



FULL PAPER

Efficient dehydration of primary amides to nitriles catalyzed by phosphorus-chalcogen chelated iron hydrides

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A series of phosphorus-chalcogen chelated hydrido iron (II) complexes **1–7**, (*o*-(R'₂P)-*p*-R-C₆H₄Y)FeH (PMe₃)₃ (**1**: R = H, R' = Ph, Y = O; **2**: R = Me, R' = Ph, Y = O; **3**: R = H, R' = ^{*i*}Pr, Y = O; **4**: R = Me, R' = ^{*i*}Pr, Y = O; **5**: R = H, R' = Ph, Y = S; **6**: R = Me, R' = Ph, Y = S; **7**: R = H, R' = Ph, Y = Se), were synthesized. The catalytic performances of **1–7** for dehydration of amides to nitriles were explored by comparing three factors: (1) different chalcogen coordination atoms Y; (2) R' group of the phosphine moiety; (3) R substituent group at the phenyl ring. It is confirmed that **5** with S as coordination atom has the best catalytic activity and **7** with Se as coordination atom has the poorest catalytic activity among complexes **1**, **5** and **7**. Electron-rich complex **4** is the best catalyst among the seven complexes and the dehydration reaction was completed by using 2 mol% catalyst loading at 60 °C with 24 hr in the presence of (EtO)₃SiH in THF. Catalyst **4** has good tolerance to many functional groups. Among the seven iron complexes, new complexes **3** and **4** were obtained via the O-H bond activation of the preligands *o*-^{*i*}Pr₂P(C₆H₄)OH and *o*-^{*i*}Pr₂P-*p*-Me-(C₆H₄)OH by Fe(PMe₃)₄. Both **3** and **4** were characterized by spectroscopic methods and X-ray diffraction analysis. The catalytic mechanism was experimentally studied and also proposed.

KEYWORDS

amide, dehydration, iron hydride, nitrile, phosphorus-chalcogen ligand

1 | INTRODUCTION

Nitriles are important chemical raw materials and are widely used in daily life such as synthetic fibers,^[1] synthetic fragrance,^[2] bioactive substances^[3] and liquid crystal materials.^[4] Nitriles are also important intermediates in organic chemical transformations because nitrogen atom can be introduced in production molecules. For instance, polyamides could be prepared via the reaction of carbonyl compounds with nitriles.^[5] The reactions of aziridine with the coordinated nitriles, e.g. [PtCl₂(RCN)₂], gave rise to (aziridino)amines by forming

C-N bonds.^[6] The combination of tris (pentafluorophenyl)borane and nitriles lead to the Lewis acid/base adduct with a substantial increase in the C ≡ N bond strength.^[7] Tetrazoles and oxadiazolines could also be synthesized using coordinate nitriles through [2 + 3] cycloaddition.^[8,9]

However, how to prepare nitriles efficiently is still a challenge for synthetic chemists. Because amides are cheap and easy to obtain, dehydration of amides to nitriles has become one of the effective methods in this field. Traditionally, some harsh dehydrating reagents such as TiCl₄,^[10] SOCl₂^[11] or POCl₃^[12] were used for this

process. However, on the one hand, these substances themselves are not environmentally friendly; on the other hand, the reactions with these substances might bring some harmful byproducts. In addition, the condition of most of the transformation is not mild. For example, with chlorosulfonic acid as dehydrating agent the aldioximes could be obtained from Beckmann rearrangement.^[13] The EtOPOCl₂/DBU system was confirmed as a convenient dehydrating agent for the conversion of primary amides to nitriles.^[14] The amides could also be dehydrated to nitriles via simultaneous action of triphenylphosphine, carbon tetrachlorides and trimethylamine.^[15]

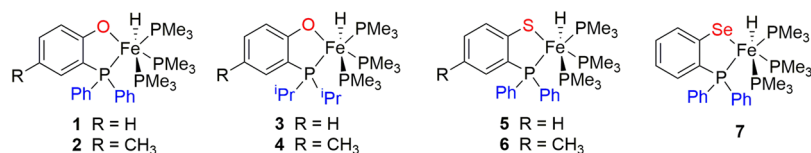
In recent years, large efforts have been put into the development of transition-metal catalyzed dehydration of amides (e.g. Ru, V, Pd, U).^[16] In 2008, Nagashima reported the first example of a transition-metal-catalyzed Si-H bond activation leading the dehydration of amides to afford the nitriles.^[16a] After two years Kaneda group designed a monomeric vanadium oxide on hydrotalcite as an effective heterogeneous catalyst for the highly efficient dehydration of amides to related nitriles.^[16b] For a decade, replacing precious metals with earth-abundant metals (e.g. Fe, Co, Ni) is getting more and more attention. Iron, being the most abundant transition metal and displaying low toxicity, is an effective alternative. In 2009, the first iron-catalyzed dehydration of primary amides to nitriles with (EtO)₂MeSiH as a dehydrating agents was developed by Beller. Beller considered that the elimination of silyl ether is the key step in the catalytic mechanism.^[17] In 2012, Beller group also found that [Et₃NH][HFe₃(CO)₁₁] could catalyze the dehydration of benzamide to phenyl nitrile in 90% yield while benzamide could be reduced to benzamine with two catalysts [Et₃NH][HFe₃(CO)₁₁] / Fe (OAc)₂ in 70% yield. (EtO)₂MeSiH was used for both catalytic systems.^[18] In the same year, Enthaler used the simple zinc salt [Zn(OTf)₂] as a Lewis acid catalyst to complete the reaction of primary amides into the corresponding nitriles with MSTFA (N-methyl-N-(trimethylsilyl) trifluoroacetamide) as a dehydrating agent.^[19] Before this, his group also introduced FeCl₂·4H₂O/MSTFA system to dehydrate the primary amides to nitriles.^[20] Some carbonyl iron compounds such as [Fe₃(CO)₁₂] and [Fe(CO)₅] could also be used to dehydrate amides to amines in the presence of silanes.^[21]

In past few years, we found that some hydrido iron complexes synthesized in our group could catalyze the dehydration reactions of amides to afford nitriles.^[22,23] Amide substrates were catalytically dehydrated to the corresponding nitriles by hydrido thiophenolato iron (II) complexes [cis-Fe(H)(SAr)(PMe₃)₄] using (EtO)₃SiH as an efficient dehydrating agent in the yield up to 93%.^[22] It was confirmed that the hydrido silyl iron complex, [(*o*-Ph₂PC₆H₄SiMe₂)Fe(H)(PMe₃)₃], is a good dual catalyst for both hydrosilylation of carbonyl complexes and dehydration of benzamides.^[23] In 2015, we prepared [P, S]-chelated iron hydrides (**5** and **6**, SCHEME 1) and found that they could be used as catalysts for hydrosilylation of aldehydes and ketones.^[24] The [P, Se]-chelated iron hydride (**7**, Scheme 1) was also obtained via Se-H bond activation.^[25] However, both [P, S]- or [P, Se]-chelated iron hydrides for dehydration of amides to nitriles as catalysts have not been studied. The [P, O]-chelated iron hydrides (**1** and **2**, Scheme 1) were published by Klein in 2004.^[26] The catalytic activity of complexes **1–2** for dehydration of amides to nitriles has also not been explored. In order to further expand the types of catalysts and compare electronic and steric effect of the hydrido iron (II) complexes with different chalcogen coordination atoms on the dehydration of amides to nitriles, in this paper seven phosphorus-chalcogen chelated hydrido iron (II) complexes **1–7** were synthesized and the catalytic performances of **1–7** for dehydration of amides to nitriles were explored. Among them iron hydrides (**3** and **4**, Scheme 1) were new and were completely characterized.^[26]

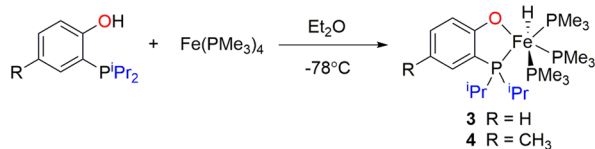
2 | RESULTS AND DISCUSSION

2.1 | Synthesis of [P, Y]-chelated (Y = O, S and se) hydrido iron (II) complexes 1–7

Complexes **1** and **2** were prepared according to the method by Klein.^[26] Complexes **5** and **6** can be obtained with the method reported in the reference.^[24] We disclosed the synthesis of complex **7** in 2017.^[25] The ligands *ortho*-diisopropylphosphinophenols were synthesized according to the literature.^[27] The combination of Fe(PMe₃)₄ with *ortho*-diisopropylphosphinophenols in diethyl ether afforded complexes **3** and **4** (Scheme 2).



SCHEME 1 Seven catalysts

SCHEME 2 Synthesis of **3** and **4**

Complexes **3** and **4** were fully characterized by IR, NMR (¹H, ³¹P and ¹³C) and X-ray diffraction analysis.

In the IR spectrum of **3** the typical Fe-H vibration appeared at 1907 cm⁻¹. This suggests that the O-H bond was cleaved. The strong vibration of coordinated PMe₃ appeared at 935 cm⁻¹. In the ¹H NMR spectrum of **3** the hydrido resonance was situated at -9.54 ppm as a dddd peak (²J_{Pd}H = 79.3 Hz, ²J_{Pc}H = 73.9 Hz, ²J_{Pb}H = 52.3 Hz, ²J_{Pa}H = 37.5 Hz)^[26] caused by the coupling with four P atoms. In the ³¹P NMR spectrum of **3** (Figure 1) four sets of signals were identified at 13.1 (dt), 21.3 (ddd), 39.0 (dt) and 78.2 (ddd) ppm in the integral ratio of 1: 1: 1: 1. This implies that the four P atoms are in different chemical environments. The two dt peaks belong to P_a and P_c atoms while the two ddd peaks were caused by P_d and P_b atoms.^[26] For complex **4** the similar spectroscopic results were obtained.

The molecular structures of **3** and **4** were determined by single crystal X-ray diffraction analysis (Figure 2 and 3). In Figure 2 the Fe atom is centered in a distorted octahedral coordination geometry. Three trimethylphosphine ligands are in *fac*-mode. Because the hydrido H has the strongest *trans*-influence and O atom has the weakest *trans*-influence, Fe1-P4 (2.2403 Å) is the longest and Fe1-P3 (2.1752 Å) is the shortest Fe-P bond among the four Fe-P bonds. The bite angle P1-Fe1-O1 is 83.68(5)°. These structural characteristics are similar with those of

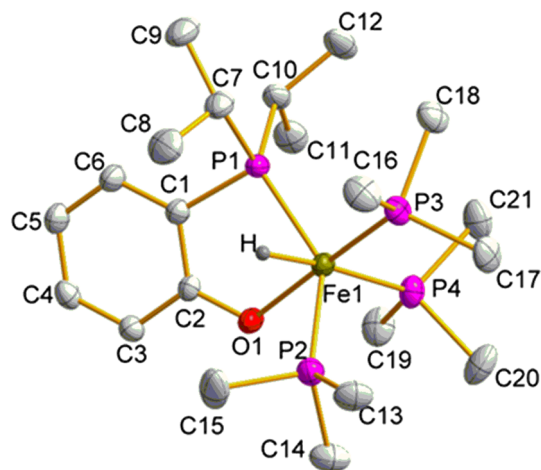


FIGURE 2 Molecular structure of **3**. The thermal ellipsoids are displayed at the 50% probability level, and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Fe1-P1 2.2319(7), Fe1-P2 2.2157(7), Fe1-P3 2.1752(7), Fe1-P4 2.2403(7), Fe1-O1 2.0382(16), Fe1-H 1.55(4); P1-Fe1-O1 83.68(5), O1-Fe1-P2 77.31(5), P2-Fe1-P3 98.51(3), P3-Fe1-P1 98.71(3), P4-Fe1-H 175(1)

the derivative iron complexes.^[26] The Fe-H bond (1.55(4) Å) is slightly longer than a normal Fe-H bond (~1.42 Å).^[28] Complex **4** has a similar molecular structure (Figure 3) with **3** but Fe1-H (1.46(3) Å) in **4** is a little bit shorter than that in **3**.

2.2 | Catalytic activities of 1–7 for dehydration of amides

Complexes **1–7** as catalysts were used in dehydration of amides to nitriles (Scheme 3). Initially, *p*-chlorobenzamide was selected as a template substrate

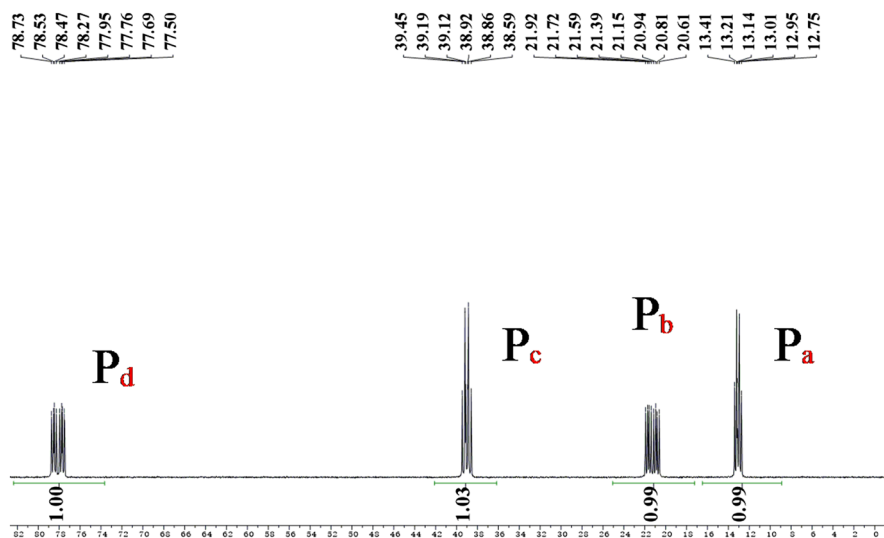
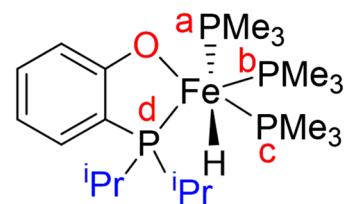


FIGURE 1 ³¹P NMR spectrum of **3**



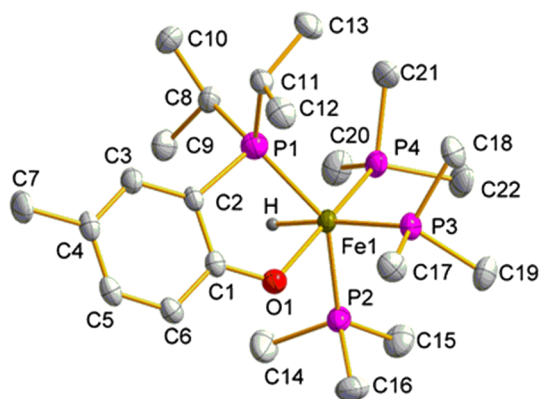
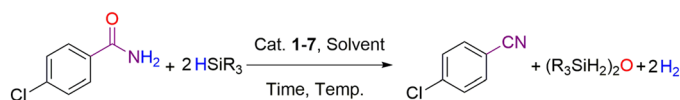


FIGURE 3 Molecular structure of **4**. The thermal ellipsoids are displayed at the 50% probability level, and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Fe1-P1 2.2392(5), Fe1-P2 2.2249(5), Fe1-P3 2.2251(5), Fe1-P4 2.1710(5), Fe1-O1 2.0209(12), Fe1-H 1.46(3); P1-Fe1-O1 83.68(4), O1-Fe1-P2 76.10(4), P2-Fe1-P4 97.60(2), P4-Fe1-P1 98.603(19), P3-Fe1-H 174.5(10)

to screen the catalytic conditions (Table 1). Under the same catalytic conditions, **2** is a better catalyst than **1** (entries 1 and 2, Table 1). This might be interpreted with the introduction of *para*-methyl group in **2**. When the diphenyl groups were replaced by the diisopropyl groups, significantly better catalytic activities of **3** and **4** were observed in comparison with those of **1** and **2** (entries 3 and 4, Table 1). If the coordination O atom in **1** or **2** was replaced by S atom (**5** or **6**), the conversions are not satisfactory comparing with the results of **3** and **4** (entries 5 and 6, Table 1) but better than those of **1** and **2**. Complex **7** with Se-coordination has the lowest conversion of 56% (entry 7, Table 1). It can be deduced that the strong coordination ability makes this complex more stable. In comparison with the results of entries 1, 5 and 7, it can be concluded hydrido iron complex **5** with S as coordination atom has the best catalytic activity while hydrido iron complex **7** with Se as coordination atom has the poorest catalytic activity among the three complexes **1**, **5** and **7**. From the results of entry 1 to entry 7 it can be concluded **4** is the best catalyst among the 7 complexes under the same catalytic conditions. When the reaction with **4** as catalyst was conducted at different temperatures, it was found that **4** is a better catalyst than **3** (entries 8 and 9, Table 1). When the reaction temperature was further lowered to 50 °C, only 65%

conversion was reached (entry 10, Table 1). Therefore, it can be concluded that the optimized temperature is 60 °C. When the reaction time was reduced from 24 hr to 22 or 20 hr, the conversion was also reduced (entries 11 and 12, Table 1). Lower conversion (67%) was detected when the catalyst loading was reduced to 1 mol% (entry 13, Table 1). In order to explore the effect of the amount of silanes on the conversion, (EtO)₃SiH in different molar ratios were added to the catalytic mixture (entries 14–16, Table 1). It can be seen that the ratio of 1: 3 (substrate: silane) is the best and the reaction temperature is crucial. We also found that (EtO)₃SiH is the best dehydrating agent for this catalytic system in comparing with Et₃SiH, Ph₃SiH, Ph₂SiH₂ and PMHS (polymethyl hydrosiloxane) (entries 17–22, Table 1). When the catalytic reaction was conducted in different media (pentane, diethyl ether, toluene, CH₃CN, THF, DMSO, DMF and benzene), it was found that THF was the best solvent (entries 21–27, Table 1). Up to now, the optimized catalytic conditions can be summarized as follows: 2 mol % of catalyst **4** at 60 °C in the presence of 3 equiv of (EtO)₃SiH in THF to react 24 hr (entry 9, Table 1). The control experiment under the optimized catalytic conditions showed that there was no conversion without complex **4** (entry 28, Table 1).

Under the optimized catalytic conditions, the scope of the substrates was expanded (Table 2). The aromatic substrates with special functional groups, such as halogeno-, amino-, nitro-, phenolic hydroxyl and C=C group, have good isolated yields (72–93%). Some substrates with electron-donating group, such as methyl or methoxy group, could reach good yields (69–84%). Heterocyclic substances, 2-pyridinecarboxamide and thiophene-2-carboxamide, could only be dehydrated in 61 and 57% yields. In the catalytic process, both nitro- and C=C groups could not be reduced and remained unchanged. Interestingly, when a group was attached to the *ortho*-position of the amides group, such as *o*-chlorobenzamide and *o*-methylbenzamide, the reaction yields are significantly poorer than those of the substrates with the same group at the *meta*- or *para*-position, such as *p*-chlorobenzamide and *m*-methylbenzamide. We consider that the steric effect plays an important role for these results due to the large steric hindrance of the two isopropyl group in **4**. The steric effect hinders the interaction of the hydrido hydrogen with the amino group of the amides.



SCHEME 3 Catalytic dehydration of amides to nitriles

TABLE 1 Optimization of catalytic reaction conditions^a

Entry	Cat	Loading (mol)	silane	solvent	Temp.(°C)	Time(h)	Conv. ^b (%)
1	1	2%	(EtO) ₃ SiH	THF	80	24	64
2	2	2%	(EtO) ₃ SiH	THF	80	24	81
3	3	2%	(EtO) ₃ SiH	THF	80	24	95
4	4	2%	(EtO) ₃ SiH	THF	80	24	96
5	5	2%	(EtO) ₃ SiH	THF	80	24	79
6	6	2%	(EtO) ₃ SiH	THF	80	24	84
7	7	2%	(EtO) ₃ SiH	THF	80	24	56
8	3	2%	(EtO) ₃ SiH	THF	60	24	89
9	4	2%	(EtO) ₃ SiH	THF	60	24	94
10	4	2%	(EtO) ₃ SiH	THF	50	24	65
11	4	2%	(EtO) ₃ SiH	THF	60	22	85
12	4	2%	(EtO) ₃ SiH	THF	60	20	69
13	4	1%	(EtO) ₃ SiH	THF	60	24	67
14	4	2%	(EtO) ₃ SiH ^c	THF	60	24	33
15	4	2%	(EtO) ₃ SiH ^d	THF	60	24	95
16	4	2%	(EtO) ₃ SiH ^d	THF	50	24	57
17	4	2%	Et ₃ SiH	THF	60	24	0
18	4	2%	Ph ₃ SiH	THF	60	24	25
19	4	2%	Ph ₂ SiH ₂	THF	60	24	7
20	4	2%	PMHS	THF	60	24	51
21	4	2%	(EtO) ₃ SiH	Pentane	60	24	71
22	4	2%	(EtO) ₃ SiH	Et ₂ O	60	24	85
23	4	2%	(EtO) ₃ SiH	Toluene	60	24	90
24	4	2%	(EtO) ₃ SiH	CH ₃ CN	60	24	61
25	4	2%	(EtO) ₃ SiH	DMSO	60	24	89
26	4	2%	(EtO) ₃ SiH	DMF	60	24	57
27	4	2%	(EtO) ₃ SiH	Benzene	60	24	88
28	4	0	(EtO) ₃ SiH	THF	60	24	0

^aCatalytic reaction condition: *p*-chlorbenamide (1.0 mmol), hydrosilane (3.0 mmol) and 1–7 (2% mmol) in 2 ml THF, T°C, t h.

^bDetermined by GC with dodecane as internal standard.

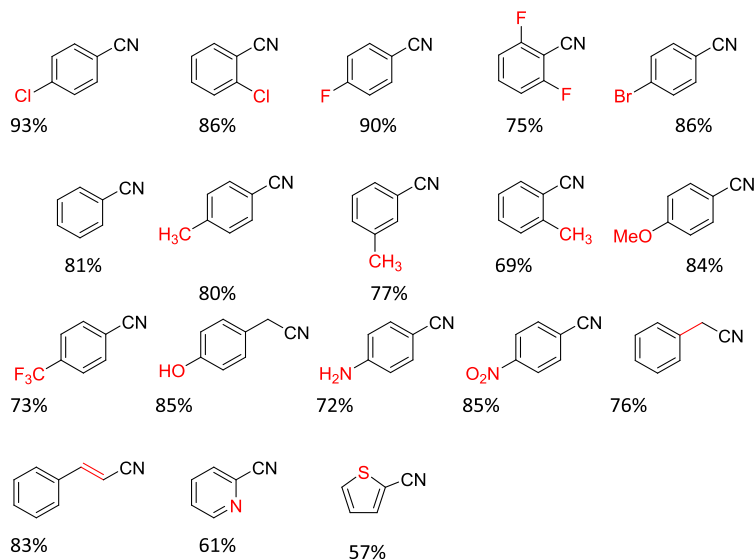
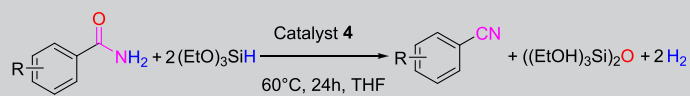
^chydrosilane (2.0 mmol).

^dhydrosilane (4.0 mmol).

3 | MECHANISM DISCUSSION

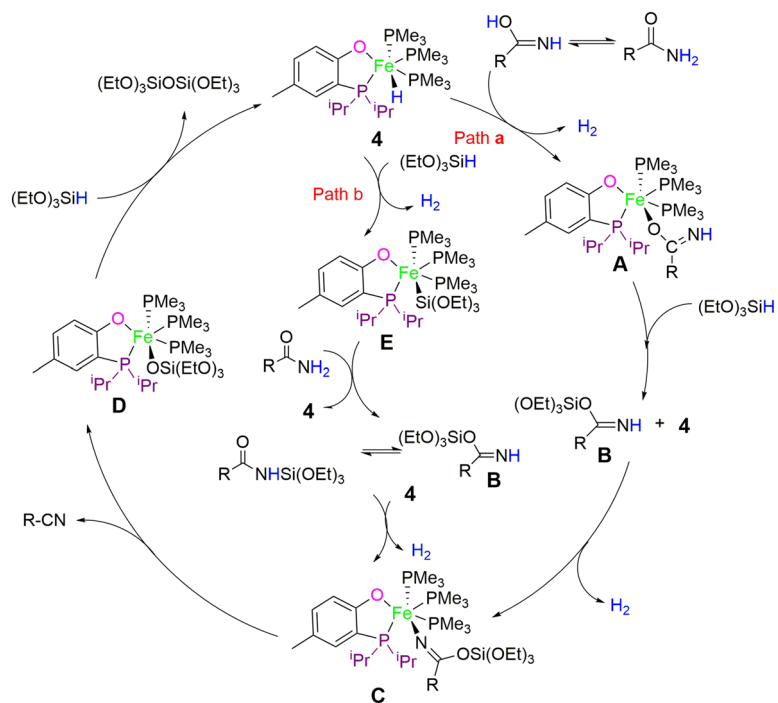
Beller proposed a mechanism for dehydration of primary amides involving the formation of disilyl imidate and the elimination of disiloxane steps.^[17] This proposal becomes a presentative mechanism for this kind catalytic transformations. In 2018, Buchwald reported an overview of amide-to-nitrile conversion supported by theoretical calculation and single crystal X-ray diffraction of intermediate.^[29] Inspired by these literatures, we proposed a process of tautomerization of primary amides at the beginning of this reaction (Scheme 4). There are two possible paths for this

reaction, Path **a** and Path **b**. For Path **a**, **4** reacts with acetimidic acid, the tautomer of amide, to give rise to intermediate **A** with the release of hydrogen gas. Intermediate **A** interacts with (EtO)₃SiH affords intermediate **B** with the formation of **4**. The “acidic” H of **B** reacts with the “basic” H of **4** to produce intermediate **C** with the formation of H₂. β-Elimination of **C** delivers intermediate **D** with the production of nitrile. Finally, the reaction of **D** with (EtO)₃SiH gives rise to disilyl ether with the recovery of **4**. Path **b** is another alternative. At first, **4** reacts with (EtO)₃SiH to afford intermediate **E** with the release of H₂. **E** interacts with amide to delivers **B** with the formation of **4**. The

TABLE 2 Products of dehydration of primary amides to nitriles^{a,b}

^aCatalytic reaction conditions: amide (1 mmol), (EtO)₃SiH (3 mmol), Catalyst 4 (2 mol%) in 2 ml THF, 60 °C, 24 hr.

^bIsolated yield.

**SCHEME 4** Proposed mechanism

combination of **4** and **B** produces intermediate **C** and H_2 . The next two steps of Path **b** are the same as those in Path **a**.

In order to explore the mechanism of the reaction experimentally, stoichiometric reaction of complex **4** with 4-methoxybenzamide or $(EtO)_3SiH$ were respectively carried out. When **4** reacted with 4-methoxybenzamide, the vibration of Fe-H bond disappeared by the detection of infrared spectra (see SIII). When complex **4** reacted with $(EtO)_3SiH$, the vibration of Fe-H bond still existed. Therefore, we consider that Path **a** is possible. In addition, the release of H_2 was confirmed by GC.

4 | CONCLUSIONS

In this work, two new *ortho*-diisopropylphosphino phenolato iron (II) hydrides **3** and **4** were prepared and fully characterized by spectroscopic methods. In order to compare different chalcogen coordination atoms and the electronic as well as the steric effects on the catalytic activities of the iron hydrides, the catalytic performance of complexes **1–7** for the dehydration of amides was explored. The catalytic experiments indicate complex **5** with S as coordination atom has the best catalytic activity and complex **7** with Se as coordination atom has the poorest catalytic activity among the three complexes **1**, **5** and **7**. Higher yields could be obtained when diphenyl groups were replaced by diisopropyl groups in comparison the data of **1** and **2** with those of **3** and **4**. When the results of **1** and **2**, **3** and **4** as well as **5** and **6** are compared, it could be found that the introduction of methyl group on the benzene ring can also increase the catalytic activity of the complex. Among the seven complexes, **7** is the poorest catalyst while **4** is the best catalyst. We think that **4** is the most electron-rich complex among them. With **4** as catalyst this catalytic system has excellent tolerance to halogeno-, amino-, nitro-, phenolic hydroxyl, C=C group. 18 Amide substrates were transformed to the related nitriles in the isolated yields of 57–93%. A catalytic mechanism was proposed and experimentally studied.

5 | EXPERIMENTAL

5.1 | General procedures and materials

All air-sensitive reactions were carried out under anhydrous and nitrogen atmospheric conditions by a standard Schlenk technique. Solvents were distilled with sodium under nitrogen atmosphere. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$), as obtained from Nujol mulls between

KBr disks, were recorded on a Bruker ALPHA FT-IR instrument. 1H , ^{13}C , ^{31}P spectra were completed by using Bruker Avance 300 MHz spectrometers. GC was recorded on a Fuli 9790 instrument. Melting points were measured in capillaries sealed under N_2 . $Fe(PMe_3)_4$ was synthesized by literature.^[30] All the amides and silanes were purchased and used without further purification.

5.2 | Synthesis of 3

A solution of 2-diisopropylphosphinophenol (0.79 g, 3.75 mmol) in 30 ml Et_2O was slowly added to a solution of $Fe(PMe_3)_4$ (1.35 g, 3.75 mmol) in 40 ml Et_2O at $-78\text{ }^\circ\text{C}$, forming an orange mixture. After stirring at room temperature for 18 h, the turbid orange solution was evaporated under reduced pressure and the red powder was extracted with *n*-pentane and diethyl ether. Complex **3** (1.15 g, 2.33 mmol) was obtained as red crystals in the yield of 62%. M.p.: $144\text{--}145\text{ }^\circ\text{C}$. IR (Nujol mull, $4000\text{--}400\text{ cm}^{-1}$): 3053, 3011 ν (ArH), 1907 ν (Fe-H), 935 ν (PMe_3). 1H NMR: (300 MHz, benzene- d_6 , 300 K/ppm) δ : -9.54 (dddd, $^2J P_dH = 79.3\text{ Hz}$, $^2J P_cH = 73.9\text{ Hz}$, $^2J P_bH = 52.3\text{ Hz}$, $^2J P_aH = 37.5\text{ Hz}$, FeH, 1H); 1.14 (dd, $J = 12.0, 6.0$, PCHCH₃, 3H), 1.26 (dd, $J = 12.0, 6.0$, PCHCH₃, 3H), 1.49 (dd, $J = 12.0, 6.0$, PCHCH₃, 3H), 1.62 (dd, $J = 12.0, 6.0$, PCHCH₃, 3H); 2.38–2.56 (m, PCH(CH₃)₂, 2H); 0.98 (d, PMe_3 , $J = 6.0\text{ Hz}$, 9H), 1.38 (d, PMe_3 , $J = 6.0\text{ Hz}$, 18H); 6.60–7.49 (m, ArH, 4H). ^{31}P NMR (121 MHz, benzene- d_6 , 300 K/ppm) δ 13.1 (dt, $J = 31.5, 24.2\text{ Hz}$, P_aMe_3 , 1P), 21.3 (ddd, $J = 24.2, 40.0, 93.8\text{ Hz}$, P_bMe_3 , 1P), 39.0 (dt, $J = 40.0, 31.5\text{ Hz}$, P_cMe_3 , 1P), 78.2 (ddd, $J = 24.2, 31.5, 93.8\text{ Hz}$, P_d iPr_2 , 1P). ^{13}C NMR (75 MHz, benzene- d_6 , 300 K/ppm) δ : 19.8 (t, $J = 2.8\text{ Hz}$, PCHCH₃), 20.9 (d, $J = 5.8\text{ Hz}$, PCHCH₃), 21.9 (d, $J = 3.0\text{ Hz}$, PCHCH₃), 22.3 (m, PMe_3), 29.7 (dt, $J = 30.0, 7.2\text{ Hz}$, PMe_3), 28.5 (s, PMe_3), 29.7 (dd, $J = 30.0, 7.2\text{ Hz}$, PCHCH₃), 110.7 (d, $J = 4.8\text{ Hz}$, Ar-C), 118.2 (d, $J = 6.2\text{ Hz}$, Ar-C), 124.3 (d, $J = 7.2\text{ Hz}$, Ar-C), 124.9 (d, $J = 7.2\text{ Hz}$, Ar-C), 129.4 (d, $J = 2.0\text{ Hz}$, Ar-C), 177.8 (ddd, $J = 20.8, 7.1, 2.0\text{ Hz}$, Ar-C). Anal. calcd for $C_{21}H_{46}FeOP_4$ (494.34 g mol^{-1}): C, 51.02; H, 9.38. Found: C, 51.25; H, 9.27.

5.3 | Synthesis of 4

A solution of 2-diisopropylphosphino-5-methylphenol (0.8 g, 3.61 mmol) in 30 ml Et_2O was slowly added to a solution of $Fe(PMe_3)_4$ (1.30 g, 3.61 mmol) in 40 ml Et_2O at $-78\text{ }^\circ\text{C}$, forming an orange mixture. After stirring at room temperature for 18 hr, the turbid orange solution was evaporated under reduced pressure and the red

powder was extracted with *n*-pentane and diethyl ether. Complex **4** (1.3 g, 2.56 mmol) was obtained as red crystals in the yield of 71%. M.p.: 124–126 °C. IR (Nujol mull, 4000–400 cm⁻¹): 3132 ν (ArH), 1906 ν (Fe–H), 932 ν (PMe₃). ¹H NMR: (300 MHz, benzene-d₆, 300 K/ppm) δ –9.53 (dddd, ²*J* PH = 79.7 Hz, ²*J* PH = 74.4 Hz, ²*J* PH = 52.3 Hz, ²*J* PH = 37.6 Hz, FeH, 1H), 1.17 (dd, *J* = 12.0, 6.0, PCHCH₃, 3H), 1.29 (dd, *J* = 12.0, 6.0, PCHCH₃, 3H), 1.53 (dd, *J* = 12.0, 6.0, PCHCH₃, 3H), 1.65 (dd, *J* = 12.0, 6.0, PCHCH₃, 3H), 2.45 (s, Ar-CH₃, 3H), 2.47–2.59 (m, PCHCH₃, 2H), 0.99 (d, *J* = 6.0 Hz, PMe₃, 9H), 1.39 (d, *J* = 6.0 Hz, PMe₃, 9H), 1.41 (d, *J* = 6.0 Hz, PMe₃, 9H), 6.86–7.53 (m, ArH, 3H). ³¹P NMR (121 MHz, benzene-d₆, 300 K/ppm) δ 13.1 (dt, *J* = 31.5, 47.2 Hz, PMe₃, 1P), 21.1 (ddd, *J* = 94.4, 40.0, 24.2 Hz, PMe₃, 1P), 38.9 (dt, *J* = 41.1, 64.1 Hz, PMe₃, 1P), 78.2 (ddd, *J* = 93.2, 33.9, 24.2 Hz, P ⁱPr₂, 1P) ppm, ¹³C NMR (75 MHz, benzene-d₆, 300 K/ppm) δ : 20.9 (s, PCHCH₃), 21.9 (d, *J* = 2.3 Hz, PCHCH₃), 22.3 (m, PMe₃), 27.0 (d, *J* = 18.2 Hz, PMe₃), 28.5 (s, PMe₃), 29.6 (dd, *J* = 30.0, 7.2 Hz, PCHCH₃), 117.8 (d, *J* = 6.8 Hz, Ar-C), 118.3 (d, *J* = 4.7 Hz, Ar-C), 123.9 (d, *J* = 7.2 Hz, Ar-C), 124.4 (d, *J* = 7.3 Hz, Ar-C), 129.1 (d, *J* = 2.4 Hz, Ar-C), 130.6 (s, Ar-CH₃), 176.0 (dd, *J* = 20.7, 7.1 Hz, Ar-C). Anal. calcd for C₂₂H₄₈FeOP₄ (508.37 g mol⁻¹): C, 51.98; H, 9.52. Found: C, 51.79; H, 9.61.

5.4 | General procedure for the dehydration of primary amides to nitriles

Under a nitrogen atmosphere, 1 mmol primary amides was weighed into a 20 ml Schlenk tube containing a magnetic stirrer. Then, 3 mmol (EtO)₃SiH, 1 ml THF and 2% mmol catalysts were added to the tube. The tube was stirred under 60 °C for 24 hr. The conversion was determined by GC with *n*-dodecane as internal standard. The mixture was extracted with petroleum ether, dried over anhydrous sodium sulfate and evaporated under reduced pressure. Column chromatography was used with petroleum ether as developing solvent.

5.5 | Single crystal X-ray diffraction

Bruker Apex II single crystal diffractometer was used with a Ga K α radiation (λ = 1.34143) and a CCD area detector. The structure was solved using the charge-flipping algorithm, as implemented in the program SUPERFLIP^[31] and refined by full-matrix least-squares techniques against F₂ (SHELXL)^[32] through the OLEX interface.^[33] 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-1897323 (**3**) and 1865449 (**4**) contain the 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).

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CONFLICT OF INTEREST

There are no conflicts to declare.

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SUPPORTING INFORMATION

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