

Lewis acid promoted dehydration of amides to nitriles catalyzed by [PSiP]-pincer iron hydrides

Guoliang Chang¹ | Xiaoyan Li¹  | Peng Zhang¹ | Wenjing Yang¹ | Kai Li¹ | Yajie Wang¹ | Hongjian Sun¹  | Olaf Fuhr² | Dieter Fenske²

¹School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, Jinan, 250100, People's Republic of China

²Institut für Nanotechnologie (INT) und Karlsruher Nano Micro Facility (KNMF), Karlsruher Institut für Technologie (KIT), Hermann von Helmholtz Platz 1, 76344, Eggenstein Leopoldshafen, Germany

Correspondence

Hongjian Sun, School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, Jinan 250100, China.
Email: hjsun@sdu.edu.cn

Funding information

National Natural Science Foundation of China, Grant/Award Numbers: 21372143, 21572119

The dehydration of primary amides to their corresponding nitriles using four [PSiP]-pincer hydrido iron complexes **1–4** [(2-Ph₂PC₆H₄)₂MeSiFe(H)(PMe₃)₂ (**1**), (2-Ph₂PC₆H₄)₂HSiFe(H)(PMe₃)₂ (**2**), (2-(iPr)₂PC₆H₄)₂HSiFe(H)(PMe₃)₂ (**3**) and (2-(iPr)₂PC₆H₄)₂MeSiFe(H)(PMe₃)₂ (**4**)] as catalysts in the presence of (EtO)₃SiH as dehydrating reagent was explored in the good to excellent yields. It was proved for the first time that Lewis acid could significantly promote this catalytic system under milder reaction conditions than other Lewis acid-promoted system, such as shorter reaction time or lower reaction temperature. This is also the first example that dehydration of primary amides to nitriles was catalyzed by silyl hydrido iron complexes bearing [PSiP]-pincer ligands with Lewis acid as additive. This catalytic system has good tolerance for many substituents. Among the four iron hydrides **1** is the best catalyst. The effects of substituents of the [PSiP]-pincer ligands on the catalytic activity of the iron hydrides were discussed. A catalytic reaction mechanism was proposed. Complex **4** is a new iron complex and was fully characterized. The molecular structure of **4** was determined by single crystal X-ray diffraction.

KEYWORDS

amide, dehydration, iron hydride, Lewis acid, nitrile

1 | INTRODUCTION

Nitrile group, as one of the key structural motifs, is an important class of functionalities in organic and industrial chemistry, advanced materials, pharmaceuticals, pigments and agrichemicals.^[1–5] Therefore, the development of synthetic strategies toward nitriles is attracting continuous interest of chemists. In traditional synthetic methods, stoichiometric acidic dehydrating or basic reagents,^[2,6] azides,^[6–8] or amine oxidation reagents^[9] were used. However, the drawbacks of these processes are obvious, such as harsh reaction conditions, toxic reagents and unfavorable formation of side products. The dehydration of primary amides catalyzed by transition metal complexes represents one of the well-

documented and promising strategies for synthesis of nitriles. At the beginning, the precious metals as catalysts were used for this process.^[10,11] Nevertheless, due to the toxicity and high prices of the precious metals, people have begun to look for cheap metal catalyst. During last decades, several cheaper and less-toxic catalysts have been applied in the dehydration of primary amides to nitriles.^[12–14] Especially, iron complexes have becoming more and more attractive for chemists because of high abundance, low-cost and environmental friendliness.^[13] In 2011, Sortais and Darcel reported a well-defined NHC iron complex catalyzed dehydration of amides to nitriles and investigated the related mechanism.^[15] In the same year, Enthaler described the iron-catalyzed dehydration of amides using M-methyl-N-

(trimethylsilyl)trifluoroacetamide (MSTFA) as the dehydration reagents.^[16] Moreover, we have made some achievements in the field of dehydration of amides to nitriles with hydrido iron complexes as catalysts. In 2016, we disclosed that hydrido thiophenolato iron (II) complexes could be used as efficient catalysts for dehydration of primary amides to nitriles.^[17] After two years, we found that dehydration of amides to nitriles could also be catalyzed by silyl hydrido iron (II) complexes in good to excellent yields.^[18] Meanwhile, it was confirmed that MSTFA as dehydration reagent is an excellent trimethylsilyl-transfer compound.^[19,20] The fluoride-catalyzed (metal-free) dehydration of primary amides using silanes as dehydrating reagents was published by Beller's group.^[21] In 2011, Enthaler also described a copper-catalyzed dehydration of primary amides to form nitriles.^[22] Last year, Buchwald presented a silylative dehydration of primary amides to nitriles using copper-hydrides as catalyst.^[23]

Over the years, it has been known that Lewis acids can promote some metal catalyzed organic transformations.^[24,25] Lewis acids were also used for dehydration of amides to nitriles^[14,20,26] but more stringent reaction conditions, such as higher temperature or longer reaction time, limit their application. It was also found that primary amides could transfer to the related nitriles by ZnCl₂ in CH₃CN/H₂O medium under microwave irradiation.^[27] After we have studied the dehydration of amides to nitriles with hydrido iron or cobalt complexes as catalysts,^[7-18,28] now we want to know if Lewis acids can promote these catalytic systems. Therefore, in order to expand the scope of the application of these hydrido iron complexes, four [PSiP]-pincer iron hydrides **1-4** were

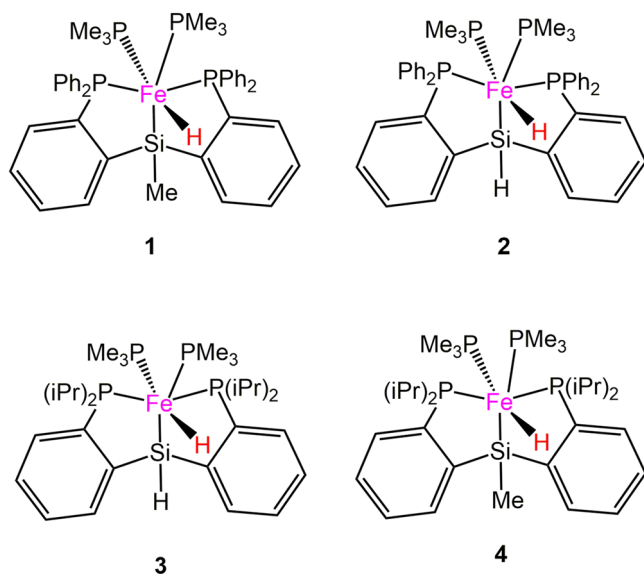


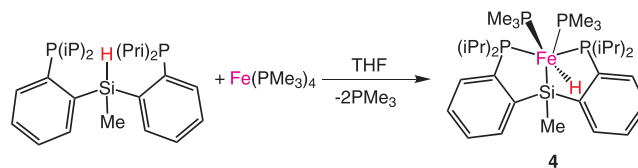
FIGURE 1 Selected silyl tridentate iron Complexes

synthesized (Figure 1) and their catalytic activities for dehydration of amides to nitriles were explored. It was also confirmed for the first time that Lewis acids could promote this catalytic dehydration process. Among the four iron hydrides, complex **4** is new. The influence of the substituents at P and Si atom on the catalytic activity of the iron hydrides were also discussed.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of [PSiP]-pincer iron hydrides **1-4**

Complexes **1-3** were prepared according to the literature procedures.^[29,30] Complex **4** was obtained from the combination of bis(*o*-(diisopropylphosphino)phenyl) methylsilane with Fe (PMe₃)₄ in THF at 0 °C under Ar atmosphere (Scheme 1). Complex **4** was fully characterized by ¹H, ¹³C and ³¹P NMR, IR and X-ray diffraction as



SCHEME 1 Preparation of Complex **4**

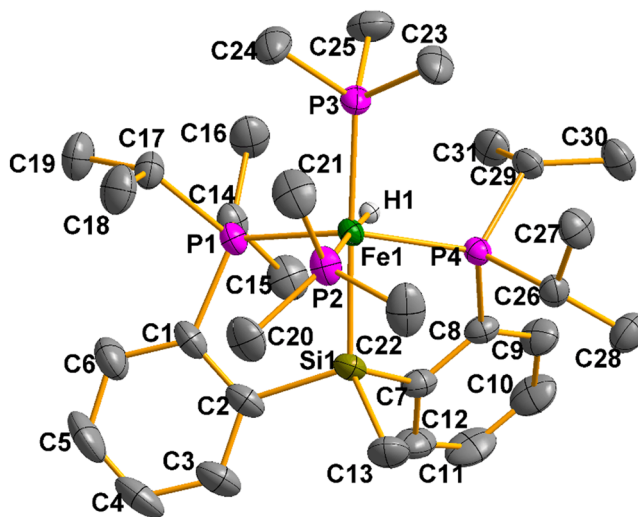


FIGURE 2 ORTEP plot of complex **4** at the 50% probability level (most of hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1 P1 2.2362(1), Fe1 P2 2.2443(1), Fe1 P3 2.2713(1), Fe1 P4 2.2463(1), Fe1 Si1 2.3106(1), Fe1 H1 1.53(2), P1 Fe1 P2 105.32(4), P1 Fe1 P3 99.92(4), P4 Fe1 P3 99.18(5), P4 Fe1 Si1 79.48(5), P1 Fe1 Si1 82.13(4), P1 Fe1 P3 99.92(4), P1 Fe1 P4 134.77(3), P1 Fe1 Si1 82.13(4), P3 Fe1 Si1 177.93(3), P2 Fe1 H1 177.50(9), Si1 Fe1 H1 92.40(9)

well as elemental analysis. In the IR spectrum of **4**, a typical ν (Fe-H) stretching band was found at 1839 cm^{-1} . In the ^1H NMR spectrum of **4**, a “td” signal at -14.56 ppm for the hydrido H was formed by (PH)-coupling with four P atoms (J (PH) = 18 and 75 Hz) while two doublets for two PMe_3 ligands were observed at 1.13 and 1.25 ppm, respectively. This indicates that two PMe_3 ligands are chemically different. The spectroscopic characteristics are comparable with those of complex **1**.^[30] In the ^{31}P NMR

spectrum of **4** a “dt” peak at 1.7 and a multiplet peak at 6.3 ppm for the two PMe_3 ligands and a doublet at 88.7 ppm for $-\text{P}^i\text{Pr}_2$ groups were recorded in the integral ratio of 1 (PMe_3): 1 (PMe_3): 2 ($-\text{P}^i\text{Pr}_2$). The molecular structure of **4** was determined by single crystal X-ray diffraction (Figure 2).

Complex **4** has a distorted octahedral geometry with an iron atom in the center. The axial bond angle P2-Fe1-H1 is $177.50(9)^\circ$, deviated from 180° . The sum of

TABLE 1 Iron catalyzed dehydration of *p* chlorobenzamide^a

The reaction scheme shows *p*-chlorobenzamide (a benzene ring with a chlorine atom at the para position and a $-\text{C}(=\text{O})\text{NH}_2$ group) reacting with Complex 1-4, solvent, and silane to produce *p*-chlorobenzonitrile (a benzene ring with a chlorine atom at the para position and a $-\text{CN}$ group).

Entry	Catalyst	Loading (mol%)	Silane	Solvent	T(°C)	Time(h)	Conv. (%) ^b	Yield (%) ^c
1	1	0	(EtO) ₃ SiH	THF	60	24	0	0
2	1	2	(EtO) ₃ SiH	THF	60	24	79	76
3	2	2	(EtO) ₃ SiH	THF	60	24	74	70
4	3	2	(EtO) ₃ SiH	THF	60	24	71	66
5	4	2	(EtO) ₃ SiH	THF	60	24	69	65
6	1	5	(EtO) ₃ SiH	THF	60	24	92	89
7	1	1	(EtO) ₃ SiH	THF	60	24	65	59
8	1	2	Et ₃ SiH	THF	60	24	55	50
9	1	2	Ph ₂ SiH	THF	60	24	59	54
10	1	2	Ph ₃ SiH	THF	60	24	57	52
11	1	2	PhSiH ₃	THF	60	24	51	44
12	1	2	TMDS	THF	60	24	60	55
13	1	2	PMHS	THF	60	24	60	54
14 ^d	1	2	(EtO) ₃ SiH	THF	60	24	51	47
15 ^e	1	2	(EtO) ₃ SiH	THF	60	24	50	44
16	1	2	(EtO) ₃ SiH	dioxane	60	24	70	67
17	1	2	(EtO) ₃ SiH	benzene	60	24	37	30
18	1	2	(EtO) ₃ SiH	DMSO	60	24	72	68
19	1	2	(EtO) ₃ SiH	isopropanol	60	24	53	47
20	1	2	(EtO) ₃ SiH	CH ₃ Cl	60	24	43	38
21	1	2	(EtO) ₃ SiH	CH ₂ Cl ₂	60	24	61	57
22	1	2	(EtO) ₃ SiH	THF	40	24	32	24
23	1	2	(EtO) ₃ SiH	THF	60	6	57	51
24	1	2	(EtO) ₃ SiH	THF	60	12	66	62
25	1	2	(EtO) ₃ SiH	THF	25	12	11	<5
26	1	2	(EtO) ₃ SiH	THF	40	12	30	24

^aCatalytic reaction conditions: amide (1.0 mmol), (EtO)₃SiH (3.0 mmol) and **1** (0.02 mmol) in 2 ml THF, T °C, t h.

^bDetermined by GC analysis. *n* Dodecane as internal standard (1.0 mmol).

^cIsolated yield.

^d2 eq. Silane.

^e4 eq. Silane.

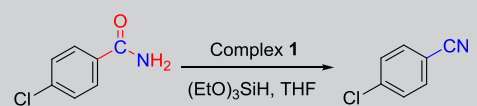
equatorial coordination bond angles (P1-Fe1-P3 (99.92°), P3-Fe1-P4 (99.18°), Si1-Fe1-P4 (79.48°) and Si1-Fe1-P1 (82.13°)) is 360.71°, slightly deviated from 360°. The length of Fe1-H1 bond is 1.53(2) Å, almost same (1.55(4) Å) with that of complex **1**.^[30] Among the four Fe-P bonds Fe1-P3 (2.2713(1) Å) is the longest due to the strongest *trans*-influence of the Si atom in comparison with that of H and P atom.

2.2 | Catalytic activities of complexes **1-4**

The catalytic performance of complexes **1-4** was evaluated for dehydration reduction of amides to nitriles. At the beginning, *p*-chlorobenzamide as a model substrate was treated with hydrosilane in the presence of catalytic amount of the iron hydride in THF (Table 1). In order to get optimized reaction conditions, a series of reaction parameters, such as catalyst loading, solvent, reaction temperature, silane and reaction time, were evaluated.

No *p*-chlorobenzonitrile was detected in the absence of catalyst (Entry 1, Table 1). 2 mol% of complex **1** could afford 76% yield (Entry 2, Table 1). However, when complex **1** was replaced by complexes **2-4**, lower yields (65% - 70%) were obtained (Entries 3-5, Table 1) but the decline from **2** to **3** is not significant. This result indicates that the *isopropyl* groups at P atoms are not obviously beneficial to reductive dehydration of primary amides to nitriles in comparison to the phenyl groups (**1** vs. **4**; **2** vs **3**) at P atoms while the influence of the methyl group at Si atom on the catalytic activity of the complexes is uncertain (**1** vs. **2**; **4** vs. **3**). When the catalyst loading was increased to 5 mol%, the yield was increased to 89% (Entry 6, Table 1). With the decrease of the catalyst loading (1 mol%) the yield (59%) declined significantly (Entry 7, Table 1). Surprisingly, the yields were greatly reduced when (EtO)₃SiH was replaced by other silanes, such as Et₃SiH, PhSiH₃, Ph₂SiH₂, Ph₃SiH, TMDS and PMHS as the hydrogen sources (Entries 8-13, Table 1). Moreover, no better yield could be obtained with 2 or 4 equiv. of

TABLE 2 Lewis acid promoted dehydration of *p* chlorobenzamide^a



Entry	Catalyst	Loading (mol%)	Lewis Acid	T(°C)	Time (h)	Yield (%) ^b
1	1	2	ZnCl ₂	25	8	38
2	1	2	ZnCl ₂	60	12	79
3	1	2	ZnCl ₂	40	12	77
4	1	2	ZnBr ₂	40	12	81
5	1	2	CuI	40	12	52
6	1	2	CuBr	40	12	<10
7	1	2	CuCl	40	12	<10
8	1	2	Cu (acac) ₂	40	12	<10
9	1	2	FeCl ₃	40	12	<10
10	1	2	MgCl ₂	40	12	<10
11	1	2	ZnBr ₂ (8%)	40	12	37
12	1	2	ZnBr ₂ (20%)	40	12	59
13	1	2	ZnBr ₂ (50%)	40	12	67
14	1	1	ZnBr ₂	40	12	62
15	1	2	ZnBr ₂	40	24	85
16	1	2	ZnBr ₂	40	30	89
17	1	2		40	30	34
18		0	ZnBr ₂	40	30	0

^aCatalytic reaction conditions: amide (1.0 mmol), (EtO)₃SiH (3.0 mmol), Lewis acid (1.2 mmol) and **1** (0.02 mmol) in 2 ml THF, T °C, t h.

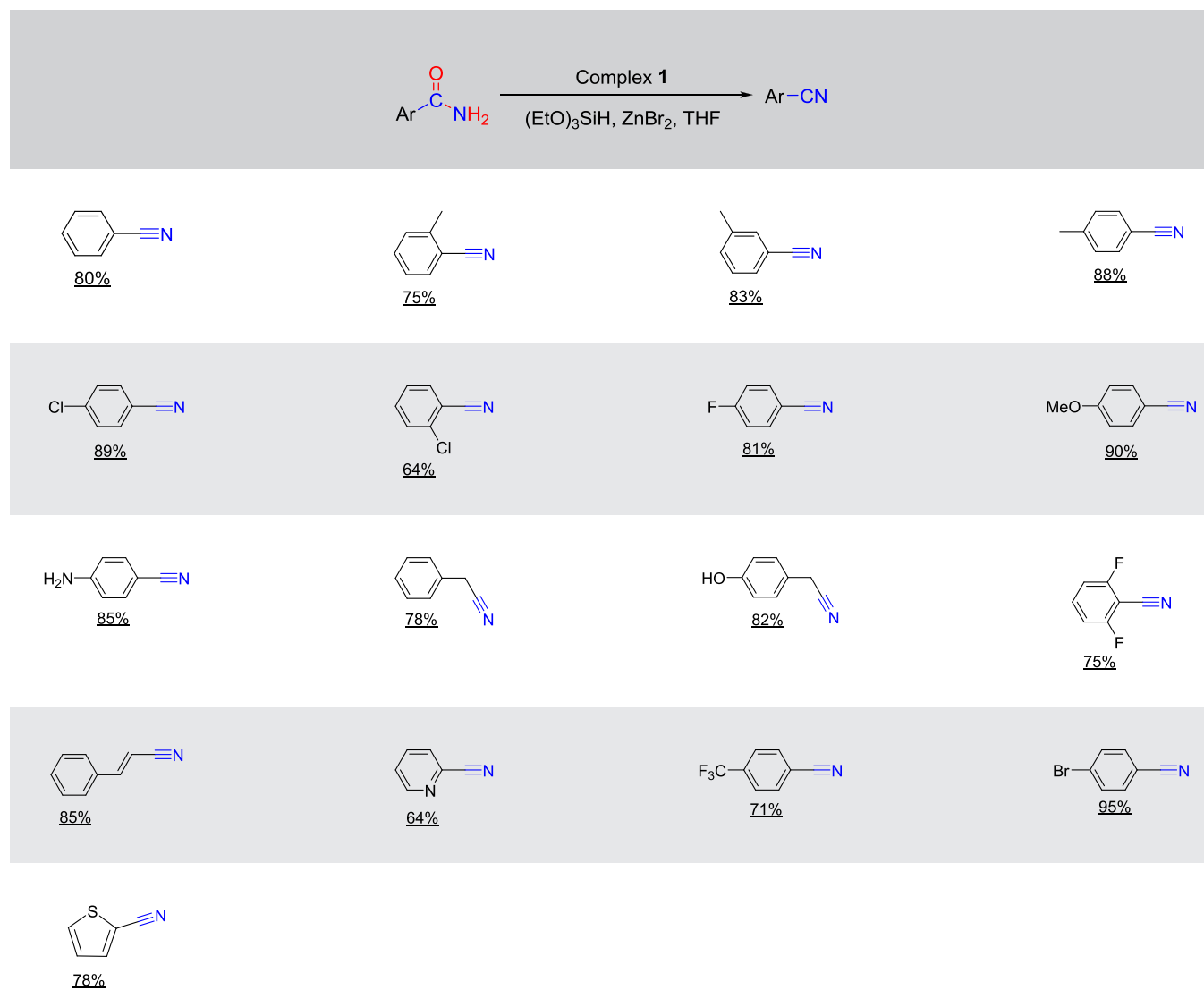
^bIsolated yield.

silane (Entries 14–15, Table 1). THF was proved to be the best reaction medium in comparison with dioxane, benzene, DMSO, isopropanol, CH₃Cl and CH₂Cl₂ (Entries 16–21, Table 1). Lower reaction temperature brought poorer yield (Entry 22, Table 1). When the reaction time was shortened, the yield became worse (Entries 23 and 24, Table 1). When we compare the results of entries 25 and 26 in Table 1 with those of entries 1 and 3 in Table 2, we can find that Lewis acids ZnCl₂ promoted the catalytic process obviously. When different Lewis acids were added into this catalytic system, it was found that ZnBr₂ is the best Lewis acid for this catalytic system (Entries 3–10, Table 2). When the amount of ZnBr₂ was decreased, the yields were decreased remarkably (Entries 11–13, Table 2). From entry 14 to entry 16 we can

conclude that the optimized catalytic conditions are: complex **1** as catalyst, catalyst loading 2 mol%, ZnBr₂ as Lewis acid (1.2 equiv.), 40 °C, 30 hr in THF. If we compare entries 16 (Yield 89%) and 17 (Yield 34%) in Table 2, we can know that Lewis acid ZnBr₂ promoted this catalytic reaction significantly. Without catalyst **1** the yield is very poor in the presence of ZnBr₂ (entry 18, Table 2).

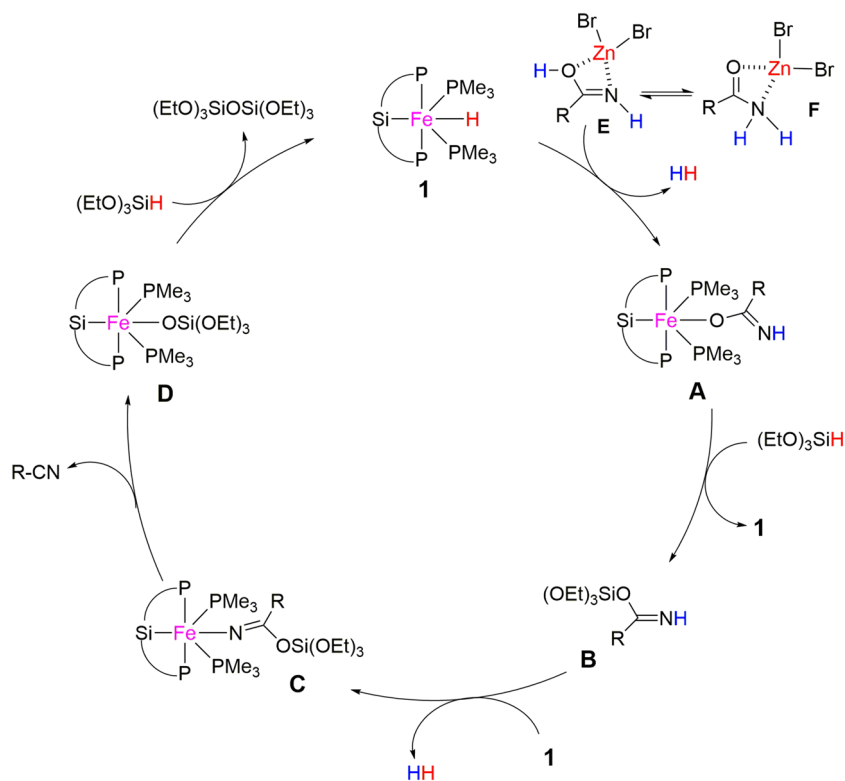
Under the optimized reaction condition the scope of the substrates for dehydration of amides to nitriles was explored (Table 3). As shown in Table 3, aromatic, and heteroaromatic as well as aliphatic nitriles could be prepared in moderate to excellent yields from the corresponding primary amides under the optimized conditions. These results reveal that this catalytic system has wide applicability for dehydration of amides to nitriles.

TABLE 3 The dehydration of amides to nitriles catalyzed by complex **1**^{a,b}



^aCatalytic reaction conditions: amide (1.0 mmol), ZnBr₂ (1.2 mmol) (EtO)₃SiH (3.0 mmol) and complex **1** (0.02 mmol) in 2 ml THF, 40 °C, 30 hr.

^bIsolated yield.



SCHEME 2 A proposed catalytic mechanism

Whether it is a substrate with electron-withdrawing group (Cl- and F-) or with electron-donating group (Me-, MeO- and -NH₂), it has a good yield. *p*-Trifluoromethylbenzamide has only 71% yield because -CF₃ is a very strong electron-withdrawing group. Cinnamonitrile was synthesized from cinnamamide in 85% yield while C=C bond remained unchanged. It must be noted that the addition of Lewis acid played an important role for this catalytic process. These results demonstrate that this catalytic system has good tolerance for some substituents and the catalytic conditions are milder than other Lewis acid-promoted system, with shorter reaction time or lower reaction temperature.^[28–30]

2.3 | Catalytic mechanism

Based on the mechanism reported by Beller^[31] and Buchwald^[23] we propose a mechanism in Scheme 2 for this dehydration of amides to nitriles catalyzed by [PSiP]-pincer iron hydrides. At the beginning of the catalytic cycle, ZnBr₂ as Lewis acid supports the tautomerization of amide (F) to imine (E) form because the strong electron-withdrawing ability of Lewis acid (ZnBr₂) makes the hydrogen atom on the hydroxyl group more acidic. This is conducive to the first acid(H⁺)-base(H⁻) reaction. E reacts with **1** to afford **A** with the release of

H₂. The interaction of **A** with (EtO)₃SiH gives rise to **B** and **1** through substitution. Intermediate **C** is formed from the combination of **B** and **1**. β-Elimination of **C** delivers nitrile as the final product with the formation of **D**. The ligand replacement of coordinated OSi(OEt)₃ group by hydrido H produces ((EtO)₃Si)₂O with the recovery of **1**.

3 | CONCLUSIONS

[PSiP]-pincer hydrido iron complexes **1–4** were synthesized and complex **4** is a new compound. The efficient silane-based reductive dehydration of amides to nitriles with complexes **1–4** as catalysts was explored in moderate to excellent yields. It was proved for the first time that Lewis acid could significantly promote this catalytic system under milder reaction conditions than other Lewis acid-promoted system, such as shorter reaction time or lower reaction temperature. This is also the first example that dehydration of primary amides to nitriles was catalyzed by silyl hydrido iron complexes bearing [PSiP]-pincer ligands with Lewis acid as additive. This catalytic system has good tolerance for some substituents. The catalytic effect of [PSiP]-pincer ligand system on the conversion of amide to nitrile is similar to that of thiophenolato ligand system^[17] and is better than that

of selenophenolato ligand system.^[32] A proposed mechanism was discussed.

4 | EXPERIMENTAL

4.1 | General procedures and materials

Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Solvents were dried by metal sodium 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. NMR spectra were recorded using Bruker Avance 300 MHz spectrometers. GC was recorded on a Fuli 9790 instrument. Melting points were measured in capillaries sealed under N₂ and were uncorrected. Elemental analyses were carried out on an Elementar Vario ELIII instrument. All the amides were purchased and used without further purification. The purity of the triethoxysilane used is 95%. Fe (PMe₃)₄^[33] and complexes **1–3**^[29,30] were prepared according to literature procedures. The ligand of bis(*o*-(diisopropylphosphino)phenyl)methylsilane was prepared via a modified procedure according to the literature.^[34]

4.2 | Synthesis of **4**

Under Ar, Fe (PMe₃)₄ (0.51 g, 1.41 mmol) in 30 ml toluene was added into a solution of ligand bis(*o*-(diisopropylphosphino)phenyl)methylsilane (0.60 g, 1.39 mmol) in 30 ml of toluene at 0 °C. The mixture was warmed slowly to room temperature and stirred at room temperature for 24 hr. The toluene was discarded under Ar. The residue was washed with *n*-pentane and diethyl ether. Orange crystals (0.67 g, 82%) were obtained from diethyl ether solution. Dec.: > 135 °C. Anal. Calc. for C₃₁H₅₈FeP₄Si (638.62 g/mol): C, 58.30; H, 9.15. Found: C, 58.05; H, 9.40. IR (Nujol mull, cm⁻¹): 3046 (ArH), 1839 (Fe-H), 1508 (ArC=C), 943 (PMe₃). ¹H NMR (300 MHz, C₆D₆, 300 K, δ/ppm): -14.86 (td, *J* = 18.0 Hz, *J* = 72.0 Hz, 1H, Fe-H), 0.29 (s, SiCH₃, 3H), 0.83 (q, *J* = 3.0 Hz, PCHCH₃, 6H), 0.98 (q, *J* = 3.0 Hz, PCHCH₃, 12H), 1.08 (q, *J* = 3.0 Hz, PCHCH₃, 6H), 1.12 (d, *J* = 9.0 Hz, PCH₃, 9H), 1.25 (d, *J* = 3.0 Hz, PCH₃, 9H), 1.90–1.96 (m, PCHCH₃, 2H), 2.47–2.49 (m, PCHCH₃, 2H), 7.08 (d, *J* = 6.0 Hz, 2H, Ar-H), 7.19 (q, *J* = 9.0 Hz, 2H, Ar-H), 7.25 (d, *J* = 6.0 Hz, 2H, Ar-H), 7.94 (d, *J* = 6.0 Hz, 2H, Ar-H). ³¹P NMR (121 MHz, C₆D₆, 300 K, δ/ppm): 1.7 (dt, *J* = 46.3, 16.4 Hz, 1P, PMe₃), 6.3 (m, 1P, PMe₃), 88.7 (d, *J* = 12.1 Hz, 2P, PⁱPr). ¹³C NMR (75 MHz,

C₆D₆, 300 K, δ/ppm): 160.2 (Ar-C), 150.4 (Ar-C), 130.8 (Ar-C), 125.6 (Ar-C), 33.9–34.2 (m, PCHCH₃), 32.4 (s, Si-CH₃), 27.6–29.9 (m, PCHCH₃), 20.8 (d, *J* = 10.0 Hz, PCH₃), 20.1 (d, *J* = 24.0 Hz, PCH₃).

4.3 | X-ray crystal structure determination

Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer equipped with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The crystal was kept at 298.15 K during data collection. Using Olex2,^[35] the structure was solved with the Superflip^[36] structure solution program using Charge Flipping and refined with the XL^[37] refinement package using Least Squares minimization. A summary of crystal data, data collection parameters, and structure refinement details is given in the Supporting Information. CCDC-1571321 (**4**) contains 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).

4.4 | Catalytic dehydration of primary amides

The primary amide (1.0 mmol), Lewis acid (1.2 mmol) and (EtO)₃SiH (0.50 g, 3.0 mmol) were added into a 25 ml Schlenk tube containing a solution of catalyst in 2 ml of THF. The reaction mixture was stirred for 30 hr at 60 °C or 40 °C. The products were purified according to literature procedures by Beller.^[21] The NMR of all products was listed in the Supporting Information.

ACKNOWLEDGMENTS

We gratefully acknowledge the support by NSF China No. 21572119 and 21372143.

CONFLICT OF INTEREST

There are no conflicts to declare.

FUNDING INFORMATION

National Natural Science Foundation of China, Grant/Award Number: NSF China No. 21572119 and 21372143.

ORCID

Xiaoyan Li  <https://orcid.org/0000-0003-0997-0380>

Hongjian Sun  <https://orcid.org/0000-0003-1237-3771>

REFERENCES

- [1] B. R. Pitta, O. W. Steward, F. F. Fleming, *J. Org. Chem.* **2018**, *83*, 2753.
- [2] D. T. Mowry, *Chem. Rev.* **1948**, *42*, 189.
- [3] G. Barker, M. R. Alshawish, M. C. Skilbeck, I. Coldham, *Angew. Chem. Int. Ed.* **2013**, *52*, 7700.
- [4] F. F. Fleming, L. Yao, P. C. Ravikumar, L. Funk, B. C. Shook, *J. Med. Chem.* **2010**, *53*, 7902.
- [5] G. Yan, Y. Zhang, J. Wang, *Adv. Synth. Catal.* **2017**, *359*, 4068.
- [6] S. E. Ellzey, C. H. Mack, W. J. Connick, *J. Org. Chem.* **1967**, *32*, 846.
- [7] W. E. McEwen, W. E. Conrad, C. A. Vanderwerf, *J. Am. Chem. Soc.* **1952**, *74*, 1168.
- [8] G. I. Koldobskii, V. A. Ostrovskii, B. V. Gidaspov, *Russ. Chem. Rev.* **1978**, *47*, 1084.
- [9] Y. Huang, X. D. Chong, C. B. Liu, Y. Liang, B. Zhang, *Angew. Chem. Int. Ed.* **2018**, *57*, 13163.
- [10] S. Hanada, Y. Motoyama, H. Nagashima, *Eur. J. Org. Chem.* **2008**, *2008*, 4097.
- [11] S. Das, S. Zhou, D. Addis, S. Enthaler, K. Junge, M. Beller, *Top. Catal.* **2010**, *53*, 979.
- [12] S. Sueoka, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2010**, *46*, 8243.
- [13] (a) I. Bauer, H. J. Knölker, *Chem. Rev.* **2015**, *115*, 3170. (b) D. Wei, C. Darcel, *Chem. Rev.* **2019**, *119*, 2550. (c) M. H. Al Huniti, M. P. Croatt, *Asian J. Org. Chem.* **2019**. <https://doi.org/10.1002/ajoc.201900343> (d) N. S. Shaikh, *Chemistry Select* **2019**, *4*, 6753. (e) S. Elangovan, S. Quintero Duque, V. Dorcet, T. Roisnel, L. Norel, C. Darcel, J. B. Sortais, *Organometallics* **2015**, *34*, 4521.
- [14] Y. Y. Wang, L. Y. Fu, H. M. Qi, S. W. Chen, Y. H. Li, *Asian J. Org. Chem.* **2018**, *7*, 367.
- [15] D. Bezier, G. T. Venkanna, J. B. Sortais, C. Darcel, *Chem Cat Chem* **2011**, *3*, 1747.
- [16] S. Enthaler, *Eur. J. Org. Chem.* **2011**, 4760.
- [17] B. Xue, H. Sun, Y. Wang, T. Zheng, X. Li, O. Fuhr, D. Fenske, *Cat. Com.* **2016**, *86*, 148.
- [18] S. Ren, S. Xie, T. Zheng, Y. Wang, S. Xu, B. Xue, X. Li, H. Sun, O. Fuhr, D. Fenske, *Dalton Trans.* **2018**, *47*, 4352.
- [19] S. Enthaler, *Chem. Eur. J.* **2011**, *17*, 9316.
- [20] S. Enthaler, S. Inoue, *Chem. Asian J.* **2012**, *7*, 169.
- [21] S. Zhou, K. Junge, D. Addis, S. Das, M. A. Beller, *Org. Lett.* **2009**, *11*, 2461.
- [22] S. Enthaler, M. Weidauer, *Catal. Lett.* **2011**, *141*, 1079.
- [23] R. Liu, M. Bae, S. L. Buchwald, *J. Am. Chem. Soc.* **2018**, *140*, 1627.
- [24] M. L. Yuan, J. H. Xie, Q. L. Zhou, *Chem Cat Chem* **2016**, *8*, 3036.
- [25] A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers, H. M. Tuononen, *Nat. Chem.* **2014**, *6*, 983.
- [26] W. Yao, H. Fang, Q. He, D. Peng, G. Liu, Z. Huang, *J. Org. Chem.* **2019**, *84*, 6084.
- [27] K. Manjula, M. A. Pasha, *Synth. Commun.* **2007**, *37*, 1545.
- [28] S. Ren, Y. Wang, F. Yang, H. Sun, X. Li, *Cat. Com.* **2019**, *120*, 72.
- [29] P. Zhang, X. Li, X. Qi, H. Sun, O. Fuhr, D. Fenske, *RSC Adv.* **2018**, *8*, 14092.
- [30] S. Wu, X. Li, Z. Xiong, W. Xu, Y. Lu, H. Sun, *Organometallics* **2013**, *32*, 3227.
- [31] S. Zhou, D. Addis, S. Das, K. Junge, M. Beller, *Chem. Commun.* **2009**, 4883.
- [32] T. Zheng, Y. Wang, Z. Yang, H. Sun, X. Li, *Chin. J. Org. Chem.* **2019**, *39*, 2941.
- [33] H. H. Karsch, *Chem. Ber.* **1977**, *110*, 2699.
- [34] H. Y. Fang, Y. K. Choe, Y. H. Li, S. Shimada, *Chem. Asian J.* **2011**, *6*, 2512.
- [35] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
- [36] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.
- [37] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *A64*, 112.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.