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

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Five [PSiP]-pincer iron hydrides **1–5**, [(2-$Ph_2PC_6H_4)_2HSiFe(H)(PMe_3)_2$ (**1**), (2-$Ph_2PC_6H_4)_2MeSiFe(H)(PMe_3)_2$ (**2**), (2-$Ph_2PC_6H_4)_2PhSiFe(H)(PMe_3)_2$ (**3**), (2-$(iPr)_2PC_6H_4)_2HSiFe(H)(PMe_3)$ (**4**), and (2-$(iPr)_2PC_6H_4)_2MeSiFe(H)(PMe_3)_2$ (**5**)], were used as catalysts to study the effects of pyridine *N*-oxide and the electronic properties 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 the initiator at 30 °C because the addition of pyridine *N*-oxide is beneficial for the formation of an 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.

Introduction

The homogeneous hydrosilylation catalysis for the reduction of carbonyl compounds as a significant route to synthesize organic alcohols attracts extensive investigation in laboratory, academic, and industrial settings.[1] It was reported in the past decade that low-cost and environment friendly iron complexes as catalysts could be used in the reduction of aldehydes, ketones and other unsaturated species.[2,3] The development on the 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 the 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(oxazolinylphenyl)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 that 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 catalysts to increase the 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 of the reduction processes. Driess found that the iron complexes bearing silicon-based ligands could also be used as catalysts for the 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 the 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 the hydrosilylation of carbonyl compounds between 50 and 70 °C.[13] Until now, in our reported work, the catalytic mechanism catalyzed by iron hydrides was

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†Electronic supplementary information (ESI) available: The table of selected crystallographic data and original IR, ^1H NMR, ^{31}P NMR, and ^{13}C NMR spectra of complex **3** and catalytic products. CCDC 1936211. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/D0DT00392A

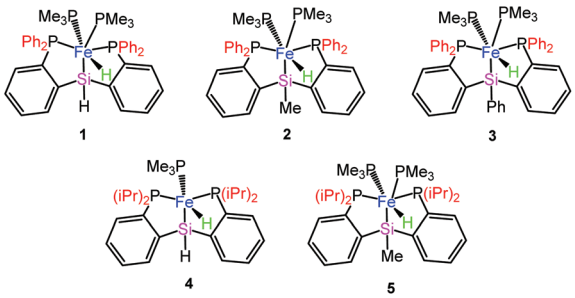


Fig. 1 [PSiP] pincer iron(II) silyl hydrides **1–5**.

not experimentally verified. Inspired by the catalytic mechanism reported by Nikonov,[18] we consider that the formation of unsaturated hydrido iron species *via* the dissociation of the PMe_3 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 PMe_3 ligands. With this assumption, we add pyridine *N*-oxide as the initiator to enhance the dissociation of the PMe_3 ligands due to the production of stable O PMe_3. 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 (Fig. 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 the initiator because this is beneficial for the formation of coordinatively unsaturated hydrido iron species by the reaction of PMe_3 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 the 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* the dissociation of the ligand is the first and key step in the catalytic mechanism. Complex **4** shows the best catalytic activity among the five complexes.

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 literature methods.[19–21] Complex **3** was synthesized by the reaction of $Fe(PMe_3)_4$ with the [PSiP]-pincer preligand, $(2\text{-}Ph_2PC_6H_4)_2SiPhH$ (Scheme 1).

In the IR spectrum of complex **3**, the typical vibration (2134 cm^{-1}) of the Si–H bond of the preligand, $(2\text{-}Ph_2PC_6H_4)_2SiPhH$, disappeared while the ν(Fe–H) stretching band was found at 1837 cm^{-1}. The hydrido resonance in the

Scheme 1 Preparation of complex **3**.

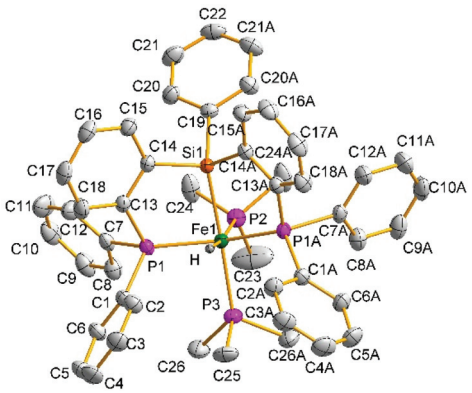


Fig. 2 Molecular structure of complex **3**.

^1H NMR spectrum of complex **3** appeared at −17.35 ppm as a "tdd" peak with the coupling constant J_{PH} = 71.4, 25.8, and 6.9 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** (–PPh_2) in the ^{31}P NMR spectrum of complex **3**. Meanwhile, X-ray diffraction was used to confirm the octahedral configuration of complex **3** (Fig. 2). The crystallographic data for complex **3** are listed in Table S1.† In the molecular structure of complex **3**, the Fe1–P3 bond length (2.2629(6) Å) 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) Å) due to the strong *trans*-influence of the Si atom.

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

In 2013, we initially confirmed that complex **2** could efficiently catalyze the 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 the initiator to study the catalytic hydrosilylation of carbonyl compounds. Meanwhile, the effect of the substituent groups of the ligands on the 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 the solvent and $(EtO)_3SiH$ as the reducing agent. From Table 1, we know that benzaldehyde does not undergo conversion without a catalyst (entry 1, Table 1). At 30 °C with 1 mol% of catalyst loading, the five iron complexes have a conversion of only 9–29% within 6 h (entries 2–6, Table 1). Under these con-

Table 1 Catalytic activity of complexes **1–5** towards the hydrosilylation of benzaldehyde[a]

Entry	Catalyst	Catalyst loading (mol%)	Pyridine *N* oxide (mol%)	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), $(EtO)_3SiH$ (1.2 mmol) and *n* dodecane (internal standard) (1.0 mmol), 2 mL THF, 30 °C.

ditions, 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 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 PMe_3 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 the rate-determining step. In addition, the electron-donating isopropyl group is beneficial for the dissociation of the 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-coordinated iron(II) intermediate is not stable. However, if the amount of pyridine *N*-oxide was decreased 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 4 h or 2 h, the conversion declined significantly (entries 14–15, Table 1). When the reaction time was extended to 8 h, 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 mentioned in Table 1 because ketones are less reactive than aldehydes. However, the catalytic

Table 2 Catalytic activity of complex **4** for the hydrosilylation of acetophenone[a]

Entry	Pyridine *N* oxide (mol%)	*T* (°C)	Time (h)	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

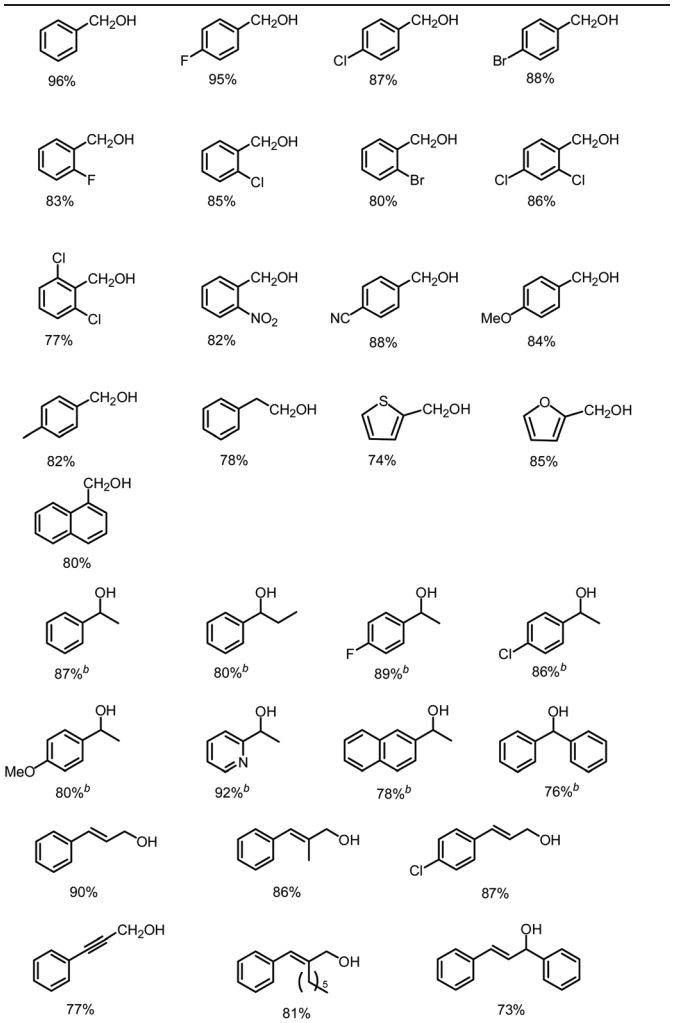
[a] Reaction conditions: acetophenone (1.0 mmol), **4** (0.01 mmol), pyridine *N* oxide, $(EtO)_3SiH$ (1.2 mmol) and *n* dodecane (internal standard) (1.0 mmol), 2 mL THF.

temperature of the 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 4 h, 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 on the phenyl rings were selected as 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 on 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 high yields. Furthermore, alcohols with halogen groups at the *para*-position were formed in higher yields due to the small steric effect. The alcohols containing strong electron-withdrawing groups, such as $-NO_2$ and –CN, were produced in good yields while the aldehydes with the electron-donating substituents, such as –Me and 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 highlight of this catalytic system is the significant reduction of the catalytic reaction temperature caused by the addition of pyridine *N*-oxide.

Compared to aldehydes, the reduction of ketones is more difficult and requires more stringent reaction conditions. With pyridine *N*-oxide as the initiator, the hydrosilylation of ketones was realized in good yields at 50 °C within 6 h. 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 substituents (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 the catalyst and $(EtO)_3SiH$ as the hydrogen source at 30 °C. The conversion of benzaldehyde is 97% while the conversion of acetophe-

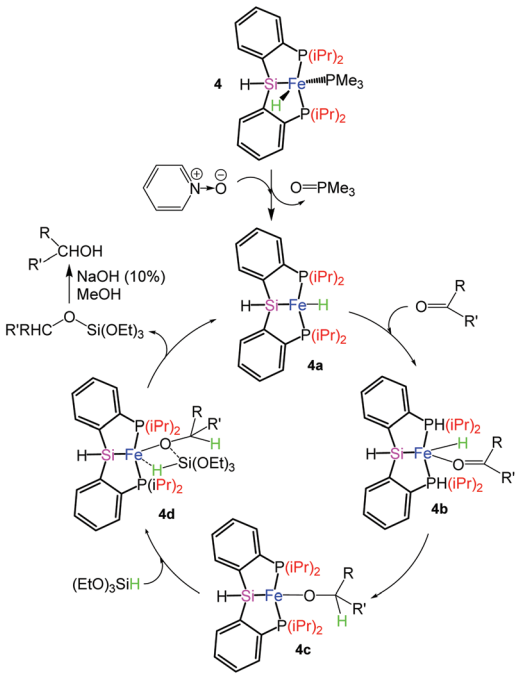
Table 3 Catalytic hydrosilylation of carbonyl compounds with **4** as catalyst[a]



[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 (0.01 mmol) and pyridine *N* oxide (0.05 mmol) in 2 mL THF at 50 °C for 6 h.

none is only 2%. The results show that the aldehyde group is easier to reduce than the ketone group.

The selective hydrogenation reduction of the C C and C O bonds in α,β-unsaturated aldehydes or ketones is of great importance in organic synthesis. To our delight, this catalytic system has good selectivity for the 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 a yield of 73%.



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

Mechanism discussion

Based on our experimental results and literature reports,[18] we proposed a catalytic mechanism with complex **4** as the catalyst for the 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 the intermediate **4b**. After that, the coordinate carbonyl group is inserted into the Fe–H bond to afford the intermediate **4c**. In the presence of $(EtO)_3SiH$, complex **4c** can be converted into the 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 the 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 O 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**.

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 the same activity as complex **4** without pyridine *N*-oxide. The electron-donating groups (the isopropyl groups on the P atom) make complexes **4** and **5** more catalytically active. Among the five complexes, complex **3** was new whose molecular structure 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 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded by using a Bruker ALPHA FT-IR instrument. The NMR spectra were recorded using Bruker Avance 300 MHz spectrometers. GC was recorded by using a Fuli 9790 instrument. The melting point was measured in capillaries sealed under N_2 and was uncorrected. Elemental analyses were carried out by using 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 was 95% and tetraethoxysilane accounted for the remaining 5%. The silanes were purchased from J&K scientific. The [PSiP]-pincer preligand {bis[*o*-(diphenylphosphino)phenyl] phenylsilane},[23] $Fe(PMe_3)_4$[24] and complexes **1**, **2**, **4** and **5** (ref. 19–21) were prepared according to literature procedures.

Synthesis of hydrido iron(II) complex 3

At 0 °C, $Fe(PMe_3)_4$ (0.36 g, 1 mmol) in 25 mL of toluene was added to a solution of $(2\text{-}Ph_2PC_6H_4)_2SiPhH$ (0.63 g, 1 mmol) in 35 mL of toluene under a N_2 atmosphere. The mixture was warmed to room temperature and the color of the solution showed no obvious change. After being stirred at room temperature for 24 h, 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 $C_{48}H_{52}FeP_4Si$ (836.77 g mol^{-1}): 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 (PMe_3). ^1H NMR (300 MHz, C_6D_6, 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 PCH_3, 9H), 1.07 (s, PCH_3, 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).^{31}P NMR (121 MHz, C_6D_6, 300 K, δ/ppm): 88.8 (t, J = 32.2 Hz, 2P, P^iPr), 5.2 (q, J = 29.8 Hz, 1P, PMe_3), 1.3 (q, J = 18.9 Hz, 1P, PMe_3). ^{13}C NMR (75 MHz, C_6D_6, 300 K, 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, PMe_3–*C*), 22.59 (dd, J = 2.3, 17.3 Hz, PMe_3–*C*).

Single crystal X-ray diffraction

A Bruker Apex II single crystal diffractometer with Ga Kα radiation (λ = 1.34143) and a CCD area detector was used. The structure was solved using the charge-flipping algorithm, as implemented in the program SUPERFLIP[25] and refined by full-matrix least-squares techniques against F^2 (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.†

Representative experimental procedure for the 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 room temperature, CH_3OH (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 Et_2O (30 mL × 2). The combined organic phases were dried over anhydrous $NaSO_4$, 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 $PhCH_2OH$ as a colorless liquid.

Conflicts of interest

There are no conflicts to declare.

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