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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.

**Keywords:** Diphosphinito pincer ligand / C-H activation / Iron Hydride / Cobalt /Hydrosilylation / *Trimethyphosphine*

† Electronic Supplementary Information (ESI) available:characterization of all compounds; crystallographic information files CCDC 977103 (**2**), 980722 (**4**), 980723 (**3**) and 980724 (**5**) See DOI:

[a] The first two authors contributed to this paper equally.

## 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 low cost and toxicity, C-H bond functionalization by iron,[5] cobalt[6] and nickel[7] complexes attracted 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 (**Figure 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 (**Figure 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 (**Figure 1. c**).[20] Recently, Wendt reported a series of new $POC_{sp3}OP$-supported nickel(II) complexes (**Figure 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 (**Figure 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.

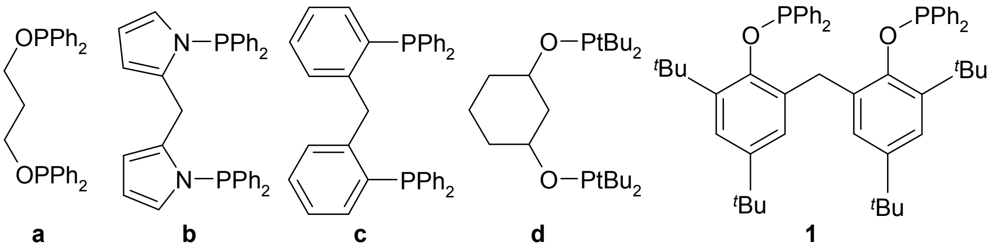


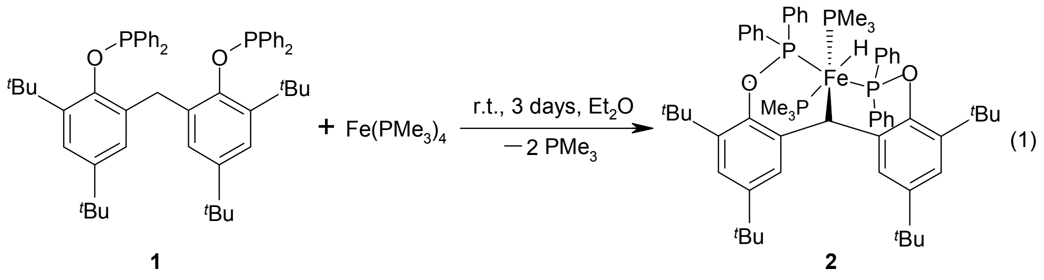
**Figure 1**. [PCP]-pincer ligand

## Results and Discussion

### 1. 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,8d], 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 (eq. (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.

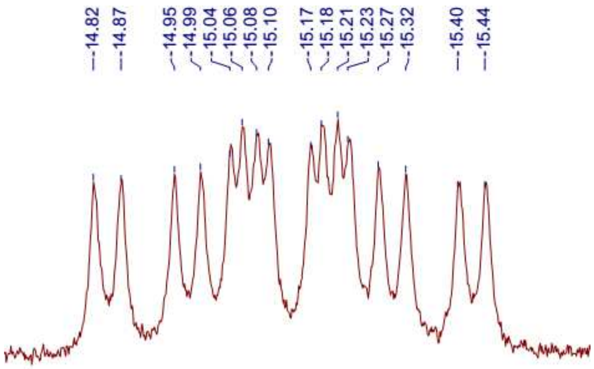


**Figure 2**. Characteristic resonance of the hydrido hydrogen of **2** in $^{1}$H NMR

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 $^{1}$H NMR spectrum is registered at -15.13 ppm with the coupling constants of $^{2}J_{\mathrm{PH}}$ of 69, 48, 38 and 14 Hz (**Figure 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]

The configuration of **2** was confirmed by X-ray structure analysis (**Figure 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)$^{o}$ 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 atoms. This result is similar to that of our early report.[19] Complex **2** has a low-spin Fe(II) center.

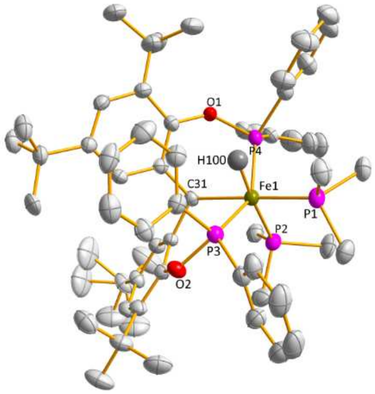
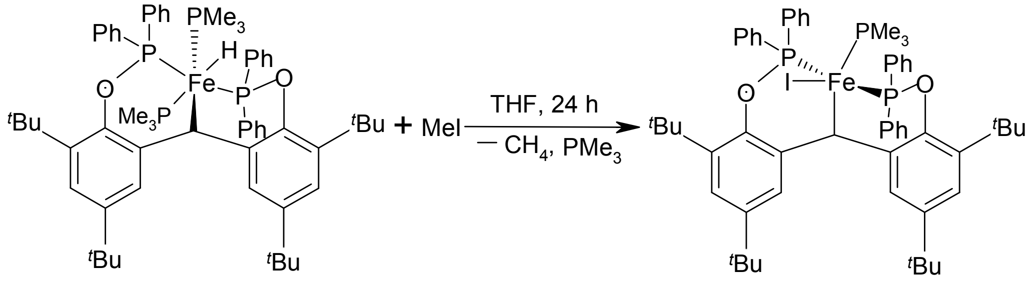


**Figure 3**. ORTEP plot of complex **2** at the 50% probability level (hydrogen atoms except for Fe−H are omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1-P4 2.141(1), Fe1-P3 2.142(1), Fe1-C31 2.165(3), Fe1-P1 2.231(1), Fe1-P2 2.269(1), Fe1-H100 1.50(3); C31-Fe1-P1 177.67(9), P2-Fe1-H100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



**2** **3** (2)

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

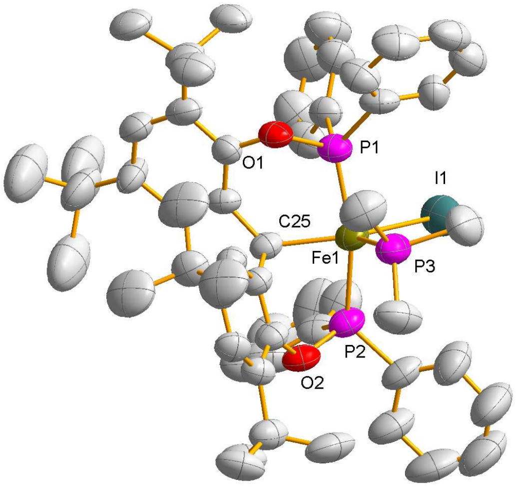
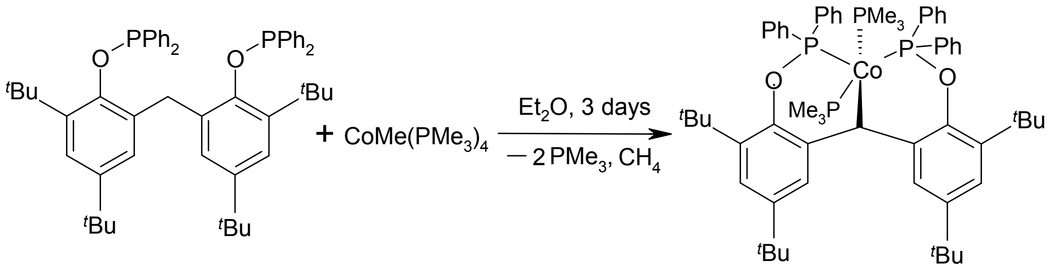


**Figure 4**. ORTEP plot of complex **3** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1-P1 2.194(2), Fe1-P2 2.239(2), Fe1-P3 2.422(3), Fe1-I1 2.699(2), C25-Fe1 2.095(8); C25-Fe1-I1 143.6(2), C25-Fe1-P3 115.2(2), P3-Fe1-I1 101.25(8),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

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 Supporting Information). This result was confirmed by X-ray crystallography. **Figure 4** shows the molecular structure of complex **3**. It has a trigonal bipyramidal coordination geometry with P1-Fe1-P2 = 160.6(1)$^o$ in the axial direction. The sum of the bond angles (C25-Fe1-I1 = 143.6(2)$^o$, C25-Fe1-P3 = 115.2(2)$^o$ and P3-Fe1-I1 = 101.25(8)$^o$) centered at the Fe atom in the equatorial plane is 360.1$^o$. This indicates that the four atoms [Fe1C25I1P3] are almost in one plane.

## 2. Reaction of $CoMe(PMe_3)_4$ with $(POCH_2OP)$ (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 (eq. (3)).



**1** **4**

(3)

The $^1H$ NMR spectrum of complex **4** in $C_6D_6$ 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 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 (**Figure 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)$^o$ 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]

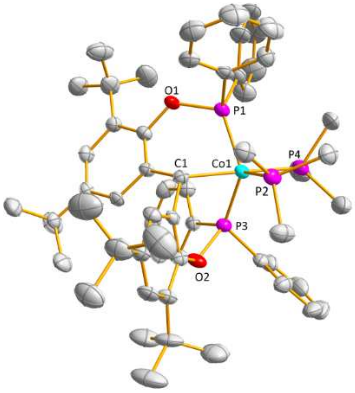
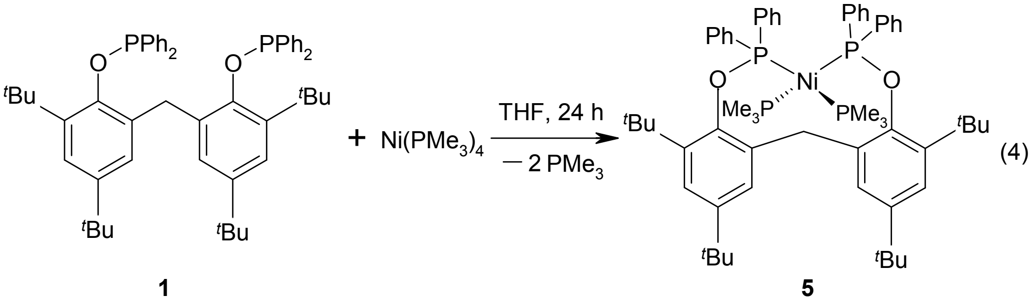


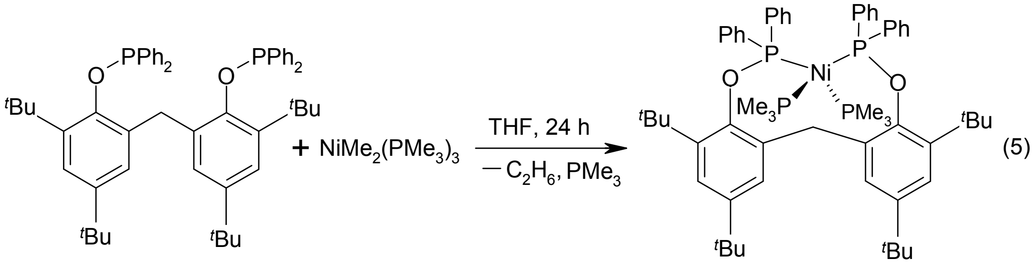
**Figure 5**. ORTEP plot of complex **4** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1-P3 2.118(1), Co1-C1 2.133(4), Co1-P1 2.144(1), Co1-P4 2.213(1), Co1-P2 2.254(1); P3-Co1-C1 82.1(1), P3-Co1-P1 130.80(4), C1-Co1-P1 81.5(1),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

### 3. 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 (eq. (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$^o$C in the yield of 87%. No $C_{sp3}$-H bond activation product could be observed.



In the $^1$H 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 $^1$H 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. 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 $C_2H_6$ (eq. (5)).



**1** **5**

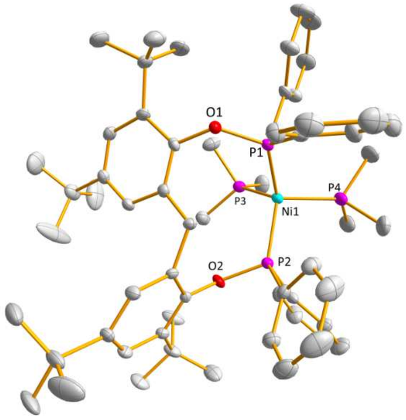


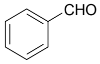
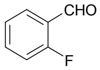
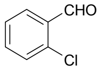
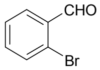
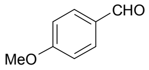
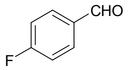
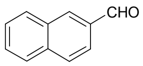
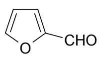
**Figure 6**. ORTEP plot of complex **5** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni1-P1 2.1572(8), Ni1-P2 2.1595(8), Ni1-P4 2.1955(8), Ni1-P3 2.1960(9); P1-Ni1-P2 119.50(3), O1-P1-Ni1 125.69(7), O2-P2-Ni1 117.24(8), C13-O1-P1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

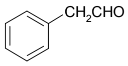
## 4. Catalytic application of hydrido iron complex 2

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

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

**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 |

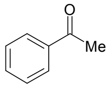
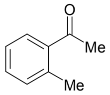
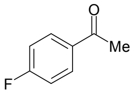
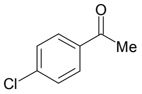
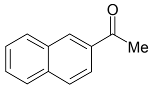
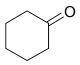
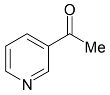
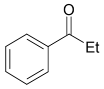
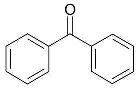
[a] Reaction conditions: RCHO (1.0 mmol), $(EtO)_3SiH$ (1.2 mmol), complex **2** (0.010 mmol), 1.0 mL THF, 65 °C. Under the given conditions, all the aldehydes were completely converted to the corresponding silyl ethers (monitored by TLC and GC).

Besides aldehydes, different ketones were also tested under these catalytic hydrosilylation conditions (eq. (7)). It was confirmed that acetophenone could be entirely converted into the product even within 5h 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 48h. 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]

$$\mathrm{RR'C{=}O} + \mathrm{(EtO)_3SiH} \xrightarrow[\mathrm{THF}]{1\ \mathrm{mol}\ \%\ \mathbf{2}} \mathrm{RR'CHOSi(OEt)_3} \xrightarrow[\mathrm{MeOH}]{10\%\ \mathrm{NaOH}} \mathrm{RR'HCOH} \quad (7)$$

**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 $^{o}$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$_2$OP) 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, 27c] $Ni(PMe_3)_4$,[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$_2$OP) (**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$^o$C. After 6h at 0$^o$C the reaction solution turned brown yellow from tan. After 20h 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): C, 70.79; H, 8.06. Found: C, 70.68; H, 8.09. IR (Nujol, cm$^{-1}$): 3046 $\nu$(ArH), 1959 $\nu$(Fe−H), 1573 $\nu$(ArC=C), 938 $\rho$(PMe$_3$). $^1$H NMR (C$_6$D$_6$, 300 K, ppm): -15.13 (dddd, $J_{P\text{-}H}$ = 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*-(C*H*$_3$)$_3$C), 1.25 (s, 9H, *p*-(C*H*$_3$)$_3$C), 1.42 (s, 9H, *o*-(C*H*$_3$)$_3$C), 1.85 (s, 9H, *o*-(C*H*$_3$)$_3$C), 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$_6$D$_6$, 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$_6$D$_6$, 300K, 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*-(*C*H$_3$)$_3$C) 31.7 (s, *p*-(*C*H$_3$)$_3$C), 31.8 (s, *o*-(*C*H$_3$)$_3$C), 32.6 (s, *o*-(*C*H$_3$)$_3$C), 34.1 (s, *p*-(CH$_3$)$_3$*C*), 34.2 (s, *p*-(CH$_3$)$_3$*C*), 34.9 (s, *o*-(CH$_3$)$_3$*C*), 35.8 (s, *o*-(CH$_3$)$_3$*C*), 118.5 – 152.9 (m, aromatic-*C*).

**Synthesis of (POCHOP)FeI(PMe$_3$) (3)** CH$_3$I (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$^o$C. After 4d the yellow color disappeared and the solution turned red. After 5d at 30$^o$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): C, 64.01; H, 6.71. Found: C, 64.13; H, 6.78. IR (Nujol, $cm^{-1}$): 3030 $\nu$(ArH), 1584 $\nu$(C=C), 940 $\rho$($PMe_3$); $\chi$ (20°C) = $5.108 \times 10^{-6}$ emu/(g Oe).

**Synthesis of (POCHOP)Co($PMe_3$)$_2$ (4).** At -78°C, (POCH$_2$OP) (**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 30h, the reaction mixture turned dark red. After 3d, 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): C, 70.65; H, 7.94. Found: C, 70.58; H, 7.99. IR (Nujol, $cm^{-1}$): 3034 $\nu$(ArH), 1580 $\nu$(C=C), 942 $\rho$($PMe_3$). $^1H$ NMR ($C_6D_6$, 283K, 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, $p$-($CH_3$)$_3$C), 1.35 (s, 9H, $p$-($CH_3$)$_3$C), 1.46 (s, 9H, $o$-($CH_3$)$_3$C), 1.84 (s, 9H, $o$-($CH_3$)$_3$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$_2$OP)Ni($PMe_3$)$_2$ (5).** (POCH$_2$OP) (**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): C, 70.59; H, 8.03. Found: C, 70.51; H, 8.11. IR (Nujol, $cm^{-1}$): 3025 $\nu$(ArH), 1580 $\nu$(C=C), 938 $\rho$($PMe_3$). $^1H$ 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) = 44.8Hz, 2P, *P*Me$_3$), -16.4 (dt, $^2J$(PP) = 44.8Hz, 2P, *P*Ph2); $^{13}C$ NMR ($C_6D_6$, 300K, 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 d. 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 $^1H$ NMR and $^{13}C\{^1H\}$ NMR spectra of the primary alcohol products are provided in the Supporting Information.

**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, 2.0 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 Supporting Information.

**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 ($\lambda$ = 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 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 1**. CCDC 977103 (**2**), 980722 (**4**), 980723 (**3**) and 980724 (**5**) for complexes **2, 3, 4** and **5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

**Table 1. 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 | P2(1)/n | P-1 | P-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 | 31954 | 31275 | 16636 | 23118 |
| no. of unique data | 12629 | 11240 | 11687 | 10325 |
| $R_{int}$ | 0.0793 | 0.0939 | 0.0694 | 0.0638 |
| $\theta_{max}$, deg | 27.560 | 25.000 | 25.500 | 25.688 |
| $R_1$ (I >2σ(I)) | 0.0569 | 0.0847 | 0.0535 | 0.0442 |
| $wR_2$ (all data) | 0.1701 | 0.3013 | 0.1445 | 0.0845 |

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# TOC

# 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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