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Pyridine N-oxide promoted hydrosilylation of carbonyl compounds catalyzed by [PSiP]-pincer iron hydrides

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Abstract

Five [PSiP]-pincer iron hydrides **1** – **5**, [(2-Ph₂PC₆H₄)₂HSiFe(H)(PMe₃)₂ (**1**), (2-Ph₂PC₆H₄)₂MeSiFe(H)(PMe₃)₂ (**2**), (2-Ph₂PC₆H₄)₂PhSiFe(H)(PMe₃)₂ (**3**), (2-(iPr)₂PC₆H₄)₂HSiFe(H)(PMe₃)₂ (**4**), and (2-(iPr)₂PC₆H₄)₂MeSiFe(H)(PMe₃)₂ (**5**)], were used as catalysts to study the effects of pyridine N-oxide and electronic property of [PSiP]-ligands on the catalytic hydrosilylation of carbonyl compounds. It was proved for the first time that this catalytic process could be promoted with pyridine N-oxide as initiator at 30 °C because the addition of pyridine N-oxide is beneficial for the formation of unsaturated hydrido iron complex, which is the key intermediate in the catalytic mechanism. Complex **4** as the best catalyst shows excellent catalytic performance. Among the five complexes, complex **3** was new and the molecular structure of complex **3** was determined by single crystal X-ray diffraction. A proposed mechanism was discussed.

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† Electronic supplementary information (ESI) available: The table of selected crystallographic data and original IR, ¹H NMR, ³¹P NMR, and ¹³C NMR spectra of complex **3** and catalytic products. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXXXXX

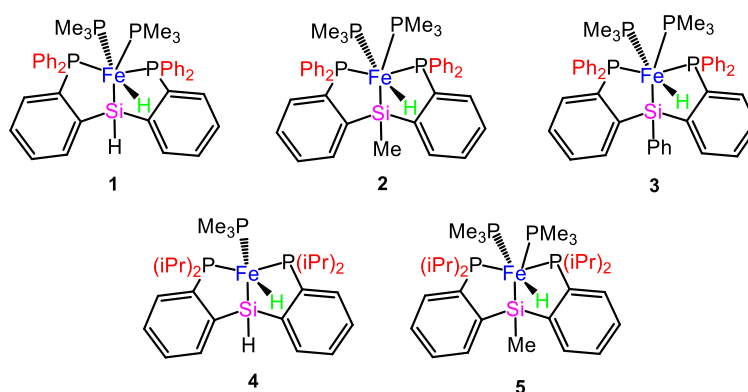
Introduction

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The homogeneous hydrosilylation catalysis for reduction of carbonyl compounds as a significant route to synthesize organic alcohols attracts extensive investigation in laboratory, academic field and industrial settings.¹ It was reported in the past decade that low-cost and environment friendly iron complexes as the catalysts could be used in the reduction of aldehydes, ketones and the other unsaturated species.²⁻³ The development on iron-catalyzed hydrosilylation reactions of carbonyl bonds was well summarized in the review articles.⁴⁻⁶ The pioneering work for the first asymmetric iron-catalyzed hydrosilylation of acetophenone by Brunner was reported in 1990.⁷ Nishiyama and Furuta disclosed that the combination of ferrous acetate and multi-nitrogen-based ligands could efficiently catalyze hydrosilylation of ketones to give the corresponding alcohols in high yields including asymmetric catalysis.⁸ In 2010, Nishiyama reported the synthesis of chiral alcohols from aldehydes catalyzed by a combination of iron(II) acetate and chiral bis(oxazolinyphenyl)amine ligands.⁹ Guan and co-workers in 2011 disclosed the hydrosilylation reaction of a variety of aldehydes and ketones with the iron hydrido complexes bearing the [PCP]-pincer ligands as catalysts.¹⁰ Sortais described several iron complexes which catalyzed the hydrosilylation of aldehydes and ketones upon visible light activation in 2012.¹¹ In 2014, the group of Guan used cationic iron complexes as the catalysts to increase catalytic activity toward the hydrosilylation reduction of aldehydes and ketones.¹² In 2018, our group also investigated the reduction of aldehydes and ketones with iron hydrides bearing a [PPP]-pincer ligand as catalysts.¹³ In addition, the design of catalysts played an important role in the activity and selectivity for the reduction processes. Driess found that iron complexes bearing silicon-based ligands could also be used as catalysts for hydrosilylation of carbonyl compounds.¹⁴⁻¹⁵ It has been proved that the transition metal complexes bearing phosphine-based [PSiP]-pincer silyl ligands as versatile pre-catalysts could be used in the reduction of unsaturated compounds in recent years. The main reason for such remarkable reactivity and catalytic activity of the [PSiP]-pincer silyl metal complexes is that ligands have potent σ -donating characters and strong

trans-influence in transition-metal chemistry.¹⁶ Furthermore, these two strategies can promote the formation of electron-rich and coordinatively-unsaturated complexes.¹⁷

In the past few years, we reported that some hydrido iron complexes could catalyze hydrosilylation of carbonyl compounds between 50 – 70 °C.¹³ Until now, in our reported work, the catalytic mechanism catalyzed by iron hydrides was not experimentally verified. Inspired by the catalytic mechanism reported by Nikonov,¹⁸ we consider that the formation of unsaturated hydrido iron species formed via dissociation of the PMe₃ ligand for our catalytic systems should be the first step in the related catalytic mechanism. Therefore, we guess that the catalytic reaction could be also promoted by taking measures to promote the dissociation of PMe₃ ligands. With this assumption we add pyridine N-oxide as initiator to enhance the dissociation of PMe₃ due to the production of stable O=PMe₃. In addition, in order to compare the catalytic activities of complexes with different groups, in this paper five hydrido [PSiP]-pincer iron complexes **1** – **5** were synthesized (**Figure 1**). Among them, complex **3** was new and was completely characterized and the molecular structure of **3** was determined by single crystal X-ray diffraction. It has been confirmed for the first time that the catalytic reactions with complexes **1** – **5** as catalysts could be significantly promoted with the addition of pyridine N-oxide as initiator because this is beneficial to the formation of coordinatively-unsaturated hydrido iron species by the reaction of PMe₃ with pyridine N-oxide. To our delight, the catalytic reactions could be realized in good to excellent yields even at 30 °C. In 2013 we reported that complex **2** could be used as catalyst for the hydrosilylation of carbonyl compounds at 60 °C.¹⁹ It is obvious that the addition of pyridine N-oxide decreased the reaction temperature significantly. This result indicates that the formation of unsaturated hydrido iron intermediate via dissociation of ligand is the first and key step in the catalytic mechanism. Complex **4** shows the best catalytic activity among the five complexes.



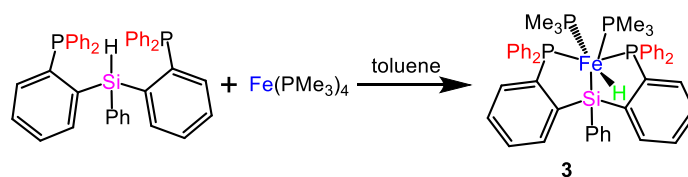
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Figure 1 [PSiP]-pincer iron(II) silyl hydrides **1 – 5**

Results and Discussion

Synthesis and characterization of complexes **1 - 5**

The synthesis and characterization of complexes **1**, **2**, **4** and **5** were realized according to the literature method.¹⁹⁻²¹ Complex **3** was synthesized by the reaction of $\text{Fe}(\text{PMe}_3)_4$ with [PSiP]-pincer preligand, (2- $\text{Ph}_2\text{PC}_6\text{H}_4$) $_2\text{SiPhH}$ (**Scheme 1**).



Scheme 1 Preparation of complex **3**

In the IR spectrum of complex **3**, the typical vibration (2134 cm^{-1}) of the Si–H bond of the preligand, (2- $\text{Ph}_2\text{PC}_6\text{H}_4$) $_2\text{SiPhH}$, disappeared while the $\nu(\text{Fe–H})$ stretching band was found at 1837 cm^{-1} . The hydrido resonance in the ^1H NMR spectrum of complex **3** appeared at -17.35 ppm as “tdd” peak with the coupling constant $J_{\text{PH}} = 71.4, 25.8, 6.9\text{ Hz}$. Three different phosphorus signals at 1.3, 5.2 and 88.8 ppm appeared in the integral ratio of 1 (PMe_3) : 1 (PMe_3) : 2 ($-\text{PPh}_2$) in the ^{31}P NMR spectrum of **3**. Meanwhile, X-ray diffraction was used to confirm the octahedral configuration of complex **3** (**Figure 2**). The crystallographic data for complex **3** was listed in Table S1. In the molecular structure of **3**, Fe1-P3 bond length ($2.2629(6)\text{ \AA}$) is longer than the other three Fe-P bonds (Fe1-P1 = $2.1970(3)$; Fe1-P1a = $2.1970(3)$ and Fe1-P2 = $2.2344(6)\text{ \AA}$) due to the strong *trans*-influence of the Si atom.

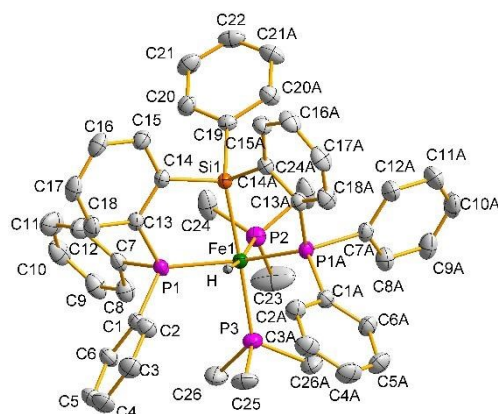


Figure 2 Molecular structure of complex **3**

Pyridine N-oxide promoted catalytic performance of iron(II) hydrides **1 - 5** for hydrosilylation of aldehydes and ketones

In 2013 we initially confirmed that complex **2** could efficiently catalyze hydrosilylation of carbonyl compounds at 60 °C.¹⁹ On this basis, in order to verify that the formation of coordinatively-unsaturated hydrido iron species is the key step we selected complexes **1 – 5** as catalysts and pyridine N-oxide as initiator to study catalytic hydrosilylation of carbonyl compounds. Meanwhile, the effect of substituent groups of the ligands on catalytic activity of the five complexes was also explored.

Initially, benzaldehyde as a model substrate was studied to evaluate the catalytic activity of complexes **1 – 5** (**Table 1**). According to our early experience we used THF as solvent and (EtO)₃SiH as the reducing agent. From **Table 1** we know that benzaldehyde has no conversion without catalyst (entry 1, **Table 1**). At 30 °C with 1 mol% of catalyst loading the five iron complexes have the conversion only between 9 – 29% within 6 h (entries 2 – 6, **Table 1**). Under this condition both complex **4** and **5** have better catalytic activity (entries 5 – 6, **Table 1**). It is surprising that, with the addition of pyridine N-oxide the conversions reached between 32 – 98 % under the same conditions (entries 7 – 11, **Table 1**). Among the five complexes, complex **4** is the best catalyst and the yield increased from 25% (without pyridine N-oxide) to 98% (with pyridine N-oxide) (entries 5 and 10, **Table 1**). The addition of pyridine N-oxide greatly facilitates the dissociation of PMe₃ with the formation of stable phosphine oxide. These

results indicate that, as we expected, the dissociation of PMe_3 ligand to form the active coordinatively unsaturated hydrido iron intermediate is the first step. Obviously, it is also rate-determining step. Additionally, electron-donating isopropyl group is beneficial for the dissociation of PMe_3 ligand and the formation of the active coordinatively unsaturated intermediate. Compared to complex **5**, it is clear that the coordinatively unsaturated intermediate of complex **4** is more active because the tetra-coordinate iron(II) intermediate is not stable. However, if the amount of pyridine N-oxide was declined to 1 mol% from 5 mol%, the conversion declined sharply (entry 12, **Table 1**). When the amount of pyridine N-oxide was increased to 10 mol%, the conversion of the reaction remained almost unchanged (entry 13, **Table 1**). When the reaction time was reduced to 4h or 2h, the conversion was declined significantly (entries 14 - 15, **Table 1**). When the reaction time was extended to 8h, the conversion could not be improved significantly (entry 16, **Table 1**). Therefore, the conclusion is that the addition of pyridine N-oxide can significantly improve the yields of the reaction only at 30 °C.

It was proved that the hydrosilylation of acetophenone could also be significantly promoted by the addition of pyridine N-oxide at 50 °C (entries 1 – 2, **Table 2**). The reaction temperature is higher than that in **Table 1** because ketones are less reactive than aldehydes. However, the catalytic temperature of hydrosilylation of ketones (at 50 °C) is still lower than that in the literature.¹¹ When the reaction time at 50 °C was shortened to 4h, the conversion decreased significantly (entry 3, **Table 2**). If the reaction temperature was 30 °C, the conversion declined sharply although the reaction time was extended to 12 h (entries 4 – 5, **Table 2**).

More aldehydes with different substituents at the phenyl rings were selected as the substrates to extend the scope of this catalytic system under the optimized catalytic condition (**Table 3**). It was found that this catalytic system is tolerant to both electron-withdrawing groups and electron-donating groups at the phenyl rings. The alcohols with either mono-substituted or bis-substituted and either *ortho*-substituted or *para*-substituted halogen groups were obtained from their corresponding aldehydes in the high yields. Furthermore, the alcohols with halogen groups at *para*-position were formed in higher yields due to the small steric effect. The alcohols containing strong

electron-withdrawing group, such as $-\text{NO}_2$ and $-\text{CN}$, were produced in good yields while the aldehydes with the electron-donating substituents, such as $-\text{Me}$ and $\text{MeO}-$, seemed to render the reaction poorer. The aliphatic alcohol (as 2-phenylethanol) was also isolated in good yield in this system. The heterocyclic alcohols also had good yields. Meanwhile, the yield of 1-naphthylmethanol was satisfactory, too. Compared with the previous reports, the bright spot of this catalytic system is the significant reduction of catalytic reaction temperature caused by the addition of pyridine N-oxide.

Table 1. Catalytic activity of **1** – **5** for hydrosilylation of benzaldehyde^a

Entry	Catalyst	Catalyst loading	Pyridine N-oxide	Time (h)	Conv. (%)
1	1	0	5	6	0
2	1	1	0	6	13
3	2	1	0	6	19
4	3	1	0	6	9
5	4	1	0	6	25
6	5	1	0	6	29
7	1	1	5	6	52
8	2	1	5	6	59
9	3	1	5	6	32
10	4	1	5	6	98
11	5	1	5	6	85
12	4	1	1	6	82
13	4	1	10	6	99
14	4	1	5	4	90
15	4	1	5	2	77
16	4	1	5	8	99

^a Reaction conditions: benzaldehyde (1.0 mmol), $(\text{EtO})_3\text{SiH}$ (1.2 mmol) and *n*-dodecane (internal standard)(1.0mmol), 2mL THF, 30 °C.

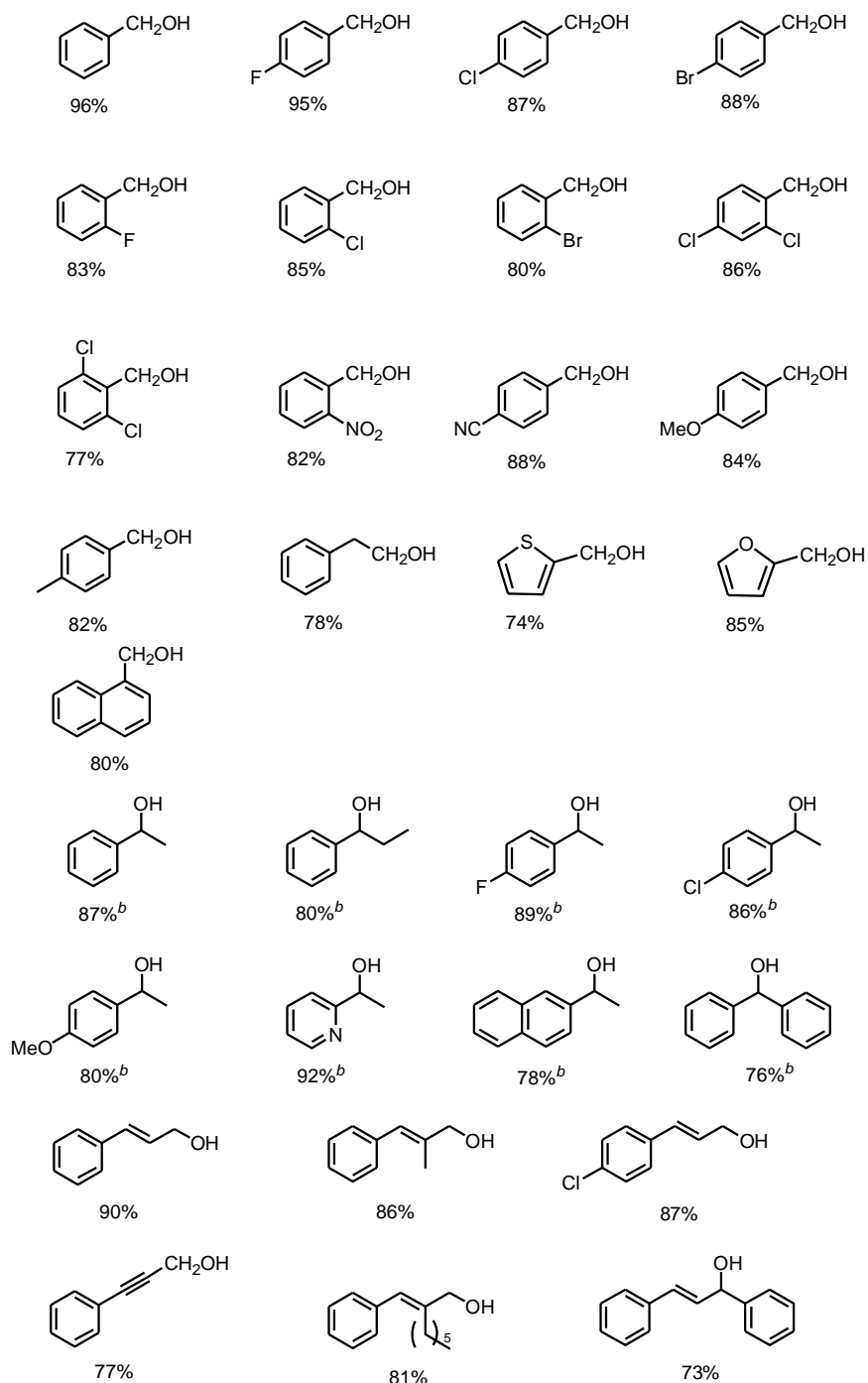
Table 2. Catalytic activity of **4** for hydrosilylation of acetophenone^a

Entry	pyridine N-oxide	T	Time	Conv.
1	0	50	6	41
2	5	50	6	89
3	5	50	4	66
4	5	30	6	47
5	5	30	12	62

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^a Reaction conditions: acetophenone (1.0 mmol), **4** (0.01 mmol), pyridine N-oxide, (EtO)₃SiH (1.2mmol) and *n*-dodecane (internal standard) (1.0 mmol), 2mL THF.

Table 3. Catalytic hydrosilylation of carbonyl compounds with **4** as catalyst^a



^a Reaction conditions: substrate (1.0 mmol), (EtO)₃SiH (1.2 mmol), **4** (0.01mmol) and pyridine N-oxide (0.05 mmol) in 2 mL THF at 30°C for 6 h in isolated yields.

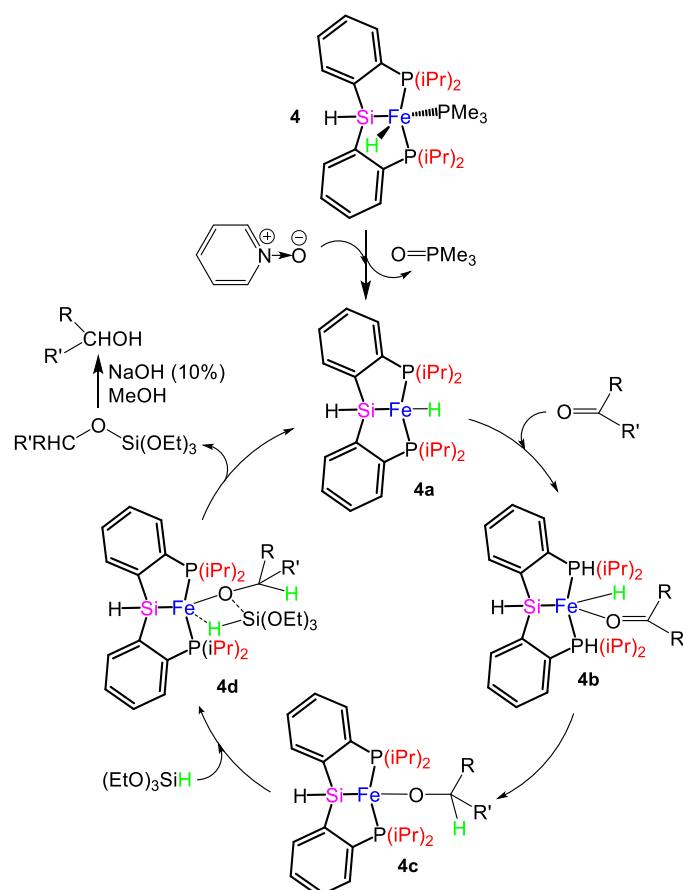
^b For ketones: substrate (1.0 mmol), (EtO)₃SiH (1.2 mmol), **4** (0.01mmol) and pyridine N-oxide (0.05 mmol) in 2 mL THF at 50°C for 6 h.

Compared to aldehydes, the reduction of ketones is more difficult and required more stringent reaction conditions. With pyridine N-oxide as initiator the

hydropyridylation of ketones was realized in good yields at 50 °C within 6h. From **Table 3** it can be concluded that the secondary alcohols could be isolated from the related ketones in moderate to excellent yields. The yield of alcohol with electron-donating substituent (MeO-) is lower than those of the alcohols with electron-withdrawing groups (F- and Cl-). The heterocyclic ketone (2-acetyl pyridine) was transferred to the related alcohol in excellent yield. 2-Acetonaphthone and benzophenone are also suitable for this catalytic system. We have tested the reaction of benzaldehyde and acetophenone (1:1) with complex **4** as catalyst and (EtO)₃SiH as hydrogen source at 30 °C. The conversion of benzaldehyde is 97% while the conversion of acetophenone is only 2%. The results show that aldehyde group is easier to be reduced than ketone group.

The selective hydrogenation reduction of the C=C and C=O bond in α,β -unsaturated aldehydes or ketones is of great importance in organic synthesis. To our delight, this catalytic system has good selectivity for reduction of α,β -unsaturated aldehydes and ketones (**Table 3**). The cinnamyl alcohol was obtained via the reduction of the corresponding cinnamaldehydes. In this process the C=C bond remained unchanged. Meanwhile, 4-chloro cinnamyl alcohol and α -hexyl cinnamyl alcohol were obtained in excellent yields. It must be emphasized that α -bromo cinnamaldehyde reacted with (EtO)₃SiH to afford 3-phenyl-2-propyn-1-ol via the elimination of HBr (77%, **Table 3**). In addition, α,β -unsaturated ketone is also applicable to this system and 1,3-diphenyl-2-propenol was isolated in the yield of 73%.

Mechanism Discussion



Scheme 2 Proposed mechanism with complex **4** as catalyst for hydrosilylation of carbonyl compounds

Based on our experimental results and literature reports,¹⁸ we proposed a catalytic mechanism with complex **4** as catalyst for hydrosilylation of carbonyl compounds (**Scheme 2**). At the beginning, in the presence of pyridine N-oxide, a trimethylphosphine ligand was dissociated from complex **4** to form an active intermediate **4a**. The coordinatively unsaturated **4a** combines with a substrate molecule to form intermediate **4b**. After that, the coordinate carbonyl group is inserted into the Fe-H bond to afford intermediate **4c**. In the presence of $(\text{EtO})_3\text{SiH}$, complex **4c** can be converted into an intermediate **4d** with a four-membered ring [FeOSiH]. The silylation product was formed by σ -metathesis reaction via **4d** and the real catalyst **4a** was regenerated for next catalytic cycle. We have monitored the reaction between complex **4** and pyridine N-oxide using the *in situ* NMR and IR. We found the signal at 31.8 ppm for $\text{O}=\text{PMe}_3$ ²² in the *in situ* ^{31}P NMR and a new signal at -10.16 ppm for hydrido hydrogen in the *in situ* ^1H NMR. In addition, a novel vibration for Fe-H bond appeared

at 1937 cm^{-1} in the *in situ* IR spectrum when pyridine N-oxide was added into the solution of complex **4**. We consider that these experimental results support the formation of complex **4a**.

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Conclusion

Five [PSiP]-pincer silyl iron hydrides **1** – **5** were used as catalysts for the hydrosilylation of carbonyl compounds. It was proved for the first time that the addition of pyridine N-oxide could greatly promote the catalytic reactions and reduce the reaction temperature from 60 °C to 30 °C in the case of aldehydes. This result explains that the dissociation of PMe_3 to form the coordinatively unsaturated intermediate is an important step in the catalytic process. Among complexes **1** – **5**, complex **4** is the best catalyst in the presence of pyridine N-oxide but complex **5** has almost similar activity as complex **4** without pyridine N-oxide. The electron-donating groups (the isopropyl groups at the P atom) make complexes **4** and **5** more catalytically active. Among the five complexes, complex **3** was new and the molecular structure of complex **3** was determined by single crystal X-ray diffraction. A proposed mechanism was discussed.

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 ($4000 - 400 \text{ cm}^{-1}$), 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 point was measured in capillaries sealed under N_2 and was uncorrected. Elemental analyses were carried out on an ElementarVario EL III instrument. All the aldehydes, ketones and α , β -unsaturated carbonyl compounds were purchased and used without further purification. The purity of the triethoxysilane used is 95%, the other 5% is tetraethoxysilane. The silanes were purchased from J&K scientific.

[PSiP]-pincer preligand {bis[*o*-(diphenylphosphino)phenyl] phenylsilane}₂ Fe(PMe₃)₄²⁴ and complexes **1**, **2**, **4** and **5**¹⁹⁻²¹ were prepared according to literature procedures.

Synthesis of hydrido iron(II) complex **3**

At 0 °C, Fe(PMe₃)₄ (0.36 g, 1 mmol) in 25 mL toluene was added to a solution of (2-Ph₂PC₆H₄)₂SiPhH (0.63 g, 1 mmol) in 35 mL of toluene in N₂ atmosphere. The mixture was warmed to room temperature and the color of solution has no obvious change. After stirred at room temperature for 24h, the solution was evaporated to dryness at reduced pressure. The residue was washed by two portions of 10 ml of cold *n*-pentane. Complex **3** (0.63 g, 0.75 mmol) was isolated as an orange powder in a yield of 75%. Crystals suitable for X-ray diffraction were obtained from *n*-pentane solution through recrystallization. dec.: >147 °C. Anal. Calc. for C₄₈H₅₂FeP₄Si (836.77 g/mol): C, 68.90; H, 6.26. Found: 69.19; H, 6.15. IR (Nujol mull, cm⁻¹): 3045 (Ar-H), 1837 (Fe-H), 1583 (C=C), 939 (PMe₃). ¹H NMR (300 MHz, C₆D₆, 300 K, δ/ppm): -17.55 (tdd, *J* = 71.4, 25.8, 6.9 Hz, 1H, Fe-*H*), 0.68 (d, *J* = 6.0 Hz PCH₃, 9H), 1.07 (s, PCH₃, 9H), 6.62 - 6.81 (m, 20H, Ar-*H*), 6.27 - 6.58 (m, 11H, Ar-*H*), 8.11 (d, *J* = 7.4 Hz, 2H). ³¹P NMR (121 MHz, C₆D₆, 300K, δ/ppm): 88.8 (t, *J* = 32.2 Hz, 2P, PⁱPr), 5.2 (q, *J* = 29.8 Hz, 1P, PMe₃), 1.3 (q, *J* = 18.9 Hz, 1P, PMe₃). ¹³C NMR (75 MHz, C₆D₆, 300K, δ/ppm) 157.08 (s, Ar-*C*), 151.61 (s, Ar-*C*), 142.53 (s, Ar-*C*), 136.13 (s, Ar-*C*), 132.58 (t, *J* = 4.5 Hz, Ar-*C*), 131.61 (t, *J* = 9.7 Hz, Ar-*C*), 130.59 (s, Ar-*C*), 127.91 (s, Ar-*C*), 125.58 (s, Ar-*C*), 125.70 (s, Ar-*C*), 125.46 (t, *J* = 3.0 Hz), 124.27 (s, Ar-*C*), 25.25 (dd, *J* = 1.5, 17.3 Hz, PMe₃-*C*), 22.59 (dd, *J* = 2.3, 17.3 Hz, PMe₃-*C*).

Single crystal X-ray diffraction

Bruker Apex II single crystal diffractometer was used with a Ga K α radiation ($\lambda = 1.34143$) and a CCD area detector. The structure was solved using the

charge-flipping algorithm, as implemented in the program SUPERFLIP²⁵ and refined by full-matrix least-squares techniques against F² (SHELXL)²⁶ through the OLEX interface.²⁷ 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-1936211 (**3**) 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).

Representative experimental procedure of catalytic reduction of aldehydes and ketones

A 25 mL Schlenk tube was charged with a mixture of PhCHO (1.0 mmol), HSi(OEt)₃ (1.2 mmol), pyridine N-oxide (0,05 mmol) and complex **4** (0.01 mmol) in 2 mL of THF. The reaction vessel was stirred at 30 °C for 6 h. The progress of the reaction was monitored by GC. After cooling to the room temperature, CH₃OH (2 mL) and 10% NaOH (3 mL) were added to the tube. After stirring for 24 h at 60 °C, the product was extracted with Et₂O (30 mL × 2). The combined organic phases were dried over anhydrous NaSO₄, filtered, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel (petroleum ether (60–90 °C) / ethyl acetate 5:1, v/v) to afford PhCH₂OH as a colorless liquid.

Mechanism study

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

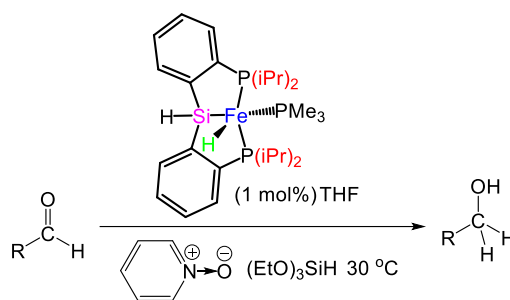
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TOC

Pyridine N-oxide promoted hydrosilylation of carbonyl compounds catalyzed by [PSiP]-pincer iron hydridesGuoliang Chang^a, Peng Zhang^a, Wenjing Yang^a, Shangqing Xie^a, Hongjian Sun^a, Xiaoyan Li^{a,*}, Olaf Fuhr^b, Dieter Fenske^b

- 21 aldehydes
- Isolated yields: 78 – 95%
- Pyridine N-oxide as initiator
- Lower reaction temperature: 30 °C