An Air-Stable N-Heterocyclic [PSiP] Pincer Iron Hydride and an Analogous Nitrogen Iron Hydride: Synthesis and Catalytic Dehydration of Primary Amides to Nitriles

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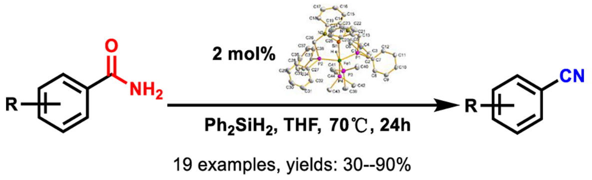


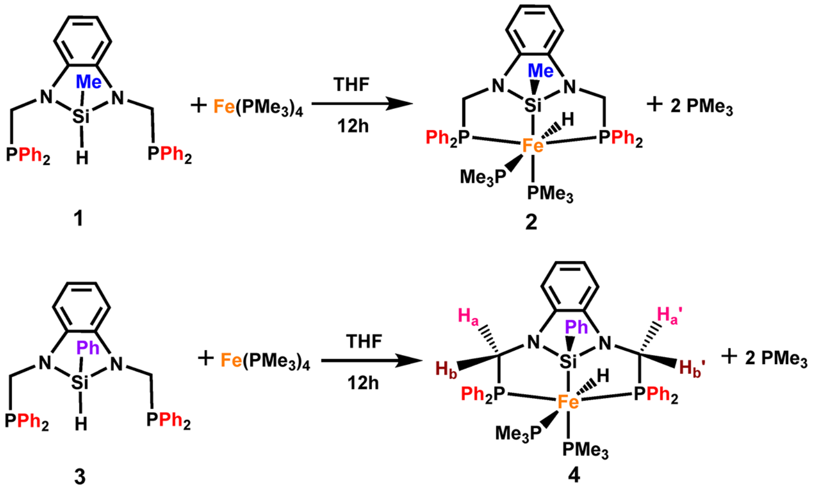
ABSTRACT: An air stable N heterocyclic PSiP pincer iron hydride $\mathrm{FeH(PMe_3)_2(SiPh(NCH_2PPh_2)_2C_6H_4)}$ (**4**) was synthesized by Si−H activation of a Ph substituted [PSiP] pincer ligand. The analogous strong electron donating ^{i}Pr substituted [PSiP] pincer ligand was prepared and introduced into iron complex to give an iron nitrogen complex $\mathrm{FeH(N_2)(PMe_3)(SiPh(NCH_2P^{i}Pr_2)_2C_6H_4)}$ (**6**). Both **4** and **6** showed similar high efficiency for catalytic dehydration of primary amides to nitriles. Air stable iron hydride **4** was the best catalyst for its stabilization and convenient preparation. A diverse range of cyano compounds including aromatic and aliphatic species was obtained in moderate to excellent yields. A plausible catalytic reaction mechanism was proposed.

■ INTRODUCTION

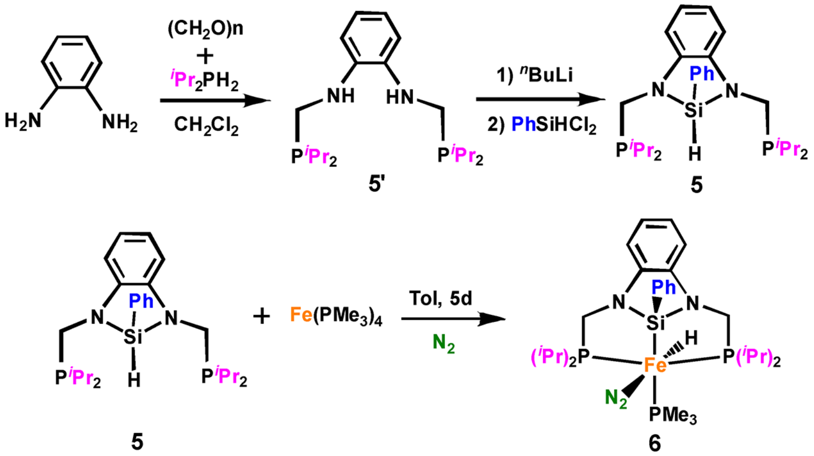
Pincer complexes have attracted extensive attention among transition metal complexes, for their excellent potential application in catalytic reactions.[1] These complexes permit the activation of small molecules without changing the structures.[2] This makes them ideal for developing efficiently catalytic systems based on earth abundant and environmentally friendly metals, such as Fe, Co, Ni, etc. In a variety of pincer complexes, cyclometalated phosphine based [PSiP] pincer complexes[3] are remarkable owing to silicon atom as a superior donor. The coordination of Si atom can stabilize higher oxidation states of the metal center and labilize coordinatively unsaturated species through strong *trans* influence. Almost all the research on [PSiP] pincer complexes is around the same rigid ligand skeleton, $(2\ \mathrm{R_2}\mathit{P}\mathrm{C_6H_4})_2\mathit{Si}\mathrm{R}$, and focuses on the precious transition metals. The study related to base transition metals, especially abundant element Fe, is relatively rare. In 2017, Nishibayashi reported an iron nitrogen complex bearing the [PSiP] pincer ligand, $(2\ \mathrm{Cy_2}\mathit{P}\mathrm{C_6H_4})_2\mathit{Si}\mathrm{R}$, toward nitrogen fixation.[4] After one year, Turculet utilized the same [PSiP] pincer ligands to synthesize novel iron hydrides for catalytic hydrogenation of alkenes.[5] Our group has also made some breakthroughs in this field by means of the similar [PSiP] pincer ligands to realize transfer hydrogenation of aldehydes.[6] It is worth noting that [PSiP] pincer complexes have multitudinous variations in the electronic and steric features of both axial and equatorial donors. These characteristics have potential utility in catalysis.

The nitrile functional groups are privileged functionality for synthesis of pharmaceuticals, agrochemicals, and polymers.[7] Accordingly, selective introduction of nitrile groups into molecules is of great interest to the synthetic organic chemists. One popular approach has been the dehydration of primary amides to nitriles utilizing dehydrating reagents. Acetonitrile has been widely explored as a dehydrating reagent. Recent major advances in this area include the development of different catalysts, such as phosphine oxide, palladium compounds, and dimethyl sulfoxide (DMSO).[8−11] Nevertheless, silanes as the other type of dehydrating reagent have attracted more and more attention, because the activity of various transition metal complexes to insert into the Si−H bonds permits the formation of electrophilic silicon species and hydrides, acting as reactive intermediates to promote the dehydration of primary amides and to generate hydrogen gas to facilitate the catalytic processes.[12] In 2008 the first silane based dehydration of primary amides was reported by Nagashima using a triruthenium carbonyl complex as the catalyst and bifunctional organosilane 1,2 bis(dimethylsilyl) ethane as the dehydrating reagent.[13] After that, other transition metal complexes, in particular, base transition metal complexes, were widely used as efficient catalysts for the dehydration of primary amides to nitriles with the assistance of silane. Darcel and Sortais reported the synthesis and activity of NHC containing Knolker type iron complexes toward the dehydration of primary amides with the inexpensive poly(hydromethylsiloxane) (PMHS) as dehydrating reagents.[14] Buchwald and co workers disclosed a copper(II)

Scheme 1. Synthesis of Iron Hydrides 2 and 4



Scheme 2. Synthesis of the Iron Nitrogen Hydride 6



catalyzed reaction under mild and efficient conditions for the dehydration of amides with dimethoxymethylsilane (DMMS).[15] We presented that the hydrido thiophenolato iron(II) catalyzed dehydration of primary amides could be achieved at lower temperature (60 °C) in the presence of triethoxysilane.[16] Soon afterward, it was confirmed that the [CNC] pincer hydrido cobalt(III) complexes as catalysts could also be used to dehydrate primary amides to nitriles. This is similar to hydrido iron(II) catalyst.[17] Recently, we reported that the classical [PSiP] pincer iron hydride $(2\ Ph_2PC_6H_4)_2$ Me*Si*Fe(H)$(PMe_3)_2$ was an efficient catalyst to dehydration of primary amides with the assistance of Lewis acid at 40 °C for 40 h.[18]

On the basis of the above research, we attempt to design novel [PSiP] pincer ligands to synthesize [PSiP] pincer iron hydrids, even iron nitrogen complexes, and to explore the catalytic activity of these complexes for dehydration of primary amides. Recently, we reported that the N heterocyclic σ silyl [PSiP] pincer ligand **1** could stabilize iron hydride **2** (Scheme 1).[19] As a continuation of the research, we prepared two novel [PSiP] pincer ligands **3** and **5** (Scheme 2) with the replacement of the methyl group attached to the silicon atom by phenyl group and the phenyl groups attached to the phosphine atoms by isopropyl groups in ligand **1**.[20] The corresponding N heterocyclic [PSiP] pincer iron hydrides **4** and **6** were obtained from the reaction of **3** and **5** with $Fe(PMe_3)_4$, respectively (Scheme 2). It was found that iron hydride **4** was an efficient catalyst for the dehydration of primary amides to nitriles with Ph_2SiH_2 as the dehydrating reagent.

■ RESULTS AND DISCUSSION

Synthesis of Iron Hydride 4. According to the literature reports,[19,20] [PSiP] pincer ligand **3** was synthesized (Scheme 1). Novel iron hydride **4** as yellow precipitate was obtained in 80% yield by the reaction of ligand **3** with $Fe(PMe_3)_4$ in tetrahydrofuran (THF). Iron hydride **4** exhibited considerable stability compared to iron hydride **2**. Even after 2 d at 70 °C in THF in the air, the decomposition of **4** was not observed. The crystals of **4** were stable in the air for several weeks. The single crystals of **4** were isolated from its THF/diethyl ether (Et_2O) solution at room temperature.

In the IR spectrum of **4** one strong band for Fe−H bond at 1873 cm^{-1} was recorded, while the Fe−H stretching band of **2** was registered at 1840 cm^{-1}.[19] This hypsochromic shift (33 cm^{-1}) can be explained by the weaker σ donating ability of the Ph group on the silicon atom to the iron center in **4** in comparison with that of the methyl group in **2**. This leads to an electron poorer iron center in complex **4** and also demon strates that the Fe−H bond in **4** is stronger than the Fe−H bond in **2**. This might be a reason why **4** is more stable than **2**.

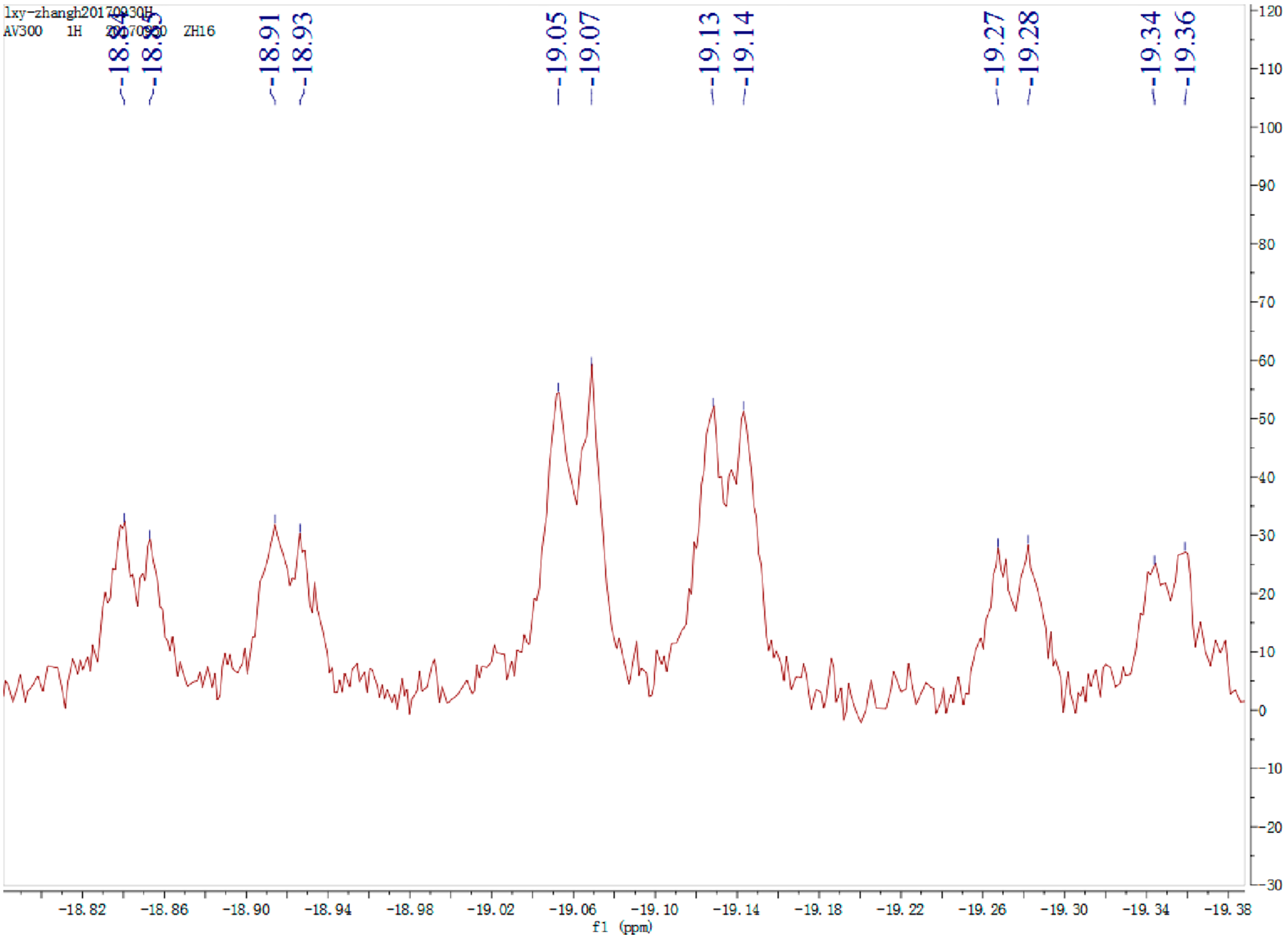


Figure 1. Hydrido resonance of **4** in C_6D_6.

The hydrido resonance of complex **4** in the ^1H NMR spectrum shows a triplet of doublets of doublets (tdd) peak at −19.10 ppm with the coupling constants J_{PH} = 66, 24, 6 Hz (Figure 1). In comparison to that (−18.70 ppm) of iron hydride **2**,[19] the upfield shift (0.40 ppm) indicates that the electron density at the iron center in complex **4** is lower than that in iron hydride **2**. In addition, the resonance of the hydrido hydrogen splits into a triplet coupled by two chemically equivalent P atoms of the $-PPh_2$ groups, and every peak of the triplet further splits into a doublet of doublets by two chemically different P atoms of the PMe_3 ligands. Two H atoms of the same methylene group in complex **4** can be distinguished due to the steric effect (Figure 2). This is different from the hydrogen atoms of the methylene group of ligand **3**. A pseudotriplet was observed, since Ha atom was coupled by Hb atom and then coupled with the nearby phosphorus atom of the $-PPh_2$ groups. However, the chemical shifts of Ha and Ha′ of **4** are much different from those of Hb and Hb′. The coupling pattern is also similar to that of iron hydride **2**.

Single crystal X ray diffraction study identified a distorted hexacoordinate octahedral geometry about iron with a PMe_3 ligand *trans* to the hydrido ligand and another PMe_3 ligand occupying the position *trans* to the Si atom of the pincer ligand (Figure 3). If we assume that P3−Fe1−H is the axis, the axial bond angle is 168.2(8)°, deviated from 180°. The sum of the coordinate bond angles within the equatorial plane is 352.1(2)°, deviated from 360°. On account of the strong *trans* influence of the Si and H atoms, Fe1−P4 (2.2706(5) Å) and Fe1−P3 (2.2278(6) Å) are remarkably longer than the other two Fe−P bonds, namely, Fe1−P1 (2.2105(5) Å) and Fe1−P2 (2.2059(5) Å), respectively. The Fe−H bond distance (1.43(2) Å) of complex **4** is within the expected range and shorter than that in complex **2** (1.47 Å). This result is consistent with data of the IR spectra of both **4** and **2**.

Synthesis of Iron Nitrogen Hydride 6. Nowadays, more and more chemists have hammered at designing and synthesizing novel pincer ligands with strong electron donating groups. These ligands can coordinate with transition metals to enhance the nucleophilic ability of metal complexes for better participation in a bond activation process.[21] Given the strong electron donating ability of the isopropyl group, the novel [PSiP] pincer ligand **5** with isopropyls substituting phenyls on the phosphorus atoms was synthesized intentionally (Scheme 2). Ligand precursor **5′** was obtained by the reaction 1,2 diaminobenzene with freshly prepared $^iPr_2PCH_2OH$ from $^iPr_2PH$ and paraformaldehyde under neat condition. Subsequent reaction of **5′** with $PhHSiCl_2$ induced the formation of ^iPr substituted [PSiP] pincer ligand **5**.

The combination of ligand **5** with $Fe(PMe_3)_4$ in toluene provided iron nitrogen hydride **6** as yellow crystals in 32% yield (Scheme 2). Surprisingly, unlike iron hydride **4**, iron nitrogen hydride **6** is a nitrogen complex owing to the strong electron donating isopropyl groups, which enhance the

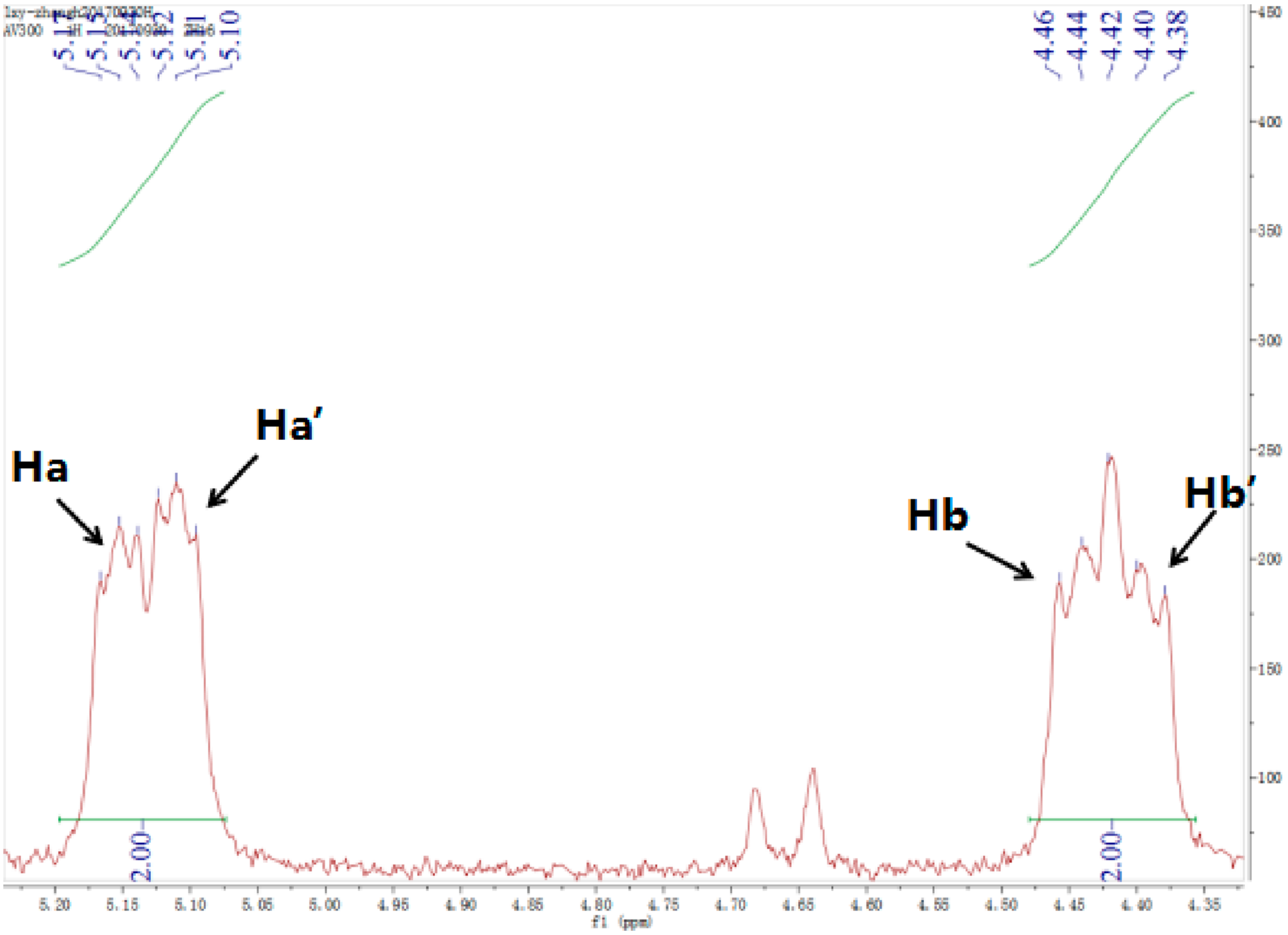


Figure 2. Coupling pattern of the $-CH_2-$ group of **4** in C_6D_6.

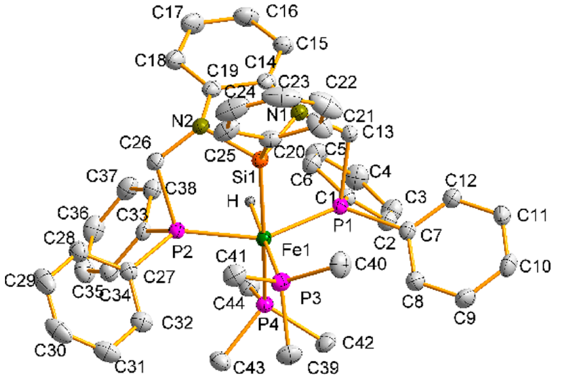


Figure 3. Molecular structure of **4**. The ORTEP representation is shown at the 50% probability level (most H atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1−P1 2.2105(5), Fe1−P2 2.2059(5), Fe1−P3 2.2278(6), Fe1−P4 2.2706(5), Fe1−H1 1.43(3); P1−Fe1−P4 92.150(19), P1−Fe1−Si1 82.592(19), P2−Fe1−P4 94.25(2), P2−Fe1−Si1 83.13(2), H1−Fe1−P3 168.2(8).

electron density of the central Fe atom, leading to the formation of the π back bond between the Fe center and N_2 ligand. Compared with complex **4**, the IR signal (1887 cm^{-1}) of the Fe−H bond in **6** is hypsochromically shifted. This shows that the electron density at the Fe center in **6** is a little lower than that at the Fe atom in **4**. The signal of coordinate N≡N bond in the IR spectrum of **6** at 2049 cm^{-1} falls within the normal range of the nitrogen complex.[22] The hydrido resonance of complex **6** in the ^1H NMR spectrum (Figure 4) shows a triplet of doublets (td) peak at −20.64 ppm with the coupling constants J_{PH} = 60, 24 Hz. In comparison with that of complex **4** the replacement of a PMe_3 ligand by N_2 coordination results in this upfield shift. The hydrido hydrogen splits into a triplet coupled by two chemically equivalent P atoms of the $-P^iPr_2$ groups. Furthermore, this triplet splits into a doublet coupled by the P atom of PMe_3 ligand. As expected, a doublet at 110.6 ppm for two $-^iPr$ groups and a triplet at 1.8 ppm for the PMe_3 ligand were recorded in the ^{31}P NMR spectrum of **6**.

The crystals suitable for X ray diffraction study were obtained from a concentrated diethyl ether solution of complex **6** at 0 °C. As in **4**, the iron center of **6** is also in a distorted octahedral geometry with a bound N_2 *trans* to the hydrido ligand and a PMe_3 ligand occupying the position *trans* to the Si atom of the pincer ligand (Figure 5). The N≡N bond distance (1.118(5) Å) in **6** is within the expected range of the nitrogen complexes.[22] Fe1−P1 (2.2837(12) Å) is longer than Fe1−P2 (2.2343(12) Å) and Fe1−P3 (2.2398(12) Å) because of the strong *trans* influence of the Si atom.

Catalytic Activities of Complexes 2, 4, and 6 for Dehydration of Primary Amides. With hydrido [PSiP] pincer iron(II) complexes **2** and **4** and iron nitrogen hydride **6** as catalysts, the catalytic activity for the dehydration of primary

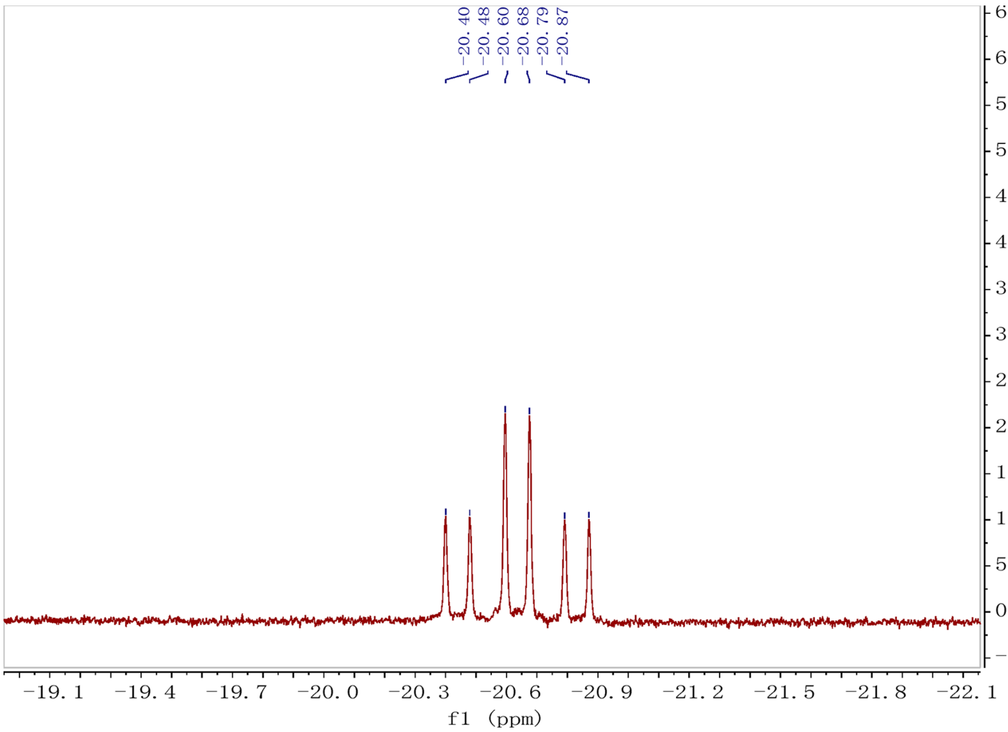


Figure 4. Hydrido resonance of **6** in C_6D_6.

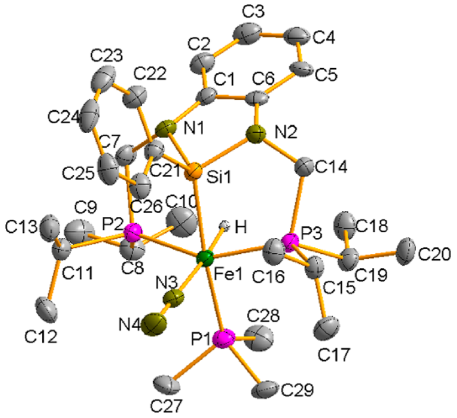
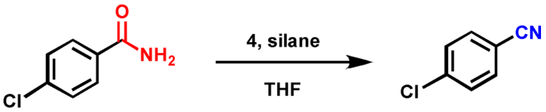


Figure 5. Molecular structure of **6**. The ORTEP representation is shown at the 50% probability level (most H atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe−N3 1.807(4), N3−N4 1.118(5), Fe−H 1.44(4), Fe−P1 2.2837(12), Fe−P2 2.2343(12), Fe−P3 2.2398(12); N3−Fe1−H 174(2), Si1−Fe1−P3 80.65(4), P3−Fe1−P1 97.25(5), P1−Fe1−P2 97.78(5), P2−Fe1−Si1 80.19 (4).

amides to nitriles was evaluated with 4 chlorobenzamide as substrate and 3 equiv of Ph_2SiH_2 as dehydrating agent (Table 1). To our surprise, all three catalysts were comparable with each other and have high efficiency up to 94% conversion on the condition of 2 mmol % catalyst and 3 equiv of Ph_2SiH_2 in THF at 70 °C (Table 1, entries 2−4). Considering the convenient preparation, higher yield, and stability to the air, iron hydride **4** was selected as the optimal catalyst for dehydration of primary amides to nitriles. On the contrary, the reaction could not be performed without catalyst (Table 1, entry 1). An increase of the loading of catalyst **4** from 2 to 4 mmol % resulted in a small improvement of the conversion (from 94 to 95%) (Table 1, entries 3 and 7). When the amount of iron hydride **4** was reduced to 0.5 mmol %, the conversion was very low (26%) (Table 1, entry 5). A moderate conversion (52%) was achieved by using 1 mmol % catalyst (Table 1, entry 6). The results with different hydrosilanes are shown in Table 1 (entries 3, 8−11). $(EtO)_3SiH$ achieved a satisfactory effect (Table 1, entry 8) compared to that with Ph_2SiH_2 as the dehydrating agent (Table 1, entry 3). If $(EtO)_2SiMeH$ was used as the dehydrating agent, the trial showed only 40% conversion (Table 1, entry 9). With Ph_3SiH or Et_3SiH as the dehydrating agent, no conversion was observed (Table 1, entries 10 and 11). Therefore, Ph_2SiH_2 was selected as the dehydrating agent due to its excellent conversion and lower toxicity. When the reaction was performed in the presence of 1 equiv of Ph_2SiH_2, low conversion (50%) was observed. (Table 1, entry 13). However, the dehydration using 2 equiv of Ph_2SiH_2 showed a promising 85% conversion (Table 1, entry 12). The effect of solvents on the conversion was investigated (Table 1, entries 14−17). Complex **4** has no catalytic activity in nonpolar solvent (Table 1, entry 17). In this regard, we reasoned that the polar solvents (dimethylformamide (DMF), THF, or dioxane) could better solubilize iron hydride **4** (Table 1, entries 14−16). When the reaction temperature was lowered to 23, 50, and 60 °C, **4** showed less efficiency (28%−37%) (Table 1, entries 18−20). If we compare the conversions with different reaction times (Table 1, entries 3, 21−23), we can find 24 h is the optimized reaction time.

Under the optimized reaction conditions (Table 1, entry 3), we investigated the scope of the substrates and the application limitation of the catalytic system for the dehydration of primary amides. The isolated yields of the different nitriles were listed in Table 2. The steric hindrance of the amides has a significant negative influence on the yields, especially for the aromatic amides bearing an *ortho* group. For example, 2 chlorobenzamide and *o* toluamide showed moderate yields

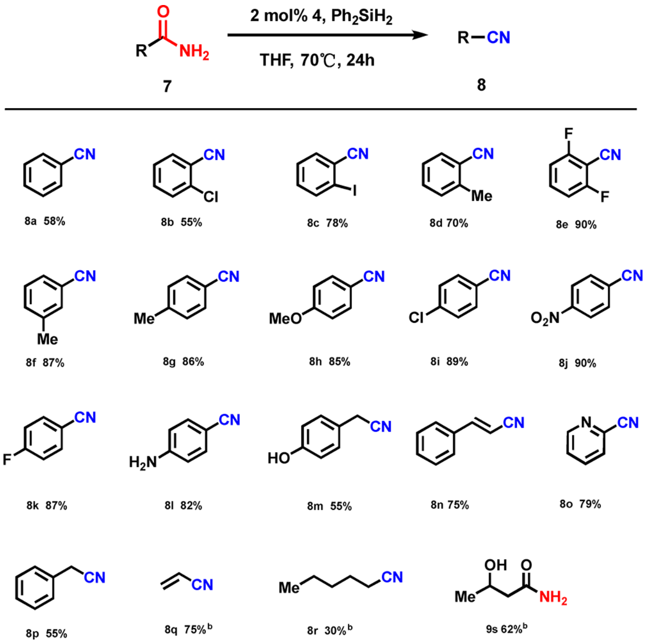
Table 1. Exploration of Conditions for Amide Dehydration[a]



entry	catalyst	loading (mol %)	silanes	loading (equiv)	solvent	temp (°C)	conv[b] (%)
1			Ph_2SiH_2	3	THF	70	0
2	**2**	2	Ph_2SiH_2	3	THF	70	93
3	**4**	2	Ph_2SiH_2	3	THF	70	94
4	**6**	2	Ph_2SiH_2	3	THF	70	94
5	**4**	0.5	Ph_2SiH_2	3	THF	70	26
6	**4**	1	Ph_2SiH_2	3	THF	70	52
7	**4**	4	Ph_2SiH_2	3	THF	70	95
8	**4**	2	$(EtO)_3SiH$	3	THF	70	90
9	**4**	2	$(EtO)_2SiMeH$	3	THF	70	40
10	**4**	2	Ph_3SiH	3	THF	70	0
11	**4**	2	Et_3SiH	3	THF	70	0
12	**4**	2	Ph_2SiH_2	2	THF	70	85
13	**4**	2	Ph_2SiH_2	1	THF	70	50
14	**4**	2	Ph_2SiH_2	3	Dioxane	70	93
15	**4**	2	Ph_2SiH_2	3	DMSO	70	75
16	**4**	2	Ph_2SiH_2	3	DMF	70	72
17	**4**	2	Ph_2SiH_2	3	toluene	70	0
18	**4**	2	Ph_2SiH_2	3	THF	23	28
19	**4**	2	Ph_2SiH_2	3	THF	50	36
20	**4**	2	Ph_2SiH_2	3	THF	60r	37
21	**4**	2	Ph_2SiH_2	3	THF	70	74[c]
22	**4**	2	Ph_2SiH_2	3	THF	70	83[d]
23	**4**	2	Ph_2SiH_2	3	THF	70	94[e]

[a] 4 Clorobenzamide (1.0 mmol), $(EtO)_3SiH$ (3.0 mmol), and **4** (0.04 mmol) in 3 mL of THF, 24 h. [b] Determined by GC with *n* dodecane as internal standard (1.0 mmol). [c] 20 h. [d] 22 h. [e] 26 h.

Table 2. Scope and Limitation of Catalytic Dehydration of Amides[a]

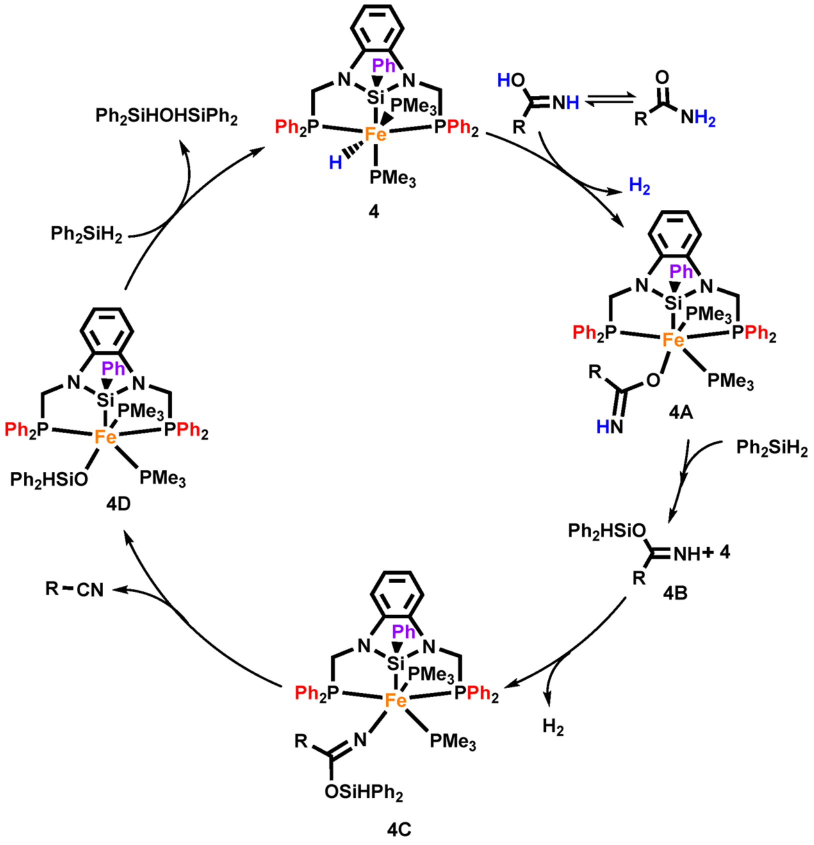


[a] Amide (1.0 mmol), Ph_2SiH_2 (3.0 mmol), and **4** (0.02 mmol) in 3 mL of THF, 70 °C, 24 h; isolated yields. [b] Dioxane, 120 °C; determined by GC with *n* dodecane as internal standard (1.0 mmol).

(Table 2, **8b**−**8d**). The aromatic amides with *para* groups were converted to the corresponding nitriles in good yields (Table 2, **8g**−**8l**). Interestingly, 2 cyanopyridine could be obtained in the yield of 79%. It is noteworthy that the yields were very low when aliphatic amides were used as substrates (Table 2, **8q**−**9s**). The strong electron withdrawing group at the benzene ring provided excellent yield (Table 2, **8e**, **8i**−**8k**). The yields could be improved to some extent when the temperature was increased from 70 to 120 °C. For example, the dehydration of hexanamide did not occur at 70 °C, while the yield was increased to 30% at 120 °C. Acrylonitrile was observed in the dehydration of acrylamide. This is similar to the result of the dehydration of cinnamamide. This indicates that the C═C double bond could not be reduced under the given conditions. However, the product of the dehydration of acetoacetamide is 3 hydroxybutyramide. This illustrates that the carbonyl group of acetoacetamide was selectively reduced prior to the amide group with this catalytic system.

Compared with the recent advances in catalyzing the dehydration of primary amides, the iron nitrogen complex **6** as catalyst is refreshing. The nitrogen iron hydride **6** had a similar catalytic effect compared to that of iron hydride **4** (Table 1, entries 3 and 4). According to the literature, it is the first example that iron nitrogen complex is applied in catalytic dehydration of amides. Although the expansion of substrates was dependent on iron hydride **4** rather than iron nitrogen complex **6** due to the stabilization and convenient preparation of **4**, the comparable catalytic activity of the iron nitrogen complex **6** provided insight into the catalytic mechanism. A possible reaction mechanism with dissociation of PMe_3 or N_2

Scheme 3. Proposed Catalytic Mechanism



as the first step and the coordination of the substrate as the second step can be excluded. If this assumption is correct, the catalytic activity of **6** should be stronger than that of **4**. The reason is that dinitrogen dissociation is easier than phosphine dissociation.

On the basis of the literature reports,[12,15,23−26] a plausible mechanism is proposed for the dehydration of primary amides to nitriles catalyzed by iron hydride **4** (Scheme 3). At the beginning of the process, tautomerization[12] of primary amides leads to the reaction of the acetimidic acid, the tautomer of amide, with the hydrido H ligand to form intermediate **4A** accompanied by the release of H_2, which was detected by gas chromatography (GC) (Supporting Information, Figure S40). Subsequently, **4A** reacts with Ph_2SiH_2 to produce intermediate **4B** and with the regeneration of catalyst **4**. The acid/base reaction between **4B** and **4** affords **4C** with the release of H_2. The product nitrile is obtained via β elimination of **4C** with the generation of intermediate **4D**. Catalyst **4** is regenerated from the interaction of **4D** with Ph_2H_2Si with the formation of disilyl ether. Unfortunately, our efforts to isolate intermediate **4A** failed. At the same time, we also implemented the stoichiometric reaction of Ph_2SiH_2 with **4**, and the reaction did not work.

■ CONCLUSION

In summary, an air stable pincer iron hydride **4** was synthesized from Ph substituted N heterocyclic σ silyl pincer preligand **3** and $Fe(PMe_3)_4$. When the Ph groups in **3** were replaced by the strong electron donating groups $-^iPr$, iron nitrogen hydride **6** could be obtained by the reaction with $Fe(PMe)_4$. The molecular structures of **4** and **6** were determined by single crystal X ray diffraction. Both **4** and **6** showed efficient catalytic activity for dehydration of primary amides, while iron hydride **4** was preferable for its stability and convenience in preparation. The catalytic system provided a variety of aromatic and aliphatic nitriles in moderate to excellent yields and tolerated the presence of halides, nitro group, pyridyl group, alkenes, and so on, with a small limitation in aliphatic amides. A plausible mechanism for the dehydration of primary amides was proposed and partially experimentally verified.

■ EXPERIMENTAL SECTION

General Procedures and Materials. All reactions were performed under an inert nitrogen atmosphere utilizing the standard Schlenk techniques. THF, toluene, dioxane, *n* pentane, and diethyl ether were dried by distillation from Na benzophenone under nitrogen. DMF and DMSO were dried by molecular sieves. $Fe(PMe_3)_4$ was prepared according to the literature.[27] Iron hydride **2**, preligand **3**, and preligand **5′** were synthesized by the literature methods.[19,20,28] All other chemicals were purchased and utilized without further purification. GC was recorded on a Fuli 9790 instrument. Infrared spectra (4000−400 cm^{-1}), as obtained from Nujol mulls between KBr disks, was recorded on a Bruker ALPHA Fourier transform infrared (FT IR) instrument. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on 300 or 500 MHz Bruker instruments.

Synthesis of Iron Hydride 4. A solution of preligand **3** (1 mmol, 0.6084 g) in THF (35 mL) was mixed with a solution of $Fe(PMe_3)_4$ (1.1 mmol, 0.3962 g) in THF (30 mL) at room temperature, and a yellow precipitate was obtained from the mixed solution gradually. After the solution was stirred for 12 h, the volatiles were removed under reduced pressure, and the residue was washed several times with THF. Iron hydride **4** (0.8 mmol, 0.6531 g) was isolated as yellow powder in 80% yield. The crystals of **4** were isolated from the mixture solution of THF and diethyl ether at room temperature. Anal. Calcd for $C_{44}H_{52}FeN_2P_4Si$ (816.74 g mol^{-1}): C, 64.71; H, 6.42; N, 3.43. Found: C, 64.98; H, 6.34; N, 3.01%. mp >198 °C dec. IR (Nujol, KBr, cm^{-1}): 3054 (Ar−H), 1873 (Fe−H), 943 (PMe_3). ^1H NMR (300 MHz, C_6D_6, δ, ppm): −19.01 (tdd, J = 66, 24, 6 Hz, 1H, Fe *H*), 0.47 (d, 9H, P*Me*$_3$), 1.06 (d, 9H, P*Me*$_3$), 4.42 (m, 2H, PC*HaHb*N), 5.11 (m, 2H, PC*Ha'Hb'*N), 6.70−7.26 (m, 20H, C_6H_5), 7.81 (s, 4H, C_6H_4). ^{31}P NMR (121 MHz, C_6D_6, δ, ppm): 13.1 (m, 1P, *P*Me$_3$), 21.3 (m, 1P, *P*Me$_3$), 110.0 (m, 2P, *P*Ph$_2$).

Synthesis of Iron Nitrogen Hydride 6. A solution of ^{n}Bu Li (34.4 mmol, 13.78 mL) was added dropwise to a stirred solution of preligand **5′** $C_6H_4(NHCH_2P^iPr_2)_2$ (14.1 mmol, 5.1 g) in Et_2O (60 mL) at 0 °C. After it warmed to room temperature, the reaction continued for 8 h. Dichlorophenylsilane (16.9 mmol, 3.0 mL) was added to the stirred solution, and then the resultant suspension was stirred for 3 d. The supernatant was filtrated, and volatiles were removed under reduced pressure, leaving a sticky oil. The solubility of ligand **5** was extremely good even in *n* pentane, and no further purification was achieved. A solution of ligand **5** (1 mmol, 0.472 g) in toluene (35 mL) was mixed with a solution of $Fe(PMe_3)_4$ (1.1 mmol, 0.396 g) in toluene (30 mL) at −78 °C and then returned to room temperature gradually. After the solution was stirred for 12 h, the reaction temperature was elevated to 60 °C. The reaction lasted 5 d, and then the volatiles were removed under reduced pressure. The residue was extracted with *n* pentane and diethyl ether. Yellow crystals of **6** were obtained at room temperature from its *n* pentane solution. Anal. Calcd for $C_{29}H_{51}FeN_4P_3Si$ (632.61 g mol^{-1}): C, 55.06; H, 8.13; N, 8.86. Found: C, 54.78; H, 8.34; N, 9.01%. mp >160 °C dec. IR (Nujol, KBr, cm^{-1}): 2925 (Ar−H), 2049 (N≡N), 1887 (Fe−H), 952 (PMe_3). ^1H NMR (300 MHz, C_6D_6, δ, ppm): −20.64 (td, J = 60, 24 Hz, 1H, Fe *H*), 0.78 (m, 6H, PCH*CH*$_3$*CH*$_3$), 0.90 (m, 6H, PCH*CH*$_3$*CH*$_3$), 1.22 (m, 6H, PCH*CH*$_3$*CH*$_3$), 1.33 (m, 6H, PCH*CH*$_3$*CH*$_3$), 1.17 (d, 9H, P*Me*$_3$), 1.16 (d, 9H, P*Me*$_3$), 1.74 (m, 4H, PC*H*CH$_3$CH$_3$), 3.48 (m, 2H, PC*H*$_2$N), 3.38 (m, 2H, PC*H*$_2$N), 6.92−7.13 (m, 4H, C$_6$*H*$_4$), 7.33−8.28 (m, 5H, C$_6$*H*$_5$). ^{31}P NMR (121 MHz, C_6D_6, δ, ppm): 1.8 (t, J = 30 Hz, 1P, *P*Me$_3$), 21.3 (d, J = 30 Hz 2P, *P*^{i}Pr$_2$). ^{13}C NMR (75 MHz, C_6D_6, δ, ppm): 17.69 (s, PCHCH$_3$), 19.99 (s, PCHCH$_3$), 20.40 (s, PCHCH$_3$), 20.61 (t, J = 2.25 Hz, PCHCH$_3$), 21.81 (d, J = 18 Hz, PCH3), 28.20 (q, J = 6.25 Hz, PCHCH$_3$), 30.76 (t, J = 4.5 Hz, PCHCH$_3$), 51.10 (dt, J = 9, 13.5 Hz, NCH$_2$P), 110.59 (s, Ar), 117.86 (s, Ar), 126.91 (s, Ar), 134.73 (s, Ar), 146. 58 (s, Ar), 147.91 (s, Ar), 148.00 (s, Ar).

General Procedure for the Dehydration of Amides to Nitriles. A 25 mL dried Schlenk tube including hydride **4** (0.005−0.04 mmol) was added to primary amides (1.0 mmol). After the Schlenk tube was purged with nitrogen, hydrosilanes (1−3 mmol) and anhydrous solvent (3 mL) were added, respectively. The mixture was stirred at corresponding temperature for 24 h. The product was purified on the basis of the literature.[24]

X-ray Structure Determination. Single crystal X ray diffraction data for the complexes were collected on a Stoe StadiVari (**4**) or XtaLAB Synergy, Dualflex, HyPix (**6**) diffractometer equipped with a Mo Kα radiation (λ = 0.710 73 Å) or Ga Kα radiation (λ = 1.341 43) and a charge coupled device (CCD) area detector. The structures were solved using the charge flipping algorithm, as implemented in the program SUPERFLIP,[29] and refined by full matrix least squares techniques against F^2 (SHELXL) through the OLEX interface. 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. CCDC Nos. 1947311 (**4**) and 1909696 (**6**) contain the supplementary crystallographic data for this paper. Additional crystallographic information is available in the Supporting Information.

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Notes

The authors declare no competing financial interest.

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