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Synthesis of [POCOP]-pincer iron and cobalt complexes *via* C_{sp3}–H activation and catalytic application of iron hydride in hydrosilylation reactions†

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C_{sp3}–H bond activation in diphosphinito pincer ligand $(Ph_2PO(o\text{-}C_6H_2\text{-}(4,6\text{-}{}^tBu_2)))_2CH_2$ (**1**) ($POCH_2OP$) was achieved by $Fe(PMe_3)_4$ and $CoMe(PMe_3)_4$ to afford complexes (POCHOP)Fe(H) $(PMe_3)_2$ (**2**) and (POCHOP) $Co(PMe_3)_2$ (**4**) under mild conditions. Hydrido iron complex **2** reacted with iodomethane *via* the elimination of methane to deliver complex (POCHOP)FeI(PMe_3) (**3**). The ligand replacement in $Ni(PMe_3)_4$ by **1** gave rise to nickel(0) complex $(POCH_2OP)Ni(PMe_3)_2$ (**5**) without C_{sp3}–H bond activation of the pincer ligand (**1**). It was confirmed that the hydrosilylation of aldehydes and ketones could be effectively catalyzed by hydrido iron complex **2**. Complexes **2–5** were characterized by spectroscopic methods and X-ray single crystal diffraction analysis.

Introduction

Owing to high efficiency and atom economy for organic synthesis, C–H bond activation and functionalization has become one of the most attractive areas in organic chemistry. Compared with C_{sp2}–H bond activation, C_{sp3}–H activation is much more difficult due to the high bond energy and weakly coordinating nature. In this field, most of the work has focused on precious metals, such as Pd,[1] Ru,[2] Rh,[3] Ir[4] *etc.* Because of the low cost and toxicity, C–H bond functionalization by iron,[5] cobalt[6] and nickel[7] complexes attracts more and more researchers' attention. Pincer ligands have a double chelation structure. This induces C_{sp3}–H bond activation much easier *via* double cyclometalation.[8] Therefore, pincer complexes of transition metals can be prepared *via* C_{sp3}–H bond activation.

Hydrido iron complexes as catalysts or key intermediates play important roles in a wide variety of catalytic processes. Nevertheless, these hydrido iron complexes are usually so reactive that they cannot be isolated or even identified.[9] To date, few stable hydrido iron complexes have been synthesized and employed as catalysts for a number of reactions, such as hydrogenation,[10–13] hydrosilylation,[14,15] hydrogen-transfer reaction,[16] the oxidation of alcohols.[17] The hydrosilylation reaction of aldehydes and ketones generates silyl ethers with Si–H bond addition to carbonyl compounds. The hydrolysis of the silyl ether gives rise to the corresponding alcohol. This process can be used as a convenient alternative to the reduction of unsaturated compounds under mild reaction condition.

In 2009, we reported the C_{sp3}–H bond activation of a [POCOP]-pincer ligand with an aliphatic backbone (Fig. 1(a)) by low-valent iron and cobalt complexes under mild conditions.[18] A hydrido [PNCNP]-pincer iron complex was also isolated through C_{sp3}–H bond activation of *N*,*N*′-bis(diphenylphosphino)dipyrromethane (Fig. 1(b)).[19] When the diphosphine PCP ligand $(Ph_2P\text{-}(C_6H_4))_2CH_2$ was treated with $Fe(PMe_3)_4$, the C_{sp3}–H activation product $[(Ph_2P\text{-}(C_6H_4))_2CH]Fe(H)(PMe_3)_2$ was obtained at room temperature (Fig. 1(c)).[20] Recently, Wendt reported a series of new $POC_{sp3}OP$-supported nickel(II) complexes (Fig. 1(d)).[21] On the basis of our early work, we synthesized another ($POCH_2OP$)-pincer ligand having a relatively rigid backbone with two phenyl rings (Fig. 1(1)). An iron hydride was obtained by oxidative addition of the C_{sp3}–H bond of the methylene group to the iron(0) center and its catalytic property in hydrosilylation of aldehydes and ketones was also explored.

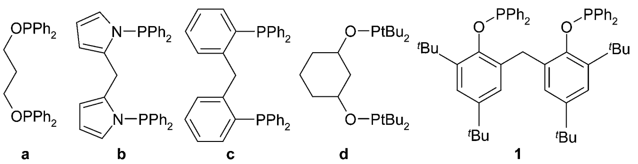

Fig. 1 [PCP]-pincer ligand.

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† Electronic supplementary information (ESI) available: Characterization of all compounds. CCDC 977103 and 980722–980724. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra00072f

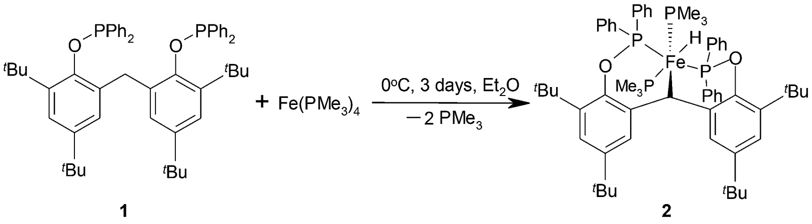
‡ The first two authors contributed to this paper equally.

Results and discussion

Reaction of Fe(PMe_3)$_4$ with ($POCH_2OP$) (1)

In most cases, C_{sp3}–H bond activation in a pincer ligand was realized by precious metals, such as Ru,[8a] Rh,[8b] Ir,[8c,d] Pd,[8e] *etc.* It is confirmed that even $PdCl_2(PhCN)_2$ failed to realize the C_{sp3}–H bond activation in a similar ligand.[22] Until now, there have been only a few examples of hydrido iron complexes formed through the activation of the C_{sp3}–H bond of a [PCP]-pincer ligand.[18–20]

Mixing a diethyl ether solution of ($POCH_2OP$) (**1**) with Fe(PMe_3)$_4$ under an atmosphere of nitrogen afforded hydrido iron complex **2** as yellow crystals in 56% yield after stirring (eqn (1)). Complex **2** is stable more than 48 h when exposed to the air at room temperature.



(1)

The reaction starts with double replacement of the two trimethylphosphine ligands by two phosphorus atoms of ligand **1**. This ligand substitution shortens the distance of the iron(0) atom to the central C_{sp3}–H bonds of the methylene group in **1** and enables the Fe(0) center to activate the C_{sp3}–H bond *via* oxidative addition by cyclometalation. Hydrido iron(II) complex **2** is formed through double chelation.

A typical ν(Fe–H) stretching band at 1959 cm^{-1} was found in the IR spectrum of **1**. In the ^{31}P NMR spectrum of complex **2**, one doublet of doublets (two –PPh_2) at 15.1 ppm and two triplets (two PMe_3) at 6.7 and 6.4 ppm are consistent with the molecular structure. The resonance of the hydrido hydrogen as a dddd peak in the ^1H NMR spectrum is registered at −15.13 ppm with the coupling constants of $^2J_{PH}$ of 69, 48, 38 and 14 Hz (Fig. 2). It is not clear why this coupling is incompatible with those of the ^{31}P NMR. This coupling pattern is also different from our early reports.[19,20]

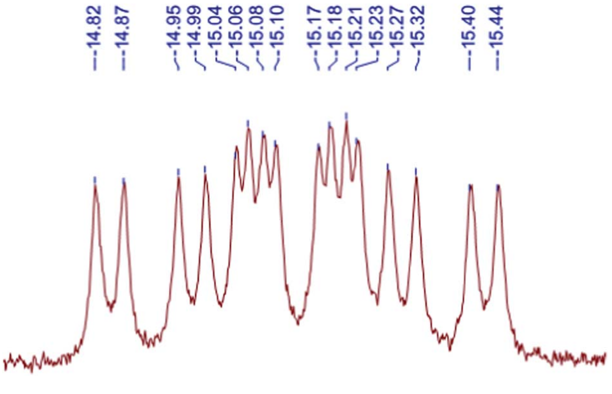


Fig. 2 Characteristic resonance of the hydrido hydrogen of **2** in ^1H NMR.

The configuration of **2** was confirmed by X-ray structure analysis (Fig. 3). Two six-membered metallacycles with a considerable ring bending are formed through two phosphorous atoms of the PPh_2 groups and a metalated C_{sp3} atom. The iron atom is centered in a slightly distorted octahedral geometry. H100 atom was located with the diffraction data of the experiments. Bond angle P3–Fe1–P4 of 142.88(4)° bends towards to the hydrido ligand due to the smaller space requirement of the hydrido hydrogen. The Fe1–C31 distance (2.165(3) Å) is within the range of Fe–C_{sp3} bonds.[23] Both Fe–P1 distance (2.231(1) Å) and Fe–P2 distance (2.269(1) Å) are longer than Fe1–P3 distance (2.142(1) Å) and Fe1–P2 distance (2.141(1) Å), presumably due to the strong *trans*-influence of the hydrido H and C (sp3) atoms being greater than that of the phosphorus

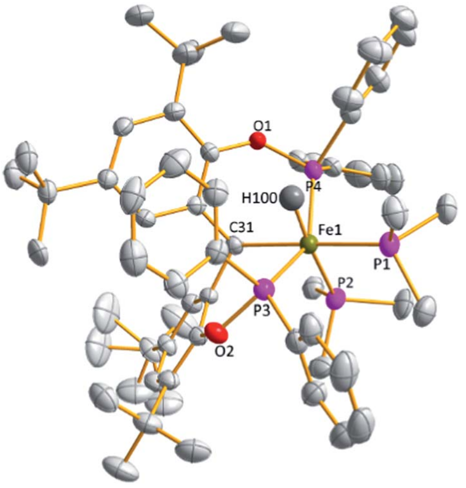
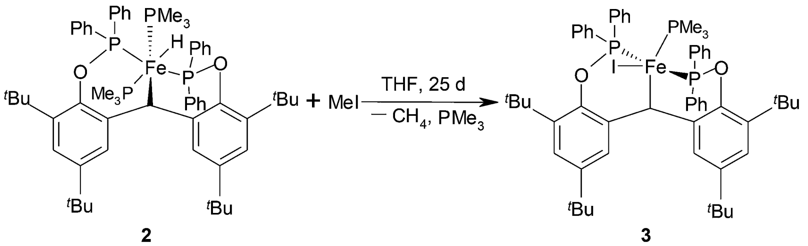


Fig. 3 ORTEP plot of complex **2** at the 50% probability level (hydrogen atoms except for Fe–H are omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1–P4 2.141(1), Fe1–P3 2.142(1), Fe1–C31 2.165(3), Fe1–P1 2.231(1), Fe1–P2 2.269(1), Fe1–H100 1.50(3); C31–Fe1–P1 177.67(9), P2–Fe1–H100 170(1), P4–Fe1–C31 81.74(9), P3–Fe1–C31 81.99(9).

atoms. This result is similar to that of our early report.[19] Complex **2** has a low-spin Fe(II) center.



(2)

The reaction of **2** with iodomethane afforded an unsaturated coordinated complex **3** as red crystals with the release of a methane molecule (eqn (2)) in the yield of 87%.

The ^{1}H NMR spectrum of **3** indicates that complex **3** is paramagnetic. From the results of the magnetization measurements for complex **3** it can be calculated that there are two unpaired electrons in complex **3**. This result is in accordance with a paramagnetic iron(II) complex (d^6) having a trigonal bipyramidal configuration (see ESI†). This result was confirmed by X-ray crystallography. Fig. 4 shows the molecular structure of complex **3**. It has a trigonal bipyramidal coordination geometry with P1–Fe1–P2 = 160.6(1)° in the axial direction. The sum of the bond angles (C25–Fe1–I1 = 143.6(2)°, C25–Fe1–P3 = 115.2(2)° and P3–Fe1–I1 = 101.25(8)°) centered at the Fe atom in the equatorial plane is 360.1°. This indicates that the four atoms [Fe1C25I1P3] are almost in one plane.

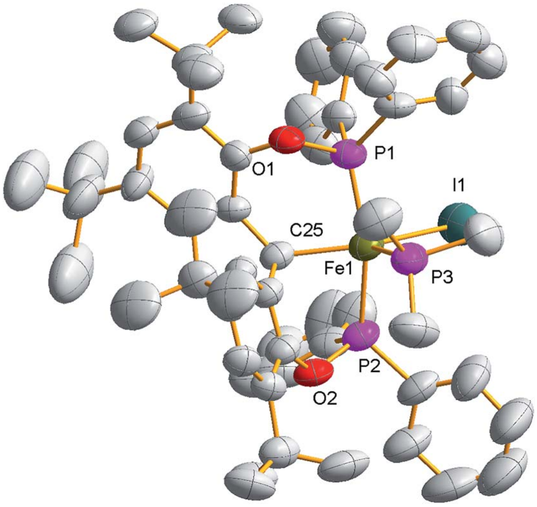
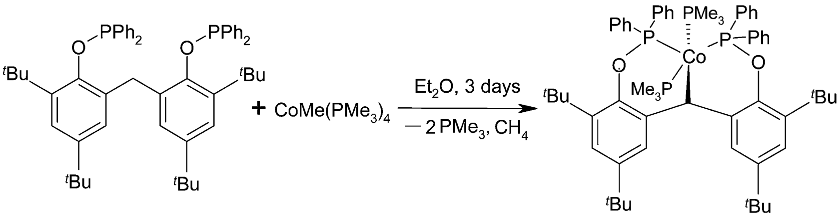


Fig. 4 ORTEP plot of complex **3** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1–P1 2.194(2), Fe1–P2 2.239(2), Fe1–P3 2.422(3), Fe1–I1 2.699(2), C25–Fe1 2.095(8); C25–Fe1–I1 143.6(2), C25–Fe1–P3 115.2(2), P3–Fe1–I1 101.25(8), P1–Fe1–I1 91.89(8), P2–Fe1–I1 91.73(8), C25–Fe1–P1 85.8(2), C25–Fe1–P2 80.0(2).

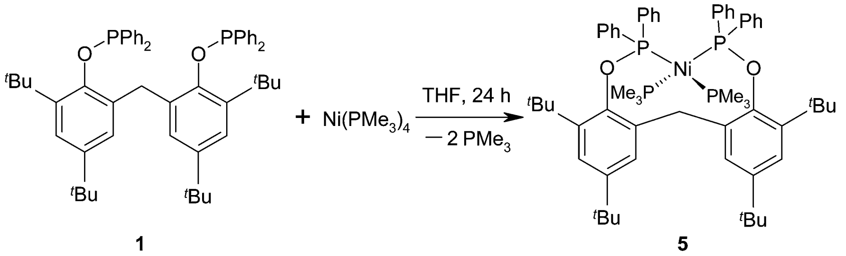
Reaction of CoMe(PMe$_3$)$_4$ with (POCH$_2$OP) (1)

CoMe(PMe$_3$)$_4$ reacted with pincer ligand **1** to form the C$_{sp3}$–H bond activation product **4** with the elimination of a methane molecule (eqn (3)).



(3)

The ^{1}H NMR spectrum of complex **4** in C$_6$D$_6$ at 10 °C indicated that the proton resonance of the CH group appear at 6.12 ppm. In comparison with the related resonance at 3.88 ppm in the similar [PNC(H)NP]Co(PMe$_3$)$_2$ complex this is a significant downfield shift.[19] The proton resonances of two types of PMe$_3$ groups were recorded as one doublet at 0.78 and a triplet at 0.96 ppm with the coupling constants of 3.0 and 6.0 Hz respectively. The ^{31}P NMR spectrum shows a triplets for two PMe$_3$ at −4.5



(4)

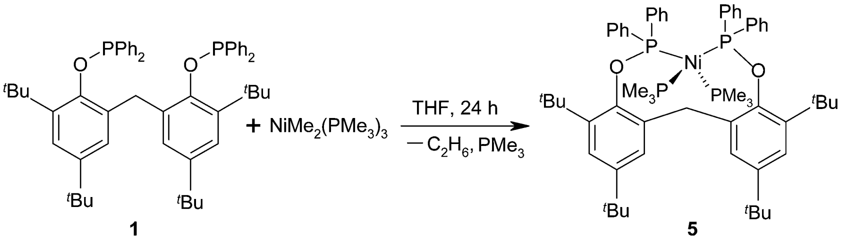
ppm with the coupling constants $^2J(PP) = 78$ Hz and a singlet for the two diphenylphosphanyl groups at 17.7 ppm.

The molecular structure of complex **4** was determined by X-ray single crystal diffraction (Fig. 5). Two six-membered cobaltocycles with a considerable ring bending are formed through two phosphorous atoms of the PPh_2 groups and a metalated C_{sp3} atom. The central cobalt atom is situated in a disordered trigonal bipyramid with C1–Co1–P4 = 175.9(1)° in the axial direction. The Co1–C1 distance (2.133(4) Å) is within the range of Co–C_{sp3} bonds (2.03–2.15 Å).[24] The structure of complex **4** is comparable with that of [PNC(H)NP]Co$(PMe_3)_2$.[19]

Reaction of $Ni(PMe_3)_4$ or $NiMe_2(PMe_3)_4$ with ($POCH_2OP$) (1)

Mixing a THF solution of ($POCH_2OP$) (**1**) with $Ni(PMe_3)_4$ afforded nickel(0) complex **5** *via* ligand substitution (eqn (4)). After all solvents were removed under vacuum, the residual powder was extracted with pentane and diethyl ether. Complex **5** crystallized from diethyl ether at 0 °C in the yield of 87%. No C_{sp3}–H bond activation product could be observed.

In the ^1H NMR spectrum of complex **5**, the resonance of the two hydrogens of the methylene group was shifted to 6.49 ppm from 4.09 ppm in the free ligand **1**. This downfield shift can be explained in terms of an increased deshielding of the methylene protons because the formation of a metallacycle results in an additional ring current, which opposes the external field.[25] In the ^{31}P NMR spectrum two types of signals with the integral intensity of 1 : 1 demonstrate two kinds of phosphorus atoms. Both the ^1H and ^{31}P NMR indicate that C_{sp3}–H bond activation did not occur. The molecular structure of complex **5** was confirmed by X-ray single crystal diffraction (Fig. 6). A ten-membered metallacycle is formed in **5** and every bond angle of the ring is approximately in 120°. The central nickel atom has a distorted tetrahedron coordination geometry. The bond angles P1–Ni1–P2 (119.50(3)°), P1–Ni1–P3 (106.47(3)°), P1–Ni1–P4 (109.63(3)°), P2–Ni1–P3 (107.91(3)°), P2–Ni1–P4 (101.93(3)°) and P3–Ni1–P4 (111.39(3)°) are approximately close to 109.5°. The four Ni–P bond distances are within the region of literature values.[15,19] The distance (3.62 Å) between the Ni and the methylene C_{sp3} atom indicates that there is no chemical interaction between them. The reaction of ligand **1** with $NiMe_2(PMe_3)_4$ gave the same product with the elimination of C_2H_6 (eqn (5)).



(5)

Catalytic application of hydrido iron complex 2

Hydrido iron complexes bearing pincer ligands have been utilized in hydrosilylation reactions of aldehydes and ketones.[14,15] We found that complex **2** could be used as catalyst in the hydrosilylation of aldehydes (eqn (6)). In the presence of 1 mol% of **2** with $(EtO)_3SiH$ as the hydrogen source in THF at 65 °C, aldehydes could be completely converted into the corresponding silyl ether. The related alcohols were obtained by following basic hydrolysis of the silyl ether. Nine aldehydes were investigated (Table 1). Electron-donating group appeared to make the hydrosilylation reactions sluggish (entry 5). On the

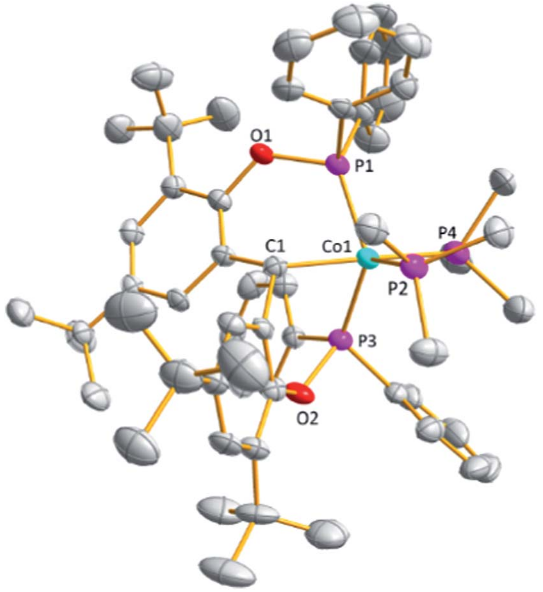


Fig. 5 ORTEP plot of complex **4** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1–P3 2.118(1), Co1–C1 2.133(4), Co1–P1 2.144(1), Co1–P4 2.213(1), Co1–P2 2.254(1); P3–Co1–C1 82.1(1), P3–Co1–P1 130.80(4), C1–Co1–P1 81.5(1), P3–Co1–P4 94.73(5), C1–Co1–P4 175.9(1), P1–Co1–P4 98.83(5), P3–Co1–P2 117.80(4), C1–Co1–P2 89.5(1), P1–Co1–P2 108.08(4), P4–Co1–P2 94.24(5).

contrary, electron-withdrawing group at the *para*-position turned out to accelerate the reduction (entry 6). *ortho*-Positioned groups hindered the process (entries 2–4).

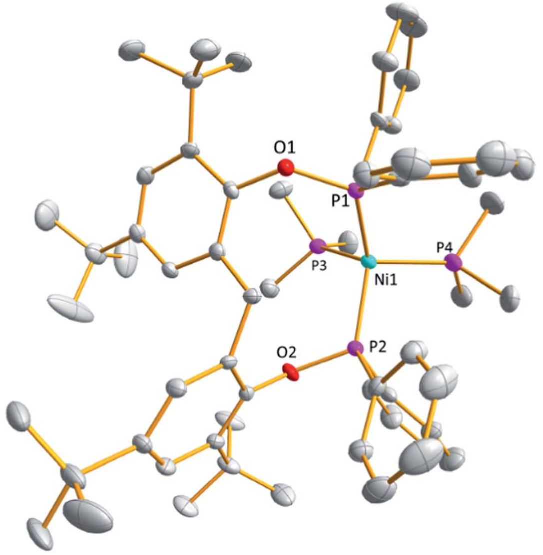
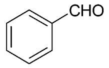
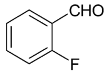
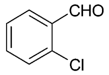
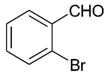
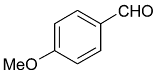
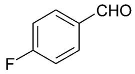
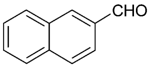
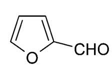
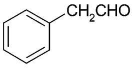


Fig. 6 ORTEP plot of complex **5** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni1–P1 2.1572(8), Ni1–P2 2.1595(8), Ni1–P4 2.1955(8), Ni1–P3 2.1960(9); P1–Ni1–P2 119.50(3), O1–P1–Ni1 125.69(7), O2–P2–Ni1 117.24(8), C13–O1–P1 127.6(2), C21–O2–P2 129.1(2), P4–Ni1–P3 111.39(3).

Table 1 Catalytic hydrosilylation of aldehydes with **2**[a]

Entry	Substrate	Time (h)	Isolated yields (%)
1		2	92
2		16	91
3		26	87
4		18	90
5		16	81
6		1.5	90
7		16	81
8		2.5	86
9		18	88

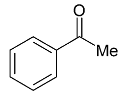
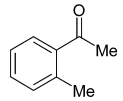
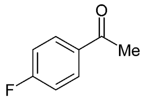
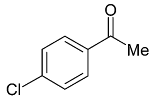
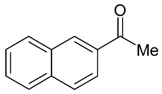
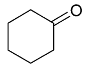
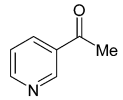
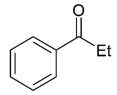
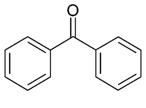
[a] Reaction conditions: RCHO (1.0 mmol), $(EtO)_3SiH$ (1.2 mmol), complex **2** (0.010 mmol), 1.0 mL THF 65 °C. Under the given conditions, all the aldehydes were completely converted to the corresponding silyl ethers (monitored by TLC and GC).

$$\mathrm{RCHO} + (\mathrm{EtO})_3\mathrm{SiH} \xrightarrow[\mathrm{THF}]{1\ \mathrm{mol\%}\ \mathbf{2}} \mathrm{RCH_2OSi(OEt)_3} \xrightarrow[\mathrm{MeOH}]{10\%\ \mathrm{NaOH}} \mathrm{RCH_2OH} \tag{6}$$

Besides aldehydes, different ketones were also tested under these catalytic hydrosilylation conditions (eqn (7)). It was confirmed that acetophenone could be entirely converted into the product even within 5 h with a catalyst loading of 2 mol% of complex **2** (Table 1, entry 1). In some cases, reasonable yields could be obtained with a catalyst loading of 2 mol% (Table 2). In most cases, the ketones are less reactive than the aldehydes. Additionally, several ketones could not be completely converted even after 48 h. Substitutents at the *para*- or *ortho*-positions reduced the rate of the reaction for both electron-withdrawing and electron-donating groups (entries 2–4). These results are consistent with Guan's work.[14] It is proposed that this catalytic system has a similar mechanism with those of the early reports.[26]

$$\mathrm{RR'C{=}O} + (\mathrm{EtO})_3\mathrm{SiH} \xrightarrow[\mathrm{THF}]{2\ \mathrm{mol\%}\ \mathbf{2}} \mathrm{RR'CHOSi(OEt)_3} \xrightarrow[\mathrm{MeOH}]{10\%\ \mathrm{NaOH}} \mathrm{RR'HCOH} \tag{7}$$

Table 2 Catalytic hydrosilylation of ketones with **2**[a]

Entry	Substrate	Time (h)	Conversation by GC (%)	Isolated yield (%)
1		5	99	88
2		48	92	71
3		10	99	81
4		48	57	43
5		48	74	63
6		18	99	79
7		48	43	37
8		18	99	86
9		48	49	39

[a] Reaction conditions: RCOR′ (1.0 mmol), $(EtO)_3SiH$ (1.2 mmol), complex **2** (0.020 mmol), 2.0 mL THF 65 °C.

Conclusion

We investigated the reactions of the diphosphinito pincer ligand $(Ph_2PO(o\text{-}C_6H_2\text{-}(4,6\text{-}^tBu_2)))_2CH_2$ (**1**) ($POCH_2OP$) with the electron-rich low-valent iron, cobalt, and nickel complexes supported by trimethylphosphine. The C_{sp3}–H bond activation of **1** was achieved by iron(0) complex $Fe(PMe_3)_4$ and cobalt(I) complex $CoMe(PMe_3)_4$. The hydrido iron complex (POCHOP) $Fe(H)(PMe_3)_2$ (**2**) reacted with iodomethane to give rise to an iodo iron(II) complex. The catalytic property of the hydrido iron(II) complex **2** was explored in hydrosilylation of aldehydes and ketones.

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 on a Bruker ALPHA FT-IR instrument. NMR spectra were recorded using Bruker Avance 300 and 400 MHz spectrometers. GC-MS was recorded on a TRACE-DSQ instrument, and GC was recorded on a Fuli 9790 instrument. A 2900 Series AGM Magnetometer was used to measure the magnetic susceptibility. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer. Melting points were measured in capillaries sealed under N_2 and were uncorrected. Elemental analyses were carried out on an Elementar Vario ELIII instrument. The compounds $(Ph_2PO(o\text{-}C_6H_2\text{-}(4,6\text{-}^tBu_2)))_2CH_2$ (**1**),[19] $Fe(PMe_3)_4$,[27a] $CoMe(PMe_3)_4$,[27b,c] $Ni(PMe_3)_4$,[27d] $NiMe_2(PMe_3)_3$,[27e] were prepared according to literature procedures.

Caution! $(EtO)_3SiH$ is flammable and highly toxic by inhalation and may cause skin irritation and blindness.

Synthesis of (POCHOP)Fe(H)$(PMe_3)_2$ (2)

($POCH_2OP$) (**1**) (0.82 g, 1.03 mmol) in 25 mL of diethyl ether was mixed with $Fe(PMe_3)_4$ (0.42 g, 1.15 mmol) in 30 mL of diethyl ether at 0 °C. After 6 h at 0 °C the reaction solution turned brown yellow from tan. After 20 h a small amount of yellow powder precipitated. After 3 days, the volatiles were removed under reduced pressure and the residue was extracted with pentane and diethyl ether. Compound **2** (0.56 g, 0.56 mmol) was isolated as yellow crystals in 56% yield from diethyl ether at 0 °C. Dec. >179 °C. Anal. calcd for $C_{59}H_{80}FeO_2P_4$ (1000.96 g mol^{-1}): C, 70.79; H, 8.06. Found: C, 70.68; H, 8.09. IR (Nujol, cm^{-1}): 3046 ν(ArH), 1959 ν(Fe–H), 1573 ν(ArC=C), 938 $\rho(PMe_3)$. ^1H NMR (C_6D_6, 300 K, ppm): −15.13 (dddd, J_{P-H} = 69, 48, 38 and 14 Hz, 1H, Fe*H*), 0.62 (s, 9H, P*Me*$_3$), 0.81 (d, 9H, $^2J(PH) = 6$ Hz, P*Me*$_3$), 0.99 (s, 9H, $p\text{-}(CH_3)_3C$), 1.25 (s, 9H, $p\text{-}(CH_3)_3C$), 1.42 (s, 9H, $o\text{-}(CH_3)_3C$), 1.85 (s, 9H, $o\text{-}(CH_3)_3C$), 5.74 (s broad, 1H, C*H*), 7.07–7.53 (m, *Ar*, 18H), 8.08–8.33 (m, *Ar*, 6H); ^{31}P NMR (C_6D_6, 300 K, ppm): 15.1 (dd, $^2J(PP) = 37.5$ Hz, $^2J(PP) = 12.1$ Hz, 2P, *P*Ph$_2$), 6.7 (t, $^2J(PP) = 22.0$ Hz, 1P, *P*CH$_3$), 6.4 (t, $^2J(PP) = 22.0$ Hz, 1P, *P*CH$_3$); ^{13}C NMR (C_6D_6, 300 K, ppm): 21.5 (d, $^1J(PC) = 9.7$ Hz, P*C*H$_3$), 24.4 (d, $^1J(PC) = 8.2$ Hz, P*C*H$_3$), 31.6 (s, $p\text{-}(CH_3)_3C$) 31.7 (s, $p\text{-}(CH_3)_3C$), 31.8 (s, $o\text{-}(CH_3)_3C$), 32.6 (s, $o\text{-}(CH_3)_3C$), 34.1 (s, $p\text{-}(CH_3)_3C$), 34.2 (s, $p\text{-}(CH_3)_3C$), 34.9 (s, $o\text{-}(CH_3)_3C$), 35.8 (s, $o\text{-}(CH_3)_3C$), 118.5–152.9 (m, aromatic-*C*).

Synthesis of (POCHOP)FeI(PMe_3) (3)

CH_3I (0.05 g, 0.35 mmol) was injected into the solution of **2** (0.30 g, 0.30 mmol) in 20 mL THF and stirred at 30 °C. After 4 days the yellow color disappeared and the solution turned red. After 5 days at 30 °C, the volatiles were removed under reduced pressure and the residue was dissolved in pentane. Compound **3** (0.27 g, 0.26 mmol) was isolated as red crystals in 87% yield from pentane at 0 °C. Dec. >114 °C. Anal. calcd for $C_{56}H_{70}FeIO_2P_3$ (1050.78 g mol^{-1}): C, 64.01; H, 6.71. Found: C, 64.13; H, 6.78. IR (Nujol, cm^{-1}): 3030 ν(ArH), 1584 ν(C=C), 940 $\rho(PMe_3)$; χ (20 °C) = 5.108×10^{-6} emu per g Oe.

Synthesis of (POCHOP)Co(PMe_3)$_2$ (4)

At −78 °C, ($POCH_2OP$) (**1**) (0.67 g, 0.84 mmol) in 25 mL of diethyl ether was treated with $CoMe(PMe_3)_4$ (0.35 g, 0.92 mmol) in 30 mL of diethyl ether at 0 °C. After 30 h, the reaction mixture turned dark red. After 3 days, the volatiles were removed under reduced pressure and the residue was dissolved with pentane. All manipulations were finished under 10 °C. Compound **4** (0.35 g, 0.35 mmol) was isolated as red crystals in 42% yield from pentane at 0 °C. Dec. >152 °C. Anal. calcd for $C_{59}H_{79}CoO_2P_4$ (1003.03 g mol^{-1}): C, 70.65; H, 7.94. Found: C, 70.58; H, 7.99. IR (Nujol, cm^{-1}): 3034 ν(ArH), 1580 ν(C=C), 942 ρ(PMe_3). ^{1}H NMR (C_6D_6, 283 K, ppm): 0.78 (d, ^2J(PH) = 3 Hz, 9H, P*Me*$_3$), 0.96 (vt, 9H, ^2J(PH) = 6 Hz, P*Me*$_3$), 1.08 (s, 9H, *p*-(C*H*$_3$)$_3$C), 1.35 (s, 9H, *p*-(C*H*$_3$)$_3$C), 1.46 (s, 9H, *o*-(C*H*$_3$)$_3$C), 1.84 (s, 9H, *o*-(C*H*$_3$)$_3$C), 6.12 (s, 1H, C*H*), 6.93–8.41 (m, *Ar*, 18H); ^{31}P NMR (C_6D_6, 283 K, ppm): 17.7 (bs, 2P, *P*Ph$_2$), −4.5 (t, ^2J(PP) = 78 Hz, 2P, *P*CH$_3$).

Synthesis of ($POCH_2OP$)Ni(PMe_3)$_2$ (5)

($POCH_2OP$) (**1**) (0.57 g, 0.72 mmol) in 25 mL of THF was mixed with $Ni(PMe_3)_4$ (0.27 g, 0.72 mmol) in 25 mL of THF with stirring at room temperature for 24 h. The reaction mixture turned orange from yellow. After removal of the volatiles under reduced pressure, the residue was extracted with pentane and diethyl ether. Compound **5** (0.63 g, 0.62 mmol) was isolated as orange crystals in 87% yield from diethyl ether at 0 °C. Dec. >121 °C. Anal. calcd for $C_{59}H_{80}NiO_2P_4$ (1003.82 g mol^{-1}): C, 70.59; H, 8.03. Found: C, 70.51; H, 8.11. IR (Nujol, cm^{-1}): 3025 ν(ArH), 1580 ν(C=C), 938 ρ(PMe_3). ^{1}H NMR (C_6D_6, 300 K, ppm): 1.10 (d, 18H, ^2J(PH) = 3.0 Hz, P*Me*$_3$), 1.28 (s, 18H, *p*-(C*H*$_3$)$_3$C), 1.45 (s, 18H, *o*-(C*H*$_3$)$_3$C), 6.49 (s, 2H, C*H*$_2$), 7.16–7.91 (m, *Ar*, 24H); ^{31}P NMR (C_6D_6, 300 K, ppm): 144.2 (dd, ^2J(PP) = 44.8 Hz, 2P, *P*Me$_3$), −16.4 (dt, ^2J(PP) = 44.8 Hz, 2P, *P*Ph2); ^{13}C NMR (C_6D_6, 300 K, ppm): 23.8 (m, P*Me*$_3$), 31.2 (s, *p*-(*C*H$_3$)$_3$C), 31.6 (s, *o*-(*C*H$_3$)$_3$C), 34.3 (s, *p*-(CH$_3$)$_3$*C*), 35.4 (s, *o*-(CH$_3$)$_3$*C*), 122.5–152.5 (m, aromatic-*C*). The reaction of $NiMe_2(PMe_3)_3$ was carried out by a procedure similar to above in 89% yield.

General procedure for the catalytic hydrosilylation of aldehydes

To a 25 mL Schlenk tube containing a solution of **2** (10.0 mg, 0.01 mmol) in 1 mL of THF were added an aldehyde (1.0 mmol) and $(EtO)_3SiH$ (0.20 g, 1.2 mmol). The reaction mixture was stirred at 65 °C until there was no aldehyde left (monitored by TLC and GC-MS). The reaction was then quenched by MeOH (1 mL) and a 10% aqueous solution of NaOH (5 mL) with vigorous stirring at 50 °C for about 2 days. The organic product was extracted with Et_2O, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The alcohol product was further purified using flash column chromatography. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of the primary alcohol products are provided in the ESI.†

General procedure for the catalytic hydrosilylation of ketones

Ketones were reduced following a similar procedure to the one used for aldehydes except that **2** (20.0 mg, 0.02 mmol) in 2 mL of THF were added. The ^{1}H NMR and ^{13}C {^{1}H} NMR spectra of the secondary alcohol products are provided in the ESI.†

X-ray crystal structure determinations

The single crystals of all complexes for X-ray single crystal diffraction were obtained from their *n*-pentane solutions at low temperature. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer equipped with graphite monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). During collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentz polarization effects and empirical absorption with the SADABS

Table 3 Crystallographic data for complexes **2**, **3**, **4** and **5**

	2	**3**	**4**	**5**
Empirical formula	$C_{59}H_{80}FeO_2P_4$	$C_{56}H_{70}FeIO_2P_3$	$C_{59}H_{79}CoO_2P_4$	$C_{59}H_{80}NiO_2P_4$
Fw	1000.96	1050.78	1003.03	1003.82
Cryst syst	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*2(1)/*n*	*P*2(1)/*n*	$P\bar{1}$	$P\bar{1}$
a, Å	21.067(4)	16.196(3)	12.437(2)	14.2600(5)
b, Å	12.873(3)	12.997(3)	13.462(2)	14.5978(6)
c, Å	22.808(5)	30.608(6)	19.727(3)	15.3049(7)
R, deg	90.00	90.00	94.511(3)	96.364(3)
β, deg	115.18(3)	97.19(3)	104.832(2)	92.785(3)
γ, deg	90.00	90.00	91.585(3)	118.212(3)
V, Å^3	5598.0(19)	6392(2)	3178.7(8)	2771.5(2)
Z	4	4	2	2
D_x, g cm^{-3}	1.188	1.092	1.048	1.203
No. of rflns collected	31 954	31 275	16 636	23 118
No. of unique data	12 629	11 240	11 687	10 325
R_{int}	0.0793	0.0939	0.0694	0.0638
θ_{max}, deg	27.560	25.000	25.500	25.688
R_1 ($I > 2\sigma(I)$)	0.0569	0.0847	0.0535	0.0442
wR_2 (all data)	0.1701	0.3013	0.1445	0.0845

program.[28] The structures were resolved by direct or Patterson methods with the SHELXS-97 program and were refined on F^2 with SHELXTL.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and were refined using a riding model. A summary of crystal data, data collection parameters, and structure refinement details is given in Table 3.†

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