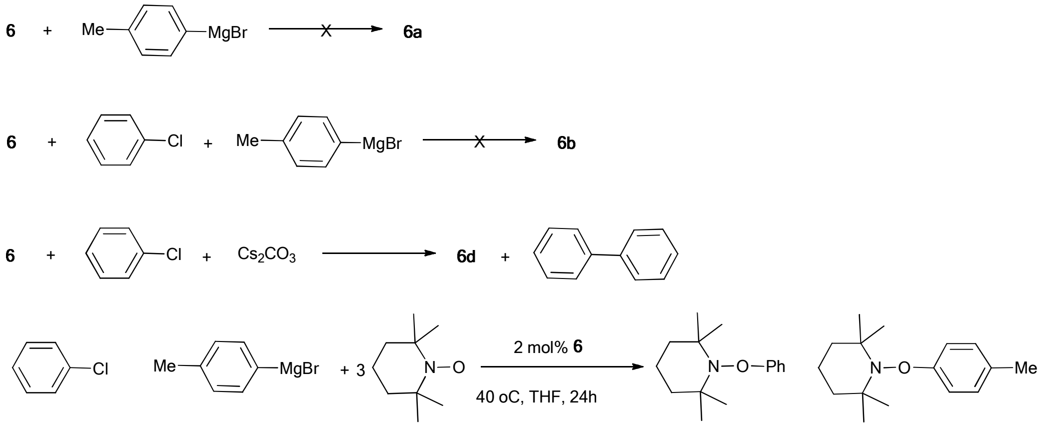

Scheme 4 Investigation of the mechanism

In order to better understand the different catalytic activities of complexes **6** and **3** for the Kumada coupling reaction, different reactions with complex **6** were designed to explore the mechanism (**Scheme 4**). Initially we guessed that the catalytic reaction mechanism should be similar to that of the reaction catalyzed by complex **3**.[24] In this case the catalytic reaction processed according to Path **a** in **Scheme 5**. In order to identify intermediates **6a** and **6b**, two experiments were conducted. In the first experiment complex **6** reacted with 1 equivalent of (4-methylphenyl)magnesium bromide. Unfortunately, we were not able to isolate intermediate **6a**. It is likely that **6a** is very unstable. In the second experiment, complex **6** reacted with stoichiometric phenyl chloride and (4-methylphenyl) magnesium bromide together but we did not obtain **6b**. In the third reaction, complex **6** reacted with one equivalent of phenyl chloride in the presence of Cs_2CO_3 as a base to replace (4-methylphenyl) magnesium bromide. To our surprise, complex **6d** as a cobalt(II) chloride was isolated and structurally characterized. At the same time, the coupling product (bisphenyl) was also detected in the solution using MS analysis. This result indicates that this reaction processed possibly according to a radical mechanism (Path **b**), rather than an oxidative addition process (Path **a**) as we initially proposed.

To verify whether the radical intermediate R’· was involved in the reaction, the inhibition experiment of chlorobenzene with (4-methylphenyl)magnesium bromide in the presence of catalyst **6** was conducted with the addition of

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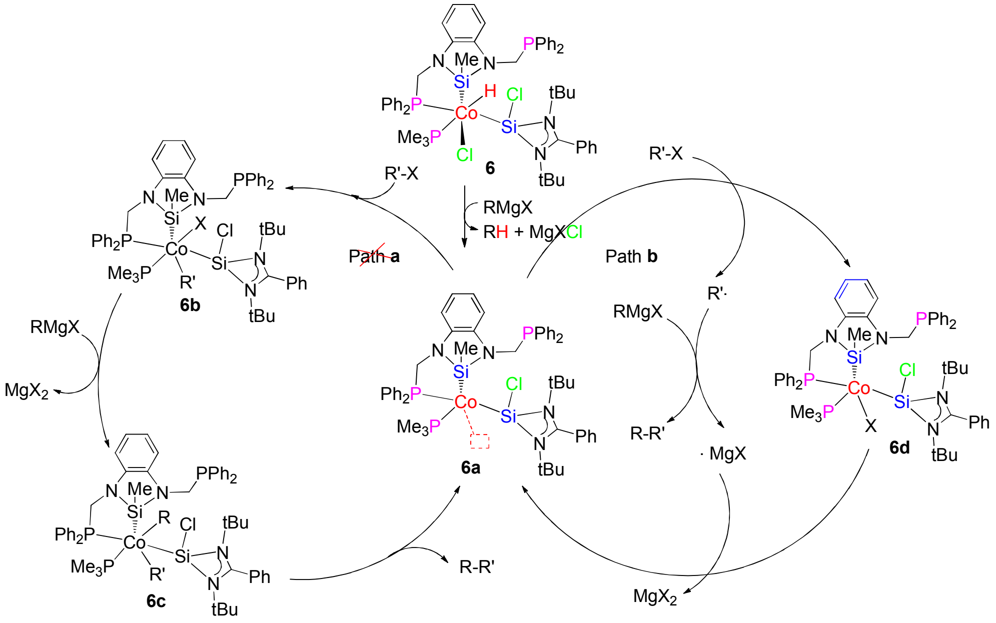
2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv), a catcher for the hydrocarbon radical. As expected, the TEMPO capture products of phenyl radical and 4-methyl-phenyl radical were detected by MS on one hand and no C,C-coupling product was found by GC detection on the other hand. This indicates that the reaction underwent a radical mechanism.



Scheme 5. Proposed mechanism for Kumada coupling reactions.

On the basis of these experimental results and different reaction mechanisms for Kumada cross-coupling reactions in the related literatures,[24,28-33] a radical mechanism Path **b** was proposed in **Scheme 5**. At first, the precatalyst complex **6** reacted with Grignard reagent to form an intermediate **6a** with one vacant coordination site. The reaction of **6a** and R'-X provided silylene cobalt(II) chloride **6d** with the formation of radical R'· via homolytic cleavage. The combination of R'· with Grignard reagent RMgX furnished radical ·MgX and the final product R-R'. The last step is the reaction of radical ·MgX with **6d** to deliver the byproduct MgX_2 with the recovery of the real catalyst **6a**.

The structure of intermediate **6d** was determined by single crystal X-ray diffraction (**Figure 4**). The central Co atom has a penta-coordinated geometry. The τ_5 value (0.464) indicates that the molecular structure of **6d** is a little bit more like tetragonal pyramid.[25] The Co1–Cl1 bond distance is 2.4050(10) Å. As complexes **5** and **6**, the Co-Si$_{silylene}$ distance (Co1-Si2 = 2.164(2) Å) is shorter than the Co-Si$_{silyl}$ distance (Co1-Si1 = 2.260(2) Å) due to the back-bonding from Co to Si$_{silylene}$.

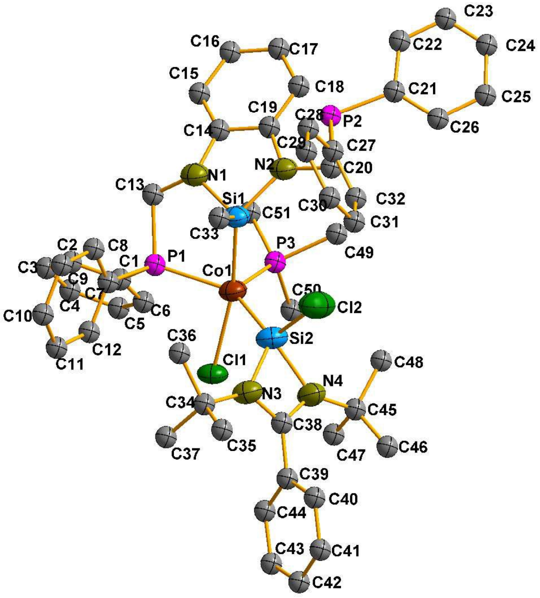


Figure 4. Molecular structure of complex **6d**. ORTEP plot of complex **6d** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1-Cl1 2.405(1), Co1-P1 2.210(1), Co1-P3 2.202(2), Co1-Si1 2.260(1), Co1-Si2 2.164(2); Si2-Co1-P1 137.90(6), Si2-Co1-P3 118.41(7), P3-Co1-P1 103.42(6), Si1-Co1-Cl1 165.73(5).

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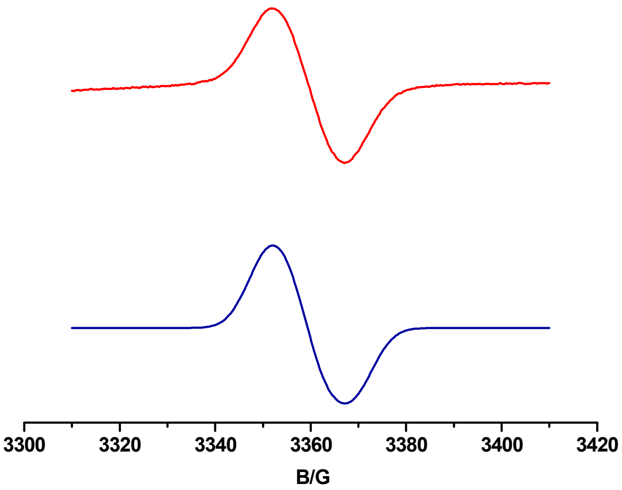

Figure 5. The EPR spectrum of **6d** (top) and simulation (bottom). $g = 2.002$.

Solution of intermediate **6d** in *n*-pentane, where the five-coordinate silylene cobalt(II) chloride is expected to dominate, yielded X-band EPR spectrum at room temperature (**Figure 5**). The EPR spectrum, centered at $g = 2.002$, was moderately narrow (fwhh ≈ 20 G) without resolved hyperfine interactions, as expected for strongly delocalized spin systems. It does, however, provide further evidence that the rotated cobalt in complex **6d** is cobalt(II) atom. This result is also consistent with the computational study of complex **6d**.

Conclusion

In summary, the first silylene hydrido Co(III) complex **6** was synthesized by the reaction of 1,3-siladiazoles $HSiMe(NCH_2PPh_2)_2C_6H_4$ (**1**) with the electron-rich NHSi Co(I) chloride **5** via the chelate-assisted Si-H activation. We also have successfully demonstrated that chlorosilylene **4** is an excellent ligand for cobalt center in comparison with the phosphine ligands. The coordination ability of **4** was so strong that the [PSiP] pincer coordination mode was destroyed and became a common chelating coordination with one arm free. Compared with the related complex **3** supported only by trimethylphosphine, complex **6** as catalyst supported by both chlorosilylene and trimethylphosphine exhibited the more efficient performance for

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the Kumada cross-coupling reactions. A novel catalytic radical mechanism was suggested and experimentally verified. As an intermediate silylene cobalt(II) chloride **6d** was isolated and structurally characterized.

Experimental section

General procedures and materials. All air sensitive and volatile materials were processed using standard vacuum techniques. *n*-Pentane, diethyl ether, THF and toluene were dried according to known methods and distilled under nitrogen prior to use. $CoCl(PMe_3)_3$,[34] chlorosilylene,[35] $HSiMe(NCH_2PPh_2)_2C_6H_4$[36] and complex **3**[37] were prepared according to the literature methods. The Grignard reagents were prepared by reacting the corresponding aryl bromide and magnesium in THF according to the known methods[4] and were titrated before use. All of the aryl halides were freshly distilled. Infrared spectra (4000-400 cm^{-1}) were obtained from Nujol mulls between KBr disks and recorded on a Bruker ALPHA FT-IR instrument. ^{1}H, $^{13}C\{1H\}$, $^{31}P\{1H\}$, and $^{29}Si\{1H\}$ NMR spectra were recorded using Bruker Avance 300 MHz, 400 MHz, 500 MHz and 600 MHz spectrometers. GC was tested with *n*-dodecane as an internal standard. Elemental analyses were carried out on an Elementar Vario ELIII.

Synthesis of complex 5. A solution of $CoCl(PMe_3)_3$ (0.60 g, 1.86 mmol) in diethyl ether (40 mL) was added slowly to a solution of chlorosilylene **4** (1.11 g, 3.72 mmol) in diethyl ether (40 mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred for 8 h to get a brown solution. After filtration, red crystals of **5** were obtained from the diethyl ether solution at -20℃. Yield: 1.52 g (98%). Dec. >168 ℃. $C_{36}H_{64}Cl_3CoN_4P_2Si_2$ (836.34 g/mol): calcd. C 51.70, H 7.71, N, 6.70; found C 52.19, H 7.47, N 6.26. IR (Nujol mull, KBr, cm^{-1}): 3056 ν(H-C=C), 1521 ν(C=C), 943 $\rho(PCH_3)$. ^{1}H NMR (300 MHz, C_6D_6, 298 K, ppm): 0.84 (s, 36H, $C(C\mathit{H}_3)_3$), 0.87 (s, 18H, $P(C\mathit{H}_3)_3$, 6.99 - 7.10 (m, 10H, Ar-*H*). ^{31}P NMR (121 MHz, C_6D_6, 298 K, ppm): 25.6 (s). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): 14.1 ($C(CH_3)_3$); 22.5 ($P\boldsymbol{C}H_3$); 29.0 ($C(\mathit{C}H_3)_3$); 32.8 ($P\mathit{C}H_3$); 51.1 ($\mathit{C}(CH_3)_3$); 53.1

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($C(CH_3)_3$); 125.1 (C_{arom}), 125.6 (C_{arom}), 126.4 (C_{arom}), 127.2 (C_{arom}), 128.5 (C_{arom}), 129.0 (C_{arom}), 129.3 (C_{arom}), 129.6 (C_{arom}), 140.7 (N*C*N), 152.8 (N*C*N). ^{29}Si NMR (79.45 MHz, C_6D_6, 298 K, ppm): 30.0 (s).

Synthesis of complex 6. A solution of $HSiMe(NCH_2PPh_2)_2C_6H_4$ (**1**) (0.90 g, 1.64 mmol) in THF (30 mL) was added slowly to a solution of complex **5** (1.37 g, 1.64 mmol) in THF (30 mL) at -78 °C. The reaction mixture was allowed to stir for 18 h at room temperature. The solvents were removed under vacuum condition. The residue was extracted with 30 mL of diethyl ether and filtered. Yellow crystals of **6** were obtained at 0 ℃. Yield: 1.52 g (92%). m.p.: 137 - 138 ℃. $C_{51}H_{64}Cl_2CoN_4P_3Si_2$ (1012.03 g/mol): calcd. C 60.53, H 6.37, N 5.54; found C 59.97, H 6.65, N 5.26. IR (Nujol mull, KBr, cm^{-1}): 3056 ν(H-C=C), 1917 ν(H-Co), 948 ρ(PCH_3). ^{1}H NMR (300 MHz, C_6D_6, 298 K, ppm): -12.49 (dd, $^2J_{P,H}$ = 57 Hz, $^2J_{P,H}$ = 18 Hz, 1H, Co-*H*), 0.81 (s, 3H, SiCH_3), 0.91 (s, 18H, $C(CH_3)_3$), 1.19 (d, $^2J_{P,H}$ = 6 Hz, 9H, $P(CH_3)_3$), 4.15 (m, 2H, CH_2), 4.45 (m, 2H, CH_2), 6.54 - 7.12 (m, 20H, Ar-H), 7.68 - 8.15 (m, 9H, Ar-H). ^{31}P NMR (121 MHz, C_6D_6, KBr, ppm): -6.0 (s, 1P, $P(CH_3)_3$), 13.3 (s, 1P, *P*Ph_2), 77.9 (s, 1P, *P*Ph_2). ^{13}C NMR (150 MHz, C_6D_6, δ/ppm): 29.8 (Si*C*H3), 30.8 ($C(CH_3)_3$), 31.2 (PCH_3), 46.6 (CH_2), 53.9 (CH_2), 55.0 ($C(CH_3)_3$), 127.9 (C_{arom}), 128.1 (C_{arom}), 128.1 (C_{arom}), 128.3 (C_{arom}), 128.3 (C_{arom}), 128.4 (C_{arom}), 129.5 (C_{arom}), 129.8 (C_{arom}), 130.5 (C_{arom}), 133.6 (C_{arom}), 133.7 (C_{arom}), 134.5 (C_{arom}), 134.6 (C_{arom}), 134.7 (C_{arom}), 134.7 (C_{arom}),141.7 (N*C*N). ^{29}Si NMR (79.45 MHz, C_6D_6, δ/ppm): 10.0 (m, Si^{II}), 68.1 (m, Si ^{IV}).

Synthesis of complex 6d. Chlorobenzene (0.048 g, 0.38 mmol) was added slowly to a solution of complex **6** (0.39 g, 0.38 mmol) in THF (30 mL) at -78 °C. A solution of Cs_2CO_3 (0.25 g, 0.76 mmol) in THF (30 mL) was then added to the above mixture. The reaction mixture was allowed to stir for 18 h at room temperature. THF was removed under vacuum condition. The residue was extracted with 30 mL of diethyl ether and filtered. Yellow crystals of **6d** were obtained at 0 ℃. Yield: 0.58 g (60%).

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m.p.: 127 - 128 ℃. $C_{51}H_{63}Cl_2CoN_4P_3Si_2$ (1011.02 g/mol): calcd. C 60.59, H 6.28, N 5.54; found C 60.87, H 6.69, N 5.32. IR (Nujol, KBr, cm^{-1}): 3052 ν(H-C=C), 948 $\rho(PCH_3)$.

Representative experimental procedure for the Kumada cross-coupling reaction. Under a nitrogen atmosphere, chlorobenzene (0.106 g, 1.00 mmol) was weighed into a 20 mL Schlenk tube containing a magnetic stirrer and complex **6** (1 mL, 0.02 mmol/mL in THF). (4-Methylphenyl)magnesium bromide (1 mL, 1.23 mmol/mL in THF) was slowly dripped into the tube. The reaction mixture was stirred at 50 °C for 48 h. After cooling, the mixture was quenched with 6 mL of H_2O. The product was extracted with 50 ml diethyl ether for three times and dried over Na_2SO_4. After filtration, volatile materials were evaporated in vacuo. The crude product was purified by column chromatography over silica gel with a mixture of petroleum ether and ethyl acetate (200 : 1) as eluent to provide the product.

X-ray Structure Determination. Intensity data were collected on a Stoe Stadi Vari (**5**), Bruker P4 (**6**) or STOE IPDS2 (**6d**) diffractometer. Using Olex2,[38] the structure was solved with the ShelXS[39] structure solution program using Direct Methods and refined with the ShelXL[40] refinement package using Least Squares minimization. CCDC-1551142 (**5**), 1548758 (**6**) and 1560796 (**6d**) contain supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the website at DOI: .... The table of selected crystallographic data and original IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR and ^{29}Si NMR spectra of complexes **5, 6, 6d** and coupling products.

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TOC

Synthesis and Catalytic Activity of N-Heterocyclic Silylene (NHSi) Cobalt Hydride for Kumada Coupling Reactions

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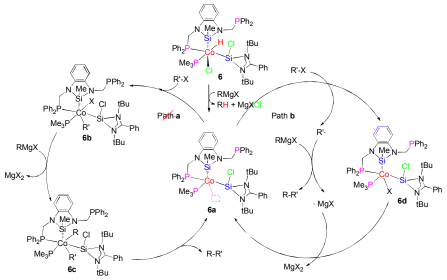

The first silylene Co(III) hydride **6**, an efficient catalyst for Kumada cross-coupling reactions, was prepared via Si-H activation.