Synthesis and structure of silylene iron complex

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Dedicated to Professor Dieter Fenske on the occasion of his 80th birthday.

Four phosphorus-chalcogen chelated hydrido iron(II) complexes **5**–**8** (*o*-(Ph_2P)-*p*-R-C_6H_4Y)Fe(H)(PMe_3)$_3$ (**5**: R=H, Y=S; **6**: R=Me, Y=S; **7**: R=H, Y=O and **8**: R=Me, Y=O) were used to synthesize the corresponding silylene hydrido iron(II) complexes. It was found that complexes **5**–**6** reacted with chlorosilylene **1** to give the silylene iron(II) hydrides **9**–**10** as ligand replacement products of trimethylphosphine by chlorosilylene **1**. Under the same reaction conditions, complex **7** or **8** reacted with chlorosilylene **1** to afford a disilylene iron(I) chloride **11**. Complex **11** can also be synthesized through the reaction of Fe(PMe_3)$_4$ with chlorosilylene **1**. The molecular structures of complexes **9**–**11** were determined by single crystal X-ray diffraction analysis.

Introduction

Silylenes, the heavier congeners of carbenes, have unique σ-donating/π-accepting and steric hindrance properties. Transition metal (TM) complexes containing silylene ligands not only exhibit rich diversity in coordination chemistry, such as coordination modes, spatial properties and electronic structures, but also exhibit high catalytic activity in organic synthesis and homogeneous catalysis. In recent years, the design and synthesis of novel stable silylene ligands and the construction of their metal complexes have attracted more and more attention.[1]

Since roesky reported the synthesis of chlorosilylene ligand **1** in 2006,[2] clochlorosilene ligand **1** has been used as a monodentate ligand and applied in the coordination chemistry of transition metals, such as the construction of silylene complexes of Fe,[3] Ti,[4] Cr, Mo, W,[5] Mn, Re[6] and Cu.[7]

Recently, our research group synthesized silylene Co(I) chloride **2** and silylene Co(III) hydride **4** respectively (Scheme 1 >). It was found that silylene Co(III) hydride **4** is a better catalyst for Kumada cross-coupling reactions compared with the Co(III) hydride supported only by trimethylphosphine ligands.[8]

We designed and prepared several [P, S]/[P, O] chelate iron(II) hydrides supported by trimethylphosphine ligands. The experiments indicate that these iron hydrides can catalyze hydrosilylation reactions of aldehydes/ketones and dehydration of amides to form nitriles.[9] In order to study the influence of introduction of silylene ligand on property of iron hydride, the reactions of complexes **5**–**8** with chlorosilylene **1** were investigated and the corresponding silylene iron complexes **9**–**11**

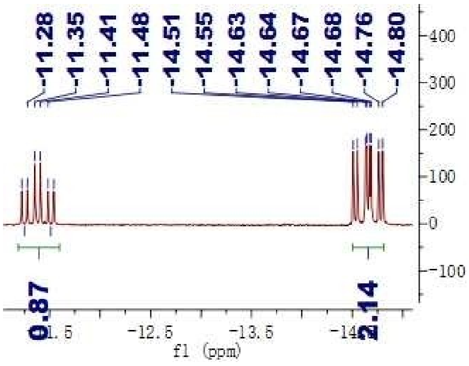

Figure 1. The hydrido signal of complexes **9** and **9a**

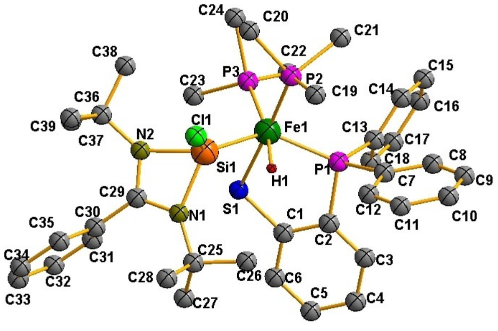

Figure 2. Molecular structure of complex **9**. Most hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1–H1 1.56(2), Fe1–P1 2.2227 (5), Fe1–P2 2.1989(5), Fe1–P3 2.2496(5), Fe1–Si1 2.1709(5), Fe1–S1 2.3295(5); P2–Fe1–S1 177.14(2), Si1–Fe1–H1 60.1(9), P1–Fe1–P3 107.08(2), Si1–Fe1–P3 110.15(2), P1–Fe1–H1 81.4(9).

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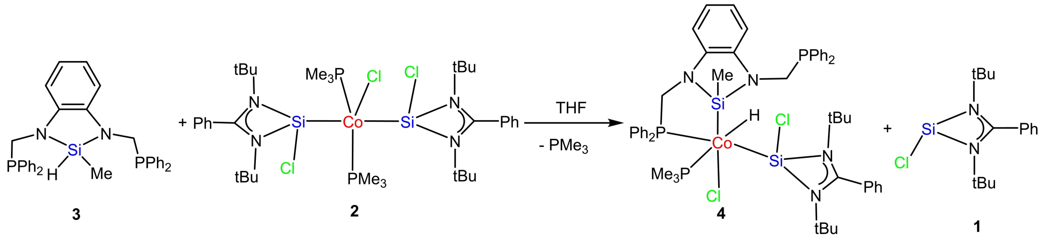


Scheme 1. Synthesis of silylene Co complexes **2** and **4**.

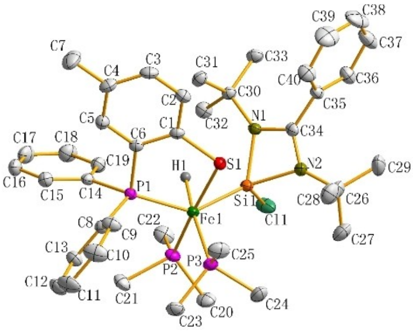


Figure 3. Molecular structure of complex **10**. Most hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1—H1 1.48(2), Fe1—P1 2.2128 (5), Fe1—P2 2.1991(5), Fe1—P3 2.2530(5), Fe1—Si1 2.1926(5), Fe1—S1 2.3258(5); P2—Fe1—S1 173.34(2), Si1—Fe1—H1 88.0(8), P1—Fe1—P3 101.77(2), Si1—Fe1—P3 113.05(2), P1—Fe1—H1 61.8(7).

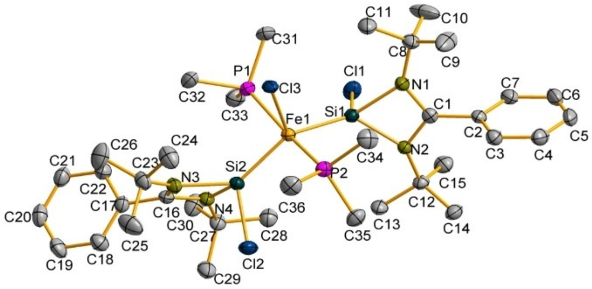
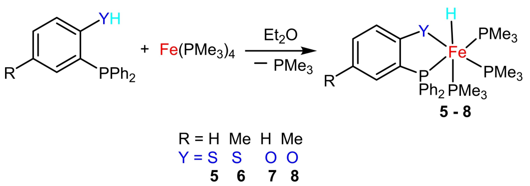


Figure 4. Molecular structure of complex **11**. ORTEP plot of complex **11** at the 50 % probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Fe1—Cl3 2.4168(9), Fe1—P1 2.2305(9), Fe1—P2 2.2256(9), Fe1—Si1 2.1854(10), Fe1—Si2 2.1827(10); Si2—Fe1—Cl3 111.36(4), Si2—Fe1—Si1 138.76(4), Si1—Fe1—Cl3 109.88(3), P2—Fe1—P1 165.01(4).



Scheme 2. Synthesis of iron hydride **5**–**8**.

were isolated and characterized. The mechanism of formation of complex **11** was discussed.

Results and Discussion

According to early reported method,[9] four phosphorus-chalcogene chelated hydrido iron (II) complexes **5**–**8** were synthesized via Y—H activation (Scheme 2).

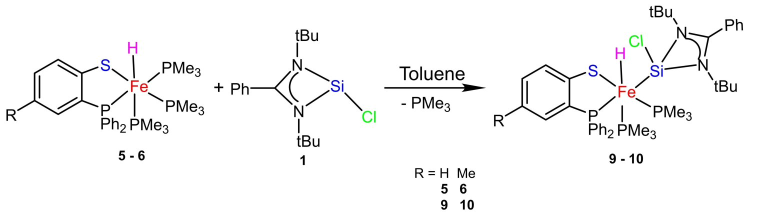
1. Reactions of phosphorus-thiophenolato hydrido iron(II) complexes 5–6 with chlorosilylene 1

The reactions of hydrido iron complexes **5**–**6** with chlorosilylene **1** in toluene resulted in the formation of silylene hydrido iron(II) complexes **9** and **10** as orange red crystals in the yields of 49 % (**9**) and 31 % (**10**), respectively (Scheme 3). Silylene iron complexes **9** and **10** are the ligand replacement products of trimethylphosphine by chlorosilylene **1**. Complexes **9** and **10** were completely characterized by spectroscopic methods. The molecular structures of complexes **9** and **10** were confirmed by single crystal X-ray diffraction analysis.

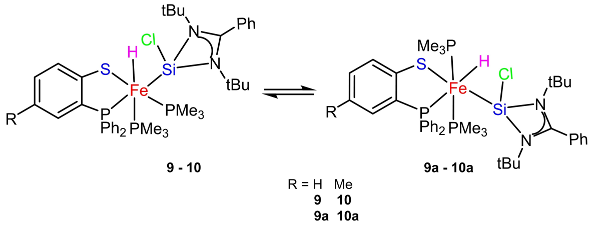
In the IR spectrum of complex **9** the Fe—H vibration is registered at 1875 cm^{-1}. Compared with the infrared signal of Fe—H of complex **5** without silylene ligand at 1845 cm^{-1}, this is a hyperchromic shift.[9a] In the ^1H NMR spectrum of complex **9**, the hydrido signal has two peak shapes, a ddd peak at −14.66 ppm and a td peak at −11.38 ppm, respectively. The integral ratio of the two peaks is about 2. : 1 (Figure 1).

After careful study, we found that the ^1H NMR signals of other groups of complex **9** can also be divided into two groups, with an integral ratio of 2:1. Similarly, the ^{31}P and ^{29}Si NMR spectra of complex **9** also have two groups of signals with an integral ratio of about 2:1. All this information explains that complex **9** is unstable in solution and exists in two isomers of **9** and **9a** (Scheme 4). The ratio of **9** and **9a** is about 2:1 in solution.

In the ^1H NMR spectrum, one group of the signals belongs to complex **9**. The hydrido signal of complex **9** appears at -14.66 ppm as a ddd peak coupled by three P atoms with the coupling constants of 40, 36 and 12.5 Hz. These data are very close to the literature values.[10] The signals of two *tert*-butyl groups in the chlorosilylene ligand as singlets are situated at 1.53 and 1.31 ppm, respectively. The signals of H atoms in the

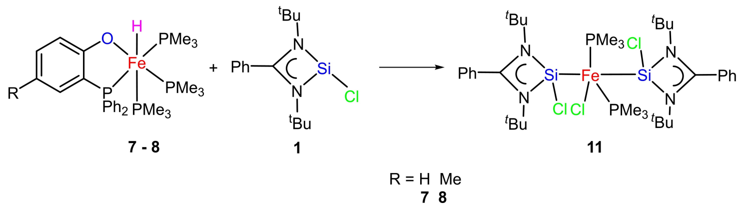


Scheme 3. Synthesis of complexes **9**–**10**.

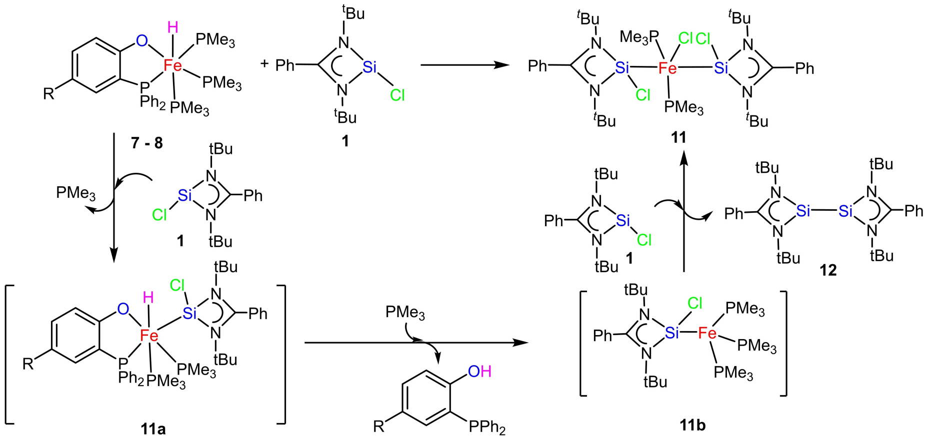


Scheme 4. Isomerization of complexes **9** and **10**.

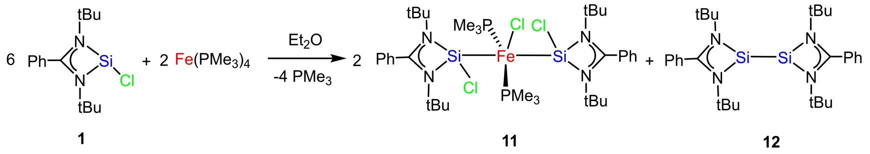
two PMe_3 ligands are split into doublets at 1.50 and 1.25 ppm, respectively, and the coupling constants are 9.0 and 6.0 Hz. In the ^{31}P NMR spectrum, there are three groups of phosphorus signals at 93.3 ppm, a ddd peak with the coupling constants of 27, 11 and 3 Hz; at 30.0 ppm, a ddd peak with the coupling constants of 54, 27 and 2 Hz; at 6.4 ppm, a dd peak with the coupling constants of 54 and 11 Hz. The integral ratio of the three groups of peaks is 1:1:1. In the ^{29}Si NMR spectrum of **9**, a multiplet at 24.8 ppm was formed under the influence of P



Scheme 5. Synthesis of complex **11**.



Scheme 6. Proposed formation mechanism of **11**.



Scheme 7. Direct synthesis of complex **11**.

atoms. The chemical shift value has an upfield shift in comparison with the corresponding value of bis(silylene) iron hydride,[10] which indicates that the electron cloud density on the silicon atom in complex **9** is relatively large. Another set of signals belongs to isomer complex **9a**. The hydrido signal as a td peak is at -11.38 ppm with the coupling constants of 39 and 17 Hz. This illustrates that two PMe_3 ligands have the same chemical environment in complex **9a**. In addition, three P signals (1:1:1) as dd peaks were registered at 95.0 ppm with the coupling constants of 47 and 8 Hz, at 26.9 ppm with the coupling constants of 47 and 26 Hz; at 8.6 ppm with the coupling constants of 26 and 9 Hz, respectively. In the ^{29}Si NMR spectrum of complex **9a**, a multiplet at 10.5 ppm was found.

The molecular structure of complex **9** was further confirmed by single crystal X-ray diffraction analysis (Figure 2). The iron atom is located in the center of the distorted octahedron configuration. The bond length of Fe–H bond is 1.56 (2) Å, which is in the normal range of Fe–H bond lengths. If the axial position is P2–Fe1–S1 with the bond angle of 177.14 (2)°, close to 180 °, P3, Si1, H1 and P1 atoms form the equatorial plane. The sum of coordination bond angles centered on Fe atom in the plane is 358.8°, deviated from 360°. The bond length of Fe1–Si1 (2.1709 Å) is within the normal range (2.15–2.37 Å) of $Fe{-}Si_{silylene}$ bonds.[10,11]

Like complex **9**, the solid of complex **10** is very stable in air. Similarly, we also carried out complete spectroscopic characterization and single crystal structure analysis of complex **10**. In the IR spectrum of complex **10**, the stretching vibration of Fe–H bond is at 1838 cm^{-1}. This is bathochromic shift in comparison with the Fe–H signal of complex **9.** The NMR signals of complex **10** are similar to those of complex **9**. There is also isomerization for complex **10** in the solution (Scheme 4), and the ratio of the two isomers in the solution is also 2:1. Single crystal X-ray diffraction analysis confirms that the molecular structure of complex **10** is similar to that of complex **9** (Figure 3). The bond length of Fe1–P3 (2.2530(5) Å) is slightly longer than that of Fe1–P1 (2.2128(5) Å) and Fe1–P2 (2.1991(5) Å), which can be attributed to the strong *trans*-influence of the hydrido ligand. The lengths of Fe–Si and Fe–H bonds of complex **10** are comparable with those of complex **9**.

2. Reactions of phosphorus-phenolato hydrido iron(II) complexes 7–8 with chlorosilylene 1

Unlike complexes **5** and **6**, complex **7** or **8** reacted with chlorosilylene **1** under the same reaction conditions without substitution reaction, but formed a penta-coordinated bissilylene iron(I) complex **11** (Scheme 5). Complex **11** is paramagnetic. The molecular structure of complex **11** was determined by single crystal X-ray diffraction analysis (Figure 4). In the molecular structure of complex **11**, the central Fe atom forms a penta-coordinated distorted triangular bipyramidal geometry with two Si(II) atoms, two P atoms and one Cl atom on five vertices. The two P atoms are in the axial position, and the P2–Fe1–P1 bond angle is 165.01(4)° with a deviation of 180°. The axial direction is basically perpendicular to the equatorial plane determined by Fe1, Si1, Si2 and Cl3 atoms. The sum of the coordination bond angles (Si2–Fe1–Cl3 = 111.36(4)°, Si2–Fe1–Si1 = 138.76(4)° and Si1–Fe1–Cl3 = 109.88(3)°) on the equatorial plane is exactly 360°. This shows that the coplanarity of the four atoms (Fe1Si1Si2Cl3) is very good. Due to the π-backdonation from Fe to $Si_{silylene}$ atoms, the bond lengths of the two Fe–Si(II) (Fe1–Si1 = 2.1854(10) and Fe1–Si2 = 2.1827(10) Å) are significantly shorter than the reported Fe–Si(IV) bond lengths (2.2643 ~ 2.331 Å).[12] The bond length of Fe1–Cl3 (2.4168(9) Å) is slightly longer than that of Co–Cl bond in similar compound of cobalt (2.4025(8) Å).[8]

The possible mechanism of formation of complex **11** is proposed in Scheme 6. Ligand replacement of PMe_3 of complex **7** or **8** by chlorosilylene **1** gives rise to intermediate **11a**. Reductive elimination of **11a** affords Fe(0) intermediate **11b** with the release of the chelate ligand 2-(diphenylphosphanyl)phenol. It is believed that compared with complexes **9**–**10**, the electronegativity of O atom in complex **11a** is larger. In addition, chlorosilylene **1** is a good π-acceptor. These two factors lead to instability of intermediate **11a** due to the lack of electrons at central iron atom, so the reductive elimination reaction occurs. The iron(0) intermediate **11b** is unstable and transfers to Fe(I) complex **11** in the presence of chlorosilylene **1** via single electron oxidative addition with the formation of bissilylene **12** as byproduct. The formation of bissilylene **12** was confirmed by GC-MS. It was found that bissilylene iron(I) complex **11** could also be obtained from the reaction of chlorosilylene **1** with $Fe(PMe_3)_4$ with **12** as byproduct (Scheme 7).

In order to study the catalytic activity of iron hydride after the introduction of silylene, we preliminarily explored the catalytic activity of complexes **9**–**10** for the hydrosilylation of aldehydes and ketones. The results show that under the same catalytic conditions, the activity of silylene complexes **9**–**10** is very poor and the conversions are less than 20% compared with the corresponding phosphine complexes **5**–**6**. We will further study the catalytic activity of silylene complexes **9**–**10** for other synthetic reactions.

Conclusions

Four phosphorus-chalcogen chelated hydrido iron(II) complexes **5**–**8** (o-(Ph_2P)-p-R-C_6H_4Y)Fe(H)(PMe_3)$_3$ (**5**: R=H, Y=S; **6**: R=Me, Y=S; **7**: R=H, Y=O and **8**: R=Me, Y=O) were used to synthesize the corresponding silyene hydrido iron(II) complexes. Complexes **5**–**6** reacted with chlorosilylene **1** to give rise to the silyene iron hydrides **9**–**10** as ligand replacement products of trimethylphosphine by chlorosilylene while complex **7** or **8** reacted with chlorosilylene **1** under the same reaction conditions to deliver complex **11**, a disilylene iron(I) chloride. Complex **11** can also be obtained from the reaction of $Fe(PMe_3)_4$ with chlorosilylene **1**. The formation mechanism of complex **11** was proposed. The molecular structures of complexes **9**–**11** were determined by single crystal X-ray diffraction analysis.

Experimental Section

General procedures and materials: Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were 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 and 400 MHz spectrometers. GC was tested with *n*-dodecane as an internal standard. Elemental analyses were carried out on an Elementar Vario ELIII. Fe(PMe$_3$)$_4$,[13] chlorosilylene,[2] and complexes **5**–**8**[9] were prepared according to the literature methods.

Synthesis of complex 9: A solution of chlorosilylene **1** (0.63 g, 2.15 mmol) in toluene (30 mL) was added slowly to a solution of **5** (1.15 g, 2.15 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 16 h to get a red solution. The solvents were removed under vacuum condition. The residue was extracted with 60 mL of pentane and filtered. Orange red crystals of **9** were obtained at −20 °C. Yield: 0.84 g (49 %). $C_{39}H_{56}ClFeN_2P_3SSi$ (797.21 g/mol): calcd. C 58.76, H 7.08, N 3.51; found C 59.17, H 6.95, N 3.26. IR (Nujol mull, KBr, cm^{-1}): 1875 ν(Fe–H), 1612 ν(C=N), 1569, 1521 ν(C=C), 954 ρ(PMe$_3$). Complex **9** is unstable and has isomers in C$_6$D$_6$. The ratio of **9** : **9 a** is 2:1. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K, δ/ppm): 8.47 (m, 6H, Ar–*H*), 8.19–7.98 (m, 7H, Ar–*H*), 7.63 (td, *J* = 8 Hz, 2.0 Hz, 5H, Ar–*H*), 7.38–7.29 (m, 10H, Ar–*H*), 7.14 (t, *J* = 5 Hz, 11H, Ar–*H*), 7.11–6.95 (m, 15H, Ar–*H*), 6.83 (t, *J* = 7 Hz, 1H, Ar–*H*), 6.70 (t, *J* = 7 Hz, 2H, Ar–*H*),1.69 (s, 9H, ^{t}*Bu*) (**9 a**), 1.57 (dd, *J* = 6 Hz, 9H, P*Me*$_3$) (**9 a**), 1.53(s, 18H, ^{t}*Bu*) (**9**), 1.50 (dd, *J* = 9 Hz, 18H, P*Me*$_3$) (**9**), 1.31 (s, 18H, ^{t}*Bu*) (**9**), 1.25 (dd, *J* = 6 Hz, 18H, P*Me*$_3$) (**9**), 1.11 (dd, *J* = 6 Hz, 9H, P*Me*$_3$) (**9 a**), 0.94 (s, 9H, ^{t}*Bu*) (**9 a**), −11.38 (td, *J* = 39 Hz, 17 Hz, 1H, Fe–*H*) (**9 a**), −14.66 (ddd, *J* = 40 Hz, 36 Hz, 12 Hz, 2H, Fe–*H*)(**9**). ^{31}P {^{1}H} NMR (121 MHz, C$_6$D$_6$, 298 K, δ/ppm): 95.0 (dd, *J* = 47 Hz, 8 Hz, 1P, *P*Ph$_2$)(**9 a**), 93.3 (ddd, *J* = 27 Hz, 11 Hz, 3 Hz, 2P, *P*Ph$_2$) (**9**), 30.0 (ddd, *J* = 54 Hz, 27 Hz, 2 Hz, 2P, *P*Me$_3$) (**9**), 26.9 (dd, *J* = 47 Hz, 26 Hz, 1P, *P*Me$_3$) (**9 a**), 8.6 (dd, *J* = 26 Hz, 9 Hz, 1P, *P*Me$_3$) (**9 a**), 6.4 (dd, *J* = 54 Hz, 11 Hz, 2P, *P*Me$_3$) (**9**). ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, 298 K, δ/ppm): 170.8 (N*C*N), 162.6 (*C*arom), 162.1 (*C*arom), 160.9 (*C*arom), 160.4 (*C*arom), 145.8 (*C*arom), 143.2 (*C*arom), 142.8 (*C*arom), 141.4 (*C*arom), 141.0 (*C*arom), 138.7 (*C*arom), 138.0 (*C*arom), 136.8 (*C*arom), 136.6 (*C*arom), 133.8 (*C*arom), 133.7 (*C*arom), 133.5 (*C*arom), 133.2 (*C*arom), 133.0 (*C*arom), 132.1(*C*arom), 131.4 (*C*arom), 130.7 (*C*arom), 129.7 (*C*arom), 129.5 (*C*arom) (*C*arom), 129.1 (*C*arom), 128.0 (*C*arom), 127.8 (*C*arom), 127.4 (*C*arom), 120.5 (*C*arom) (*C*arom), 119.7 (*C*arom), 55.1 (*C*(CH$_3$)$_3$), 54.8 (*C*(CH$_3$)$_3$), 54.4 (*C*(CH$_3$)$_3$), 53.6 (*C*(CH$_3$)$_3$), 32.1 (C(*C*H$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 26.6 (d, *J* = 15 Hz, P(*C*H$_3$)$_3$), 25.8 (d, *J* = 20 Hz, P(*C*H$_3$)$_3$), 23.0 (d, *J* = 20 Hz, P(*C*H$_3$)$_3$), 22.0 (d, *J* = 19 Hz, P(*C*H$_3$)$_3$). ^{29}Si NMR (59.59 MHz, C$_6$D$_6$, 298 K, δ/ppm) δ 24.8 (m, 2Si) (**9**), 10.5 (m, 1Si) (**9 a**).

Synthesis of complex 10: The synthetic method of complex **10** is the same as that of complex **9**. Yield:0.22 g (31 %). $C_{40}H_{58}ClFeN_2P_3SSi$ (811.24 g/mol): calcd. C 59.22, H 7.21, N 3.45; found C 59.46, H 7.35, N 3.27. IR (Nujol mull, cm^{-1}): 1838 ν(Fe–H), 1585, 1529 ν(C=C), 954 ρ(PMe$_3$). ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K, δ/ppm): 8.53 (m, 6H, Ar–*H*), 8.16 (d, *J* = 8 Hz, 2H, Ar–*H*), 8.10–8.03 (m, 2H, Ar–*H*), 7.95 (dd, *J* = 8 Hz, 3 Hz, 2H, Ar–*H*), 7.73–7.61 (m, 4H, Ar–*H*), 7.45–7.31 (m, 10H, Ar–*H*), 7.12–7.02 (m, 18H, Ar–*H*), 6.97–6.86 (m, 10H, Ar–*H*), 2.06 (s, 3H, C*H*$_3$) (**10 a**), 1.96 (s, 6H, C*H*$_3$) (**10**), 1.70 (s, 9H, ^{t}*Bu*) (**10 a**), 1.57 (d, *J* = 9 Hz, 9H, P*Me*$_3$) (**10 a**), 1.54 (s, 18H, ^{t}*Bu*) (**10**), 1.51 (d, *J* = 6 Hz, 18H, P*Me*$_3$) (**10**), 1.34 (s, 18H, ^{t}*Bu*)(**10**), 1.25 (d, *J* = 9 Hz, 18H, P*Me*$_3$) (**10**), 1.12 (d, *J* = 6 Hz, 9H, P*Me*$_3$) (**10 a**), 0.98 (s, 9H, ^{t}*Bu*) (**10 a**), −11.40 (td, *J* = 39 Hz, 18 Hz, 1H, Fe–*H*) (**10 a**), −14.63 (ddd, *J* = 39 Hz, 36 Hz, 15 Hz, 2H, Fe–*H*) (**10**). ^{1}P {^{1}H} NMR (121 MHz, C$_6$D$_6$, 298 K, δ/ppm): 94.9 (dd, *J* = 47 Hz, 8 Hz, 1P, *P*Ph$_2$) (**10 a**), 93.1 (dd, *J* = 26 Hz, 11 Hz, 2P, *P*Ph$_2$) (**10**), 30.1 (dd, *J* = 54 Hz, 26 Hz, 2P, *P*Me$_3$) (**10**), 26.9 (dd, *J* = 47 Hz, 25 Hz, 1P, *P*Me$_3$) (**10 a**), 8.7 (dd, *J* = 25 Hz, 8 Hz, 1P, *P*Me$_3$) (**10 a**), 6.4 (dd, *J* = 54 Hz, 11 Hz, 2P, *P*Me$_3$) (**10**). ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, 298 K, δ/ppm): 171.2 (N*C*N), 171.1 (N*C*N), 159.2 (*C*arom), 158.6 (*C*arom), 157.4 (*C*arom), 156.9 (*C*arom), 146.0 (*C*arom), 143.4 (*C*arom), 143.2 (*C*arom), 142.8 (*C*arom), 141.6 (*C*arom), 141.2 (*C*arom), 136.9 (*C*arom), 136.7 (*C*arom), 134.0 (*C*arom), 133.8 (*C*arom), 133.7 (*C*arom), 133.4 (*C*arom), 133.1 (*C*arom), 133.0 (*C*arom), 132.3 (*C*arom), 132.2 (*C*arom), 131.8 (*C*arom), 130.8 (*C*arom), 130.0 (*C*arom), 129.9 (*C*arom), 129.8 (*C*arom), 129.6 (*C*arom), 129.4 (*C*arom), 129.1 (*C*arom), 128.8 (*C*arom), 128.7 (*C*arom), 128.6(*C*arom), 128.4 (*C*arom), 126.8 (*C*arom), 126.7(*C*arom), 55.2 (*C*(CH$_3$)$_3$), 54.9 (*C*(CH$_3$)$_3$), 54.4 (*C*(CH$_3$)$_3$), 53.6 (*C*(CH$_3$)$_3$), 32.1 (C(*C*H$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 26.6 (d, *J* = 20 Hz, P(*C*H$_3$)$_3$), 25.8 (d, *J* = 20 Hz, P(*C*H$_3$)$_3$), 23.0 (d, *J* = 20 Hz, P(*C*H$_3$)$_3$), 22.0 (d, *J* = 20 Hz, P(*C*H$_3$)$_3$). ^{29}Si NMR (59.59 MHz, C$_6$D$_6$, 298 K, δ/ppm): 24.3 (m, 2Si)(**10**), 9.7 (m, 1Si)(**10 a**).

Synthesis of complex 11: Method a: A solution of chlorosilylene **1** (0.63 g, 2.15 mmol) in toluene (30 mL) was added slowly to a solution of **7** (1.11 g, 2.15 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 16 h to get a dark-red solution. The solvents were removed under vacuum condition. The residue was extracted with 40 mL of diethyl ether and filtered. Red crystals of **11** were obtained at 0 °C. 0.40 g (0.44 mmol, 20 %). Complex **11** can also be synthesized through the reaction of chlorosilylene **1** with **8**. $C_{36}H_{64}Cl_3FeN_4P_2Si_2 \cdot C_4H_{10}O$ (907.35 g/mol): calcd. C 52.95, H 8.22, N 6.17; found C 53.16, H 8.35, N 3.27. IR (Nujol mull, KBr, cm^{-1}): 1615 ν(C=N), 1522 ν(C=C), 941 ρ(PCH$_3$). **Method b**: A solution of Fe(PMe$_3$)$_4$ (0.60 g, 1.67 mmol) in diethyl ether (40 mL) was slowly added to a solution of chlorosilylene **1** (1.47 g, 5.01 mmol) in diethyl ether (40 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 24 h to get a dark-red solution. The solvents were removed under vacuum condition. The residue was extracted with 30 mL of pentane and 60 mL of diethyl ether. Red crystals of **11** were obtained at 0 °C. 0.95 g (1.05 mmol, 63 %).

X-ray Crystal Structure Determinations: Single crystal X-ray diffraction data of complexes **9**–**11** were collected on a STOE STADIVARI Cu (λ = 1.54186 Å) or XtaLAB Synergy, Dualflex, HyPix Mo (λ = 0.71073 Å) or Stoe StadiVari Mo (λ = 0.71073 Å) diffractometers. Using Olex2,[14] the structure was solved with ShelXS[15] structure solution program using Direct Methods and refined with the ShelXL[16] refinement package using Least Squares minimization. CCDC 1561101 (**9**), 1851883 (**10**) and 2154120 (**11**) 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).

Acknowledgements

We gratefully acknowledge the support by the natural science foundation of Shandong province ZR2019MB065/ZR2021MB010.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: silylene iron hydride · N-heterocyclic silylene · thiophenolato iron(II) complex · phenolato iron(II) complex

[1] a) S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.* **2012**, *3*, 659; b) B. Blom, D. Gallego, M. Driess, *Inorg. Chem. Front.* **2014**, *1*, 134; c) L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez, D. Polo, *Coord. Chem. Rev.* **2015**, *300*, 1; d) S. Raoufmoghaddam, Y.-P. Zhou, Y. Wang, M. Driess, *J. Organomet. Chem.* **2017**, *829*, 2; e) Y.-P. Zhou, M. Driess, *Angew. Chem.* **2019**, *131*, 2.

[2] a) C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem. Int. Ed.* **2006**, *45*, 3948; b) S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123.

[3] B. Blom, S. Enthaler, S. Inoue, E. Irran, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 6703.

[4] B. Blom, M. Driess, D. Gallego, S. Inoue, *Chem. Eur. J.* **2012**, *18*, 13355.

[5] R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *J. Am. Chem. Soc.* **2012**, *134*, 2423.

[6] R. Azhakar, S. P. Sarish, H. W. Roesky, J. Hey, D. Stalke, *Inorg. Chem.* **2011**, *50*, 5039.

[7] G. Tan, B. Blom, D. Gallego, M. Driess, *Organometallics* **2014**, *33*, 363.

[8] X. Qi, H. Sun, X. Li, O. Fuhr, D. Fenske, *Dalton Trans.* **2018**, *47*, 2581.

[9] a) B. Xue, H. Sun, X. Li, *RSC Adv.* **2015**, *5*, 52000; b) K. Li, H. Sun, W. Yang, Y. Wang, S. Xie, X. Li, O. Fuhr, D. Fenske, *Appl. Organomet. Chem.* **2020**, e5337.

[10] S. Li, Y. Wang, W. Yang, K. Li, H. Sun, X. Li, O. Fuhr, D. Fenske, *Organometallics* **2020**, *39*, 757.

[11] X. Qi, T. Zheng, J. Zhou, Y. Dong, X. Zuo, X. Li, H. Sun, O. Fuhr, D. Fenske, *Organometallics* **2019**, *38*, 268.

[12] a) S. Wu, X. Li, Z. Xiong, W. Xu, Y. Lu, H. Sun, *Organometallics* **2013**, *32*, 3227; b) Z. Xiong, X. Li, S. Zhang, Y. Shi, H. Sun, *Organometallics* **2016**, *35*, 357.

[13] H. H. Karsch, *Chem. Ber.* **1977**, *110*, 2699.

[14] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

[15] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[16] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3.